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## **Review of Bi<sub>2</sub>O<sub>3</sub>-based glasses for electronics and related applications**

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### **Abstract**

The present work critically reviews the scientific and patent literature on low-melting bismuth-based oxide glass frits in materials for electronics, sensors and related applications such as sealing glasses, solar cells, architectural and automotive glass, the main motivation being to replace lead-based materials by environmentally more benign ones. Due to similar glass-forming properties of Bi and Pb, Bi-based glasses are the closest "drop-in" alternative for lead-bearing formulations, and are therefore actually replacing them in many applications, helped also by previous experience with Bi-containing materials in thick-film technology and component metallisations. The outstanding issues are discussed, e.g. matching the lowest processing temperatures achieved by the classical lead-based glasses without sacrificing durability and stability, as well as stability vs. chemical reduction. Finally, consideration is also given to special "heavy" glasses (often containing Bi and Pb together) that are useful in fields such as optics, superconductors and nuclear technology, as well as to specific Bi<sub>2</sub>O<sub>3</sub>-containing crystalline compounds.

**Keywords:** Glasses; Bismuth; Bi<sub>2</sub>O<sub>3</sub>; Electronics; Optics; Thick-film technology; Sensors

*Note. Parts of this work are based on a previous conference paper<sup>1</sup>.*

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## 1. Introduction

### 1.1. Low-melting glasses in electronics and other applications

As for ceramics, inorganic glasses, glass-ceramic and glaze materials have long gone beyond their traditional uses to address a wide array of modern technological challenges,<sup>2-43</sup> in fields such as electrical engineering / electronics / sensors,<sup>9-32</sup> solar energy,<sup>42, 43</sup> protective and decorative coatings,<sup>20, 27-35</sup> optics / optical telecommunications,<sup>36, 37</sup> structural mechanics,<sup>8</sup> medical,<sup>38</sup> nuclear technology,<sup>6, 7</sup> superconductors<sup>39</sup> and microfluidics.<sup>40, 41</sup>

Due to performance and cost criteria, most standard glasses have relatively high softening points. However, there are many technological applications where a low softening temperature is required, in order to lower energy expenditure, avoid damaging devices in contact with the glass during processing or ensure compatibility with other materials:

- Hermetic sealing of packages, lamps, electrical feedthroughs and semiconductor devices<sup>13, 14, 16, 17, 19, 44, 45</sup>
- Hermetic sealing and mechanical attachment of sensors<sup>23, 27</sup> (Figure 1)
- Encapsulation of semiconductor devices<sup>29, 30</sup>
- Overglazing of automotive, packaging and architectural glass<sup>33, 34, 46-48</sup>
- Photovoltaic (PV) solar cell technology – conductors & contacts<sup>42, 43, 49-53</sup>
- Enamelling of aluminium in architecture and home appliances<sup>35, 54-58</sup>
- Thick-film (TF) electronics and other devices<sup>21, 22, 24, 25, 27, 59</sup> on various substrates:<sup>60</sup> glasses for resistor (TFR),<sup>61, 62</sup> conductor,<sup>63, 64</sup> overglaze, dielectric<sup>65</sup> and sealing<sup>15-19</sup> materials (Figure 1, section 1.3); especially, special low-firing compositions for fabrication of circuits and sensors on glass or metals<sup>1, 28, 66-72</sup>

For these applications, glasses are often formulated as frits (i.e. finely divided powder), which may be applied – dispersed in a suitable medium – onto a substrate by various methods such as slip casting, screen printing, roller / curtain coating, spraying, dispensing and electrophoresis, or as preforms for sealing. Classically, the aforementioned applications have to a great extent used lead-based glasses, which have a rather unique combination of desirable properties,<sup>10-12</sup> as will be discussed hereafter in section 1.3. Table 1 compiles the compositions and melting points / processing temperatures of selected classical low-melting lead-based glasses.

Figure 1 shows a thick-film integrated pressure sensor<sup>27</sup> that illustrates many of the aforementioned applications: hermetic sealing of the sensing membrane combined with mechanical attachment and electrical contact, encapsulation through an hermetic dielectric of a wetted surface, conductors, resistors and overglazes.

**Table 1. Representative compositions (cation%\*) of low-melting lead-based glasses. Temperatures = melting points (eutectics) or processing temperatures (others).**

Applications	Temp. [°C]	Pb [%]	Zn [%]	Bi [%]	Al [%]	B [%]	Si [%]	Others	Code
(Eutectics)†	493	52	-	-	-	48	-		PDC-0282
	484	49	-	-	-	41	10		PDC-0741
	739	30	-	-	-	-	70		PDC-5173
Sealing (stable) <sup>73</sup>	390-410	52	8	-	-	40	-		Sck-11
	410-430	42	7	-	-	51	-		Sck-16
	480-500	40	-	-	11	31	18		Sck-27
Sealing (crystallising) Hiz <sup>74</sup> / Bob <sup>75</sup>		45	17	-	3	31	4		Hiz-C3
		43	17	-	3	32	5		Hiz-C5
	420-450	48	15	-	3	30	4		Hiz-C9
		46	17	-	-	32	5		Bob-00
"Classical" TFR frits Pru <sup>62, 76-81</sup> H81 <sup>82</sup>		19	-	-	18	49	14		Pru-F5
		31	-	-	13	-	56		Pru-F7
		36	-	-	2	-	62		Pru-F8
	800-900	40	-	-	-	-	60		H81-01
		26	-	-	5	28	41		H81-04
		33	-	-	2	-	65		H81-05
		22	-	-	4	24	33	17Li 1Zr	H81-10
Low-firing TFR frits <sup>67-69, 71, 83-86</sup>	700-750	23	-	-	3	58	16		L-V2
	550-625	37	-	-	4	32	27		L-V6
	430-550	48	-	-	5	36	11		L-V8
Conductor frits	600-850	9	-	7	-	18	10		C-1 <sup>87</sup>
		15	-	36	-	14	15	20 Ca	C-2 <sup>88</sup>
"Crystal" Glass <sup>89, 90</sup>	≈ 850	11	-	-	-	1	68	1 Na 19 K 0.2 As	Hyn-LC

\*Compositions on a cation basis, i.e.. LiO<sub>0.5</sub>, NaO<sub>0.5</sub>, PbO, ZnO, BiO<sub>1.5</sub>, AlO<sub>1.5</sub>, BO<sub>1.5</sub>, SiO<sub>2</sub>, etc..

†PDC = Phase diagrams for ceramists (figure nr. given): 1-2066<sup>91</sup>, 2067-4149<sup>92</sup>, 4150-4999<sup>93</sup>, 5000-5590<sup>94</sup>.

While most low-melting glasses are used on a substrate or for sealing, there are several significant "bulk" applications of low-melting or relatively low-melting glasses:

- Lead "crystal" glass<sup>89</sup>
- Glasses for nuclear waste immobilisation<sup>6, 95-98</sup>
- Leaded CRT tube glass<sup>89</sup>
- Superconductor synthesis - bulk or film - via the glass-ceramic route<sup>39, 99-105</sup>
- Heavy metal oxide (HMO) glasses with high refraction indices and far infrared (IR) transmission for optical devices & communications<sup>36, 106-128</sup>
- HMO glasses for gamma radiation shielding<sup>129-135</sup>

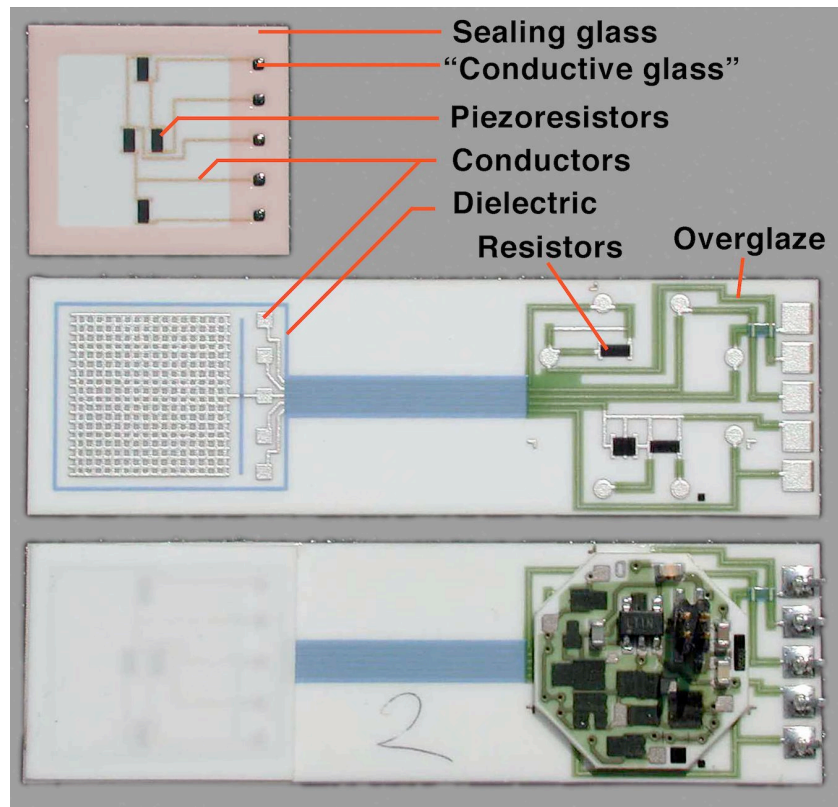


Figure 1. Example thick-film circuit - piezoresistive pressure sensor<sup>27</sup> - showing typical involved materials. Reddish tint added to sealing glass to enhance visibility; "conductive glass" seal = low-firing TFR composition.

## 1.2. Main performance criteria

The performance criteria in selecting a low-melting glass depend on the application. A short overview is given in Table 2 (layers & sealing) and Table 3 (bulk) for the aforementioned applications. In contrast to most "film" applications, most of the "bulk" examples listed above depend specifically on the presence in the glass of HMOs, rather than just require a reliable low-melting glass. In optics, heavy, polarisable cations such as Pb<sup>2+</sup> and Bi<sup>3+</sup> impart to the glass a high diffraction index, a high dispersion, strong nonlinear effects, and better IR transmission,<sup>12, 36, 112</sup> whereas CRT and gamma radiation shielding benefits from the strong absorption of ionising radiation by heavy elements.<sup>11, 129, 130</sup>

**Table 2. Requirements for (relatively) low-melting glasses for layers and seals. "-" = normally not important; "+" = significant; "++" = critical.**

Application	Property	Low process temperature	High service temperature	Thermal expansion matching	Good chemical durability	Good electrical insulation
Hermetic package sealing		+ / ++ <sup>a</sup>	+	+ / ++ <sup>b</sup>	+ <sup>d</sup>	-
Sensor sealing & fastening		+	+ / ++ <sup>c</sup>	++	+ <sup>d</sup>	- / + <sup>e</sup>
Encapsulation of semiconductors		++ <sup>f</sup>	+	++ <sup>g</sup>	+ <sup>d</sup>	++ <sup>h</sup>
Enamelling		- / + <sup>i</sup>	- / +	++ <sup>b</sup>	+ / ++ <sup>j</sup>	-
TF – overglazes		+ <sup>i</sup>	- / +	+ <sup>b</sup>	+ / ++ <sup>j,k</sup>	+ / ++
TF – resistors		- / + <sup>i</sup>	+ / ++	+ <sup>b</sup>	- / +	-
TF - conductors		- / + <sup>i</sup>	-	-	- / +	-
TF - dielectrics		- / + <sup>i</sup>	+ / ++	++	+	++ <sup>h</sup>

- (a) Critical for sealing organic parts & semiconductors / thin-film devices.
- (b) Match not critical for thin layers on planar substrates – avoid tensile stresses.
- (c) Stress relaxation → risk of signal drift.
- (d) Depends on environment; protection of seal with organics sometimes possible.
- (e) Often significant due to seal overlapping conductor tracks – see Figure 1.
- (f) Critical to avoid degradation.<sup>45</sup>
- (g) Difficult combination of low process temperature & low thermal expansion, especially directly on chip, achieved through fillers.<sup>18</sup>
- (h) Surface states in semiconductors also important<sup>29, 30</sup> – reduce / avoid alkalis, which are mobile under electric field.
- (i) Important on sensitive substrates / other layers, e.g. glass, metals, pre-fired TFRs.
- (j) Critical for underwater applications<sup>27</sup> or for automotive.<sup>48</sup>
- (k) Needed for acid plating baths.

### **1.3. PbO in low-melting frits & thick-film technology**

Thick-film electronics makes wide use of glassy compounds, used as main components of overglazes, permanent binders for dielectrics and resistors, and also as frits / adhesion promoters for conductors.<sup>21, 22, 24, 59, 61-65</sup> Note that the technology and materials are very similar for other applications such as architectural / automotive / solar-cell overglazes and conductors.

For conductors, resistors and overglazes (and relatively old dielectrics), most classical low-melting frits are based on the PbO-B<sub>2</sub>O<sub>3</sub> (lead borate) system, with mainly SiO<sub>2</sub>, ZnO and Al<sub>2</sub>O<sub>3</sub> additions. Several phase diagrams and property maps exist for these systems.<sup>21, 91-93, 136-144</sup>

Table 1 gives several representative "traditional" glass compositions, compared with that of traditional leaded "crystal" glass<sup>89</sup> and some representative eutectic compositions in the phase diagrams. Throughout this work, compositions are given on a cation basis unless specified otherwise, as by Dumbaugh and Lapp,<sup>36</sup> this convention facilitates comparison with Bi<sub>2</sub>O<sub>3</sub>-based glasses when PbO is replaced by approximately equimolar amounts of "BiO<sub>1.5</sub>".

By altering the composition, the properties, especially the processing temperature and the tendency to crystallise, can be easily and reliably tuned. Low-melting glasses in this system, which have a composition relatively close to the PbO-B<sub>2</sub>O<sub>3</sub> binary eutectic, allow a reduction in binder glass amount in TF conductors, and/or a decrease of processing temperatures down to ca. 400°C for low-temperature TF conductors, dielectrics, overglazes and resistors,<sup>67, 72, 85, 86</sup> for glass sealing ("solder glasses") of cathode ray tubes (CRTs) and flat panel displays (FPDs), or for glass encapsulation of semiconductor devices.<sup>15, 16, 73, 74</sup>

Low-melting glasses in the lead zinc borosilicate system can be formulated as essentially "stable", i.e. with little or no crystallisation during firing or sealing, or devitrifying, i.e. forming significant amounts of crystalline phase and thus conserving dimensional stability upon later reheating. These latter crystallising glasses are referred to as glass ceramics, vitroceramics, or "cements" in glass-sealing parlance. In these compositions, devitrification is usually favoured by high amounts of ZnO, whereas B<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> tend to stabilise the glassy state (Table 1). To achieve even lower processing temperatures and / or promote wetting, compounds such as CuO, Fe<sub>2</sub>O<sub>3</sub>, Bi<sub>2</sub>O<sub>3</sub>, V<sub>2</sub>O<sub>5</sub>, WO<sub>3</sub>, MoO<sub>3</sub> and fluorine (batched as CaF<sub>2</sub>, PbF<sub>2</sub>, ZnF<sub>2</sub>, BiF<sub>3</sub>...) can be added to the glass formulation.<sup>19, 75, 145-152</sup> Interestingly, fluorine, which is effective in lowering the processing temperature, was found to have better compatibility with glasses where a sizeable amount of PbO was replaced by Bi<sub>2</sub>O<sub>3</sub>.<sup>149</sup> Very low processing temperatures may be reached by glasses largely based on PbO-TeO<sub>2</sub>,<sup>45</sup> PbO-V<sub>2</sub>O<sub>5</sub><sup>145, 147, 148</sup> and especially SnO-SnF<sub>2</sub>-PbO-PbF<sub>2</sub>-P<sub>2</sub>O<sub>5</sub>.<sup>153</sup>

Glass frits are often used in conjunction with other materials that act as fillers (Table 4): insulating powders for dielectrics / overglazes / encapsulation / sealing glasses,<sup>18, 67, 145, 147, 149-152, 154</sup> conductive oxides for resistors,<sup>61, 62, 155-157</sup> metal powders & adhesion promoters for conductors,<sup>63, 64, 88, 158-160</sup> pigments, ... Even for applications such as sealing, encapsulation or thick-film overglazes, where they are not intrinsically required, fillers are often found necessary or advantageous in practice, mainly to adjust the coefficient of thermal expansion (CTE) of the deposited material to that of the substrate(s) – see Donald's review<sup>20</sup> for an extensive list of filler CTEs. The filler can also be used as a nucleating agent to better control the crystallisation process of a devitrifying glass. Alternatively or additionally, chemical and mechanical stabilisation of a glass can be obtained by reaction with the filler; an example is the reaction of lead-bearing glass with TiO<sub>2</sub> and MoO<sub>3</sub>,<sup>161, 162</sup> yielding both an increase of the filler volume (by formation of PbTiO<sub>3</sub> / PbMoO<sub>4</sub>) and of the glass softening point (by the resulting depletion of glass PbO content).



Correctly formulated, both stable and devitrifying lead-based glasses achieve an excellent combination of very consistent and reliable properties, relatively large processing windows, acceptable corrosion resistance and low processing temperatures, all this without requiring, in their composition, alkaline oxides, which are detrimental for insulating properties (due to the mobility of alkaline ions under electric fields) and chemical durability, and impart a high CTE that is deleterious in most cases (except for substrates with CTE > ≈10 ppm K<sup>-1</sup>). Due to these advantages, which have been recognised for a long time (see supplement 10), these lead-based glasses have achieved widespread use, and have been the object of extensive studies and reviews.<sup>10-12</sup>

An overview of the current status of commercial thick-film compositions is given in

Table 5; modern multilayer dielectric compositions such as ESL 4913 are commonly lead-free,<sup>163</sup> and recently-introduced (relatively) low-melting overglaze materials use Bi<sub>2</sub>O<sub>3</sub> instead of PbO. Surprisingly, even an old composition such as Ag:Pd conductor DP 9473 uses a Bi<sub>2</sub>O<sub>3</sub>-based glass.<sup>164</sup>

**Table 3. Requirements for low-melting "bulk" glasses. "-" = normally not important; "+" = significant; "++" = critical**

Application	Property	Low process temperature	Optical properties	Radiation shielding	Good chemical durability
"Crystal" glass (see Table 1)		+ <sup>a</sup>	++ <sup>b</sup>	-	+ / ++ <sup>c</sup>
CRT tube		+ <sup>a</sup>	- <sup>d</sup>	++ <sup>d</sup>	- / +
Optical devices		+ <sup>a</sup>	++ <sup>e</sup>	-	- / +
γ-ray shielding		+ <sup>a</sup>	+ <sup>f</sup>	++	- / +
Waste immobilisation		+ <sup>a</sup>	-	+	++ <sup>c</sup>

**Notes:** (a) minimal volatilisation of toxic / radioactive compounds<sup>89,95</sup> & stresses in large parts / bonds; (b) good transparency & high refractive index; (c) minimal leaching of toxic and radioactive components; (d) browning of glass unimportant for tube part; shielding against X-rays required; (e) depending on application: high refractive index, IR transparency, nonlinearity, luminescence efficiency; (f) conservation of transparency despite high radiation doses.

**Table 4. Representative materials / fillers used in conjunction with glass frits.**

Type	Application / function	Examples
<b>Insulating filler</b>	Dielectrics / enamels, sealing glasses, encapsulation & overglazes: CTE adjustment of composite, glass nucleating agent, reactive stabilisation, colouring	β-eucryptite, cordierite, zircon, mullite, PbTiO <sub>3</sub> , Al <sub>2</sub> O <sub>3</sub> , SiO <sub>2</sub> (amorphous); <sup>149-151</sup> NZP family; <sup>147</sup> Fe <sub>2</sub> O <sub>3</sub> , SiO <sub>2</sub> (quartz, cristobalite); <sup>67-69, 71</sup> CaF <sub>2</sub> ; <sup>154, 165</sup> TiO <sub>2</sub> †, MoO <sub>3</sub> †
<b>Conducting oxide</b>	Resistors: conductive phase <sup>61, 62, 156</sup>	RuO <sub>2</sub> , IrO <sub>2</sub> ; <sup>157</sup> (Pb,Bi,...) <sub>2</sub> Ru <sub>2</sub> O <sub>7-y</sub> , (Ca,Sr,Ba)RuO <sub>3</sub> ; <sup>155</sup> SnO <sub>2</sub> :Sb <sup>166</sup>
<b>Metal</b>	TF conductors: conductive / solderable / bondable phase	Ag, AgPd, Au, Pt, Ni, Cu <sup>60, 64</sup> + other alloys
<b>Bonding oxides</b>	Thick-film conductors: fluxing & bonding to substrate	PbO, Bi <sub>2</sub> O <sub>3</sub> , CuO, ZnO, CdO; <sup>60, 64, 158, 159</sup> (Ni,Co,Fe)O <sub>y</sub> <sup>160</sup>

† React with PbO in glasses to give PbTiO<sub>3</sub> and PbMoO<sub>4</sub><sup>161, 162</sup> – may also react likewise with Bi<sub>2</sub>O<sub>3</sub>.

**Table 5. Qualitative composition (+++ = high, ++ = medium, + = low, ? = very low or absent) of commercial thick-film inks ( $T_f$  = firing temperature\*): dielectrics<sup>167</sup> (compared with LTCC†),<sup>168-170</sup> conductor<sup>164</sup> and resistor.<sup>85</sup> Boron most likely present in all these compositions, but not always detectable by the analysis methods – mentioned where explicitly formulated / detected.**

Type	Supplier code #	$T_f^*$ [°C]	Pb	Ba Sr	Ca	Zn	Bi	Al	Si	Other
"Classical" overglazes	ESL G-481	600	+++			++			++	Cr
	Her IP065	850	+++		+			++	++	Cr
Pb-free overglazes	Her CL90-8325	620				+++	+++			Cr
	ESL 4771P	625					+++		+	Cr
Sealing glass	ESL 4026A	725	+++						+++	
Old Pb-bearing dielectrics	ESL 4904	850	+++		++			++	+++	Co
	ESL 4903	850	+++		+++			+++	+++	Fe, Zr
Modern multi-layer dielectrics	DP QM42	850		+++	+	+++		++	++	Co Ti Zr
	ESL 4913	850		+++	++	+++			++	Co Fe Ti Zr
LTCC	Bosch	875			++			+++	+++	B, Na
	Her CT700	875	?	+++	+	+		++	+++	B, Mg, Na
	DP 951	875	+		++				+++	B, Na
Dielectrics for steel substrates	Her GPA	850			+++	+++		++	++	Co Ti
	ESL 4924	850		++	+++	+		++	++	Co Fe
	ESL 4916	850		++	++				++	Mg Co Zr Ti
Conductor§	DP 9473	850				++	+++	+	++	
Resistor§	DP 2041	850	+++			+		+	++	Zr

\* Used firing temperature for sample processing, i.e. not necessarily the one specified by the manufacturer.

† LTCC = Low-temperature cofired ceramic.

‡ DP: DuPont Microcircuit Materials (Bristol, UK); ESL: ElectroScience Laboratories (King of Prussia, PA, USA); Her: Heraeus Precious Metals, Thick-film division (Hanau, DE)

§ Glass part only.

#### **1.4. The trend away from lead**

In recent times, there is a trend towards removing lead from electronic materials due to its toxicity (see supplement 11), a move spurred by the enactment of the European Union RoHS (Restriction of Hazardous Substances) directive.<sup>171</sup> This has already largely taken place in the field of metallic solders, where the Sn-Ag-Cu alloy ("SAC") has become the standard to replace the classical Sn-Pb-(Ag) eutectic.<sup>172</sup> Although glasses in electronics are mentioned under the list of exemptions,<sup>173</sup> the directive requires this list to be periodically reviewed in the future, and further restrictions on the use of lead-bearing glasses are therefore likely in the medium term. Moreover, cadmium, also a popular addition to low-melting glass frits, must be abandoned.

In contrast to the case of metallic lead and its simple, relatively soluble compounds such as litharge & massicot (PbO), minium (Pb<sub>3</sub>O<sub>4</sub>) and ceruse (2PbCO<sub>3</sub>·Pb(OH)<sub>2</sub>), lead in well-prepared glasses and glazes was traditionally considered to be stably bound, and therefore not a health concern, provided the composition was well formulated, and, for glazes, sufficiently fired.<sup>174</sup> This perception drastically changed after the widely publicised 1991 work of Graziano & Blum,<sup>175</sup> who demonstrated that important amounts of lead could be leached out of "crystal" glass over time by (acidic) wines and spirits. This alarming report was later somewhat contradicted by more realistic tests,<sup>176</sup> while other research<sup>177</sup> showed that water dredged from Pb-contaminated sediments remained well within the official limits, and, more to our point, that lead-bearing LTCC (low-temperature cofired ceramic) compositions could even exhibit good biocompatibility.<sup>178, 179</sup> However, although human exposure to lead and corresponding blood levels have drastically dropped in recent times, the ongoing controversy over the effects of low lead levels, especially for children,<sup>89</sup> will likely generate additional regulatory pressure on its uses (see supplement 11). In the case of "crystal" glass, this has led to research activity towards lead-free substitutes,<sup>90</sup> which showed that most of the properties of original "crystal" could be largely duplicated (although the working range was somewhat smaller), while guaranteeing minimal leaching of potentially dangerous substances.

The situation of glasses in electronics might seem less critical, due to the smaller volumes involved and to the fact that contact with foodstuffs or beverages is (usually) not specified. However, electronic glasses often require lower processing temperatures and only little or no alkali ions are tolerable when good insulating properties are required. Therefore, they can contain much higher amounts of lead than "crystal" ( $\geq 24\%$  mass): ca. 65% for classical 850°C-firing TFRs<sup>62</sup> and up to ca. 85% mass for sealing glasses<sup>12, 15, 16, 73, 74, 150</sup> and low-firing TFRs<sup>85, 86</sup> (Table 1). This results in much lower stability against dissolution in acids,<sup>140, 141</sup> which again raises the issue of contamination of groundwater from disposed electronics waste. Moreover, very low-temperature electronic encapsulant and sealing glasses may contain even more dangerous metals such as Cd and Tl.<sup>165</sup> Therefore, especially for these applications, alternative materials are needed. Finally, even if the final product may be considered stable, occupational exposure during processing is always a concern.

In thick-film electronics, removal of lead started in the 1980s with multilayer dielectrics, where traditional ceramic-filled glass formulations have given way to crystallisable types, which can be formulated lead-free.<sup>163</sup> More recently there has been an effort to remove lead from frits in conductors,<sup>180</sup> overglazes<sup>181</sup> and sealing glasses,<sup>182</sup> and commercial lead-free compositions have become widely available (see

Table 5). However, resistors (and to some extent sealing glasses and overglazes) have lagged behind in this trend, due to the exceptionally easy processing of lead-based glasses and the considerable development work required for entirely new TFR series. Lead-free glasses were widely used in the 1970s...1980s, including for resistors, due to the then considerable

development of nitrogen-firing thick-film systems.<sup>183-189</sup> However, these materials have largely fallen into disfavour, due mainly to performance and reliability problems, especially in ensuring proper organic vehicle burnout.<sup>190</sup>

While "lead-free" is an important aspect in the present review, glasses containing both Bi<sub>2</sub>O<sub>3</sub> and PbO are also included, as they are relevant for specialised applications.

## **2. Low-melting frits – alternative systems**

After the "classical" lead-based glasses (see previous sections), a short discussion of the potential oxide glass substitutes based on elements other than bismuth is given in this section. The reader is referred to other reviews for halide, chalcogenide (non-oxide) and chalcogenide glasses.<sup>37, 191-194</sup>

### **2.1. Borate / borosilicate / silicate glasses**

Several glass systems have been proposed to replace lead-bearing frits. In the case of multilayer dielectrics for "standard" (firing at 850...900°C) thick-film technology, crystallising glasses containing mainly CaO-Al<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>, forming phases such as anorthite or celsian, have largely displaced lead-bearing types in both screen-printed 850°C-firing multilayer dielectrics<sup>163</sup> and LTCC,<sup>9, 168, 169</sup> with mostly improved performance, and therefore provide a satisfactory solution.

A complete lead-free cofirable TFR + LTCC system for processing at 900°C has been implemented by Bosch in its production of car ECUs (engine control units).<sup>169</sup> This system is based on two glasses: an anorthite-crystallising CaO-Al<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> glass (as in the case of dielectrics),<sup>163</sup> and a lower-melting Na<sub>2</sub>O-B<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> one, which probably acts as a binder. In spite of its good properties, its extension to a general-purpose TFR system would be unlikely, as the complicated reactions involved in its processing require a very rigid and tightly controlled manufacturing process: as the resistor has a higher CTE than the substrate, it has to be co-fired with its overglaze, which imparts a protective compressive stress. Such very standardised processes may probably also be used by the chip resistor manufacturers to produce lead-free components.

There have been some attempts at making general-purpose TFRs based on similar glasses, with RuO<sub>2</sub><sup>195-198</sup> and ruthenate perovskites,<sup>197, 199-202</sup> or pyrochlores<sup>82, 203</sup> as conducting phases, which have partly resulted in promising properties, albeit with problems of high process sensitivity and the requirement of a large amount of – expensive – conducting RuO<sub>2</sub>.

The high encountered process sensitivity is expected, as these glasses tend to be not so "well-behaved"<sup>29, 198, 204-207</sup> as lead-based ones, which may be formulated to be virtually non-crystallising,<sup>45, 73</sup> the glass-forming range and stability of the lead-free glasses is in general more limited, and the processing range is restricted to relatively higher-temperature applications than for lead-bearing ones – or other properties such as CTE matching and durability are compromised. Therefore, the abovementioned lead-free glasses are not applicable to compositions requiring very low processing temperatures in applications such as low-firing TFR overglazes and sealing glasses in flat screens.<sup>206, 207</sup>

Nevertheless, silicate, borosilicate or borophosphate glasses have found large-scale low-temperature applications such as the overglazing of architectural and automobile glass<sup>34, 46, 47</sup>, and enamelling of aluminium.<sup>35, 47, 54-57, 208</sup> In these applications, the processing window between sufficient melting of the glass and degradation of the substrate is narrow, and firing schedules are tightly controlled, so a very wide stability range against crystallisation is not necessary. Moreover, significant amounts of alkali oxides, which are detrimental for insulator

dielectric applications, are tolerated within the limits set by their detrimental effect on corrosion resistance; in enamels for aluminium, they impart a desirable high CTE to the glass.

## **2.2. Phosphate glasses**

Phosphate glasses<sup>209, 210</sup> are an interesting alternative, as they usually have low working temperatures. On the other hand, high CTE and water absorption are potential issues. An example low-melting system is Na<sub>2</sub>O-Cu<sub>2</sub>O-CuO-P<sub>2</sub>O<sub>5</sub>,<sup>211</sup> but chemical durability is only passable and it contains a high alkali content, limiting its use in electronics.

Many promising phosphate glasses are based on / derived from the ZnO-P<sub>2</sub>O<sub>5</sub> system, with additives such as B<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, MgO, CaO, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, V<sub>2</sub>O<sub>5</sub> and Nb<sub>2</sub>O<sub>5</sub>.<sup>97, 212-216</sup> For instance, Nb<sub>2</sub>O<sub>5</sub> additions were claimed to allow sealing glasses with processing temperatures as low as 500°C, while retaining good durability and moderate CTE values.<sup>216</sup> Explorative TFRs have also been formulated with such glasses, yielding, however, compatibility problems with Ag terminations.<sup>214, 216</sup> As in borosilicates, a good combination of low processing temperature, stability and durability is imparted by PbO, and corresponding lead iron phosphate glasses have drawn interest for vitrification of high-level radioactive waste; avoidance of PbO is possible for this application if somewhat higher processing temperatures can be accepted.<sup>6, 95, 97, 98</sup>

## **2.3. Glasses based on divalent tin**

A major breakthrough towards low-melting phosphate frits was achieved with the SnO-ZnO-P<sub>2</sub>O<sub>5</sub> system.<sup>182, 217</sup> SnO, with Sn in the unusual +2 oxidation state, seems to behave in a similar manner as PbO, without the toxicity problems. In fact, comparing simple binary SnO, PbO and ZnO phosphate glasses, SnO gives the lowest glass transition temperatures, in the order SnO < PbO < ZnO.<sup>218, 219</sup> Thus, SnO-ZnO-P<sub>2</sub>O<sub>5</sub> glasses (with more SnO than ZnO) can achieve flow characteristics similar to those of traditional lead-based frits<sup>182</sup>, while remaining lead- and alkali-free and having acceptable chemical durability. A recent review<sup>219</sup> of SnO-based glasses shows that low-melting properties are also found in tin(II) borate and silicate glasses, and, like PbO, SnO allows very wide glass-forming ranges with the glass forming oxides, because it can partly behave as a glass former at high concentrations. Substituting part of the O<sup>2-</sup> anions by F<sup>-</sup> or Cl<sup>-</sup><sup>220, 221</sup> can further reduce processing temperatures (usually at the expense of durability, greatly improved by additions of none other than Pb),<sup>153</sup> while posing less migration problems than the alkali ions often present in other low-melting glass compositions.

Although these glasses seem very promising, there are issues about their rather large thermal expansion,<sup>182</sup> mediocre adhesion to silicates such as float glass<sup>222</sup> and mechanical properties.<sup>150</sup> Moreover, the +2 valence state of Sn, which is not stable in ambient air, raises two important processing issues. First, processing in air is preferable (cost & burnout of the organic vehicle), but can oxidise Sn<sup>2+</sup> to Sn<sup>4+</sup>, leading to devitrification and halting densification. This issue can be solved by replacing some of the SnO with low-valence oxides of transition metals such as Mn, Co and Fe, which would protect Sn<sup>2+</sup> by acting as buffers that stabilise the oxygen activity in the glass to low values while being preferentially oxidised, as has been patented for Mn.<sup>223</sup> This, however, raises the second issue: such glasses, once they achieve densification, have a reducing character for anything they encapsulate, as evidenced by the tendency of Cu ions to be reduced to metal.<sup>219</sup> Although this opens up interesting applications such as base-metal thick-films, compatibility with some applications such as existing RuO<sub>2</sub> / ruthenate-based thick-film resistors will be problematic, due to likely reduction of the Ru compounds to metal (2SnO + RuO<sub>2</sub> → 2SnO<sub>2</sub> + Ru). Finally, the presence of metals in several coexisting valence states can degrade the insulating characteristics of



dielectrics based on these glasses.<sup>224-228</sup> One interesting open point relevant for this work is the possible substitution of Pb by Bi as an additive to achieve water-durable ultra low-melting tin fluorophosphate glasses,<sup>153, 220</sup> i.e. whether Bi oxifluoride in glass is first at all thermodynamically compatible with Sn<sup>2+</sup> (not reduced to metal) and, if this is the case, yields similar improvements in durability as Pb while maintaining a low processing temperature.

## **2.4. Other systems**

Finally, other more "exotic" systems must be mentioned, such as glasses containing important amounts of TeO<sub>2</sub>, V<sub>2</sub>O<sub>5</sub>, Nb<sub>2</sub>O<sub>5</sub>, Ta<sub>2</sub>O<sub>5</sub>, MoO<sub>3</sub>, and WO<sub>3</sub>, with TeO<sub>2</sub>, V<sub>2</sub>O<sub>5</sub>, and MoO<sub>3</sub> giving especially low-melting compositions.<sup>45, 73, 113, 120, 123, 126, 229-241</sup> Although toxicity of V<sub>2</sub>O<sub>5</sub> is a cause of concern (supplement 11), these oxides are useful as additives in small amounts, to improve adhesion, wetting and durability, suppress crystallisation in glasses and reduce working temperatures.<sup>35, 56-58, 146, 198, 207, 216, 222, 242</sup>

## **2.5. Discussion**

From the above considerations, one can conclude that replacement of lead-based frits by the abovementioned systems – of which several examples are summarised in Table 6 – may be achieved for applications not requiring a too demanding combination of good insulating properties (e.g. alkali-free), wide processing window, high durability and low processing temperatures; enamelling / overglazing aluminium and glass for protective, functional and decorative purposes, as well as TF dielectric and LTCC compositions, are good examples of successful large-scale replacement of lead-bearing glasses by borosilicate/ silicate compositions. However, durability is often problematic if low processing temperatures are specified.<sup>33</sup>

In electronics, mass-produced chip resistors and co-fired LTCC devices including resistors may also be manufactured lead-free using similar glasses. However, it would be difficult to achieve a general-purpose thick-film system with a comfortable processing window using these materials.

Phosphate and SnO-based glasses, especially those derived from the SnO-ZnO-P<sub>2</sub>O<sub>5</sub> system modified with transition metal oxides, are very promising, and their flow characteristics can resemble those of lead-based frits, but they represent a very radical departure from the heretofore-applied chemistry, especially due to their intrinsically reducing character. This may lead, through the likely resulting presence of mixed-valence transition metal oxides, to degradation of the insulating properties of dielectrics. Also, TFRs, currently based on (most likely incompatible) RuO<sub>2</sub> would have to be formulated anew, using compatible conductive phases based on compounds such as reduced/doped SnO<sub>2</sub>, Fe<sub>3</sub>O<sub>4</sub>, MoO<sub>2</sub> and WO<sub>2</sub>. Finally, the high water affinity of phosphate glasses<sup>209</sup> is an issue which cannot be ignored if well-defined, high-reliability electronic materials are to be manufactured.

**Table 6. Some low-melting lead-free glass systems (without Bi), with typical glass transition temperature  $T_g$ .  $R_2O = (Li,Na,K)_2O$ ;  $RO = (Ca,Sr,Ba,Zn)O$ .**

System	$T_g$ [°C]	Applications & notes
SnO-SnF <sub>2</sub> -P <sub>2</sub> O <sub>5</sub> <sup>220</sup>	180	Very low-temperature sealing, compatible with organics Poor durability; volatilisation; Sn(II) - see below
SnO-ZnO-P <sub>2</sub> O <sub>5</sub> <sup>182</sup>	300	Low-temperature sealing Sn <sup>II</sup> unstable in air & incompatible with RuO <sub>2</sub>
ZnO-Al <sub>2</sub> O <sub>3</sub> -SiO <sub>2</sub> -P <sub>2</sub> O <sub>5</sub> - ... <sup>214</sup> R <sub>2</sub> O-RO-Al <sub>2</sub> O <sub>3</sub> -B <sub>2</sub> O <sub>3</sub> -SiO <sub>2</sub> <sup>195, 196, 200, 203</sup> RO-Al <sub>2</sub> O <sub>3</sub> -B <sub>2</sub> O <sub>3</sub> -SiO <sub>2</sub> <sup>82, 197-199, 201, 202</sup>	≈400- 600	Experimental TFRs - high process sensitivity & other issues Overglazes (TF, architecture, ...)
(ZnO-)Fe <sub>2</sub> O <sub>3</sub> -P <sub>2</sub> O <sub>5</sub> <sup>6, 97</sup>	≈500	Nuclear waste immobilisation; higher working temperature than PbO-Fe <sub>2</sub> O <sub>3</sub> -P <sub>2</sub> O <sub>5</sub> , but successful
R <sub>2</sub> O-TiO <sub>2</sub> -SiO <sub>2</sub> -V <sub>2</sub> O <sub>5</sub> -P <sub>2</sub> O <sub>5</sub> <sup>35, 57, 58</sup>		Enamels for aluminium; toxic V <sub>2</sub> O <sub>5</sub> (supplement 11) hard to remove
BaO-ZnO-B <sub>2</sub> O <sub>3</sub> <sup>206</sup> ZnO-B <sub>2</sub> O <sub>3</sub> -MoO <sub>3</sub> /WO <sub>3</sub> <sup>207</sup>	≈500	Relatively high working temperature; BaO somewhat toxic (supplement 11); limited glass stability with MoO <sub>3</sub> /WO <sub>3</sub> additions
CaO-Al <sub>2</sub> O <sub>3</sub> -B <sub>2</sub> O <sub>3</sub> -SiO <sub>2</sub> + Na <sub>2</sub> O-B <sub>2</sub> O <sub>3</sub> -SiO <sub>2</sub> <sup>243</sup>	≈650 ≈600	Duplex lead-free glass for resistors co-fired with LTCC - fired at 900°C

## 3. Bismuth glasses

### 3.1. Introduction

In contrast to the abovementioned lead-free glasses, Bi<sub>2</sub>O<sub>3</sub> appears a quite promising "drop-in" replacement for PbO, as also evidenced by comparing the commercial lead-free and lead-based thick-film overlazes (

Table 5). The intentional use of bismuth in glasses is by far not as old as that of lead (supplement 10), but the similarity of Bi<sub>2</sub>O<sub>3</sub> and PbO was immediately noticed in the early studies;<sup>129, 244-247</sup> akin to PbO, Bi<sub>2</sub>O<sub>3</sub> belongs to the class of "conditional glass formers": while it does not by itself readily form a glass, it can be incorporated in very large quantities in the classical glass forming oxides SiO<sub>2</sub>, B<sub>2</sub>O<sub>3</sub> and P<sub>2</sub>O<sub>5</sub> and GeO<sub>2</sub>,<sup>2, 110, 245, 246, 248</sup> where it acts as a glass modifier at low concentrations, but partly as a glass former at higher ones. These glasses may in turn incorporate, under standard glass-making conditions, large amounts of alkaline earth (especially SrO and BaO) and transition metal oxides (e.g. ZnO, Fe<sub>2</sub>O<sub>3</sub>, CuO<sub>y</sub>, MnO<sub>y</sub>, CoO<sub>y</sub>), as well as PbO, with small additions enhancing vitrification.<sup>73, 122, 129, 246, 248-272</sup> Other possible additives are alkalis<sup>247, 248</sup> and rare earths.<sup>273-278</sup> Vitrification in different systems is detailed more fully in the following section (3.2). Representative compositions are given in Table 7, and a system-property reference index of studied systems is given in Table 8 for borates, Table 9 for silicates, germanates and phosphates, Table 10 for other systems and Table 11 for binary systems without network formers; systems with several network formers are attributed on a following priority basis: B<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, GeO<sub>2</sub>, TeO<sub>2</sub>, V<sub>2</sub>O<sub>5</sub> and MoO<sub>3</sub>.

One fortunate difference with lead is the much lower toxicity of bismuth, which compares well in this respect with other potential substitutes, as discussed in supplement 11. A less fortunate aspect, however, is the somewhat lower fluxing ability, as can be inferred from the higher overall bonding of Bi<sup>3+</sup> vs. Pb<sup>2+</sup>: simple substitution of PbO with "BiO<sub>1.5</sub>" leads to higher processing temperatures, as illustrated by the stable liquidus (Figure 2) and glass transition temperatures ( $T_g$ , Figure 3). This may be seen as well on the ternary PbO-Bi<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub> phase diagram,<sup>279</sup> where the ternary eutectic composition lies very close to the PbO-B<sub>2</sub>O<sub>3</sub> join, at ca. 45 Pb + 4 Bi + 51 B on a cation basis. Therefore, most studies and developed low-melting glasses are based on the Bi<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub> binary, which combines a wide vitrification range with relatively low processing temperatures, with ZnO, SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> being the most common additions. One must however note that comparison on the basis of equilibrium diagrams should be made with caution, given the slow equilibration in many Bi<sub>2</sub>O<sub>3</sub>-containing systems, attributed to mesomorphism in the melt<sup>280</sup> and illustrated in corresponding metastable phase diagrams.<sup>280-282</sup>

Scientific work has been matched by technical use, the first patent dating from as early as 1945.<sup>283</sup> In the early patents,<sup>49, 87, 146, 283-288</sup> Bi<sub>2</sub>O<sub>3</sub> was introduced in component / ceramic metallisations for its fluxing and wetting properties. The glass frits usually contained PbO and/or CdO – their elimination was at the time not an issue – and the patents gave conflicting information about how Bi<sub>2</sub>O<sub>3</sub> should best be added to obtain maximal adhesion: included in the glass frit, "presintered" with it, added separately to the paste, or even be present both in the glass and as a separate addition. Ensuring good adhesion to alumina without any alkali oxides, CdO and PbO was reported to be problematic, but possible by replacing some SiO<sub>2</sub> by GeO<sub>2</sub>.<sup>288</sup> Starting from 1980, a string of early Soviet patents,<sup>289-293</sup> from what is now the Belarusian State Technological University, disclose a family of low-melting or intermediate glass frits based on the ZnO-Bi<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> system, with optional Li<sub>2</sub>O, Na<sub>2</sub>O, MgO, BaO, CuO and CdO, Al<sub>2</sub>O<sub>3</sub> additions, and claiming a better chemical resistance and a lower coefficient of thermal expansion (CTE) than analogous lead borosilicate frits. These glasses



(Table 7-B80/B82/B83/B89), featuring moderate to high Bi content, processing temperatures down to ca. 500°C, and designed specifically for application in electronics, overglazing and sealing,<sup>289-294</sup> can truly be considered as the base for the "modern" Bi-based frits. More recent patents disclose usually similar compositions for glazes & enamels,<sup>295-302</sup> TF conductors,<sup>250, 303-305</sup> resistors<sup>251</sup> and overglazes,<sup>306, 307</sup> plasma display panel (PDP) dielectrics,<sup>308</sup> conductors<sup>305, 309, 310</sup> and low-melting sealing glasses.<sup>311-314</sup>

The closeness of PbO and Bi<sub>2</sub>O<sub>3</sub> may be seen by comparing, on a cation basis, some glasses taken from Table 1 (standard & low-fire resistor and non-crystallising sealing compositions) with corresponding Bi-based analogues (Table 7). Both types belong to the so-called "fragile glasses", i.e. with a strong dependence of properties on temperature around  $T_g$ .<sup>253, 315</sup>

Bi-based oxide glasses are already making strong inroads in commercial architectural<sup>33</sup> & automotive overglazes,<sup>48</sup> as well as thick-film compositions (

Table 5). Besides these lead-free substitutes, Bi<sub>2</sub>O<sub>3</sub>-based HMO glasses have found potential applications – partly together with PbO – in nuclear physics (scintillators, gamma-ray shielding windows),<sup>129-135</sup> optics,<sup>36, 106-109, 111-128</sup> magnetic materials<sup>316</sup> and glass-ceramic semi/superconductors.<sup>99-102</sup> However, in spite of their significance, compositions based on Bi<sub>2</sub>O<sub>3</sub> have drawn only scant attention – if mentioned at all – in classical "mainstream" reviews of glasses.<sup>2-6, 20</sup>

### **3.2. Glass formation**

A comparison of the vitrification ranges of Bi<sub>2</sub>O<sub>3</sub> and PbO (and a few SnO examples) with common and uncommon glass formers, as found by various authors, is given in Table 12 for nominally binary systems, as a function of the estimated rate of cooling from the melt. This rate, indicated as a subscript for each limiting composition, is expressed in this work as a "quenching index"  $Q$ , equal to the base 10 logarithm of the estimated cooling rate:

$$Q = \log_{10}(\text{estimated cooling rate in K s}^{-1})$$

The reader is reminded that the indicated cooling rates are approximate at best, educated guesses at the worst; the method for estimating / determining  $Q$  is discussed in supplement 14. Please also refer to section 4.1 for stability upon re-heating, and to more extensive work on PbO-<sup>10-13, 16, 19</sup> and SnO-based<sup>219</sup> glasses.

#### *Origins of discrepancies in indicated data*

As seen in Table 12, some values are clearly in conflict, as exemplified by studies on air-cooled gram-size samples<sup>245</sup> yielding a larger vitrification range than others on quenched ones.<sup>244</sup> Partial volatilisation of some components, especially PbO, Bi<sub>2</sub>O<sub>3</sub>, B<sub>2</sub>O<sub>3</sub> and P<sub>2</sub>O<sub>5</sub>, can account for some of these discrepancies, especially for quenching studies, which tend to involve small, open melts. Also, the large apparent discrepancy involving the extensive early work of Janakirama-Rao<sup>246</sup> is tentatively attributed to the graphical representation; if Bi<sub>2</sub>O<sub>3</sub> is taken as "BiO<sub>1.5</sub>" (to make it comparable to the other oxides), a convention sometimes seen in the literature<sup>36, 112</sup> and used in the present review, their results become closer to that of other work.

This said, the by far most common cause of extended reported vitrification ranges can be traced to small but significant amounts of SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and other impurities (in porcelain, fireclay, etc.) leached from crucibles,<sup>118, 317</sup> so some of the examined compositions are most likely not strictly binary. Therefore, the borate systems are marked in Table 12 by a crucible-specific suffix (where specified) after the quenching index.

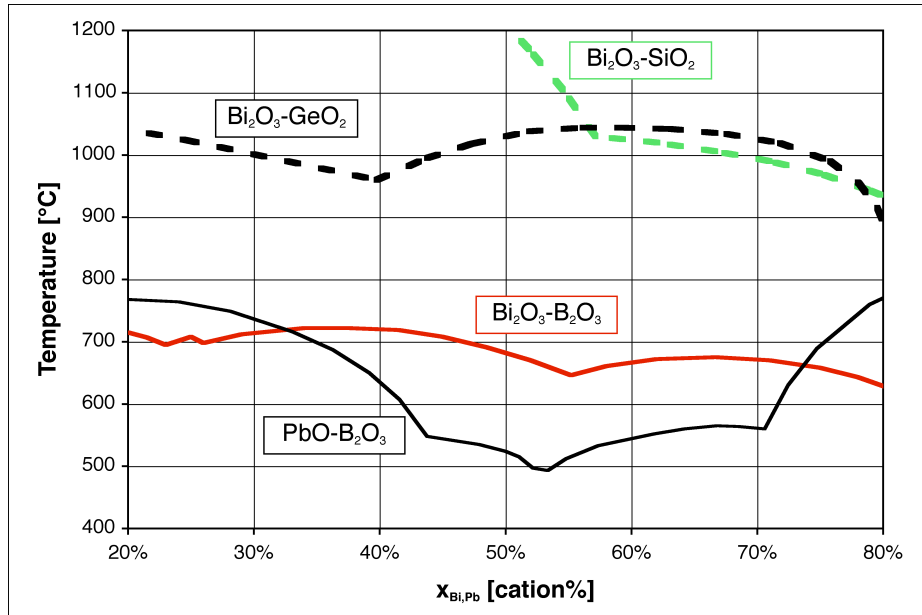


Figure 2. Liquidus temperatures of binary systems – redrawn from phase diagrams  $\text{Bi}_2\text{O}_3$ - $\text{SiO}_2$ ,<sup>281</sup>  $\text{Bi}_2\text{O}_3$ - $\text{GeO}_2$  (PDC-2359),  $\text{Bi}_2\text{O}_3$ - $\text{B}_2\text{O}_3$  (PDC-323), and  $\text{PbO}$ - $\text{B}_2\text{O}_3$  (PDC-282).

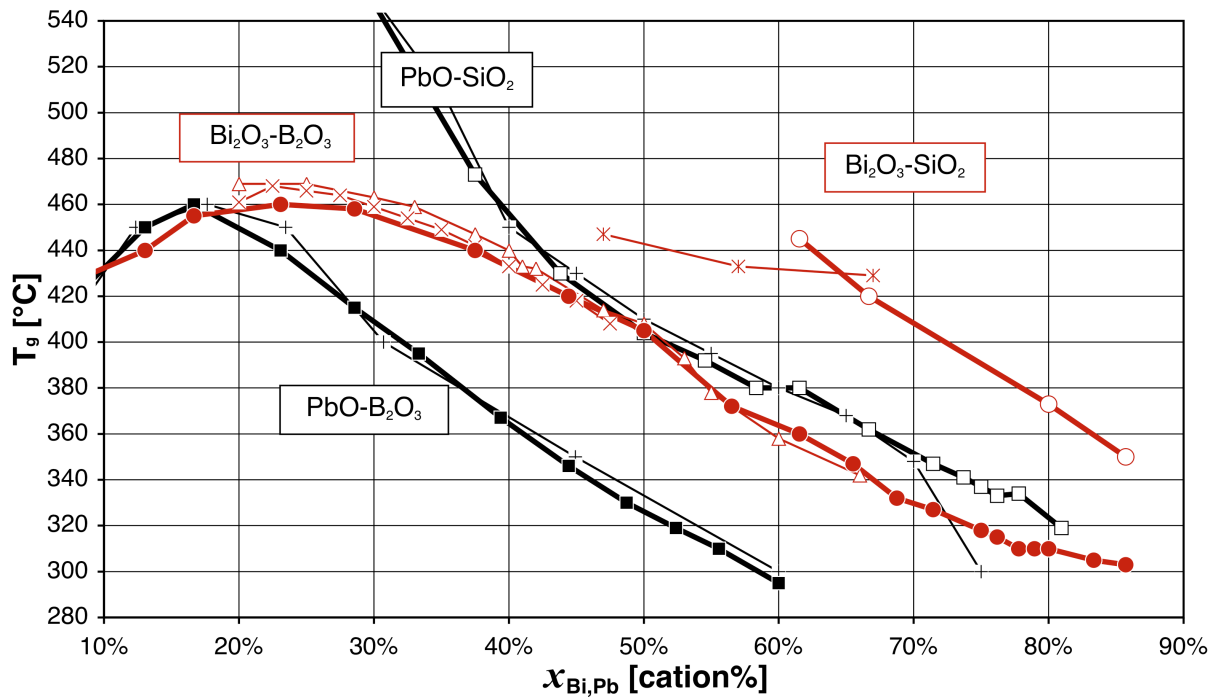


Figure 3. Glass transition temperatures  $T_g$  of binary systems according to George et al.<sup>248</sup> (heavy lines), compared with other work -  $\times$ <sup>318</sup>  $\Delta$ <sup>317</sup>  $+$ <sup>141</sup>  $*$ <sup>319</sup>.

**Table 7. Bismuth glass compositions, in cation mole%.**

Code	Zn [%]	Bi [%]	Al [%]	B [%]	Si [%]	Other [%]	Other [%]
B80-1	11.8	44.2	-	38.7	5.3	-	Early "stable" low-T frits <sup>289</sup> T <sub>s</sub> ≈405-435°C
B80-2	16.4	51.8	-	19.2	12.6	-	
B80-3	2.7	54.0	-	23.8	19.5	-	
B82-1	7.6	46.8	6.5	34.4	2.9	1.8 Mg	Mg + Al: improved durability <sup>290</sup>
B82-2	14.2	46.7	2.7	23.4	4.5	2.7 Mg	
B82-3	5.5	44.9	2.8	38.7	5.1	2.8 Mg	
B89-1	15.2	48.4	-	30.3	4.5	1.6 Ba	Ba: improved hardness <sup>293</sup> T <sub>s</sub> ≈400°C
B89-2	18.4	48.5	-	24.7	6.9	1.6 Ba	
B89-3	8.8	47.0	-	35.4	7.4	1.3 Ba	
Don-01	-	34.1	13.4	30.7	21.8	-	TFR overglaze <sup>307</sup>
Don-04	5.2	36.3	20.7	18.2	19.5	-	
Fri-1	12.5	39.6	7.5	12.8	27.6	-	Overglaze <sup>48</sup> 1='Zn'; 2='ZnTi'
Fri-2	6.2	39.6	7.5	12.8	27.5	6.4 Ti	
Hg-010	20.0	39.5	2.5	27.4	9.1	1.0 La, 0.5 Gd	Magnetic head seals <sup>314</sup>
Hg-018	29.1	37.2	1.0	25.1	7.3	0.4 Ln*	
Hg-026	15.0	56.5	2.4	16.5	2.1	0.1 Er	
Hg-071	20.0	39.8	2.5	27.5	10.1	0.1 La	
Hg-141	21.0	42.0	1.0	26.8	4.5	4.2 Na, 0.5 La	
Hg-203	20.7	48.1	0.3	24.2	2.4	8.5 Na	FPD seals <sup>314</sup>
Hg-324	20.6	52.3	0.6	21.5	2.7	1.1 Ca, 1.0 Sr	
Hm-02	-	82.4	-	-	17.6	-	TFR frits, blended to formulate resistive composites <sup>251</sup>
Hm-03	-	46.2	-	-	23.1	30.8 Cu	
Hm-04	13.3	66.7	-	-	20.0	-	
Hm-05	-	66.7	-	-	20.0	13.3 Cu	
Hm-06	46.2	-	-	-	23.1	30.8 Co	
Hm-09	58.8	-	-	-	17.6	23.5 Fe	
Hm-11	4.6	6.8	5.8	57.6	11.8	1.4 Mg, 11.7 Ba, 0.3 Cu	

(Continued on next page)

(Table 7. Bismuth glass compositions, in cation mole%. – *continued from previous page*)

<b>Code</b>	<b>Zn</b> [%]	<b>Bi</b> [%]	<b>Al</b> [%]	<b>B</b> [%]	<b>Si</b> [%]	<b>Other</b> [%]	<b>Note</b> [%]
Hw-0	25.6	47.3	0.6	24.3	1.9	0.3 Ba†	Conductor frit <sup>320</sup>
Hy-29	19.1	33.3	0.2	-	45.7	0.1 Mg, 1.5 Ca, 0.1 Cu	TFR overglaze <sup>321</sup> TFR matrix <sup>322</sup>
Jeo-1	20.7	47.4	20.4	6.1	-	2.7 Na, 2.7 Ag	PV§ <sup>53</sup>
Jeo-1'	19.2	44.0	3.8	27.7	-	2.5 Na, 2.7 Ag	
L-Bi08	10.0	45.0	4.0	35.0	6.0	-	Experimental Bi-based frits (our work) <sup>1, 323</sup>
L-Bi09	10.0	50.0	4.0	30.0	6.0	-	
L-Bi11	15.0	45.0	4.0	30.0	6.0	-	
L-Bi12	15.0	40.0	4.0	35.0	6.0	-	
L-Bi16	5.0	50.0	4.0	35.0	6.0	-	
L-Bi17	15.0	50.0	4.0	25.0	6.0	-	
LTS-1	10.6	25.1	-	17.8	1.4	39.7 Pb, 3.2 Cu 2.2 Fe, 11 F <sub>2</sub> ‡	Low-T sealing (+Pb) 1: N14; <sup>149</sup> 2: C <sup>242</sup>
LTS-2	5.9	4.5	-	28.2	-	52.2 Pb, 2.8 Cu, 4.7 Fe 1.4 Te, 0.3 Mn, 3 F <sub>2</sub> ‡	
Lvx-1	-	6.2	-	7.7	25.6	38.4 Na, 2.9 K, 4.5 Li 0.9 Ba, 13.7 Ti	Enamel for Al <sup>56</sup>
Nch-1	16.1	43.8	-	35.5	2.0	2.7 Sr	FPD Seal <sup>312</sup>
Rad-1	-	15.2	-	-	29.4	55.4 Pb	γ-ray shielding 1: #211, 2: #218 <sup>129</sup> 3: #14 <sup>130</sup>
Rad-2	-	21.3	-	-	16.5	62.2 Pb	
Rad-3	-	73.7	-	21.1	-	5.3 Pb	
Sck-30	30.6	8.2	-	61.2	-	-	Early Zn-Bi-B <sup>73</sup>
Smt-7	-	64.5	-	33.3	2.1	0.1 Ce	NL optics <sup>112</sup>
Usu-05	17.7	59.0	-	23.0	-	0.3 Ce	FPD seal "Si-free" <sup>311</sup>
Usu-06	20.6	54.4	-	24.6	-	-	
Usu-09	11.3	60.7	-	27.7	-	-	
Usu-10	17.6	52.5	-	29.6	-	-	
Usu-11	20.7	48.3	-	30.7	-	-	

\*Ln = lanthanide mix.

†Only sum Si+Al+Ba given in reference – "educated guess" according to Table 18.

‡Fluorine expressed as replaced oxygen fraction, i.e. F<sub>2</sub> / (O + F<sub>2</sub>); usually inaccurate due to volatilisation losses.

§Possible error in paper – bottom formulation more likely.

**Table 8. System-property index: borates**

Oxide system	Properties*
Bi-B	$P^{282, 318} V^{110, 244, 245, 247, 270, 315, 317, 318, 324, 325} S^{247, 254, 317, 326, 327} T_g^{110, 248, 275, 315, 317, 318}$ $T_s^{254, 324} T_x^{110, 275, 317, 318, 326} \alpha^{254, 318, 324} \rho^{110, 248, 254, 315, 317, 318, 324, 327-329} n^{318, 324, 325, 327, 329-331}$ $E+\eta^{315} m^{317, 327} N^{332} L^{325, 329, 331} \epsilon^{324} \sigma^{328} W^{110, 247, 254, 317, 327, 331, 332} \mu^{132, 133, 254, 333} \gamma^{143}$
Li-Bi-B	$V^{247, 248, 334, 335} S+n+W^{334, 335} \rho^{248, 334, 335}$
Li-K-Bi-B-V	$S+T_g+\rho+W^{336}$
Li-Zn-Bi-B	$S+V+W+\rho+\sigma^{337, 338} T_g+W+R^{337}$
Li-Cd-Bi-B	$S+W+\rho+\sigma^{338}$
Na-Bi-B	$V+S+W^{247}$
Na-Bi-Fe-B	$V+X+T_g+T_x+\sigma^{339}$
Na-Bi-B-Mo	$n+W^{340}$
K-Bi-B	$V^{247}$
K-Bi-Fe-B	$V+\rho+\sigma^{341-343} T_g^{343}$
Mg-Bi-B	$P^{344}$
Ca-Bi-B	$P^{345} T_g+T_x+\epsilon+\sigma^{269}$
Sr-Bi-B	$P^{346} V^{246, 258, 346} W+\rho+\sigma^{258}$
Ba-Bi-B	$P^{347, 348} V^{246, 258, 270, 349} S^{266, 349, 350} T_g^{349} T_x^{349} E+H^{266} W+\rho^{258, 266, 349, 350} \sigma^{258} S+N^{351}$
Ba-Zn-Bi-Al-B-Sb	$\alpha+T_g+T_s+T_x+W+\sigma^{271}$
Pb-Bi-B	$P^{279} V^{246, 253, 259, 261} R+S^{352} S+W+T_s+\alpha^{254} T_g^{253, 259, 261, 352} E^{253, 259, 261} H^{253} \rho^{130, 254, 259, 261, 352} \mu^{130}$
Pb-Bi-B-Si†	$W+L^{353}$
Pb-Zn-Bi-B-Si	$S+X+T_s+\alpha+H+W+\rho^{256}$
Zn-Bi-B‡	$P^{354} V^{122, 246, 264} S^{122, 264, 266, 355} T_g^{260, 355} m+\alpha+s+\epsilon^{355} E+H^{266} W+\rho^{122, 264, 266} R^{122}$
Zn-Bi-B-Si	$V+\alpha^{257, 289, 314} T_g^{257} T_s^{257, 289, 293} D^{289} H^{293} \sigma^{289, 293}$
Zn-Bi-B-Si-Ba	$\alpha+T_s+T_x+H+D+\sigma^{293}$
Zn-Bi-Fe-B	$V^{316}$
Zn-Bi-Al-B-Sb	$\alpha+T_g+T_s+T_x+W+\sigma^{271}$
Cu-Bi-B	$P^{356} V^{132, 249} T_g+T_s+\alpha+\rho^{132, 249} T_x+D+H+\epsilon+\sigma^{249} S+W+R+\mu^{132}$
Y-Bi-B	$V+S+p+W^{274}$
La-Bi-B	$T_g+T_x+\alpha+H+\rho^{275}$
Sm-Bi-B	$X+T_g+T_x+L^{273}$
Eu-Bi-B	$X+S+W^{276, 357} \rho^{357}$
Eu-Bi-Al-B	$V+S+T_g+T_x+W^{277}$
Gd-Bi-Al-B	$V+S+W^{278}$
Gd-Bi-B-Mo	$V+S+\rho+E+H+n+W^{358}$
Er-Bi-B	$T_g+T_x+\alpha+H+\rho^{275}$
Bi-Fe-B	$V+T_g^{252} T_s+T_x+\epsilon^{272} W^{255, 272} \rho+\sigma^{252, 272} S+X+W+R+R^{255}$
Bi-Ga-B	$S+T_g+T_x+R^{359, 360} n+W+\rho^{119, 359, 360} L^{119}$
Bi-B-Si	$V^{112, 263, 361, 362} S^{362} T_g+T_x^{263, 362} W^{112, 361, 362} n^{112, 362} N^{112} R^{362}$
Bi-B-Ti	$V+T_g+T_x^{363}$
Bi-B-Ti-Nb	$V+X+T_g+T_x+\epsilon^{364}$

\*P: phase diagram; V: vitrification; S: structure; X: crystallisation (see also T<sub>x</sub>); b: Mössbauer spectroscopy; m: nuclear magnetic resonance (NMR); p: electron paramagnetic/spin resonance (EPR/ESR); s: sintering; T<sub>g</sub>: glass transition temperature; T<sub>s</sub>: softening point; T<sub>x</sub>: crystallisation temperature; α: CTE; c: heat capacity; E: elasticity; η: viscosity; ρ: density; γ: surface tension; D: chemical durability; H: hardness and/or strength; n: refraction index; W: optical transmission; N: optical nonlinearity; L: luminescence / amplification / upconversion; R: Raman spectra; ε: dielectric properties; σ: electrical conductivity; μ: interaction with ionising radiation.

†Also +Sb fining agent.

‡Error in Kim et al.<sup>260</sup> –  $T_g/T_{liquidus} \approx 2/3$ , authors used °C instead of K.

**Table 9. System-property index: silicates, germanates & phosphates.**

Oxide system	Properties (symbols: see Table 8)
Bi-Si	$P^{281, 365} V^{107, 131, 244, 245} S+T_s+W+R+\mu^{131} T_g^{131, 248, 319} T_x^{366} \rho^{248, 319, 329} n^{329} \sigma^{319, 366}$
K-Bi-Si	$T_x+\sigma^{366}$
Pb-Bi-Si	$V+\rho+\mu^{129} \rho+H+W^{367}$
Bi-Si-Ti-Nb	$V+X+T_g+T_x+\varepsilon^{364}$
Bi-Ge	$P^{280} V^{231, 245} T_g^{319} T_x^{366, 368} \rho^{319, 329} W^{231, 368} n^{329} \sigma^{319, 366}$
Bi-Ge-V	$V+W^{231}$
K-Bi-Ge	$T_x+\sigma^{366}$
Pb-Bi-Ge	$V+\rho+\alpha+T_g+T_x^{369}$
Pb-Bi-Ga-Ge	$T_g+T_x^{121} W+L^{121, 125, 370} R^{370}$
Pb-Bi-Ga-Ge-F*	$T_g+T_x+R+L^{371}$
Zn-Bi-Ge	$V+\rho+D+W^{372}$
Bi-Cr-Ge	$V+S+p^{373}$
Eu-Bi-Ge	$V+S+W^{374}$
Bi-P	$V^{244, 375, 376} \rho^{329, 375, 376} \alpha+T_g+T_x+D+W^{375} E^{376} n^{329, 375} p^{377}$
Bi-Fe-P	$S+b+\rho+\sigma+\varepsilon^{228}$
Li-Bi-P	$V+T_g+\rho+W^{378}$
Zn-Bi-P	$V+S+T_g+\rho^{262, 265, 267} \alpha^{265} m+T_x+R^{262} W^{265, 267} D^{262, 267}$

\*Also with fluoride additions.

**Table 10. System-property index: tellurites, vanadates, molybdates & other\*.**

Oxide system	Properties (symbols: see Table 8)
Bi-Te	$P^{379} V^{244, 245}$
Bi-Te-Ti	$P^{380} V+S+T_g+T_x+R+p^{240}$
Bi-Te-Nb	$V+X+T_g+T_x+p^{113}$
Bi-Te-W	$V+W+\rho^{123, 126} S+T_g+\alpha+R+p^{126} n+N^{123}$
Ba-Bi-Te	$V+S+T_g+T_x+\alpha+n+W+R^{120}$
Zn-Bi-Te	$V+n+W+N+p^{241}$
Bi-Te-V	$T_g+E+p^{239}$
Pb-Bi-Te-V	$T_s+\alpha+\sigma+\varepsilon^{45}$
Bi-V	$V^{231, 238, 244} T_g+T_x+p^{238} W^{231}$
Bi-Fe-V	$V+S+b+T_g+T_s+T_x+W^{233}$
Bi-Fe-Mo	$V+S+b+T_g+T_s+T_x+W^{234}$
Bi-V-Mo	$V+T_g+T_x^{232, 235} S^{232}$
Pb-Bi-Mo	$V+X+W^{115}$
Li-Ba-Bi	$V+T_g+T_x+W^{381}$
Li-Pb-Bi	$V+T_g+T_x+\rho+W^{382}$
Ca-Sr-Pb-Cu-Bi	$X+\sigma^{104}$
Sr-Pb-Bi	$W+L^{117}$
Pb-Ba-Zn-Bi	$V+\rho+n+W^{36}$
Pb-Cd-Bi-Fe	$V+T_g+\alpha+\rho+n+W+\sigma+\varepsilon^{36}$
Pb-Cu-Bi	$P^{383} V+S+T_g+T_x+W^{103}$
Pb-Bi-Mn-[Al <sup>#</sup> ]	$S+W+R^{384}$
Pb-Bi-Ga	$V^{36, 128} \alpha+\sigma+\varepsilon^{36} S^{111, 371, 385, 386} R^{371, 385, 386} L^{127, 371} \rho+n+W^{36, 128, 387} T_g+T_x^{371, 387}$

\*Binary systems without glass formers: see Table 11. #Probable Al<sub>2</sub>O<sub>3</sub> contamination from crucible.

**Table 11. Glasses without standard network formers: binary systems.**

Oxide system	Range* (%left cation)			Properties (symbols: see Table 8)
Bi-Li	65-75 <sub>2,0</sub> <sup>388</sup>	63-77 <sub>2,6</sub> <sup>381</sup>	15-80 <sub>7,0</sub> <sup>389</sup>	V <sup>381, 388, 389</sup> T <sub>g</sub> +T <sub>x</sub> <sup>389</sup> S <sup>388</sup>
Bi-Ba	X <sub>2,6</sub> <sup>244</sup>	X <sub>1,0; 2,0</sub> <sup>270</sup>	70-98 <sub>3,5</sub> <sup>270</sup>	P <sup>270</sup> V <sup>244, 270</sup>
Bi-Pb	X <sub>2,6</sub> <sup>244</sup>	18-89 <sub>3,5</sub> <sup>108</sup>	40-85 <sub>4,5</sub> <sup>115</sup>	V <sup>108, 115, 244</sup> T <sub>g</sub> +T <sub>x</sub> <sup>108</sup> W+R <sup>384,†</sup>
Bi-Cu (Pb-Cu)	43-82 <sub>4,5</sub> <sup>390</sup>	46-95 <sub>3,5</sub> <sup>108</sup>	(30-90 <sub>3,5</sub> <sup>108</sup> )	V+T <sub>x</sub> <sup>108, 390</sup> T <sub>s</sub> <sup>108</sup> S+T <sub>g</sub> +p+W+p <sup>390</sup>
Bi-Mn	67-95 <sub>3,5</sub> <sup>108</sup>			V+T <sub>s</sub> +T <sub>x</sub> <sup>108</sup>
Bi-Fe	69-94 <sub>3,2</sub> <sup>391</sup>			V+T <sub>g</sub> +p+σ+ε <sup>391</sup>
Bi-Ti	75-89 <sub>3,5</sub> <sup>108</sup>			V+T <sub>s</sub> +T <sub>x</sub> <sup>108</sup>
Bi-Ga	57-80 <sub>2,6</sub> <sup>106</sup>			V <sup>106</sup> S (neutron & XRD & Pb-Ga) <sup>109</sup>

\*Vitrification range; X = none found.

†Probable Al<sub>2</sub>O<sub>3</sub> contamination from crucible.

### Binary systems

The binary Bi<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub> system has been studied most extensively, and vitrifies easily at low cooling rates.<sup>318</sup> A minimal amount of Bi<sub>2</sub>O<sub>3</sub> is seen to be necessary due to the miscibility gap in the phase diagram<sup>110</sup> (which also exists with PbO-Bi<sub>2</sub>O<sub>3</sub><sup>136</sup> and many other borates), setting a practical limitation for technical purposes to above ca. 19% Bi<sub>2</sub>O<sub>3</sub>, the end of the gap. It is nevertheless possible to achieve apparently homogeneous vitrification throughout this range if quenching sufficiently fast from above the gap.<sup>110</sup>

For the "strict" Bi<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub> binary, the extensive and well-controlled work of Becker<sup>318</sup> (very large melts, controlled cooling, noble metal crucibles, 20-43% Bi<sub>2</sub>O<sub>3</sub>) is deemed the most reliable for slow cooling. At intermediate cooling rates, the maximum Bi content is around 60%,<sup>118, 244, 317</sup> with 66% achievable for splat quenching.<sup>317</sup> Going to twin roller quenching increases the vitrification range further, to 0-88% Bi.<sup>110, 248</sup>

The Bi<sub>2</sub>O<sub>3</sub>-rich ends of the glass-forming ranges with B<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> are often reported to be quite different from each other, and also from the values for PbO. However, as noticed by Dumbaugh and Lapp,<sup>36</sup> this is due to the arbitrary selection of the "molecules" PbO, Bi<sub>2</sub>O<sub>3</sub>, B<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub>; on a cation basis, these limits (Pb vs. Bi and B vs. Si) become more similar, as illustrated by the results of fast quenching experiments by Stehle, George et al.,<sup>110, 248</sup> where the four systems were examined in the same conditions; for Bi<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>, a maximum of ca. 85% Bi is obtained.

To summarise the data on binary systems with the common glass formers (B<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, P<sub>2</sub>O<sub>5</sub>, GeO<sub>2</sub>), the vitrification ranges (in cation%) of Bi<sub>2</sub>O<sub>3</sub> and PbO appear similar, although a direct comparison is difficult due to the spread in experimental data and the paucity of experiments under the same conditions. The maximum Bi<sub>2</sub>O<sub>3</sub> content is smaller with GeO<sub>2</sub>, and even more with P<sub>2</sub>O<sub>5</sub>; the Bi<sub>2</sub>O<sub>3</sub>-P<sub>2</sub>O<sub>5</sub> system has therefore attracted limited attention. The reverse is seen for SnO, where vitrification is especially favourable with P<sub>2</sub>O<sub>5</sub>, resulting in glasses based on the SnO-P<sub>2</sub>O<sub>5</sub> system being another promising substitute to lead-based ones (see section 2.3).

With the unconventional network formers, vitrification is more difficult in general, and more severe quenching must be applied; comparing with PbO, vitrification appears to be more difficult for Bi<sub>2</sub>O<sub>3</sub> with TeO<sub>2</sub> and V<sub>2</sub>O<sub>5</sub>, while the reverse is true with MoO<sub>3</sub>. Under fast to very fast quenching, binary glasses may be obtained with Li<sub>2</sub>O, BaO, PbO, CuO<sub>y</sub>, MnO<sub>y</sub> and Ga<sub>2</sub>O<sub>3</sub>.



### *Complex systems with traditional network formers*

As mentioned earlier, even small amounts of Al<sub>2</sub>O<sub>3</sub> and especially SiO<sub>2</sub> leached from the crucible considerably facilitate vitrification in the Bi<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub> system. This synergistic vitrification is confirmed by experiments with B ≈ Si, where 74% Bi may be achieved by conventional melting and casting,<sup>361</sup> i.e. much more than in either the Bi<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub> or Bi<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> binary system. This is also true for low SiO<sub>2</sub> & Al<sub>2</sub>O<sub>3</sub> additions: a 65 BiO<sub>1.5</sub> + 33 BO<sub>1.5</sub> + 2SiO<sub>2</sub> composition vitrifies easily when casting large plates,<sup>112</sup> as does 70 BiO<sub>1.5</sub> + 25 BO<sub>1.5</sub> + 3 SiO<sub>2</sub> + 3 AlO<sub>1.5</sub> under moderate quenching.<sup>324</sup> Such modifications are therefore very useful for low-melting glasses rich in Bi<sub>2</sub>O<sub>3</sub>, as they stabilise the glass with only limited impact on processing temperature.<sup>314</sup>

Synergistic vitrification also occurs, for a given network former, when replacing on a cation basis part of the Bi<sub>2</sub>O<sub>3</sub> with other alkaline earth and transition metal oxides. This occurs in spite of a generally poorer vitrification with these oxides (except PbO) taken individually than with Bi<sub>2</sub>O<sub>3</sub>, and is seen for borates with SrO,<sup>246, 258, 346</sup> BaO,<sup>246, 258, 270, 349</sup> PbO,<sup>130, 246, 279</sup> ZnO<sup>246, 354, 355, 392</sup> and CuO<sub>y</sub>.<sup>249</sup> Figure 4, redrawn on a cation basis from the original studies,<sup>249, 354</sup> illustrates the case of the Bi<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub> binary extended with ZnO and CuO<sub>y</sub>: there is clearly an optimum in substitution that minimises the required amount of network former. This composition "hump" roughly agrees with low-melting zones in the corresponding ternary equilibrium diagrams.<sup>354, 356</sup> In commercial low-melting glasses based on ZnO-Bi<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub> (Table 7, Hg-Nch-Ussu), the Zn:Bi ratio – in practice also influenced by other considerations such as acid resistance – is commonly 0.2...0.7. In most cases, Zn is preferred over Cu due to the easy occurrence of mixed valence in the latter, leading to semiconductivity in Cu-rich glasses<sup>249</sup> – a drawback mainly for insulators. This said, excluding PbO and alkalis, Zn and Cu apparently give the lowest melting points in the ternary phase diagrams, with the deepest eutectics somewhat below 600°C; the BaO-Bi<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub> system, for instance,<sup>347, 348</sup> apparently is fully solid at 600°C. Going one step further in complexity, mixing both network formers and modifier, allows a further decrease in the required amount of the former, as seen for PbO-ZnO-Bi<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> glasses,<sup>256</sup> in line with the general trend towards more difficult crystallisation of multicomponent glasses.

In contrast to these oxides, an extension of the glass-forming range to lower B<sub>2</sub>O<sub>3</sub> contents is not seen with the light alkali elements Li, Na and K (Figure 5);<sup>247</sup> the effect for small substitutions of BiO<sub>1.5</sub> by alkalis is neutral up to ca. 25% LiO<sub>0.5</sub>, then the minimum B<sub>2</sub>O<sub>3</sub> required for vitrification rises sharply; this threshold is much lower (ca. 3%) for NaO<sub>0.5</sub> and practically zero for KO<sub>0.5</sub>. Under fast cooling in the more complex R<sub>2</sub>O-ZnO-Bi<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub> (R=Li, Na, K) system, a deleterious effect on vitrification was also observed, with a similar, but less pronounced trend of the size of the vitrification domain (Li>Na>K).<sup>392</sup> Qualitatively, this agrees with the relatively stringent limits set on alkali content in the patents of Hasegawa et al.,<sup>313, 314</sup> as discussed in section 4.1.

While small amounts of rare-earth additions are common for luminescence studies, the effect of larger quantities on vitrification Bi<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub> have been less studied; especially, experiments where Bi<sub>2</sub>O<sub>3</sub> is systematically replaced by Ln<sub>2</sub>O<sub>3</sub> (Ln = rare earth and Y, except Ce) are lacking. Experiments by Pascuta et al.,<sup>276-278, 357</sup> while extensive, were carried out on relatively unstable glasses with a low amount of B<sub>2</sub>O<sub>3</sub> (20...33% BO<sub>1.5</sub>), requiring fast quenching; they could replace ca. 25% to 35% of the whole glass, on a cation basis, by GdO<sub>1.5</sub> or EuO<sub>1.5</sub> (they achieving similar results with GeO<sub>2</sub> as a network former<sup>374</sup>). Stabilisation of the glass was also observed with 5% Fe<sub>2</sub>O<sub>3</sub>.<sup>255</sup> Compositions reported by this group for this and other systems<sup>255, 274, 276-278, 357, 374, 384, 393, 394</sup> must be taken with caution, however, as they used very high melting temperatures (1100°C and above) in Al<sub>2</sub>O<sub>3</sub> crucibles and their



reported glass-forming ranges – >90% BiO<sub>1.5</sub> for moderate quenching! - seem too high (see Table 12); their compositions are therefore likely to be shifted by reaction or volatilisation.

For more stable glasses (Bi<sub>2</sub>O<sub>3</sub>·2B<sub>2</sub>O<sub>3</sub>), vitrification is easy and therefore not affected by small Ln<sub>2</sub>O<sub>3</sub> additions; however, strong suppression of crystallisation upon reheating was observed for 5% La<sub>2</sub>O<sub>3</sub> and 3% Er<sub>2</sub>O<sub>3</sub>.<sup>275</sup> In the patent literature (complex glasses based on ZnO-Bi<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub>), maximal rare earth content is reported to be at ca. 4 to 8%, lower-melting glasses being more sensitive.<sup>314</sup>

For the less-studied silicates and germanates, a wide maximum in synergistic vitrification range is achieved when mixing Bi<sub>2</sub>O<sub>3</sub> with PbO<sup>129, 367, 369</sup> or PbO & some BaO<sup>107</sup> and, while systematic studies are lacking, successful incorporation of large amounts of alkaline earth / transition metal oxides with low network former content is reported;<sup>246, 250, 251</sup> for instance Janakirama-Rao reports facile vitrification of 31 RO + 62 BiO<sub>1.5</sub> + 7 SiO<sub>2</sub>, where R = Sr, Ba, Pb or Zn, i.e. with a much lower amount of SiO<sub>2</sub> than needed for vitrification in the binary systems, and similar results when adding two oxides (CdO & WO<sub>3</sub>, PbO & MnO<sub>y</sub>, PbO & CuO<sub>y</sub>) to the Bi<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> binary.<sup>246</sup> In comparison, the PbO-SiO<sub>2</sub> system is also quite tolerant for substitution of PbO by NiO, ZnO, MnO<sub>y</sub> and FeO<sub>y</sub>,<sup>395</sup> – though a decrease of required SiO<sub>2</sub> is not observed for small substitutions, in contrast to the Bi<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub> system.

Data on alkali additions is not as complete as with borates. At <10% (cation) Si, R<sub>2</sub>O-Bi<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> is reported not to vitrify for R = Li, Na or K (as with borates), but to vitrify easily with R = Rb or Cs, even with a very large (>50%) degree of substitution of Bi by R.<sup>246</sup>

Extensions of the glass-forming range by other oxides also occur with vanadates (Fe<sub>2</sub>O<sub>3</sub><sup>234</sup>), molybdates (PbO<sup>115</sup>, Fe<sub>2</sub>O<sub>3</sub><sup>234</sup>) and even gallates (PbO & CdO<sup>36</sup>). In the case of phosphates, vitrification with ZnO occurs over a wider range than with Bi<sub>2</sub>O<sub>3</sub>, but a synergistic effect is achieved nonetheless, albeit in this case with less Bi<sub>2</sub>O<sub>3</sub> than ZnO.<sup>262</sup>

#### *Glasses without network formers*

Besides providing new insights in glass formation, glasses without traditional network formers are of interest for optical applications (section 5.1), provided other light-element oxides with strong oxygen bonding (especially Al<sub>2</sub>O<sub>3</sub>) are absent.

Although early attempts to make glasses of Bi<sub>2</sub>O<sub>3</sub> without at least a very small amount of true network formers were unsuccessful,<sup>244, 246</sup> several such binary systems were later successfully vitrified under twin roller quenching (Table 11), and melts with Li<sub>2</sub>O and Ga<sub>2</sub>O<sub>3</sub> were observed to actually vitrify under relatively moderate quenching.

Adding more components facilitates glass formation, of which several examples are given in Table 13. Extension of the Li<sub>2</sub>O compositions to systems such as Li<sub>2</sub>O-BaO/PbO-Bi<sub>2</sub>O<sub>3</sub> significantly facilitates vitrification.<sup>381, 382</sup> Khalilov<sup>107</sup> systematically modified glasses based on Bi<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> with binary or more complex combinations of PbO, BaO, CdO, ZnO, and MgO, under moderate quenching (cast in metallic moulds and covered with plates), and SiO<sub>2</sub>-free Bi<sub>2</sub>O<sub>3</sub>-PbO-BaO-CdO-ZnO (+optional MgO) glasses were obtained; as the mixtures were melted in Pt crucibles, contamination by SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> or B<sub>2</sub>O<sub>3</sub> can safely be excluded. Other similar systems are SrO-PbO-Bi<sub>2</sub>O<sub>3</sub><sup>117</sup> and CaO-SrO-PbO-Bi<sub>2</sub>O<sub>3</sub>-CuO<sub>y</sub><sup>99</sup> (useful for processing superconductors via the glass-ceramic route – see section 5.3), and PbO-CdO-Bi<sub>2</sub>O<sub>3</sub>-Fe<sub>2</sub>O<sub>3</sub>.<sup>36</sup> Ga<sub>2</sub>O<sub>3</sub> was found to be particularly useful to promote glass formation, with the relatively simple PbO-Bi<sub>2</sub>O<sub>3</sub>-Ga<sub>2</sub>O<sub>3</sub> system exhibiting easy vitrification over a wide composition range and even allowing casting of large objects.<sup>36, 106, 386</sup>

**Table 12. Glass-forming range\* of Bi<sub>2</sub>O<sub>3</sub> and PbO/SnO† binary systems with network-forming oxides, with quenching index *Q* and crucible‡ indicated as subscript.**

Network former	Limit	Bi <sub>2</sub> O <sub>3</sub> (as BiO <sub>1.5</sub> )*				PbO* ( <i>SnO</i> )†	
B <sub>2</sub> O <sub>3</sub> (as BO <sub>1.5</sub> )	Min	25 <sub>1.5§</sub> <sup>246</sup>	22 <sub>1.2P</sub> <sup>247</sup>	22 <sub>1.0</sub> <sup>245</sup>	20 <sub>-1.8N</sub> <sup>318</sup>	11 <sub>1.0</sub> <sup>245</sup>	11 <sub>2.0</sub> <sup>246</sup>
		19 <sub>1.2A</sub> <sup>315</sup>	19 <sub>1.0S</sub> <sup>270</sup>	19 <sub>3.5S</sub> <sup>270</sup>	0 <sub>5.2N</sub> <sup>110</sup>		
	Max	43 <sub>-1.8N</sub> <sup>318</sup>	57 <sub>1.2A</sub> <sup>315</sup>	57 <sub>2.6N</sub> <sup>244</sup>	60 <sub>2.0N</sub> <sup>317</sup>	60 <sub>0.6</sub> <sup>129</sup>	62 <sub>1.0</sub> <sup>245</sup>
		60 <sub>2.6</sub> <sup>325</sup>	65 <sub>1.0</sub> <sup>245</sup>	66 <sub>3.0N</sub> <sup>317</sup>	67 <sub>1.5#</sub> <sup>246</sup>	67 <sub>2.6N</sub> <sup>397</sup>	80 <sub>1.5</sub> <sup>246</sup>
		68 <sub>1.2P</sub> <sup>247</sup>	70 <sub>1.6P</sub> <sup>324</sup>	70 <sub>2.6S</sub> <sup>396</sup>	70 <sub>1.0S</sub> <sup>270</sup>	89 <sub>5.2N</sub> <sup>248</sup>	
		75 <sub>2.0A</sub> <sup>357</sup>	75 <sub>2.0A</sub> <sup>274</sup>	75 <sub>1.2P</sub> <sup>254</sup>	80 <sub>1.2P</sub> <sup>132</sup>		
	80 <sub>1.6A</sub> <sup>332</sup>	80 <sub>2.0S</sub> <sup>270</sup>	88 <sub>5.2N</sub> <sup>110</sup>	96 <sub>3.5S</sub> <sup>270</sup>	60 <sub>2.5Sn</sub> <sup>398</sup>		
SiO <sub>2</sub>	Min					0 <sup>136</sup>	
	Max	51 <sub>0.6</sub> <sup>129</sup>	57 <sub>2.6</sub> <sup>244</sup>	63 <sub>1.0</sub> <sup>245</sup>	61 <sub>1.6</sub> <sup>118</sup>	60 <sub>0.6</sub> <sup>129</sup>	65 <sub>1.3N</sub> <sup>395</sup>
GeO <sub>2</sub>	Min	67 <sub>1.8</sub> <sup>107</sup>	85 <sub>5.2N</sub> <sup>248</sup>	95 <sub>1.2P</sub> <sup>131</sup>		67 <sub>1.0</sub> <sup>245</sup>	82 <sub>5.2N</sub> <sup>248</sup>
		0 <sub>5.4</sub> <sup>231</sup>	30 <sub>0.0N</sub> <sup>369</sup>			0 <sub>0.0N</sub> <sup>369</sup>	
	Max	43 <sub>0.0N</sub> <sup>369</sup>	51 <sub>1.0</sub> <sup>245</sup>	55 <sub>2.6N</sub> <sup>369</sup>	57 <sub>3.4</sub> <sup>372</sup>	46 <sub>0.0N</sub> <sup>369</sup>	57 <sub>1.0</sub> <sup>245</sup>
P <sub>2</sub> O <sub>5</sub> (as PO <sub>2.5</sub> )	Min	70 <sub>5.4</sub> <sup>231</sup>	80 <sub>1.6A</sub> <sup>374</sup>	89 <sub>2.0A</sub> <sup>374</sup>	92 <sub>4.2</sub> <sup>368</sup>	67 <sub>2.6N</sub> <sup>369</sup>	
	Max	≈0 <sub>0.6</sub> <sup>376</sup>	40 <sub>0.6</sub> <sup>376</sup>	40 <sub>2.6</sub> <sup>244</sup>	45 <sub>1.2</sub> <sup>375</sup>	0 <sub>1.0</sub> <sup>245</sup>	58 <sub>1.6Sn</sub> <sup>182</sup>
TeO <sub>2</sub>	Min					45 <sub>1.0</sub> <sup>245</sup>	
	Max	X <sub>1.0</sub> <sup>245</sup>	0 <sub>2.6</sub> <sup>244</sup>			11 <sub>1.0</sub> <sup>245</sup>	
V <sub>2</sub> O <sub>5</sub> (as VO <sub>2.5</sub> )	Min	X <sub>1.0</sub> <sup>245</sup>	19 <sub>2.6</sub> <sup>244</sup>			22 <sub>1.0</sub> <sup>245</sup>	
	Max	0 <sub>2.6</sub> <sup>244</sup>	0 <sub>4.0</sub> <sup>238</sup>	0 <sub>5.4</sub> <sup>231</sup>		0 <sub>4.0</sub> <sup>238</sup>	
MoO <sub>3</sub>	Min	18 <sub>2.6</sub> <sup>244</sup>	29 <sub>4.0</sub> <sup>238</sup>	40 <sub>5.4</sub> <sup>231</sup>		43 <sub>4.0</sub> <sup>238</sup>	
	Max	28 <sub>4.5</sub> <sup>115</sup>				X <sub>4.5</sub> <sup>115</sup>	
		53 <sub>4.5</sub> <sup>115</sup>				X <sub>4.5</sub> <sup>115</sup>	

\*Limits given as cation% of Bi, Pb or Sn. X: no glass-forming domain found.

†Values for SnO systems (more data in review<sup>219</sup>) given in same column as PbO, in *italic* and with ‘Sn’ suffix.

‡Crucible types: S: SiO<sub>2</sub> crucible; A: Al<sub>2</sub>O<sub>3</sub>; P: porcelain or similar; N: noble metal.

# Assumed Bi<sub>2</sub>O<sub>3</sub> is in fact represented as BiO<sub>1.5</sub> in the diagrams.

**Table 13. Glasses without standard network formers: complex systems**

System (oxide cations)		Composition (typ., cation%)	<i>Q</i>
Li-Ba-Bi <sup>381</sup>	Fu-1	22 Li + 12 Ba + 67 Bi	2.6
Sr-Pb-Bi <sup>117</sup>		14 Sr + 29 Pb + 57 Bi	2.0
Pb-Cd-Bi-Fe	Dmb-H	40 Pb + 15 Cd + 20 Bi + 25 Fe	1.2
Zn-Bi-Fe <sup>316</sup>		11 Zn + 40 Bi + 49 Fe	4.2
Pb-Zn-Cd-Bi-Ba	Khv-12	5 Ba + 14 Pb + 8 Zn + 9 Cd + 64 Bi	1.8
<i>Idem</i> + Mg <sup>107</sup>	Khv-13	4 Ba + 14 Pb + 7 Zn + 8 Cd + 64 Bi + 3 Mg	1.8
Pb-Bi-Ga <sup>36</sup>	Dmb-EO	40 Pb + 35 Bi + 25 Ga	1.2
Pb-Bi-Ga <sup>128</sup>	McC-1	31 Pb + 39 Bi + 30 Ga	1.6
	McC-2	23 Pb + 59 Bi + 18 Ga	1.6
Cd-Bi-Ga <sup>36</sup>	Dmb-IV	15 Cd + 70 Bi + 15 Ga	1.2
Ba-Zn-Bi-Ga <sup>36</sup>	Dmb-D	10 Ba + 10 Zn + 24 Pb + 56 Bi	1.2
Ca-Sr-Pb-Bi-Cu <sup>99</sup>	HTS-1	22 Ca + 22 Sr + 5 Pb + 33 Cu + 18 Bi	2.9

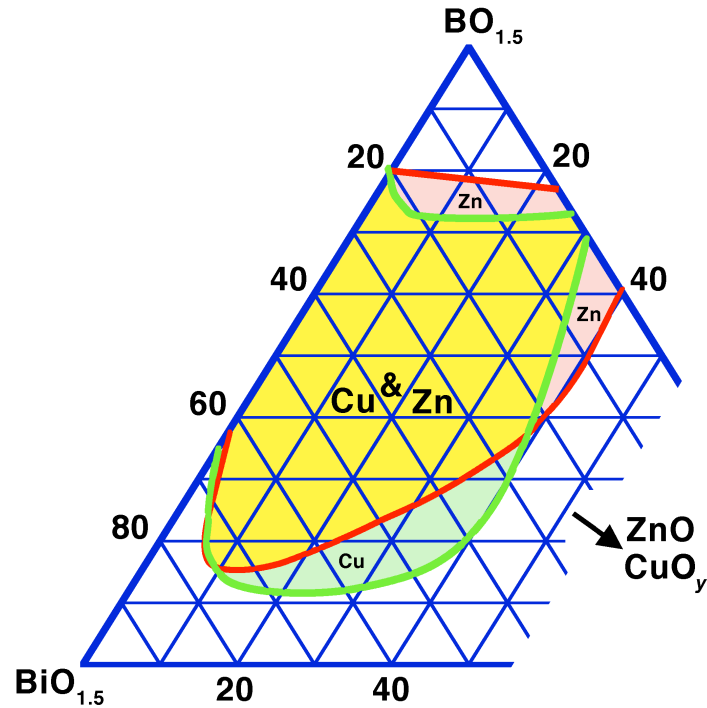


Figure 4. Vitrification range in the  $\text{Bi}_2\text{O}_3$ - $\text{B}_2\text{O}_3$ - $\text{ZnO}^{354}/\text{CuO}_y^{249}$  systems (cation basis).

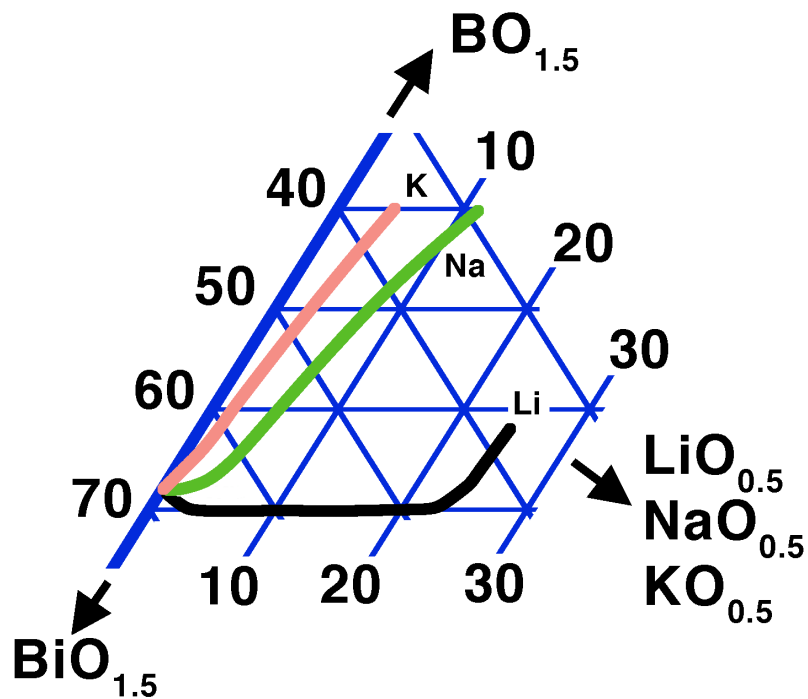


Figure 5. Effect of  $\text{R}_2\text{O}$  on min.  $\text{B}_2\text{O}_3$  in the  $\text{R}_2\text{O}$ - $\text{Bi}_2\text{O}_3$ - $\text{B}_2\text{O}_3$  ( $\text{R}=\text{Li}, \text{Na}, \text{K}$ ) systems.<sup>247</sup>

### *Conclusions*

The following remarks may be derived from the data on glass formation:

- Bi<sup>3+</sup>, akin to Pb<sup>2+</sup>, is a large, polarisable ion; both, while not vitrifying alone, behave as conditional network formers, requiring "abnormally" low amounts of true network formers for successful vitrification at moderate cooling rates.
- The Bi<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub> system appears to be the most promising basis for the fabrication of stable lead-free Bi<sub>2</sub>O<sub>3</sub> glasses with low processing temperatures, but does not allow by itself processing temperatures as low as those of the corresponding PbO-B<sub>2</sub>O<sub>3</sub> system.
- In the Bi<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub> system, adding low amounts of SiO<sub>2</sub> and other oxides such as ZnO, Al<sub>2</sub>O<sub>3</sub>, and Fe<sub>2</sub>O<sub>3</sub> also stabilises the glass without largely increasing processing temperatures. Further studies, however, are needed to better define glass stability as a function of composition, especially upon re-heating, which is critical for TF processes (see section 4.1 for some information in this regard).
- Mixing several oxides of large, polarisable cations, such as Bi<sub>2</sub>O<sub>3</sub>, PbO and BaO tends to stabilise the glasses and/or lower the required amount of true network formers; adding limited amounts of other transition metal or rare earth oxides furthers this trend.
- Using rapid cooling, glasses containing Bi<sub>2</sub>O<sub>3</sub> and PbO may be formed in the complete absence of true network formers. The PbO-Bi<sub>2</sub>O<sub>3</sub>-Ga<sub>2</sub>O<sub>3</sub> system provides an especially favourable base for such HMO glasses.

### **3.3. Glass structure**

#### *General considerations*

Since the "anomalous" ease of vitrification of Bi<sub>2</sub>O<sub>3</sub> with standard network formers, similar to that of PbO, was noticed in early work,<sup>244-246</sup> numerous studies have been devoted to elucidating the structure of Bi<sub>2</sub>O<sub>3</sub>-based glasses, using methods such as X-ray diffraction (XRD), Fourier-transform infrared (FTIR), Raman, electron paramagnetic/spin resonance (EPR/ESR), Mössbauer, X-ray absorption (XAS / EXAFS) and magic-angle-spinning nuclear magnetic resonance (MAS-NMR) spectroscopy. A good knowledge of structural features is required to efficiently correlate glass properties with chemical data;<sup>327, 329, 399-401</sup> this is especially important for borate glasses, given the different possible forms and structures assumed by borate anions.<sup>402</sup>

#### *Bonding in crystalline compounds*

To provide additional insight into the structural features of Bi<sub>2</sub>O<sub>3</sub>-based glasses, a survey of a range of relevant and related crystalline oxides, where atomic positions may be precisely determined, was carried out (supplement, section 13). Even in crystalline oxides, Bi<sup>3+</sup> adopts a wide variety of asymmetric, disordered and often ill-defined coordination polyhedra, presumably due to its high polarisability<sup>400</sup> and stereochemically active "lone pair" electrons, and bonding with oxygen is fairly covalent. An overview of idealised typical oxygen coordination shells observed around Bi<sup>3+</sup> cations, in the crystalline oxides examined in the supplement, is given in Figure 6, with the corresponding descriptions in Table 14. The lone pair may strongly deform the oxygen coordination shell (6-Oct33), and often replaces an oxygen anion to "fill" the corresponding vacancy (3-PyM, 4-BPy / 4-PyM, 5-Py14). Recently, the lone-pair concept has been revisited in the light of diffraction data and spectroscopic studies of band structure, coupled with detailed computational modelling<sup>403</sup> (see other

references in supplement 13); the lone pair is found to stem from interaction of both metal valence *s* and *p* orbitals, mediated by oxygen 2*p* ones.

In compounds, Bi<sup>3+</sup> tends to have coordination number (CN) values of typ. 5-7, but with very varying bond lengths and presumably strengths, with only a slight tendency to reduction to typ. 5 at high Bi<sup>3+</sup> concentrations. This reduction has little effect in practice as it only eliminates very long, weak bonds. CN = 3 is found only exceptionally, such as for a minority of Bi<sup>3+</sup> cations in the defective sillenite  $\gamma$ -Bi<sub>2</sub>O<sub>3</sub>.

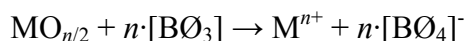
Pb<sup>2+</sup> and Sn<sup>2+</sup> are fundamentally similar to Bi<sup>3+</sup>, also being lone-pair cations. However, Sn<sup>2+</sup> has relatively well-defined coordination shells and tends to low coordination number (CN) values, ca. 3. Pb<sup>2+</sup>, being larger and more polarisable, behaves in a more similar way to Bi<sup>3+</sup> in compounds; CN is similar to that of Bi<sup>3+</sup> at low concentrations, but drops to 3 or 4 in Pb-rich compounds. Bi<sup>3+</sup> has more asymmetric bonding, having fairly high strongest-bond valences in the range 0.8-1.3, compared to 0.6-0.7 for Pb<sup>2+</sup> (supplement, Table 36).

### *Borate glasses*

The binary  $x \cdot \text{Bi}_2\text{O}_3 + (1-x) \cdot \text{B}_2\text{O}_3$  system has been studied most extensively; there is general agreement on several features.<sup>248, 317, 318, 350, 355, 394, 402</sup>

With addition of Bi<sub>2</sub>O<sub>3</sub> in B<sub>2</sub>O<sub>3</sub>, the original B<sub>2</sub>O<sub>3</sub> network, constituted of [B<sub>3</sub>O<sub>6</sub>] boroxol rings and [BO<sub>3</sub>] triangles (written B<sub>Δ</sub>, i.e. CN = 3), is initially strengthened – as in other borate glasses – by conversion of part of the B<sub>Δ</sub> groups to tetrahedral [BO<sub>4</sub>] ones (B<sub>T</sub>, CN = 4), as shown in Figure 7. Boroxol rings persist only in compositions with very low Bi<sub>2</sub>O<sub>3</sub> content, and disappear for  $x > 25\%$ . This initial increase in the degree of bonding results – as in other borate glasses – in an increase of  $T_g$  (Figure 3, Table 15) and network compacity<sup>248, 318</sup> up to  $x \approx 20\text{-}25\%$ .

At low  $x$ , an "ideal" modifier cation M<sup>*n*+</sup> with valence *n*, incorporated as its oxide MO<sub>*n*/2</sub>, is fully incorporated by creation of tetrahedral units:



where "Ø" is the usual convenient symbol<sup>350, 352, 404</sup> for an oxygen ion making a bridging link between two network former cations (and therefore corresponding to half an oxygen atom in formulae, sometimes written "O<sub>1/2</sub>"<sup>398</sup>). Ideally, the fraction  $N_4$  of [BØ<sub>4</sub>] tetrahedra is  $n \cdot x / (1-x)$ , a relation obeyed at  $n \cdot x < \text{ca. } 25\%$  by alkali<sup>405</sup> and large alkaline earth (Sr, Ba)<sup>404</sup> oxide additives. In contrast,  $N_4$  is much lower than expected for Bi<sub>2</sub>O<sub>3</sub>, hinting at very different behaviour from that of an ideal modifier, presumably stemming from stronger preference for retaining direct covalent Bi-O bonds over more "diffuse" ones with [BØ<sub>4</sub>] tetrahedra. This behaviour also matches that of SnO, and of other intermediate oxides such as CdO and ZnO.<sup>398</sup> In contrast, with PbO (Figure 7),  $N_4$  behaves closer to ideal at low  $x$ .

For  $x > \text{ca. } 25\%$ ,  $N_4$  further rises, but borate units are progressively depolymerised, as B-O-B linkages are replaced by weaker B-O-Bi ones, resulting in a drop of  $T_g$ . This behaviour is very different from simple alkali and alkaline earth borate glasses,<sup>404, 405</sup> where the peaks of  $T_g$  and  $N_4$  roughly coincide. PbO and SnO borate glasses also exhibit the same anomalies (Table 15), but they are much less pronounced; the exceptional structural feature in binary Bi<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub> glasses is a very broad peak of  $N_4 \approx 45\%$ , which essentially extends throughout the "useful" composition range. It is therefore assumed that Bi<sup>3+</sup> at least partly enters the network already at low  $x$  values, and the borate network progressively adapts with increasing  $x$ .<sup>402</sup> The same is also true, but to a lesser extent, for Pb<sup>2+</sup> and Sn<sup>2+</sup>, given the lower discrepancy between the  $T_g$  and  $N_4$  peaks.



It is interesting to compare the maximum single-bond valence range for Bi<sup>3+</sup> (0.8-1.3) and Pb<sup>2+</sup> (0.6-0.7) in crystalline compounds with the oxygen bonding deficit for different types of bonding and different boron coordinations, accounting for the variability of ca. ±0.05 seen for a given B-O bond in crystalline compounds (see Table 16 and supplement 13, Table 36). Allowing for total variability of two B-O bonds, i.e. ±0.1 for a given Ø, some of the strongest Pb-O bonds (0.6-0.7) may still be taken up by the bonding deficit of bridging oxygen anions bound to two borate tetrahedra (≈0.5+0.1). This is not enough for the strongest Bi-O bonds, which will therefore favour direct linkage to the "terminal" oxygen anions of higher nominal valence, 1.00 or 1.25 (Table 16), the bridging oxygen ions in B<sub>Δ</sub>-Ø-B<sub>T</sub> and B<sub>T</sub>-Ø-B<sub>T</sub> links being able to take up the weaker bonds for both cations. This speculative interpretation, which still requires confirmation, agrees well with observed behaviour at low *x*: Bi<sup>3+</sup> has much higher deviations from "ideal-modifier" behaviour of *N*<sub>4</sub> than Pb<sup>2+</sup>, and *T*<sub>g</sub> is similar for both cations at same *x*, in spite of the higher valence of Bi<sup>3+</sup>. Also, the preference of Bi<sup>3+</sup> for higher CNs and bond disorder agrees with conservation of high *N*<sub>4</sub> values (i.e. mixed B<sub>Δ</sub>+B<sub>T</sub>) in a wide *x* range, compared to the more ordered crystalline phases and to PbO, which has lower valence and favours lower CNs (Figure 7).

Anomalies in properties<sup>317, 318, 350</sup> such as density and *T*<sub>g</sub> yield other hints on the structure; they are often correlated with compositions close to that of crystalline phases in the corresponding oxide systems. Based on this observation, a tendency to form local groupings in the glass similar to those that exist in the crystals was also postulated for the BaO-Bi<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub> system,<sup>350</sup> as typically found in borate glasses.<sup>402</sup> Comparing data on glassy and crystallised Bi<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub> samples on Figure 7, however, one can see that this structural similitude progressively breaks down at high *x* values, where Bi<sub>2</sub>O<sub>3</sub> becomes the dominant species and obviously assumes the function of network former, with significant amounts of O<sup>2-</sup> anions not bound to boron (i.e. only to Bi<sup>3+</sup>) identified at ca. *x* ≥ 65%.<sup>255, 394</sup>

In these Bi<sub>2</sub>O<sub>3</sub>-rich compositions, in spite of extensive characterisation work with well-controlled samples, there are significant discrepancies in the reported *N*<sub>4</sub> values, as illustrated in Figure 7; the work of Terashima et al. used by Dimitrov<sup>327</sup> seems somewhat at odds with that of Bajaj et al.<sup>317</sup> (and previous work cited by the latter<sup>247</sup>), although the same method (MAS-NMR) was used in both cases and sample fabrication appeared to be well-controlled (moderate melting temperatures and noble metal crucibles). Residual impurities<sup>317</sup> could possibly account for some of the discrepancies, as well as thermal history (quenching rate and subsequent annealing), which significantly influences glass properties<sup>376</sup> and even structure (see discussion on "polyamorphism"<sup>280, 317</sup>); interestingly, Terashima's data lies roughly halfway between Bajaj's for glassy and crystallised samples.

Given the differences in *N*<sub>4</sub> between crystalline and glassy samples, shifts of the CN of Bi<sup>3+</sup> in glass vs. in crystals can also be expected, but Bi<sup>3+</sup> is less sensitive in this respect than Pb<sup>2+</sup>, as seen in supplement 13. In fact, most structural studies<sup>132, 255, 275, 276, 326, 352, 359, 360</sup> in the binary or almost binary Bi<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub> system favour retention of "distorted [BiO<sub>6</sub>] octahedra" throughout the composition range, and low-CN groups are not seen in Bi<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub> glasses at least up to *x* ≈ 70%. Above this level, presence of a minority of [BiO<sub>3</sub>] groups has been reported<sup>357, 394</sup> (threshold uncertain due to likely significant contamination from the Al<sub>2</sub>O<sub>3</sub> crucible), in line with the structure of high-Bi<sub>2</sub>O<sub>3</sub> crystalline boron sillenite Bi<sub>12</sub>(Bi<sub>0.25</sub>B<sub>0.50</sub>)O<sub>19.125</sub>, (see supplement 13). This agrees well with [BiO<sub>3</sub>] groups appearing together with sillenite crystallisation for ca. *x* ≥ 65% in heat-treated glasses.<sup>276, 394</sup> The reported presence of [BiO<sub>3</sub>] groups at moderate Bi contents in borate, borosilicate<sup>362</sup> and aluminoborate<sup>277, 278</sup> glasses is doubtful, and most likely results from IR peak misassignment, expected [BiO<sub>3</sub>] peaks lying at ≈480 and 840 cm<sup>-1</sup>.<sup>276, 357, 374, 394</sup>

Substituting some of the Bi<sub>2</sub>O<sub>3</sub> with compounds such as ZnO, PbO and BaO<sup>350, 352, 355</sup> yields results very similar to that of Bajaj & Bishay,<sup>247, 317</sup> as shown for Zn in Figure 7, with only slight offsets due to the elemental substitution. Ba<sup>2+</sup> enters the glass as a modifier,<sup>266</sup> while Zn<sup>2+</sup> may do the same at low concentrations,<sup>266</sup> but forms [ZnO<sub>4</sub>] tetrahedra at high ones.<sup>122, 406</sup>

Concerning more complex systems, presence of [BiO<sub>3</sub>] groups is reported in (Li<sub>2</sub>O)-ZnO-Bi<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub><sup>264, 337, 406</sup> and Li<sub>2</sub>O-Bi<sub>2</sub>O<sub>3</sub>-(B<sub>2</sub>O<sub>3</sub>)<sup>334, 335</sup> glasses only at high Bi<sub>2</sub>O<sub>3</sub> and low B<sub>2</sub>O<sub>3</sub> contents, Bi<sup>3+</sup> being otherwise present as [BiO<sub>6</sub>] only.

Compared to Bi<sup>3+</sup>, the coordination of Pb<sup>2+</sup> is somewhat more ordered and much more dependent on  $x$  in binary borate glasses, according to XRD and MAS-NMR studies:<sup>397</sup> CN is 6 up to ca.  $x = 25\%$ , then decreases continuously, reaching 3 for  $x \geq \approx 55\%$ , which is matched by a corresponding decrease of average bond length from  $\approx 300$  down to 233 pm. Pb<sup>2+</sup> is therefore roughly present as [PbO<sub>6</sub>] octahedra and behaves somewhat as a classical modifier at low  $x$ , and progressively switches at higher  $x$ , well within the vitrification range, to [PbO<sub>3</sub>] network-forming trigonal pyramids (3-PyM), with fewer, stronger Pb-O bonds. However, while the average bond length found for [PbO<sub>3</sub>] agrees well with bonding in Pb-rich crystalline compounds (supplement 13), the corresponding length for [PbO<sub>6</sub>] is clearly too long, which suggests bonding is also somewhat inhomogeneous at low  $x$  (existence of shorter bonds). This, together with  $N_4$  being slightly less than ideal and  $T_g$  starting to drop at lower  $x$  values than the CN, hints at some departure of Pb<sup>2+</sup> from pure modifier behaviour, even at low  $x$ , albeit to a much lesser extent than Bi<sup>3+</sup>. At high  $x$ , there is also some ambiguity in the 3-PyM configuration, as there are additional, weaker bonds, as seen in the crystals;<sup>407</sup> the configuration can be viewed as 4-PyM (more 3+1, with one longer bond), with additional, much longer ones above the pyramid apex.

#### *Silicate and germanate glasses*

The case of silicate<sup>408</sup> and germanate<sup>231, 374, 393, 409</sup> glasses is much simpler, as the [SiO<sub>4</sub>] and [GeO<sub>4</sub>] tetrahedra are conserved when Bi<sub>2</sub>O<sub>3</sub> is added, with no reported formation of [GeO<sub>6</sub>] octahedra as found in the alkaline germanate glasses. The only change is gradual weakening of the original network, as attested by the continuous drop of  $T_g$  with increasing  $x$  in the  $x \cdot \text{BiO}_{1.5} + (1-x) \cdot (\text{Ge}, \text{Si})\text{O}_2$  system, as shown in Figure 3 for silicates. Absence of [GeO<sub>6</sub>] octahedra was also reported in complex germanate glasses, with V<sub>2</sub>O<sub>5</sub>,<sup>231</sup> Ga<sub>2</sub>O<sub>3</sub><sup>359, 360</sup> and PbO-Ga<sub>2</sub>O<sub>3</sub><sup>370</sup> additions.

Bi<sup>3+</sup> is generally reported as being present in the form of [BiO<sub>6</sub>] groups, but also as [BiO<sub>5</sub>], from XAS spectra and molecular dynamics (MD) calculations.<sup>408</sup> Given the very high disorder around Bi<sup>3+</sup>, this difference in reported structure is probably not very significant. As for borates, no [BiO<sub>3</sub>] groups were found to high  $x$  values (80%) in Bi<sub>2</sub>O<sub>3</sub>-GeO<sub>2</sub>(-Eu<sub>2</sub>O<sub>3</sub>) glasses. On the other hand, after heat treatment and crystallisation, [BiO<sub>3</sub>], [BiO<sub>6</sub>], [GeO<sub>4</sub>] and [GeO<sub>6</sub>] groups appeared, with Bi<sub>2</sub>GeO<sub>5</sub>, Bi<sub>4</sub>Ge<sub>3</sub>O<sub>12</sub> and unidentified peaks seen in the XRD spectra.<sup>374</sup> Neither [BiO<sub>3</sub>] 3-PyM pyramids nor [GeO<sub>6</sub>] octahedra exist in the identified crystalline structures (supplement 13), but this apparent conflict may be resolved for [BiO<sub>3</sub>], assuming some of the unidentified crystalline phase is the [BiO<sub>3</sub>]-containing Ge sillenite Bi<sub>12</sub>GeO<sub>20</sub>, whose formation would be expected at  $x = 80\%$ , as seen in borates.<sup>276, 394</sup> The presence of [GeO<sub>6</sub>] is more doubtful, as it is also absent in sillenite and Bi<sub>2</sub>Ge<sub>3</sub>O<sub>9</sub> as well, but could be possible in the residual glass due to the thermal history or in an unidentified metastable phase.

The existence of [GeO<sub>6</sub>] groups in PbO-GeO<sub>2</sub> glasses has been reported, albeit to a much lower extent than in the alkali germanates,<sup>12, 410</sup> but more recent work<sup>409</sup> concludes to all Ge<sup>4+</sup>

being in [GeO<sub>4</sub>] tetrahedra. There is basic consensus that Pb<sup>2+</sup> forms [PbO<sub>3/4</sub>] (3/4-PyM) pyramids in Pb-rich PbO-SiO<sub>2</sub><sup>407, 411, 412</sup> and PbO-GeO<sub>2</sub><sup>413</sup> glasses. On the other hand, Pb<sup>2+</sup> coordination at lower lead contents has been questioned recently. CN = 6 was found at up to 40% PbO in PbO-GeO<sub>2</sub><sup>410</sup> and progressive switch from network modifier to former behaviour (presumably [PbO<sub>6</sub>] → [PbO<sub>3/4</sub>]) up to 40% PbO in PbO-SiO<sub>2</sub>.<sup>414</sup> Somewhat at odds with these results, Pb<sup>2+</sup> was found to form [PbO<sub>3/4</sub>] pyramids down to 30% PbO in PbO-SiO<sub>2</sub>,<sup>412</sup> a behaviour similar to that found in SnO-SiO<sub>2</sub> glasses, where Sn<sup>2+</sup> essentially appears in 3-PyM coordination, with CN only slightly increasing at low SnO contents.<sup>415</sup>

### *Phosphate glasses*

The binary Bi<sub>2</sub>O<sub>3</sub>-P<sub>2</sub>O<sub>5</sub> system has received only scant attention due to its limited vitrification range, which probably stems from easy crystallisation of high-melting BiPO<sub>4</sub>.<sup>377</sup> Bi<sub>2</sub>O<sub>3</sub> is therefore mostly found as an additive (intended or as waste<sup>96, 98</sup>) in multicomponent glasses.

Replacing part of Fe<sup>3+</sup> in a 40Fe<sub>2</sub>O<sub>3</sub>-60P<sub>2</sub>O<sub>5</sub> glass with isovalent Bi<sup>3+</sup> is found to effect only limited changes to the structure;<sup>228</sup> expectedly, the phosphate groups are mostly present as Q<sub>1</sub> pyrophosphate units,<sup>209, 210</sup> and both Fe<sup>3+</sup> and Bi<sup>3+</sup> are present as hexacoordinated octahedral units. Similar incorporation as [BiO<sub>6</sub>] was determined for ZnO-Bi<sub>2</sub>O<sub>3</sub>-P<sub>2</sub>O<sub>5</sub><sup>262, 265, 267</sup> and Li<sub>2</sub>O-Bi<sub>2</sub>O<sub>3</sub>-P<sub>2</sub>O<sub>5</sub><sup>378</sup> glasses. As for the other systems, Bi<sub>2</sub>O<sub>3</sub> was concluded to behave partly as a network former. In comparison, SnO in 3-PyM coordination can also enter the glass network, being able to vitrify with fully depolymerised phosphate groups.<sup>218</sup>

### *Gallate glasses*

Ga<sup>3+</sup> is found to form [GaO<sub>4</sub>] tetrahedral groups in HMO glasses throughout the ternary PbO-Bi<sub>2</sub>O<sub>3</sub>-Ga<sub>2</sub>O<sub>3</sub><sup>109, 111, 385, 386</sup> and Bi<sub>2</sub>O<sub>3</sub>-Ga<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub><sup>359, 360</sup> systems, as well as more complex PbO-(PbF<sub>2</sub>)-Bi<sub>2</sub>O<sub>3</sub>-Ga<sub>2</sub>O<sub>3</sub>-GeO<sub>2</sub><sup>370, 371</sup> compositions, with good agreement of Ga-O bond lengths with those found in crystals.<sup>109, 111</sup> As in other HMO-rich systems, Bi<sup>3+</sup> and Pb<sup>2+</sup> are reported to form "[BiO<sub>6</sub>]" groups and [PbO<sub>3/4</sub>] (3/4-PyM) pyramids respectively, with a higher degree of disorder around Bi<sup>3+</sup>.

In these glasses, coordination around Bi<sup>3+</sup> and Pb<sup>2+</sup> has been examined more extensively. Assignment of Raman bands for Bi-O bonds<sup>360</sup> agrees with the Bi<sup>3+</sup> bonding in crystals (Supplement 13, deformed 5-Py14 pyramids), with a short apical bond, and 2 groups of unequal bonds on either side of the pyramid base. The last, much weaker bond assigned in glasses to complete a "[BiO<sub>6</sub>] octahedron" could actually correspond to a pair, as found in the 7-Py142 configuration often reported in crystals. These results also agree very well with detailed neutron & XRD studies of a binary 80BiO<sub>1.5</sub>+20GaO<sub>1.5</sub> glass,<sup>109</sup> which yield CN ≈ 5 for Bi<sup>3+</sup>, with roughly 1, 2 and 2 oxygen anions at 213, 224 and 252 pm respectively. Obviously, CN of Bi<sup>3+</sup> stays high even for a very Bi-rich glass, influencing the CN of Pb<sup>2+</sup> in the ternary PbO-Bi<sub>2</sub>O<sub>3</sub>-Ga<sub>2</sub>O<sub>3</sub> system, which was found to decrease from 3.5 for Bi-free glasses to 3.0 for Bi-rich ones.<sup>111</sup> This is logical, as the higher oxygen CN of Bi<sup>3+</sup> creates a severe oxygen shortage, which is partly compensated by decrease of Pb<sup>2+</sup> CN. Nevertheless, in all these HMO-rich glasses, CN > 2 for oxygen, with CN = 3.5 for the binary 80BiO<sub>1.5</sub>+20GaO<sub>1.5</sub> glass.

### *Other glasses*

Vanadate<sup>231, 232</sup> and molybdate<sup>232, 234</sup> glasses exhibit a change of network former coordination polyhedra when adding Bi<sub>2</sub>O<sub>3</sub>: [VO<sub>5</sub>] trigonal bipyramids and [MoO<sub>6</sub>] octahedra are converted to [VO<sub>4</sub>] and [MoO<sub>4</sub>] tetrahedra respectively. Tellurates are even more complex, and tend to integrate only little Bi<sub>2</sub>O<sub>3</sub>, together with a 3<sup>rd</sup> oxide; the original irregular [TeO<sub>4</sub>] trigonal bipyramid (4-BPy, Te<sup>4+</sup> also being a lone-pair ion) of TeO<sub>2</sub> is partly converted,



depending on Bi<sub>2</sub>O<sub>3</sub> and other oxides, to [TeO<sub>3</sub>] (3-PyM) pyramids and [TeO<sub>3+1</sub>] polyhedra.<sup>120, 126, 237, 239, 240</sup> Bi<sup>3+</sup> is reported to form "[BiO<sub>6</sub>]" groups, as with standard network formers.

#### *Glasses without network formers*

Structural studies on systems where mainly Bi<sub>2</sub>O<sub>3</sub> forms the network are relatively scarce. In Li<sub>2</sub>O-Bi<sub>2</sub>O<sub>3</sub> glasses, a disordered local structure, analogous to crystalline Bi<sub>2</sub>O<sub>4</sub>, was assumed; it was rationalised that the nominal additional oxygen was provided by Li<sub>2</sub>O, and even very atypical partial oxidation to Bi<sup>5+</sup> (see supplement 12), the rest being compensated by defects.

Structural analysis of glasses based on a nominal 89BiO<sub>1.5</sub>+11PbO formulation, probably contaminated with Al<sub>2</sub>O<sub>3</sub> from the crucible and optionally doped with MnO<sub>y</sub>, expectedly yields coordination of Pb<sup>2+</sup> as [PbO<sub>3/4</sub>] (3/4-PyM) groups. Bi<sup>3+</sup> was found in the Mn-free glass mainly as [BiO<sub>6</sub>] groups, with a minority of [BiO<sub>3</sub>]. However, the reported exclusive formation of [BiO<sub>3</sub>] pyramids in Mn-doped glass must be taken with caution, as this does not correspond to any relevant Bi-based compound.

#### *Conclusions*

Concerning the coordination of Bi<sup>3+</sup> in glass, most infrared and Raman spectroscopic studies on conclude that Bi<sup>3+</sup> essentially forms distorted [BiO<sub>6</sub>] (CN ≈ 6) octahedral-like configuration, with little variation of CN over a wide concentration range; a minority of [BiO<sub>3</sub>] pyramids is found only in very Bi-rich compositions, in agreement with their presence in the sillenite crystalline structure (see supplement 13). The term "[BiO<sub>6</sub>] octahedron" must be taken with proper caution, as coordination around Bi<sup>3+</sup> tends to be ill-defined; more dedicated studies<sup>109, 408</sup> yield CN ≈ 5 with nonuniform bond lengths, corresponding to a deformed octahedron with an oxygen vertex replaced by the Bi<sup>3+</sup> lone pair E and thus yielding a [BiO<sub>5</sub>E] unit (Figure 8, 5-Py14 configuration). This agrees well with assignment of Raman bands;<sup>360</sup> the additional Raman band attributed to a further, weaker bond could in fact correspond to two such bonds, matching the 7-Py142 configuration often found in crystalline compounds.

The high CN maintained by Bi<sup>3+</sup> to high concentrations necessitates a CN of O<sup>2-</sup> greater than 2, apparently violating the classical rules for glass formation.<sup>416</sup> This is also true for Pb<sup>2+</sup> and Sn<sup>2+</sup>, which have lower CN but lower valence as well. However, in contrast to Bi<sup>3+</sup> and Sn<sup>2+</sup>, coordination around Pb<sup>2+</sup> is seen – at least in some cases such as the PbO-Bi<sub>2</sub>O<sub>3</sub>-Ga<sub>2</sub>O<sub>3</sub> and PbO-B<sub>2</sub>O<sub>3</sub> systems – to be more dependent on the local environment and available oxygen to bond to.

A comparison of the analogous divalent and trivalent lone-pair cations (Table 17) sheds new light into their structural features and trends. In line with original predictions,<sup>416</sup> the rigid 3-PyM oxygen coordination shell of the lightest trivalent cation, As<sup>3+</sup>, makes it a classical network former, as is (almost) the case for Sb<sup>3+</sup>, whose coordination is somewhat less rigid.<sup>417, 418</sup> Sn<sup>2+</sup> is relatively rigid and favours a similar coordination, but intrinsically cannot form a glass on its own due to its valence being lower than its CN. Note that As<sup>3+</sup>, Sb<sup>3+</sup> and Sn<sup>2+</sup> are not stable in air, and Sn<sup>2+</sup> tends to disproportionate into Sn<sup>0</sup> and Sn<sup>4+</sup>.

The larger polarisable cations, Pb<sup>2+</sup> and Bi<sup>3+</sup> have much more variable and disorderly coordination shells, with CN behaving somewhat the same way as in crystals, i.e. being somewhat concentration-dependent for Pb<sup>2+</sup>, and less so for Bi<sup>3+</sup>. Nevertheless, a tendency remains to form a limited number (3-4) of comparatively stronger bonds. One can speculatively view this inhomogeneous metal-oxygen bonding as a reflection of the ambiguous behaviour of these cations, as both network formers (through the stronger metal-

oxygen bonds) and network modifiers (through the weak ones); considering the strong bonds only reduces the CN of oxygen, making it more compatible with classical rules of glass formation. More studies are clearly needed to arrive at a better definition of these complex and disordered coordination environments, possibly assisted by MD simulations<sup>408</sup> coupled with cation-oxygen interactions based on recent revisions<sup>403</sup> (see also supplement 13) of lone-pair bonding in crystals.

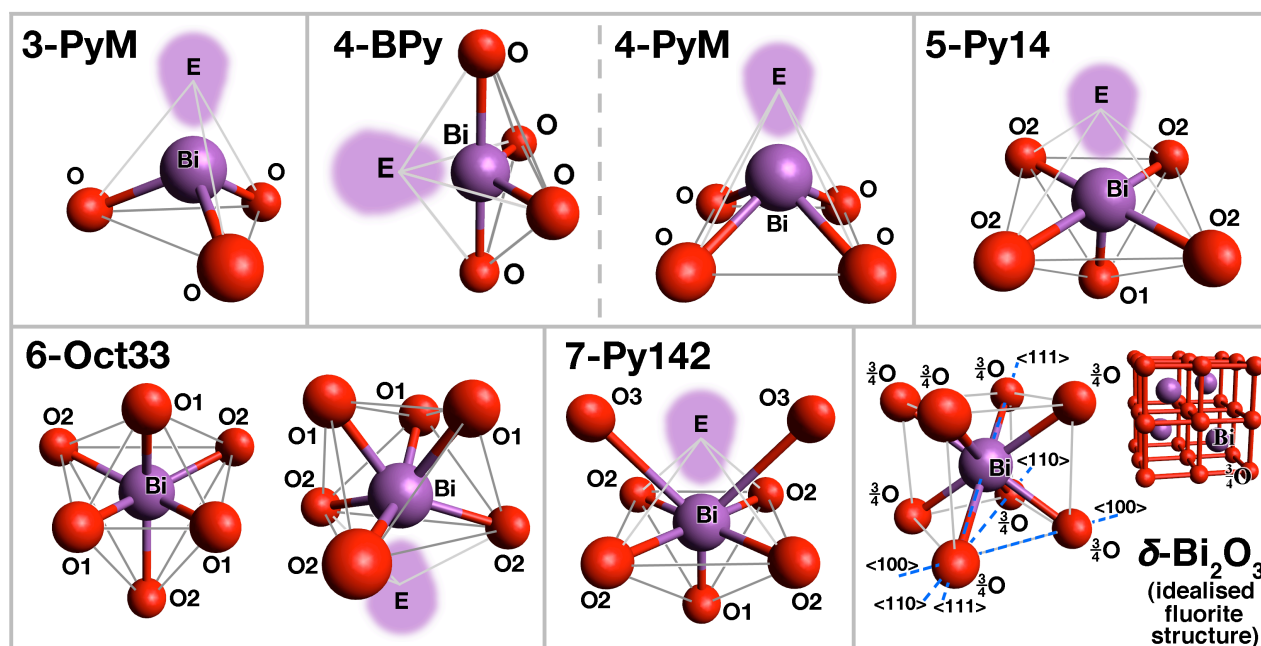


Figure 6. Some oxygen coordination shells around Bi observed in crystalline oxides (see supplement 13 and Table 14). E =  $\text{Bi}^{3+}$  lone-pair electrons.

Table 14. Description of oxygen coordination shells around Bi observed in crystalline oxides (see supplement 13 and Figure 6). E stands for the  $\text{Bi}^{3+}$  lone-pair electrons.

Designation	Description
3-PyM	Trigonal pyramid with Bi apex / $\text{Bi}(\text{O}_3\text{E})$ tetrahedron
4-Py13	Trigonal pyramid with base around Bi ( $\text{O}_1$ = apex, $3 \times \text{O}_2$ = base; E directed opposite to apex, through base) / $\text{Bi}(\text{O}_4\text{E})$ trigonal bipyramid
4-BPy	Face-sharing bipyramid with Bi apex / $\text{Bi}(\text{O}_4\text{E})$ trigonal bipyramid
4-PyM	Square pyramid with Bi apex / $\text{Bi}(\text{O}_4\text{E})$ square pyramid
5-Py14	Square pyramid with base around Bi ( $\text{O}_1$ = apex, $4 \times \text{O}_2$ = base; E directed opposite to apex, through base) / $\text{Bi}(\text{O}_5\text{E})$ octahedron
6-Oct	Octahedron (in general)
6-Oct33	Irregular octahedron with 3 short ( $\text{O}_1$ ) and 3 long ( $\text{O}_2$ ) bonds (E through the large triangle formed by $3 \times \text{O}_2$ )
6-Oct222	Another form of irregular octahedron, with bond lengths in 2+2+2 order
7-Py142	Same as 5-Py14, with 2 additional longer bonds ( $\text{O}_3$ ) below the pyramid base
7-PyM34	Same as 3-PyM, with 4 longer, irregular bonds opposite of apex
7-PyM43	Same as 4-PyM, with 3 longer, irregular bonds opposite of apex
$\delta\text{-Bi}_2\text{O}_3$	Idealised cubic oxygen shell in the high-temperature $\delta$ polymorph of $\text{Bi}_2\text{O}_3$ (fluorite structure), with 6/8 oxygen site occupation and possible vacancy arrangements
8-C26s	Cubic environment ( $\delta\text{-Bi}_2\text{O}_3$ with all oxygen sites occupied), with two shorter bonds along [111], i.e. apparently symmetric
9-Pr333	Tricapped trigonal prism, asymmetric, with three triangles of different bonding lengths

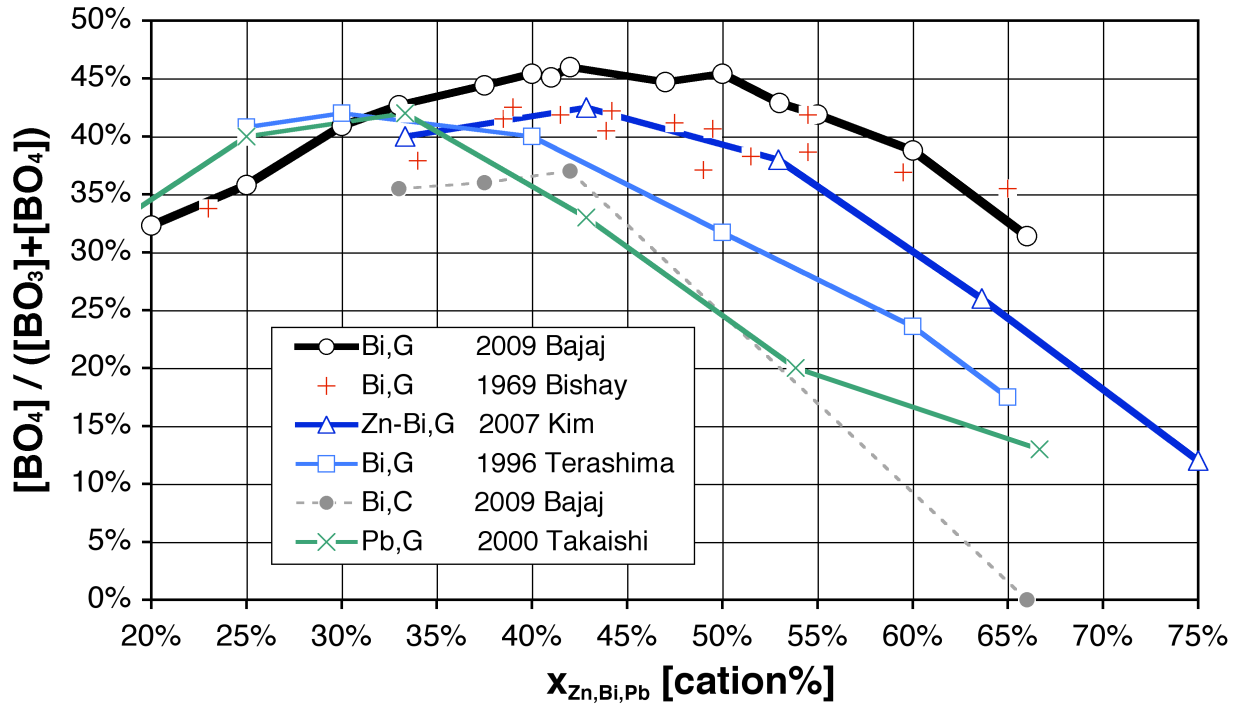


Figure 7. [BO<sub>4</sub>] tetrahedra fraction  $N_4$  in boron coordination polyhedra ([BO<sub>3</sub>] and [BO<sub>4</sub>]), for Bi<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub> glass ( $\circ^{317} + \square^{247}$ ) & crystallised glass ( $\bullet^{317}$ ), (Zn·Bi<sub>2</sub>O<sub>3</sub>)-B<sub>2</sub>O<sub>3</sub> glass ( $\Delta^{355}$ ) and PbO-B<sub>2</sub>O<sub>3</sub> glass ( $\times^{397}$ ).

Table 15.  $T_g$  and  $N_4$  peaks in binary  $x \cdot (\text{BiO}_{1.5}, \text{SbO}_{1.5}, \text{PbO}, \text{SnO}) - (1-x) \cdot \text{BO}_{1.5}$  glasses.

System	Bi <sub>2</sub> O <sub>3</sub> - B <sub>2</sub> O <sub>3</sub> <sup>317</sup>	Sb <sub>2</sub> O <sub>3</sub> - B <sub>2</sub> O <sub>3</sub> <sup>418</sup>	PbO - B <sub>2</sub> O <sub>3</sub> <sup>397</sup>	SnO - B <sub>2</sub> O <sub>3</sub> <sup>398</sup>
Peak $T_g$ (x)	469°C (23%)	300°C (50%)	460°C (17%)	384°C (23%)
Peak $N_4$ (x)	≈45% (38-50%)	11% (50%)	42% (30%)	28% (33%)
"Ideal" x	25%	(see note)	33%	33%

Note. Sb<sub>2</sub>O<sub>3</sub> (Sb<sup>3+</sup>) is close to being a true glass former – B<sub>T</sub> possibly due to observed presence of Sb<sup>5+</sup> ions.

**Table 16. Nominal bonding deficit of oxygen anions in borate glasses vs. structure.**

Oxygen bond	O / Ø nominal bonding deficit [valence units]
B <sub>Δ</sub> – Ø – B <sub>Δ</sub>	0.00
B <sub>Δ</sub> – Ø – B <sub>T</sub>	0.25
B <sub>T</sub> – Ø – B <sub>T</sub>	0.50
B <sub>Δ</sub> – O <sup>-</sup>	1.00
B <sub>T</sub> – O <sup>-</sup>	1.25
O <sup>2-</sup>	2.00

**Table 17. Oxygen coordination trends of "lone-pair" cations vs. concentration x.**

Shell	+2		x	+3	
	Ion	Coord. <sup>a</sup>		Coord. <sup>a</sup>	Ion
4s <sup>2</sup>	-	-	(All)	3-PyM	As <sup>3+</sup>
5s <sup>2</sup>	Sn <sup>2+</sup>	3-PyM	(All)	3-PyM	Sb <sup>3+</sup>
6s <sup>2</sup>	Pb <sup>2+</sup>	3/4-PyM <sup>b</sup> ≈6 <sup>d</sup>	High Low	5-Py14 <sup>c</sup> ≈5-7 <sup>d</sup>	Bi <sup>3+</sup>

**Notes**

- a) Coordination shells: see Figure 6 & Table 14  
 b) 4-PyM often 3+1 (1 longer bond)  
 c) 5-Py14 often 1+2+2 (1 short, 2 medium, 2 long bonds); exceptionally 3-PyM as in sillenites.  
 d) Variable, disordered oxygen coordination shells, more so for Bi<sup>3+</sup> than for Pb<sup>2+</sup>

### **3.4. Oxidoreduction issues**

Possible reduction of Bi<sup>3+</sup> to metal during glass preparation,<sup>118</sup> and later during processing, for instance through transient reducing conditions brought about by binder burnout, is even more pronounced than for Pb<sup>2+</sup>, as Bi<sub>2</sub>O<sub>3</sub> is even less stable towards reduction than PbO.<sup>59, 419-422</sup> This can be a problem for processing, especially of low-melting glasses due to difficulty in burning out the organics. One must however mention that precious metal oxides used in TFRs, such as RuO<sub>2</sub>, are even much less stable towards reduction (see PDC-5015) than Bi<sub>2</sub>O<sub>3</sub>, so Bi<sub>2</sub>O<sub>3</sub> reduction is not the limiting problem overall for standard air-firing thick-film electronics.<sup>423</sup> Finally, a moderate sensitivity to reduction actually can be beneficial in some respects, especially solderability of conductors (see section 4.5).

Unfortunately, information about the thermodynamics of Bi<sub>2</sub>O<sub>3</sub> (and other oxides) in glasses is rather limited: polarimetric studies were carried out<sup>424</sup> on a borosilicate glass with very low (0.25% mol) Bi<sub>2</sub>O<sub>3</sub> additions, but the results are not directly applicable to glasses where Bi<sub>2</sub>O<sub>3</sub> is one of the main components, as those concerned in the present work. Nevertheless, recent reduction experiments<sup>366, 408, 425-427</sup> and results of high-temperature firing<sup>118, 375</sup> do confirm easy reduction and formation of Bi<sup>0</sup> nanoparticles, or, for glasses doped with low amounts Bi, presumably reduced species, whose nature is still subject to debate.<sup>428-430</sup>

Control of reduction, as in more common industrial glasses, may be achieved by "fining agents", i.e. oxidoreduction buffers that inhibit reduction to Bi<sup>0</sup> under practical firing conditions; this has been shown to be successful with low Sb, As, Ce or Cu additions,<sup>112, 114, 273, 361, 431</sup> with CeO<sub>2</sub> often found in the patent literature.<sup>311, 314, 432</sup> Alternatively, using a fugitive oxidant such as KClO<sub>4</sub> and KNO<sub>3</sub> allows controlled reduction and precipitation of Bi<sup>0</sup> nanoparticles to create a well-defined surface plasmon resonance (SPR) band.<sup>427</sup> Additionally, the other main glass constituents, by affecting the overall basicity of the glass, will also somewhat influence the tendency of Bi<sup>3+</sup> towards reduction.<sup>399, 430</sup>

Finally, further oxidoreduction issues involving interaction with adjacent layers, such as adhesion on metal (section 4.4), staining of glasses by in-diffusion from Ag conductors (4.2) and contacts to PV cells (4.5), as well as optical properties, are discussed in the corresponding sections. Also, a strong point is made in supplement 12 against – except in unusual circumstances – the occasionally reported presence of significant amounts of Bi<sup>5+</sup> in glasses.

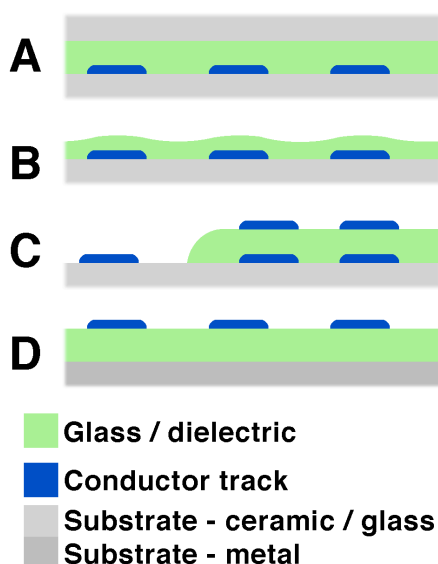
## 4. Applications in layer form

This section discusses in more detail the application of Bi<sub>2</sub>O<sub>3</sub>-based glasses, using thick-film or similar technology, to electronics, automotive and architectural glass, display panels and photovoltaics. Uses in bulk form are discussed in section 5. The present discussion will mostly concentrate on materials covering the low processing temperature range, the main application of the Bi<sub>2</sub>O<sub>3</sub>-based glasses and the PbO-based ones they should replace.

Parts 4.1 to 4.4 discuss applications of insulating glass-based layers in the four main configurations illustrated in Figure 8, each corresponding to a specific role for the glass-based layer and determining the required behaviour during firing and the insulating characteristics: A) sealing, B) overglazing / enamelling, C) multilayer dielectrics and D) dielectrics for insulating metal substrates. Part 4.1 also discusses glass stability upon refiring, as low-temperature sealing is the most demanding application in this respect. Finally, parts 4.5 and 4.6 discuss conductors / metallisations, and TFRs respectively.

### 4.1. Sealing & glass stability during reflow

Sealing stands apart from the other applications in that the sealing material must ideally be able to flow extensively during processing, in contrast to the other applications, where densification only is to be achieved. In the classical leaded sealing glasses, some of the PbO is often replaced by Bi<sub>2</sub>O<sub>3</sub> to improve flowability,<sup>150, 151, 242</sup> stability against devitrification and compatibility with temperature-lowering fluoride additions,<sup>149</sup> or even strength,<sup>152</sup> However, as discussed in section 3.1, replacing most or all of the PbO by Bi<sub>2</sub>O<sub>3</sub> results in increased viscosity,<sup>149</sup> which may in most cases be mitigated by alkaline or fluoride additions to the extent durability and stability is not excessively degraded. As possible conductors going through the seal are usually only in a side-by-side configuration (Figure 8A), insulating properties should not be critical in most applications, except in PDPs,<sup>181, 308</sup> where conductors are on both sides.



**Figure 8.** Typical configurations / roles for dielectric glass-based layers: A) sealing glass; B) overglaze; C) multilayer dielectric; D) insulating dielectric on metallic substrate.



Sealing glass may be formulated to be either stable or devitrifying.<sup>15, 18, 74</sup> Ideally, devitrifying seals yield the best properties, but they also tend to have tight processing requirements, limited flowability and are usually not applicable for low-temperature sealing, where "composite" glasses are used, i.e. stable glasses with low-expansion fillers to adjust the CTE.<sup>18</sup> In any case, extensive flow must be insured without or before crystallisation, which means sealing is arguably the most demanding application in terms of glass stability. In terms of glass formulation, this requirement tends to be in contradiction with the need for low softening temperature, as discussed hereafter.

Glass stability and devitrification in the Bi<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub> binary system, which is the basis for most of the commercial formulations, has been the object of several studies.<sup>110, 317, 318, 326</sup> Except the oldest study,<sup>110</sup> they agree on a practical stability optimum near 45% BiO<sub>1.5</sub>, in agreement with the break in the liquidus temperature (Figure 2), vs. falling  $T_g$  (Figure 3); this somewhat lower optimum than Figure 2 would suggest lies in crystallisation of the metastable phase BiBO<sub>3</sub>.<sup>318</sup>

As discussed in section 3.2, small additions of other network formers and modifiers, as well as oxides such as Fe<sub>2</sub>O<sub>3</sub> and lanthanides, hinder crystallisation; ZnO-Bi<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> compositions specified in the early Soviet patents (Table 7; B80, B82 and B89), reported there as non crystallising and containing no alkalis, provide a good starting basis for low-temperature sealing glasses, and the overwhelming majority of the subsequent research and patent literature report very similar compositions.

Hasegawa et al.,<sup>313, 314</sup> in their patent applications, performed arguably the most extensive discussion – although very empirical and on a weight basis – of composition optimisation and stability in this system; the resulting restrictions, converted to a cation molar percentage basis, are given in Table 18 and discussed hereafter.

The indicated data are according the second application,<sup>314</sup> which specifies a minimum amount of Al<sub>2</sub>O<sub>3</sub> (recognising its beneficial effect on glass stability), and introduces a second, more restrictive composition range for low-temperature FPD sealing with fillers, which apparently requires even better stability against crystallisation. This can be due to the filler possibly promoting crystallisation and the sealing temperature lying in the range where crystallisation is most apt to occur; sealing processes that require stronger capillary flow or firing of conductors / resistor frits occur at higher temperatures where crystallisation is less likely, i.e. slightly below or even above the liquidus.

Overall, the requirements stated in Table 18 and corresponding compositions (Table 7-Hg) correlate fairly well with glass formation (section 3.2) and properties (3.1), as well as with our own preliminary reflow stability experiments, performed with glass frits printed on alumina and glass and summarised in Figure 9. The main network former is B<sub>2</sub>O<sub>3</sub>, to minimise processing temperatures, with SiO<sub>2</sub> and preferably some Al<sub>2</sub>O<sub>3</sub> being added to improve stability.

The beneficial effects of mixing B<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> are illustrated by comparing with other work where either B<sub>2</sub>O<sub>3</sub> or SiO<sub>2</sub> were used alone,<sup>311, 355, 433</sup> densification is reported to be problematic, with a strong tendency to crystallisation.<sup>355, 433</sup> Crystallisation problems may also be inferred from a higher sealing temperature, in spite of a low filler volume fraction.<sup>311</sup> In accordance with Table 18<sup>314</sup>, using a very low amount of SiO<sub>2</sub> in SrO-ZnO-Bi<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub> (Nch-01), is reported to yield a devitrified seal, albeit with enough prior flow to achieve successful densification.<sup>312</sup>



Table 18. Composition ranges and ratios specified for sealing glass stability.<sup>314</sup>

Cation	Limits "Magnetic head" High flow, without fillers [cation %], low-high		Limits "FPD seal" Low flow, with fillers [cation %], low-high	
	Zn	7	– 29	16
Bi	23	– 59	39	– 52
B	13	– 29	15	– 32
Si	1.3	– 22	2.4	– 9
Al	0.2	– 4	0.2	– 4
Zn/B ratio	35	– 120	47	– 107
Al/Si ratio	1	– 59	1	– 59
Li	0.0	– 13	0.0	– 16
Na	0.0	– 10	0.0	– 16
K	0.0	– 9	0.0	– 6
Li+Na+K	0.0	– 19	0.0	– 16
Mg	0.0	– 15	0.0	– 7
Ca	0.0	– 13	0.0	– 11
Sr	0.0	– 10	0.0	– 6
Ba	0.0	– 9	0.0	– 4
Mg+Ca+Sr+Ba	0.0	– 20	0.0	– 12
Ln, Ce	0.1	– 8	0.1	– 4

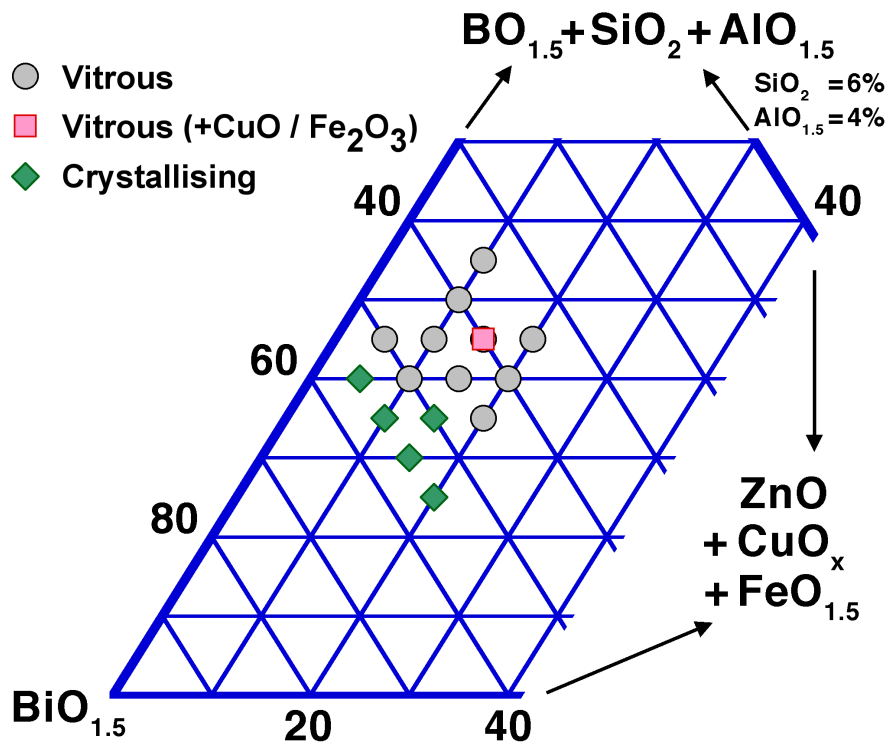


Figure 9. Results, in cation%, of our experiments on stability of Bi<sub>2</sub>O<sub>3</sub>-based glasses in TF firing cycles (belt oven, 45 min total time with 10 min at peak, 400-700°C).

Stability is improved by low levels of ZnO and alkaline earth additions, and degraded by excessive amounts, in line with vitrification studies (see e.g. Figure 4) and other work.<sup>263</sup> The stated maximum amounts of alkaline earths should be taken with caution, as they were added without regard to ZnO; a more pertinent test would be to add them with corresponding reduction of ZnO, i.e. keeping Zn + alkaline earths constant. Rare earths (Ln), including cerium, are stated to improve mechanical strength, an advantage compounded by CeO<sub>2</sub> being a useful fining agent (section 3.4), and a low level of lanthanides providing stability vs. devitrification.<sup>275</sup> One not mentioned compound is Fe<sub>2</sub>O<sub>3</sub>, which is reported, together with CuO<sub>y</sub> / MnO<sub>y</sub>, to be a useful alternative to Al<sub>2</sub>O<sub>3</sub> against devitrification in modern very low-melting lead-bearing sealing glasses,<sup>149, 151, 242</sup> interestingly, Fe<sub>2</sub>O<sub>3</sub> seems to stabilise Bi<sub>2</sub>O<sub>3</sub>-based glasses as well.<sup>255</sup> These effects are expected to strongly depend on composition, i.e. formed crystalline phase(s) according to phase diagram, i.e. borates for low-melting glasses. In higher-melting, essentially Bi<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> glasses, crystallisation of Bi<sub>2</sub>SiO<sub>5</sub> has been found to be promoted by Cr<sub>2</sub>O<sub>3</sub>, but inhibited by CuO<sub>y</sub> and MnO<sub>y</sub>.<sup>301</sup>

Practical sealing examples, taken from the patent literature,<sup>149, 242, 311, 314</sup> given in Table 19, illustrate the potential of the new Bi-based glasses (Hg-203/324 / Usu-5) for low-temperature sealing, well below the softening point of common float glass, and thus clearly demonstrates their industrial usefulness.

On the other hand, these examples also illustrate the remaining gap with the Pb-bearing frits (LTS) for ultra low-temperature sealing of electronic and optical devices at temperatures compatible with some engineering polymers, e.g. glass fibre coatings,<sup>242</sup> in spite of these compositions not containing any alkalis. However, further studies combining fluxing additives such as F<sup>-</sup>, TeO<sub>2</sub>, V<sub>2</sub>O<sub>5</sub>, Nb<sub>2</sub>O<sub>5</sub>, and MoO<sub>3</sub> with stabilising agents (Ln<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, ...), i.e. optimisation similar to that of the lead-bearing frits, should yield further progress in lowering achievable sealing temperatures.

## **4.2. Overglazing / enamelling**

Low-melting glassy layers (overglazes, or enamels) find a large palette of applications in electronics,<sup>291, 302, 307, 321</sup> displays,<sup>181</sup> automotive / architectural / container glass<sup>33, 47, 432</sup> and cookware / dishware / chinaware,<sup>47, 56</sup> as protective and decorative layers. Examples and properties are given in Table 20.

In TF electronics, overglazes protect resistors against humidity, and Ag-rich conductors against electrochemical migration, thereby improving circuit reliability.<sup>63, 434</sup> Other functions useful during processing are solder masking and protection of resistors against acid electrochemical plating baths. As for sealing, conductors are absent or lie side-by-side (Figure 8B); excellent electrical insulation characteristics are therefore in most cases not necessary, and minor alkali additions are usually allowed.

The choice of a TF overglaze is a balance between limiting the shift in resistor characteristics and guaranteeing a sufficient level of protection. Both standard (e.g. ESL 4771P,

Table 5) and acid-resistant (such as Her CL90-8325, roughly equivalent to lead-bearing ESL-481) lead-free overglazes are now available from most thick-film materials suppliers. For very low required processing temperatures, one may use the sealing glasses discussed in the previous section, adding fillers to increase strength / abrasion resistance or to match the CTE to that of the substrate, or slightly higher-firing glasses.<sup>291</sup>

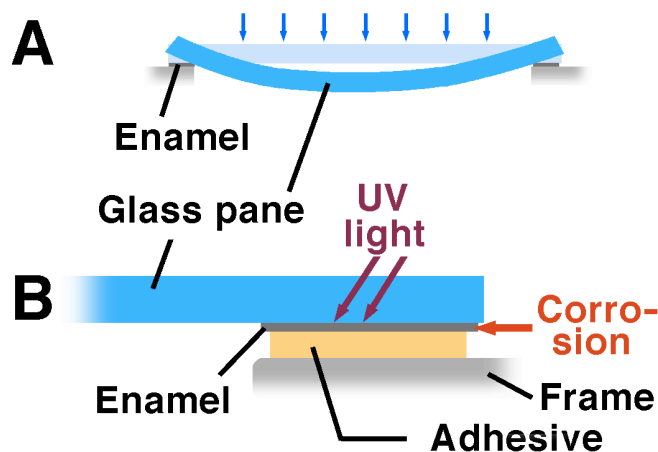
**Table 19. Composite sealing glasses (compositions: see Table 7).**

Glass	Filler & vol.%	T <sub>s</sub> <sup>*</sup> [°C]	T <sub>seal</sub> <sup>*</sup> [°C]	CTE <sub>glass</sub> [ppm K <sup>-1</sup> ]	CTE <sub>seal</sub> [ppm K <sup>-1</sup> ]
Hg-203 <sup>314</sup>	Cordierite 62% (40) <sup>††</sup>	410	460	10.8	7.2
Hg-324 <sup>314</sup>	ZrSiO <sub>4</sub> 58% (50) <sup>††</sup>	422	472	10.4	6.9
Usu-5 <sup>311</sup>	ZrSiO <sub>4</sub> 32% <sup>†</sup>	-	500	(11)	7.9
LTS-1 <sup>149</sup>	Cordierite 30% ZrSiO <sub>4</sub> 10%	297 <sup>#</sup>	360	13.3	6.4
LTS-2 <sup>242</sup>	PbTiO <sub>3</sub> 18%	235 <sup>#</sup>	<350	(15)	

**Notes.** † Calculated assuming glass density ≈6'500 kg/m<sup>3</sup> – †† values for Hg-203/324 (examples 6A and 6D) in original work dubious (too high) – confusion with volume fraction (40 / 50%) likely. \* T<sub>s</sub> = Littleton softening point, at which viscosity η is 10<sup>6.6</sup> Pa s; T<sub>seal</sub> = sealing temperature. # LTS-1 estimated as T<sub>g</sub>+50 K; LTS-2 as flow point-30 K.

**Table 20. Overglaze / enamel / dielectric properties (glass compositions: see Table 7).**

Glass	Firing temp. [°C]	Description
Hy-29 <sup>321</sup>	650	Acid-resistant TFR overglaze
Don-01/04 <sup>307</sup>	620	As above; low TFR drift
Fri-1 <sup>48</sup>	700	Forms Zn <sub>2</sub> SiO <sub>4</sub> & Bi <sub>4</sub> (SiO <sub>4</sub> ) <sub>3</sub> , poor acid durability
Fri-2 <sup>48</sup>	700	As above, +Bi <sub>4</sub> Ti <sub>3</sub> O <sub>12</sub> ; durability limited by glass
Lvx-1 <sup>56</sup>	560	Enamel for aluminium alloys
L-Bi12 <sup>323</sup>	525-625	Filled with ≈40% vol. Al <sub>2</sub> O <sub>3</sub> / SrTiO <sub>3</sub> , poor refire stability



**Figure 10. Application of enamel to automotive glass, as (A) anti-stick layer during forming and (B) adhesive protection layer. Redrawn from Sakoske.<sup>47</sup>**

As for the older lead-bearing glasses, acid-resistant types require a higher firing temperature, ca. 600°C, than standard ones. However, extensive publications on the chemistry and properties of Bi-based TFR overglazes are still lacking, although some examples are available in the patent literature (Table 20, Hy-29<sup>321</sup> & Don-01/04<sup>307</sup> for the ≈600°C-firing types); information may be garnered, for the low-firing (≤550°C) type, from sealing glasses.<sup>289, 290, 293, 313, 314</sup>

A related application is the overglazing of displays (FPDs), where, besides providing suitable protection, the overglaze must avoid excessive degradation of the transparent conductor, usually indium tin oxide (ITO) on the glass. This is achieved using low-firing glasses similar to the sealing types, with a low level of In<sub>2</sub>O<sub>3</sub>, SnO<sub>2</sub> and SbO<sub>y</sub> additives.<sup>297, 308</sup>

Low-firing TF circuits (e.g. for FPDs) mostly use pure or almost pure Ag conductors, as Pd tends to oxidise in the intermediate firing range,<sup>64</sup> which raises the issue of staining by interdiffusion of Ag<sup>+</sup> and probable reprecipitation of Ag<sup>0</sup>. This is prevented by Cu<sup>308, 435</sup> and Cr<sup>306</sup> additions, presumably through oxidoreduction mechanisms.

Compared to consumer electronics, automotive and architectural enamels are exposed to much more severe outdoors environments, such as acid rain.<sup>33, 47, 48</sup> In a way typical of the high-volume cost-sensitive automotive industry, single window-rim dark enamel coating fulfils multiple roles, as illustrated in Figure 10: A) anti-stick agent during forming of the panel, and B) hiding of the adhesive and its protection against ultraviolet (UV) light. Moreover, to optimise costs, the enamel must fire and achieve anti-stick properties reliably during the heating step required for forming of the window pane (650-700°C<sup>47, 436</sup>), and be sufficiently resistant to atmospheric attack to avoid requiring extra protective layers.

Such enamels have recently undergone extensive development, as attested in the patent literature.<sup>298, 299, 301, 432, 436-439</sup> Firing temperatures are in the 600-675°C range suitable for glass processing. First compositions were mainly glassy, relying on pigments to provide anti-stick properties, but have been replaced by crystallising compositions optimised to achieve the best chemical durability. In this respect, the trend has gone from Zn borates<sup>437</sup> to Zn/Bi silicates<sup>438-440</sup> and finally to mixed Bi (Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub>, Bi<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>, Bi<sub>2</sub>Ti<sub>3</sub>O<sub>9</sub>) & other (Zn, V-Bi) titanates,<sup>302, 436</sup> which are claimed to exhibit better chemical resistance to acid attack. This is generally in accordance with the investigations of Fredericci et al.,<sup>48</sup> who report increasing acid resistance going from Zn silicate to Bi silicate to Bi titanate phases, and the facile crystallisation of titanate phases.<sup>48, 363</sup> Other compounds with "acidic" oxides such as V<sub>2</sub>O<sub>5</sub>, Nb<sub>2</sub>O<sub>5</sub>, Ta<sub>2</sub>O<sub>5</sub>, MoO<sub>3</sub> and WO<sub>3</sub>, alone or mixed,<sup>364</sup> may probably have similar beneficial effects on acid resistance, but the composition must also be tuned in order to ensure sufficient durability of the remaining glass phase.

When coating glass or ceramics, an important issue is the degradation of the strength of the glass substrate by application of the enamel.<sup>47, 441</sup> This is not specific to Bi-based glasses, as similar effects have also been observed by our group on ceramic TF circuits with "classical" lead-bearing materials.<sup>442</sup> The implications are significant, as automotive windshields play a structurally important role in cars, and TF electronics are used in high-reliability, safety-critical applications.

### **4.3. Insulating dielectrics**

As reliable crystallisable lead-free dielectrics are readily available for standard 850°C firing conditions,<sup>163</sup> Bi-based glasses are mainly applied to low-firing insulating layers for circuitry on glass (FPDs / PDPs)<sup>181, 308, 431</sup> or metal.<sup>71, 323</sup> Typical configurations are multilayer circuits and crossovers (Figure 8C), as well as the deposition of complete circuits on metal (D).

Dielectrics may be formulated essentially the same way as filled sealing glasses, with the difference that some sort of "stabilisation" is desirable. Otherwise, the dielectric (e.g. L-Bi12, Table 20) tends to reflow upon subsequent firing of conductors and resistors. Stabilisation may be achieved by crystallisation (spontaneous or filler-nucleated)<sup>312</sup> and/or by chemical reaction with the filler, as successfully experimented with PbO-bearing glasses.<sup>161, 162</sup> Bi<sub>2</sub>O<sub>3</sub> should react similarly, with the "acidic" oxides mentioned in the previous section; tuning the reactivity may be achieved by varying the glass composition, as well as the chemistry, amount and particle size of reactive filler.

#### **4.4. Dielectrics on metal substrates**

Commercial thick-film dielectrics / enamels for firing onto stainless steel exist (see

Table 5), but, as the porcelain-enamelled steel they replace, they require high processing temperatures unsuitable for sensors or application to substrates such as titanium (limited by oxidation) or aluminium (limited by melting),<sup>68, 71</sup> and low-firing dielectrics must be used.

However, dielectrics on metal face one important issue stemming from the reducing conditions (section 3.4) at the substrate-dielectric interface; to ensure good adhesion, the formation of soft and low-melting metallic Bi and Pb should be avoided. Pre-oxidation of the metal is not always possible or useful due to reasons such as manufacturing process requirements, insufficient oxide adhesion or thickness. Moreover additional reducing conditions may be generated, on alloys forming Cr<sub>2</sub>O<sub>3</sub> scales such as stainless steels, by chromate formation (Cr<sup>3+→6+</sup>) with glass components such BaO, PbO and Bi<sub>2</sub>O<sub>3</sub>,<sup>443, 444</sup> although Cr may also remain as Cr<sup>3+</sup> in the glass.<sup>373</sup> Therefore, a generally applicable approach on metallic substrates consists in including significant amounts of transition metals that may be partially reduced in the glass (Fe<sup>3+→2+</sup>, Mn<sup>4+→3+→2+</sup>, Co<sup>3+→2+</sup>, Cu<sup>2+→1+</sup>), and that are moreover not deleterious when fully reduced to metal; Co is in fact found in dielectrics for steel substrates (

Table 5). As the situation is very similar to PbO, it is surmised that our previous experiments with Pb-based glasses, where Fe<sub>2</sub>O<sub>3</sub> additions were successfully applied,<sup>68, 71</sup> may be extended to Bi-based ones.

It must be mentioned no adhesion problems were encountered on Al alloys,<sup>445</sup> in spite of the very strong reducing power of Al; it is surmised that formation of Al<sub>2</sub>O<sub>3</sub> rapidly results in the effective stoppage of oxygen diffusion, and hence limited interaction with the substrate, a hypothesis supported by the absence of oxidoreduction buffers in commercial enamels for Al.<sup>56</sup>

The high CTE some metals, such as austenitic stainless steel (17 ppm K<sup>-1</sup>) and aluminium alloys (23) constitutes an additional issue, causing warping of thin substrates and excessive stress build-up in the dielectric. This may be corrected by suitable high-expansion fillers such as quartz, cristobalite, CaF<sub>2</sub> and AlPO<sub>4</sub>, using chemical particle coating techniques if chemical reactions must be limited. In contrast, ferritic low-alloy or stainless steel (≈11 ppm K<sup>-1</sup>) and Ti alloys (8-10) are reasonably well matched with low-melting Bi-based frits (8-11).

As a final note, commercial lead- and alkali-free bilayer low-firing dielectrics on aluminium substrates have recently become available,<sup>446</sup> but no detailed studies on their composition has been carried out to date.

#### 4.5. Metallisations & thick-film conductors

Metallisations and conductors for electroceramic components such as resistors, capacitors voltage limiters, for solar cells, for automotive window heaters and thick-film conductors fundamentally share the same technology, i.e. the starting material is a finely-divided conductor powder such as Ag, Ag:Pd, Au, Cu, with oxide and/or glass frit additive that promote densification and bonding to the substrate.<sup>21, 60, 63, 64, 447-451</sup> While traditional lead borosilicate frits are widely used, application of Bi-based frits in conductors is hardly new, with the 1<sup>st</sup> patent going back to 1945,<sup>283</sup> and such conductors being widely in use by the early 1970's<sup>88, 449, 452</sup> – see also

Table 5. Mixed PbO-Bi<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> glass frits have also been used, and Bi<sub>2</sub>O<sub>3</sub> is also added in its own right, without nominally being part of a glass frit,<sup>158, 159, 288, 310, 452-457</sup> in order to impart good adhesion by reacting with the substrate and potentially also with the metals, as well as for promoting liquation in fritless conductors.<sup>158, 457, 458</sup> Its reactivity with 96%-Al<sub>2</sub>O<sub>3</sub> (+ 3.8% SiO<sub>2</sub> & 0.2% CaO; mass%), 99.9%-Al<sub>2</sub>O<sub>3</sub> and BeO has been extensively studied.<sup>459</sup> Bi<sub>2</sub>O<sub>3</sub> does react with Al<sub>2</sub>O<sub>3</sub>, but reaction with the SiO<sub>2</sub> contained in the glass phase of 96%-Al<sub>2</sub>O<sub>3</sub> is dominant below 850°C. Finally, Bi<sub>2</sub>O<sub>3</sub> (and PbO) may also be added to conductor metallisations for electroceramics that contain these elements, in order to control the chemical interactions.<sup>451</sup> The technical importance of integrating elements in the frit or adding them separately is not clear, i.e. avoidance of patent infringement may also play an important role...

The rather low affinity to oxygen of bismuth makes it easily reduced, at least partially, during firing or soldering. It is believed that partial reduction of Bi and Cu and partition between noble metal and oxides favours the formation of bridging bonds and thereby good adhesion.<sup>88, 159, 251</sup> Solderability is of course also favourably impacted, but aged adhesion of solder pads can be affected if reduction of bismuth by tin in solder proceeds in service,<sup>64, 449</sup> a problem that may be mitigated by incorporation of Bi<sub>2</sub>O<sub>3</sub> into other oxides or glass frit (initially or during firing) or by adding oxides that act as barriers against this reaction.<sup>160, 456</sup> Bi<sub>2</sub>O<sub>3</sub> may also lead to formation of lossy semiconducting interfacial reaction products at electrocomponent interfaces<sup>310</sup> and, in popular Ag-Pd metallisations, reinforce the problematic oxidation of Pd to PdO at intermediate temperatures by formation of Bi<sub>2</sub>PdO<sub>4</sub>, retarding Pd reduction at high temperatures.<sup>64, 460</sup>

The above considerations are summarised in Table 21. Relatively recent work<sup>159, 180, 250, 433, 455, 456</sup> details both fritless and fritted (Table 7, Hw-00) Bi-containing Pb-free silver-based conductors, and such conductors have recently become much more widely available from thick-film materials suppliers.

The case of solar cell front-side Ag metallisations is rather special: the traditionally PbO-bearing glass frit must dissolve the antireflective layer (normally SiN<sub>x</sub>) and ideally create a good ohmic contact with the underlying n-type silicon emitter<sup>43, 50</sup> in a highly non-equilibrium dissolution-oxidoreduction-precipitation process. The overall reaction sequence has been shown to involve dissolution of Ag into the glass and reduction by Si to form crystallites, but the exact conduction mechanism – some direct connections or only tunnelling in a similar fashion to TFRs (next section) and the role of PbO in the frit are still somewhat elusive<sup>43</sup>. Nevertheless, successful substitution of PbO by Bi<sub>2</sub>O<sub>3</sub> has been demonstrated recently, with presence of Ag ions in the glass enhanced by prior incorporation into the frit as Ag<sub>2</sub>O (Jeo-1, or Jeo-1' if Al<sub>2</sub>O<sub>3</sub> and B<sub>2</sub>O<sub>3</sub> mistakenly inverted in the paper, as is likely)<sup>53</sup> or by firing in pure oxygen.<sup>52</sup> These results allow removal of lead from what has become a high-volume industry.



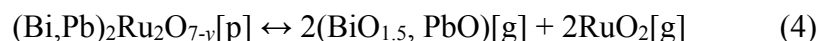
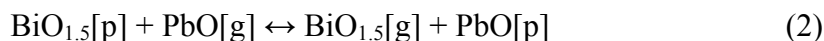
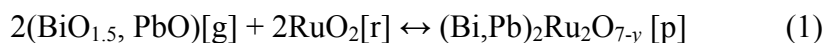
**Table 21. Advantages & issues of Bi in conductors and component metallisations.**

Advantages (+) and possible problems (-)	
+	Lower reaction temperature; better liquation
+	Solderability
+	Conductor adhesion (on firing)
-	Conductor adhesion (aged) in contact with Sn-based solder
+	Interface with electroceramics (control of reactions)
-	Interface with electroceramics (possible formation of lossy layers)
-	Worse oxidation of Pd in Ag-Pd conductors

#### 4.6. Glasses for thick-film resistors

Current "cermet" thick-film resistor (TFR) compositions consist of a granular conductive phase dispersed in a glassy insulating matrix,<sup>59, 61, 62, 461-465</sup> with additives to control the electrical properties;<sup>466, 467</sup> conduction occurs by percolation through the conductive grain network, with intergrain transport through a nm-thin glass film, thought to occur by tunnelling, essentially accounting for the overall resistivity (Figure 11).<sup>84, 463, 468-474</sup> In classical TFR series, the conductive phase is mainly ruthenium oxide (RuO<sub>2</sub>) and/or its pyrochlore compounds with PbO and Bi<sub>2</sub>O<sub>3</sub>, lead and bismuth ruthenate (Pb<sub>2</sub>Ru<sub>2</sub>O<sub>7-y</sub> and Bi<sub>2</sub>Ru<sub>2</sub>O<sub>7</sub>), and the glassy matrix is a high-lead lead borosilicate glass (Figure 12).<sup>59, 62, 475</sup> Ruthenates give a higher resistivity than RuO<sub>2</sub>,<sup>423</sup> and the composition of the glass also has a strong effect, both on the stability of ruthenates vs. RuO<sub>2</sub> and directly on the resistivity.<sup>464, 476</sup> Alternative conductive phases for resistors can be based on IrO<sub>2</sub> (properties similar to RuO<sub>2</sub>, more expensive),<sup>477, 478</sup> and compounds with CaO, SrO and BaO, which have the perovskite structure, are also possible.<sup>155</sup> The synthesis and properties of RuO<sub>2</sub>, IrO<sub>2</sub>, their pyrochlore compounds and similar substances have been extensively studied.<sup>155, 203, 479-489</sup> They belong to the class of electrically conductive oxides, which have been (very) extensively reviewed.<sup>490</sup>

Such a complex resistor chemistry suggests possible particle-glass chemical reactions, as Bi<sub>2</sub>O<sub>3</sub> and PbO may be both in the glass and in the particles, and the configuration before firing may not be the equilibrium one. This is common in commercial systems, which frequently combine (Pb,Bi)<sub>2</sub>Ru<sub>2</sub>O<sub>7-y</sub> as the (initial) conductive phase dispersed in lead borosilicate glass, giving rise to exchange of Bi<sub>2</sub>O<sub>3</sub> and PbO between the glass and the conducting phase as well as decomposition reactions.<sup>61, 62, 465, 491, 492</sup> One may write the following main chemical equilibria:



where: [g] – glass phase

[r] – conductive particles: rutile RuO<sub>2</sub> (or IrO<sub>2</sub>) phase

[p] – conductive particles: pyrochlore ruthenate (or iridate) phase

Equation (1) relates to the equilibrium between the pyrochlore ruthenate phase and the simple rutile oxide, and (2) describes the equilibrium composition of the pyrochlore phase relative to that of the glass; (3) and (4) relate to dissolution into / precipitation from the glass, which are quantitatively small due to the low solubility of  $\text{RuO}_2$  in the glass,<sup>493, 494</sup> but may nevertheless play an important role in the electrical properties.<sup>495</sup> Reactions of type (1) and (2) have indeed been observed experimentally,<sup>61, 62, 465, 491</sup> and a detailed study, for  $\text{PbO}$  only, established lead ruthenate was stable / formed only at moderate temperatures in glasses with lead concentrations much higher than that used in commercial systems;<sup>464</sup> this was confirmed in our studies on model  $\text{RuO}_2$ -glass TFRs.<sup>85, 496</sup> Therefore, most ruthenate-based formulations are not at thermodynamic equilibrium during firing. However, even in model systems where the conducting phase is thermodynamically stable (in practice, those formulated using  $\text{RuO}_2$ ), the glass composition strongly influences the resistivity.<sup>476, 496</sup>

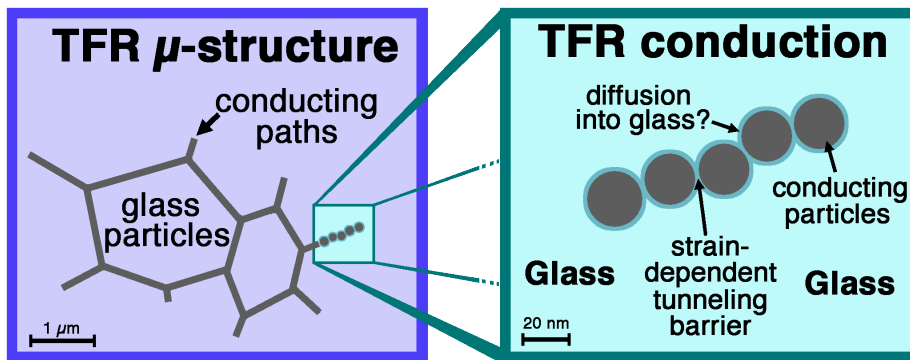


Figure 11. Microstructure and conduction mechanism of TFRs.<sup>1</sup>

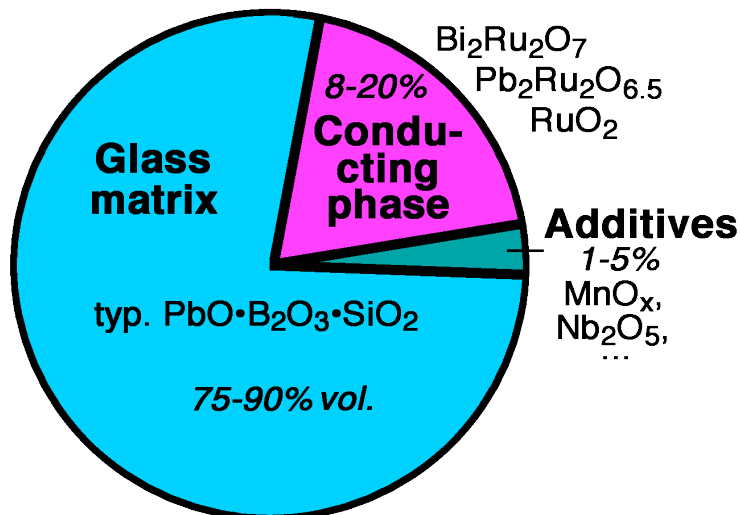


Figure 12. Typical composition (without temporary vehicle / binder) of thick-film resistors with lead borosilicate glass matrix.<sup>1</sup>

It must be additionally noted that the oxygen stoichiometry of Pb<sub>2</sub>Ru<sub>2</sub>O<sub>7-y</sub> is reported to be  $x = 0.5$ ,<sup>483, 484</sup> which implies an average valence of +2.5 for Pb (or +4.5 for Ru?) in this compound. This adds a further complication, as formation / decomposition of lead ruthenate may involve a change of the oxidation state of Pb, requiring exchange of oxygen with the firing atmosphere, an implication supported by results of TFR annealing studies in different atmospheres.<sup>497, 498</sup> On the other hand, Bi and Ru essentially have the same valence in Bi<sub>2</sub>Ru<sub>2</sub>O<sub>7</sub> as in the individual oxides Bi<sub>2</sub>O<sub>3</sub> and RuO<sub>2</sub>; while Bi<sub>2</sub>Ru<sub>2</sub>O<sub>7</sub> transforms at low temperatures to Bi<sub>3</sub>Ru<sub>3</sub>O<sub>11</sub>,<sup>460, 499</sup> formally linked with a slight oxidation, this transformation is apparently not observed in thick-film resistors, and does not involve a change of the Bi:Ru stoichiometry (Bi<sub>2</sub>Ru<sub>2</sub>O<sub>7</sub> made by high-temperature synthesis is actually reported to be slightly nonstoichiometric, Bi<sub>2</sub>Ru<sub>2</sub>O<sub>6.9</sub> or Bi<sub>1.9</sub>Ru<sub>2</sub>O<sub>6.9</sub> – see supplement 13 – but this does not necessarily apply to "resistor-grade" nanopowders calcined at lower temperatures,<sup>483, 488</sup> whose stoichiometry would require further study).

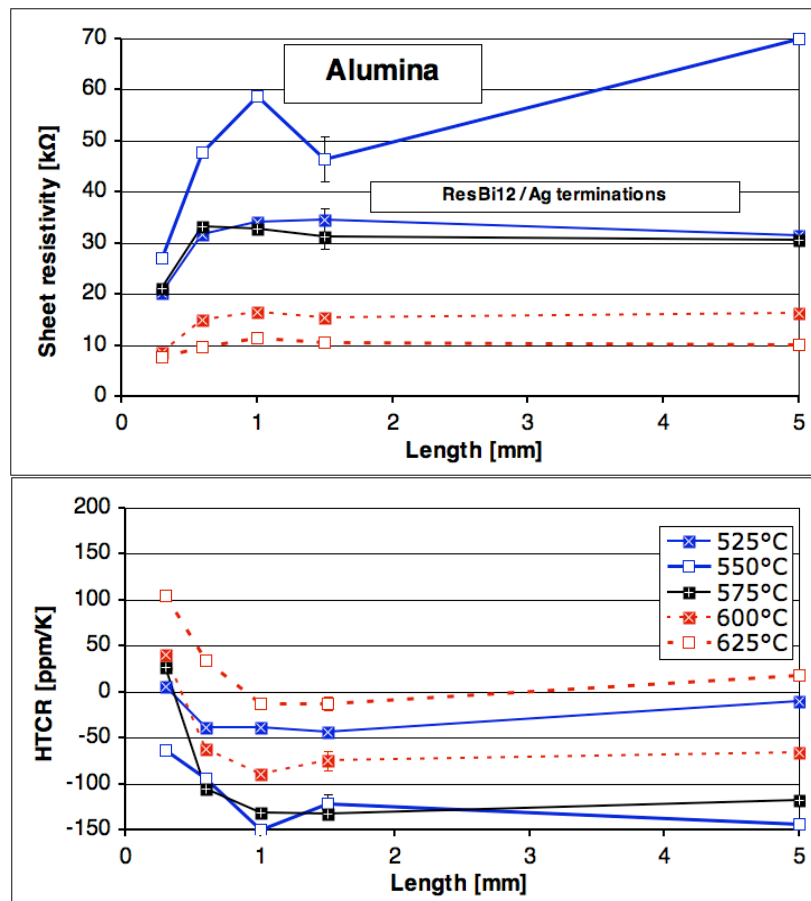


Figure 13. Sheet resistivity at 25°C and temperature coefficient (*HTCR*, 25...100°C), vs. length and firing temperature, of experimental TFRs fired on Al<sub>2</sub>O<sub>3</sub> with Ag terminations.<sup>1</sup>

Therefore, it would seem logical to use a Bi-based glass in order to enhance resistor stability to firing, given the otherwise similar properties to Pb-based glasses. This would also lessen the property changes that classical resistors formulated with Pb-based frits encounter when fired with Bi-containing terminations.<sup>79, 500</sup> Therefore, it is not surprising that several such compositions have been patented<sup>251</sup> (Table 7, Hm). Nevertheless, making the switch is not trivial, given the intricacies of TFR chemistry. Recently, first encouraging results – some of which by our group – have been published on lead-free TFRs with bismuth-based glasses and RuO<sub>2</sub> conducting particles,<sup>1, 70, 322, 323</sup> for both standard 850°C<sup>251, 322</sup> and relatively low (ca. 600°C) firing temperatures<sup>1, 70, 323</sup> (see also Table 7, Hm/Hy/L-Bi12). The former is useful for application as standard thick-film resistors, while the latter may be used for low-firing compositions suitable for firing onto glass or high-strength temperature-sensitive metallic alloys to fabricate high-performance force and pressure sensors.<sup>1, 68, 69, 71</sup> An example of our results is given in Figure 13, for resistors consisting of LPM-Bi12 glass with 11% by mass of RuO<sub>2</sub> (≈9% volume fraction) without additives. The results are very encouraging, featuring reproducible properties at firing temperature ≥550°C and moderate, normal termination effects, i.e. without the increase of resistivity at the terminations<sup>77, 79</sup> seen with the equivalent lead-bearing systems.<sup>69</sup>

Several aspects must be studied carefully for Bi<sub>2</sub>O<sub>3</sub>-based glasses to become a standard matrix for TFRs. First, thermodynamic properties of RuO<sub>2</sub>, Bi<sub>2</sub>Ru<sub>2</sub>O<sub>7</sub> and related compounds in regard to Bi-based glasses must be known, especially the solubility of RuO<sub>2</sub> in glass and the equilibrium between oxide and ruthenate, as was investigated in the lead-based systems.

Additionally, as oxides of transition metals such as Ti, Zr, Nb, Mn, Fe, Cu and Zn are often added to control the temperature coefficient of resistance (TCR), it is important to know their possible interactions with Bi<sub>2</sub>O<sub>3</sub> and RuO<sub>2</sub>. This has been the object of several studies, in pure oxide form, for ZnO,<sup>501</sup> TiO<sub>2</sub>,<sup>502</sup> CuO,<sup>503</sup> and NiO.<sup>504</sup> The Bi<sub>2</sub>Ru<sub>2</sub>O<sub>7</sub> phase has been shown to be able to incorporate a significant amount of divalent transition metals (MO) as nominally (Bi<sub>2-x</sub>M<sub>x</sub>)Ru<sub>2</sub>O<sub>7-x/2</sub> solid solutions, which seems to be a major difference with Pb<sub>2</sub>Ru<sub>2</sub>O<sub>7-y</sub>, where such solid solutions were not detected with CuO.<sup>505</sup> For tetravalent TiO<sub>2</sub>, there is some disagreement as to the extent of Bi<sub>2</sub>(Ru,Ti)<sub>2</sub>O<sub>7</sub> solid solutions.<sup>482, 502</sup> Additionally, one must note that these studies only give clues to the observed behaviour in real thick-film resistor systems, because a) the activities of the oxides are different when dissolved in glass, and b) thick-film resistors are usually non-equilibrium systems.

A more long-term potential development would be the avoidance of costly precious metals, by using other metallic (or almost metallic) oxides and compounds as conductive phases, of which a very wide variety exists,<sup>490</sup> or metal borides, silicides etc. To circumvent the often-observed processing issues with nitrogen-firing thick-film resistors,<sup>183-189, 190, 506</sup> air-firing systems should be developed. Several promising studies using molybdenum oxides have been carried out towards this goal,<sup>507-512</sup> with the most recent embodiment<sup>512</sup> having achieved transition to a bismuth glass frit, paving the way to low-cost lead-free resistors. These compositions are air-fireable, because the conductive phase, MoO<sub>2</sub> and/or other intermediate oxides (which are unstable in air) form in situ, after densification of the glass frit, by reduction of MoO<sub>3</sub>. This is brought about by a suitable reducing agent, usually boron. Another base metal conductive filler successfully investigated with bismuth glasses is SnO<sub>2</sub>:Sb,<sup>166</sup> which seems however more suitable for higher ranges of surface resistance (> 100 kΩ), in line with the semiconductive properties of this filler.

## 5. Other applications

### 5.1. Optics

Heavy metal ions such as Bi<sup>3+</sup>, Pb<sup>2+</sup> and Tl<sup>+</sup> feature a unique combination of properties: high mass and polarisability, together with low bond strength. For optical applications of HMO materials, be it in glassy, ceramic or single-crystal form, this translates into high refractive indices  $n$  (Table 22), dispersion and optical non-linear susceptibility  $\chi^{(3)}$ , as well as low phonon energies.<sup>36, 112, 124, 128, 329, 371</sup> In addition, low levels of partly reduced Bi in both Bi-based and other glasses have been found to display broad IR luminescence, with possible application to optical amplification<sup>353, 428-430</sup> (see also discussion in supplement section 12). HMO glasses are a promising alternative to fluorides,<sup>37, 192, 193</sup> due to their better chemical durability.

IR cut-off wavelength is related to the highest-frequency bond vibrations / maximum phonon energy. Therefore, HMO glasses for light amplification, and especially for far-IR transmission, should contain no standard network formers (B<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, P<sub>2</sub>O<sub>5</sub>) or light intermediates with strong bonding such as Al<sub>2</sub>O<sub>3</sub>. Although GeO<sub>2</sub> constitutes a good drop-in replacement for SiO<sub>2</sub>, much better infrared performance can be obtained (Table 22) with non-standard formers such as Ga<sub>2</sub>O<sub>3</sub> in the PbO-Bi<sub>2</sub>O<sub>3</sub>-Ga<sub>2</sub>O<sub>3</sub> system<sup>36, 371</sup> and TeO<sub>2</sub> in Bi<sub>2</sub>O<sub>3</sub>-TeO<sub>2</sub>-WO<sub>3</sub>,<sup>123</sup> and even systems entirely without glass formers such as Li<sub>2</sub>O-[BaO/PbO]-Bi<sub>2</sub>O<sub>3</sub><sup>381, 382, 388</sup> and SrO-PbO-Bi<sub>2</sub>O<sub>3</sub>.<sup>117</sup> Considerable care must be exercised when melting Bi-containing glasses for optical applications, as they are quite susceptible to reduction by trace organics or excessive melting temperatures (section 3.4), and to contamination by crucibles.<sup>36, 387</sup> Reduction or Pt pickup leads to darkening / staining of the glass, while even relatively low contamination by oxides such as SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> will introduce high-frequency vibrations into the network, degrading far-IR transmission.

Obtaining a high refractive index and non-linear susceptibility, on the other hand, only involves the average glass properties, allowing limited use of standard network formers and thereby greatly facilitating vitrification. Synergistic vitrification through mixing of SiO<sub>2</sub>, B<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub> and substituting some Bi<sub>2</sub>O<sub>3</sub> by ZnO (section 3.2) allows maximisation of HMO content; recent results on glasses optimised this way<sup>116</sup> yield  $n = 2.31$  at 633 nm and  $\chi^{(3)} = 4.9 \times 10^{-11}$  esu at 748 nm. The glass composition was not specified exactly, but mentioned as Bi<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>, and is probably close to Smt-7 (Table 7). The high and very fast response of these glasses makes them very promising for high-frequency fully optical switching.<sup>112</sup>

In the case of upconversion, recent measurements<sup>119, 371</sup> indicate that average properties (phonon density) rather than maximal phonon energy dominates efficiency, which is supported by the good results achieved by others with doped/codoped HMO glasses containing a low amount of network formers,<sup>121, 124, 125, 325, 370</sup> usually GeO<sub>2</sub> given its lower impact on performance. An additional advantage of Bi<sub>2</sub>O<sub>3</sub>-based HMO glasses for this application is their good compatibility with lanthanide additions (section 3.2).

Finally, the above considerations, though essentially focussed on glasses, are also applicable to similar crystalline (single-crystal, ceramic or glass-ceramic) compounds, of which many exhibit promising optical properties.<sup>351</sup>

### 5.2. Gamma-ray protection glasses

Due to their ideal combination of high  $\gamma$ -ray absorption coefficient (imparted by their large atomic mass) and good glass-forming ability as oxides, Pb and Bi are useful in  $\gamma$ -ray-absorbing windows in the nuclear industry and high-energy physics.<sup>129-135</sup> Requirements for these glasses are in general similar to that for nonlinear optics: a HMO glass is needed for a

good attenuation factor, but moderate concentrations of traditional network formers (B<sub>2</sub>O<sub>3</sub> & SiO<sub>2</sub>) are allowed, facilitating fabrication of the thick parts needed for good shielding.

An early study of was carried out by Brekhovskikh in the PbO-Bi<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> system;<sup>129</sup> ternary glasses down to ca. 17% SiO<sub>2</sub> and with density > 8'000 kg m<sup>-3</sup> could be manufactured (Rad-1), but practical considerations (need for casting in thick sections requires ca. 30% SiO<sub>2</sub>, Rad-2). An analogous borate glass (Rad-4, ≈21% BO<sub>1.5</sub>) was formulated<sup>130</sup>, but no indication was given on its castability in thick sections. The claim of a Bi<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> glass with ≈95% cation Bi is<sup>131</sup> is dubious, as the indicated density of 7'284 kg/m<sup>3</sup> corresponds to ca. 70% Bi,<sup>248</sup> In the light of section 3.2, maximising HMO content in a Bi-based Pb-free glass would most likely best be achieved in a more complex system, such as SrO-BaO-ZnO-Bi<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>. Compared to PbO,  $\gamma$ -ray attenuation coefficients with Bi<sub>2</sub>O<sub>3</sub> are similar<sup>129, 134</sup> (the apparent observed increase when substituting PbO with Bi<sub>2</sub>O<sub>3</sub><sup>130</sup> is simply due to the "molecular" formulation, where Bi is counted twice vs. Pb), yielding a progressive increase in HMO content from 69% to 79% on a cation basis.

**Table 22. Optical properties of HMO glasses.**

Code	Refractive index $n^\dagger$	IR transmission cut-off [ $\mu\text{m}$ ] <sup>*</sup>	Density [g cm <sup>-3</sup> ]
Dmb-H	2.6 <sub>589</sub>	7.8 <sub>30/2.0</sub>	7.90
Dmb-EO	2.5 <sub>589</sub>	7.0 <sub>30/2.0</sub>	8.19
Dmb-IV	2.4 <sub>589</sub>	6.8 <sub>30/2.0</sub>	8.29
Dmb-D	2.5 <sub>589</sub>	6.0 <sub>50/2.0</sub>	8.9
Fu-1		8.0 <sub>35/0.7</sub>	
McC-1	2.32 <sub>633</sub>		8.1
McC-2	2.40 <sub>633</sub>		8.4

Notes. † At wavelength [nm] indicated in index. \* Transmission [%] and thickness [mm] given in index.

**Table 23. Compositions of selected BiSCCO superconductors, given in cation molar proportions.  $z = \text{Pb}/(\text{Pb}+\text{Bi})$ .**

Code	$z$	Pb+Bi	Sr	Ca	Cu	Other	Notes
HTS-1 <sup>99</sup>	20%	2	2	2	3	-	
HTS-2 <sup>101</sup>	20%	2	2	2	3	0.1Mo	& other dopants
HTS-3 <sup>102</sup>	20%	4	3	3	4	-	
HTS-4 <sup>104</sup>	0%	4	3	3	4	0.1Al	Mix of phases

Note: oxides = PbO, BiO<sub>1.5</sub>, SrO, CaO, CuO <sub>$\gamma$</sub>  ( $\gamma$  preparation-dependent), AlO<sub>1.5</sub> & MoO<sub>3</sub>.



This said, the main issue with  $\gamma$ -ray protection glasses lies with radiation-induced darkening, for which results are relatively unclear.<sup>131-133, 135</sup> Significant darkening in the short-wavelength portion of the visible spectrum was observed after 2.5 kGy from <sup>60</sup>Co, but no systematic trend vs. composition was observed for Bi<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub> glasses,<sup>133</sup> which is also the case for Bi<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> glasses after 10, 20 and 40 kGy <sup>60</sup>Co.<sup>131</sup> This darkening on the other hand was absent or very low in the visible for Bi<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub> glasses optionally doped with CuO<sub>y</sub> after up to 50 kGy <sup>60</sup>Co.<sup>132</sup> Although these latter results are very encouraging, systematic studies of the mechanisms of radiation-induced damage and of the good resistance against it of some glasses, including doping / impurity effects, still need to be carried out to reliably achieve low-darkening Bi-based glasses.

### **5.3. Bi<sub>2</sub>O<sub>3</sub> in (glass-)ceramics and crystals**

A short discussion is given in this section of Bi<sub>2</sub>O<sub>3</sub> in five types of crystalline materials: 1) piezoceramics, 2) ionic and mixed conductors with high oxygen mobility, 3) high-temperature superconductors, 4) scintillators, and 5) ferroelectric memories. Besides these applications, Bi<sub>2</sub>O<sub>3</sub> is a component of many electroceramics, in both the active crystalline phase or as a sintering aid,<sup>9</sup> and compounds such as bismuth ruthenates (Bi<sub>2</sub>Ru<sub>2</sub>O<sub>7</sub> / Bi<sub>3</sub>Ru<sub>3</sub>O<sub>11</sub>), besides being a useful conductive phase for thick-film resistors (see section 4.6), are envisioned as chemical catalysts and electrodes.<sup>499, 513</sup> Bismuth vanadate (BiVO<sub>4</sub>) is a relatively new yellow pigment that provides an alternative to toxic Pb- and Cd-based pigments,<sup>514</sup> and crystalline bismuth borates have interesting optical properties,<sup>351</sup> akin to the corresponding glasses (see section 5.1). A quite extensive list of Bi<sub>2</sub>O<sub>3</sub>-based compounds and corresponding applications is given in recent work,<sup>403, 515</sup> together with an extensive discussion on their structural features (some of which are also discussed in supplementary section 13, as they yield insight into the structure of the corresponding glasses). Finally, it is worth mentioning that derivatives of the analogous chalcogenide, Bi<sub>2</sub>Te<sub>3</sub>, are the dominant room-temperature thermoelectric materials.<sup>516</sup>

#### *1) Piezoceramics*

Besides glass, the main application of PbO-bearing materials is arguably PZT = Pb(Zr,Ti)O<sub>3</sub> and similar ceramics, mainly used for their large piezoelectric or electrostrictive properties. As these ceramics are present in many small essentially disposable electronic devices, considerable effort has been devoted to finding lead-free substitutes with at least acceptable performance. Recently, complex mixtures of Bi<sub>2</sub>O<sub>3</sub> perovskite compounds such as Bi<sub>0.5</sub>(Na,K)<sub>0.5</sub>TiO<sub>3</sub> & Bi(Fe,Sc)O<sub>3</sub> with (Ba,Sr)TiO<sub>3</sub> & (Na,K)NbO<sub>3</sub> have given rise to promising materials achieving strains comparable to that of the classical PZT ceramics, although many issues remain.<sup>517, 518</sup> Note that bismuth titanate (Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub>) is also a piezoceramic, albeit a specialised, high-temperature and low-activity one.

#### *2) Ionic and mixed ionic-electronic conductors with high oxygen mobility*

The high-temperature disordered defect-fluorite cubic  $\delta$ -Bi<sub>2</sub>O<sub>3</sub> phase contains a very large amount of disordered oxygen vacancies – it may in fact be written as Bi(O<sub>3/4</sub>□<sub>1/4</sub>)<sub>2</sub>, i.e. with 1/4 of the oxygen anion sublattice randomly empty – and therefore exhibits exceptionally high ionic conductivity. Although  $\delta$ -Bi<sub>2</sub>O<sub>3</sub> is only stable above 730°C, Takahashi et al.<sup>519</sup> established that this disordered phase may be stabilised at lower temperatures – much like cubic zirconia – by various dopants, thus giving birth to a new family of solid electrolyte materials<sup>519-522</sup> with high ionic conductivity at moderate temperatures. For instance, Bi<sub>2</sub>O<sub>3</sub> solid solutions stabilised by oxides such as Y<sub>2</sub>O<sub>3</sub> or Er<sub>2</sub>O<sub>3</sub> have ionic conductivities exceeding 1 S/m at 500°C, more than 20× that of cubic or tetragonal zirconia, and more recent "BIMEVOX" materials with an oxygen-deficient Aurivillius structure have even higher

conductivity. However, as all Bi<sub>2</sub>O<sub>3</sub>-based materials, these ionic conductors have limited stability towards reduction, and their use is limited in solid-oxide fuel cell (SOFC) applications. Nevertheless, they may still be used to this end, provided the reduction potential is limited or a thin protective layer of another electrolyte material is used on the reducing side. In addition, Bi<sub>2</sub>O<sub>3</sub> ionic and mixed ionic-electronic conductors may find other important applications such as air-side electrodes for SOFCs, chemical electrodes, oxygen sensing and oxygen extraction from air.<sup>521, 523</sup>

### *3) High-temperature superconductor (HTS) materials*

The discovery of high-temperature (>100 K) superconductivity in the Bi-Sr-Ca-Cu oxide ("BiSCCO") family (with possible substitution of Bi by Pb)<sup>99, 524, 525</sup> having low melting points opened up the possibility of greatly easier processing of these materials. In fact, these HTS compounds have compositions (examples in Table 23) corresponding to the "heavy-metal oxide" glasses,<sup>36</sup> and are therefore amenable to processing by the vitroceraic route, i.e. glass melting and quenching, followed by shaping and finally crystallisation and annealing to yield the superconducting phase<sup>39, 99, 101, 102, 104, 105</sup> with zero-resistance temperatures in excess of 100 K under optimal conditions.<sup>101</sup> Low concentrations of suitable dopants do not significantly enhance the superconducting properties, but are added to facilitate processing and yield more consistent products. Reported melting temperatures are in the 1100-1300°C range, with long-term annealing around 850°C to form the superconducting phase(s). These materials feature rather high resistivity in their glassy state,<sup>100</sup> in contrast to amorphous Bi<sub>3</sub>Ru<sub>3</sub>O<sub>11</sub>.<sup>499</sup>

Besides these materials, doping BaBiO<sub>3</sub> (with Bi in mixed +3 and +5 valence) with K or Pb yields (Ba,K)BiO<sub>3</sub> or Ba(Bi,Pb)O<sub>3</sub> respectively, yields superconductors with transition temperatures up to 30 K that are of theoretical interest due to their simple cubic structure.<sup>526</sup>

### *4) Scintillators*

In addition to heavy glasses potentially improving scintillation efficiency,<sup>36</sup> crystals such as Bi<sub>4</sub>Ge<sub>3</sub>O<sub>12</sub>, Bi<sub>4</sub>Si<sub>3</sub>O<sub>12</sub> and their solid solutions<sup>368, 527, 528</sup> are useful as  $\gamma$ -ray scintillators, the active ion in this case being directly Bi<sup>3+</sup> (i.e. "self-activated"). Potential preparation of Bi<sub>4</sub>Ge<sub>3</sub>O<sub>12</sub> by the glass-ceramic route has been explored.<sup>368</sup>

### *5) Ferroelectric memories*

Besides being useful as a piezoceramic, PZT in thin-film form is also of interest for non-volatile ferroelectric memories. However, it was soon realised that its sensitivity to so-called fatigue, i.e. degradation upon repeated switching, was an important issue, although alleviated by the use of oxide electrode contacts.<sup>529</sup> This problem was largely solved by the introduction of Aurivillius-type layered perovskite compounds derived from Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub> such as Bi<sub>3.25</sub>La<sub>0.75</sub>Ti<sub>3</sub>O<sub>12</sub> (simple substitution with La),<sup>530</sup> SrBi<sub>2</sub>Ta<sub>2</sub>O<sub>9</sub><sup>531</sup> or SrBi<sub>4</sub>Ti<sub>4</sub>O<sub>15</sub>,<sup>532</sup> which feature vastly improved switching endurance.

## 6. Conclusions

The many examples discussed in this review show that replacement of lead by bismuth in TF and related glass frits seems the most feasible route in the short to middle term. In fact, this is already happening in several important industries such as electronics, displays and automotive / architectural glass, in spite of the still considerable technological issues. Moreover, promising new applications are currently undergoing development in the sensors and optics field.

The considerably higher price of bismuth, ca. 10× that of lead<sup>533</sup> should not constitute a problem in many high-added-value applications, where a relatively low overall volume of material is used, such as TF electronics, sensor cells and specialised optics. Moreover, Bi is not expected to replace lead in high-volume applications such as vehicle batteries, and only to a very modest extent in electronic solders, Bi-Sn and similar low-melting eutectic solder having only limited use. The same applies for use of Pb-Bi eutectic (LBE) coolants.<sup>422</sup>

For thick-film electronics, the very strong increase in prices of all noble metals (Ag, Pd, Pt, Ru) in recent times<sup>533</sup> is therefore a much more pressing issue for conductor and resistor materials. Development should be concentrated on new materials which reduce or altogether avoid their use, as has already been initiated for resistors.<sup>166, 512</sup> On the other hand, the price of Bi can be a factor in high-volume and very cost-sensitive architectural and automotive applications,<sup>47</sup> so further developments to reduce its use in these sectors are likely.

From a scientific point of view, more well-controlled experimental data is necessary for bismuth-based glasses, as the reported results, especially on glass stability and properties, are somewhat conflicting, even for the simplest systems. Detailed studies on devitrification, separately assessing the composition-dependent dynamics of crystal nucleation and growth, are strongly needed as well, especially in the practically important low-melting borosilicates and HMO gallate systems.

Also, the very disordered structure Bi<sup>3+</sup> adopts within the glass network – and how it is influenced by glass composition and thermal history – requires further clarification, especially in the light of recent structural studies<sup>403</sup> on the peculiar behaviour of "lone-pair" ions such as Bi<sup>3+</sup>, Sb<sup>3+</sup>, Pb<sup>2+</sup> and Sn<sup>2+</sup> (see also supplementary section 13). Apparently, PbO-based glasses and two important envisioned substitutes, those based on Bi<sub>2</sub>O<sub>3</sub> and on SnO, share fundamental structural features. Extending the detailed structural studies and computer modelling to glasses would lead to a clearer picture of how glass formation and structure are affected by the stereochemically active lone pair, the valence and the polarisability.

Finally, it must be noted that this review has only dealt with relatively standard glassmaking techniques of Bi-based glasses; chemical methods such as solution coating of powders, nanopowder synthesis or sol-gel casting<sup>534</sup> constitute promising alternative routes, potentially allowing the manufacture of novel glasses and glass-matrix composites with a degree of control not achievable by standard methods.

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## 9. Description of supplementary material

The supplements consist of the following sections:

- **Supplement 10** gives a **historical perspective** of lead and bismuth in oxide glasses, including the development of awareness of the toxicity of lead and of the need to strongly limit exposure to this element.
- **Supplement 11** presents and discusses the **comparative toxicity** of the elements found in common and special oxide glasses. This provides a rough guide to potential hazards and adequate formulation, bearing in mind that chemical (leaching) resistance must also be considered.
- **Supplement 12** discusses the **valence of bismuth** in oxide glasses, usually taken to be Bi<sup>3+</sup>, in the light of the occasionally reported presence of Bi<sup>5+</sup>. A strong case is made against significant presence of Bi<sup>5+</sup> species in most glasses processed by melting and quenching, with the possible exception of some very alkaline formulations melted at moderate temperatures. Hence, the darkening observed in glasses melted at high temperatures is rather attributed to the formation of reduced species.
- **Supplement 13** compiles and discusses the **bonding and oxygen coordination** of Bi<sup>3+</sup>, compared to Pb<sup>2+</sup> and Sn<sup>2+</sup>, in crystalline oxides, including pure or doped polymorphs of Bi<sub>2</sub>O<sub>3</sub>, compounds (borates, silicates, germanates, phosphates) lying close to or within the glass-forming range, and the pyrochlore-structure conducting phases. This provides useful supporting information for the discussion on glass structure, in section 3.3.
- **Supplement 14** describes the assumptions used in this work to determine a rough estimate – when not given by the authors – of the **cooling rate** of the glass after melting. The cooling rate influences the vitrification ability (section 3.2), but may also somewhat affect the properties, which will be further influenced by annealing.
- The additional bibliography for the supplements is given in supplemental section 15.

## 10. Lead and bismuth in glass – a historical perspective

This section gives a short historical perspective on the use of lead and bismuth in glasses – and awareness of the toxicity of lead – taken from several reference works.<sup>5, 89, 535-546</sup> A summarised timeline may be found in Table 24, and a few representative compositions are given in Table 25.

### 10.1. Lead and bismuth in glasses

Glassy materials were first obtained sometime before 3000 BC by in-situ glazing reaction between a siliceous body (bulk stone or ground quartz – faience) and an alkali-lime powder. Early colours were limited copper blue and manganese black, together with the ubiquitous iron brown.<sup>5, 542, 543</sup> With the introduction of true bulk glass around 1500 BC<sup>542, 543</sup> came a progressive extension of the available colour range, and, for the first time, introduction of low amounts of lead, albeit only to colour the glass yellow by forming lead antimonate (Pb<sub>2</sub>Sb<sub>2</sub>O<sub>7</sub>). As considerable excess Pb was added over Sb, some of the glasses had a low (1-2 cation mol%) content of PbO,<sup>543</sup> which however was of little practical significance.

Introduction of leaded glazes came only shortly before the current era (4<sup>th</sup>-1<sup>st</sup> century BC), in China and Rome, despite lead being known for millennia before.<sup>541, 547</sup> Over time, depending on availability of lead and application, both lead silicate and lead-alkali silicate glazes (optionally containing alkaline earth) came to be produced, and their advantages over comparable alkali glasses (better wetting, better glass & hydrolytic stability, lower thermal expansion, higher refractive index & gloss, easier processing) were well recognised.<sup>541, 544</sup> Al<sub>2</sub>O<sub>3</sub> was found in significant proportions in most compositions, hinting that ancient glassmakers were already aware of its beneficial effect on glass stability,<sup>81</sup> in fact, some modern TFR boron-free glasses bear a striking similitude to these ancient glazes (Table 25, Tit-T5 vs. Table 1, Pru-F8, summing Pb+R2). Lead was used only in glazing (or small objects) at this stage, however, with more classical glasses already having composition very similar to that of modern container glass (see Krk-1/3/5). This restriction was probably due to the leaded glasses being very aggressive towards the crucibles owing to the high fluxing ability of PbO, an issue hindering large-scale fabrication by standard glass melting that is well documented in early studies.<sup>536-538</sup>

The 1600s saw the publication of Antonio Neri's monumental book on glass technology, *L'Arte Vetraria* (1612); this work was widely expanded, commented and translated in the following century,<sup>5, 536</sup> reflecting the technological advances in European glass production. The end of the 17<sup>th</sup> century saw the large-scale introduction and expansion of leaded "crystal" glass, first in England, then in whole Europe.<sup>5</sup>

In contrast, to lead, the intentional use of bismuth is relatively recent, dating from 1400s Renaissance Europe, being mentioned in trading and mining concession documents shortly before 1500 AD,<sup>548</sup> documented identification of bismuth extraction techniques is be found in Agricola's *Bermannus*<sup>549</sup> and *De Re Metallica*,<sup>535</sup> where its mining and separation are described. Bismuth was most likely used in early type alloys, as exemplified from a 1568 description of the type founder trade (*Der Schriffgießer*).<sup>550</sup>

<i>Ich geuß die Schrifft zu der Druckrey</i>	I cast the type for printing
<i>Gemacht auß Wißmat / Zin und Bley</i>	Made from bismuth, tin and lead

Around similar times, Bi also appeared in some renaissance Italian glazes, albeit in small amounts, as a component of lustre, e.g. colour induced by nanoparticles precipitated out of the glass matrix during reduction firing.<sup>551</sup> In this case, the precipitated phase was cosalite, Pb<sub>2</sub>Bi<sub>2</sub>S<sub>5</sub>, and there is no indication Bi was added for glassmaking per se. However, in a more recent glass-making manual by Zimmermann (undated, ca. 1700, included in the expanded French translation of *L'Arte Vetraria*<sup>536</sup>), the inclusion of Bi<sub>2</sub>O<sub>3</sub> in cobalt blue glazes is recommended to enhance their aspect, presumably due to its fluxing role and convenient simultaneous presence in that particular ore.

The first rigorous accounts of scientific experiments on Bi date from the 18<sup>th</sup> century, exemplified by the work of Geoffroy the Younger, building on the previous studies of Pott,<sup>537</sup> who noted considerable similitude with lead in both the metallic and oxide (herein described as "*chaux*" – i.e. "lime") forms:

- 1) Low melting point as a metal
- 2) Weight gain upon "calcination", i.e. oxidation in air
- 3) Ready vitrification to a glass "without addition"
- 4) As a glass, strong "erosion of crucibles", but somewhat lower than with lead
- 5) Slow crystallisation of the glass to "massicot" in 2 hours
- 6) Aptitude of the glass to vitrify and entrain base metal oxides out of precious metal ores during cupellation

Geoffroy also noted the main difference between bismuth and lead metal, e.g. the brittleness of bismuth. Observations 3-6 are interesting for glass formation. For (3), although we now know that vitrification of pure PbO and Bi<sub>2</sub>O<sub>3</sub> does not occur in pure form, and that Geoffroy's samples were therefore – unsurprisingly for that time – contaminated, his findings nevertheless demonstrate the unusually strong glass-forming properties of these compounds, which were to be rigorously investigated for Bi<sub>2</sub>O<sub>3</sub> by Heynes and Rawson only ca. 200 years later.<sup>244</sup> This good ability for vitrification is compounded by the apparently low tendency of the formed glasses to crystallise (5) and the strong fluxing ability, i.e. solubility of other oxides to form low-melting glasses (4 & 6).

Bismuth, however, was not used significantly in glass until the middle of the 20<sup>th</sup> century, when it was introduced in the formulation of metallisations (see section 4.5). This is easily attributed to lead being much better known and more available, having even higher fluxing power in glass and not yet being a major health concern there (leaded petrol and interior paint being much more pressing issues – see next section).

Around 1800, astronomy was a major driving force for the development of technical glasses, which culminated in the experiments of Faraday,<sup>538</sup> who developed both PbO-B<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> glasses and manufacturing techniques to ensure large, homogeneous and quite colour-free melts. His preferred glass composition is quite similar, somewhat lower-melting, to the main low-firing TFR composition developed by our group (Table 25 – Krk-7 vs. L-V6), the main difference being the absence of Al<sub>2</sub>O<sub>3</sub>.

The end of the 19<sup>th</sup> century saw massive developments in glass technology, which, among others, led to the development of low-melting leaded "solder" glasses.<sup>10-12, 14-17, 19</sup> An overview of the investigated compositions since this period is given by Mazurin.<sup>552, 553</sup>

## 10.2. Awareness of lead as a toxic substance

Although health problems related to lead have been mentioned throughout antiquity and the middle ages,<sup>539, 540, 545, 546</sup> their precise cause was not always well identified. This stems from many factors: lack of knowledge of chemistry, generally poor health and the presence of several toxic elements besides lead, such as mercury, arsenic and cadmium, especially in mining. For example, Agricola<sup>535</sup> specifically mentions the toxic effects of mines in general on workers and the adjacent environment (he even mentions the latter as a useful hint when searching for a metalliferous vein!), but in most cases does not precisely identify harmful substances, except for vermilion (HgS); his mention of some types of *cadmia* and *pompholyx* (zinc minerals) being toxic probably stems more from the variable content of lead or cadmium associated with the relatively harmless zinc. Several ancient authors did however warn against ingestion of leaded compounds such as minium (Pb<sub>3</sub>O<sub>4</sub>), ceruse (2PbCO<sub>3</sub>·Pb(OH)<sub>2</sub>) and litharge (PbO), and drinking water from leaded pipes.<sup>89, 539, 546</sup> This, however, did not deter the ancient Romans from making heavy use of sapa contaminated with lead acetate – Pb(CH<sub>3</sub>COO)<sub>2</sub>, also known as sugar/salt of Saturn in ancient texts – as a sweetener and preservative for food and wine, resulting in widespread intoxication; contamination resulted from boiling down the sapa in lead kettles.<sup>89, 539, 540, 546</sup> The ban on lead-containing sapa, first enacted by several authorities in the 1400s, was actually one of the first legal restrictions against lead use, but the use of lead-adulterated drinks, as well as that of lead compounds in medicine to combat infections (not so surprising given the paucity of alternatives at this time), continued into the 19<sup>th</sup> century.<sup>539, 540</sup>

Nevertheless, firm evidence of the toxic effects of lead came to be clearly established in the 1800s, as attested by the comprehensive 1839 treatise on lead poisoning by Tanquerel des Planches,<sup>539</sup> based on his own observations of patients, animal experiments and an extensive literature survey. As awareness of this rose, lead came to be progressively removed from interior paint and canned food. Nonetheless, use of lead continued to rise, culminating in its widespread diffusion, from 1923 on, into the atmosphere through the addition to petrol (USA: gasoline) of tetraethyl lead, Pb(CH<sub>2</sub>CH<sub>3</sub>)<sub>4</sub>, as an anti-knock and engine valve seat protection agent. This source alone dominated the average human exposure to lead for the next decades, until its progressive phase-out from the 1970s onward.<sup>89, 540, 546, 554</sup> Now that tetraethyl lead is banned in all developed countries, older contaminants such as interior leaded paints have again become a dominant issue in some countries such as the USA, where the ban came relatively late (1978), and are the subject of controversy and litigation, namely over the opportunity to systematically remediate homes or simply keep the old paints safe (e.g. "lead-free" vs. "lead-safe") and the degree of accountability of present and former leaded paint manufacturers.<sup>545, 555, 556</sup> Auto batteries, the dominant application of lead nowadays, are not considered an important source of exposure provided they are handled and recycled properly.

With lead now also banned from large-scale application in electronic solders (specialised applications remain allowed),<sup>171, 173</sup> lead in glass has come under more focus (section 1.4), due to the ongoing controversy over the subclinical effects of very low lead exposure levels, i.e. subtle alterations of cognitive behaviour, especially of children.<sup>89, 545, 557</sup> The resulting trend towards further decreasing lead exposure is one of the major motivations for the development of many of the bismuth-based glasses reviewed in the present work.

**Table 24. Timeline of lead- & bismuth glass development**

≈10000 BC	1 <sup>st</sup> ceramic materials (pottery)
<3500 BC	Lead (metal) first used <sup>89</sup>
≈3000 BC	First glassy materials (glazes, faience) <sup>542, 543</sup>
≈1500 BC	First bulk glasses; extension of available colour range <sup>542, 543</sup>
≈300 BC -	First leaded glazes and small glass objects in China and Rome <sup>541, 547</sup>
≈100 BC	Widespread use of – and intoxication by – lead in ancient Rome <sup>540</sup>
1000 AD	Lead-alkali tin-opacified glazes in the Middle East <sup>541, 544</sup>
1400s	Bi mined specifically, used in typesetting <sup>535, 548, 550</sup> Bi in glass lustre, as cosalite (Pb <sub>2</sub> Bi <sub>2</sub> S <sub>5</sub> ) <sup>551</sup> First local bans of sapa made in lead kettles, i.e. containing lead acetate, in wine <sup>540</sup>
1500s	Documentation of Bi mining and extraction <sup>535, 549</sup>
1600s	<i>L'Arte Vetraria</i> (1612), extensively expanded, commented and translated; beginning of bulk lead "crystal" glass <sup>5, 536</sup>
1700s	Inclusion of Bi mentioned in cobalt blue glaze making <sup>536</sup> Many studies linking the use of lead tools in the elaboration of drinks with disease, and assorted bans on this practice <sup>539, 540</sup>
1757	Scientific experiments on Bi <sup>537</sup> , including 1 <sup>st</sup> vitrification of Bi <sub>2</sub> O <sub>3</sub> (most probably contaminated by SiO <sub>2</sub> )
1800 (ca.)	Systematic studies on optical flint glass; crown-flint achromatic pairs <sup>5</sup> Bismuth compounds first used in medicine <sup>558, 559</sup>
1830	Publication of Faraday's experiments on PbO-B <sub>2</sub> O <sub>3</sub> -SiO <sub>2</sub> optical glass <sup>5, 538</sup>
1839	Extensive treatise on lead-induced diseases <sup>539</sup>
1900 (ca.)	Very wide range of technical glasses <sup>5</sup> First bans of lead in interior paint (France, Belgium, Austria) <sup>546</sup>
1923	Tetraethyl lead introduced in petrol <sup>546, 554</sup>
1945	Bi <sub>2</sub> O <sub>3</sub> used in metallisation patent <sup>283</sup>
1960 (ca.)	Basic studies of Bi <sub>2</sub> O <sub>3</sub> glasses <sup>129, 244-246</sup> 1 <sup>st</sup> lead-free Bi-based glass, with alcalis <sup>285</sup> Discovery of massive lead contamination through petrol <sup>546, 554</sup>
1970s	Bi <sub>2</sub> O <sub>3</sub> in "standard" AgPd thick-film metallisations, such as DP 9473 Start of phase-out of leaded petrol <sup>554</sup>
1980	First low-melting, alkali- & Pb-free glasses based on Bi <sub>2</sub> O <sub>3</sub> <sup>289-294, 452</sup>
1990s	Widespread introduction of Pb-free glasses Bi <sub>2</sub> O <sub>3</sub> gains importance in glass research (since 1980s) <sup>553</sup>
2002	EU RoHS directive passed <sup>171</sup>
2003	Bi proven to be (very slightly) unstable – no practical significance <sup>560</sup>
2006	EU RoHS directive in force – use of lead prohibited with exemptions <sup>173</sup>



**Table 25. Historical oxide glass compositions on a cation basis. R1=Na+K; R2=Mg+Ca[+Cu]; R3=Al[+Fe+Mn]. Modern glasses in italic.**

Code	R1	R2	R3	Pb	B	Si	Other	Note
	[%]	[%]	[%]	[%]	[%]	[%]	[%]	
Krk-1 <sup>5</sup>	29.0	8.2	4.2	-	-	58.0	0.6 S	Egypt, 1500 BC
Krk-3 <sup>5</sup>	27.2	8.9	3.1	-	-	61.0		Sudan, ≈250 AD
<i>Krk-5<sup>5</sup></i>	<i>23.7</i>	<i>10.4</i>	<i>1.9</i>	-	-	<i>64.0</i>		<i>Container glass</i>
<i>Krk-6<sup>5</sup></i>	<i>22.2</i>	<i>11.1</i>	-	-	-	<i>66.7</i>		<i>"Std." soda-lime</i>
Krk-7 <sup>5</sup>	-	-	-	34.4	47.3	18.2		Faraday, optical
<i>L-V6</i>			4.3	36.8	31.5	27.4		<i>Low-firing TFR</i>
Tit-T5	1.2	5.5	6.6	30.3		56.5		Glaze†
<i>Pru-F8</i>	-	-	2.3	36.3		<i>61.4</i>		<i>TFR glass</i>

† Ref. 909.38.5 in original work

## 11. Toxicity of elements in glasses

This section gives a small comparison of the respective toxicity of different elements found in oxide (and some chalcogenide) glasses. Oxides of Na, K, Mg, Ca, Al, Si and P are of essentially no concern, and therefore are not included.

Table 26 gives an overview of element / representative compound toxicological data, based on indications gathered from product datasheets and governmental / international agencies such as the USA Agency for Toxic Substances Disease Registry (ATSDR), the United Nations (UN) World Health Organisation (WHO) and the latter's International Agency for Research on Cancer (IARC). Especially, comprehensive toxicological profiles from the ATSDR were examined,<sup>557, 561-569</sup> as well as WHO drinking water recommendations.<sup>570</sup>

The acronyms PEL, TLV and REL are related air contamination levels, given by different USA governmental agencies. Here, the values are expressed as "TWA", i.e. time-weighted averages over a 40h workweek.

- PEL (permissible exposure limit): maximum allowed exposure level in workplace air (8-hour average), as defined by the Occupational Safety and Health Administration (OSHA), i.e. the legally binding limit in the USA
- TLV (threshold limit value): maximum level, as recommended by the American Conference of Governmental Industrial Hygienists (ACGIH)
- REL (recommended exposure limit): maximum level, as recommended by the National Institute of Occupational Safety and Health (NIOSH)

The TLV and REL values may be lower than the legally binding PEL, if the corresponding agencies feel the latter does not fully guarantee a risk-free environment.

The permissible level in water is that recommended by the WHO for drinking water unless indicated otherwise.

The MSDSs (material safety datasheets)<sup>571</sup> were taken for relatively neutral compounds, selected to avoid extra hazards not pertinent to glassmaking, i.e. reactivity in the metallic state

or excessive basicity as an oxide (especially applies to Sr and Ba). Also, multiple entries are given for compounds whose toxicity strongly depends on oxidation state (As and Sb, another well-known example being Cr).

Based on this information, one can roughly classify the elements according to a decreasing order of concern:

- Cadmium and arsenic must clearly be avoided, as their toxicity is much higher than that of other substances (a very low level of As might be acceptable as a fining agent).
- Lead is next in line, especially given its tendency to bioaccumulate and apparently low subclinical toxicity threshold (see previous section).
- Vanadium, often touted as a "safe" replacement of lead for low-melting glasses, can actually pose a strong health concern, given its toxicity. However, the main hazard from completed glass seals would be water leaching, and the tolerable V concentration in water is much higher than that for Pb. These considerations are reinforced by the abundance of V, and its natural presence in the human body (although it has no apparent biological role in humans, it is an essential element for some organisms), and apparent non-toxicity at moderate levels.<sup>565, 572-574</sup> Therefore its use as a relatively low-level additive in glass is not a cause of concern.
- Selenium, akin to V, is quite toxic, but is not expected to be used in large amounts, especially in Bi-based oxide glasses; also, it is an essential trace element,<sup>569, 573</sup> and therefore should not pose concern in practice, unless for glasses rich in SeO<sub>2</sub>.
- Barium, antimony, molybdenum and tungsten, while toxic in high amounts, are not a cause of concern at the low levels expected to result from glass leaching. Mo is actually an important trace element,<sup>573</sup> and Sb, in spite of its similitude with As, is much less toxic and actually used in medication;<sup>567, 575-579</sup> expected use in glasses is mainly at a low level (<1%), as a fining agent (section 3.4), although higher levels can be used given the good glass-forming characteristics of Sb<sub>2</sub>O<sub>3</sub>.<sup>327</sup>
- According to recent research, bismuth is much less toxic than lead,<sup>580, 581</sup> and, though recently proven to be radioactive, its half life of 2·10<sup>19</sup> years allows its consideration as stable for all practical purposes.<sup>560</sup> Bi has a long been used in medication, and is still widely applied for this purpose,<sup>558, 559, 579, 582, 583</sup> with a good safety record at the prescribed dosages.
- Strontium, niobium and tantalum apparently have very low toxicity.<sup>561, 584-586</sup> Sr is a good partial or total substitute for more toxic Ba, although somewhat less polarisable, and Nb/Ta are useful in some glass formulations.<sup>113, 216, 301, 364</sup>
- Tellurium, in spite of it having no known biological function, has apparently low toxicity,<sup>587</sup> which is fortunate, as it is an important component in specialised "heavy" glasses (see section 5.1).
- Boron is a somewhat particular case, given the apparently conflicting classification of B<sub>2</sub>O<sub>3</sub> and H<sub>3</sub>BO<sub>3</sub> as "toxic", coupled with very high permissible levels. The classification as toxic stems from the reproductive toxicity of very high levels of ingested boron, but significant doses may otherwise be absorbed without problems<sup>564, 573</sup>, as illustrated by the high permissible levels in air and water and the ubiquity of B in nature. B is therefore not considered problematic for any reasonably durable glass.

From the above considerations, the use of glasses such as those based on ZnO-Bi<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> should not pose significant health problems in most applications, i.e. except when

exposed to very aggressive media or implanted in the body. Nevertheless, toxicity and leaching issues – as well as emissions during manufacturing steps such as glass melting – should always be borne in mind when formulating glasses.

**Table 26. Toxicological information for different elements found in glasses: air (PEL / TLV / REL) and ambient water exposure levels; carcinogenic potential (IARC) and safety classification according to materials safety datasheet (MSDS) of indicated compound. See text and notes for further clarification.**

Element	PEL [ $\mu\text{g}\cdot\text{m}^{-3}$ ]	TLV [ $\mu\text{g}\cdot\text{m}^{-3}$ ]	REL [ $\mu\text{g}\cdot\text{m}^{-3}$ ]	Water [ $\mu\text{g}\cdot\text{l}^{-1}$ ]	IARC <sup>a</sup>	MSDS	Classification <sup>b</sup>
Sr	/	/	/	4'000 <sup>d</sup>	-	SrCO <sub>3</sub>	/
Ba	500 <sup>c</sup>	500 <sup>c</sup>	500 <sup>c</sup>	700	-	BaCO <sub>3</sub>	Xn
B	15'000 <sup>e</sup>	10'000 <sup>e</sup>	10'000 <sup>e</sup>	300	-	H <sub>3</sub> BO <sub>3</sub>	T <sup>f</sup>
V	100	50	50	100 <sup>g</sup>	2B	V <sub>2</sub> O <sub>5</sub>	T, N
Nb	-	-	-	-	-	Nb <sub>2</sub> O <sub>5</sub>	Xi
Ta	-	-	-	-	-	Ta <sub>2</sub> O <sub>5</sub>	/
Mo	-	-	-	70	2B	MoO <sub>3</sub>	Xn
W	1'000	1'000	-	-	-	WO <sub>3</sub>	Xn
Cd	5	2 <sup>h</sup>	-	3	1	CdO	T+, N
Pb	50	50	50	10	2A	PbCO <sub>3</sub>	T, N
As	10	10	2	10	1	As <sub>2</sub> O <sub>3</sub>	T+
						As <sub>2</sub> O <sub>5</sub>	T
Sb	500	500	500	5	2B	Sb <sub>2</sub> O <sub>3</sub>	Xn
						Sb <sub>2</sub> O <sub>5</sub>	Xi
Bi	-	-	-	-	-	Bi <sub>2</sub> CO <sub>5</sub>	-
Se	200	200	200	10	3	SeO <sub>2</sub>	T, N
Te	-	-	-	-	-	TeO <sub>2</sub>	-

(a) 1 = demonstrated carcinogenic; 2A/B = probably/possibly carcinogenic; 3 = not classifiable

(b) T+ = very toxic; T = toxic; Xn = harmful; Xi = irritant; N = dangerous for the environment

(c) Soluble Ba only; BaSO<sub>4</sub> : 10 mg/m<sup>3</sup> (REL/TLV) ; 15 mg/m<sup>3</sup> (PEL)

(d) Sr: according to ATSDR<sup>561</sup>

(e) Expressed as B<sub>2</sub>O<sub>3</sub>

(f) Classified toxic due to reproductive effects at much lower doses than that for systemic toxicity

(g) Rough estimate based on 1.8 mg/day intake limit & 4...220  $\mu\text{g}/\text{L}$  reported surface water concentration

(h) Expressed as Cd in Cd compounds

## 12. Oxidation state of Bi species in glasses

This section discusses the valence of Bi in oxide glasses, i.e. the existence of species differing from the usual trivalent state. A strong case is made in favour of predominantly reduced species in the case of departure from the nominal Bi<sup>3+</sup> valence, and against significant formation of Bi<sup>5+</sup> species, as occasionally reported, except possibly in very special cases. Also, the nature of these reduced species is briefly discussed.

### Introduction

In recent work on the optical properties, mainly luminescence, of Bi-containing glasses (both Bi-based and Bi-doped), somewhat conflicting conclusions have been made as to the origin of these phenomena. While most authors clearly seem to favour defects stemming from reduced species<sup>353, 428, 429, 588-591</sup>, others disagree and postulate significant or even dominant amounts of Bi<sup>5+</sup><sup>359, 360, 592-595</sup>, often basing on the results of XAFS or XPS studies.

### Oxide compounds with pentavalent bismuth

Akin to lead(IV), there are instances where Bi does occur in higher oxidation states than +3:

- Although isolation of well-defined, stoichiometric, anhydrous Bi<sub>2</sub>O<sub>5</sub> is exceedingly difficult,<sup>596-598</sup> compounds such as BiO<sub>2</sub> (stoichiometric and nonstoichiometric variants) and Bi<sub>4</sub>O<sub>7</sub><sup>597-599</sup> may be prepared by wet chemical methods – with Bi<sub>4</sub>O<sub>7</sub> crystallised by heating at high oxygen pressures – and tend to show separate Bi<sup>3+</sup> and Bi<sup>5+</sup>, rather than "average" (delocalised) sites. Decomposition temperatures to mainly trivalent Bi<sub>2</sub>O<sub>3</sub> are low, lying between 300 and 400°C, with a small amount of pentavalent Bi (oxygen excess) possibly persisting in sillenite-type β-Bi<sub>2</sub>O<sub>3</sub>.<sup>600</sup> In comparison, preparation of PbO<sub>2</sub> is quite facile,<sup>601</sup> and the decomposition temperature in air of Pb<sub>3</sub>O<sub>4</sub> to PbO is higher, ca. 560°C.<sup>602</sup> In oxides, the lower stability of Bi<sup>5+</sup> vs. Pb<sup>4+</sup> follows the trend set by As<sup>5+</sup> vs. Ge<sup>4+</sup>, and Sb<sup>5+</sup> vs. Sn<sup>4+</sup> in the periodic table.
- In the synthesis of conductive bismuth noble metal pyrochlores such as Bi<sub>2</sub>Ru<sub>2</sub>O<sub>7</sub> by wet chemical methods, excess Bi may be incorporated, presumably into the "B" site in higher-valence form, nominally yielding the solid solution Bi<sup>III</sup><sub>2</sub>(Ru,Bi<sup>IV</sup>)<sub>2</sub>O<sub>7</sub>, the same being possible with Pb to form Pb<sup>II</sup><sub>2</sub>(Ru,Pb<sup>IV</sup>)<sub>2</sub>O<sub>6.5</sub>,<sup>483</sup> although there is some doubt about the valence of Ru (see below). Low-temperature, oxidising conditions were used in this work, i.e. soluble bismuth nitrate salts<sup>603</sup> and oxygen sparging. In both compounds, about half of the Ru may be substituted by Bi or Pb. However, these substituted forms are probably not stable at high temperature, excess Pb being clearly shown to severely degrade thermal stability<sup>483</sup> and no significant excess Bi being seen in Bi<sub>2</sub>Ru<sub>2</sub>O<sub>7</sub> prepared by standard calcination. Additionally, there is some doubt about the valence of Pb, Bi, and Ru, as studies on Bi<sub>3</sub>Ru<sub>3</sub>O<sub>11</sub>, which is stable vs. Bi<sub>2</sub>Ru<sub>2</sub>O<sub>7</sub> below 950°C in air, tend to attribute the valence increase stemming from the excess oxygen to Ru,<sup>460, 513, 604, 605</sup> a conclusion that is also supported by the existence of La<sub>3</sub>Ru<sub>3</sub>O<sub>11</sub>,<sup>606</sup> where La is clearly trivalent.
- In crystalline compounds such as perovskites and related structures, studies of the ternary equilibria of Bi<sub>2</sub>O<sub>3</sub> / Bi<sub>2</sub>O<sub>5</sub> with alkaline earth oxides show that pentavalent bismuth may be stabilised in the octahedral "B" sites by large alkaline earth "A" cations. Stability is favoured both by large "A" cations and large A:B ratios, i.e. a more basic environment, as attested by systems with CaO<sup>607, 608</sup>, SrO<sup>609, 610</sup>, and BaO<sup>611</sup>. With CaO, only trivalent bismuth is seen under normal oxygen pressures. With SrO, pentavalent bismuth compounds such as Sr<sub>6</sub>Bi<sub>4</sub>O<sub>15</sub> and Sr<sub>6</sub>Bi<sub>2</sub>O<sub>11</sub> do exist at moderate temperatures for Sr:Bi > 1; however, the 1:1 compound yields Sr<sub>2</sub>Bi<sub>2</sub>O<sub>5</sub>, with trivalent bismuth only. BaO has expectedly an even better stabilising effect for

higher valence of Bi; thus, BaBiO<sub>3</sub> may be prepared by standard ceramic methods and is essentially oxygen-stoichiometric below ca. 875°C.<sup>611, 612</sup> This is also true of more complex oxides, such as Ba(In<sub>0.5</sub>Ta<sub>0.5-x</sub>Bi<sub>x≤0.05</sub>)<sup>613</sup>, Sr<sub>2</sub>BiNdO<sub>6</sub>,<sup>614</sup> Ba<sub>2</sub>BiYO<sub>6</sub> and Ba<sub>2</sub>BiDyO<sub>6</sub>.<sup>615</sup> Again, a strong similitude with lead may be noted, as stabilisation of tetravalent lead is also seen in the corresponding compounds with the alkaline earth oxides,<sup>66, 616-620</sup> and tendentially occurs more readily than for higher Bi oxidation states. Going even further, one can observe that such stabilisation of "unusual" higher oxidation states by large alkaline and alkaline earth ions (or in some cases by Pb<sup>2+</sup> or Bi<sup>3+</sup>) is also found for many polyvalent transition metal oxide compounds, yielding species such as Cr<sup>4+/6+</sup>, Mn<sup>4+</sup>, Fe<sup>4+</sup>, Co<sup>3+/4+</sup>, Ni<sup>3+</sup> and Cu<sup>2+/3+</sup>.<sup>444, 621-624</sup>

- Single alkalis have a lower stabilising effect on pentavalent bismuth than alkaline earths in oxide compounds; substances such as NaBiO<sub>3</sub>, KBiO<sub>3</sub>, or (Ba<sub>1-x</sub>K<sub>x</sub>)BiO<sub>3</sub> with  $x$  above ~0.5, require wet chemical synthesis,<sup>596</sup> high-pressure conditions,<sup>625</sup> or anodic electrodeposition.<sup>626</sup> Compounds with a more basic stoichiometry such as Na<sub>3</sub>BiO<sub>4</sub> may be prepared by more classical routes, albeit at moderate temperatures (600°C in 1 atm O<sub>2</sub>, then 700°C in sealed capsules).<sup>627</sup> In all cases, reported synthesis or decomposition temperatures under ambient pressures are below ca. 900°C.
- The pure compound Bi<sub>2</sub>O<sub>3+x</sub> itself is reported to be slightly oxygen-deficient ( $x = -0.033$ ) in the melt equilibrated with air at 895°C, and also in the different crystalline polymorphs.<sup>628</sup> Detailed structural studies on metastable  $\gamma$ -Bi<sub>2</sub>O<sub>3</sub><sup>629</sup> and other similar compounds,<sup>630, 631</sup> which have a defective sillenite structure, also indicated Bi<sup>5+</sup> to be essentially absent, the formal higher charge of the tetrahedral sites being compensated by oxygen vacancies making space for the "too large" Bi<sup>3+</sup> cation and its "lone pair" electrons. On the other hand, for solid oxygen-ion electrolytes consisting of the high-temperature cubic  $\delta$ -Bi<sub>2</sub>O<sub>3</sub> phase stabilised by 20-50 mol% Er<sub>2</sub>O<sub>3</sub>, a slight oxygen excess,  $x = +0.005$  to  $+0.022$ , depending on the Er<sub>2</sub>O<sub>3</sub> content, has been reported in air around 800°C,<sup>632</sup> in agreement with the results for similar Bi<sub>2</sub>O<sub>3</sub>-Y<sub>2</sub>O<sub>3</sub> and with the conductivity being p-type in ambient air.<sup>519, 521</sup> However, this represents at most a small oxygen excess, and the possibility this may be due to impurities cannot be totally excluded, given the rather high reactivity of Bi<sub>2</sub>O<sub>3</sub> with other oxides.

#### *Pentavalent bismuth in glasses?*

Clearly, the above examples indicate that, in traditional high-temperature (above ca. 900°C) synthesis, Bi<sup>5+</sup> occurs only in rather special circumstances: very basic environments, not too high temperatures and high oxygen pressures. In glasses prepared from the melt, significant amounts of Bi<sup>5+</sup> species, if any, would therefore only be expected to occur in compositions very rich in alkalis (alkaline earth oxides require higher melting temperatures), stabilised by minimal amounts, if at all, of B<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub>. An example of such compositions is the Li<sub>2</sub>O-Bi<sub>2</sub>O<sub>3</sub> system,<sup>388, 389</sup> with optional BaO,<sup>381</sup> PbO<sup>382</sup> or small B<sub>2</sub>O<sub>3</sub><sup>334</sup> additions, and "excess oxygen" has indeed been reported in these glasses at high Li<sub>2</sub>O concentrations,<sup>388</sup> but such compositions are very atypical and would find limited practical uses due to their moisture sensitivity.

Less basic conditions rapidly destabilise Bi<sup>5+</sup>, as attested by the results of adding B<sub>2</sub>O<sub>3</sub> to the BaO-Bi<sub>2</sub>O<sub>3</sub> system<sup>347, 351, 611, 633</sup>: the higher Bi valence seen in BaBiO<sub>3</sub> is no longer found in the compositionally closest compounds, BaBiBO<sub>4</sub> and Ba<sub>3</sub>BiB<sub>3</sub>O<sub>9</sub>, which essentially contain Bi<sup>3+</sup> only.

This view is also confirmed by the electrochemical series determined for a more traditional, but still quite alkali-rich, Li<sub>2</sub>O-Na<sub>2</sub>O-MgO-B<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> glass<sup>424</sup>. Even at the relatively



moderate temperature of 1100°C, Bi<sup>5+</sup> is not found; the equilibrium in air lies ca. at the Sb<sup>5+</sup>/Sb<sup>3+</sup> boundary, so a significant amount of Bi<sup>5+</sup>, which is much less stable than Sb<sup>5+</sup>, would only be expected at higher oxygen pressures, lower temperatures and more alkali-rich glasses (stabilisation of oxidised species by alkalis is illustrated by the comparison of their redox potential in two different Na<sub>2</sub>O-SiO<sub>2</sub> glass melts<sup>634</sup>). Recent sol-gel experiments on insertion of Bi metal, oxide and sulphide nanoparticles into a Na<sub>2</sub>O-B<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> glass (Na:Bi:Si ≈ 2:6:9)<sup>534</sup>, although performed at moderate temperatures (400-600°C) in oxygen, did not lead to detected formation of Bi<sup>5+</sup> species (it must be noted that the particular experimental procedure somewhat limited the interaction of Bi species with the glass). This is not surprising, given the well-known low stability towards reduction of Bi<sub>2</sub>O<sub>3</sub>, both pure and in compounds,<sup>421, 422, 424, 519-521, 635</sup> also attested by its easy precipitation from glass as metal particles upon exposition to a reducing gas at moderate temperatures.<sup>366, 408, 425, 534, 636</sup>

#### *Nature of reduced species in Bi<sub>2</sub>O<sub>3</sub>-containing glasses*

Detailed investigations on the origins of the intense colouration and near-infrared (NIR) luminescence of bismuth glasses clearly show they are correlated<sup>637</sup> and both stem from the presence of reduced species introduced by corresponding conditions: acidic melts,<sup>375, 426, 588</sup> high temperatures,<sup>118, 353, 375, 426, 591, 637</sup> low oxygen pressures,<sup>591</sup> using reducing starting reagents or introduction of small amounts of Bi metal.<sup>426, 637</sup> A direct confirmation is the presence of metallic Bi nanoparticles in the more reduced glasses, as evidenced by SEM, TEM and XRD.<sup>118, 353, 361, 426, 427</sup> Conversely, classical fining agents (i.e. that act as redox buffers, preventing excessive reduction) such as Sb<sub>2</sub>O<sub>3</sub>, As<sub>2</sub>O<sub>3</sub> and CeO<sub>2</sub> efficiently suppress both.<sup>118, 273, 353, 361, 638</sup> Coloration and nanoparticles formation may also be suppressed by additives that generate oxygen in the melt such as KNO<sub>3</sub> and KClO<sub>4</sub>.<sup>427</sup>

While these facts establish that the aliovalent species in glasses (except possibly the abovementioned very alkaline, low-temperature melts) are reduced with respect to the usual Bi<sup>3+</sup> state, the exact nature of the intermediate species, if any, between Bi<sup>0</sup> metallic nanoparticles and Bi<sup>3+</sup> still is vividly debated, based on chemical, structural and luminescence studies; species such as Bi<sup>2+</sup>,<sup>429, 588</sup> Bi<sup>+</sup>,<sup>637</sup> subvalent polycations,<sup>591, 637</sup> or even dissolved Bi<sup>0</sup> atoms or clusters<sup>353</sup> have been postulated, in line with species found in molten salt solutions.<sup>639</sup> It must also be borne in mind that the glasses are far out of equilibrium (possibly incomplete equilibration of the melt with ambient oxygen, rapid cooling after melting, stress-relieving anneal), making the reduced species most likely highly dependent on the preparation conditions.

Concerning the XAFS results<sup>595</sup> interpreted to show the presence of Bi<sup>5+</sup> ions, the overwhelming experimental evidence favouring reduced Bi species in glasses melted at high temperatures calls into question<sup>588</sup> the use of X-ray absorption data to determine valence: the information returned, i.e. bond length and coordination, cannot be used alone to unambiguously determine the exact valence of Bi, especially in the light of the strong tendency towards local structural disorder.

#### *Conclusions*

The experimental evidence confirms the presence of reduced (valence < 3) Bi species as the source of colour and luminescence in most cases: such properties are favoured by reducing conditions: high melting temperatures, absence of fining agents, reducing atmospheres and a more acidic glass chemistry, culminating in the precipitation of Bi<sup>0</sup> metallic nanoparticles. Most practical glasses will have a chemistry similar to those where such phenomena are observed (with additions such as fining agents to suppress their occurrence when transparency



is sought). Therefore, the existence of significant amounts of pentavalent bismuth is deemed very unlikely in most melt-derived glasses.

On the other hand, the presence of some Bi<sup>5+</sup> in very basic melts at moderate temperatures cannot be totally ruled out, nor in glasses prepared by "unconventional" low-temperature methods such as sol-gel synthesis or thin-film deposition.

The chemistry of the reduced species present in Bi glasses – other than Bi<sup>0</sup> particles – has not at present been fully understood; more detailed work is clearly needed to elucidate how these species form, as a function of the degree of reduction of the melt and the subsequent cooling and annealing phases.

### **13. Coordination of bismuth in crystalline oxides**

In the aim to provide insight into the structure of Bi<sub>2</sub>O<sub>3</sub>-based glasses, this section shortly reviews the coordination of bismuth in crystalline oxides, concentrating on those oxides having the most relevance for glass formation, i.e. mixed compounds of Bi<sub>2</sub>O<sub>3</sub> (Bi essentially trivalent) with the classical glass-forming oxides. Pure or near-pure Bi<sub>2</sub>O<sub>3</sub>, as well as conducting compounds such as Bi<sub>2</sub>Ru<sub>2</sub>O<sub>7</sub>, are also treated. It is shown that due to its stereochemically active "lone-pair" electrons, Bi<sup>3+</sup> oxygen coordination polyhedra exhibit a wide array of disordered and asymmetrical geometries, even in crystalline compound. As expected, similar behaviour is seen in the other "lone-pair" ions Pb<sup>2+</sup> and Sn<sup>2+</sup>.

#### *Introduction*

The concept of ionic radii, as published in the tables by Shannon,<sup>640</sup> has been mostly very helpful in the study of ceramic structures. However, even at the time of publication (1976), Shannon noted that some cations posed considerable problems when considering them as spheres: Pb<sup>2+</sup> (somewhat), and especially Sn<sup>2+</sup> and Bi<sup>3+</sup>. He already correctly identified these problems as stemming from their "lone pair" character, derived from outer *s* states (Sn<sup>2+</sup>: 5*s*<sup>2</sup>; Pb<sup>2+</sup> and Bi<sup>3+</sup>: 6*s*<sup>2</sup>). However, the exact nature of the involved orbital mixing, required for the "lone pair" to become stereochemically active (pure *s* states have spherical symmetry), has long been elusive. Recent electronic structure calculations and corresponding experiments have shed new light on this matter, yielding a complex picture involving interaction between both *s* and *p* orbitals in the metal valence shell, mediated by oxygen 2*p* ones; these studies were also extended to other lone-pair cations and chalcogenide anions, and good predictions of the appearance or not of a stereochemically active lone pair for a several metal-chalcogenide compounds could be made.<sup>403, 641-643</sup> Such a stereochemically active lone pair results in strong bonding asymmetry and attendant structural distortions, which are expected to limit, in this case, the usefulness of simplified concepts such as bond-valence parameters<sup>644</sup> in calculating the effective bond strengths.

This supplement lists and comments some of the features found in the different structures of crystalline compounds: the oxide, Bi<sub>2</sub>O<sub>3</sub> (pure and slightly doped), as well as compositions more typical of those found in glasses, i.e. especially borates and silicates. This should yield useful insight on local Bi<sup>3+</sup> oxygen coordination polyhedra in glasses. A few salient examples of the coordination polyhedra seen in the crystalline compounds discussed in this supplement are illustrated in Figure 6; the stereochemically active lone pair, denoted "E", may be seen as "repelling" the oxygen atoms in its vicinity, or even as taking the place of a bond, resulting in Bi(O<sub>*x*</sub>E) polyhedra.

### Polymorphism in Bi<sub>2</sub>O<sub>3</sub>

Bi<sub>2</sub>O<sub>3</sub> has four common phases, denoted  $\alpha$ ,  $\beta$ ,  $\gamma$  and  $\delta$ , of which monoclinic  $\alpha$ -Bi<sub>2</sub>O<sub>3</sub> is stable below 729°C, and cubic  $\delta$ -Bi<sub>2</sub>O<sub>3</sub> above this temperature, the  $\beta$  and  $\gamma$  phases being metastable and their obtention possible by light doping, controlled cooling of  $\delta$ -Bi<sub>2</sub>O<sub>3</sub>, or low-temperature chemical synthesis. A fifth  $\epsilon$  phase has recently been grown by a hydrothermal method.<sup>515, 629, 642, 645-648</sup> Atomic configurations and Bi-O distances are given for the  $\alpha$ ,  $\beta$  and  $\delta$  polymorphs, and a common " $\beta$ " ionic conductor phase<sup>649</sup>, in Table 27. The data for the sillenite compounds (ideally Bi<sub>24</sub>M<sub>2</sub>O<sub>40</sub>, where M is a tetravalent cation), of which  $\gamma$ -Bi<sub>2</sub>O<sub>3</sub> is a defective variant, are listed in Table 28.

#### $\alpha$ - and $\beta$ -Bi<sub>2</sub>O<sub>3</sub>

Monoclinic  $\alpha$ -Bi<sub>2</sub>O<sub>3</sub>, the phase stable in ambient conditions, has two distinct Bi sites (Bi1 & Bi2, respectively with 5 and 6 neighbouring oxygen anions (Table 27 & Figure 8, good agreement between different sources), with both coordination polyhedra being strongly distorted with respect to their idealised geometry. In the square pyramid around Bi1, the shortest apex bond (212 pm) is almost matched by the bonds on one side of the base (220 & 221 pm), whereas the bonds on the other side of the base are much longer (253 & 263 pm). The same is true for the asymmetric octahedron around Bi2, especially for the three longer bonds, which span a wide range of distances (243-279 pm).

The metastable tetragonal  $\beta$ -Bi<sub>2</sub>O<sub>3</sub> phase, which can be prepared by decomposing Bi<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> at  $\approx 380^\circ\text{C}$ <sup>650</sup> or sublimation/condensation,<sup>651</sup> may be thought of as a distorted and ordered (oxygen vacancies) version of the high-temperature cubic  $\delta$  polymorph.<sup>650</sup> The reported Bi-O distances (Table 27) are in very good agreement, and also similar to that observed for Bi1 in  $\alpha$ -Bi<sub>2</sub>O<sub>3</sub>. The oxygen coordination shell around Bi, shown in Figure 14, is a prime example of the difficulty of unambiguously specifying the coordination of Bi, stemming from the strong distortions, wide range of bond lengths and stereochemically active lone pair. Here, several coordination polyhedra may reasonably be considered (see also Figure 6 & Table 14):

- Octahedron: if all oxygen ions and the lone pair E are counted as vertices
- Square pyramid (5-Py14, very deformed): if either O2<sup>e</sup> or E is omitted
- Face-sharing trigonal bipyramid (4-BPy): if both O2<sup>e</sup> and E are omitted

#### $\delta$ -Bi<sub>2</sub>O<sub>3</sub>

Cubic  $\delta$ -Bi<sub>2</sub>O<sub>3</sub> is traditionally reported to crystallise in the fluorite (CaF<sub>2</sub>) structure with only  $\frac{3}{4}$  of oxygen positions filled (Figure 6) and the corresponding oxygen vacancies completely disordered. This ideal Bi(O<sub>1.5</sub>□<sub>0.5</sub>) formula suggests a very high oxygen ion conductivity. In practice, both conductivity and entropy are indeed close to that of the liquid phase,<sup>646</sup> and this material is the best solid oxygen ionic conductor known to date. Although it is stable only at high temperature,  $\delta$ -Bi<sub>2</sub>O<sub>3</sub> or closely related phases may be stabilised to lower temperatures (in the same way as cubic ZrO<sub>2</sub>) by appropriate doping to yield useful ionic oxygen conductors, albeit with lower conductivity than the pure material.<sup>519-522, 632, 651-654</sup> More detailed structural studies yielded a somewhat more complicated structure than a simple fluorite lattice with random oxygen vacancies. To account for the observed neutron diffraction data, local shifts of all<sup>645</sup> or some<sup>653</sup> of the oxygen anions with respect to their average positions were postulated, with stabilised Bi<sub>2</sub>O<sub>3</sub> (doped with 27% Y<sub>2</sub>O<sub>3</sub>) exhibiting an even wider variety of possible oxygen displacements.<sup>653</sup> As the possible dynamic shifts are averaged out over time, the material retains a cubic symmetry overall. However, recent experiments and calculations<sup>403, 642, 643, 648, 655, 656</sup> strongly suggest that on an instantaneous and local basis, there is strong departure from the overall symmetry, leading to a coordination

around Bi and Bi-O distances that strongly resemble that of the ordered  $\alpha$  and  $\beta$  polymorphs. The exact local structure is still a matter of debate.

#### *$\gamma$ -Bi<sub>2</sub>O<sub>3</sub> and the sillenite family*

Doping Bi<sub>2</sub>O<sub>3</sub> with a small amount of oxides of widely varying cation sizes and valences, such as ZnO, CdO, PbO, B<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, Ga<sub>2</sub>O<sub>3</sub>, Tl<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, ZrO<sub>2</sub>, SiO<sub>2</sub>, GeO<sub>2</sub>, CeO<sub>2</sub>, V<sub>2</sub>O<sub>5</sub>, P<sub>2</sub>O<sub>5</sub> and As<sub>2</sub>O<sub>5</sub><sup>630, 631, 651, 652, 657, 658</sup> stabilises the body-centred cubic sillenite structure, which is isostructural with the metastable  $\gamma$  polymorph of pure Bi<sub>2</sub>O<sub>3</sub>.<sup>629</sup> Sillenites are classified as "ideal" if they correspond to the formula Bi<sub>12</sub>MO<sub>20</sub> (unit cell: Bi<sub>24</sub>M<sub>2</sub>O<sub>40</sub>), where M is a smaller tetravalent metal, or "defect" otherwise, the latter category therefore including pure  $\gamma$ -Bi<sub>2</sub>O<sub>3</sub>.<sup>629, 631, 659</sup>

Two distinct cation sites ("Bi" and "M") exist in the sillenite structure. The oxygen coordination shell around Bi<sup>3+</sup> in the Bi site consists of distorted square pyramids (5-Py14, see Figure 6 & Table 14), and the corresponding distances (to apex; to the 4 bases) are given in Table 28. Two oxygen ions lie further, at ca. 300-310 pm, and taking them in consideration as well would yield a distorted 7-Py142 structure.<sup>629, 630, 657, 659</sup> The Bi-O distances are very similar as in the 5-Py14 polyhedra of  $\alpha$ - and  $\beta$ -Bi<sub>2</sub>O<sub>3</sub>: the shortest oxygen is 200-210 pm distant and is at the pyramid apex, and the pyramid base is strongly distorted, with one side having only slightly longer bonds than with the apex and the other side much longer ones.

In ideal sillenites, the M site is filled with cations having a valence of +4 (e.g. Si<sup>4+</sup> or Ge<sup>4+</sup>) or a cation mix of same average valence, and surrounded by an oxygen tetrahedron. However,  $\gamma$ -Bi<sub>2</sub>O<sub>3</sub> and sillenites doped at low levels contain Bi ions in the M site as well, and analyses have not detected significant amounts of Bi<sup>5+</sup><sup>629, 631, 652, 659</sup> (see also discussions in the previous section). This implies accommodation of Bi<sup>3+</sup> in the much too small tetrahedral M sites (that accept cations as small as B<sup>3+</sup>!), and again illustrates the effect of the lone pair: in this case, Bi<sup>3+</sup> takes the 3-PyM configuration (Figure 6 & Table 14), i.e. the nominal MO<sub>4</sub> tetrahedron is replaced by BiO<sub>3</sub>E, with an oxygen anion replaced by a vacancy "filled" by the Bi<sup>3+</sup> lone pair E, accompanied by a local shift of the large Bi<sup>3+</sup> cation away from the three remaining oxygen anions. This yields short average Bi-O distances in the 198 to 209 pm range, as determined by neutron diffraction,<sup>629, 659</sup> which is realistic given the fact that there are only 3 bonds. As each Bi<sup>3+</sup> at the M site entails "replacement" of a corresponding oxygen anion by the Bi<sup>3+</sup> lone pair E, the general formula for sillenite stoichiometry determined by Valant & Suvorov<sup>631</sup> for all M valences may be written Bi<sub>12</sub>(Bi<sub>0.8-n-x</sub>M<sup>n+</sup><sub>5x□0.2-(5-n-x)</sub>)(O<sub>19.2+n-x</sub>E<sub>0.8-n-x</sub>), which corresponds to complete occupation of the oxygen sites if the lone pairs E of the Bi<sup>3+</sup><sub>M</sub> cations are taken into account. The very flexible bonding of Bi<sup>3+</sup> can also allow some departure from stoichiometry, as required due to charge or size considerations, e.g. cations too large for the M site or interstitial oxygen.<sup>629, 630</sup>

#### *Compounds related to glass-forming compositions*

After examining the strong disordering effects of the Bi<sup>3+</sup> lone pair on pure or doped Bi<sub>2</sub>O<sub>3</sub>, we now turn to compositions more relevant to our main subject, i.e. compounds of Bi<sub>2</sub>O<sub>3</sub> with glass-forming oxides such as B<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, GeO<sub>2</sub> and P<sub>2</sub>O<sub>5</sub>. The coordination around Bi<sup>3+</sup> for some compounds is listed in Table 29. For comparison purposes, the same is given around Pb<sup>2+</sup> in Table 30, and Sn<sup>2+</sup> in Table 31, and around other cations in Table 32, for analogous compounds. Finally, the coordination shells around B<sup>3+</sup> are listed for examined compounds in Table 33, and those around Si<sup>4+</sup>, Ge<sup>4+</sup> and P<sup>5+</sup> is given in Table 34.

The tendency for disorder and asymmetry around Bi<sup>3+</sup>, seen in pure and doped Bi<sub>2</sub>O<sub>3</sub>, is confirmed in the compounds with the glass-forming oxides, with a very rich variety of oxygen coordination shells (even in a single compound such as Bi<sub>4</sub>B<sub>2</sub>O<sub>9</sub><sup>660</sup>), and often three bonds

significantly shorter than the rest, as in the idealised 6-Oct33 structure. Three shorter bonds are also often seen for nominally different coordinations (e.g. 4-PyM & 5-Py14), resulting in strong deformations of these polyhedra. There are some other less-common motifs, though, such as 2 or 4 shorter bonds. It must be borne in mind that the strong disorder makes coordination assignment for Bi a rather arbitrary choice; this is especially seen in borates, and could be linked to the Bi<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub> system being a good basis for glasses.

It must also be noted that some of the structures have unrealistically long reported Bi-O bonds, such as SrBi<sub>2</sub>B<sub>2</sub>O<sub>7</sub><sup>661</sup> and Ba<sub>3</sub>BiP<sub>3</sub>O<sub>12</sub>.<sup>662</sup> The authors in this case suppose local disordered displacements that are not seen in the average structure, but are reflected as anomalously large thermal parameters. Such local displacements would be in line with current understanding of  $\delta$ -Bi<sub>2</sub>O<sub>3</sub> and observed static disorder in pure and doped Bi<sub>2</sub>Ru<sub>2</sub>O<sub>7</sub>.<sup>663</sup>

It is difficult to see any salient tendency of Bi coordination with compound composition, except possibly somewhat smaller coordination numbers at high Bi contents, as seen in silicate/germanate compounds and in line with tendencies postulated for glasses (see section 3.3 of main paper).

Concerning bonding of oxygen, compositions such as (Ca,Sr)Bi<sub>2</sub>B<sub>2</sub>O<sub>7</sub><sup>661</sup> and Bi<sub>3</sub>B<sub>5</sub>O<sub>12</sub><sup>664</sup> lie at the threshold where O<sup>2-</sup> anions appear, that are not bonded to any glass-forming cation polyhedra.

*Comparison with lone-pair Pb<sup>2+</sup>, Sn<sup>2+</sup>, as well as modifiers without lone pairs*

In analogous compounds, Pb<sup>2+</sup> (Table 30) and Sn<sup>2+</sup> (Table 31) cations exhibit strong similitude with Bi<sup>3+</sup>, i.e. markedly asymmetric bonding brought about by the stereochemically active lone pair. There are some differences, though: the coordination shells tend to be less disordered, especially for the smaller, less polarisable Sn<sup>2+</sup>.

For Pb<sup>2+</sup>, there is a marked tendency for low-coordination bonding at high Pb contents, whereas such a trend is much less clear-cut for Bi<sup>3+</sup>. Distorted octahedra (6-Oct33) are seen in a compound where Pb content is relatively low (Pb<sub>6</sub>B<sub>10</sub>O<sub>21</sub>), also in line with what is postulated for glasses. At high Pb contents, the type of low-coordination bonding is also different: Pb<sup>2+</sup> favours pyramids with itself at its apex, with a triangular (3-PyM) or square (4-PyM) base. In the latter case, the square is often rather "3+1" in complex PbO compounds, with one bond significantly longer than the others, in contrast to the more symmetrical pure PbO, both forms having regular (litharge) or "2+2" bonding (massicot). A "direct comparison" of Bi<sup>3+</sup> and Pb<sup>2+</sup> is possible for the compound PbBiBO<sub>4</sub>, which contains both ions and actually lies in the glass-forming range (see section 3.2 in main paper): Pb<sup>2+</sup> adopts a clear threefold 3-PyM coordination (or 6-Oct33, but with 3 very long additional Pb-O bonds), whereas the coordination around Bi<sup>3+</sup> is clearly much more octahedral (6-Oct33), the difference between both groups of three bonds being much smaller for Bi<sup>3+</sup>.

It is difficult to establish tendencies for Sn<sup>2+</sup>, as the structures of only a few phosphate compounds were found, given the tendency in many systems for Sn<sup>2+</sup> to disproportionate to Sn<sup>0</sup> and Sn<sup>4+</sup>. Nevertheless, the observed behaviour of Sn<sup>2+</sup> is logical with respect to Pb<sup>2+</sup>: the tendency for threefold coordination as 3-PyM pyramids is very strong (except in pure SnO, whose litharge form keeps the 4-PyM coordination), and the Sn-O distances are much less variable and slightly shorter than the Pb-O ones. Sn<sup>2+</sup> therefore appears to be the most "ordered" cation of the three, however retaining the asymmetry stemming from the stereochemically active lone pair, in line with the results of analyses on glasses<sup>219</sup> and structural modelling.<sup>403</sup> In fact, the latter modelling work predicts the lone pair character of Sn<sup>2+</sup> to be more pronounced than that of Pb<sup>2+</sup> and Bi<sup>3+</sup>.

In comparison with the lone-pair cations, modifiers such as Ca<sup>2+</sup>, Sr<sup>2+</sup>, Ba<sup>2+</sup> and La<sup>3+</sup> (Table 32) expectedly tend to adopt more symmetrical, nondirectional geometries characteristic of ionic bonding, i.e. a larger coordination number, and no especially short bonds. In line with the compounds ZnBi<sub>2</sub>B<sub>2</sub>O<sub>7</sub> and CaBiGaB<sub>2</sub>O<sub>7</sub> being relatively poor in B<sub>2</sub>O<sub>3</sub>, Zn<sup>2+</sup> and Ga<sup>3+</sup> adopt a tetrahedral oxygen environment, as they would do in corresponding glasses when they partly enter the network backbone.

#### *Coordination of glass-forming oxides*

The borates follow the usual trends seen in both glasses and crystalline compounds: 1) initial conversion of bridging BO<sub>3</sub> triangles to bridging BO<sub>4</sub> tetrahedra and attendant increase in connectivity, 2) progressive depolymerisation of the borate network by replacing bridging oxygen ions with terminal ones, 3) reversion to BO<sub>3</sub> groups, with 2 & 3 occurring somewhat concomitantly. This may be seen in a list of example compounds.

- BaB<sub>4</sub>O<sub>11</sub>: half BO<sub>3</sub> and BO<sub>4</sub> groups, 3D borate network (typical of phase 1)
- BiB<sub>3</sub>O<sub>6</sub>: beyond phase 1 – layered borate network (mixed BO<sub>3</sub> and BO<sub>4</sub>), with Bi<sup>3+</sup> in between
- CaBiGaB<sub>2</sub>O<sub>7</sub> & ZnBi<sub>2</sub>B<sub>2</sub>O<sub>7</sub>: layered mixed network of borate (resp. fully BO<sub>4</sub> & half BO<sub>3</sub>/BO<sub>4</sub>) and gallate/zincate tetrahedra, with Ca<sup>2+</sup> and Bi<sup>3+</sup> in between
- (Ca,Sr)Bi<sub>2</sub>B<sub>2</sub>O<sub>7</sub>: BO<sub>3</sub> triangles only interlinked via Bi<sup>3+</sup>, layered structure
- PbBiBO<sub>4</sub>: BO<sub>3</sub> triangles, stronger bonding by Pb-O and Bi-O network.

In practice (see section 3.2 and Figure 9), glasses would have a glass former cation fraction roughly in the range from 3:4 (e.g. BiB<sub>3</sub>O<sub>6</sub>) down to ca. 1:3 (e.g. PbBiBO<sub>4</sub>), i.e. beyond phase 1 up to complete conversion into isolated BO<sub>3</sub> groups. However, borate glasses behave somewhat differently from crystalline compounds, as shown in Figure 7, retaining considerable fractions of BO<sub>4</sub> tetrahedra down to low B<sup>3+</sup> contents, which implies additional Bi-O-B bonds.

In all these examined "glass-forming" compositions, Ge<sup>4+</sup> and P<sup>5+</sup> behaved the same as Si<sup>4+</sup> (as did Ga<sup>3+</sup> and Zn<sup>2+</sup>) forming GeO<sub>4</sub> tetrahedra. Comparing the typical metal-oxygen bond lengths in these tetrahedra, we get B<sup>3+</sup>: 148; P<sup>5+</sup>: 153; Si<sup>4+</sup>: 163; Ge<sup>4+</sup>: 174; Ga<sup>3+</sup>: 183, Zn<sup>2+</sup>: 194 pm. These distances agree well, within ca. 2 pm, with those calculated from the crystal radii.<sup>640</sup> For P<sup>5+</sup>, the absence of irregular bonding stemming from double P=O bonds was due to the compounds all being outside the ultraphosphate range.<sup>209, 210</sup>



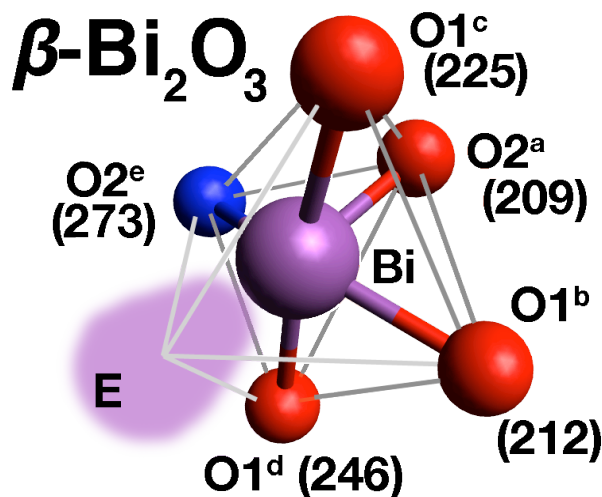
**Table 27. Oxygen around Bi in the  $\alpha$ ,  $\beta$  and  $\delta$  phases of Bi<sub>2</sub>O<sub>3</sub> & derived phase.**

Compound	Coordination (see Figure 6)	Distances [pm]
$\alpha$ -Bi <sub>2</sub> O <sub>3</sub>	5-Py14 (Bi1)	212; 220, 221, 253, 263 <sup>656</sup> 213; 221, 222, 255, 263 <sup>645</sup> 208; 217, 221, 254, 263 <sup>665</sup>
	6-Oct33 (Bi2)	213, 220, 228; 243, 257, 279 <sup>a 656</sup> 213, 220, 228; 242, 256, 279 <sup>645</sup> 214, 222, 229; 248, 254, 280 <sup>665</sup>
$\beta$ -Bi <sub>2</sub> O <sub>3</sub>	4-BPy (5-Py14)	209; 212, 225, 245, (273) <sup>648</sup> 209; 212, 225, 247, (273) <sup>650</sup>
	$\delta$ -Bi <sub>2</sub> O <sub>3</sub>	(Various)
231( $\times$ 4.06); 245( $\times$ 1.94) <sup>b648</sup>		
231( $\times$ 2.56); 245( $\times$ 3.44) <sup>b653</sup>		
231( $\times$ 4.50); 310( $\times$ 1.50) <sup>b645</sup>		
Bi <sub>2-2x</sub> Sr <sub>2x</sub> O <sub>3-x</sub> <sup>c</sup> (x=0.235)	4-Py13	201; 231( $\times$ 3) <sup>649</sup>

a) Calculated from their data; not mentioned in the original paper.

b) Measured at 750-760°C, within the stability limit of the  $\delta$  polymorph; average distances and coordination assumed based on random site occupation, without taking local rearrangements into account.

c) Example of relatively common " $\beta$ " layered Bi<sub>2</sub>O<sub>3</sub>-based ionic conductor phase.



**Figure 14. Oxygen coordination polyhedron around Bi in  $\beta$ -Bi<sub>2</sub>O<sub>3</sub>, with O numbered according to crystal lattice positions, and Bi-O distances indicated in pm.**<sup>648, 656</sup>



**Table 28. Sillenites – Bi coordination and Bi-O distances of Bi at normal "Bi" sites.**

Compound <sup>a</sup>	Coordination	Bi-O distances [pm]
$\gamma$ -Bi <sub>2</sub> O <sub>3</sub> = Bi <sub>12</sub> (Bi <sub>0.8</sub> □ <sub>0.2</sub> )(O <sub>19.2</sub> E <sub>0.8</sub> ) <sup>b 629</sup>	5-Py14 <sup>f</sup>	205; 240, 228, 246, 256
Bi <sub>12</sub> SiO <sub>20</sub> <sup>c 658</sup>	5-Py14 <sup>f</sup>	206; 222, 220, 262, 265
Bi <sub>12</sub> GeO <sub>20</sub> <sup>c 657, 659</sup>	5-Py14 <sup>f</sup>	207; 221, 222, 262, 262 <sup>659</sup> 208; 222, 223, 262, 264 <sup>657</sup>
Bi <sub>12</sub> (Fe <sub>0.35</sub> P <sub>0.59</sub> □ <sub>0.06</sub> )O <sub>20</sub> <sup>c 659</sup>	5-Py14 <sup>f</sup>	208; 221, 221, 261, 271
Bi <sub>12</sub> (Bi <sub>0.50</sub> Ga <sub>0.50</sub> )(O <sub>19.50</sub> E <sub>0.50</sub> ) <sup>b 659</sup>	5-Py14 <sup>f</sup>	207; 222, 225, 257, 263
Bi <sub>12</sub> (Bi <sub>0.50</sub> Fe <sub>0.50</sub> )(O <sub>19.50</sub> E <sub>0.50</sub> ) <sup>b 659</sup>	5-Py14 <sup>f</sup>	207; 222, 224, 257, 262
Bi <sub>12</sub> (Bi <sub>0.67</sub> Zn <sub>0.33</sub> )(O <sub>19.33</sub> E <sub>0.67</sub> ) <sup>b 659</sup>	5-Py14 <sup>f</sup>	207; 222, 225, 256, 262
Bi <sub>12</sub> (Ti <sub>0.90</sub> □ <sub>0.10</sub> )(O <sub>19.80</sub> □ <sub>0.20</sub> ) <sup>d 659</sup>	5-Py14 <sup>f</sup>	207; 222, 223, 261, 261
Bi <sub>12</sub> (Bi <sub>0.25</sub> B <sub>0.50</sub> □ <sub>0.25</sub> )(O <sub>19.125</sub> E <sub>0.25</sub> □ <sub>0.625</sub> ) <sup>d 630</sup>	5-Py14 <sup>f</sup>	209; 217, 221, 263, 272
Bi <sub>12</sub> (Bi <sub>0.03</sub> V <sub>0.89</sub> □ <sub>0.08</sub> )O <sub>20</sub> [O <sub>0.27</sub> ] <sup>e 659</sup>	6-Oct33	209, 219, 222; 258, 260, 274

a) E = oxygen vacancy "filled" with Bi<sup>3+</sup> lone pair; □ = "unfilled" vacancy.

b) Stoichiometric according to Valant & Suvorov,<sup>631</sup> i.e. with oxygen sites filled by O<sup>2-</sup> or replaced by Bi<sup>3+</sup> lone pairs E

c) Ideal sillenite, with average M valence = 4

d) Nonstoichiometric – cation- & oxygen-deficient

e) Nonstoichiometric – interstitial excess oxygen [O]

f) 5-Py14 coordination or 7-Py142 if two additional O anions at ≈300-310 pm taken into account

### *Behaviour of Bi<sup>III</sup> ruthenates and other compounds*

Lone-pair behaviour potentially has important implications for the properties of many technologically important oxides, such as the pyrochlore-structure ruthenates Pb<sub>2</sub>Ru<sub>2</sub>O<sub>6.5</sub> and Bi<sub>2</sub>Ru<sub>2</sub>O<sub>7</sub>, and other compounds such as Bi<sub>3</sub>Ru<sub>3</sub>O<sub>11</sub>, the pyrochlores being used in TFRs as the conductive phase (section 4.6), and both bismuth ruthenates being useful as electrodes and catalysts.<sup>499, 513, 605</sup> Diffraction studies (Table 35) indicate that the coordination around Bi<sup>3+</sup> in Bi<sub>2</sub>Ru<sub>2</sub>O<sub>7</sub> and Bi<sub>3</sub>Ru<sub>3</sub>O<sub>11</sub> is apparently similar to that in analogous lanthanide compounds, nominally yielding the same symmetry and close bond lengths. However, in the case of Bi<sub>2</sub>Ru<sub>2</sub>O<sub>7</sub>, both pure and doped, detailed Rietveld refinement of neutron diffraction spectra<sup>663</sup> reveals significant static displacive disorder of Bi<sup>3+</sup> and linked oxygen, most likely stemming from the Bi<sup>3+</sup> lone pair. This picture correlates well with the significant structural anomalies in bond lengths and angles seen in ruthenium pyrochlores of Pb<sup>II</sup> and Bi<sup>III</sup>, compared to those of lanthanides<sup>666, 667</sup> (similar anomalies are seen for Tl<sup>III</sup>, but involve different electronic phenomena<sup>403</sup>). These compounds lying close to the boundary between insulators and conductors, these anomalies, by slightly altering the electronic band structure, render Pb<sup>II</sup>, Bi<sup>III</sup> and Tl<sup>III</sup>, as well as mixed<sup>482, 485</sup> pyrochlores conducting, whereas lanthanide ruthenates (Ln<sub>2</sub>Ru<sub>2</sub>O<sub>7</sub>) are semiconductors.<sup>482, 666-668</sup> In contrast to the pyrochlores, Bi<sub>3</sub>Ru<sub>3</sub>O<sub>11</sub> and La<sub>3</sub>Ru<sub>3</sub>O<sub>11</sub> differ more subtly in their electric properties, both being metallic.<sup>669</sup> In these materials, which would deserve further structural studies similar to those performed on Bi<sub>2</sub>Ru<sub>2</sub>O<sub>7</sub>,<sup>663</sup> one of both Bi<sup>3+</sup>/La<sup>3+</sup> sites (9-Pr333) is more "suited" to asymmetric lone-pair ions.

Important properties of other compounds, such as catalyst activity of Bi<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub><sup>403</sup> and biochemistry of Bi-based medicinal compounds,<sup>559</sup> may also depend on lone-pair character, although electronegativity may also play a role. Therefore, the respective roles of electronegativity and lone-pair character in determining the structure and different properties (conductivity, catalytic activity, etc.) of materials should be better examined. The fact they are distinct is illustrated by a recent empirical attempt at correlating the lattice parameter of a large list of pyrochlore compounds with ionic radii corrected by electronegativity only.<sup>670</sup> Whereas the calculated values are in general quite successful in predicting the lattice parameter, large errors are seen for many compounds containing lone-pair ions, such as Bi<sup>3+</sup>, Pb<sup>2+</sup> and Te<sup>4+</sup>.

### *Bond valence analysis*

Bond valence sums<sup>644</sup> were calculated for selected coordination shells in compounds corresponding to glass-forming compositions (borates and one silicate), and are listed in Table 36. As this approach does not account for bond anisotropy, calculated bond valence sums – and especially individual bond valences – are expected to be imprecise for Bi<sup>3+</sup> and Pb<sup>2+</sup>. For BO<sub>3</sub> triangles and BO<sub>4</sub> tetrahedra, this method provides an estimation of the allowed degree of variation in individual bond strengths.

Overall, the calculated valence sums agree relatively well with nominal values, with expectedly more summation errors for Bi<sup>3+</sup>. The strongest estimated individual Bi<sup>3+</sup>-O<sup>2-</sup> bond valence ranges from 0.8 to 1.3 in the examined compounds, and the repartition of the individual bond valences is extremely variable, in line with the disordered valence shells typically found around Bi<sup>3+</sup>. Compared to Bi<sup>3+</sup>, the Pb<sup>2+</sup> strongest-bond valence range (ca. 0.6-0.7) is shifted to lower values and exhibits less variability. Also, the contributions beyond the 3<sup>rd</sup> (or 4<sup>th</sup>) bond are very small, which agrees well with the 3-PyM and 4-PyM coordination often found for Pb<sup>2+</sup>. For the much less polarisable B<sup>3+</sup> the bond valences are close to their nominal values (1.00 for Bi<sup>3+</sup><sub>Δ</sub> and 0.75 for Bi<sup>3+</sup><sub>T</sub>, in triangular and tetrahedral coordination respectively). Nevertheless, variations up to ca. ±0.05 are common, and ±0.10 is

found in some compounds. This gives an idea of the bonding "flexibility" of borate coordination shells.

### *Conclusions*

Having examined a wide range of compounds, including pure and doped Bi<sub>2</sub>O<sub>3</sub>, compounds related to glass-forming compositions and conducting ruthenates, it is clear that even in crystalline oxides, Bi<sup>3+</sup> tends to adopt rather a very wide array of unusual, asymmetric and often ill-defined oxygen coordination shells, often comprising 3 (but also sometimes 2 or 4) short bonds, with a variable number of longer ones. This behaviour, which promotes lattice distortions or local disorder, is related to the stereochemically active lone-pair of Bi<sup>3+</sup>, a concept that has been revised recently to involve strong covalent bonding, with mixing not only of metal *s* and *p* electrons, but also O *2p* ones. This lone-pair character and covalent bonding of Bi<sup>3+</sup>, and their effects on crystal structures, are found to be very similar to that of Pb<sup>2+</sup> and Sn<sup>2+</sup>, which suggests that the good glass-forming characteristics of PbO-, Bi<sub>2</sub>O<sub>3</sub> and SnO-based compositions are thereby related. There are some differences, though: of the three cations, Bi<sup>3+</sup> tends to have the most disordered coordination shells, with varying numbers and geometries of both "short" and "long" bonds. Pb<sup>2+</sup> is somewhat more ordered, and has a stronger tendency, at high concentrations, to adopt lower oxygen coordination numbers (3 or 3+1, sometimes 4) in the form of metal-capped pyramids (3/4-PyM). Sn<sup>2+</sup> behaves in a similar, but even more ordered way, with three almost equidistant bonds (3-PyM) favoured by the examined compounds.

Bond valence analysis (which must be regarded with caution in its isotropic formulation<sup>644</sup>) yields different valence distributions for Bi<sup>3+</sup> and Pb<sup>2+</sup>, confirming that Pb<sup>2+</sup> coordination shells tend to be better defined and that Pb<sup>2+</sup> is compatible with small (3/4) coordination numbers. The strongest-bond valence for Bi<sup>3+</sup> is not only (expectedly) higher than for Pb<sup>2+</sup>, but also more variable. These differences are expected to have important effects on glass structure, especially the borates due to the possible change in B<sup>3+</sup> coordination shells.

It must be noted that other lone-pair cations are also relevant for glass formation, such as Tl<sup>+</sup>, As<sup>3+</sup>, Sb<sup>3+</sup>, Se<sup>4+</sup> and Te<sup>4+</sup>, but only TeO<sub>2</sub>, and possibly some Sb<sub>2</sub>O<sub>3</sub>, are expected to be used in appreciable quantities in specialised glasses, due to toxicity concerns (see supplement 11).

**Table 29. Approximate coordination type around Bi<sup>3+</sup> and Bi-O distances, for different Bi<sup>III</sup>-containing silicate, germanate, borate and phosphate compounds. Several entries per compound indicate distinct Bi locations.**

Compound & ref.	Coordination	Bi-O distances [pm]
(Bi <sub>1.9</sub> La <sub>0.1</sub> )SiO <sub>5</sub> <sup>671</sup>	4-PyM†	232(×4)
Bi <sub>2</sub> SiO <sub>5</sub> <sup>671</sup>	4-PyM	214, 226, 231, 253
Bi <sub>2</sub> GeO <sub>5</sub> <sup>672</sup>	4-PyM	215, 225, 228, 266
Bi <sub>4</sub> Si <sub>3</sub> O <sub>12</sub> <sup>a 673</sup>	6-Oct33	213(×3); 262(×3)
Bi <sub>4</sub> Ge <sub>3</sub> O <sub>12</sub> <sup>a 673</sup>	6-Oct33	215(×3); 262(×3)
Bi <sub>2</sub> Ge <sub>3</sub> O <sub>9</sub> <sup>674</sup>	6-Oct33	214(×3); 274(×3)
Bi <sub>4</sub> B <sub>2</sub> O <sub>9</sub> <sup>660</sup>	6-Oct	214, 220, 233, 245, 251, 268
	7-Py142	233; 229, 231, 237, 264; 252, 268
	7-Py1222	219; 222, 243; 236, 250; 286, 287
	7-PyM43	220, 225, 231, 235; 266, 278, 287
BaBiBO <sub>4</sub> <sup>351</sup>	5-Py14	199; 223, 228, 253, 264
PbBiBO <sub>4</sub> <sup>675</sup>	6-Oct222	218, 220; 235, 240; 250, 259
CaBi <sub>2</sub> B <sub>2</sub> O <sub>7</sub> <sup>661</sup>	7-PyM43	214 <sup>b</sup> , 221, 223, 263; 275, 283, 309
	7-PyM43	205 <sup>b</sup> , 220, 228, 250; 278, 297, 311
SrBi <sub>2</sub> B <sub>2</sub> O <sub>7</sub> <sup>661</sup>	?	215 <sup>b</sup> , 247, 251, 267, 273, 280, 295, 318
		219 <sup>b</sup> , 253, 259, 264, 264, 271, 283, 308
ZnBi <sub>2</sub> B <sub>2</sub> O <sub>7</sub> <sup>676</sup>	6-Oct33	217, 222, 232; 244, 257, 268
	6-Oct33	214, 217, 226; 252, 269, 279
CaBiGaB <sub>2</sub> O <sub>7</sub> <sup>676</sup>	8-? <sup>d</sup>	222, 228, 239, 247, 251, 265, 269, 286
BaBi <sub>2</sub> B <sub>4</sub> O <sub>10</sub> <sup>633</sup>	7-Py142	211; 217, 234, 240, 263; 273, 289
	7-Py142	214; 224, 227, 234, 260; 290, 313
Bi <sub>3</sub> B <sub>5</sub> O <sub>12</sub> <sup>664</sup>	6-Oct33	209, 220(×2); 271, 275(×2)
	7-BPy43	211, 224, 226, 233; 279, 279, 280
BiB <sub>3</sub> O <sub>6</sub> <sup>677</sup>	6-Oct222	209(×2); 239(×2); 263(×2)
Ba <sub>3</sub> BiP <sub>3</sub> O <sub>12</sub> <sup>a 662</sup>	6-Oct33	238(×3); 278(×3)
	6-Oct33	260(×3); 281(×3)
Bi <sub>2</sub> P <sub>4</sub> O <sub>13</sub> <sup>678</sup>	8-2222 <sup>e</sup>	218, 219; 231, 236; 266, 267; 276, 280

a) Eulytite structures.

b) Nearest oxygen is a single Bi-O-Bi link in these structures (O mostly bonded to both Bi).

c) Probably only average structure according to authors – local distortions / displacements (especially of Bi) strongly suspected from the neutron diffraction data.

d) Bi in ill-defined BiO<sub>8</sub> coordination; structure = Ga<sub>2</sub>B<sub>4</sub>O<sub>7</sub><sup>5-</sup> layers with 2Ca<sup>2+</sup> & 2Bi<sup>3+</sup> in ordered interlayer positions.

e) Distorted irregular dodecahedron with strongly asymmetric bonding (closest O on one side).

**Table 30. Approximate coordination type around Pb<sup>2+</sup> and Pb-O distances, for some Pb<sup>II</sup>-containing oxides. Several entries per compound indicate distinct Pb locations.**

Compound	Coordination	Pb-O distances [pm]
PbO (litharge) <sup>679</sup>	4-PyM	230(4×)
PbO (massicot) <sup>680</sup>	4-BPy <sup>a</sup>	222, 225, 248(2×)
Pb <sub>2</sub> SiO <sub>4</sub> <sup>681</sup>	3-PyM	218, 218, 227 (298, 298, 328)
	4-PyM	221, 224, 230, 278 (306, 320, 320)
	3-PyM	234, 234, 247 (290, 290, 324)
	3-PyM	223, 226, 232 (282, 283, 283)
Pb <sub>2</sub> (Si <sub>1-x</sub> Ge <sub>x</sub> )O <sub>4</sub> <sup>681</sup> (x = 0.24)	3-PyM	213, 230, 230 (296, 308, 325)
	4-PyM	228, 229, 234, 264 (322, 324, 332)
	4-PyM	219, 222, 237, 272 (290, 330)
PbSiO <sub>3</sub> (alamosite) <sup>682</sup>	4-PyM	224, 239, 246, 263 (284, 303)
	3-PyM	228, 229, 260
	4-PyM	223, 225, 247, 247
PbBiBO <sub>4</sub> <sup>675</sup>	4-PyM	230, 231, 247, 258
	3-PyM	231, 231, 233 (279, 288, 300) <sup>b</sup>
Pb <sub>6</sub> B <sub>10</sub> O <sub>21</sub> <sup>683</sup>	6-Oct33	228, 229, 255; 276, 285, 294
	6-Oct33	223, 239, 244; 279, 281, 293
	4-PyM	230, 233, 238, 248 (300, 319, 326)
Pb <sub>3</sub> P <sub>2</sub> O <sub>8</sub> <sup>c 684</sup>	6-Oct	261(2×), 262(2×), 275(2×)
	7-PyM34	233, 245, 250; 274, 281, 289, 289

a) As often, intermediate form between 4-BPy and 4-PyM, but closer to former.

b) Can be seen as very distorted 6-Oct33, with the Pb<sup>2+</sup> cation actually lying somewhat beyond the plane constituted of the 3 "far" O<sup>2-</sup> anions, so can also be described as twice 3-PyM (near+far).

c) Low-temperature, low-symmetry form.

**Table 31. Approximate coordination type around Sn<sup>2+</sup> and Sn-O distances, for some Sn<sup>II</sup>-containing oxides. Several entries per compound indicate distinct Sn locations.**

Compound	Coordination	Sn-O distances [pm]
SnO (litharge-type) <sup>685</sup>	4-PyM	222.4(4×)
Sn <sub>3</sub> P <sub>2</sub> O <sub>8</sub> <sup>686</sup>	3-PyM	212, 212, 212 (296, 298)
	3-PyM	208, 210, 212 (305)
	3-PyM	215, 223, 232 (286, 286)
β-Sn <sub>2</sub> P <sub>2</sub> O <sub>7</sub> <sup>687</sup>	3-PyM	211, 219, 223 (286, 286)
	3-PyM	213, 214, 223
	3-PyM	212, 213, 213
	3-PyM	214, 214, 215

**Table 32. Approximate coordination around other cations.**

Compound & ref.	Coordination	Cation-O distances [pm]
CaBi <sub>2</sub> B <sub>2</sub> O <sub>7</sub> <sup>661</sup>	CaO <sub>8</sub>	232, 232, 240, 245, 247, 256, 275, 287
CaBiGaB <sub>2</sub> O <sub>7</sub> <sup>676</sup>	CaO <sub>8</sub>	240(2×), 247, 248, 253(2×), 258(2×)
CaBi <sub>2</sub> B <sub>2</sub> O <sub>7</sub> <sup>676</sup>	CaO <sub>6(+2)</sub> <sup>†</sup>	232, 232, 240, 245, 247, 256 (275, 286)
SrBi <sub>2</sub> B <sub>2</sub> O <sub>7</sub> <sup>661</sup>	SrO <sub>6(+2)</sub> <sup>†</sup>	244, 248, 250, 253, 254, 256, (261, 289)
BaBiBO <sub>4</sub> <sup>351</sup>	BaO <sub>9</sub>	271, 278, 278, 279, 286, 287, 288, 288, 304
Ba <sub>3</sub> BiP <sub>3</sub> O <sub>12</sub> <sup>662</sup>	BaO <sub>9</sub>	267(3×), 270(3×), 301(3×)
BaBi <sub>2</sub> B <sub>4</sub> O <sub>10</sub> <sup>633</sup>	BaO <sub>12</sub>	275, 275, 275, 275, 285, 286, 288, 291, 309, 312, 314, 319
BaB <sub>4</sub> O <sub>7</sub> <sup>688</sup>	BaO <sub>9</sub>	261, 267, 269, 269, 276, 287, 298, 300, 308
BaB <sub>4</sub> O <sub>7</sub> <sup>688</sup>	BaO <sub>10</sub>	272, 283, 286, 290, 294, 296, 298, 301, 307, 312
LaBO <sub>3</sub> <sup>689</sup>	LaO <sub>9</sub>	245, 249(2×), 260(2×), 263(2×), 272(2×)
ZnBi <sub>2</sub> B <sub>2</sub> O <sub>7</sub> <sup>676</sup>	ZnO <sub>4</sub>	193, 194, 195, 197
CaBiGaB <sub>2</sub> O <sub>7</sub> <sup>676</sup>	GaO <sub>4</sub>	183(4×)

<sup>†</sup> Ca coordination relatively well ascertained, Sr more doubtful due to possible local atomic displacements – see note c of Table 29.



Table 33. Coordination around B<sup>3+</sup> in examined oxides.

Compound & ref.	Cation <sup>†</sup>	(B,Si,Ge,P)-O distances [pm]	Avg. [pm]
LaBO <sub>3</sub> <sup>689</sup>	B <sup>3+</sup> <sub>Δ</sub>	137, 137, 137	137.3
Bi <sub>4</sub> B <sub>2</sub> O <sub>9</sub> <sup>660</sup>	B <sup>3+</sup> <sub>Δ</sub>	137, 137, 139	137.5
	B <sup>3+</sup> <sub>Δ</sub>	133, 135, 146	
PbBiBO <sub>4</sub> <sup>675</sup>	B <sup>3+</sup> <sub>Δ</sub>	136, 137, 142	138.2
BaBiBO <sub>4</sub> <sup>351</sup>	B <sup>3+</sup> <sub>Δ</sub>	137, 138, 139	138.3
ZnBi <sub>2</sub> B <sub>2</sub> O <sub>7</sub> <sup>676</sup>	B <sup>3+</sup> <sub>Δ</sub>	133, 134, 140	135.5
	B <sup>3+</sup> <sub>T</sub>	146, 148, 151, 153	149.4
CaBiGaB <sub>2</sub> O <sub>7</sub> <sup>676</sup>	B <sup>3+</sup> <sub>T</sub>	142, 148, 157(2×)	151.0
	B <sup>3+</sup> <sub>Δ</sub>	136, 137, 140	137.5
BaBi <sub>2</sub> B <sub>4</sub> O <sub>10</sub> <sup>633</sup>	B <sup>3+</sup> <sub>T</sub>	144, 147, 149, 149	148.1
	B <sup>3+</sup> <sub>T</sub>	146, 147, 147, 156	
	B <sup>3+</sup> <sub>T</sub>	143, 144, 151, 154	
	B <sup>3+</sup> <sub>Δ</sub>	134, 139, 140	
Bi <sub>3</sub> B <sub>5</sub> O <sub>12</sub> <sup>664</sup>	B <sup>3+</sup> <sub>Δ</sub> (2×)	134, 135, 142	137.3
	B <sup>3+</sup> <sub>T</sub>	144, 148, 148, 149	147.3
	B <sup>3+</sup> <sub>T</sub>	139, 148, 150, 151	
	B <sup>3+</sup> <sub>Δ</sub> (2×)	134, 137, 141	
BiB <sub>3</sub> O <sub>6</sub> <sup>677</sup>	B <sup>3+</sup> <sub>T</sub>	144(2×), 149(2×)	146.5
	B <sup>3+</sup> <sub>Δ</sub>	137, 138, 140	136.8
BaB <sub>4</sub> O <sub>7</sub> <sup>688</sup>	B <sup>3+</sup> <sub>Δ</sub>	134, 135, 137	
	B <sup>3+</sup> <sub>Δ</sub>	136, 138, 143	
	B <sup>3+</sup> <sub>Δ</sub>	130, 136, 140	
	B <sup>3+</sup> <sub>T</sub>	146, 149, 151, 152	
	B <sup>3+</sup> <sub>T</sub>	141, 145, 151, 151	
	B <sup>3+</sup> <sub>T</sub>	141, 144, 148, 153	
	B <sup>3+</sup> <sub>T</sub>	144, 147, 157, 148	

<sup>†</sup> Coordinations: Δ = B in BO<sub>3</sub> triangle; T = B in BO<sub>4</sub> tetrahedron.

**Table 34. Coordination around Si<sup>4+</sup>, Ge<sup>4+</sup> and P<sup>5+</sup> in examined oxides.**

Compound & ref.	Cation <sup>†</sup>	(B,Si,Ge,P)-O distances [pm]	Avg. [pm]
(Bi <sub>1.9</sub> La <sub>0.1</sub> )SiO <sub>5</sub> <sup>671</sup>	Si <sup>4+</sup> <sub>T</sub>	159(2×), 166(2×)	162.8
Bi <sub>2</sub> SiO <sub>5</sub> <sup>671</sup>	Si <sup>4+</sup> <sub>T4</sub>	160, 163(2×), 170	164.0
Pb <sub>2</sub> SiO <sub>4</sub> <sup>681</sup>	Si <sup>4+</sup> <sub>T</sub>	159, 164, 170, 171	164.0
Bi <sub>4</sub> Si <sub>3</sub> O <sub>12</sub> <sup>a 673</sup>	Si <sup>4+</sup> <sub>T</sub>	162(4×)	161.9
PbSiO <sub>3</sub> <sup>682</sup>	Si <sup>4+</sup> <sub>T</sub>	162, 163, 164, 167	162.9
		161, 162, 163, 166	
		160, 161, 162, 163	
Pb <sub>2</sub> (Si <sub>1-x</sub> Ge <sub>x</sub> )O <sub>4</sub> <sup>681</sup> (x = 0.24)	(Si,Ge) <sup>4+</sup> <sub>T</sub>	161, 161, 162, 170	163.5
		163, 165, 167, 171	164.5
Bi <sub>2</sub> GeO <sub>5</sub> <sup>672</sup>	Ge <sup>4+</sup> <sub>T</sub>	167(2×), 184(2×)	175.7
Bi <sub>4</sub> Ge <sub>3</sub> O <sub>12</sub> <sup>a 673</sup>	Ge <sup>4+</sup> <sub>T</sub>	174(4×)	173.6
Bi <sub>2</sub> Ge <sub>3</sub> O <sub>9</sub> <sup>674</sup>	Ge <sup>4+</sup> <sub>T</sub>	171(2×), 175, 177	173.8
Ba <sub>3</sub> BiP <sub>3</sub> O <sub>12</sub> <sup>662</sup>	P <sup>5+</sup> <sub>T</sub>	151(4×)	151.2
		152(4×)	
Bi <sub>2</sub> P <sub>4</sub> O <sub>13</sub> <sup>678</sup>	P <sup>5+</sup> <sub>T</sub>	151, 152, 153, 159	154.0
		149, 151, 156, 159	
Pb <sub>3</sub> P <sub>2</sub> O <sub>8</sub> <sup>c 684</sup>	P <sup>5+</sup> <sub>T</sub>	148, 154, 154, 156	153.0
		150, 151, 152, 159	
Sn <sub>2</sub> P <sub>2</sub> O <sub>7</sub> <sup>687</sup>	P <sup>5+</sup> <sub>T</sub>	151, 151, 152, 160	153.6
		151, 152, 153, 161	
		151, 151, 152, 161	

† Coordination: T = tetrahedral.

**Table 35. Approximate coordination type and cation-oxygen distances, for Bi<sub>2</sub>O<sub>3</sub> compounds with RuO<sub>2</sub> and related compositions.**

Compound & ref.	Cation	Coordination	Bi-O distances [pm]
Bi <sub>3</sub> Ru <sub>3</sub> O <sub>11</sub> <sup>604, 605</sup>	Bi <sup>3+</sup>	8-C26s	237(×2), 248(×6) <sup>605</sup> 245(×2), 251(×6) <sup>604</sup>
		9-Pr333	224(×3); 262(×3); 277(×3) <sup>605</sup> 221(×3); 260(×3); 282(×3) <sup>604</sup>
La <sub>3</sub> Ru <sub>3</sub> O <sub>11</sub> <sup>606</sup>	La <sup>3+</sup>	8-C26s	237(×2), 256(×6)
		9-Pr333	234(×3); 268(×3); 286(×3)
Bi <sub>2</sub> Ru <sub>2</sub> O <sub>6,9</sub> <sup>605</sup>	Bi <sup>3+</sup>	8-C26s	223(×2), 258(×6)
Bi <sub>1.9</sub> Ru <sub>2</sub> O <sub>6,9</sub> <sup>663</sup>			
Pr <sub>2</sub> Ru <sub>2</sub> O <sub>7</sub> <sup>666</sup>	Pr <sup>3+</sup>	8-C26s	223(×2), 255(×6)

Table 36. Bond-valence analysis<sup>644</sup> of selected coordination shells.

Compound & ref.	Cation <sup>†</sup>	Valence sum	Bond valences
PbBiBO <sub>4</sub> <sup>675</sup>	Bi <sup>3+</sup>	3.04	0.79, 0.75, 0.49, 0.42, 0.33, 0.26
	Pb <sup>2+</sup>	2.11	0.59, 0.58, 0.56, 0.16, 0.13, 0.09
	B <sup>3+</sup> <sub>Δ</sub>	2.92	1.04, 0.99, 0.89
BaBiO <sub>4</sub> <sup>351</sup>	Bi <sup>3+</sup>	3.13	1.31, 0.69, 0.60, 0.31, 0.22
	B <sup>3+</sup> <sub>Δ</sub>	2.90	0.99, 0.97, 0.94
CaBi <sub>2</sub> B <sub>2</sub> O <sub>7</sub> <sup>661</sup>	Bi <sup>3+</sup>	2.88	0.87, 0.72, 0.68, 0.23, 0.17, 0.14, 0.07
	Bi <sup>3+</sup>	3.10	1.11, 0.74, 0.60, 0.33, 0.15, 0.09, 0.06
	B <sup>3+</sup> <sub>Δ</sub>	3.06	1.04, 1.03, 0.98
	B <sup>3+</sup> <sub>Δ</sub>	2.99	1.01, 0.99, 0.99
ZnBi <sub>2</sub> B <sub>2</sub> O <sub>7</sub> <sup>676</sup>	Bi <sup>3+</sup>	2.93	0.81, 0.71, 0.54, 0.39, 0.27, 0.20
	Bi <sup>3+</sup>	2.99	0.88, 0.82, 0.63, 0.31, 0.20, 0.15
	B <sup>3+</sup> <sub>Δ</sub>	3.06	1.04, 1.03, 0.98
	B <sup>3+</sup> <sub>T</sub>	2.99	1.01, 0.99, 0.99
BaBi <sub>2</sub> B <sub>4</sub> O <sub>10</sub> <sup>633</sup>	Bi <sup>3+</sup>	3.21	0.94, 0.80, 0.51, 0.43, 0.23, 0.18, 0.12
	Bi <sup>3+</sup>	3.05	0.88, 0.67, 0.61, 0.46, 0.26, 0.11, 0.06
	B <sup>3+</sup> <sub>Δ</sub>	2.97	1.04, 0.99, 0.93
	B <sup>3+</sup> <sub>T</sub>	3.04	0.83, 0.77, 0.73, 0.72
	B <sup>3+</sup> <sub>T</sub>	2.93	0.79, 0.77, 0.76, 0.60
	B <sup>3+</sup> <sub>T</sub>	2.98	0.85, 0.81, 0.69, 0.63
BiB <sub>3</sub> O <sub>6</sub> <sup>677</sup>	Bi <sup>3+</sup>	3.37	1.01, 1.01, 0.45, 0.45, 0.23, 0.23
	B <sup>3+</sup> <sub>Δ</sub>	2.99	1.09, 1.00, 0.90
	B <sup>3+</sup> <sub>T</sub>	3.11	0.83, 0.83, 0.72, 0.72
Bi <sub>4</sub> Si <sub>3</sub> O <sub>12</sub> <sup>673</sup>	Bi <sup>3+</sup>	3.43	0.91, 0.91, 0.91, 0.23, 0.23, 0.23
	Si <sup>4+</sup>	4.05	1.01, 1.01, 1.01, 1.01
Pb <sub>6</sub> B <sub>10</sub> O <sub>21</sub> <sup>683</sup>	Pb <sup>2+</sup>	1.98	0.64, 0.62, 0.31, 0.17, 0.14, 0.11
	Pb <sup>2+</sup>	2.03	0.73, 0.47, 0.41, 0.16, 0.15, 0.11
	Pb <sup>2+</sup>	2.01	0.60, 0.55, 0.48, 0.37

<sup>†</sup> Boron coordinations: Δ = BO<sub>3</sub> triangle; T = BO<sub>4</sub> tetrahedron.

## 14. Estimation of cooling rates

During cooling between the melting point of the glass (i.e. the liquidus temperature in the equilibrium phase diagram) and the glass transition temperature  $T_g$ , vitrification is in kinetic competition with the processes of nucleation of crystallites and – if nucleation has occurred – crystallite growth. Therefore, the glass forming ability of "borderline" systems strongly depends on the cooling rate through critical temperature range where nucleation and growth may occur. The true cooling rate inside the glass is difficult to estimate accurately, so the indicated values should be treated with caution. In this work, the indicated cooling rate is that estimated by the authors if given in their work. "Air quenched" glasses were assumed to cool at  $\approx 1 \text{ K}\cdot\text{s}^{-1}$ . Otherwise, if the glasses were cast or pressed, the cooling rate was estimated according to the procedure defined hereafter, with the following reasonable assumptions:

- Cold wall temperatures remain essentially constant, which is reasonable for sufficiently massive moulds / plates, given that materials such as stainless steel ( $\approx 15\dots 25 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ ), aluminium (6061 alloy,  $\approx 170 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ ), brass ( $\approx 90 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ ) and bulk graphite ( $\approx 100 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ ) all have a much higher thermal conductivity than that of the glass.
- Glass thermal diffusivity was assumed to be constant, at  $0.4 \text{ mm}^2\cdot\text{s}^{-1}$  (reasonable for a "heavy" glass at high temperature).
- The initial temperatures of the glass melt and mould / wall were assumed to be  $1000^\circ\text{C}$  and  $200^\circ\text{C}$  respectively, and cooling rate is specified for  $600^\circ\text{C}$ , i.e. the middle of this range. This corresponds well to relatively low-melting glasses.
- If the glass thickness was not mentioned, it was assumed to be 5 mm for "pouring into a mould", 3 mm for "pouring onto a plate", 2 mm for "pouring and pressing", 0.5 mm for roller quenching and 0.2 mm for twin roller quenching. Fritting (i.e. pouring into water) was considered for simplicity as "pouring and pressing" with a thickness of 2 mm.

Fast cooling a glass from the melt is typically done, in ascending cooling rate, by various methods:

- Pouring into a mould
- Pouring onto a plate
- Pouring onto a plate with immediate pressing with a plate from the top
- Pouring into water, i.e. fritting
- Roller quenching
- Twin roller quenching

Cooling in the glass will occur through a thickness  $L$  (single-side cooling). For double-side cooling (casting-pressing or roller quenching),  $L$  is half the glass film thickness (Figure 15). In this case, the time-dependent temperature is the well-known Fourier series:<sup>690</sup>

$$\frac{\Delta T(x,t)}{\Delta T_0} = \frac{2}{\pi} \cdot \sum_{n=1}^{\infty} \left[ \frac{1 - (-1)^n}{n} \cdot \sin\left(\frac{n \cdot \pi \cdot x}{2L}\right) \cdot \exp\left(-\frac{D \cdot n^2 \cdot \pi^2 \cdot t}{4L^2}\right) \right]$$

Here,  $\Delta T(x,t)/\Delta T_0$  is the fractional remaining temperature difference between melting and cold-wall temperature at a distance  $x$  from the wall and time  $t$  from casting, and  $D$  is the

thermal diffusivity in the glass. Here, we are chiefly interested in the slowest-cooling part of the glass, i.e.  $x = L$ . Also, we can safely assume that the higher-order members of the series decay rapidly and become negligible. Therefore, we arrive at a much simpler expression:

$$\frac{\Delta T(L,t)}{\Delta T_0} \cong \frac{4}{\pi} \cdot \exp\left(-\frac{t}{t_c}\right), \text{ where } t_c = \frac{4L^2}{\pi^2 \cdot D} \text{ is the fundamental decay period.}$$

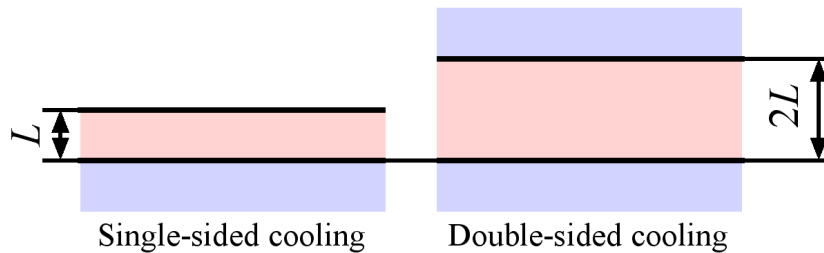
Here, we want to calculate the cooling rate  $-dT/dt$  for  $\Delta T/T_0 \approx 0.5$ , therefore:

$$t_{1/2} \cong t_c \cdot \ln \frac{8}{\pi}, \text{ which yields, with our assumptions:}$$

$$-\frac{dT}{dt}(L, t_{1/2}) \cong \frac{\Delta T_0}{2t_c} \cong \frac{400 \text{ mm}^2 \cdot \text{K} \cdot \text{s}^{-1}}{L^2}$$

In this work, the cooling rates are for convenience expressed as a "quenching index",  $Q$ :

$$Q = \log_{10} \left[ -\frac{dT}{dt}(L, t_{1/2}) \right], \text{ where the cooling rate is expressed in } \text{K s}^{-1}.$$



**Figure 15. Thickness  $L$  for single- or double-sided cooling of glass.**

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