

## Complex ceramic structures. I. Weberites

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The weberite structure ( $A_2B_2X_7$ ) is an anion-deficient fluorite-related superstructure. Compared with fluorites, the reduction in the number of anions leads to a decrease in the coordination number of the  $B$  cations (VI coordination) with respect to the  $A$  cations (VIII coordination), thus allowing the accommodation of diverse cations. As a result, weberite compounds have a broad range of chemical and physical properties and great technological potential. This article summarizes the structural features of weberite and describes the structure in several different ways. This is the first time that the stacking vector and stacking angle are used to represent the weberite structure. This paper also discusses the crystallographic relationship between weberite, fluorite and pyrochlore (another fluorite-related structure). The cation sublattices of weberite and pyrochlore are correlated by an axial transformation. It has been shown that the different coordination environment of anions is due to the alternating layering of the  $AB_3$  and  $A_3B$  close-packed cation layers. A stability field of weberite oxides is proposed in terms of the ratio of ionic radius of cations and relative bond ionicity. In addition, a selection of weberite compounds with interesting properties is discussed.

## 1. Introduction

The weberite crystal structure (space group: *Imma*, No. 74), with typical stoichiometry  $A_2B_2X_7$  ( $A$  and  $B$  are cations,  $X$  is an anion, O or F), is a type of anion-deficient fluorite superstructure ( $AX_2$ ). While several other compounds possess the same stoichiometry (pyrochlores, layered perovskites *etc.*), weberites are isomorphic with the mineral  $\text{Na}_2\text{MgAlF}_7$ . This mineral was originally found in Ivigtut in southwestern Greenland and was named after Theobald Weber (Bogvad, 1938). In 1944, Byström (1944) determined the crystal structure, basing his studies on the pyrochlore structure, which is another fluorite-related superstructure.

While the structure has a cationic sublattice arrangement similar to that found in the fluorite structure (face-centered cube), owing to distortions in the anion sublattice, the crystal structure has a high potential to accommodate diverse metals. The cations in (011) planes have nearly the same symmetry as in the hexagonal tungsten bronze (HTB) structure. In addition, the triangular network in  $\text{Na}_2B^{2+}B^{3+}F_7$  weberites, which is formed by  $B^{2+}$  and  $B^{3+}$  cations in the HTB-like planes, potentially supports various magnetically ordered systems. To date, fluorine-based weberites such as  $\text{Na}_2B^{2+}B^{3+}F_7$  and  $\text{Ag}_2B^{2+}B^{3+}F_7$  have attracted most of the attention owing to their interesting magnetic properties (Cosier *et al.*, 1970; Dance *et al.*, 1974; Frenzen *et al.*, 1992; Lalignant *et al.*, 1989; Lalignant, Ferey *et al.*, 1987; Pankhurst *et al.*, 1991; Ruchaud *et*

**Table 1**Weberite structure data (origin at *A* cations) in space group *Imma*.

Atoms	Wyckoff position	Site symmetry	Atomic position		
			<i>x</i>	<i>y</i>	<i>z</i>
A1	4 <i>d</i>	2/ <i>m</i>	0.25	0.25	0.75
A2	4 <i>a</i>	2/ <i>m</i>	0	0	0
B1	4 <i>c</i>	2/ <i>m</i>	0.25	0.25	0.25
B2	4 <i>b</i>	2/ <i>m</i>	0	0	0.5
X1	8 <i>h</i>	<i>m</i>	0	<i>y</i> <sub>1</sub>	<i>z</i> <sub>1</sub>
X2	16 <i>j</i>	1	<i>x</i> <sub>2</sub>	<i>y</i> <sub>2</sub>	<i>z</i> <sub>2</sub>
X3	4 <i>e</i>	<i>mm</i> 2	0	0.25	<i>z</i> <sub>3</sub>

X1 is at the center of *A*<sub>3</sub>*B*, X2 is in the *A*<sub>2</sub>*B*<sub>2</sub> tetrahedron and X3 is inside *A*<sub>4</sub>*B*<sub>2</sub>.

*al.*, 1992; Thompson *et al.*, 1992; Tressaud *et al.*, 1974; Heger, 1973). Investigations on *A*<sub>2</sub>*B*<sub>2</sub>*O*<sub>7</sub> weberites have mainly focused on crystallography because of the close relationship between the weberite and the pyrochlore structures (Cordfunke & Ijdo, 1988; Groen & Ijdo, 1988; Klein *et al.*, 2006; Reading *et al.*, 2002; Astafev *et al.*, 1985; Bonazzi & Bindi, 2007; Desgardin *et al.*, 1976; Grey *et al.*, 2001, 2003; Grey & Roth, 2000; Ivanov & Zavodnik, 1990). Both of the structures form three-dimensional *BX*<sub>6</sub> networks and HTB-like layers. Some compounds, for example Ca<sub>2</sub>Sb<sub>2</sub>O<sub>7</sub>, can form a metastable pyrochlore phase, which can be converted into the weberite structure by heating above 973 K (Brisse *et al.*, 1972). Recently, weberite oxides and weberite-related oxides have been reported to possess interesting physical properties (ferroelectric, dielectric and magnetic) as well as photocatalytic activity (Wakeshima *et al.*, 2004; Abe *et al.*, 2004, 2006; Cai & Nino, 2007; Cai *et al.*, 2007; Cava *et al.*, 1998; Ebbinghaus *et al.*, 2005; Ivanov *et al.*, 1998; Grey *et al.*, 2001; Lin *et al.*, 2006; Khalifah *et al.*, 1999; Nishimine *et al.*, 2004, 2005; Plaisier *et al.*, 2002; Wakeshima & Hinatsu, 2006; Hinatsu *et al.*, 2004; Harada & Hinatsu, 2002, 2001; Lam *et al.*, 2003; Wiss *et al.*, 2000; Wltschek *et al.*, 1996; Gemmill *et al.*, 2005).

There are a considerable number of publications on weberite ceramics. However, information on weberites is scattered. While presenting their work on the structure determination of Na<sub>2</sub>Fe<sub>2</sub>F<sub>7</sub>, Yakubovich *et al.* (1993) devoted more than half of the paper to a comparison of different types of weberite structures in Na<sub>2</sub>*B*<sup>2+</sup>*B*<sup>3+</sup>F<sub>7</sub> compounds and their relationship to the fluorite and the pyrochlore structures, but their discussion was limited to the crystallographic aspects. Lopatin *et al.* (1985) and Sych *et al.* (Sych, Kabanova, Garbuz *et al.*, 1988) focused on the stability-field region of these compounds. However, there is no article that correlates the structure and properties of weberites. Therefore, this paper is intended to provide a discussion of weberite ceramics, covering crystallographic aspects including the relationship between weberite, fluorite and pyrochlore, their stability field with respect to pyrochlore, and their interesting properties.

In §2 the structural features of weberite and the characteristics of weberite-like structures are discussed. Several different descriptions of the structure are given and a stacking vector and stacking angle are used for the first time to represent the weberite structure. The crystallographic relationship between the fluorite and the pyrochlore structures is

also discussed. It is also shown that the cation sublattices of pyrochlores can be transformed to the weberite-like lattice. The different stacking of neighboring *AB*<sub>3</sub> and *A*<sub>3</sub>*B* layers lead to the different coordination environments of anions in weberite and pyrochlore. A stability field is developed to predict the formation of pyrochlore and weberite oxides. In §3 ferroelectric and dielectric properties of some weberite compounds are discussed.

## 2. Crystal structure

### 2.1. Classic orthorhombic weberite

The space group of the orthorhombic weberite structure is *Imma* (No.74) with four formula units per unit cell (*Z* = 4). However, the correct space group of weberites was a subject of controversy for a long time, as it was described as both *Imma* and *Imm*2 (Sych, Kabanova & Andreeva, 1988; Haegele *et al.*, 1978; Giuseppetti & Tadini, 1978; Knop *et al.*, 1982; Byström, 1944). The detailed history of the determination of the space group has been reported by Yakubovich *et al.* (1993). The two space groups are closely related as *Imm*2 is a subgroup of *Imma*. The only evidence ruling out *Imma* was the observation of very weak (*hk*0) with *h* = 2*n* + 1 reflections. It was later proven that the existence of (*hk*0) with *h* = 2*n* + 1 reflections from Na<sub>2</sub>NiFeF<sub>7</sub> single crystals and Na<sub>2</sub>NiAlF<sub>7</sub> originated from the Renninger effect ('double reflection' process; Schmidt *et al.*, 1992; Lalignat *et al.*, 1989). Thus, there is no doubt that the true space group of the orthorhombic weberite is *Imma*. The atomic positions and site symmetry are given in Table 1.

In weberites the *A* ions sit in the 4*a* and 4*d* atomic positions with site symmetry 2/*m* and establish a coordination number of 8 with the anions. The *A* ions have two different coordination environments. The *A*1 cations (in atomic position 4*d*) lie in a highly distorted cube (or square prism) where there are two different *A*1–*X* bond lengths. The cubes are edge-shared to form a series of chains in the [100] direction. The *A*2 cations (in atomic position 4*a*) are located within bi-hexagonal pyramids in which anions are spaced at three different distances from the central cations. Each pyramid is corner-shared with two other pyramids and edge-shared with four *A*1*X*<sub>8</sub> cubes. As presented in Table 1 there are three Wyckoff positions for anions (*X*1 at 8*h*, *X*2 at 16*j* and *X*3 at 4*e*). *A*1 ions only connect to *X*1 and *X*2, while *A*2 link to all three types of anions (two *X*1, four *X*2 and two *X*3).

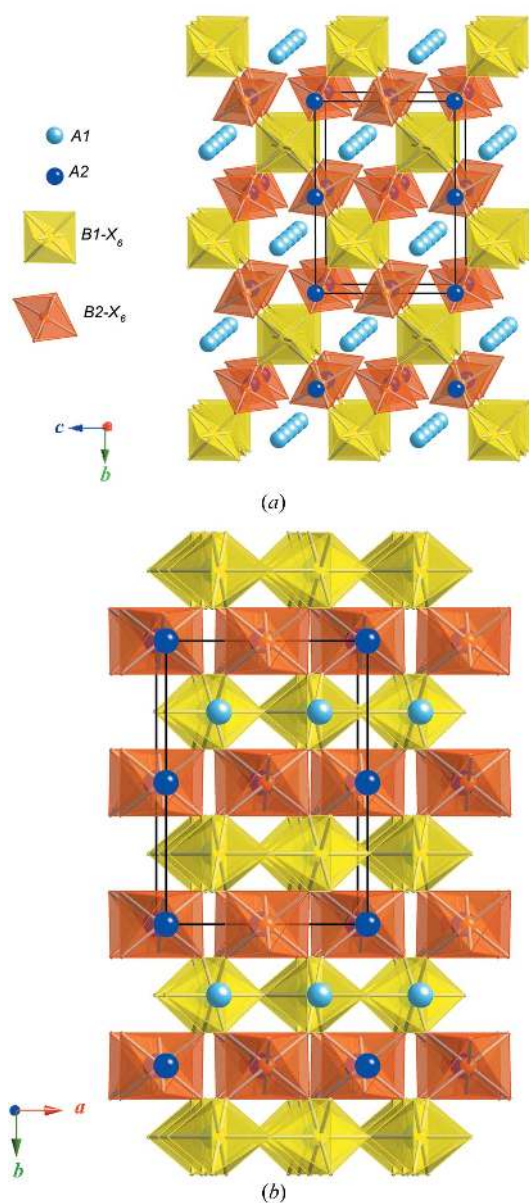
The *B* ions are located in the 4*b* and 4*c* Wyckoff positions (site symmetry 2/*m*) and have a coordination number of 6, *i.e.* *A*<sub>2</sub><sup>VIII</sup>*B*<sub>2</sub><sup>VII</sup>*X*<sub>7</sub>. The weberite structure can be described as a network of corner-shared *BX*<sub>6</sub> octahedra with the penetration of *A* cations (see Fig. 1). There are two types of *BX*<sub>6</sub> octahedra: *B*-1 (*B*<sup>2+</sup> in the case of *A*<sub>2</sub>*B*<sup>2+</sup>*B*<sup>3+</sup>F<sub>7</sub>, *A* = Na<sup>+</sup> or Ag<sup>+</sup>) in 4*c* Wyckoff positions, and *B*-2 (*B*<sup>3+</sup> in the case of *A*<sub>2</sub>*B*<sup>2+</sup>*B*<sup>3+</sup>F<sub>7</sub>) in 4*b* Wyckoff positions. Each of the six vertices of *B*-1 octahedra connects to another *B* octahedron, while only four vertices of a *B*-2 octahedron link to other *B* octahedra. The two unpaired vertices are in a *trans* configuration. As will be

discussed later, trigonal or monoclinic weberite variants cause a *cis* configuration (see Fig. 2). The *B*-1 octahedra are corner-linked to each other and form *B*-1 octahedral chains parallel to the *A*1 chains (in the [100] direction). The *B*-2 octahedra are isolated from each other and link the *B*-1 octahedral chains to form a three-dimensional octahedral network.

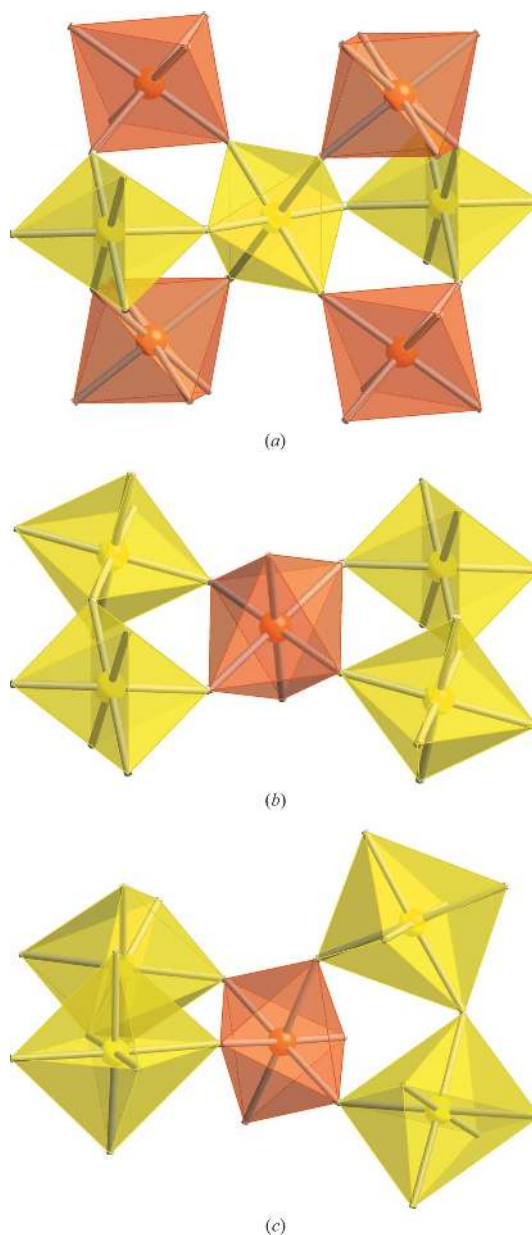
The arrangements of *A* and *B* ions lead to three different cation tetrahedra. Six anions occupy the two  $A_3B$  ( $A_3BX$ ,  $X1$ ) and four  $A_2B_2$  tetrahedral interstices ( $A_2B_2X$ ,  $X2$ ) and none are located inside the two  $AB_3$  sites ( $AB_3[]$ , where [] represents a vacant site) in a formula unit. The remaining anion ( $X3$ ) maintains four coordination and lies outside the two edge-shared  $AB_3$  tetrahedra, very close to the shared *B*–*B*

edge (see Fig. 3).  $X3$  can also be considered to sit inside the octahedron ( $A_4B_2$ ), which shares faces with two adjacent  $AB_3$  tetrahedra, and distort towards the *B*–*B* edge (Grey *et al.*, 2003).

The weberite structure can also be considered as a stacking of repeated layers or slabs. The most common way to examine the structure is to view it as stacked, alternating close-packed metal layers  $A_3B$  and  $AB_3$  on (011) parallel planes. In  $A_3B$  layers, four *A*-1 and two *A*-2 ions form a hexagonal ring with *B*-2 occupying the center. In other words the *A* cations form Kagomé-type networks. [Kagomé in Japanese means a bamboo-basket woven pattern. It is formed by interlaced triangles and each lattice point has four equivalent bonds. ‘Kagomé’ was introduced by Husimi after he and his co-



**Figure 1**  
*B*-octahedral network and *A* cations (a) in the [1, 0.04, 0.07] direction and (b) in the [0.1, 0, 1] direction; the black lines are the unit cell.

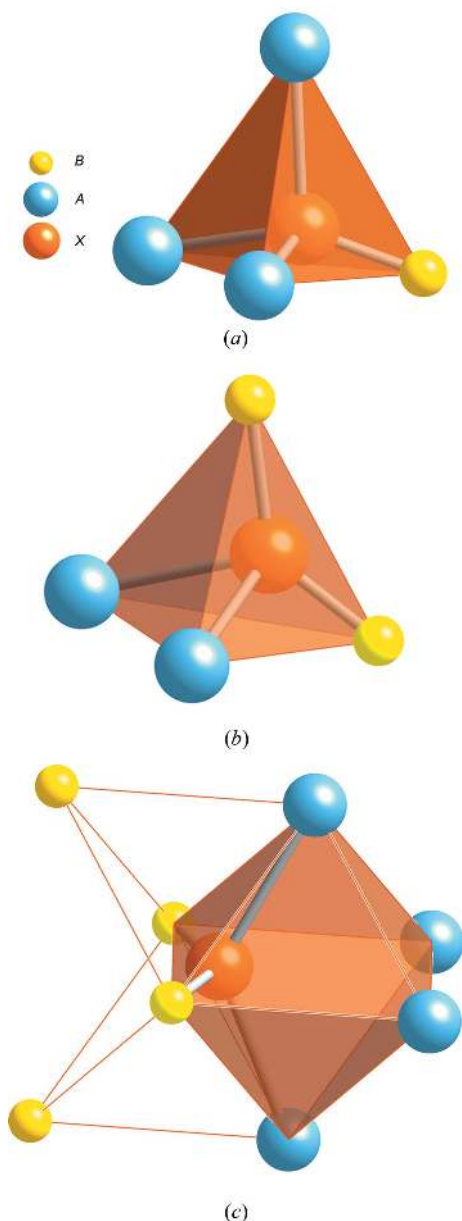


**Figure 2**  
(a) A *B*-1 octahedron in the center and its connection to another six octahedra; (b) *trans* configuration of *B*-2 octahedra; (c) *cis* configuration of *B*-2 octahedra.

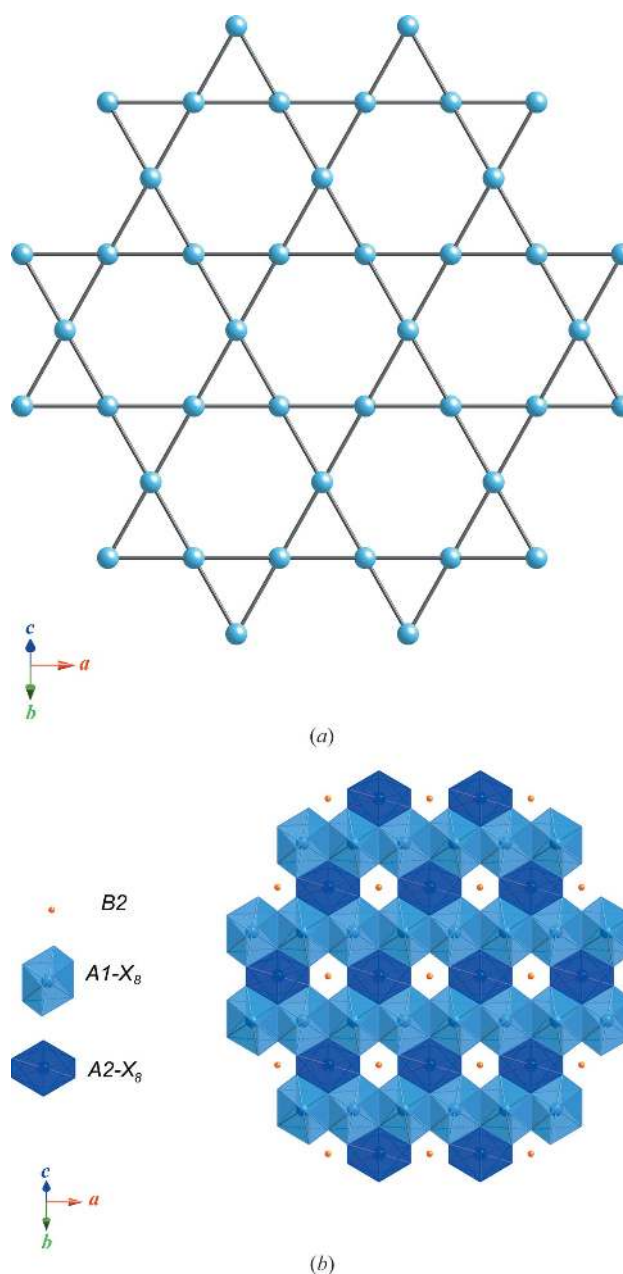
worker Syôzi found a new antiferromagnetic lattice by star-to-triangle transformation from a honeycomb lattice (Mekata, 2003). Syôzi published the first Kagomé paper in 1951 (Syozi, 1951); see Fig. 4.) In  $AB_3$  layers the  $BX_6$  octahedron arrangement is nearly identical with the basal plane of the hexagonal tungsten bronze (HTB) structures and  $A$ -2 cations are in the center of the hexagonal rings. The HTB-like layers can also be simplified by a Kagomé net representation (Fig. 5). The HTB-like layers are displaced with respect to each other by an interlayer stacking vector (SV) which is defined as the projected distance, viewed down the (pseudo-) sixfold axis, between crystallographically similar ions in adjacent layers. White (1984) and Coelho *et al.* (1997) used SV as an alternative description for zirconolite, zirkelite, pyrochlore and polymignyte. Here, SV is used to describe weberite. The

stacking vectors in the weberite structure are nearly in the  $[0\bar{1}1]$ ,  $[3\bar{1}1]$  and  $[31\bar{1}]$  directions. They are typically of the order 4 Å. The angle between successive stacking vectors (SA) is approximately  $120^\circ$ . The distance between two neighboring HTB-like layers along the (pseudo-) sixfold axis is approximately 5.8 Å. Fig. 6 shows the stacking vectors between three sequences of HTB layers.

There is yet another way to consider the weberite repeated layers. The first layer is formed by the alternating  $B$ -1 octahedral chains and  $A$ -1 distorted cube (or square prism) chains, which are in the  $[100]$  direction for classic orthorhombic weberites. In this layer the  $B$ -1 octahedra are edge-shared with



**Figure 3**  
Anion coordination: (a)  $X$ -1 in  $A_3B$ ; (b)  $X$ -2 in  $A_2B_2$ ; (c)  $X$ -3 in  $A_4B_2$ .



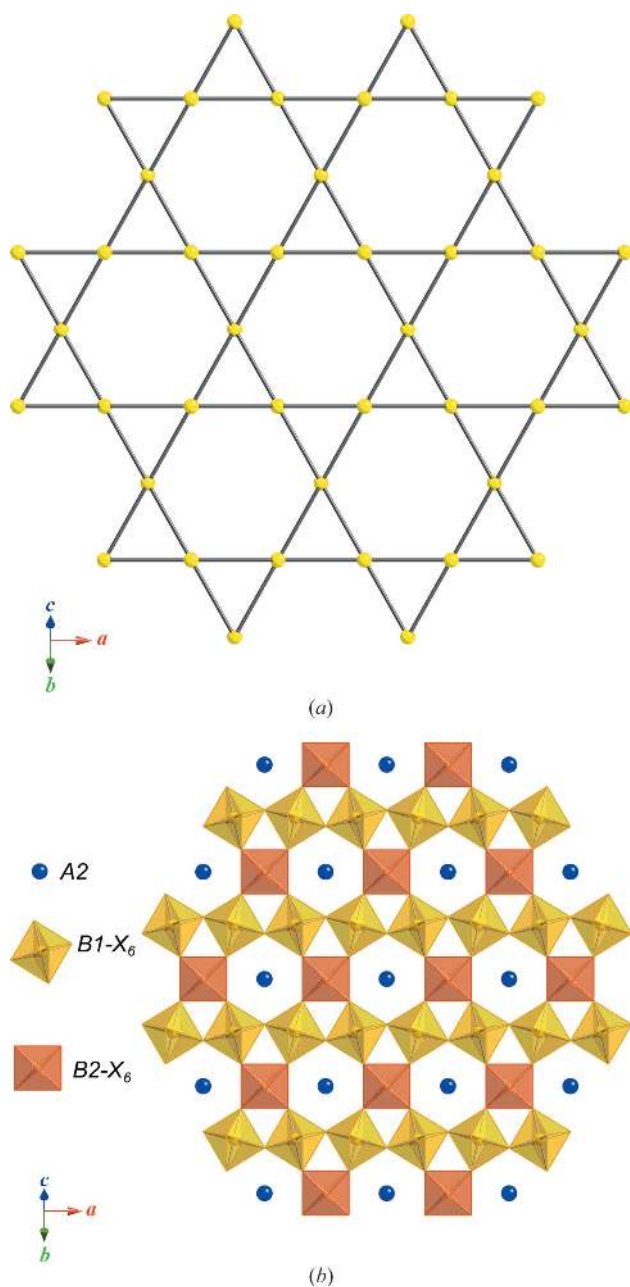
**Figure 4**  
(a) Kagomé net presentation of  $A$  cations on  $A_3B$  layers; (b)  $AX_8$  polyhedral representation of  $A_3B$  layers, which are parallel to the  $(011)$  plane.

A-1 cubes. The second layer is alternating B-2 octahedra and A-2 bi-hexagonal pyramids in the [100] direction as in Fig. 7 (Rossell, 1979; Renaudin *et al.*, 1988).

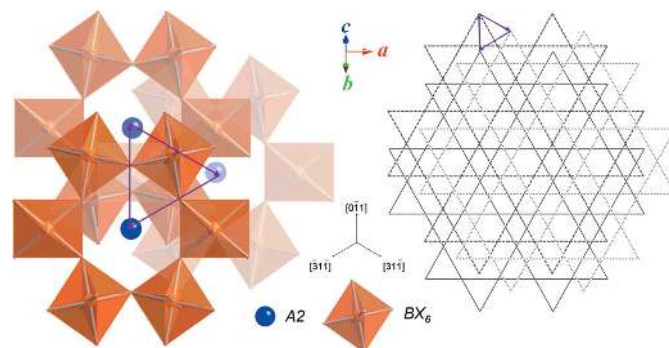
## 2.2. Relationship to fluorite and pyrochlore

Weberite and pyrochlore ( $A_2B_2X_7$ ) are both fluorite-related ( $AX_2$  or  $A_4X_8$ ) superstructures. The coordination number of A and B is the same in both structures. These two structures have a similar cationic sublattice, which is comprised of stacked cubic close-packed cation layers, the same as (111) planes in fluorite. These layers alternate between the compositions  $A_3B$  and  $AB_3$  and are parallel to (111) planes in pyrochlore and

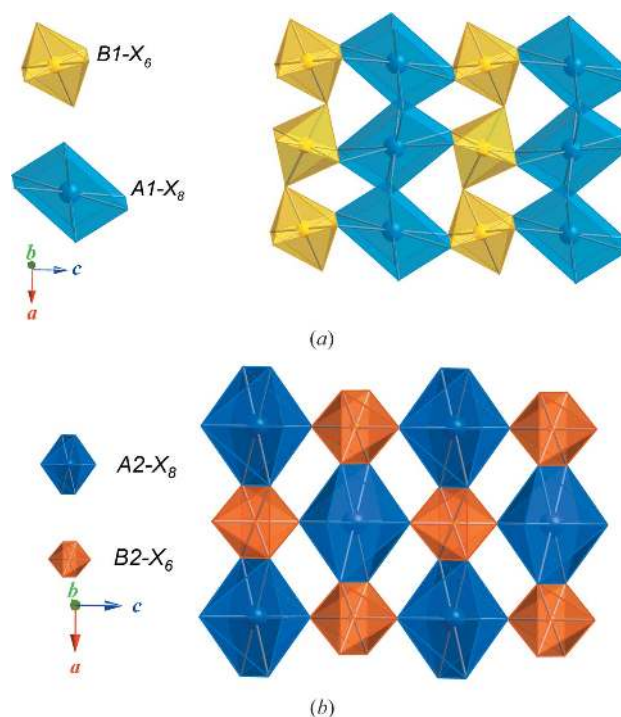
(011) planes in weberite.  $AB_3$  layers in pyrochlore can also be described as HTB-like layers. The length of SV and the value of SA of the pyrochlore structure are almost the same as weberite. However, the difference between the weberite and the pyrochlore structures is the different stacking of two successive  $AB_3$  and  $A_3B$  layers, which will be discussed later in this section. The crystallographic relationship between the weberite and the pyrochlore structures is further confirmed by the fact that the space group of weberite ( $Im\bar{m}a$ ) is a subgroup of  $Fd\bar{3}m$ , the space group of pyrochlore. If the lattice parameter of pyrochlores is  $2a$  with respect to fluorite  $a$  ( $a \approx 5 \text{ \AA}$ ), then the lattice parameters of the classic orthorhombic



**Figure 5**  
(a) Kagomé net presentation of B cations on  $AB_3$  layers; (b)  $BX_6$  polyhedral representation of  $AB_3$  layers, which are parallel to the (011) plane.



**Figure 6**  
Left: Stacking vectors (black arrows) between three sequences of HTB layers; right: Kagomé nets of three successive HTB layers (purple arrows are stacking vectors). This figure is in color in the online version of this paper.



**Figure 7**  
(a) The layer consisting of A1 and B1 lines; (b) A-2 and B-2 layers, viewed in the [010] direction.

**Table 2**  
Pyrochlore ( $A_2B_2X_6X'$ ) structure data in space group  $Imcm$ .

Atoms	Wyckoff position	Site symmetry	Atomic position		
			$x$	$y$	$z$
A	4b	2/m	0	0.5	0
	4c	2/m	0.25	0.25	0.25
B	4a	2/m	0	0	0
	4d	2/m	0.25	0.75	0.25
X	4e	mm2	0.5	$x + 0.25$	0.25
	4e	mm2	0	$x$	0.25
X'	16j	1	$x - 0.125$	0.125	$x + 0.125$
	4e	mm2	0.25	0.375	0

The  $x$  is the oxygen parameter inside the  $A_2B_2$  tetrahedral site. The value is between 0.3125 and 0.375.

weberites are approximately  $2^{1/2}a$ ,  $2a$  and  $2^{1/2}a$ . The rotation of  $45^\circ$  about the  $b$  axis of the pyrochlore cation sublattice leads to the weberite-like cation sublattice (Fig. 8). The (111) planes of pyrochlore are transformed to the (011) of the new lattice. The transformation relationship can be written as

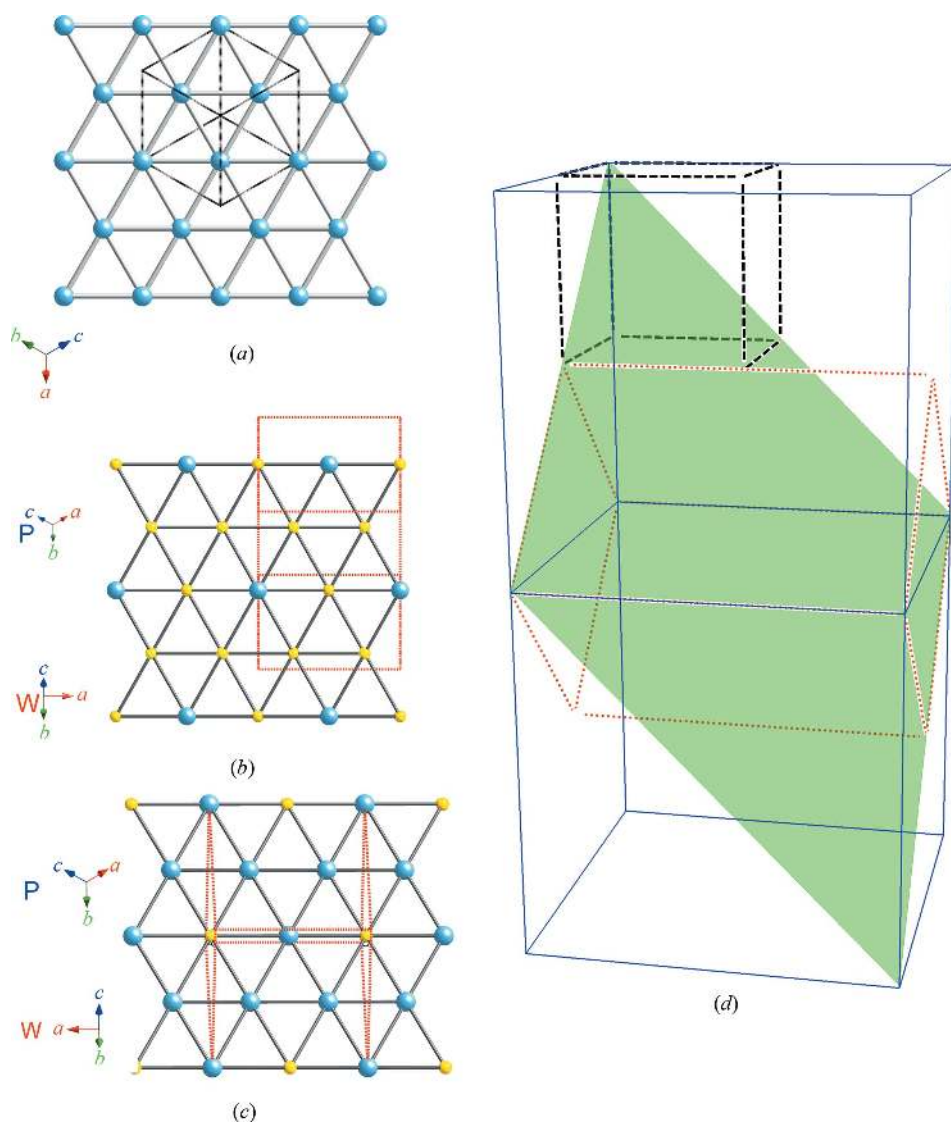
$$W = P \begin{pmatrix} 0.5 & 0 & 0.5 \\ 0 & 1 & 0 \\ -0.5 & 0 & 0.5 \end{pmatrix}. \quad (1)$$

The transformation leads to the space group  $Imcm$ , which is a different setting of  $Imma$ . The  $Imma$  lattice can be achieved by the  $90^\circ$  rotation of the coordinate system of  $Imcm$ . The transformation matrix is

$$\begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{pmatrix}. \quad (2)$$

The resulting lattice parameters in  $Imma$  are  $2a$ ,  $2^{1/2}a$  and  $2^{1/2}a$ . In order to match the weberite lattice parameters, the space group  $Imcm$  is preferred when presenting the atomic positions of pyrochlore in the weberite-like orthorhombic lattice (Table 2).

It is easy to recognize weberite and distinguish the three structures from powder diffraction. As is well known, in  $Cu K\alpha$  radiation to  $2\theta \approx 70^\circ$ , the five fluorite characteristic peaks are (111), (200), (220), (311) and (222). The (111) reflection is at  $2\theta \approx 30^\circ$  with the highest intensity. In pyrochlore, owing to the doubling of the lattice parameter with respect to fluorite, the five fluorite peaks become (222), (400), (440), (622) and (444). The appearance of several weak reflections, especially the (111) peak at  $2\theta \approx 15^\circ$ , is a major difference between the X-ray diffraction (XRD) patterns of fluorite and pyrochlore. In orthorhombic weberite, the five fluorite peaks are split, for example, the most intense  $(111)_f$  or  $(222)_p$  are split into  $(022)_w$  and  $(220)_w$ . There are several more reflections in weberite, which are systematic absences in pyrochlore, for example,  $(101)_w$  and  $(020)_w$  [corresponding to  $(200)_p$ ]. Details on the XRD reflection for fluorite, pyrochlore and



**Figure 8**  
(a) Cationic network on (111) of fluorite; (b)  $AB_3$  layer; (c)  $A_3B$  layer on (011) of weberite; dashed lines are the unit cell; (d) axial transformation of pyrochlore to weberite [black dashed lines: a fluorite cell; blue lines: double pyrochlore cells; red dotted lines: weberite lattice; green shadow  $(011)_w$  and  $(111)_p$ ]. This figure is in color in the online version of this paper.

weberite are listed in Table 3. For space reasons, only reflections up to  $(222)_f$  are presented.

It is important to recall that in fluorites, each anion is at the center of the cationic tetrahedra ( $A_4X$ ). The arrangement of  $A$  and  $B$  leads to different cation tetrahedra:  $AB_3$ ,  $A_3B$  and  $A_2B_2$  in weberites, and  $A_4$ ,  $B_4$  and  $A_2B_2$  in pyrochlores. The reason for the formation of different cation tetrahedra is that weberites and pyrochlores are different in stacking two neighboring  $AB_3$  and  $A_3B$  layers, although generally they follow the pattern of cubic close-packed cation layers. The three nearest-neighbor metal ions in these layers form pseudo-equilateral triangles. The distribution of  $A$  and  $B$  cations in  $AB_3$  layers will lead to two types of triangles:  $AB_2$  and  $B_3$ . The cations in the following  $A_3B$  layer lie above the centers of these triangles. If an  $AB_3$  layer is a reference, there are  $2^{1/2}a/2$  along  $[100]_w$  or  $[10\bar{1}]_p$  displacement in the above  $A_3B$  layer between weberite and pyrochlore. As a result, in the  $A_3B$  layer,  $A$  cations are above the center of  $AB_2$  triangles and  $B$  cations are above  $B_3$  triangles in pyrochlore, while in weberite,  $2/3 A$  ( $A-1$ ) and all  $B$  cations are above the  $AB_2$  triangles and the remaining  $A$  cations ( $A-2$ ) are above  $B_3$  triangles (see Fig. 9). Therefore, these arrangements lead to two  $AB_3$ , two  $A_3B$  and four  $A_2B_2$  in a formula unit of weberite, and in the case of pyrochlore, one  $A_4$ , six  $A_2B_2$  and one  $B_4$ . In addition, different stacking of two neighboring  $AB_3$  and  $A_3B$  layers can explain why the transformation of the pyrochlore cation sublattice into a weberite-like lattice results in a different setting of the space group.

As stated in §2.1, in a formula unit the  $X3$  anion of weberite is located outside the cation tetrahedra and leaves two  $AB_3$  tetrahedra with a vacant center. In contrast, all anions in the pyrochlore structure are inside the cation tetrahedra. Therefore, it can be argued that pyrochlore is more closely related to fluorite than weberite since the former preserves all the anions in cation tetrahedral interstices (Yakubovich *et al.*, 1993; Grey *et al.*, 2003). In weberite it is understandable that the  $X$ -deficient site is more favorable in  $B$ -rich tetrahedra ( $AB_3$  than  $A_2B_2$  and  $A_3B$ ), because  $B$  ions have a smaller coordination number (CN). However, it raises the question: why there are two  $AB_3$  tetrahedra with a vacant center and the  $X3$  is not inside the cation tetrahedra? Grey *et al.* (2003) argued that in  $\text{Ca}_2\text{Ta}_2\text{O}_7$  weberite, the sum of valence ( $\sum v/\text{CN}$ ) in  $\text{CaTa}_3$  tetrahedra is so highly over-saturated that  $\text{CaTa}_3$  cannot accommodate  $X3$ . Actually, the highly over-saturated  $AB_3$  tetrahedra occur in all weberite compounds:  $A_2^{1+}B^{2+}B^{3+}F_7$ ,  $A_2^{2+}B_2^{5+}O_7$  and  $A_2^{1+}B_2^{6+}O_7$ . The nominal sum of valence in the center of  $AB_3$  is 1.46 for  $A_2^{1+}B^{2+}B^{3+}F_7$ , 2.75 for  $A_2^{2+}B_2^{5+}O_7$ , 3.13 for  $A_2^{1+}B_2^{6+}O_7$ . Thus, anions should distort largely towards  $A$  cations to meet the required valence, which would then result in a shorter  $A-X$  distance than a  $B-X$  distance. However,  $A$  ions are larger and have a larger CN than  $B$  ions and so the  $A-X$  bond length should be larger than the  $B-X$  bond length. The end result is that anions cannot move towards  $A$  cations and the required valence cannot be achieved. By contrast, the sum of valence in the center of  $AB_3$  is under-saturated, being 0.875 for  $A_2^{1+}B^{2+}B^{3+}F_7$ , 1.58 for  $A_2^{2+}B_2^{5+}O_7$  and 1.375 for  $A_2^{1+}B_2^{6+}O_7$ . Anions are required to

**Table 3**

XRD reflections for fluorite, pyrochlore and weberite.

XRD reflections			
$hkl$ (fluorite)	$hkl$ (pyrochlore)	$hkl$ (weberite)	Corresponding pyrochlore plane
	111	011	111
		101	200
		020	020
		002	202
	220	121	220
		200	202
		112	311
	311	211	311
		031	131
111	222	022	222
		220	222
200	400	202	400
		040	040
		013	313
	331	132	331
		231	331
		103	402
		222	420
		301	402
		141	240
		123	422
		042	242
		321	422
		240	242
	333	033	333
		213	511
	511	312	511
		051	151
		004	404
220	440	242	440
		400	404
		114	513
		233	531
	531	152	351
		332	531
		251	351
		411	513
		024	424
	442	143	442
		341	442
		420	424
		303	600
		060	060
		204	602
	620	323	620
		402	602
		161	260
		134	533
	533	053	353
		431	533
		224	622
311	622	062	262
		422	622
		260	262
222	444	044	444
		440	444

move towards  $B$  cations, which is favored by the bond length argument above. As for  $A_2B_2$  tetrahedra, the sum of valence is 1.08 for  $A_2^{1+}B^{2+}B^{3+}F_7$ , 2.17 for  $A_2^{2+}B_2^{5+}O_7$  and 2.25 for  $A_2^{1+}B_2^{6+}O_7$ . In this case the sum of valence is close to the anion oxidation state.

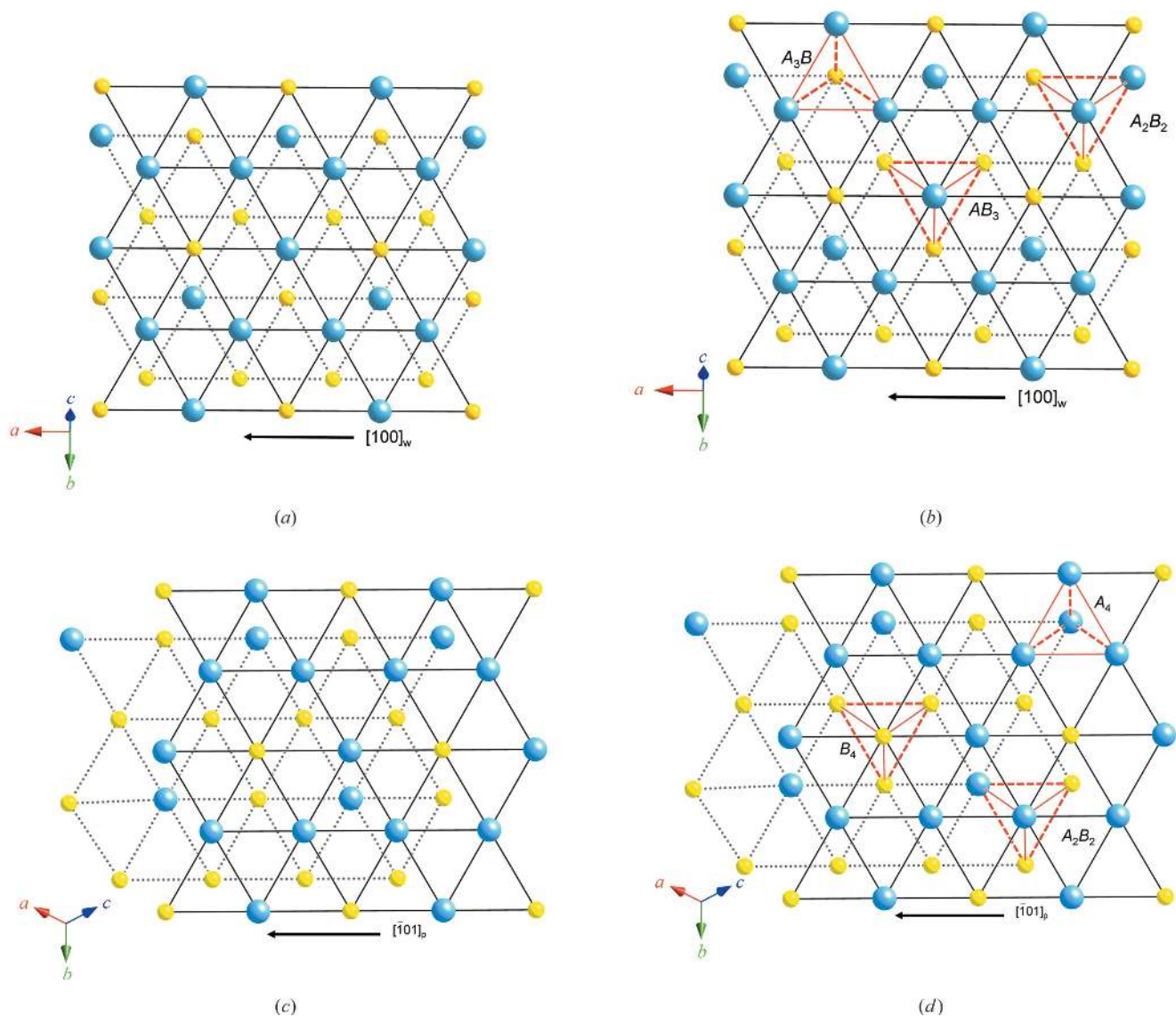
In order to check the stability of the  $X3$ , the empirical equation by Brese & O'Keeffe (1991) is used to calculate the valence of the  $X3$

$$V_i = \sum v_{ij} = \sum \exp((R_{ij} - r_{ij})/b) \quad (3),$$

where  $R_{ij}$  is the bond-valence parameter,  $r_{ij}$  is the bond distance and  $b$  is a constant. Three representative compounds were chosen for detailed analysis:  $\text{Na}_2^+ \text{Mg}^{2+} \text{Al}^{3+} \text{F}_7$ ,  $\text{Sr}_2^+ \text{Sb}_2^+ \text{O}_7$  and  $\text{Ag}_2^+ \text{Te}_2^+ \text{O}_7$ . There are few, if any, reported bond-length data for  $\text{Ag}_2 \text{B}_2 \text{F}_7$ .  $\text{Na}_2 \text{MgAlF}_7$  was chosen since it is the aristotype of the weberite compounds. The  $r_{ij}$  of  $\text{Na}_2^+ \text{Mg}^{2+} \text{Al}^{3+} \text{F}_7$  is from Knop *et al.* (1982) based on single-crystal XRD.  $\text{Sr}_2^+ \text{Sb}_2^+ \text{O}_7$  was chosen because it is a stable weberite even under high pressure and neutron diffraction data are available (Knop *et al.*, 1980; Groen & Ijdo, 1988). As for  $\text{A}_2^+ \text{B}_2^+ \text{O}_7$  compounds, only the crystal structure  $\text{Ag}_2 \text{Te}_2 \text{O}_7$  has been reported (Klein *et al.*, 2006). Table 4 lists the detailed valence information including all three anion types as well as cations by the empirical equation above using the bond-valence parameters (Brese & O'Keeffe, 1991; Brown, 2002) and the bond lengths ( $r_{ij}$ ) from the literature. The valence of

$X_3$  is close to its oxidation state in these compounds. It is worth noting that the discrepancy is small in  $\text{Ag}_2^+ \text{Te}_2^+ \text{O}_7$  for all three oxygen anions. Therefore,  $\text{A}_2^+ \text{B}_2^+ \text{O}_7$  weberites are possible.

Another significant difference is the formation of  $\text{BX}_6$  networks. All of the anions in weberites participate in the formation of  $\text{BX}_6$  octahedra, but only 6/7 of the anions in pyrochlores do. The  $\text{BX}_6$  octahedral network in both structures is fairly rigid. Therefore, in order to maintain the octahedral network it is difficult for the weberite to form vacancies at anion sites. By contrast, the pyrochlore structure tolerates  $X$  deficiency or paired  $A$  and  $X$  deficiencies relatively easily. Examples of such pyrochlore oxides are  $\text{Bi}_{1.5} \text{Zn}_{0.92} \text{Nb}_{1.5} \text{O}_{6.92}$  and  $\text{Tl}_2 \text{B}_2 \text{O}_6$  ( $B = \text{Nb}, \text{Ta}$  and  $\text{U}$ ),  $\text{Tl}_2 \text{Os}_2 \text{O}_{7-x}$  and  $\text{Pb}_2 \text{Os}_2 \text{O}_{7-x}$  (Nino, 2002; Subramanian *et al.*, 1983; Reading *et al.*, 2002). In addition, the substitution of small amounts of oxygen by  $\text{F}^-$  may prevent the formation of weberites. For example,  $\text{Ca}_2 \text{Sb}_2 \text{O}_7$  pyrochlore transforms into weberite irreversibly



**Figure 9**

$A_3B$  and  $AB_3$  slabs of (a) weberite and (b) pyrochlore. Cations connected by dotted lines are on the  $AB_3$  layer and by grey lines are on the  $A_3B$  layer. The red lines (or dotted line) show cation tetrahedra. This figure is in color in the online version of this paper.



Table 4

Examples of bond-valence sum for anions and cations by Brese and O'Keeffe.

X1 in $A_3B$ tetrahedra				X2 in $A_2B_2$ tetrahedra				X3 outside the $AB_3$ tetrahedra			
Bonds	$r_{ij}$ (Å)	$v_{ij}$	$\sum v_{ij}$	Bonds	$r_{ij}$ (Å)	$v_{ij}$	$\sum v_{ij}$	Bonds	$r_{ij}$ (Å)	$v_{ij}$	$\sum v_{ij}$
<b><math>\text{Na}_2\text{MgAlF}_7</math></b>											
Al—F	1.825	0.469		Mg—F	1.960	0.360		Mg—F	1.951	0.368	
Na2—F	2.211	0.236	0.972	Al—F	1.793	0.512	1.022	Mg—F	1.951	0.368	0.866
Na1—F	2.423	0.133		Na2—F	2.549	0.095		Na2—F	2.689	0.065	
Na1—F	2.423	0.133		Na1—F	2.749	0.055		Na2—F	2.689	0.065	
Na1 <sup>1+</sup> : $\sum v_{ij} = 0.779$ ; Na2 <sup>1+</sup> : $\sum v_{ij} = 0.981$ ; Mg <sup>2+</sup> : $\sum v_{ij} = 2.17$ ; Al <sup>3+</sup> : $\sum v_{ij} = 2.89$											
<b><math>\text{Sr}_2\text{Sb}_2\text{O}_7</math></b>											
Sb2—O	1.922	1.056		Sb1—O	1.971	0.926		Sb1—F	2.005	0.843	
Sr2—O	2.363	0.515	2.280	Sb2—O	2.202	0.512	2.151	Sb1—F	2.005	0.843	1.963
Sr1—O	2.502	0.354		Sr1—O	2.833	0.145		Sr2—F	2.850	0.138	
Sr1—O	2.502	0.354		Sr2—O	2.599	0.273		Sr2—F	2.850	0.138	
Sr1 <sup>2+</sup> : $\sum v_{ij} = 1.996$ ; Sr2 <sup>2+</sup> : $\sum v_{ij} = 2.40$ ; Sb1 <sup>5+</sup> : $\sum v_{ij} = 5.39$ ; Sb2 <sup>5+</sup> : $\sum v_{ij} = 5.34$											
<b><math>\text{Ag}_2\text{Te}_2\text{O}_7</math></b>											
Te2—O	1.825	1.281		Ag1—O	2.806	0.067		Ag2—O	2.806	0.067	
Ag2—O	2.388	0.207	1.864	Ag2—O	2.549	0.134	2.041	Ag2—O	2.806	0.067	1.983
Ag1—O	2.465	0.168		Te1—O	1.997	0.806		Te1—O	1.946	0.925	
Ag1—O	2.465	0.168		Te2—O	1.905	1.034		Te1—O	1.946	0.925	
Ag1 <sup>1+</sup> : $\sum v_{ij} = 0.939$ ; Ag2 <sup>1+</sup> : $\sum v_{ij} = 1.084$ ; Te1 <sup>6+</sup> : $\sum v_{ij} = 5.785$ ; Te2 <sup>6+</sup> : $\sum v_{ij} = 5.983$											

 $r_{ij}$  is the bond distance,  $v_{ij}$  is the bond valence.

above 973 K, but  $\text{CaNaSb}_2\text{O}_6\text{F}$  and  $\text{Ca}_{1.56}\text{Sb}_2\text{O}_{6.37}\text{F}_{0.44}$  pyrochlores are stable (Aleshin & Roy, 1962; Aia *et al.*, 1963).

### 2.3. Weberite-like structures

The weberite structures show a wide variety of different modifications including monoclinic and trigonal variants. Grey *et al.* (2003) proposed the use of the nomenclature of the International Mineralogical Association Commission New Minerals and Mineral Names (IMA-CNMMN), which was initially approved for zirconolite  $\text{CaZrTi}_2\text{O}_7$  (Bayliss *et al.*, 1989). As discussed above, the basic building unit is a slab formed by one  $A_3B$  and one  $AB_3$  layer. The differences between weberites are the crystal system and the number of slabs ( $N$ ) in a unit cell. A notation which combines  $N$  and the first letter of the crystal system is used to indicate different weberites. For example, the notation of the classic orthorhombic weberite is  $2O$  because it has two slabs in a unit cell. The reported weberites include  $2O$ ,  $2M$ ,  $3T$ ,  $4M$ ,  $5M$ ,  $6M$ ,  $6T$ ,  $7M$  and  $8O$ . Tables 5 and 6 list different types of  $A_2B_2F_7$  and  $A_2B_2O_7$  weberites, respectively.  $(\text{NaCu})\text{Cu}_2\text{F}_7$  (or  $\text{NaCu}_3\text{F}_7$ , space group  $C2/c$ ) and  $(\text{Ca}_{0.5}\text{Ln}_{1.5})(\text{Ca}_{0.5}\text{Sb}_{1.5})\text{O}_7$  (or  $\text{CaLn}_{1.5}\text{Sb}_{1.5}\text{O}_7$ , space group  $I2/m11$ , Ln = La, Pr, Nd and Y) are special  $2M$  weberites and more like pseudo- $2O$  weberites for they maintain the structural feature of  $2O$  rather than  $2M$ , as will be discussed later.  $\text{Ca}_2\text{Ta}_2\text{O}_7$ -based compounds are important in the weberite family since for  $N > 4$ , only  $\text{Ca}_2\text{Ta}_2\text{O}_7$ -based compounds have been reported. Grey and co-workers (Grey *et al.*, 1999, 2001, 2003; Grey & Roth, 2000) have shown that  $\text{Ca}_2\text{Ta}_2\text{O}_7$  compounds can crystallize into  $3T$ ,  $4M$ ,  $5M$ ,  $6T$ ,  $6M$  and  $7M$  by different doping or synthesis methods and later Ebbinghaus *et al.* (2005) also synthesized an

$8O$   $\text{Ca}_2\text{Ta}_2\text{O}_7$  single crystal using the optical floating zone method.

A significant difference between  $2O$  and non- $2O$  weberites is that the  $AB_3$  and  $A_3B$  layers are parallel to the (011) planes for  $2O$  and parallel to the (001) planes for other weberites, except for  $\text{NaCu}_3\text{F}_7$  and  $\text{CaLn}_{1.5}\text{Sb}_{1.5}\text{O}_7$  (Ln = La, Pr, Nd and Y). The formula unit ( $Z$ ) of  $\text{NaCu}_3\text{F}_7$  and  $\text{CaLn}_{1.5}\text{Sb}_{1.5}\text{O}_7$  is also consistent with  $2O$  weberites, four rather than eight, the latter the formula unit for other  $2M$  weberites. As in §2.2 the lattice parameters of  $2O$  weberites are approximately  $2^{1/2}a$ ,  $2a$  and  $2^{1/2}a$  ( $a \simeq 5$  Å, the lattice parameters for fluorite). The lattice parameters of  $2M$  weberites are nearly  $6^{1/2}a$ ,  $2^{1/2}a$  and  $6^{1/2}a$ . The  $[0\bar{1}1]$ ,  $[100]$  and  $[011]$  vectors of  $2O$  become  $[100]$ ,  $[010]$  and  $[001]$  of  $2M$ . The lattice parameter difference between  $2M$ ,  $4M$ ,  $5M$ ,  $6M$  and  $7M$  is mainly on the  $c$  axis. The lattice parameters for  $nM$  ( $n = 2, 4, 5$  and  $7$ ) are approximately  $6^{1/2}a$ ,  $2^{1/2}a$  and  $[n(6)^{1/2}/2]a$  and they are nearly  $2^{1/2}a$ ,  $6^{1/2}a$  and  $3(6)^{1/2}/a$  for  $6M$  (Grey *et al.*, 1999, 2001, 2003; Grey & Roth, 2000). The  $8O$  weberite is closely related to a monoclinic variant rather than  $2O$  in both the orientation of the  $AB_3$  and  $A_3B$  layers and the lattice parameters. The lattice parameters are nearly  $2^{1/2}a$ ,  $6^{1/2}a$  and  $4(6)^{1/2}/a$ . As for  $3T$ , the  $[100]$ ,  $[-0.5, -0.5, 0.5]$  and  $[012]$  vectors in  $2O$  are transformed into the basal vectors. The resulting lattice parameters are approximately  $2^{1/2}a$ ,  $2^{1/2}a$  and  $2(3)^{1/2}a$ . The relationship of  $2O$ ,  $2M$  and  $3T$  weberites is shown in Fig. 10. Meanwhile, the lattice parameters of  $6T$  are approximately  $2^{1/2}a$ ,  $2^{1/2}a$  and  $4(3)^{1/2}a$ , just double the length of the basal vector in the  $c$  axis.

For  $2O$  weberites there are two special types in which the body-center symmetry is lost. The first case is when  $\text{Cu}^{2+}$  is introduced into  $\text{Na}_2B^{2+}B^{3+}F_7$  at  $B-1$  sites such as  $\text{Na}_2\text{CuCrF}_7$  and  $\text{Na}_2\text{CuInF}_7$  (Kummer *et al.*, 1988; Ruchaud *et al.*, 1992). The common Jahn–Teller distortion (the  $\text{CuF}_6$  octahedra are

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**Table 5**  
List of  $A_2B_2F_7$  weberites.

Type		Space group	Z	Lattice parameters			$\beta$ (°)	$R_A$ (Å)	$R_B$ (Å)	$R_A/R_B$	Properties
				a (Å)	b (Å)	c (Å)					investigated
2O	Na <sub>2</sub> MgCrF <sub>7</sub> (Chassain, 1969)	<i>Imma</i>	4	7.39	7.15	10.20		1.18	0.667	1.768	
2O	Na <sub>2</sub> MgGaF <sub>7</sub> (Chassain, 1969)	<i>Imma</i>	4	7.42	7.16	10.16		1.18	0.67	1.761	
2O	Na <sub>2</sub> MgScF <sub>7</sub> (Chassain, 1969)	<i>Imma</i>	4	7.55	7.34	10.43		1.18	0.733	1.611	
2O	Na <sub>2</sub> MgVF <sub>7</sub> (Chassain, 1969)	<i>Imma</i>	4	7.45	7.24	10.30		1.18	0.68	1.735	
2O	Na <sub>2</sub> NiFeF <sub>7</sub> (Cosier <i>et al.</i> , 1970; Laligant <i>et al.</i> , 1989; Thompson <i>et al.</i> , 1992)	<i>Imma</i>	4	7.2338 (3)	10.3050 (3)	7.4529 (3)		1.18	0.62	1.903	Magnetic
2O	Na <sub>2</sub> NiAlF <sub>7</sub> (Tressaud <i>et al.</i> , 1974; Heger, 1973)	<i>Imma</i>	4	7.31 (2)	7.07 (2)	10.04 (2)		1.18	0.603	1.959	Magnetic
2O	Na <sub>2</sub> NiCoF <sub>7</sub> (Tressaud <i>et al.</i> , 1974; Cosier <i>et al.</i> , 1970)	<i>Imma</i>	4	7.40 (2)	7.20 (2)	10.24 (2)		1.18	0.618	1.911	Magnetic
2O	Na <sub>2</sub> NiCrF <sub>7</sub> (Hansler & Rudorff, 1970; Laligant, Ferey <i>et al.</i> , 1987)	<i>Imma</i>	4	7.183 (1)	10.224 (1)	7.414 (1)		1.18	0.653	1.808	Magnetic
2O	Na <sub>2</sub> CoGaF <sub>7</sub> (Koch & Hebecker, 1988)	<i>Imma</i>	4	7.3011 (6)	10.5436 (9)	7.3845 (7)		1.18	0.645	1.829	
2O	Na <sub>2</sub> CoInF <sub>7</sub> (Koch & Hebecker, 1988)	<i>Imma</i>	4	7.4032 (6)	10.3892 (8)	7.5302 (9)		1.18	0.745	1.5849	
2O	Na <sub>2</sub> CoScF <sub>7</sub> (Koch & Hebecker, 1988)	<i>Imma</i>	4	7.431 (1)	10.546 (1)	7.544 (1)		1.18	0.718	1.645	
2O	Na <sub>2</sub> MnTiF <sub>7</sub> (Koch & Hebecker, 1988)	<i>Imma</i>	4	7.371 (1)	10.369 (3)	7.603 (1)		1.18	0.67	1.761	
2O	Na <sub>2</sub> NiGaF <sub>7</sub> (Koch & Hebecker, 1988; Dahlke <i>et al.</i> , 1998)	<i>Imma</i>	4	7.1805 (7)	10.2433 (9)	7.4256 (7)		1.18	0.655	1.802	
2O	Na <sub>2</sub> NiInF <sub>7</sub> (Koch & Hebecker, 1988)	<i>Imma</i>	4	7.3632 (5)	10.3490 (7)	7.5274 (6)		1.18	0.745	1.584	
2O	Na <sub>2</sub> NiScF <sub>7</sub> (Koch & Hebecker, 1988)	<i>Imma</i>	4	7.3116 (7)	10.3278 (9)	7.4779 (7)		1.18	0.718	1.645	
2O	Na <sub>2</sub> MgTiF <sub>7</sub> (Koch & Hebecker, 1988)	<i>Imma</i>	4	7.3756 (8)	10.418 (1)	7.5496 (8)		1.18	0.695	1.698	
2O	Na <sub>2</sub> ZnFeF <sub>7</sub> (Koch & Hebecker, 1988)	<i>Imma</i>	4	7.281 (1)	10.446 (2)	7.459 (1)		1.18	0.645	1.829	
	Na <sub>2</sub> ZnGaF <sub>7</sub> (Koch & Hebecker, 1988)	<i>Imma</i>	4	7.2494 (7)	10.3283 (8)	7.3582 (6)		1.18	0.68	1.735	
2O	Na <sub>2</sub> ZnInF <sub>7</sub> (Koch & Hebecker, 1988)	<i>Imma</i>	4	7.4077 (6)	10.4759 (9)	7.5732 (6)		1.18	0.77	1.532	
2O	Na <sub>2</sub> ZnTiF <sub>7</sub> (Koch & Hebecker, 1988)	<i>Imma</i>	4	7.338 (1)	10.300 (2)	7.539 (1)		1.18	0.705	1.674	
2O	Na <sub>2</sub> MgFeF <sub>7</sub> (Pankhurst <i>et al.</i> , 1991; Chassain, 1969)	<i>Imma</i>	4	7.49	7.25	10.26		1.18	0.635	1.858	Magnetic
2O	Na <sub>2</sub> MgAlF <sub>7</sub> (Byström, 1944; Knop <i>et al.</i> , 1982)	<i>Imma</i>	4	7.501 (1)	9.968 (2)	7.285 (1)		1.18	0.618	1.911	
2O	Na <sub>2</sub> ZnAlF <sub>7</sub> (Dahlke & Babel, 1994)	<i>Imma</i>	4	7.092 (1)	10.092 (1)	7.337 (1)		1.18	0.6375	1.851	
2O	Ag <sub>2</sub> CuMnF <sub>7</sub> (Koch & Hebecker, 1988)	<i>Imma</i>	4	7.5006 (9)	10.5025 (9)	7.6452 (8)		1.28	0.655	1.954	
2O	Ag <sub>2</sub> CoAlF <sub>7</sub> (Koch <i>et al.</i> , 1982)	<i>Imma</i>	4	7.252	10.16	7.601		1.28	0.603	2.124	
2O	Ag <sub>2</sub> CoGaF <sub>7</sub> (Koch <i>et al.</i> , 1982)	<i>Imma</i>	4	7.313	10.35	7.678		1.28	0.655	1.954	
2O	Ag <sub>2</sub> CoInF <sub>7</sub> (Koch <i>et al.</i> , 1982)	<i>Imma</i>	4	7.544	10.72	7.851		1.28	0.745	1.718	
2O	Ag <sub>2</sub> CoScF <sub>7</sub> (Koch <i>et al.</i> , 1982)	<i>Imma</i>	4	7.497	10.64	7.789		1.28	0.718	1.784	
2O	Ag <sub>2</sub> MnAlF <sub>7</sub> (Koch <i>et al.</i> , 1982)	<i>Imma</i>	4	7.360	10.32	7.601		1.28	0.593	2.160	
2O	Ag <sub>2</sub> MnGaF <sub>7</sub> (Koch <i>et al.</i> , 1982)	<i>Imma</i>	4	7.465	10.62	7.787		1.28	0.645	1.986	
2O	Ag <sub>2</sub> MnScF <sub>7</sub> (Koch <i>et al.</i> , 1982)	<i>Imma</i>	4	7.634	10.78	7.802		1.28	0.708	1.809	
2O	Ag <sub>2</sub> NiGaF <sub>7</sub> (Koch <i>et al.</i> , 1982)	<i>Imma</i>	4	7.255	10.28	7.650		1.28	0.655	1.954	
2O	Ag <sub>2</sub> NiScF <sub>7</sub> (Koch <i>et al.</i> , 1982)	<i>Imma</i>	4	7.463	10.54	7.771		1.28	0.718	1.785	
2O	Ag <sub>2</sub> MgAlF <sub>7</sub> (Koch <i>et al.</i> , 1982)	<i>Imma</i>	4	7.197	10.01	7.571		1.28	0.618	2.073	
2O	Ag <sub>2</sub> MgGaF <sub>7</sub> (Koch <i>et al.</i> , 1982)	<i>Imma</i>	4	7.257	10.21	7.664		1.28	0.67	1.910	
2O	Ag <sub>2</sub> MgInF <sub>7</sub> (Koch <i>et al.</i> , 1982)	<i>Imma</i>	4	7.495	10.62	7.832		1.28	0.76	1.684	
2O	Ag <sub>2</sub> MgScF <sub>7</sub> (Koch <i>et al.</i> , 1982)	<i>Imma</i>	4	7.427	10.52	7.782		1.28	0.733	1.747	
2O	Ag <sub>2</sub> CuAlF <sub>7</sub> (Koch <i>et al.</i> , 1982)	<i>Imma</i>	4	7.109	10.22	7.684		1.28	0.623	2.056	
2O	Ag <sub>2</sub> CuGaF <sub>7</sub> (Koch <i>et al.</i> , 1982)	<i>Imma</i>	4	7.200	10.34	7.755		1.28	0.675	1.896	
2O	Ag <sub>2</sub> ZnAlF <sub>7</sub> (Koch <i>et al.</i> , 1982)	<i>Imma</i>	4	7.237	10.14	7.590		1.28	0.6375	2.008	
2O	Ag <sub>2</sub> ZnGaF <sub>7</sub> (Koch <i>et al.</i> , 1982)	<i>Imma</i>	4	7.303	10.32	7.688		1.28	0.68	1.882	
2O	Ag <sub>2</sub> ZnInF <sub>7</sub> (Koch <i>et al.</i> , 1982)	<i>Imma</i>	4	7.531	10.71	7.841		1.28	0.77	1.662	
2O	Ag <sub>2</sub> CoCrF <sub>7</sub> (Koch & Hebecker, 1988)	<i>Imma</i>	4	7.349 (1)	10.376 (1)	7.683 (1)		1.28	0.653	1.962	
2O	Ag <sub>2</sub> CoFeF <sub>7</sub> (Koch & Hebecker, 1988)	<i>Imma</i>	4	7.3711 (8)	10.437 (1)	7.7145 (8)		1.28	0.62	2.065	
2O	Ag <sub>2</sub> MnFeF <sub>7</sub> (Koch & Hebecker, 1988)	<i>Imma</i>	4	7.490 (1)	10.612 (2)	7.731(1)		1.28	0.61	2.098	

Table 5 (continued)

Type		Space group	<i>Z</i>	Lattice parameters				$R_A$ (Å)	$R_B$ (Å)	$R_A/R_B$	Properties investigated
				<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	$\beta$ (°)				
2O	Ag <sub>2</sub> MnInF <sub>7</sub> (Koch & Hebecker, 1988)	<i>Imma</i>	4	7.6747 (8)	10.856 (1)	7.8641 (7)		1.28	0.735	1.742	
2O	Ag <sub>2</sub> MgCrF <sub>7</sub> (Koch & Hebecker, 1988)	<i>Imma</i>	4	7.2746 (6)	10.3128 (9)	7.7060 (7)		1.28	0.668	1.918	
2O	Ag <sub>2</sub> MgFeF <sub>7</sub> (Koch & Hebecker, 1988)	<i>Imma</i>	4	7.3100 (7)	10.335 (1)	7.6972 (9)		1.28	0.635	2.016	
2O	Ag <sub>2</sub> MgTiF <sub>7</sub> (Koch & Hebecker, 1988)	<i>Imma</i>	4	7.2506 (9)	10.362 (2)	7.497 (1)		1.28	0.695	1.842	
2O	Ag <sub>2</sub> CuCrF <sub>7</sub> (Koch & Hebecker, 1988)	<i>Imma</i>	4	7.2103 (6)	10.454 (1)	7.7871 (8)		1.28	0.673	1.903	
2O	Ag <sub>2</sub> CuFeF <sub>7</sub> (Koch & Hebecker, 1988)	<i>Imma</i>	4	7.2435 (9)	10.474 (2)	7.769 (1)		1.28	0.64	2	
2O	Ag <sub>2</sub> CuInF <sub>7</sub> (Koch & Hebecker, 1988)	<i>Imma</i>	4	7.3461 (6)	10.7501 (9)	7.9098 (6)		1.28	0.765	1.673	
2O	Ag <sub>2</sub> ZnCrF <sub>7</sub> (Koch & Hebecker, 1988)	<i>Imma</i>	4	7.3165 (7)	10.362 (1)	7.6877 (8)		1.28	0.678	1.889	
2O	Ag <sub>2</sub> ZnFeF <sub>7</sub> (Koch & Hebecker, 1988)	<i>Imma</i>	4	7.359 (1)	10.409 (2)	7.706 (1)		1.28	0.645	1.985	
2O	Ag <sub>2</sub> ZnMnF <sub>7</sub> (Koch & Hebecker, 1988)	<i>Imma</i>	4	7.408 (1)	10.503 (1)	7.6972 (9)		1.28	0.66	1.939	
2O	Ag <sub>2</sub> NiAlF <sub>7</sub> (Dance <i>et al.</i> , 1974)	<i>Imma</i>	4	7.564 (6)	7.210 (6)	10.139 (15)		1.28	0.603	2.124	Magnetic
2O	Ag <sub>2</sub> NiCrF <sub>7</sub> (Dance <i>et al.</i> , 1974)	<i>Imma</i>	4	7.673 (6)	7.305 (6)	10.285 (9)		1.28	0.653	1.962	Magnetic
2O	Ag <sub>2</sub> NiFeF <sub>7</sub> (Dance <i>et al.</i> , 1974)	<i>Imma</i>	4	7.692 (6)	7.345 (6)	10.345 (9)		1.28	0.62	2.065	Magnetic
2O	Ag <sub>2</sub> NiInF <sub>7</sub> (Dance <i>et al.</i> , 1974)	<i>Imma</i>	4	7.822 (6)	7.499 (6)	10.622 (9)		1.28	0.745	1.718	Magnetic
2O-II	Na <sub>2</sub> CuInF <sub>7</sub> (Ruchaud <i>et al.</i> , 1992)	<i>Pmnb</i>	4	7.318	10.602	7.712		1.18	0.765	1.542	Magnetic
2O-II	Na <sub>2</sub> CuCrF <sub>7</sub> (Kummer <i>et al.</i> , 1988; Koch & Hebecker, 1985)	<i>Pmnb</i>	4	7.100 (1)	10.338 (1)	7.518 (1)		1.18	0.673	1.755	
2O-II	Na <sub>2</sub> CuScF <sub>7</sub> (Dahlke & Babel, 1994)	<i>Pmnb</i>	4	7.260 (1)	10.534 (1)	7.658 (1)		1.18	0.7375	1.6	
2O-III	Na <sub>2</sub> NiInF <sub>7</sub> (Frenzen <i>et al.</i> , 1992)	<i>Pmnb</i>	4	7.356	10.334	7.523		1.18	0.745	1.584	Magnetic
2O-III	Na <sub>2</sub> MgInF <sub>7</sub> (Caramanian <i>et al.</i> , 2001)	<i>Pnma</i>	4	10.435 (1)	7.345 (1)	7.533 (1)		1.18	0.76	1.553	Magnetic
2M	Na <sub>2</sub> CuGaF <sub>7</sub> (Ruchaud <i>et al.</i> , 1992)	<i>C2/c</i>	8	12.325 (5)	7.318 (1)	12.780 (5)	109.29 (2)	1.18	0.675	1.748	Magnetic
2M and 4M	Na <sub>2</sub> CuFeF <sub>7</sub> (Welsch & Babel, 1992; Yakubovich <i>et al.</i> , 1990; Kummer <i>et al.</i> , 1988)	<i>C2/c</i>	8	12.46 (1)	7.363 (8)	12.93 (1)	109.36 (7)	1.18	0.64	1.844	
		<i>C2/c</i>	16	12.444 (2)	7.343 (1)	24.672 (5)	99.27 (3)				
3T	Na <sub>2</sub> MnAlF <sub>7</sub> (Koch & Hebecker, 1988)		6	7.2854 (4)		17.844 (1)		1.18	0.593	1.992	
3T	Na <sub>2</sub> MnInF <sub>7</sub> (Koch & Hebecker, 1988)		6	7.6006 (3)		18.617 (1)		1.18	0.735	1.605	
3T	Na <sub>2</sub> MnScF <sub>7</sub> (Koch & Hebecker, 1988)		6	7.5442 (4)		18.479 (1)		1.18	0.708	1.668	
3T	Na <sub>2</sub> MnGaF <sub>7</sub> (Courbion <i>et al.</i> , 1988)	<i>P3<sub>1</sub>21</i>	6	7.421 (3)		18.166 (6)		1.18	0.645	1.829	
3T	Na <sub>2</sub> MnCrF <sub>7</sub> (Courbion <i>et al.</i> , 1988)	<i>P3<sub>1</sub>21</i>	6	7.401 (1)		18.091 (2)		1.18	0.6425	1.837	
3T	Na <sub>2</sub> MnVF <sub>7</sub> (Peschel & Babel, 1997)	<i>P3<sub>1</sub>21</i>	6	7.467		18.216		1.18	0.655	1.802	
3T	Na <sub>2</sub> MnFeF <sub>7</sub> (Verscharen & Babel, 1978; Cosier <i>et al.</i> , 1970; Boireau <i>et al.</i> , 1993)	<i>P3<sub>1</sub>21</i>	6	7.488 (2)		18.257 (6)		1.18	0.61	1.934	Magnetic
3T	Ag <sub>2</sub> MnInF <sub>7</sub> (Koch & Hebecker, 1988)		6	7.751 (1)		18.838 (4)		1.28	0.735	1.741	
4M	Na <sub>2</sub> CoAlF <sub>7</sub> (Boireau <i>et al.</i> , 1993; Gravereau <i>et al.</i> , 1992)	<i>C2/c</i>	16	12.378 (4)	7.210 (3)	24.019 (9)	99.67 (2)	1.18	0.613	1.927	Magnetic
4M	Na <sub>2</sub> ZnGaF <sub>7</sub> (Dahlke <i>et al.</i> , 1998)	<i>C2/c</i>	16	12.519	7.303	24.353	99.74	1.18	0.68	1.735	
4M	Na <sub>2</sub> ZnFeF <sub>7</sub> (Dahlke <i>et al.</i> , 1998)	<i>C2/c</i>	16	12.610	7.359	24.538	99.70	1.18	0.645	1.829	
4M	Na <sub>2</sub> FeVF <sub>7</sub> (Peschel <i>et al.</i> , 1995)	<i>C2/c</i>	16	12.710 (3)	7.429 (1)	24.716 (5)	100.03 (3)	1.18	0.625	1.888	
4M	Na <sub>2</sub> CoVF <sub>7</sub> (Peschel <i>et al.</i> , 1995)	<i>C2/c</i>	16	12.703 (5)	7.391 (3)	24.651 (5)	100.02 (3)	1.18	0.645	1.829	
4M	Na <sub>2</sub> FeCrF <sub>7</sub> (Peschel <i>et al.</i> , 1995)	<i>C2/c</i>	16	12.625 (3)	7.391 (1)	24.695 (5)	99.93 (3)	1.18	0.6125	1.927	
4M	Na <sub>2</sub> Fe <sub>2</sub> F <sub>7</sub> (Yakubovich <i>et al.</i> , 1993; Cosier <i>et al.</i> , 1970; Tressaud <i>et al.</i> , 1974)	<i>C2/c</i>	16	12.676 (3)	7.422 (1)	24.710 (5)	99.97 (3)	1.18	0.58	2.034	Magnetic
4M	Na <sub>2</sub> CoFeF <sub>7</sub> (Welsch & Babel, 1992; Cosier <i>et al.</i> , 1970; Tressaud <i>et al.</i> , 1974; Boireau <i>et al.</i> , 1993)	<i>C2/c</i>	16	12.622 (10)	7.360 (4)	24.516 (20)	99.71 (5)	1.18	0.62	1.903	Magnetic
4M	Na <sub>2</sub> CoCrF <sub>7</sub> (Boireau <i>et al.</i> , 1993; Peschel <i>et al.</i> , 1995)	<i>C2/c</i>	16	12.578 (3)	7.335 (1)	24.415 (5)	99.64 (3)	1.18	0.653	1.808	Magnetic
4M	Na <sub>2</sub> FeAlF <sub>7</sub> (Dahlke <i>et al.</i> , 1998; Tressaud <i>et al.</i> , 1974)	<i>C2/c</i>	16	12.426	7.278	24.206	99.99	1.18	0.563	2.098	Magnetic

**Table 6**

 List of weberite oxides with  $R_A/R_B$  and the relative ionicity of the  $A-O$  bond.

Type		Lattice parameters				$R_A$ (Å)	$R_B$ (Å)	$R_A/R_B$	$I_A/(I_B + I_A)$	Properties investigated
		$a$ (Å)	$b$ (Å)	$c$ (Å)	$\beta$ (°)					
2O	Ca <sub>2</sub> Sb <sub>2</sub> O <sub>7</sub> (Bystrom, 1945; Ivanov <i>et al.</i> , 1998; Sato <i>et al.</i> , 2002; Lin <i>et al.</i> , 2006)	7.28 7.3060 7.2900	7.44 7.4627 10.2000	10.18 10.2263 7.4500		1.12	0.6	1.86667	0.60636	Ferroelectric and photocatalytic
2O	Cd <sub>2</sub> Sb <sub>2</sub> O <sub>7</sub> (Brisse <i>et al.</i> , 1972; Bystrom, 1945)	7.21	7.33	10.14		0.9	0.6	1.5	0.56093	
2O	Sr <sub>2</sub> Sb <sub>2</sub> O <sub>7</sub> (Knop <i>et al.</i> , 1980; Groen & Ijdo, 1988; Lin <i>et al.</i> , 2006; Sato <i>et al.</i> , 2002)	7.452 7.4557 (2)	7.687 10.3708 (3)	10.381 7.6860 (1) 7.6860		1.26	0.6	2.1	0.61038	Ferroelectric and photocatalytic
2O	Pb <sub>2</sub> Sb <sub>2</sub> O <sub>7</sub> (Ivanov & Zavodnik, 1990; Ivanov <i>et al.</i> , 1998)	7.484 (1) 7.4774	7.857 (1) 7.8549	10.426 (2) 10.4250		1.29	0.6	2.15	0.54792	Ferroelectric
2O	Ca <sub>2</sub> Os <sub>2</sub> O <sub>7</sub> (Reading <i>et al.</i> , 2002; Weller <i>et al.</i> , 2003)	7.2104 (2)	10.1211 (3)	7.3813 (2)		1.12	0.575	1.94783	0.55518	Electronic
2O	Sr <sub>2</sub> Bi <sub>2</sub> O <sub>7</sub> (Knop <i>et al.</i> , 1980)	7.70	7.91	10.58		1.26	0.76	1.65789	0.58305	
2O	Ba <sub>2</sub> U <sub>2</sub> O <sub>7</sub> (Cordfunke & Ijdo, 1988)	8.1665 (15)	11.3081 (21)	8.1943 (16)		1.42	0.76	1.86842	0.5232	
2O	Na <sub>2</sub> Te <sub>2</sub> O <sub>7</sub> (Knop & Demazeau, 1981)	7.233 (5)	10.104 (7)	7.454 (5)		1.18	0.56	2.10714	0.64905	
2O	Ag <sub>2</sub> Te <sub>2</sub> O <sub>7</sub> (Klein <i>et al.</i> , 2006)	7.266 (2)	10.1430 (9)	7.6021 (17)		1.28	0.56	2.28571	0.60811	
2O	CaPbSb <sub>2</sub> O <sub>7</sub> (Ivanov <i>et al.</i> , 1998)	7.3577	7.5362	10.3521		1.205	0.6	2.00833	0.59219	Ferroelectric
2O	DyNaSb <sub>2</sub> O <sub>7</sub> (Desgardin <i>et al.</i> , 1977)	7.26 (6)	7.41 (5)	10.20 (6)		1.1035	0.6	1.83917	0.6051	
2O	GdNaSb <sub>2</sub> O <sub>7</sub> (Desgardin <i>et al.</i> , 1977)	7.29 (1)	7.47 (0)	10.20 (7)		1.1165	0.6	1.86083	0.60468	
2O	EuNaSb <sub>2</sub> O <sub>7</sub> (Desgardin <i>et al.</i> , 1977)	7.30 (0)	7.47 (2)	10.21 (4)		1.123	0.6	1.87167	0.6088	
2O	SmNaSb <sub>2</sub> O <sub>7</sub> (Desgardin <i>et al.</i> , 1977)	7.30 (8)	7.45 (7)	10.22 (7)		1.1295	0.6	1.8825	0.60636	
2O	NdNaSb <sub>2</sub> O <sub>7</sub> (Desgardin <i>et al.</i> , 1977)	7.32 (7)	7.49 (2)	10.24 (2)		1.1445	0.6	1.9075	0.60636	
2O	PrNaSb <sub>2</sub> O <sub>7</sub> (Desgardin <i>et al.</i> , 1977)	7.33 (7)	7.50 (6)	10.25 (5)		1.153	0.6	1.92167	0.58322	
2O	LaNaSb <sub>2</sub> O <sub>7</sub> (Desgardin <i>et al.</i> , 1977)	7.37 (8)	7.50 (1)	10.28 (8)		1.17	0.6	1.95	0.60594	
2O	KLuSb <sub>2</sub> O <sub>7</sub> (Klein <i>et al.</i> , 2006; Sych, Kabanova & Andreeva, 1988; Sych, Kabanova, Garbuz & Kovalenko, 1988)	7.23	10.23	7.39		1.2435	0.6	2.0725	0.60759	
2O	KYbSb <sub>2</sub> O <sub>7</sub> (Klein <i>et al.</i> , 2006; Sych, Kabanova & Andreeva, 1988; Sych, Kabanova, Garbuz & Kovalenko, 1988)	7.24	10.25	7.40		1.2475	0.6	2.07917	0.61077	
2O	KErSb <sub>2</sub> O <sub>7</sub> (Klein <i>et al.</i> , 2006; Sych, Kabanova & Andreeva, 1988; Sych, Kabanova, Garbuz & Kovalenko, 1988)	7.26	10.25	7.41		1.257	0.6	2.095	0.6088	
2O	KHoSb <sub>2</sub> O <sub>7</sub> (Klein <i>et al.</i> , 2006; Sych, Kabanova & Andreeva, 1988; Sych, Kabanova, Garbuz & Kovalenko, 1988)	7.26	10.25	7.42		1.2625	0.6	2.10417	0.6092	
2O	KYSb <sub>2</sub> O <sub>7</sub> (Klein <i>et al.</i> , 2006; Sych, Kabanova & Andreeva, 1988; Sych, Kabanova, Garbuz & Kovalenko, 1988)	7.26	10.25	7.43		1.2645	0.6	2.1075	0.6088	
2O	KYT <sub>2</sub> O <sub>7</sub> (Gade & Chincholkar, 1979)	7.78	10.82	7.50		1.2645	0.64	1.97578	0.5324	
2O	KDyT <sub>2</sub> O <sub>7</sub> (Gade & Chincholkar, 1979)	7.80	10.88	7.70		1.2685	0.64	1.98203	0.53282	
2O	KGdT <sub>2</sub> O <sub>7</sub> (Gade & Chincholkar, 1979)	7.84	10.86	7.72		1.2815	0.64	2.00234	0.5324	
2O	KSmT <sub>2</sub> O <sub>7</sub> (Gade & Chincholkar, 1979)	7.86	10.82	7.76		1.2945	0.64	2.02266	0.53405	
2O	NaDyV <sub>2</sub> O <sub>7</sub> (Gade & Chincholkar, 1979)	7.53	10.94	7.44		1.1035	0.54	2.04352	0.53496	
2O	NaGdV <sub>2</sub> O <sub>7</sub> (Gade & Chincholkar, 1979)	7.56	10.88	7.46		1.1165	0.54	2.06759	0.54352	
2O	NaSmV <sub>2</sub> O <sub>7</sub> (Gade & Chincholkar, 1979)	7.58	10.86	7.48		1.1295	0.54	2.09167	0.54526	
2O	NaNdV <sub>2</sub> O <sub>7</sub> (Gade & Chincholkar, 1979)	7.62	10.82	7.50		1.1445	0.54	2.11944	0.54526	
2O	NaSrSbTeO <sub>7</sub> (Burchard & Rudorff, 1979)	Not reported				1.22	0.58	2.10345	0.62891	

Table 6 (continued)

Type		Lattice parameters				Properties				
		<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	$\beta$ (°)	<i>R<sub>A</sub></i> (Å)	<i>R<sub>B</sub></i> (Å)	<i>R<sub>A</sub>/R<sub>B</sub></i>	<i>I<sub>A</sub>/(I<sub>B</sub> + I<sub>A</sub>)</i>	investigated
2O	NaCdSbTeO <sub>7</sub> (Burchard & Rudorff, 1979)	Not reported				1.04	0.58	1.7931	0.60778	
2O	NdCaSbTeO <sub>7</sub> (Burchard & Rudorff, 1979)	Not reported				1.15	0.58	1.9828	0.62694	
2O	Na <sub>0.5</sub> Cd <sub>1.5</sub> (Fe <sub>0.5</sub> Te <sub>1.5</sub> )O <sub>7</sub> (Burchard & Rudorff, 1979)	7.131	7.317	10.183		1.12	0.5575	2.00897	0.59584	
2O	Na <sub>0.5</sub> Ca <sub>1.5</sub> (Fe <sub>0.5</sub> Te <sub>1.5</sub> )O <sub>7</sub> (Burchard & Rudorff, 1979)	Not reported				1.135	0.5575	2.0358744	0.626874	
2O	Ba <sub>0.5</sub> Ca <sub>1.5</sub> (Fe <sub>0.5</sub> Te <sub>1.5</sub> )O <sub>7</sub> (Burchard & Rudorff, 1979)	7.176	7.464	10.140		1.195	0.5725	2.08734	0.627674	
2M	CaLa <sub>1.5</sub> Sb <sub>1.5</sub> O <sub>7</sub> (Au <i>et al.</i> , 2007)	7.5753 (3)	10.6870 (5)	7.5482 (3)	90.346 (3)	1.15	0.7	1.6428571	0.57329	
2M	CaPr <sub>1.5</sub> Sb <sub>1.5</sub> O <sub>7</sub> (Au <i>et al.</i> , 2007)	7.5188 (3)	10.6111 (4)	7.4952 (2)	90.315 (2)	1.1245	0.7	1.6064286	0.569502	
2M	CaNd <sub>1.5</sub> Sb <sub>1.5</sub> O <sub>7</sub> (Au <i>et al.</i> , 2007)	7.5019 (2)	10.5890 (3)	7.4770 (2)	90.298 (2)	1.11175	0.7	1.5882143	0.569502	
2M	CaY <sub>1.5</sub> Sb <sub>1.5</sub> O <sub>7</sub> (Au <i>et al.</i> , 2007)	7.3905 (1)	10.4563 (2)	7.3894 (1)	90.049 (1)	1.04425	0.7	1.4917857	0.55821	
3T	Ca <sub>1.5</sub> Mn <sub>0.5</sub> Sb <sub>2</sub> O <sub>7</sub> (Bonazzi & Bindi, 2007)	7.282 (2)		17.604 (4)		1.04	0.6	1.73333	0.59369	
3T	Mn <sub>2</sub> Sb <sub>2</sub> O <sub>7</sub> (Scott, 1990)	7.191		17.402		0.96	0.6	1.6	0.540094	
3T	Ca <sub>1.92</sub> Ta <sub>1.92</sub> Nd <sub>0.08</sub> Zr <sub>0.08</sub> O <sub>7</sub> (Grey <i>et al.</i> , 2003)	7.356 (1)		18.116 (1)		1.11956	0.61728	1.8136988	0.529853	
3T	Ca <sub>2</sub> Ta <sub>2</sub> O <sub>7</sub> (Cava <i>et al.</i> , 1998; Grey <i>et al.</i> , 1999)	7.355 (1)		18.09 (1)		1.12	0.64	1.75	0.52985	Dielectric
4M	Ca <sub>1.92</sub> Ta <sub>1.92</sub> Nd <sub>0.08</sub> Zr <sub>0.08</sub> O <sub>7</sub> (Grey <i>et al.</i> , 2003)	12.761 (1)	7.358 (1)	24.565 (1)	100.17	1.12	0.64	1.75	0.52922	
5M	Ca <sub>1.8</sub> Ta <sub>1.8</sub> Sm <sub>0.24</sub> Ti <sub>0.17</sub> O <sub>7</sub> (Grey & Roth, 2000)	12.763 (1)	7.130 (1)	30.190 (1)	94.09 (1)	1.13635	0.62743	1.81113	0.52523	
5M	Ca <sub>2</sub> Ta <sub>1.8</sub> Nb <sub>0.2</sub> O <sub>7</sub> (Grey <i>et al.</i> , 2001)	12.749 (1)	7.347 (1)	30.23 (1)	94.23 (1)	1.12	0.64	1.75	0.52866	Dielectric
6M	Ca <sub>2</sub> Ta <sub>2</sub> O <sub>7</sub> (Grey <i>et al.</i> , 1999)	7.348 (3)	12.727 (3)	36.44 (5)	95.9 (1)	1.12	0.64	1.75	0.52985	
6T	Ca <sub>1.89</sub> Ta <sub>1.86</sub> Sm <sub>0.16</sub> Ti <sub>0.1</sub> O <sub>7</sub> (Grey & Roth, 2000)	7.353 (1)		36.264 (1)		1.1792	0.63505	1.85686	0.52649	
7M	Ca <sub>2</sub> Ta <sub>1.9</sub> Nb <sub>0.1</sub> O <sub>7</sub> (Grey <i>et al.</i> , 2001)	12.714 (1)	7.370 (1)	42.45 (1)	95.75 (1)	1.12	0.64	1.75	0.52925	Dielectric
8O	Ca <sub>2</sub> Ta <sub>2</sub> O <sub>7</sub> (Ebbinghaus <i>et al.</i> , 2005)	7.3690 (2)	12.7296 (3)	48.263 (1)		1.12	0.64	1.75	0.52985	Dielectric and optical

*R* is the ionic radius from Shannon (1976),  $\chi$  is the electronegativity from Allred & Rochow (1958), *I* is the bond ionicity.

elongated perpendicular to the *B*-1 chains) in CuF<sub>6</sub> octahedra leads to the lowering of symmetry, while maintaining the orthorhombic lattice. The space group is reduced to *Pmnb*, a subgroup of *Imma* (Yakubovich *et al.*, 1993). Another case of losing *I*-centering symmetry happens when the ionic radius of *B*-2 is larger than that of *B*-1. In a classic 2O weberite structure the ionic radius of *B*-2 is equal to or smaller than that of *B*-1. When a larger *B*-2 ion appears in a weberite compound, the anions, which are shared by two *B*-1 octahedral neighbors, distort toward *B*-2 ions. As a result, the *A*-2 ions cannot hold eight-coordination and change to seven-coordination. The *B*-2 ion keeps octahedral coordination with a seventh anion relatively close to it. As in the case of Na<sub>2</sub>NiInF<sub>7</sub>, the distance between the distorted anion and *B*-2 (In<sup>3+</sup>) is only 1.3 times larger than the shortest In—F bond length in *B*-2 octahedra (Frenzen *et al.*, 1992). In a 2O weberite structure, the ratio of the two distances is higher, such as 1.97 in Na<sub>2</sub>MgAlF<sub>7</sub> or 1.83 in Ca<sub>2</sub>Os<sub>2</sub>O<sub>7</sub> (Wyckoff, 1963; Reading *et al.*, 2002). The distortion of the anion excludes the *I*-centering of the structure and results in the space group *Pnmb* (Yakubovich *et al.*, 1993). The notation of 2O-II and 2O-III is used for the first and the second condition, respectively.

One extreme case for 2O-III is Ln<sub>2</sub>(B,Ln)O<sub>7</sub> (or Ln<sub>3</sub>BO<sub>7</sub>, where Ln<sup>3+</sup> is a rare-earth element, and *B* is Os<sup>5+</sup>, Re<sup>5+</sup>, Ru<sup>5+</sup>, Re<sup>5+</sup>, Mo<sup>5+</sup>, Ir<sup>5+</sup>, Sb<sup>5+</sup>, Nb<sup>5+</sup> or Ta<sup>5+</sup>). *B*-2 ions are the same as *A* ions. As a result, the *B*-2 sites and *A*-2 sites are indistinguishable. The structure has an arrangement of BO<sub>6</sub>–LnO<sub>8</sub>

layers (much like weberites), but a different cation configuration with VII coordination between the layers (Fig. 11). Due to the fact that this type of structure does not maintain the three-dimensional BO<sub>6</sub> octahedral network, it is considered a weberite-type structure rather than the weberite structure, or sometimes it is reported as a La<sub>3</sub>NbO<sub>7</sub>-type structure (Rossell, 1979; Allpress & Rossell, 1979; Rooksby & White, 1964; Abe *et al.*, 2004, 2006; Cai & Nino, 2007; Cai *et al.*, 2007; Wakeshima *et al.*, 2004; Groen *et al.*, 1987; Wakeshima & Hinatsu, 2006; Nishimine *et al.*, 2007; Gemmill *et al.*, 2007; Khalifah *et al.*, 1999, 2000; Wiss *et al.*, 2000; Bontchev *et al.*, 2000; Harada & Hinatsu, 2001; Harada *et al.*, 2001; Nishimine *et al.*, 2005; Gemmill *et al.*, 2004, 2005; Vanberkel & Ijdo, 1986; Kahnharari *et al.*, 1995; Wltschek *et al.*, 1996; Greedan *et al.*, 1997; Lam *et al.*, 2002; Plaisier *et al.*, 2002; Lam *et al.*, 2003; Barrier & Gougeon, 2003; Hinatsu *et al.*, 2004; Vente & Ijdo, 1991). Table 7 lists examples of Ln<sub>3</sub>BO<sub>7</sub> and their properties that have been investigated. Details on the dielectric properties of Ln<sub>3</sub>NbO<sub>7</sub> have been reported and will be covered in §3.2.2.

There is a special type of weberite (*B*<sup>+2</sup>*B*<sup>+3</sup>F<sub>5</sub>·2H<sub>2</sub>O) named inverse weberite (please see Table 7 for examples). In this structure *A* cations are missing. In order to maintain charge neutrality, two H<sub>2</sub>O molecules take the place of two F<sup>−</sup> ions. This structure has the same characteristic *B* octahedral network, just like the 2O weberite structure. The space group and Wyckoff positions of *B* cations and anions are the same as

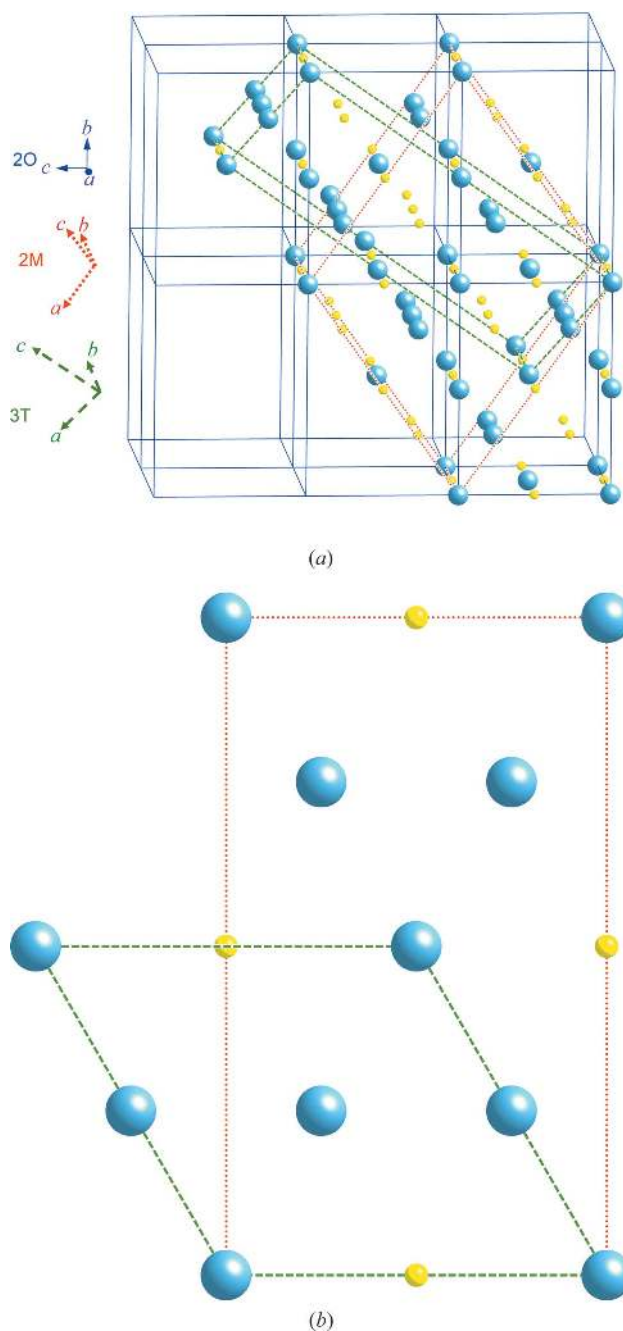
in the 2O weberite. However,  $B^{2+}$  ions take B-2 sites while  $B^{3+}$  cations lie at B-1 sites in this structure, which is opposite to the classic weberite structure (Laligant, Calage *et al.*, 1986; Laligant, Leblanc *et al.*, 1986; Laligant, Pannetier *et al.*, 1986; Laligant, Pannetier *et al.*, 1987; Weil & Werner, 2001; Leroux *et al.*, 1995; Subramanian *et al.*, 2006).

The investigation of  $Na_2B^{2+}B^{3+}F_7$  weberites indicates that the resulting structure type is determined by the size of the  $B^{2+}$

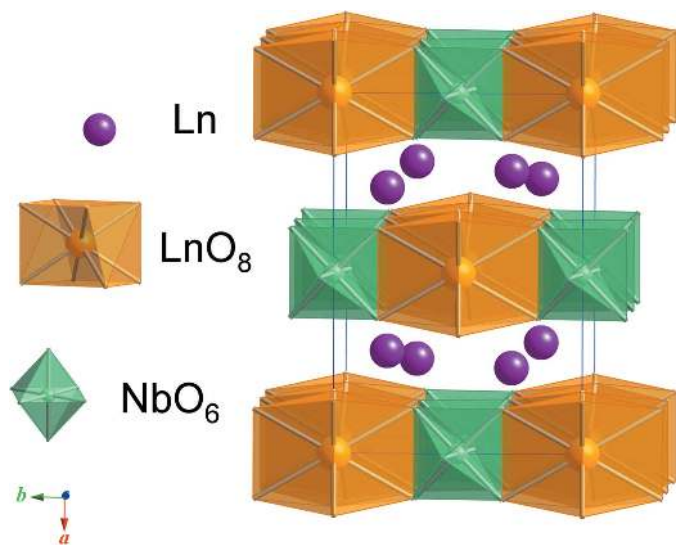
cations. With increasing ionic radius of  $B^{2+}$ , the structure changes from 2O to 2M, 4M and to 3T, gradually (Yakubovich *et al.*, 1993). As for oxide weberites, it is clear that the A cation still plays an important role, for example, 2O  $Ca_2Sb_2O_7$ , 3T  $Ca_{1.5}Mn_{0.5}Sb_2O_7$  and 3T  $Mn_2Sb_2O_7$  (Ivanov *et al.*, 1998; Bonazzi & Bindi, 2007; Scott, 1990; Butler *et al.*, 1950; Bystrom, 1945). The occurrence of the monoclinic and trigonal variants may be closely related to the ionic radius ratio of the A and B cations. However, due to the limited number of compounds reported in each weberite-like structure, it is difficult to define the factors that determine when the variants occur.

As discussed before, the unpaired vertex (terminal anions) of B-2 octahedra are in *trans* configurations in 2O weberites. The trigonal and monoclinic variants produce another type of B-2 octahedra with the *cis* configuration (see Figs. 2b and c). Grey and co-workers (Grey & Roth, 2000; Grey *et al.*, 2003) figured out that the relative position of the terminal anions is a characteristic of weberite polytypes. In 2M and 3T polytypes *cis*-B2 are only in  $A_3B$  layers, while *trans*-B2 are only in  $AB_3$  layers (Grey *et al.*, 2003; Yakubovich *et al.*, 1993). The 4M and 6T weberites have alternative *cis* and *trans* configurations in successive  $A_3B$  layers (Grey & Roth, 2000; Grey *et al.*, 2003).

Several research groups (Yakubovich *et al.*, 1993, 1990; Dahlke *et al.*, 1998; Verscharen & Babel, 1978; Welsch & Babel, 1992) proposed that the formation of B-1 chains is a characteristic of  $Na_2B^{2+}B^{3+}F_7$  weberite polytypes. The detailed description about the different stacking sequence and the orientation of B-1 chains in 2O, 2M, 3T and 4M variants has been reported by Yakubovich *et al.* (1993). Here, the discussion is expanded to include all 2O, 2M, 3T, 4M, 5M, 6M, 6T, 7M and 8O variants. There are three different orientations for B-1 chains: type  $\alpha$ , type  $\beta$  and type  $\gamma$ . These three orientations are correlated with each other by a threefold rotation.



**Figure 10** (a) Relationship between 2O, 2M and 3T weberites (origin at the  $A_2$  site); large spheres: A ions; small spheres: B ions; blue solid lines: multiple unit cells of 2O; red dotted lines: the unit cell of 2M; green dashed lines: the unit cell of 3T. (b) (001) plane of 3T (green dashed lines) and 2M [red dotted lines, also indicating (011) of 2O].



**Figure 11** Weberite-type  $Ln_3BO_7$ , viewed in the  $[0.05, 0.05, 1]$  direction. The layers of  $LnO_8$  and  $BO_6$  lines are parallel to the (001) plane. Between the layers are Ln with a coordination number of 7.

Table 7

Examples of weberite-type  $\text{Ln}_3\text{BO}_7$  and inverse weberites.

Type	Compounds	Space group	Z	Lattice parameters			Properties investigated
				$a$ (Å)	$b$ (Å)	$c$ (Å)	
Weberite type	$\text{La}_3\text{NbO}_7$ (Abe <i>et al.</i> , 2004, 2006; Allpress & Rossell, 1979)	<i>Cmcm</i>	4	11.167 (1)	7.629 (1)	7.753 (1)	Dielectric and photocatalytic
Weberite type	$\text{La}_3\text{TaO}_7$ (Allpress & Rossell, 1979; Abe <i>et al.</i> , 2004, 2006)	<i>Cmcm</i>	4	11.1863 (4)	7.6152 (3)	7.7556 (3)	Catalytic and magnetic
Weberite type	$\text{Pr}_3\text{NbO}_7$ (Vente <i>et al.</i> , 1994)	<i>Cmcm</i>	4	10.959 (1)	7.5240 (7)	7.6676 (7)	Magnetic
Weberite type	$\text{Pr}_3\text{TaO}_7$ (Vente <i>et al.</i> , 1994)	<i>Cmcm</i>	4	10.973 (1)	7.5230 (7)	7.6721 (7)	Magnetic
Weberite type	$\text{Nd}_3\text{NbO}_7$ (Cai <i>et al.</i> , 2007; Allpress & Rossell, 1979)	<i>Cmcm</i>	4	10.905 (2)	7.517 (2)	7.624 (1)	Dielectric
Weberite type	$\text{Gd}_3\text{NbO}_7$ (Cai <i>et al.</i> , 2007; Allpress & Rossell, 1979; Astafyev <i>et al.</i> , 1985)	<i>C222</i> <sub>1</sub>	4	10.610 (1)	7.521 (1)	7.550 (1)	Dielectric
Weberite type	$\text{Gd}_3\text{TaO}_7$ (Wakeshima <i>et al.</i> , 2004)	<i>C221</i> <sub>1</sub>	4	10.6259 (4)	7.5234 (3)	7.5446 (3)	Magnetic
Weberite type	$\text{Dy}_3\text{TaO}_7$ (Wakeshima <i>et al.</i> , 2004)	<i>C222</i> <sub>1</sub>	4	10.5332 (3)	7.4447 (2)	7.4816 (2)	Magnetic
Weberite type	$\text{Ho}_3\text{TaO}_7$ (Wakeshima <i>et al.</i> , 2004)	<i>C222</i> <sub>1</sub>	4	10.4873 (4)	7.4292 (3)	7.4499 (3)	Magnetic
Inverse	$\text{Fe}_2\text{F}_5(\text{H}_2\text{O})_2$ (Laligant, Pannetier <i>et al.</i> , 1986; Greneche <i>et al.</i> , 1988; Hall <i>et al.</i> , 1977)	<i>Imma</i>	4	7.447 (1)	10.8623 (2)	6.652 (1)	Magnetic
Inverse	$\text{ZnFeF}_5(\text{H}_2\text{O})_2$ (Laligant, Calage <i>et al.</i> , 1986)	<i>Imma</i>	4	7.475 (1)	10.766 (1)	6.594 (1)	Magnetic
Inverse	$\text{MnFeF}_5(\text{H}_2\text{O})_2$ (Laligant, Calage <i>et al.</i> , 1986; Laligant, Pannetier <i>et al.</i> , 1987; Greneche <i>et al.</i> , 1988)	<i>Imma</i>	4	7.5635 (2)	10.901 (1)	6.7319 (3)	Magnetic
Inverse	$\text{MnAlF}_5(\text{H}_2\text{O})_2$ (Subramanian <i>et al.</i> , 2006)	<i>Imma</i>	4	7.229 (2)	10.487 (4)	6.816 (2)	
Inverse	$\text{MgAlF}_5(\text{H}_2\text{O})_2$ (Subramanian <i>et al.</i> , 2006; Weil & Werner, 2001)	<i>Imma</i>	4	7.057 (2)	10.125 (4)	6.798 (2)	Electrical resistivity
Inverse	$\text{MnVF}_5(\text{H}_2\text{O})_2$ (Subramanian <i>et al.</i> , 2006; Leroux <i>et al.</i> , 1995)	<i>Imma</i>	4	7.607 (2)	10.912 (4)	6.728 (2)	Magnetic

For  $2O$  weberites (including  $2O$ -II and  $2O$ -III), the stacking sequence of  $B$ -1 chains is  $\alpha\alpha\alpha\dots$  (the orientation is parallel to the  $[100]$  direction). The same applies for pseudo- $2O$   $\text{NaCu}_3\text{F}_7$  and  $\text{CaLn}_{1.5}\text{Sb}_{1.5}\text{O}_7$  ( $\text{Ln} = \text{La}, \text{Pr}, \text{Nd}$  and  $\text{Y}$ ), special cases of  $2M$  (Renaudin *et al.*, 1988; Au *et al.*, 2007). The directions of the  $B$ -1 chains for  $2M$  (except  $\text{NaCu}_3\text{F}_7$  and  $\text{CaLn}_{1.5}\text{Sb}_{1.5}\text{O}_7$ ) and  $4M$  weberites are either nearly parallel to  $[110]$  (type  $\beta$ ) or  $[\bar{1}10]$  (type  $\gamma$ ). The stacking array for  $2M$  is  $\beta\gamma\beta\gamma$ , while it is  $\beta\beta\gamma\gamma\beta\beta\gamma\gamma$  for the  $4M$  polytype. As for  $3T$  and  $6T$ , the directions of the  $B$ -1 chains are nearly parallel to  $[010]$ ,  $[100]$  or  $[110]$ . The sequence of  $B$ -1 chains is  $\alpha\beta\gamma$  in  $3T$  and  $\alpha\alpha\beta\beta\gamma\gamma\alpha\alpha\beta\beta\gamma\gamma$  in  $6T$  weberites.

It is important to note that the close-packed cation layers are stacked the same as f.c.c. (face-centered cubic: cubic stacking in which the stacking sequence is  $ABCABC\dots$ ) in  $2O$ ,  $2M$ ,  $3T$ ,  $4M$  and  $6T$  polytypes. The cation layers in  $5M$ ,  $6M$ ,  $7M$  and  $8O$  polytypes ( $\text{Ca}_2\text{Ta}_2\text{O}_7$ -based compounds) are a mixture of cubic stacking and hexagonal stacking. The hexagonal stacking layers act as mirror glide planes for the cations, for example, the stacking sequence of  $5M$  is  $ABC\underline{A}CB\underline{A}CB$  in a unit cell (the underline letters indicate a hexagonal stacking; Grey *et al.*, 1999, 2001). Therefore,  $5M$ ,  $6M$ ,  $7M$  and  $8O$  polytypes are not pure weberite. The weberite blocks are separated by  $h$ -stacking layers. A simpler approach is to describe the stacking of  $c$  as cubic and  $h$  as hexagonal. The stacking sequence is  $cchccchcc$  for  $5M$  [simplified as  $(3c)h(3c)h(2c)$ , the integers indicating the number of  $c$  stacking layers],  $(5c)h(5c)h$  for  $6M$ ,  $(5c)h(7c)h$  for  $7M$  and  $(4c)h(7c)h(3c)$  for  $8O$  (Ebbinghaus *et al.*, 2005; Grey *et al.*,

1999, 2001, 2003; Grey & Roth, 2000). There are several structural features resulting from the introduction of  $h$  stacking:

- (i)  $h$  stacking only occurs in the  $\text{CaTa}_3$  cation layers;
- (ii)  $h$  stacking causes the appearance of  $B$ -3 octahedra on the  $\text{CaTa}_3$  cation layers and the neighboring  $\text{Ca}_3\text{Ta}$  cation layers, which have only one unpaired vertex ( $B$ -1 octahedra have no unpaired vertex and  $B$ -2 have two);
- (iii) in  $h$  stacking layers  $B$ -3 chains are formed, but no  $B$ -1 chains.

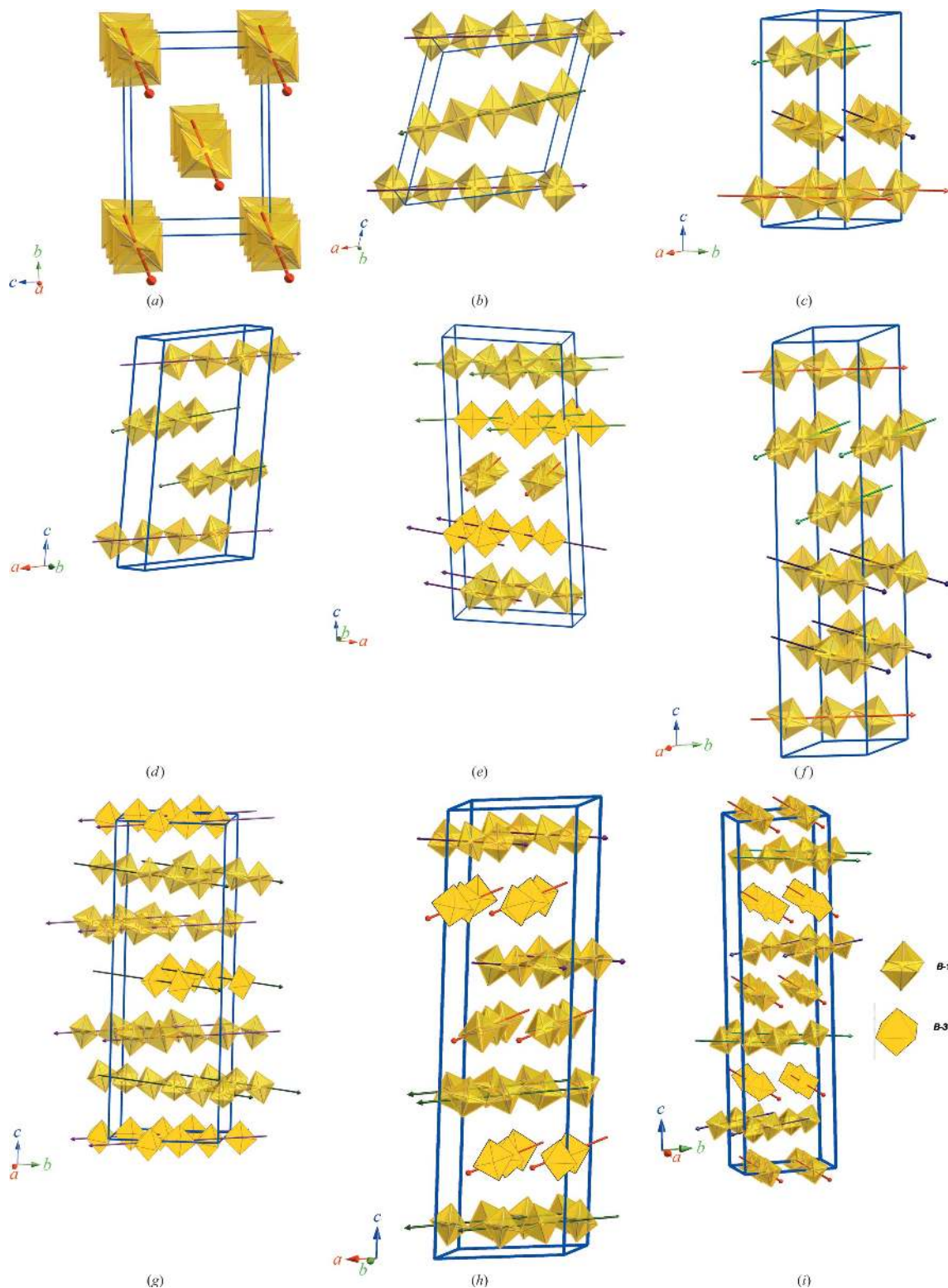
In these cases type  $\alpha$  is nearly parallel to  $[100]$  for  $8O$  or  $[010]$  for  $5M$  and  $7M$ . Type  $\beta$  is nearly parallel to  $[110]$  and type  $\gamma$  is nearly parallel to  $[\bar{1}10]$ . The directions of the  $B$  chains are  $\beta\beta\alpha\gamma\gamma$  for  $5M$ ,  $\underline{\gamma\beta\gamma\beta\gamma\beta}$  for  $6M$ ,  $\underline{\gamma\alpha\gamma\alpha\beta\alpha\beta}$  for  $7M$  and  $\underline{\alpha\beta\alpha\gamma\alpha\beta\alpha\gamma}$  for  $8O$  ( $B$ -3 chains are underlined). In summary, the stacking sequence of  $B$  chains changes with different weberite variants (see Fig. 12) and the formation of  $B$  chains is a characteristic of all weberites.

#### 2.4. Stability field

Both pyrochlores and weberites have  $BX_6$  octahedral networks. Owing to the fact that  $B$ -2 octahedra have two unpaired vertices, the  $BX_6$  octahedral network in weberite is typically less compact. Therefore, weberite has more potential to permit larger radii of  $A$  ions. Fig. 13 shows a diagram of  $R_A$  versus  $R_B$  for 159 pyrochlore oxides and 131 weberite compounds (83 weberite fluorides and 48 weberite oxides, see Tables 5 and 6 for a complete list and references). The 159

pyrochlore oxides are taken from two articles (Subramanian *et al.*, 1983; Isupov, 2000). Fig. 13 indicates that the majority of pyrochlores have  $R_A$  ranging from 0.97 to 1.13 Å, while most weberites have  $R_A$  values ranging from 1.10 to 1.30 Å.

Weberite  $Ba_2U_2O_7$  has the highest  $R_A$  value of 1.42 Å (Cordfunke & Ijdo, 1988; Shannon, 1976). This clearly shows that larger  $R_A$  values prefer the formation of the weberite (Brisse *et al.*, 1972). The ratio of  $R_A/R_B$  for the weberite is



**Figure 12**  
*B* chains in different weberite-like structures. The vectors across the octahedra indicate the orientations of the *B* chains. (a) 2O, (b) 2M, (c) 3T, (d) 4M, (e) 5M, (f) 6T, (g) 6M, (h) 7M and (i) 8O.

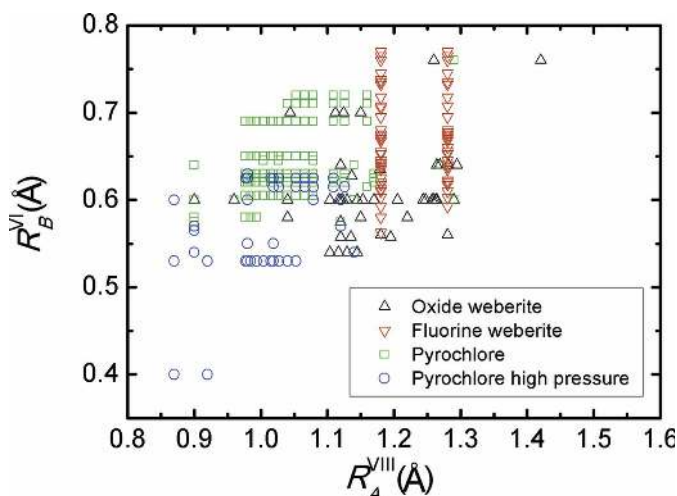


between 1.5 and 2. The two end-members are  $\text{Cd}_2\text{Sb}_2\text{O}_7$  and  $\text{Ag}_2\text{Te}_2\text{O}_7$ . However, the range of  $R_A/R_B$  for weberite greatly overlaps with the stability field for pyrochlore: 1.46–1.8 for  $A_2^{3+}B_2^{4+}\text{O}_7$  and 1.4–2.2 for  $A_2^{2+}B_2^{5+}\text{O}_7$  (Subramanian *et al.*, 1983). Therefore, the ionic radius ratio is not the only determining factor in the structural stability.

Electronegativity ( $\chi$ ) is another important factor in the field of existence, because the formation of weberites is closely related to the covalent character of the bonds (Sych, Kabanova, Garbuz *et al.*, 1988; Lopatin *et al.*, 1985; Weller *et al.*, 2003; Burchard & Rudorff, 1979). Weller *et al.* (2003) used only  $\chi_A$  and  $\chi_B$  to picture the stability field of the weberite, but their study only included a limited number of compounds. Lopatin *et al.* (1982, 1985) successfully utilized  $\chi_A$  and  $R_A/R_B$  to distinguish pyrochlores and weberites, and  $\chi_B$  and  $R_A/R_B$  to determine the different regions of the weberite and the layered perovskite. They chose Allred–Rochow (Allred & Rochow, 1958) electronegativities (which were completed by Little & Jones, 1960) because Allred–Rochow electronegativities are more precise when measuring the degree of covalent character of the bonds. Sych *et al.* (Sych, Kabanova, Garbuz *et al.*, 1988) introduced  $R_A/R_B$  versus the relative ionicity of the  $A-O$  bond, which is the ratio of the ionicity of the  $A-O$  bond to the sum of the ionicity of the  $A-O$  and  $B-O$  bonds. The ionicity of the  $A-O$  bond is calculated as

$$I_{A-O} = 1 - \exp[-0.25(\chi_A - \chi_O)^2]. \quad (4)$$

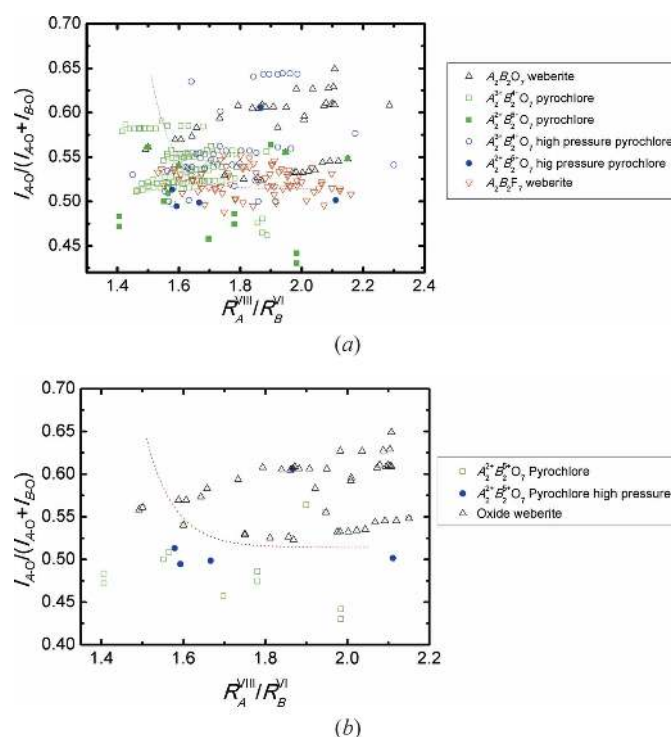
They used the electronegativities for the crystalline state calculated by Batanov (1975). The advantage of relative ionicity is that it contains the information for both  $A-O$  and  $B-O$  bonds. Therefore, the relative ionicity of  $A-O$  versus  $R_A/R_B$  is used to determine the stability field in this study, as shown in Fig. 14. Here, the electronegativities of Allred–Rochow (Allred & Rochow, 1958) and Little–Jones (Little & Jones, 1960) were used in calculating the ionicity. In Fig. 14(a) there is no obvious separation between weberites and pyrochlores. The reason for this may be that both  $A_2^{3+}B_2^{4+}\text{O}_7$  and  $A_2^{2+}B_2^{5+}\text{O}_7$  pyrochlore compounds are plotted. There are very



**Figure 13**  
Summary of  $R_A$  versus  $R_B$  for weberites (including oxide and fluorine) and pyrochlore oxides.

few, if any,  $A_2^{3+}B_2^{4+}\text{O}_7$  weberites reported. Most weberites are  $A_2^{2+}B_2^{5+}\text{O}_7$  or  $(A, A')_2^{2+}(B, B')_2^{5+}\text{O}_7$  and several  $A_2^{1+}B_2^{6+}\text{O}_7$  ( $\text{Na}_2\text{Te}_2\text{O}_7$  and  $\text{Ag}_2\text{Te}_2\text{O}_7$ ). The inclusion of  $A_2^{3+}B_2^{4+}\text{O}_7$ , particularly high-pressure phases, complicates the stability field, therefore, Fig. 14(b) only contains  $A_2^{2+}B_2^{5+}\text{O}_7$ ,  $(A, A')_2^{2+}(B, B')_2^{5+}\text{O}_7$  compounds  $\text{Na}_2\text{Te}_2\text{O}_7$  and  $\text{Ag}_2\text{Te}_2\text{O}_7$  (all weberites points in Fig. 14b are listed in Table 6). Observing the plotted data in Fig. 14(b), there is a clear separation between weberites and pyrochlores. The dashed line is for visual effect – above the line is the weberite region. Weberites prefer a higher ratio of  $I_{A-O}/(I_{A-O} + I_{B-O})$  and a higher ratio of  $R_A/R_B$  than pyrochlores.

It is worth mentioning four specific compounds:  $\text{Cd}_2\text{Sb}_2\text{O}_7$  ( $R_{\text{Cd}^{2+}} = 0.9 \text{ \AA}$ ) in the pyrochlore region, and  $\text{Ca}_2\text{Sb}_2\text{O}_7$ ,  $\text{Ca}_2\text{Os}_2\text{O}_7$  ( $R_{\text{Ca}^{2+}} = 1.12 \text{ \AA}$ ) and  $\text{Pb}_2\text{Sb}_2\text{O}_7$  ( $R_{\text{Pb}^{2+}} = 1.29 \text{ \AA}$ ) in the weberite region (Shannon, 1976). A high-pressure study has been performed on the first three compounds to investigate the transformation of the pyrochlore and weberite phases.  $\text{Cd}_2\text{Sb}_2\text{O}_7$  can form a metastable phase of weberite, which can be fully converted to pyrochlore under high pressure.  $\text{Ca}_2\text{Sb}_2\text{O}_7$  weberite is more stable than  $\text{Cd}_2\text{Sb}_2\text{O}_7$  weberite. The same high-pressure condition only results in mixed phases of  $\text{Ca}_2\text{Sb}_2\text{O}_7$  pyrochlore and weberite (Knop *et al.*, 1980). At one atmosphere,  $\text{Ca}_2\text{Sb}_2\text{O}_7$  crystallizes as a pyrochlore below 973 K, above which it transforms to a weberite (Brisse *et al.*, 1972). Meanwhile,  $\text{Ca}_2\text{Os}_2\text{O}_7$  weberite is stable and the synthesis of pyrochlore  $\text{Ca}_2\text{Os}_2\text{O}_7$  under pressure leads to calcium-deficient  $\text{Ca}_{1.7}\text{Os}_2\text{O}_7$  (Reading *et al.*, 2002; Weller *et al.*, 2003). The reported crystal structure of  $\text{Pb}_2\text{Sb}_2\text{O}_7$  also strongly depends on the synthesis conditions. Low-temperature firing or wet chemical synthesis resulted in a



**Figure 14**  
Stability field for weberite.

cubic pyrochlore phase. The cubic phase was metastable and readily transformed into weberite or rhombohedrally distorted pyrochlore (Ivanov *et al.*, 1998; Brisse *et al.*, 1972). These four compounds can crystallize as different polymorphs depending on the processing history, as presented in Fig. 14(b). It is worth noting that although the ionic radii ratio and bond ionicity are two major factors, there may be some additional crystallochemical characteristics or parameters that play a role in determining the prevalence of weberite over pyrochlore or *vice versa*. It would be interesting to perform some computational calculations (*e.g.* density functional theory) to shed light on the comparative lattice energy and stability field of pyrochlore and weberite.

### 3. Interesting properties and potential applications

For fluorine-based weberites, the magnetic properties attract most of the attention. The triangular network formed by  $B^{2+}$  and  $B^{3+}$  cations in the HTB-like planes generally support three different magnetically ordered systems:

(i) the diamagnetic  $B^{3+}$  ions separate linear chains of paramagnetic  $B^{2+}$  ions, for example, antiferromagnetic  $\text{Na}_2\text{NiAlF}_7$ ,  $\text{Na}_2\text{FeAlF}_7$  and  $\text{Na}_2\text{NiInF}_7$  (Frenzen *et al.*, 1992; Heger, 1973);

(ii) both  $B^{2+}$  and  $B^{3+}$  are paramagnetic ions, like ferromagnetic  $\text{Na}_2\text{NiFeF}_7$  and antiferromagnetic  $\text{Na}_2\text{NiCrF}_7$  (Laligant *et al.*, 1989; Thompson *et al.*, 1992; Heger, 1973; Frenzen *et al.*, 1992);

(iii) diamagnetic  $B^{2+}$  forming linear chains which isolate the paramagnetic  $B^{3+}$  such as antiferromagnetic  $\text{Na}_2\text{MgFeF}_7$  (Pankhurst *et al.*, 1991).

As for weberite oxide, various properties have been investigated including the photocatalytic properties (Abe *et al.*, 2004, 2006; Sato *et al.*, 2002; Lin *et al.*, 2006), the resistivity of  $\text{Ca}_2\text{Os}_2\text{O}_7$  weberite (Reading *et al.*, 2002), magnetic properties (Khalifah *et al.*, 1999; Wakeshima *et al.*, 2004; Wakeshima & Hinatsu, 2006), ferroelectric properties (Ivanov *et al.*, 1998; Astafev *et al.*, 1985) and dielectric properties (Cai & Nino, 2007; Cava *et al.*, 1998; Grey *et al.*, 2001). The interest in the properties is first due to the fact that the weberite structure is considered more favorable for the realisation of a ferroelectric state than the pyrochlore structure (Astafev *et al.*, 1985). The Sb-based compounds are the most investigated weberites for ferroelectric properties. Ten years ago, Cava *et al.* (1998) found that the temperature coefficients of the dielectric constant ( $TC\epsilon_r$ ) of the  $\text{Ca}_2\text{Ta}_2\text{O}_7$ – $\text{Ca}_2\text{Nb}_2\text{O}_7$  system can be close to zero. A series of investigations on  $\text{Ca}_2\text{Ta}_2\text{O}_7$ -based weberites have followed (Grey *et al.*, 1999, 2001, 2003; Grey & Roth, 2000; Ebbinghaus *et al.*, 2005).  $\text{Ln}_3\text{BO}_7$  (where Ln = rare-earth elements and B is Nb or Ta) are also interesting weberite-type compounds. The crystal structure is related to the ionic radius of  $\text{Ln}^{3+}$ , which provides a stage for the study of structure-dielectric properties relationships. This section will focus on the ferroelectric properties and dielectric properties of weberite oxides.

### 3.1. Ferroelectric properties

$\text{A}_2\text{Sb}_2\text{O}_7$  ( $A = \text{Ca}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Sr}^{2+}$ ) are perhaps the most studied weberites owing to their ferroelectric properties. Second-harmonic generation and heat-capacity measurements indicated a possible ferroelectric phase transition in  $\text{Pb}_2\text{Sb}_2\text{O}_7$ . Dielectric constants showed a thermal hysteresis around the Curie temperature ( $T_c$ ) in  $\text{Pb}_2\text{Sb}_2\text{O}_7$  (Astafev *et al.*, 1985; Milyan & Semrad, 2005). Single-crystal X-ray and powder neutron diffraction were performed in detailed crystallographic studies (Ivanov & Zavodnik, 1990; Astafev *et al.*, 1985). Below  $T_c$ , there is a slight distortion from a centrosymmetric structure and ionic displacements cause spontaneous polarization in this structure. The results indicated a non-centrosymmetric (space group  $I2cm$ ) to centrosymmetric (space group  $Imam$ , another setting of  $Imma$ ) phase transition (Astafev *et al.*, 1985; Ivanov *et al.*, 1998; Ivanov & Zavodnik, 1990).  $T_c$  depends on the A cation: 510 K for  $\text{Pb}_2\text{Sb}_2\text{O}_7$ , 110 K for  $\text{Ca}_2\text{Sb}_2\text{O}_7$  and 90 K for  $\text{Sr}_2\text{Sb}_2\text{O}_7$ . The substitution of Ca by Pb in  $\text{Ca}_2\text{Sb}_2\text{O}_7$  causes a shift of  $T_c$  towards a higher temperature: 200 K for  $\text{CaPbSb}_2\text{O}_7$  weberite. Therefore, the A sublattice seems more likely to be the ferroelectrically active one.

It is worth noting that  $\text{Pb}_2\text{Sb}_2\text{O}_7$  can also form rhombohedrally distorted pyrochlore (Brisse *et al.*, 1972). The pyrochlore phase is paraelectric even at room temperature. Actually,  $\text{Pb}_2\text{Sb}_2\text{O}_7$  weberite has a higher  $T_c$  than most Pb-based pyrochlores. These facts may serve as evidence that the weberite structure is more suitable for the appearance of the ferroelectric state (Astafev *et al.*, 1985; Isupov, 2000).

### 3.2. Dielectric properties

**3.2.1.  $\text{Ca}_2\text{Ta}_2\text{O}_7$ -based compounds.** According to Grey and co-workers (Grey *et al.*, 1999) the structure of pure  $\text{Ca}_2\text{Ta}_2\text{O}_7$  is  $3T$  weberite up to 1673 K, where it transforms to the  $7M$  polytype. The structure can be easily modified by doping and different synthesis routines (Grey *et al.*, 1999, 2001, 2003; Grey & Roth, 2000; Ebbinghaus *et al.*, 2005). One of the most interesting dielectric properties of  $\text{Ca}_2\text{Ta}_2\text{O}_7$  is that the temperature coefficient of the dielectric constant ( $TC\epsilon_r$ ) is 0 when mixing with 18 mol% of  $\text{Ca}_2\text{Nb}_2\text{O}_7$ , meeting the requirement for the application of microwave dielectrics (Cava *et al.*, 1998).  $TC\epsilon_r \simeq 0$  can be easily understood because  $TC\epsilon_r$  is negative for  $\text{Ca}_2\text{Ta}_2\text{O}_7$  ( $-444$  p.p.m.  $\text{K}^{-1}$  at 295 K) and positive for  $\text{Ca}_2\text{Nb}_2\text{O}_7$  (231 p.p.m.  $\text{K}^{-1}$  at 295 K). Extensive studies on the structure of the  $(1-x)\text{Ca}_2\text{Ta}_2\text{O}_7$ – $x\text{Ca}_2\text{Nb}_2\text{O}_7$  system have been performed by powder and single-crystal X-ray diffraction, and powder neutron diffraction (Grey *et al.*, 2001). The system forms  $7M$  weberite solid solutions up to  $x = 0.1$  and  $\text{Ca}_2\text{Nb}_2\text{O}_7$ -type solid solutions from  $x = 0.2$ – $1$ . When  $x = 0.1$ , the structure transforms into  $5M$ . The solubility limit is reached when the substitution of  $\text{Ca}_2\text{Nb}_2\text{O}_7$  increases to 15 mol% and  $\text{Ca}_2\text{Nb}_2\text{O}_7$  forms as a second phase. The presence of  $\text{Ca}_2\text{Nb}_2\text{O}_7$  thus results in  $TC\epsilon_r$  compensation, making it approximately zero.

Another interesting aspect is that most of the  $(1-x)\text{Ca}_2\text{Ta}_2\text{O}_7$ – $x\text{Ca}_2\text{Nb}_2\text{O}_7$  compounds have higher dielec-

**Table 8**

Structural comparison of three weberite-type structures (Allpress &amp; Rossell, 1979; Rossell, 1979).

	La <sub>3</sub> NbO <sub>7</sub>	Nd <sub>3</sub> NbO <sub>7</sub>	Gd <sub>3</sub> NbO <sub>7</sub>
$\Delta d_{\text{Ln-O}}/(d_{\text{Ln-O}})_{\text{av}}$ in LnO <sub>8</sub> cube (%)	13.33	7.14	13.06
Deviation of O–Ln–O angle from perfect cube (°)	–9.87–6.46	–2.37–2.47	–5.77–8.88
$\Delta d_{\text{Nb-O}}/(d_{\text{Nb-O}})_{\text{av}}$ in NbO <sub>6</sub> octahedra (%)	1.64	0.41	4.86
Deviation of O–Nb–O angle from perfect octahedra	–1.58–1.58	0.27–0.42	–5.63–5.63

$d_{\text{Ln-O}}$  and  $d_{\text{Nb-O}}$  represents the bond length between Ln<sup>3+</sup> and O<sup>2-</sup> and the bond length between Nb<sup>5+</sup> and O<sup>2-</sup>, respectively.  $\Delta d_{\text{Ln-O}}$  means the difference of longest and shortest bond length between Ln<sup>3+</sup> and O<sup>2-</sup> in LnO<sub>8</sub> distorted cubes.  $\Delta d_{\text{Nb-O}}$  is the difference of the longest and shortest bond length between Nb<sup>5+</sup> and O<sup>2-</sup> in NbO<sub>6</sub> distorted octahedra.  $(d_{\text{Ln-O}})_{\text{av}}$  is the average bond length between Ln<sup>3+</sup> and O<sup>2-</sup> in LnO<sub>8</sub> distorted cubes.  $(d_{\text{Nb-O}})_{\text{av}}$  is the average bond length between Nb<sup>5+</sup> and O<sup>2-</sup> in NbO<sub>6</sub> distorted octahedra.

tric constants (above 30) than pure Ca<sub>2</sub>Ta<sub>2</sub>O<sub>7</sub> and Ca<sub>2</sub>Nb<sub>2</sub>O<sub>7</sub> at 1 MHz (Cava *et al.*, 1998). However, another set of published dielectric constants of 5M Ca<sub>2</sub>Ta<sub>1.8</sub>Nb<sub>0.2</sub>O<sub>7</sub> and 7M Ca<sub>2</sub>Ta<sub>1.9</sub>Nb<sub>0.1</sub>O<sub>7</sub> are approximately 18 and 20 at 1 MHz, respectively, which are lower than the previous publication (Grey *et al.*, 2001). It is not clear what causes the discrepancy in dielectric constant measurement. It may be due to different firing conditions and measurement methods. Dielectric properties at radio frequency have also been investigated. The dielectric constants of 3T Ca<sub>1.6</sub>Nd<sub>0.4</sub>Ta<sub>1.6</sub>Zr<sub>0.4</sub>O<sub>7</sub>, 5M Ca<sub>2</sub>Ta<sub>1.8</sub>Nb<sub>0.2</sub>O<sub>7</sub> and 7M Ca<sub>2</sub>Ta<sub>1.9</sub>Nb<sub>0.1</sub>O<sub>7</sub> are approximately stable (18–19) from 100 kHz up to 5 GHz and reach a maximum (22, 24.5 and 26.1, respectively) at ~ 8 GHz. The dielectric constant is comparable for some important microwave dielectrics, such as BaMg<sub>1/3</sub>Ta<sub>2/3</sub>O<sub>3</sub> (~ 24; Reaney & Iddles, 2006). However, the problem with these systems is that they have low quality factors ( $Q \simeq 200$ ) for technical applications (Grey *et al.*, 2001).

It is interesting to see that 8O Ca<sub>2</sub>Ta<sub>2</sub>O<sub>7</sub>, which is synthesized by the optical floating zone melting method from 3T Ca<sub>2</sub>Ta<sub>2</sub>O<sub>7</sub> powder, has a relatively high dielectric constant (~ 60) at room temperature (Ebbinghaus *et al.*, 2005). And  $\epsilon_r$  increases to 90 at 50 K. The high dielectric constant may result from a net dipole created by the off-center Ta<sup>5+</sup> in the TaO<sub>6</sub> octahedra of the Ca<sub>3</sub>Ta layers. The shifting of Ta<sup>5+</sup> also produces two short Ta–O bonds and two long Ta–O bonds, leading to the distortion of TaO<sub>6</sub> octahedra. The high dielectric constant and the ability to tailor it are interesting for scientific study and possible electronic applications.

In addition, the crystallographic study of Nd<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> and Sm<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> doping Ca<sub>2</sub>Ta<sub>2</sub>O<sub>7</sub> has been conducted by Grey *et al.* (Grey *et al.*, 2003; Grey & Roth, 2000). The resulting phases include 3T, 4M, 5M and 6T weberites. The great structural flexibility of Ca<sub>2</sub>Ta<sub>2</sub>O<sub>7</sub>-based compounds is interesting in a crystallographic study and may have potentials in technical applications.

**3.2.2. Weberite-type Ln<sub>3</sub>NbO<sub>7</sub>.** As stated in §2.3, Ln<sub>2</sub>(Nb,Ln)O<sub>7</sub> (or Ln<sub>3</sub>NbO<sub>7</sub>, where Ln is La<sup>3+</sup>, Pr<sup>3+</sup>, Nd<sup>3+</sup> and Gd<sup>3+</sup>) is a weberite-type structure. It is an extreme case of 2O-

III weberite structure, in which A-2 and B-2 are the same. Our recent study on the dielectric properties of Ln<sub>3</sub>NbO<sub>7</sub> (Ln = La<sup>3+</sup>, Nd<sup>3+</sup> and Gd<sup>3+</sup>) showed some interesting results (Cai *et al.*, 2007; Cai & Nino, 2007). As shown in Fig. 15, all three compounds exhibited a dielectric relaxation behavior similar to that observed in pyrochlore compounds (Roth *et al.*, 2008; Nino *et al.*, 2001). The permittivity increases sharply with increasing temperature until a maximum is reached. After that, the permittivity decreases slightly with an increase in temperature. The permittivity is between 35 and 60 for La<sub>3</sub>NbO<sub>7</sub> and 34–47 for Gd<sub>3</sub>NbO<sub>7</sub> from 113 to 473 K, and is between 34 and 62 for Nd<sub>3</sub>NbO<sub>7</sub> from 113 to 673 K at 1 MHz. These three compounds have close permittivity at 113 K. The relaxation temperatures are different, 183, 473 and 323 K for La<sub>3</sub>NbO<sub>7</sub>, Nd<sub>3</sub>NbO<sub>7</sub> and Gd<sub>3</sub>NbO<sub>7</sub>, respectively. The difference in relaxation temperature indicates the possibility of tailoring the temperature at which dielectric relaxation occurs through variations in compositions. As for the origin of different dielectric relaxation temperatures, a possible explanation is provided by comparing the structure. The main difference between the structure is that in Gd<sub>3</sub>NbO<sub>7</sub> the polyhedra are more distorted (Wakeshima *et al.*, 2004; Allpress & Rossell, 1979; Rossell, 1979). In Table 8 polyhedral distortions are quantified in the deviation of bond length and bond angle. The calculation is based on the atomic positions after Rossell (1979). Nd<sub>3</sub>NbO<sub>7</sub> has nearly perfect NbO<sub>6</sub> octahedra, while Gd<sub>3</sub>NbO<sub>7</sub> has the most distorted octahedra. The LnO<sub>8</sub> cube in Nd<sub>3</sub>NbO<sub>7</sub> is the least distorted while LaO<sub>8</sub> and GdO<sub>8</sub> cubes have comparable distortion. These distortions are attributed to the ‘openness’ of the structure which causes an easier polarization of the material and results in a lower relaxation temperature (Astafyev *et al.*, 1985). Additional details on the relationship of dielectric relaxation and polyhedral distortions are ongoing and will be a matter for future publications.

Owing to the interesting dielectric loss behavior observed in Gd<sub>3</sub>NbO<sub>7</sub> its characterization includes more frequencies (1, 4, 6, 10, 30, 80, 100, 300, 800 kHz and 1 MHz), as shown in Fig. 15(c). The temperature ( $T_m$ ), at which the loss peak occurs increases with increasing measuring frequency. To better understand the phenomena, the Arrhenius function is used to model the relaxation behaviour of Gd<sub>3</sub>NbO<sub>7</sub>

$$\nu = \nu_0 \exp\left(-\frac{E_a}{k_B T_m}\right), \quad (5)$$

where  $\nu$  is the measuring frequency, the pre-exponential  $\nu_0$  is the attempt-jump frequency,  $E_a$  is the activation energy and  $k_B$  is Boltzmann’s constant.  $T_m$  is determined for each measuring frequency by fitting the loss peak to a Gaussian function. The non-symmetric tails of loss peaks are cut off during fitting. The resulting Arrhenius plot is presented in Fig. 15(d). From the linear fit,  $\nu_0 = 1.51 \times 10^{11}$  Hz, and the activation energy  $E_a$  is 0.45 eV, which is larger than typical values observed in Nb-based pyrochlores, for example 0.32 eV in Ca–Ti–Nb–O pyrochlore and 0.14 eV in Bi–Zn–Nb–O pyrochlore (Roth *et al.*, 2008; Nino, 2002). However, other ionic and dipolar compounds systems have even higher activation energies; for

example, 0.53 eV for CaF<sub>2</sub>-doped NaF and 1.02 eV for (Ba<sub>0.8</sub>Sr<sub>0.2</sub>)(Ti<sub>1-x</sub>Zr<sub>x</sub>)O<sub>3</sub> (Johnson *et al.*, 1969; Cheng *et al.*, 2004). Thus, the calculated  $E_a$  is acceptable.

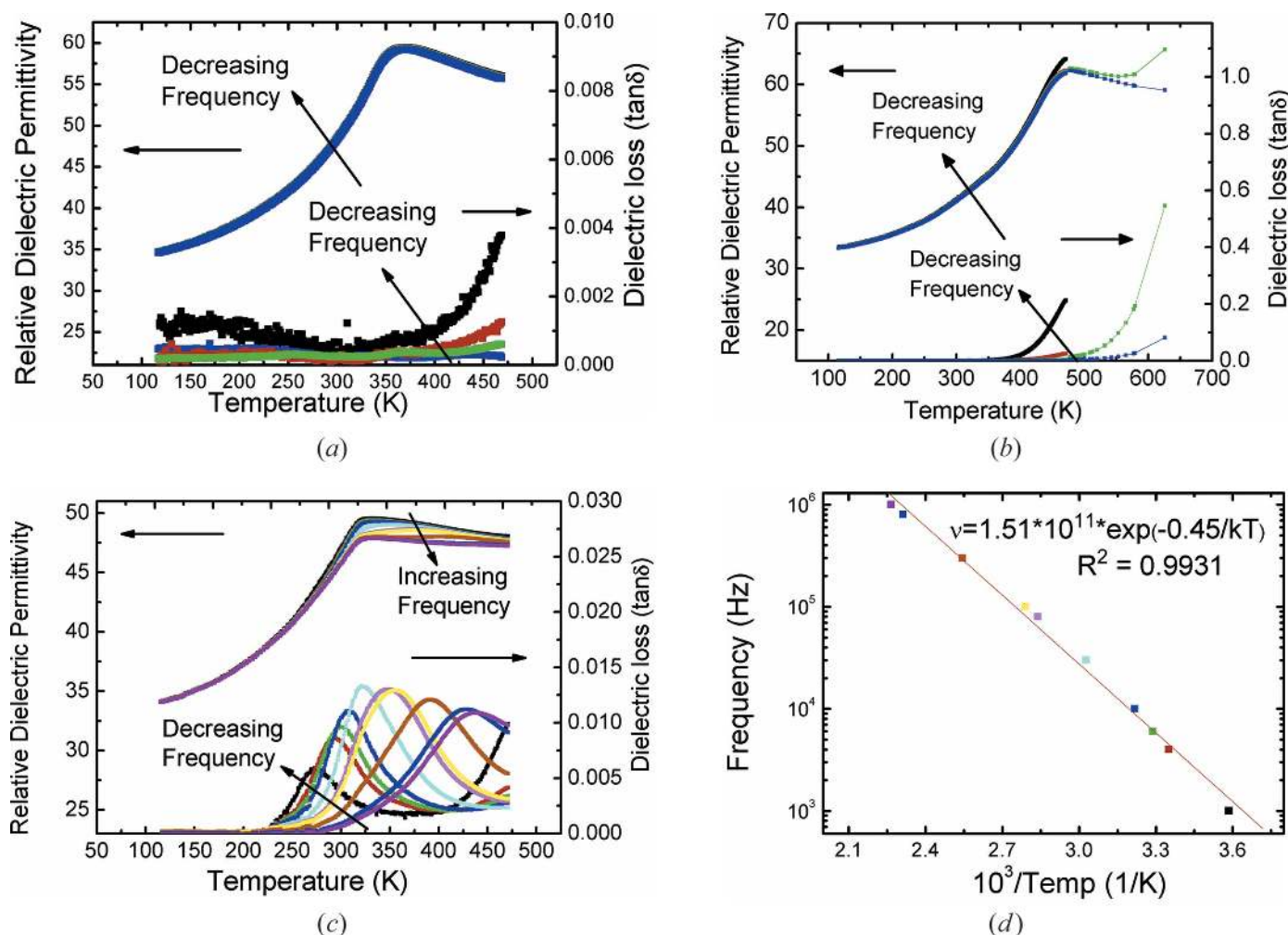
The dielectric study of Ln<sub>3</sub>NbO<sub>7</sub> compounds points to the possibility of tailoring the dielectric relaxation and develop further a paradigm for the compositional design of fluorite-related ceramics with optimized dielectric properties.

#### 4. Conclusions

There are a considerable number of weberite compounds (A<sub>2</sub>B<sub>2</sub>X<sub>7</sub>) that have been studied to date. Here the stability field in terms of the ratio of  $R_A$  and  $R_B$ , and the relative bond ionicity has been established. This structure can be interpreted in different ways. As an anion-deficient fluorite structure, it has similar close-packed cationic networks as fluorite and pyrochlore. It is presented here that the cation sublattices of the weberite and the pyrochlore structures are correlated by an axial transformation and that the different stacking inside

an AB<sub>3</sub> and A<sub>3</sub>B cation slab leads to a different coordination environment of anions in weberite and pyrochlore. There are various types of weberite-like structures. They can be distinguished by the number of AB<sub>3</sub> and A<sub>3</sub>B slabs and the crystal system. B chains are a characteristic of all weberite structures even for weberite polytypes with  $N > 4$ . The stacking sequence and the orientation of B-chains changes with respect to monoclinic and trigonal variants.

So far, investigations have primarily focused on the crystallographic aspects of weberites and some weberite compounds are reported to have interesting properties. It is clear that they are of great scientific interest. However, few studies have concentrated on the properties and possible applications. There is no doubt that weberite compounds possess various useful properties that can be tailored owing to the fact that many metal cations can be introduced into this structure as well as that a large diversity of variants exist in this structure. The realisation of the potential of weberites for electrical applications will grow as more extensive studies are conducted and knowledge of the structures increases.



**Figure 15** Dielectric properties between 1 kHz and 1 MHz of (a) La<sub>3</sub>NbO<sub>7</sub>, (b) Nd<sub>3</sub>NbO<sub>7</sub>, (c) Gd<sub>3</sub>NbO<sub>7</sub> and (d) Arrhenius analysis of Gd<sub>3</sub>NbO<sub>7</sub>.

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