Constitution and properties of ceramized fireclay refractories: II. Properties

S P CHAUDHURI* and B K BHAUMIK

Special Ceramics Section, Central Glass and Ceramic Research Institute, Calcutta 700032, India

Abstract. Low-grade fireclay refractories contain large amounts of glassy phase. The properties, e.g. mechanical strength, thermal-shock resistance, refractoriness-under-load, refractoriness and also porosity and bulk density of these refractories before and after ceramization of their glassy phase were investigated. The glassy phase was ceramized by incorporating Cr_2O_3, V_2O_5 and TiO_2 into the refractories as nucleating agents and subsequent heat-treatment. Significant improvement in mechanical strength and thermal-shock resistance of the ceramized refractories was observed.

Keywords. Fireclay; ceramization; thermomechanical properties.

1. Introduction

A refractory product made of poor-grade fireclay obviously contained large amounts of glass, but this glass was shown to undergo nucleation and crystallization (Chaudhuri and Datta 1996a, b). The glass was heat-treated by two different techniques to crystallize it. Though this process could not influence the mineralogical composition of the product significantly, a remarkable change in the microstructure was noted (Chaudhuri and Bhaumik 1997). Further, there appeared no major change in the microstructure of the products subjected to two types of heat-treatment.

In this paper some important ceramic properties, at room temperature as well as high temperature, of the poor-grade fireclay refractory products, before and after ceramization of their glassy phase by heat-treatment, are described. Attempts are made to correlate the properties with the constitution.

2. Experimental

2.1 *Sample preparation*

Briquettes of 152 mm × 25 mm × 25 mm and 64 mm × 12·5 mm × 12·5 mm rectangular dimensions and 51 mm ht × 51 mm dia cylindrical dimension were fabricated from the fireclay grog and the green fireclay.

The fireclay was mixed with the nucleating agent thoroughly by dry milling in a stainless steel pot and balls. About 80 wt.% of this mass was moistened with water to form small balls which were then dried and fired at 1300°C for 1 h in the oil-fired furnace to make grog. The grog was crushed and sieved into three size fractions, e.g. + 60 mesh(coarse), − 60 + 80 mesh (medium) and − 80 mesh (fine). This 80 wt.% grog which comprised of 45 wt.% coarse, 10 wt.% medium and 45 wt.% fine fractions

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*Author for correspondence

(Westman and Hugill 1930) was mixed with 20 wt.% green fireclay left aside. The mixture was moistened with about 12 wt.% water. The moist mixture was then charged into the cavity of the rectangular and also the cylindrical iron moulds in small instalments and compacted by vibrating the mould and tapping the mixture after each addition to fill it completely. The briquettes were released from the moulds and dried in oven. The briquettes of only fireclay without the addition of nucleating agent were similarly fabricated.

Cr_2O_3, V_2O_5 and TiO_2 were selected as nucleating agents (Chaudhuri and Bhaumik 1997) for this study and were used to the extent of 1, 3 and 10 wt.%, respectively.

Both the rectangular and cylindrical briquettes from four sets, i.e. one without the addition of nucleating agent and three incorporated with the nucleating agents, were divided equally into three groups. Group (a) was fired at 1300°C for 1 h and cooled to room temperature; group (b) was fired at 1300°C for 1 h, cooled to room temperature and then heat-treated at 1150°C for 15 h and group (c) was fired at 1300°C for 1 h, cooled to 1150°C and heat-treated at this temperature for 15 h. An oil-fired furnace was used for firing and heat-treatment of the briquettes. Therefore twelve compositions resulted due to three different heating schedules to which four sets were subjected.

2.2 *Property measurement*

The recommended ASTM methods were utilized for measurement of properties of the compositions. These methods are widely accepted in most of the laboratories and thus help comparison of the inter-laboratory results easily.

2.2a *Porosity and bulk density*:   The small rectangular briquettes (64 mm × 12·5 mm × 12·5 mm) were used for this purpose. Four briquettes of each composition were boiled under water for 2 h and cooled. The porosity and bulk density of a briquette was obtained by taking its dry wt. (D), its wt. after it was fully soaked with water (W) and the wt. of the soaked piece when suspended in water (A) and by applying Archemedes principle as follows (ASTM 1966a):

$$\text{Porosity} = \left(\frac{W-D}{W-A}\right) \times 100 \ (\%), \tag{1}$$

$$\text{Bulk density} = \left(\frac{D}{W-A}\right) \text{g/cc.} \tag{2}$$

2.2b *Mechanical strength*:   Mechanical strength of the rectangular briquettes (152 mm × 25 mm × 25 mm) was measured in terms of modulus of rupture (MOR), both at room temperature (cold) (ASTM 1966b) and at high temperature (hot) (ASTM 1966c). Both cold and hot MORs of a briquette were calculated by the following relationship (Singer and Singer 1971):

$$\text{MOR} = \frac{3WL}{2bd^2}, \tag{3}$$

where W is the breaking load, L the span between the knife edge, b the breadth of the briquette at the point of fracture and d the depth of the briquette at the point of fracture.

For calculation of cold MOR, the briquette was placed on two knife edges, 135 mm apart, and load was applied by pushing the upper knife edge across the length of the briquette by three-point bending method. The downward displacement of the knife edge was maintained at 0·5 mm/min. Four briquettes were tested for each composition.

The machine (INSTRON, Model 1185, U.K.) used for this measurement had loading range of 0–100 KN. The knife edge speed varied from 0·005–1000 mm/min with the loading accuracy of $\pm 0·1\%$ at 100 mm/min speed. The knife edge span could be varied to accommodate samples of 40 mm – 2500 mm length.

For calculation of hot MOR, the test was carried out in the Netzsch apparatus by three-point bending method and four briquettes were tested for each composition. The span between the knife edge was 135 mm. The upper knife edge was pushed across the length of the briquette at 0·5 mm/min and the load was transmitted to it at the rate of 0·15 N/mm^2 sec. The briquettes were raised to 1300°C at 5°C/min, soaked for 15 min and then ruptured one after another.

2.2c *Refractoriness-under-load (RUL)*: This test (ASTM 1966d) was conducted in an oxidizing atmosphere inside an electrically-heated furnace. The electrical resistance of porous petroleum coke granules produced heat. The cylindrical briquette 51 mm ht × 51 mm dia was seated on the dense graphite base and was guarded by magnesite tube. Pieces of graphite electrodes of arc furnace were used to transmit a static load of 2 kg/cm^2 on the sample. A pointer was attached to the loading device which recorded expansion and contraction of the sample with the rise in temperature. After the temperature attained 1000°C, further rise in temperature was obtained at the rate of 8°C/min till the end.

After the initial expansion, the temperature at which 3 mm contraction of the sample was observed was considered as the T_a value of the sample. The T_e value of the sample was the temperature at which the sample suffered a deformation of 40% of its initial length at room temperature. The temperature was measured at every 5 min interval by an optical pyrometer focused on the sample.

The RUL test of each composition was repeated twice with two briquettes.

2.2d *Thermal-shock resistance*: For this test (Chesters 1957), small rectangular (64 mm × 12·5 mm × 12·5 mm) briquettes were used. Three such briquettes of each composition were placed inside an electrically-heated muffle furnace whose temperature was raised from room temperature to 1000°C in about 3 h and maintained for 30 min. The briquettes were then allowed to cool on a refractory brick in draught-free atmosphere for 10 min. These were again introduced into the furnace and heated for further 10 min at 1000°C. This process of alternate heating followed by cooling, each cycle of 10 min duration, was repeated till the briquettes cracked and were easily separable into pieces.

The resistance to thermal shock of the sample was expressed by the number of such thermal cycles that caused the briquettes to break.

2.2e *Refractoriness*: The refractoriness of a sample was expressed by pyrometric cone equivalent (PCE) number. The sample was finely powdered in agate mortar and shaped into standard PCE cone (ASTM 1966e) by bonding with alkali-free dextrin. The sample cones and a few standard cones were alternately embedded on a refractory plaque. This assembly was inserted into an electrically-heated furnace with oxidizing

atmosphere and its temperature was raised at 150°C/h. The temperature was measured by an optical pyrometer focused on the cones.

When the tip of a sample cone and that of a standard cone simultaneously bent to touch the plaque, the PCE number of the standard cone was assigned to that of the sample cone. In some instances, however, the tip of the sample cone bent to touch the plaque a little before and a little after the tips of two standard cones of successive PCE numbers bent similarly. In such case the PCE number of the sample cone was assumed to be in between those of the two standard cones.

The PCE of each composition was determined twice by repeating the test with two cones.

3. Results and discussion

3.1 *Porosity and bulk density*

The results are shown in table 1. Each result was the average of the results of four measurements. There was marginal difference in the porosity and bulk density of the compositions belonging to group (A) and group (B) but rise in porosity and fall in bulk density were observed for compositions under group (C) compared to those for compositions under group (A). As it appeared, the compositions 4, 8 and 12, which contained TiO_2 as nucleating agent, attained lowest porosity due to their lowest

Table 1. Porosity and bulk density of different compositions.

Heating condition		Composition		Porosity (%)	Bulk density (g/cc)
		No.	Description		
Heated at 1300°C for 1 h	(A)	1	Fireclay	26·89	1·91
		2	Fireclay + 1·0 wt.% Cr_2O_3	25·53	1·79
		3	Fireclay + 3·0 wt.% V_2O_5	24·75	1·90
		4	Fireclay + 10·0 wt.% TiO_2	21·72	2·07
Heated at 1300°C for 1 h, cooled to room temp., heat-treated at 1150°C for 15 h	(B)	5	Fireclay	25·65	1·92
		6	Fireclay + 1·0 wt.% Cr_2O_3	25·93	1·94
		7	Fireclay + 3·0 wt.% V_2O_5	25·02	1·95
		8	Fireclay + 10·0 wt.% TiO_2	23·09	2·06
Heated at 1300°C for 1 h, cooled to 1150°C, heat-treated at 1150°C for 15 h	(C)	9	Fireclay	27·26	1·66
		10	Fireclay + 1·0 wt.% Cr_2O_3	30·04	1·82
		11	Fireclay + 3·0 wt.% V_2O_5	31·97	1·78
		12	Fireclay + 10·0 wt.% TiO_2	25·50	1·98

crystalline phase and highest glassy phase content (Chaudhuri and Bhaumik 1997). The ceramization process did not bring about noteworthy change in porosity and bulk density of the samples.

The possibility of closed pore formation in the test briquettes in different proportions during firing could not be ruled out. Some microcracks also appeared in the briquettes. Such pores and cracks were not penetrated by water and, therefore, caused slight variation in porosity and bulk density.

3.2 *Mechanical strength*

The cold and hot MOR values of the compositions are presented in table 2. The MOR values measured at room temperature and 1300°C are expressed as cold MOR and hot MOR, respectively. Each MOR value in the table was the mean of four MOR values.

Both the cold and hot MOR of compositions 5–8 under group (B) showed higher values than those of the corresponding compositions 1–4 under group (A). Again, cold and hot MOR of group (A) compositions (1–4) were higher than those of group (C) compositions (9–12). These results indicate that the mechanical strength of compositions in group (B) improved but that of compositions belonging to group (C) deteriorated.

It is, however, interesting to note that the difference between the cold and hot MOR values of a composition under group (C) was lower than that of a similar composition under group (B) and also group (A). It was, therefore, indicated that the group (C) compositions had the lowest mechanical strength at room temperature but these retained maximum strength at higher temperature (1300°C), the retention of strength being calculated as the percentage gain or loss in hot MOR value over the cold MOR value of any particular composition (table 2). Compositions 5–8 would be more useful because of their highest cold and hot MOR values. This had become possible by heat-treatment of the nucleated poor-grade fireclay products through heating condition (B).

Irrespective of the heating conditions, TiO_2-containing compositions gained the highest strength at room temperature (cold MOR), those containing Cr_2O_3 gained the lowest strength (cold MOR) and the V_2O_5 containing compositions had intermediate cold MOR. It was also observed that the compositions with TiO_2 had hot MOR (strength at 1300°C) that was higher than the compositions with Cr_2O_3 and V_2O_5. The hot MOR of Cr_2O_3- and V_2O_5-containing compositions were, however, reversed, i.e. compositions with Cr_2O_3 occupied the intermediate position and those with V_2O_5 the lowest (table 2). The effect of the nucleating agents on the cold and hot MOR of the compositions is shown by the following series:

$$TiO_2 > V_2O_5 > Cr_2O_3 \quad \text{(for cold MOR)}$$

$$TiO_2 > Cr_2O_3 > V_2O_5 \quad \text{(for hot MOR)}$$
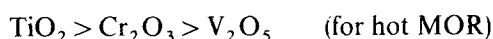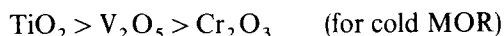
It was shown earlier (Chaudhuri and Datta 1996a) that the mullite content decreased and glass content increased from the V_2O_5- to TiO_2-nucleated compositions and the Cr_2O_3-nucleated compositions fell in between. Despite their low-mullite and high-glass concentrations, the TiO_2-nucleated compositions achieved highest strength, both cold MOR and hot MOR, due to their microstructure where mullite needles with high aspect ratio were well developed and interlocked and thus reinforced the matrix (Chaudhuri and Bhaumik 1997). The lowest cold strength (cold MOR) of the

Table 2. Mechanical strength (cold MOR and hot MOR) of different compositions.

Heating condition		Composition No.	Description	Cold MOR	s.d.*	Hot MOR	s.d.*	Difference (%)
Heated at 1300°C for 1 h	(A)	1	Fireclay	134·63	11·6	69·15	5·7	−48·6
		2	Fireclay + 1·0 wt.% Cr_2O_3	106·48	8·2	80·84	6·2	−24·1
		3	Fireclay + 3·0 wt.% V_2O_5	148·36	12·4	45·65	3·6	−69·2
		4	Fireclay + 10·0 wt.% TiO_2	165·30	13·1	100·58	7·1	−39·2
Heated at 1300°C for 1 h, cooled to room temp., heat-treated at 1150°C for 15 h	(B)	5	Fireclay	149·38	10·7	146·88	12·0	−1·7
		6	Fireclay + 1·0 wt.% Cr_2O_3	137·72	11·2	139·74	7·8	+1·5
		7	Fireclay + 3·0 wt.% V_2O_5	190·53	14·7	70·09	4·1	−63·2
		8	Fireclay + 10·0 wt.% TiO_2	201·20	14·7	146·88	10·3	−27·0
Heated at 1300°C for 1 h, cooled to 1150°C, heat-treated at 1150°C for 15 h	(C)	9	Fireclay	94·31	4·1	108·08	7·9	+14·6
		10	Fireclay + 1·0 wt.% V_2O_3	76·37	5·5	103·38	6·2	+35·4
		11	Fireclay + 3·0 wt.% V_2O_5	74·84	5·7	49·78	3·7	−33·5
		12	Fireclay + 10·0 wt.% TiO_2	118·91	7·6	96·03	6·3	−19·2

Mechanical strength (kg/cm^2)

* Standard deviation

Cr_2O_3-nucleated compositions was essentially due to their poor microstructure, which was featured by small mullite crystals but separated and thereby failed to reinforce the matrix (Chaudhuri and Bhaumik 1997). Highest concentration of mullite in the V_2O_5-nucleated compositions was responsible for their cold strength (cold MOR) to be in between that of TiO_2- and Cr_2O_3-nucleated compositions. The viscosity of the glassy phase in the matrices of V_2O_5- and Cr_2O_3-containing compositions played vital role for the reversal of their hot strength (hot MOR). Cr_2O_3 is a refractory oxide but V_2O_5 is a good fluxing oxide. Consequently, at 1300°C the viscosity of the glassy phase in the compositions with V_2O_5 was lower than that with Cr_2O_3. The low viscosity of the glassy phase in the compositions with V_2O_5 destroyed the beneficial effect of their higher mullite content, and their hot strength had fallen below that of the compositions with Cr_2O_3. The harmful effect of the low-viscous glass was excellently manifested by the difference in the cold and hot MOR values of V_2O_5-containing compositions which had been maximum among all the compositions (table 2).

3.3 *Refractoriness-under-load*

There was definite sign of improvement of refractoriness-under-load (RUL) property of the poor-grade fireclay refractory products on being nucleated and heat-treated via both the heating conditions (table 3). The average value of two measurements is reported in this table for each T_a and T_e.

Table 3. Refractoriness-under-load (RUL) of different compositions.

Heating condition		Composition		RUL		
		No.	Description	T_a(°C)	T_e(°C)	T_e-T_a(°C)
Heated at 1300°C for 1 h	(A)	1	Fireclay	1295	1450	155
		2	Fireclay + 1·0 wt.% Cr_2O_3	1285	1455	170
		3	Fireclay + 3·0 wt.% V_2O_5	1350	1480	130
		4	Fireclay + 10·0 wt.% TiO_2	1265	1425	160
Heated at 1300°C for 1 h, cooled to room temp., heat-treated at 1150°C for 15 h	(B)	5	Fireclay	1325	1495	170
		6	Fireclay + 1·0 wt.% Cr_2O_3	1300	1450	150
		7	Fireclay + 3·0 wt.% V_2O_5	1405	1510	105
		8	Fireclay + 10·0 wt.% TiO_2	1325	1455	130
Heated at 1300°C for 1 h, cooled to 1150°C, heat-treated at 1150°C for 15 h	(C)	9	Fireclay	1265	1360	95
		10	Fireclay + 1·0 wt.% Cr_2O_3	1290	1470	180
		11	Fireclay + 3·0 wt.% V_2O_5	1355	1520	165
		12	Fireclay + 10·0 wt.% TiO_2	1260	1440	180

Both the T_a and T_e values of the V_2O_5-nucleated compositions were maximum. But the compositions nucleated with TiO_2 showed T_a and T_e values which were higher than those nucleated with Cr_2O_3 under heating condition (B) and *vice versa* under heating condition(C). Another salient feature was the difference in the T_e and T_a values of the investigated compositions. Under each heating condition, this difference was found to be maximum for Cr_2O_3-nucleated compositions and minimum for V_2O_5-nucleated ones but very close to the former with the TiO_2-nucleated compositions.

The compositions with V_2O_5 had the maximum concentration of mullite, followed by compositions with Cr_2O_3 and TiO_2. The glassy matrix of the TiO_2-bearing compositions had long interlocked mullite needles but small needles of mullite were the characteristic feature of the matrices of compositions bearing Cr_2O_3 and V_2O_5.

It was observed (Higgins and Jones 1963; Pantony and Vasu 1968; Williamson 1970) that the rate of crystal growth increased with the reduction of viscosity of glass. The rate of crystal growth in a base glass (without the nucleating agent) decreased by more than 3 times due to addition of Cr_2O_3 in this glass but increased by more than 35 times due to addition of V_2O_5 in the same glass. Addition of TiO_2 in this glass also accelerated the crystal growth rate, but less than that by V_2O_5. Thus, the viscosity of glass increased due to addition of Cr_2O_3, but decreased due to addition of both TiO_2 and V_2O_5 and most drastically by V_2O_5. The viscosity of the glassy phase in the V_2O_5-nucleated compositions was therefore the lowest, while in the Cr_2O_3-nucleated compositions it was the highest and in the TiO_2-nucleated compositions it was in between. The gap between T_e and T_a values for V_2O_5-nucleated compositions was the least. The highly viscous glassy matrix of Cr_2O_3-nucleated compositions and the special microstructural attributes of TiO_2-bearing samples were essentially responsible for this comparatively large differences between their T_e and T_a values.

3.4 *Thermal-shock resistance*

The compositions (1–4) which were not heat-treated spalled within 20 cycles, but heat-treated samples (5–8) and (9–12) survived 30 cycles. So, heat treatment enhanced thermal-shock resistance of poor-grade fireclay products.

The Cr_2O_3-bearing compositions, whether heat-treated or not, showed poor resistance to thermal-shock and cracked into pieces within 4–7 cycles. Cr_2O_3 increased the refractoriness and viscosity of the glassy matrix in the samples. This rigid glass could not be strained enough to absorb the stress generated by thermal-shock (Kingery 1955; Chaudhuri and Chatterjee 1968) and these compositions had low mechanical strength (Hasselman 1963) to withstand the thermal-shock stress. These compositions, therefore, cracked only after a few thermal-shock cycles. On the contrary, comparatively high mullite content of V_2O_5-containing compositions (Chaudhuri and Bhaumik 1997), and the glassy matrix with interlocked mullite needles of TiO_2-containing compositions (Chaudhuri and Bhaumik 1997) as well as low viscosity of their glassy matrices were responsible for their greater thermal-shock resistance.

3.5 *Refractoriness*

The pyrometric cone equivalent (PCE) values of all the compositions are included in table 4. The compositions having Cr_2O_3 as the nucleating agent attained the highest

Table 4. Refractoriness (PCE) of different compositions.

Heating condition		Composition		PCE	
		No.	Description	Temp.($^{\circ}$C)	Cone no.
Heated at 1300°C for 1 h	(A)	1	Fireclay	1590	26 → 27
		2	Fireclay + 1·0 wt.% Cr_2O_3	1660	28 → 30
		3	Fireclay + 3·0 wt.% V_2O_5	1575	23 → 26
		4	Fireclay + 10·0 wt.% TiO_2	1530	20
Heated at 1300°C for 1 h, cooled to room temp., heat-treated at 1150°C for 15 h	(B)	5	Fireclay	1575	23 → 26
		6	Fireclay + 1·0 wt.% Cr_2O_3	1620	26 → 28
		7	Fireclay + 3·0 wt.% V_2O_5	1575	23 → 26
		8	Fireclay + 10·0 wt.% TiO_2	1520	19
Heated at 1300°C for 1 h, cooled to 1150°C, heat-treated at 1150°C for 15 h	(C)	9	Fireclay	1570	20 → 23
		10	Fireclay + 1·0 wt.% Cr_2O_3	1660	28 → 30
		11	Fireclay + 3·0 wt.% V_2O_5	1575	23 → 26
		12	Fireclay + 10·0 wt.% TiO_2	1525	19 → 20

value. Although Cr_2O_3 has low solubility (Williamson 1970) in glass, it increased the viscosity of the glassy phase and also its refractoriness due to its own high melting point and refractoriness. Moreover, the mullite content of the Cr_2O_3-nucleated compositions was moderate (Chaudhuri and Bhaumik 1997). These factors are mostly responsible for their highest refractoriness.

Incorporation of V_2O_5 and TiO_2 as nucleating agents in the poor-grade fireclay products and subsequent heat-treatment had but little influence on their refractoriness. The V_2O_5-containing compositions had the highest mullite content and the TiO_2-containing compositions had their glassy matrices reinforced with interlocked mullite needles. In spite of these qualities of V_2O_5- and TiO_2-nucleated compositions these showed poor refractoriness which was less than that of Cr_2O_3-nucleated ones. This is because V_2O_5 and TiO_2 are good fluxing agents and reduced the glass viscosity to a level where the conducive effects of high-mullite concentration and reinforcement of the matrix by interlocked mullite needles were outweighed at higher temperatures.

4. Conclusions

The ceramization of the glassy phase in the poor-grade fireclay refractory products by nucleation with Cr_2O_3, V_2O_5 and TiO_2 and subsequent heat-treatment brought about the following effects on their properties:

(I) The porosity and bulk density did not change significantly but these were comparable with those of high-grade fireclay products.

(II)   The mechanical strength (MOR), particularly the hot MOR, improved remarkably and was 4–5 times higher than that of high-grade fireclay products.

(III)   The refractoriness-under-load (RUL) increased substantially and was at par with that of high-grade fireclay products.

(IV)   The thermal-shock resistance (of V_2O_5- and TiO_2-nucleated compositions) increased to the extent of at least ten cycles more than that of high-grade fireclay products.

(V)   The refractoriness (PCE) (of Cr_2O_3-nucleated composition) was raised to the same level as for the high-grade fireclay products.

Acknowledgement

References

ASTM Standards 1966a Part 13 C20–46 8
ASTM Standards 1966b Part 13 C93–54 74
ASTM Standards 1966c Part 13 C583–65T 605
ASTM Standards 1966d Part 13 C16–62 1
ASTM Standards 1966e Part 13 C24–56 11
Chaudhuri S P and Chatterjee M K 1968 *Trans. Ind. Ceram. Soc.* **27** 63
Chaudhuri S P and Datta T 1996a *Bull. Mater. Sci.* **19** 373
Chaudhuri S P and Datta T 1996b *Bull. Mater. Sci.* **19** 383
Chaudhuri S P and Bhaumik B K 1997 *Bull. Mater. Sci.* **20** 949
Chesters J H 1957 *Steelplant refractories* (London: The United Steel Co. Ltd.) p. 701
Hasselman D P H 1963 *J. Am. Ceram. Soc.* **46** 534
Higgins R and Jones J B 1963 *Bull. Inst. Min. Met.* **72** 825
Kingery W D 1955 *J. Am. Ceram. Soc.* **38** 3
Pantony D A and Vasu K I 1968 *J. Inorg. Nucl. Chem.* **30** 433
Singer F and Singer S S 1971 *Industrial ceramics* (London: Chapman and Hall) p. 336
Westman A E R and Huggil H R 1930 *J. Am. Ceram. Soc.* **13** 767
Williamson J W 1970 *Min. Mag.* **37** 759