EFFECTS OF Al_2O_3: SiO_2 RATIO OF THE STARTING MIXTURE ON THE COMPOSITION ,MICROSTRUCTURE AND MECHANICAL PROPERTIES OF MULLITE PRODUCED BY REACTION SINTERING.

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ABSTRACT

Composition of mullite formed by reaction sintering mixtures of α-alumina and amorphous silica varies from 70.4 to 74.8 wt% Al_2O_3 depending on the bulk composition of the starting mixture. 3 Al_2O_3 : 2 SiO_2 stoichiometric mullite results in the best densification and finest grain size. Mullite rich in alumina (ie. 74.8 wt% Al_2O_3) exhibits rather poor densification and excessive grain growth. A small amount of silica in excess of the solubility limit, which is present in the form of a vitreous phase, has no significant effect on either the densification or the grain growth whereas a small amount of excess alumina resulting in α-alumina precipitates reduces the excessive grain growth and improves the densification of mullite rich in alumina. Mullite begins to form with a composition close to 70.4 wt% Al_2O_3 irrespective of the Al_2O_3 : SiO_2 ratio of the starting mixture. Alumina dissolves into mullite progressively after all free silica is consumed.

Mechanical strength of mullite is sensitive to its composition. Presence of a small amount of vitreous silica leads to a higher flexural strength at elevated temperatures (up to 1200 ^{o}C) and α-alumina precipitates slightly improves fracture toughness.

INTRODUCTION

Mullite is a solid solution of alumina and silica[1]. Good chemical and thermal stability, high creep resistance and refractoriness, low thermal expansion and thermal conductivity and medium strength at high temperatures are some of the attractive properties of this material. It can be synthesised at temperatures above 1300 ^{o}C using mixtures of fine alumina and silica of different crystalline forms [2,3,4,5]. Sintering of mullite is rather difficult. Pressureless sintering of fine (1 μm) mullite powders at about 1650 ^{o}C for several hours results in densifications of the order of 90% [6,7]. Therefore it is difficult to produce dense mullite by sintering of synthetic mullite powders. This shows the necessity of studies on the possibilities of producing dense mullite by reaction sintering.

The aim of this work was to study the effects of the Al_2O_3 : SiO_2 ratio of the starting mixture on the composition, microstructure and mechanical properties of mullite produced by reaction sintering mixtures of α-alumina and amorphous silica.

EXPERIMENTAL

The characteristics of amorphous silica and α-alumina which were used as starting materials are given in Table 1. The powder mixtures were prepared by attrition milling in ethanol using zirconia balls. After drying, crushing and mixing with the organic binder, powder mixtures were sieved through a 200 um sieve. Disc shape specimens (diameter : 30mm, thickness : 4mm) were prepared by uniaxial pressing under 150MPa in a floating die which is subjected to an ultrasonic vibration to improve compaction homogeneity[8].

After burning off the binder by firing up to 800 °C, the powder compacts were subjected to different predetermined heat treatments. Fired specimens were characterized by measurement of density, observation of microstructure and both qualitative and quantitative analyses of crystalline phases using X-ray diffraction techniques. Mechanical strength was measured by biaxial flexure of discs[9]. Fracture toughness was measured according to SENB method using rectangular bars (25mm x 4mm x 4mm).

RESULTS AND DISCUSSION

The effects of the $Al_2O_3 : SiO_2$ ratio of starting mixture on densification and microstructure of the final product were studied using mixtures of α-alumina and amorphous silica of different compositions, namely 68.0, 71.8, 75.0, 77.3 and 80.0 wt% Al_2O_3. According to X-ray diffraction patterns given in Figure 1 corresponding to specimens fired at 1600 °C for 10h, mullite and α-alumina are present in all samples which initially contained 75.0 wt% or more Al_2O_3. This observation is confirmed by the corresponding micrographs (Figure 2). Mullite is the only crystalline phase present in fired samples of other two compositions.

Samples of all starting compositions, fired at 1600 °C for 10h were finely ground and leached with an aqueous solution of 10% HF for 3h in order to reveal the presence of any glassy phase. A loss in weight was recorded only in the case of samples of 68.0 wt% Al_2O_3 starting composition, which indicates that there was no significant amount of glassy phase in other sintered samples. The glassy phase present in sintered samples containing 68.0 wt% Al_2O_3 transformed into cristobalite when it was crushed, ground and fired again at 1350 °C for 2h (Figure 3). This indicates that a certain amount of free silica is present in samples containing 68.0 wt% Al_2O_3 even after sintering at 1600 °C for 10h. Quantities of different phases present in sintered samples of all compositions were determined using X-ray diffraction techniques. Results of this quantitative analyses, given in Table 2, confirm that mullite is a solid solution. The range of compositions of stable mullite solid solution, calculated using the data given in Table 2, is from 70.4 to 74.8 wt% Al_2O_3. Low-alumina and high-alumina ends of this range of compositions are in good agreement with the corresponding values obtained by Aksay and Pask[10] (70.5 wt% Al_2O_3) and Aramaki and Roy[11] (74.3 wt % Al_2O_3) respectively. The mullite rich in alumina, formed in mixtures containing 75.0 wt% Al_2O_3 exhibits a peculiar grain growth leading to a microstructure consisting of both elongated grains (≃7 x 30 μm) and equiaxed grains (≃ 5 x 5 μm). In contrast, the mullite of the same chemical composition formed in mixtures containing 77.3 and 80.0 wt% Al_2O_3 consists of only equiaxed grains. This difference is caused by α-alumina grains present at intergranular positions which retard the growth of mullite grains most probably by acting as grain boundary barriers. Despite the presence of a noncrystalline silicate phase (≃ 5% in volume), the mullite rich in silica, formed in mixtures containing 68.0 wt% Al_2O_3 consists of mainly equiaxed grains (a few slightly elongated grains are present). This shows that the presence of silica in excess of the solubility limit, which results in a noncrystalline (glassy) phase has almost negligible effect on mullite grain growth compared stoichiometric mullite formed in mixtures containing 71.8 wt% Al_2O_3 consists only of equiaxed grains ($\approx 5 \times 5\ \mu m$).

Final densification of powder compacts reaction sintered according to three different firing cycles are graphically shown in Figure 4. Powder compacts containing 71.8 wt% alumina, which convert into mullite (71.8 wt% Al_2O_3 and 28.2 wt% SiO_2) recorded the highest densification whereas those containing 75.0 wt% Al_2O_3 , which convert into mixtures of mullite (74.7 wt% Al_2O_3 and 25.3 wt% SiO_2) and α-alumina recorded the poorest densification after each heat treatment. Better densification of powder compacts containing 77.3 and 80.0 wt% Al_2O_3, which also convert into mixtures of mullite(74.8 wt% Al_2O_3 and 25.2 wt% SiO_2) and α-alumina, is due to the presence of considerable amounts of free α-alumina after the completion of mullite formation.

Figure 5 shows the variation of flexural strength with chemical composition at 20(room temperature), 600, 900, and 1200 °C. The plot of room temperature flexural strength versus composition has a shape similar to that of the plot of densification versus composition (Figure 4). This close relationship between flexural strength and densification exists even at 600 °C. Therefore the low temperature mechanical strength depends more on densification than on composition. Flexural strength of products which do not contain a considerable amount of any phase other than mullite does not vary significantly with temperature up to 1200 °C. Presence of α-alumina precipitates leads to a 15 to 20 percent drop in strength at temperatures above 600 °C. Product containing 3 to 4 wt% free silica in the form of a vitreous phase shows the most remarkable dependency of flexural strength on temperature. Its strength increases with temperature from 210 MPa at 20 °C to a value in excess of 450 MPa at 1200 °C. This happens as a result of the presence of vitreous silica of high viscosity. Such a phase in a brittle polycrystalline material slows down the propagation of cracks at high temperatures as a result of the relaxation of stresses at crack tips when they enter the zones of vitreous phase of limited plasticity. Data given in Table 3 show that the fracture toughness at room temperature is slightly improved by the presence of α-alumina precipitates.

Cell dimensions of mullite vary with its composition [12,13,14]. The changes in composition of mullite can be detected by measuring the cell parameter "a" which is the most sensitive one. It increases as the Al_2O_3 content in mullite increases. According to Camaron[12], the "a" versus composition plot does not deviate from linearity even when "a" values corrected for Fe and Ti in solid solution with mullite are incorporated(Figure 6).

Cell parameters of the mullite formed in three samples of the mixture containing 75.0 wt% Al_2O_3, sintered at 1550 °C for 1min and 1h and at 1600 °C for 10h were determined by powder X-ray diffractometry. $CuK\alpha_1$ peak positions were determined with an accuracy of $\pm\ 0.0025^\circ$ relative to an α-alumina standard. Unit cell parameters of mullite calculated using a least-squares computer program and the relative amounts of other crystalline phases present determined by X-ray diffraction methods are given in Table 4. Gradual increase of "a" and "c" cell parameters with increasing sintering time and temperature indicates that the mullite formed at early stages of reaction enriches with Al_2O_3 on continued heating. The composition of mullite formed in each of the three samples was estimated using,

(1) quantitative analyses of crystalline phases present by X-ray diffraction methods (given under "x" in Table 4)

(2) values of cell parameter "a" and Figure 6(given under "y" in Table 4)

The significant difference between estimated "x" and "y" values for the composition of mullite formed in sample fired for 1min at 1550 °C could be explained by the presence of noncrystalline SiO_2 owing to the insufficient time given for the transformation of amorphous silica into cristobalite. For other two samples "x" and "y" values are in good agreement. These data show that mullite begins to form with a composition close to the silica rich end of the stable mullite solid solution and it enriches with Al_2O_3 on continued heat treating.

CONCLUSION

The range of compositions of stable mullite is from 70.4 to 74.8 wt% Al_2O_3. Mullite begins to form with the composition close to the silica rich end of the range of solid solution irrespective of the Al_2O_3:SiO_2 ratio of the starting mixture. Densification, grain growth and mechanical properties of mullite ceramic are highly dependent on composition. $3Al_2O_3.2SiO_2$ stoichiometric mullite leads to the best densification and finest grain size. Nearly dense(97%) mullite ceramic possessing moderate mechanical properties up to about 1200 °C can be produced by reaction sintering mixtures of α-alumina and amorphous silica at temperatures near 1600 °C.

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Table 1. Characteristics of starting materials

Material	Chemical analysis(wt%)					Particle size(μm) distribution		
	Al_2O_3	SiO_2	Fe_2O_3	Na_2O	CaO/ MgO	d_{10}	d_{50}	d_{90}
α-alumina	99.7	0.07	0.03	0.05	0.07	0.28	0.65	1.7
Amorphous silica	-	99.6	-	0.12	0.08	0.88	3.6	15

Table 2. Quantitative analysis of phases present in mixtures of α-alumina and amorphous silica of different compositions reaction sintered at 1600°C for 10h.

Composition of the starting mixture (wt% Al_2O_3)	Amount (in wt%) of different phases present after reaction sintering at 1600°C for 10h.			Composition of mullite (wt% Al_2O_3)
	Al_2O_3	Amorphous silica	Mullite	
68.0	-	3.4	96.6	70.4
71.8	-	-	100.0	71.8
75.0	1.0	-	99.0	74.7
77.3	10.0	-	90.0	74.8
80.0	20.5	-	79.5	74.8

Table 3. Fracture toughness of products obtained by reaction sintering at 1600°C for 10h.

Overall composition (wt% Al_2O_3)	68.0	71.8	75.0	77.3	80.0
Fracture toughness at 20°C($MNm^{-3/2}$)	2.0	2.1	1.8	2.3	2.4

Table 4. Cell dimensions of mullite formed and relative amounts of crystalline phases present in mixtures of 75.0 wt% Al_2O_3 composition reaction sintered under different conditions as indicated

Heat treatment (°C/min)	Cell parameters (Å)			Number of peaks considered for cell parameter estimation	Relative amounts of crystalline phases present		Composition of mullite (wt% Al_2O_3)	
	c	b	a		$\frac{A}{A+M}$	$\frac{C}{C+M}$	x	y
1550/1	2.8785	7.6758	7.5374	20	0.337	0.078	68.6	70.9
1550/60	2.8820	7.6858	7.5477	20	0.101	0.0	72.2	72.8
	2.8817	7.6832	7.5482	23				
	2.8821	7.6848	7.5480	25				
1600/600	2.8836	7.6824	7.5588	21	0.010	0.0	74.7	74.5
	2.8837	7.6824	7.5589	22				
	2.8835	7.6820	7.5591	23				

y: Estimated using values of cell parameter 'a' and Figure 6.
x: Estimated using [A/(A+M)] and [C/(C+M)] assuming that no vitreous phase is present. A, C and M are the quantities (by weight) of α-alumina, cristobalite and mullite respectively.

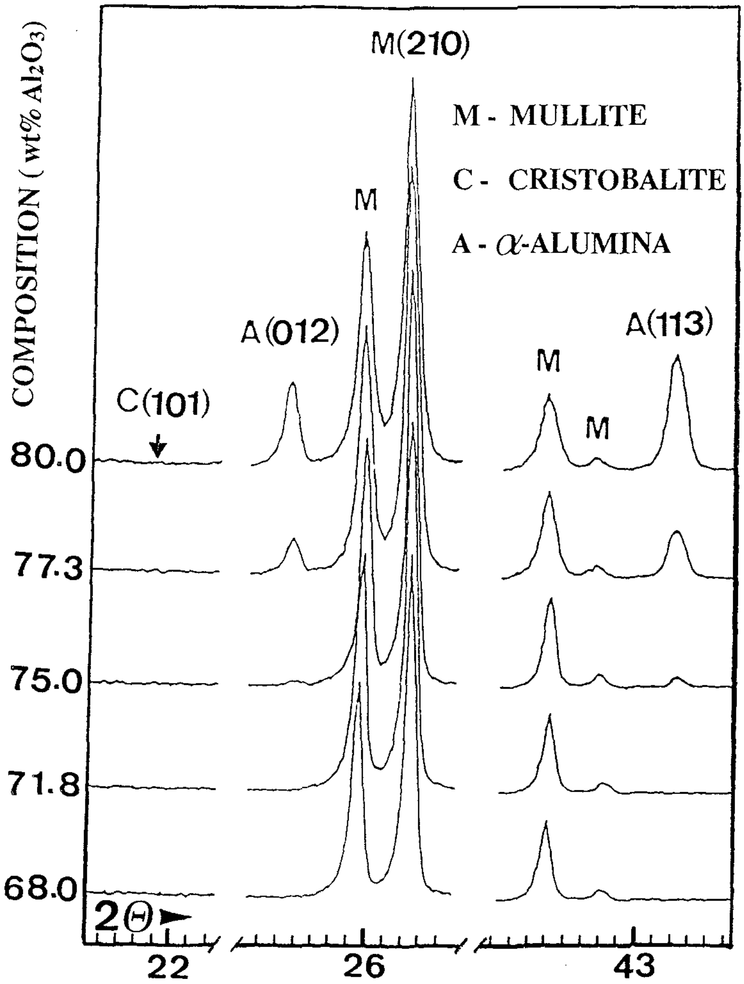

Figure 1. XRD patterns of mixtures of α-alumina and amorphous silica reaction sintered for 10h at 1600 °C.

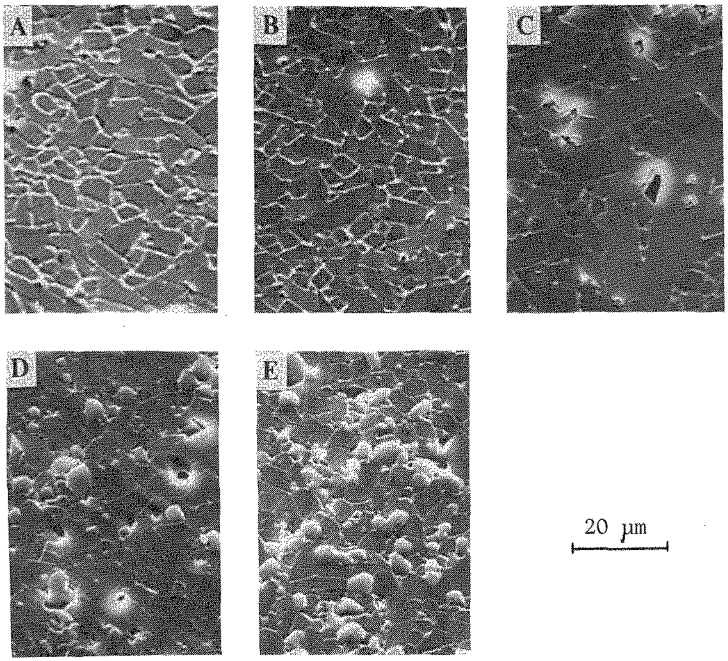

Figure 2. Microstructures of (A) 68.0, (B) 71.8, (C) 75.0, (D) 77.3, (E) 80.0 wt% Al_2O_3 compositions reaction sintered for 10h at 1600 °C.

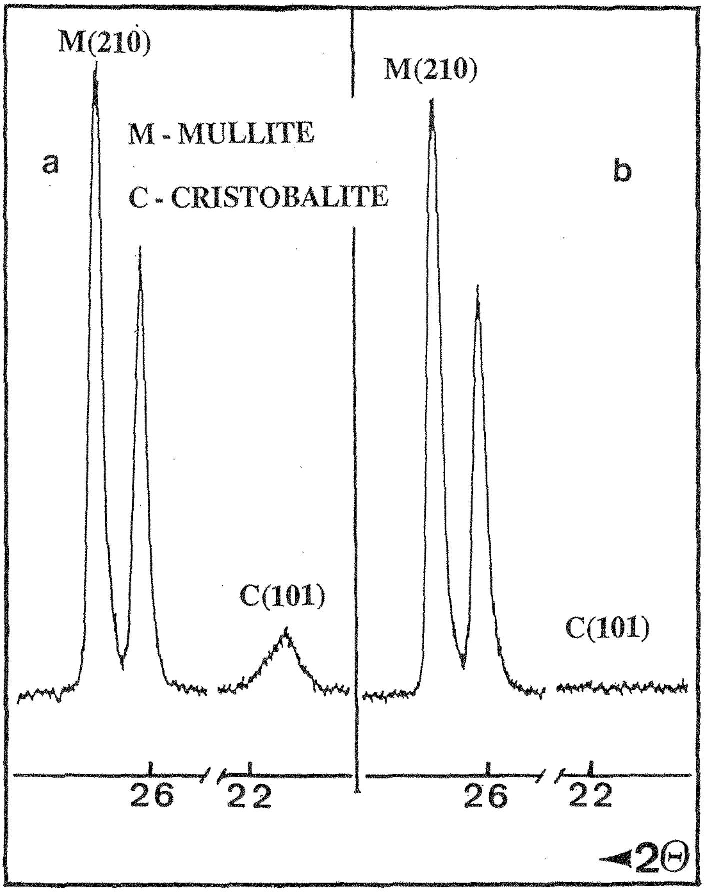

Figure 3. XRD patterns of the 68.0 wt% Al_2O_3 composition reaction sintered (1600 °C/10h) and reheated (1350 °C/2h) after (a) grinding, (b) grinding and leaching by 10% HF aqueous Solution.

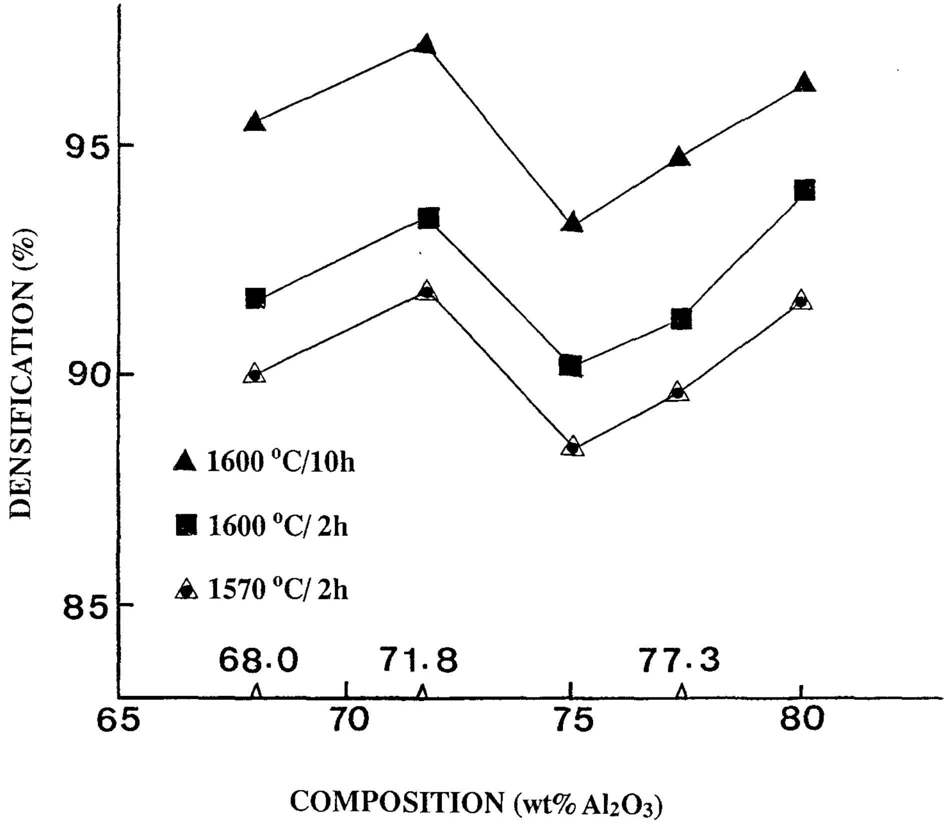

Figure 4. Densification versus composition plots for powder com pacts of α-alumina and amorphous silica,reaction sin tered under different conditions as indicated.

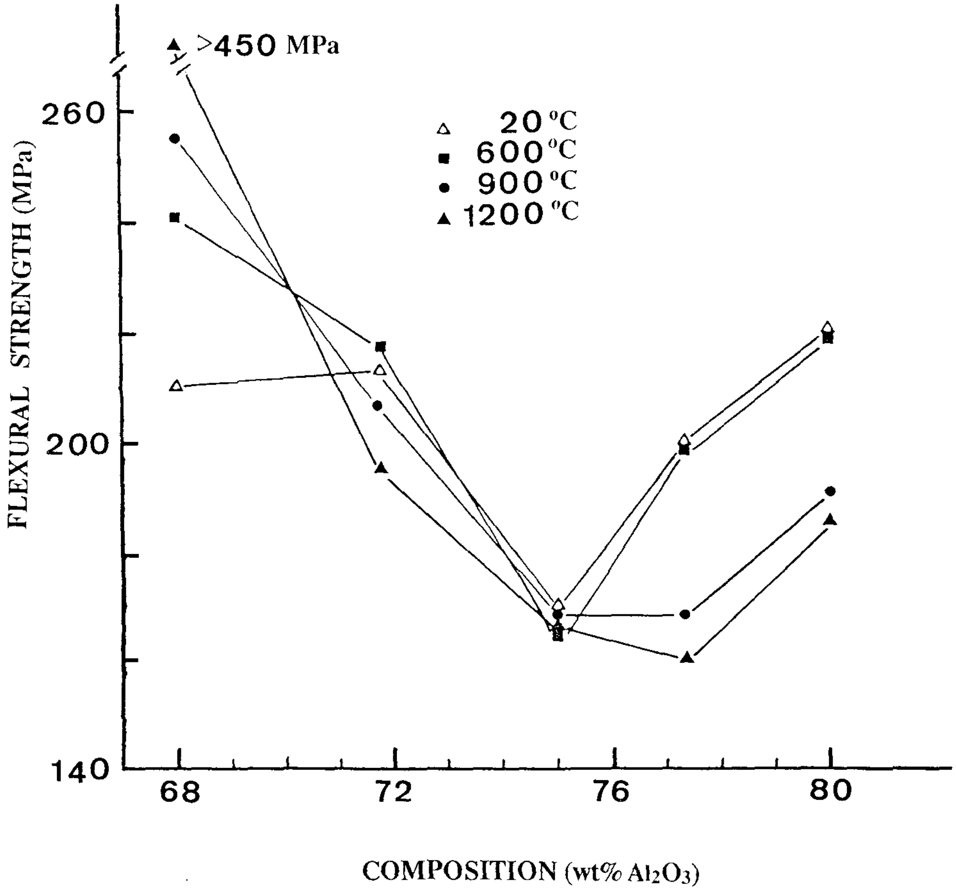

Figure 5. Flexural strength versus composition at 20, 600, 900 and 1200 °C for mullite based ceramics produced by reaction sintering for 10h at 1600 °C.

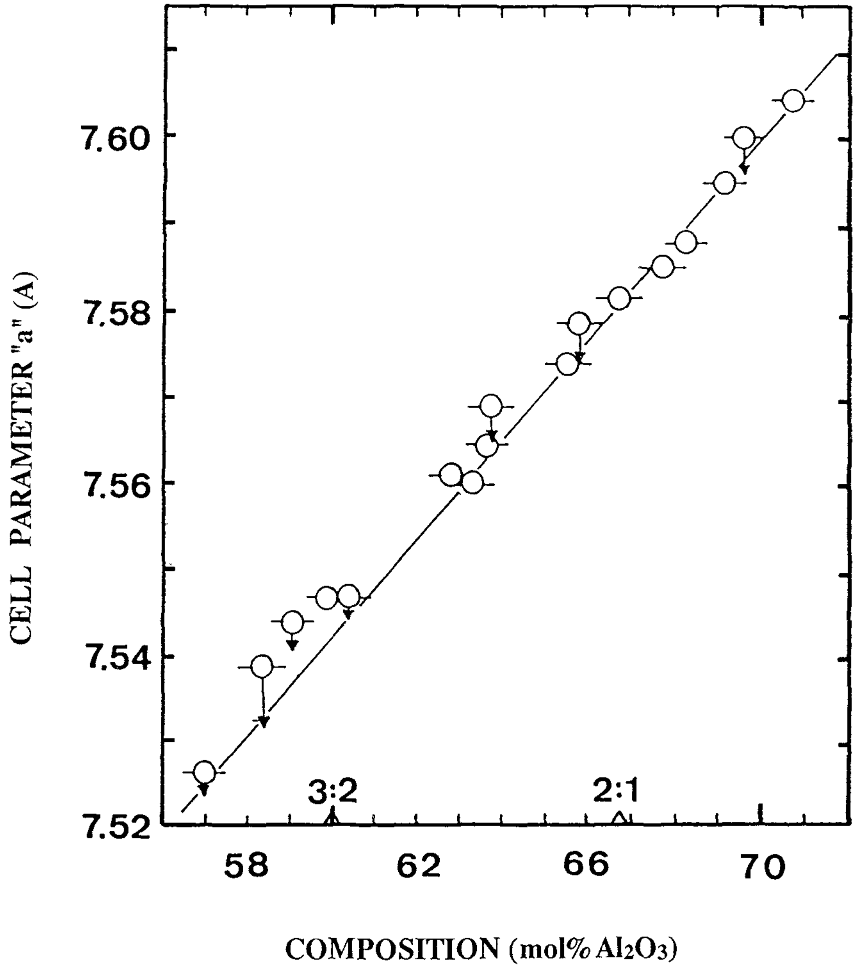

Figure 6. Cell parameter "a" versus composition for mullite (arrows indicate the values of "a" corrected for Fe and Ti in solid solution)(Ref 12).