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Two-stage densification of ultrafine transition alumina seeded with α -phase particulates

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Highly densified Al_2O_3 was prepared from a transition (mainly θ -phase) Al_2O_3 powder doped with α -seeds. Two thermal processing steps resulted in the densification and the θ - to α -phase transformation were characterized by thermomechanical analysis (TMA), porosimetry, scanning and transmission electron microscopies (SEM and TEM). The evolution of the grain growth and porosity were observed. The results showed that the first-stage densification in association with the θ - to α -phase transformation could be controlled to form ultrafine and uniform microstructures, and that would benefit the second-stage densification. The additional α -seeds do not only enhance the transformation rate and give a narrower pore size, but also allow the growth of uniform α -grains to sizes ca. 60 nm. The final densification properties of two seeded samples by thermal treatments were investigated revealing the effects of the transformation in the first stage and the influence of two sintering parameters, e.g. temperature and soaking time on the sintered microstructure.

Key words: alumina, theta phase, seeding, densification, microstructure.

Introduction

Alumina is the most widely used fine ceramics for structural and electronic applications [1]. Recently, alumina of high strength and uniform microstructure has been sought in pursuit of extreme properties for structural applications. One requires the precursory powder to have a fine particle size, avoid agglomerates, and be processed to high and uniform green density [2, 3]. However, the procedure to obtain fine crystalline and highly purified Al_2O_3 powders in the α -phase is tedious. Instead, other sources of alumina powder of high purity have been tried [4, 5]. The reasons for this relate to the cost of the refining process and the difficulty to obtain an agglomeration-free α -powder.

Transition alumina powders normally have the highest surface area and smallest crystalline size, e.g. 15~70 nm [5-7]. There are several studies reporting the phase transformation of transition aluminas, including boehmite [8], γ - [4, 9], and θ -Al₂O₃ [6]. The theta-phase is the last transition phase stable at high temperature and this will transform to α -phase above 1200°C [1].

The transformation of $\theta \rightarrow \alpha$ is considered to be a kind of nucleation and growth transformation and will be accompanied with the changes of morphology. During the transformation of the crystalline structure from the monoclinic (θ -phase) to the hexagonal (α -

phase) structure, a volume reduction of ca. 10.2% is resulted due to the higher density of α -Al₂O₃. Two morphologies of α -Al₂O₃ appeared [10, 11]. The one produced at relatively low temperature is termed "discrete" α -grains with 250~500 nm sizes. The other is in a vermicular shape by finger growth of the α -Al₂O₃ into the θ -matrix [8]. Large porous channels are possibly formed during the transformation and distributed between the growing single-crystalline α -alumina dendrites [7].

In order to reduce the abnormal grain growth of transformed α -grains, several processes have been reported in literature. High pressure may reduce the transformation temperature to as low as 800°C [5]. In addition, many studies on the effects of seeding have been tried [3, 7, 12-16], or combined with sinter forging [6] to demonstrate the influence on the transformation or capability for reducing the crystallization temperature and for enhancing densification. These reports focused on γ -Al₂O₃ or AlOOH. In the transition alumina system of $\gamma \rightarrow \alpha$, Pach *et al.* [14] have measured the heat of the transformation and report a reduction of the activation energy by 18.7 kJ/mol⁻K (12%) of the seeded gel to that of an unseeded gel sample (330~485 kJ/ mol·K). They considered that the transformation of the gel was not solely affected by the number of added α - Al_2O_3 particles (in their cases this was ca. 5×10¹¹ nuclei/cm³), but also by triggering a larger number of α -nuclei at multiple nucleation sites. A tight control of the growth of α -grains for a fine microstructure needed α -Al₂O₃ seeds of an order of 0.25 µm or less [2, 14].

In addition, the thermal process triggering the trans-

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formation also favors the mass diffusion on particle surfaces. Our previous study [17] investigated the kinetics of the $\theta \rightarrow \alpha$ transformation. The results of the transformation started from 960°C are controlled by the diffusion of oxygen in the Al₂O₃ lattice. Newly-formed α -particles show fairly fine sizes in the range of 40~60 nm. These nano-sized particles offer a very good starting point for proceeding to densification. Therefore, the objectives of the present research were set to study the effects of seeding and thermal treatment on the densification of the ultrafine Al₂O₃. An understanding of the microstructural evolution of seeded sample helps to reach a better densification and to maintain a fine grain microstructure.

Experimental

Materials and Sample Preparation

The alumina powder used in this study was a high purity (>99.95%) alumina powder (APA-0.2, Ceralox Co., USA), which has a median size 0.058 μ m (d₅₀), surface area 37±2 m²/g, contains mainly θ -phase with 4.0±1.0 wt% of α -phase [17]. Seeding particles were obtained from AKP-50 (Sumitomo Chemical, Jpn) which is an α -phase alumina with a median size of 0.4 μ m. In this study, two series of alumina pieces was prepared. The samples had either 4 wt% or 17 wt% of α -phase and were named " α 4" or " α 17", which was prepared from pure APA-0.2 or seeded with 13 wt% AKP-50.

The steps for preparing green specimens are documented in Hsiehs thesis [18]. In brief, a suspension with 8 or 30 vol% powder loading and a semicarbazide hydrochloride (S-HCl, 1.0 m% based on powder) dispersant was prepared. After mixing for 24 h with a paint shaker, the well-dispersed suspension was cast at an air pressure of 10 kg/cm³ to form a 60 mm diameter disc with a thickness of 5~7 mm. The dried green bodies which showed a relative density of $54\pm1\%$ theoretical density^{*1} (T.D.) were ready for the following tests.

Characterization

Density measurement: The bulk density of the green and sintered samples were measured by Archimedes' method following the ASTM C372-73 standard [19].

Dilatometry: Dried samples were cut to the dimensions $5\times5\times6$ mm³, and measured the thermal shrinkage measured with a dilatometer (1600°C differential dilatometer, Theta Co., USA) which was normally operated from room temperature to 1500°C with a ramping rate of 5°C/min and held for 1 h at peak temperature.

Microstructural observation: The heat treated samples were very porous, normally containing 40% porosity. Polishing of scanning electron microscopy (SEM) samples at a very moderate pressure was conducted on a diamond wheel with fixed diamond grids of average of 40 µm, and then with 15 µm. The samples between each step were ultrasonically cleaned in ethanol for a few minutes and dried in air. The fine-ground surface was then ion-milled (Ion miller, Gatan Co., Ltd.) for at least 8 h so as to remove more than a 40 µm surface layer. The SEM samples were polished to ensure a clean surface with a genuine microstructure for observation. Two SEM microscopes (Philips 515 SEM, Netherlands and Hitachi S4100 SEM, Japan) operating at 25 or 5 kV were used to characterize the features in the partiallytransformed samples. Similar polishing skill was conducted for a 3 mm-diameter TEM thin foil in a thickness of 250 µm. The ion miller then milled the foil until a small hole was observed at the center.

Results and Discussion

(1) Thermal Shrinkage of Alumina in First Stage

The densification behavior of pure alpha-Al₂O₃ (AKP-50) and two APA-0.2 samples ($\alpha 4$ and $\alpha 17$) tested at temperatures up to 1400°C are reported in Fig. 1. The green density of the two α -samples is around 54% T.D. For the transition Al_2O_3 samples, $\alpha 4$ starts to shrink at 1060°C, and the threshold temperature of shrinkage is reduced to 950°C if seeded with additional α -particles, as the $\alpha 17$ samples shows in the figure. Both transition Al₂O₃ samples (i.e. $\alpha 4$ and $\alpha 17$) perform two-stage sintering. The first shrinkage is ca. 6.8% linearly, which results from the θ - to α -Al₂O₃ phase transformation and particle-particle sintering [17]. The second shrinkage is possibly due to the densification of newly transformed α -Al₂O₃ particles and residual θ -particles. By comparison, the AKP-50 sample with a green density of 65% starts to densify at 1060°C and performs a one-stage sintering



Fig. 1. Thermal shrinkage of pure α -Al₂O₃ (AKP-50) and two θ -samples without (α -4) or with α -seed (α -17) heat-treated in a rate of 10°C/min to 1300°C.

¹The T.D. of samples was estimated from the mass ratio of θ to α phase which showed the density either 3.58 (θ -phase) or 3.987gm/cm³ (α -phase). The T.D. of as-received powder is 3.594 gm/cm³.

process below 1400°C. The linear shrinkage of the AKP sample is 13%, and the maximum rate of shrinkage is at 1220°C.

Pure and ultrafine α -phase Al₂O₃ powder can be sintered at ambient pressure to nearly full density at a temperature as low as 1200°C [2]. Good uniformity and packing in the green stage are necessary for the densification of ultrafine α -Al₂O₃ at lower temperatures. However, there are two additional requirements for the transition Al₂O₃ to achieve full densification. One is to keep the θ -phase particles free from sintering before transforming to α -phase. Then, the newly formed α particles have a chance to keep their size as small as possible. The second requirement is to control the shape of the newly-formed α -particles. Without a good growth control, the α -particles will from a porous, vermicular shape [7], which is impossible to densify below 1500°C.

A recent report [20] on the morphological evolution of the θ -particles prepared from very fine boehmite suggest they may grow to a critical size of 23 nm by thermal treatment, then transform to α -phase at a temperature between 1170°C and 1300°C. The transformation took place by the conversion of one θ -particle to one α -particle. The newly transformed α -particles would grow by a coalescence process from 17 nm to ca. 50 nm.

There are three occasions when the volume of the Al₂O₃ particles may change. The first is during the growth of the θ -particles to the critical size of 23 nm; the second is during the transformation of the θ - to α phase which will increase the density from 3.58 g/ml to 3.987 g/ml; and the last one is the sintering of the α particles. The precursor θ -particles of the present study have a size of 10~50 nm. According to Wen et al.'s transformation model [20], the θ -particles of sizes larger than 23 nm are not stable, especially in a seeding condition. The transformation of θ - to α -Al₂O₃ would cause an 11% density increment, equivalent to a 3.5% linear shrinkage. However, the first shrinkage of $\alpha 17$ and $\alpha 4$ samples in Fig. 1 is in the range 6~7% linearly. The theoretical linear shrinkage of pure θ - to α -phase transformation is obviously less than the shrinkage (6.8%) in the first stage. The shrinkage in the first stage might undergo three possible processes as mentioned previously. The specimen does simultaneously create porosity and densify during the first stage of densification. The sintering of either the θ - or newly formed α -Al₂O₃ grains could be responsible for the 6~7% dimensional reduction in the first-stage.

(2) Structural Evolution of θ - to α -Phase Transformation

The Transformation-Time-Temperature (TTT) curves of two α -samples determined at temperatures from 900°C to 1080°C are shown in Fig. 2. The samples may totally transform to α -phase at 1080°C in 4 h, but need more than 300 h at 900°C. The maximal amount of



Fig. 2. Temperature-Time-Transformation (TTT) diagram of α -4 (broken lines) or α -17 (solid lines) revealing the amounts of the α -phase transformation, either 5%, 50%, or 95%.



Fig. 3. SEM micrographs of the fracture surfaces of (a) α 4 sample sintered at 1050°C for 1 h showing 16% transformation; (b) α 4 sample sintered at 1100°C for 1 h having nearly 86% transformation.

transformation of the $\alpha 17$ sample at 950°C does not exceed 80%. There is 20% θ -phase left in the matrix.

Figure 3 gives the SEM micrographs of α 4 specimens at an early and the final stages of the transformation. The surfaces were milled by Ar⁺ ions for ca. 8 h. The features shown on the surface are thought to be free from artifacts induced by mechanical grinding. Some



Fig. 4. TEM (a) brief field and (b) centered dark field micrographs of the porous region of an 86% transformed $\alpha 4$ Al₂O₃ sample sintered at 1100°C for 1 h.

porous regions of the Al₂O₃ grains were randomly found in Fig. 3(a), where assembled with the transformed α grains with sizes still less than 0.1 µm. The transformation is heterogeneous and under interfacial control. The volume fraction of transformed α -phase in the α 4 sample was around 15~20%. The formation of the coarser grains was partially due to the hetero-transformation of θ - to α -grains and to the coarsening of the α -grains [3, 4, 17].

An 86% transformed α 4 specimen imaged by SEM is shown in Fig. 3(b) and by TEM in Fig. 4. The dense and porous regions of Fig. 3(b) correspond to the densified α -grains and residual θ -phase, respectively. Small θ -grains remain almost left in the pores, as shown in Fig. 4(a). The electron diffraction pattern (DP) of the grains in the pores was indexed according to the XRD data organized in Table 1. The grains shown in Fig. 4(a) are θ -phase with characteristic twinned structures. In addition, these fine θ -grains are surrounded with an amorphous phase of a thickness of 10 to 20 nm. Similar amorphous layers have been identified on those a4 samples processed at temperatures less than 1100°C. At present, no appropriate explanation for the formation of the amorphous layers on alumina grains exists, nor why it retards the transformation of the core θ -grains.

Figure 5 depicts the grain features of the seeded samples

	Fable 1. X-ray	Diffraction	Data of q	and a	Aluminas
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D (Å)		P (cm)	
q (%)	a (%)	K (clii)	
4.540 (18)		0.48	
	3.479 (75)	0.62	
2.837 (80)		0.76	
2.730 (65)		0.79	
2.566 (14)		0.84	
	2.552 (90)	0.85	
2.444 (60)		0.89	
	2.379 (40)	0.91	
2.315 (45)		0.93	
2.257 (35)		0.96	
	2.085 (100)	1.04	
2.019 (45)		1.07	
1.9094 (30)		1.13	
	1.740 (45)	1.24	
	1.601 (80)	1.35	
1.5426 (25)		1.40	
1.4883 (25)		1.45	
1.4526 (25)		1.49	
	1.404 (30)	1.54	
1.3883 (100)		1.56	
	1.374 (50)	1.58	



(α 17) under two major thermal treatments. One was holding at 1020°C for 10 hr. The other was holding at 1020°C for 4 hr, then slow heating to 1120°C at a ramp rate of 2 K/min. The microstructures shown on the fractured surfaces are fairly uniform. The holding at 1020°C for 10 hr has caused α 17 sample to experience more than 95% θ - to α -transformation. But the particle size remains very small. Comparing the treatment with slow heating to 1120°C, the grain size apparently grew 2 times larger, indicating the treatment between 1020°C to 1120°C to be important for the growth and densification of α -grains.

In addition to the grain size, the size distribution of the porosity of the two seeded samples is an important factor for the sintering of ultrafine Al_2O_3 . The as-molded $\alpha 4$ green sample has a size distribution identical to the sample treated at 1000°C. The porosity will grow to larger size if the treatment temperature is ≥ 1100 °C. The results of the $\alpha 4$ treated at 1100°C for a longer time (e.g. 1000.rt)^{*2} show the most frequent pore size has grown to 60 nm, which is 1.4 times more than

²1000.rt means the heat treatment is from room temperature to 1000°C at a ramping rate of 10°C/min, then ramps to 1100°C at a rate of 2°C/min



Fig. 5. SEM micrographs of the fracture surfaces of $\alpha 17$ (a) asreceived, (b) 1020.10 (which means holding at 1020°C for 10 h), and (c) 1020.4r (which means holding at 1020°C for 4 h then heating to 1120°C at a rate of 2°C/min) samples.

those treated at 1000°C (Fig. 6(a)). This pore growth in association with α -grain growth is not favored in the view of microstructural development.

The pore size distribution of $\alpha 17$ is narrower than that of $\alpha 4$, and will not change if treated at 960°C under various conditions, either at 960°C for 4 h or at 960°C for 12 hr. The distribution of the pore sizes treated at 960°C (Fig. 6) is nearly identical to those in the green stage. But, the pores which are smaller less than 21 nm may be sintered away if treated at 1020°C for a few hours. The growth of α -grains has been investigated in literature [11, 14] which suggests that this may result in different morphologies of α -grains.



Fig. 6. Pore size distribution of (a) α 4 and (b) α 17 samples treated with various annealing conditions.

Dynys and Halloran [11] reported their observation that the transformation rate of boehmite gels was 10 times slower in an unseeded gel than in a seeded θ -matrix. This resulted in the growth of vermicular α -grains, which was opposite to the discrete grains which appeared in seeded samples with a uniform microstructure. In the present study, the seeded samples (α 17) if held at 1020°C show an optimized rate of the transformation and minimal α -grain growth. The temperature 1020°C was selected for retaining the smallest α -grains before densification, of which may commence at the temperatures below 1250°C as experienced by Badker and Bailey [8] precisely at 1100°C in this θ -Al₂O₃ system.

(3) Densification and Grain Growth in Second Stage

In order to investigate the phenomena of shrinkage during the transformation and the following densification,



Fig. 7. Shrinkage curves of the $\alpha 17$ sample sintered with the profile specified in the diagram. (a) Calcined at 1020°C for 4 h, then 2°C/min to 1120°C, followed 10 °C/min to sintering temperature, the schedule was designated as "1020.4r"; (b) calcined at 1020°C for 14 h, then sintered at 1490°C for 2 h, designated "1020.10". Note that the change of the shrinkage rate in 750 min at 1020°C where corresponds to the end of θ -to- α -transformation.

two sintering tests were conducted. Both tests were planned to calcine at 1020°C for 4 h or 10 h, and then gradually heated to 1490°C, as shown in the thermal profiles of Fig. 7. The transformation of θ - to α -phase of the α 17 sample was about 65% in 4 h, but nearly complete in 10 h. The temperature control was within \pm 5°C, which was closely monitored in the experiment and shown in the insert on Fig. 7(b).

The initial shrinkage when held at 1020°C is small, 2% for 4 h. This corresponds to a volume shrinkage of 6%. The transformation of 65% α -phase, in fact, introduces about 7% porosity, which is thought in section 3.1 to be readily densified at a temperature 1020°C. This means that the transformed α -particles do not apparently sinter each other at 1020°C. Moreover, the



Fig. 8. Relative density and grain size of $\alpha 4$ and $\alpha 17$ samples calcined at 1000°C or 1020°C for 0 h, 4 h or 10 h, and then sintered at the temperatures for 2 h.

shrinkage extends at the same rate at 1020°C for as long as 10 h until the matrix totally transforms to α phase, as shown in Fig. 7(a). Therefore, the shrinkage in the period of 10~14 hr occurs entirely due to the sintering of α -particles, and experiences a lower shrinkage rate, as indicated in Fig. 7(b). It is also noted that when the temperature is greater than 1050°C, as depicted in Fig. 1 and 7(a), the shrinkage rate of the α 17 sample is dramatically enhanced possibly due to the sintering of newly-transformed α -particles.

Figure 8 gives the densification results of the α 4 and α 17 samples sintered at various temperatures for 2 h. The density results of the sintered samples show that the two seeded $\alpha 17$ samples have a higher density than that $(\alpha 4)$ without seeding at the same sintering temperature. The $\alpha 17-1020.10^{*3}$ sample densifies to 99.5% T.D. at 1490°C, which is 30°C lower than the others. Although these simples, α 4-1000.r,*⁴ α 17-1020.4r, and α 17-1020.10 have totally transformed α -phase before reaching the sintering temperature, the grain size of the samples should be different. The average grain size (Fig. 8) of the three sample is in the range of 2 to 5 µm, and hardly differs from one to the other at the same sintering temperature. The grain size of these sintered samples is only a function of the sintering temperature, but not sensitive to previous calcination history.

Figure 8 depicts that three samples have minimal sintering temperatures and reached the best density (99.5% TD). The α 17-1020.10 is 1490°C, the α 17-1020.4r is 1520°C, and the α 4-1000.r is 1550°C. Therefore, these samples were sintered at these temperatures for 0 to 4 h. The results of the relative densities and grain sizes

³1020.10 represents a treatment at 1020°C held for 10 h.

^{4&}quot;r" means the treatment to 100°C higher than the indicated temperature at a ramping rate of 2°C/min.



Fig. 9. Relative density and grain size of $\alpha 4$ and $\alpha 17$ samples calcined at 1000°C or 1020°C for 0 h, 4 h or 10 h, and then sintered at either 1490 °C, 1520 °C, or 1550 °C.



Fig. 10. SEM micrographs of (a) α 4 sintered at 1550 °C for 2 h, and (b) α 17 Al₂O₃ which were sintered at 1490°C for 1 h. Two samples were polished and thermally etched.

are shown in Fig. 9. The grain size of the α 17-1020.10 at 1490°C is less than 2.0 μ m, and this is the optimum for densification and fine grain size of the alumina.

Fig. 10 is SEM micrographs of the a4 and a17 Al_2O_3 samples sintered either at 1550°C or 1490°C for 1 h. The α 4 and α 17 samples polished and thermally etched at 1400°C for 30 min appear to have 1.5% or 0.6% porosity, respectively. A uniform microstructure of the

 $\alpha 17$ with minimal porosity was achieved with 17 wt% α -phase seeding and using the optimized calcination/sintering conditions.

Conclusions

The densification of ultrafine θ -alumina powders either seeded or non-seeded shows two-stage shrinkage. The first stage of ca. 6.8% linear shrinkage partially corresponds to the elimination of the porosity formed by the θ - to α -phase transformation. In addition, ca. 3% of linear shrinkage is due to the densification of the newly-formed α -particles in the first stage.

The microstructural evolution in association with the θ - to α -transformation is closely controlled by the treatment at 1020°C to 1120°C. The pore and grain size do not grow below 1020°C, but the seeded matrix can totally transform to α -phase in 10 h. Without seeding and temperature control, the matrix tended to form coarser α -grains and pores.

The second-stage shrinkage of the sample starts at 1050°C for seeded α 17 samples. Below this temperature, the seeded matrix only shrinks due to the θ - to α -transformation. The non-seeded α 4 sample is normally able to shrink to the same dimensions, but needs an 80°C approximately higher temperature. A nearly dense (>99.5% T.D.) and fine- grain (<2.0 µm) matrix can be achieved within the α 17 sample is calcined at 1020°C for 10 h then sintered at 1490°C for 1 h. The sintered microstructure of the α 17 is uniform and the average grain size can be as small as 2.0 µm.

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References

- W. Gitzen, "Alumina as a Ceramic Material," (Am. Ceram. Soc., 1970) Special pub. No. 4.
- T.S. Yeh and M.D. Sacks, J. Am. Ceram. Soc. 71[10] (1988) 841-44.
- 3. S. Rajendran, J. Mat. Sci. 29 (1994) 5664-5672.
- 4. G.L. Messing and M. Kumagai, Am. Ceram. Soc. Bull. 73[10] (1994) 88-91.
- R.S. Mishra, C.E. Lesher, and A.K. Mukherjee, J. Am. Ceram. Soc. 79[11] (1996) 2989-92.
- C.S. Nordahl and G.L. Messing, J. Am. Ceram. Soc. 79[12] (1996) 3149-54.
- F.D. Dynys and J.W. Halloran, J. Am. Ceram. Soc. 65[9] (1982) 442-448.
- P.A. Badkar and J.E. Bailey, J. Mat. Sci. 11 (1976) 1794-1806.
- S.J. Wu and L.C. Jonghe, J. Am. Ceram. Soc. 79[8] (1996) 2207-11.

- F.D. Dynys, M. Lungberg, and J.W. Halloran, Mat. Res. Soc., Symp. Proc. 32 (1984) 321-326.
- F.D. Dynys and J.W. Halloran, Chapter 11 in "Ultrastructure Processing of Ceramics, Glasses and Composites", ed. L.L. Hench and D.R. Ulrich, (John Wiley and Sons, N. Y., 1984).
- M. Kumagai and G.L. Messing, Comm. J. Am. Ceram. Soc. 67 (1984) C-230-C-231.
- R.A. Shelleman, G.L. Messing, and M. Kumagai, J. Non-Crystal. Sol. 82 (1986) 277-285.
- 14. L. Pach, R. Roy, and S. Komarneni, J. Mat. Res. 5 (1990) 278-285.
- J.L. McArdle and G.L. Messing, J. Am. Ceram. Soc. 76[1] (1993) 214-222.
- 16. Y. Yoshizawa and F. Saito, J. Ceram. Soc. Jpn. 104[9]

(1996) 867-871.

- H.C. Kao and W.J. Wei, J. Am. Ceram. Soc. 83[2] (2000) 362-68.
- C.L. Hsieh, Master thesis, National Taiwan University, Taipei, Taiwan (1997).
- 19. ASTM C372-73.
- 20. H.L. Wen, Y.Y. Chen, F.S. Yen, and C.Y. Huang, Nanostructured Materials 11[1] (1999) 89-101.
- 21. C.H. Bamford and C.F.H. Tipper, "Chemical Kinetics", (Elsevier Sci. Pub. Co., 1980).
- 22. S.J. Wilson and J.D.C. McConnell, J. Solid State Chem. 34 (1980) 315-322.
- 23. C.A. Shaklee and G.L. Messing, J. Am. Ceram. Soc. 77[11] (1994) 2977-2984.