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Characteristics of translucent alumina produced by slip casting method using gypsum mold

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Translucent Al_2O_3 ceramics were successfully produced by slip casting using a gypsum mold, provided that $CaSO_4$ impurities, which had penetrated into the green bodies from the gypsum mold, were removed by the wash of HCl aqueous solution. Some of the calcined Al_2O_3 compacts were washed with HCl aqueous solution before sintering the compacts and the others were not washed with HCl aqueous solution. The relative densities of the sintered Al_2O_3 ceramics with HCl treatment were higher than those of the untreated samples. Grains in the HCl-treated samples, which sintered at 1350°C, grew homogeneously with about 1 μm in diameter. When the sintering temperature was higher, the grains grew homogeneously. The sintered Al_2O_3 ceramics with the HCl treatment were translucent. The transmittance value increased from 0 to 12% with increasing wavelength from 300 to 900 nm. The Al_2O_3 ceramics with the HCl treatment did not have the transmittance when the solid contents of slurry were low. The transmittance was influenced by the solid contents of slurry. On the other hand, grains in the HCl-untreated samples, which sintered at 1350°C, grew heterogeneously with the range from 0.2 to 2 μm. The Al_2O_3 ceramics did not have the transmittance. *© 2002 Kluwer Academic Publishers*

1. Introduction

High-strength and/or translucent Al_2O_3 ceramics are important for practical application as strength-performance ceramics parts. Slip casting [1–10], a process that has been used in the forming of traditional ceramics and is cost efficient can produce large and dense green bodies with complicated shapes. Therefore, slip casting is industrially one of important forming methods.

It is well known that sintered highly pure Al_2O_3 ceramics exhibit transmittance properties [11, 12]. However, physical properties of advanced ceramics are influenced by impurities produced in the forming process. Dissolution of gypsum components from the mold contaminates the green bodies with calcium and sulfate during slip casting process. Transmittance of Al_2O_3 body is low due to contamination from the gypsum mold [13]. Therefore, it is important that the contamination is removed from green bodies to produce translucent Al_2O_3. Non-contaminated green bodies by slip casting under vacuum pressure [14–16], using resin molds [17, 18] was obtained by Mizuta *et al.* Those researchers obtained translucent Al_2O_3 ceramics by hot isostatic pressing (HIP) methods. However, slip casting using such as resin molds and HIP process is more expensive than that using gypsum molds because resin molds are difficult to produce a mold of complicated sharps and expensive, compared with gypsum molds. Therefore, gypsum molds have been used at slip casting.

The present study demonstrates that translucent Al_2O_3 ceramics can be produced by the simple chemical treatment of green compacts made by slip casting using gypsum molds. The characteristics of the sintered Al_2O_3 compacts were examined and were discussed.

2. Experimental procedure

2.1. Materials

Commercially available Al_2O_3 (99.99% purity, Taimicron TM-DAR, Taimei Chemicals Co., Ltd., Tokyo, Japan) was used in the present work. Particle size distribution was determined by light scattering and laser diffraction (Particle size analyzer, E-900, Horiba, Ltd., Kyoto, Japan). Al_2O_3 consists of ultrafine particles averaging 0.157 μm in diameter. Powders were analyzed with an X-ray diffractiometer (Rigaku, Japan). The measurements were performed under the conditions of 40 kV, 30 mA and Cu Kα ($\lambda = 1.540$ Å). Scan rate was 2.0 degree/min.

2.2. Preparation of slurry and green bodies

The rheological characteristics of the slurry were measured using a viscometer (Type E Viscometer, Tokyoseiki Co., Ltd., Japan). A chemically available deflocculant (Aron A6114, Toagousei Co., Ltd., Japan)

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that was an NH_4^+ salt of poly(methacrylic acid) was used to obtain a well dispersed slurry. The compositions of the slurry, which yielded a low viscosity at a high solids content, are shown in Table I. The slurry was mixed for 16 h in a ball-mill with both mill and balls of high-grade Al_2O_3. The slurry was degassed for 10 min before slip casting. The green bodies were formed by gypsum molds. To prepare the gypsum mold, gypsum (Wako Pure Chemical Industries, Osaka, Japan) was added to water as 70 mass% of the water content. The gypsum slurry was stirred for 1.5 min, then degassed for 3 min under vacuum. The gypsum slurry then was poured into an acrylic resin mold adjusted to a height of 4 cm and a diameter of 5 cm, and gypsum molds were produced. The gypsum mold was dried in air at 40°C before slip casting. The slip casting was carried out at 20°C. The green bodies were dried in air after slip casting and removed from the gypsum mold.

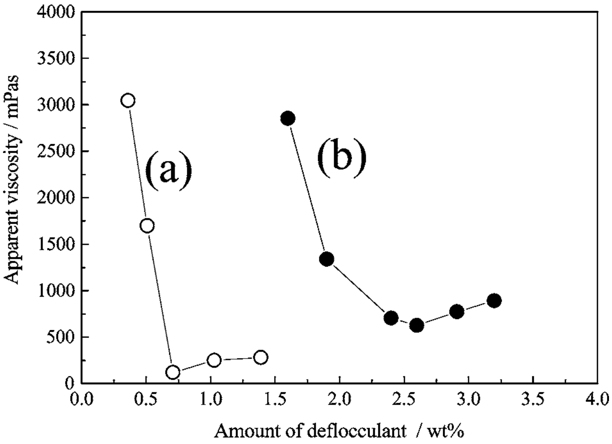


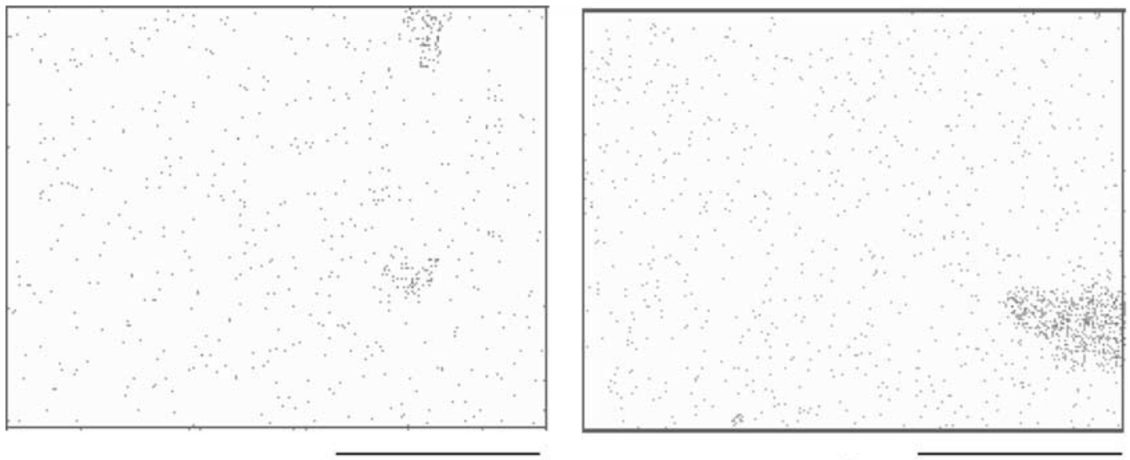
Figure 1 Relationship between a viscosity and a concentration of deflocculant in the slurry. (a): 70 wt% Al_2O_3 slurry. (b): 80 wt% Al_2O_3 slurry.

2.3. Calcining, sintering and HCl treatment

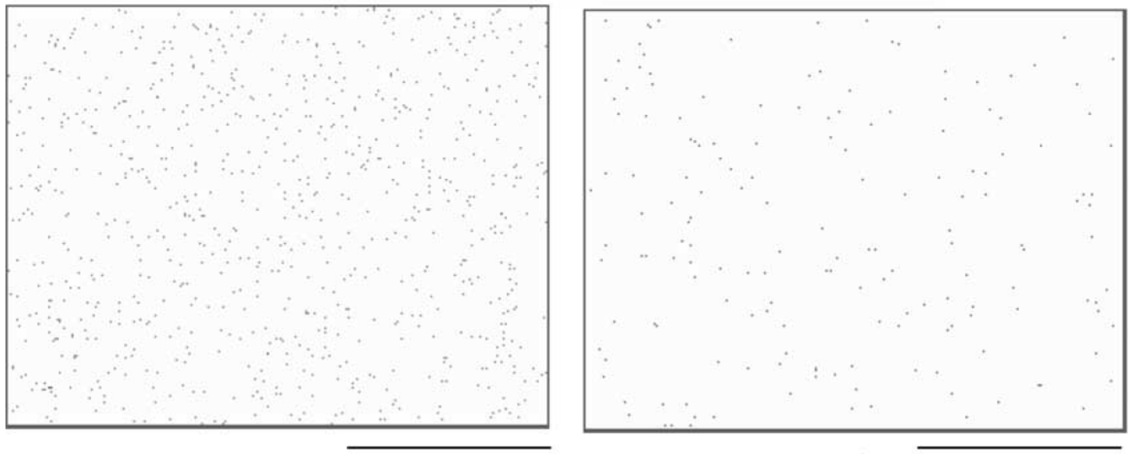
The green bodies were dried and calcined at 800°C for 2 h in air to remove deflocculant. Both the heating and the cooling rate were 100°C/h, respectively. The calcined bodies produced by slip casting using the gypsum mold were immersed in 0.9N-HCl for 1 h to remove gypsum components that had penetrated into the compacts. Then, the compacts were washed with water until HCl detection. The absence of HCl was confirmed

TABLE I Composition of the slurry

Generic	Specific	Composition (wt%)	
Alumina	TM-DAR	80	70
Water	–	20	30
Deflocculant	NH_4^+ salt of poly (methacrylic acid)	2.61	0.7



(a) Green compact 50μm (b) Sample sintered at 500°C 50μm



(c) Sample sintered at 700°C 50μm (d) Sample sintered at 800°C 50μm

Figure 2 Mapping analysis of calcium in part of the bottom of green bodies after slip casting using gypsum molds.

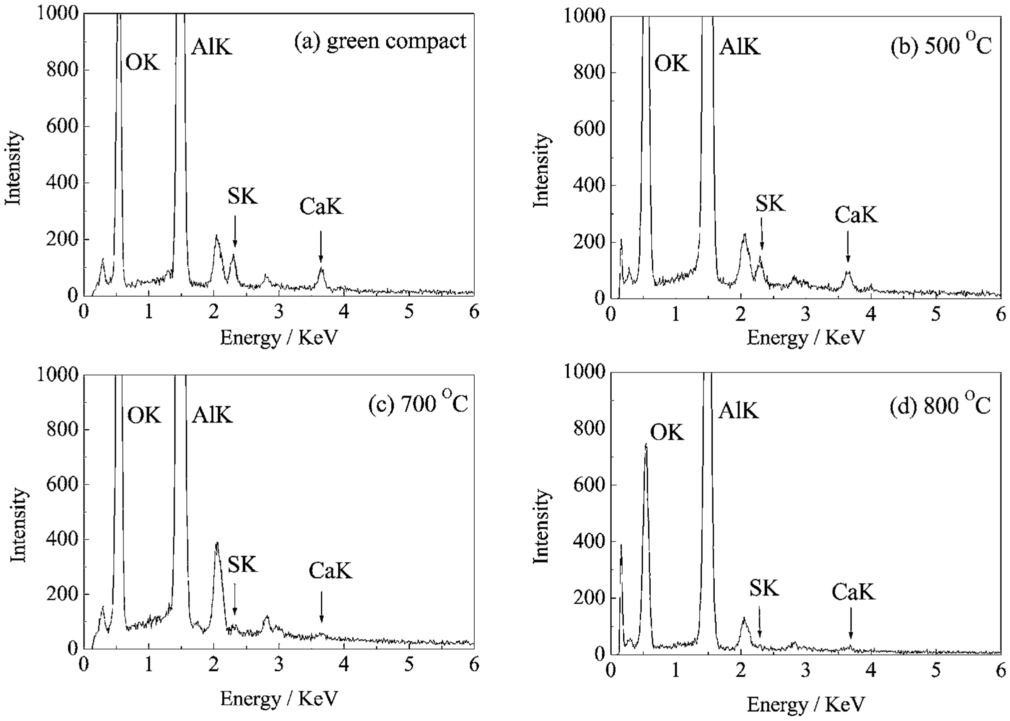


Figure 3 EDX spectra in part of the bottom of bodies after slip casting using gypsum molds.

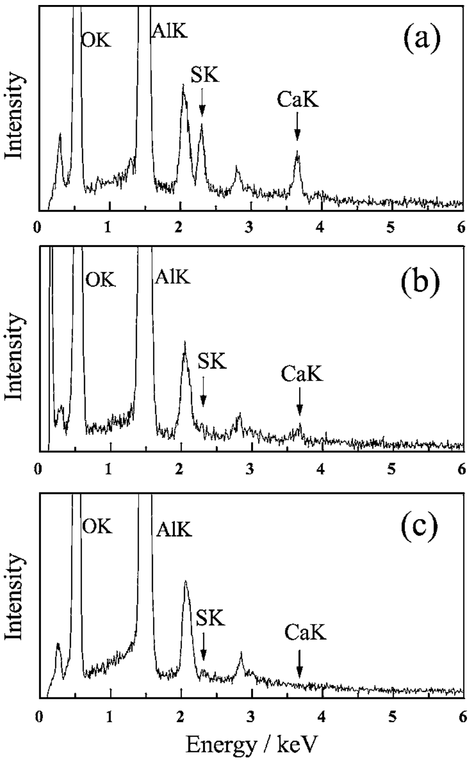


Figure 4 EDX spectra. (a) the green bodies produced by slip casting using gypsum molds, (b) the calcined bodies at 800°C, (c) the bodies washed the calcined bodies with HCl.

using $AgNO_3$ until no Cl^- detection. Finally, the HCl-washed and HCl-unwashed compacts were sintered at 1350, 1450 and 1550°C under vacuum. Both the heating and the cooling rate were 100°C/h, respectively.

2.4. Measurements

The densities of the samples were determined by the Archimedes method. The existence of gypsum

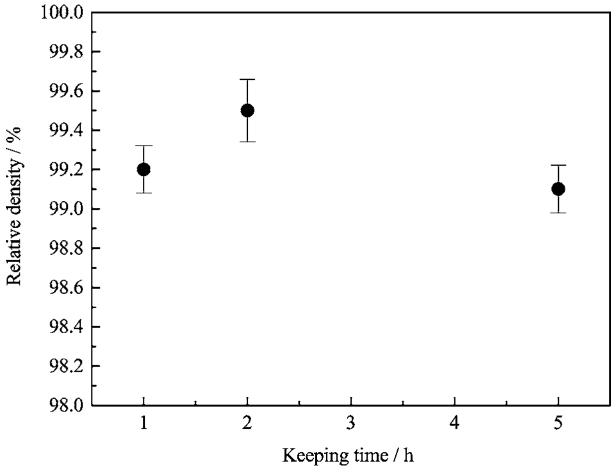


Figure 5 Relationship between the keeping time and relative density for samples sintered at 1350°C under vacuum. The sintered rate was 100°C/h.

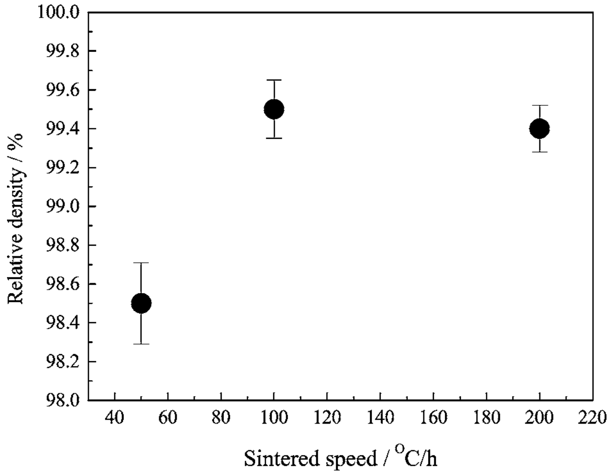


Figure 6 Relationship between the baking rate and relative density for samples sintered at 1350°C under vacuum.

components was detected using an EDX apparatus (EDAX, DX-4, USA). The optical transmittance was determined using a UV/Vis spectrometer (Perkin-Elemeter, Perkin-Elmer Corp., Lambola, France) in the range from 300 to 900 nm. The samples were cut to a thickness of 1 mm and their surfaces were polished for optical-transmittance measurements. After polishing, both the HCl-treated and the HCl-untreated samples were thermally etched at 1330, 1430 and 1530°C for 2 h. The microstructures were observed by scanning electron microscopy (SEM) (S-3500N, Hitachi, Japan).

3. Results and discussion

The compositions of the slurries are shown in Table I. The relationship between the viscosity and a concentration of deflocculant in the slurry was shown in Fig. 1. The viscosity of the slurry with 80 wt% Al_2O_3 and 20 wt% water was lowest at 2.61 wt% of added deflocculant. On the other hand, the viscosity of the slurry with 70 wt% Al_2O_3 and 30 wt% water was lowest at 0.7 wt% of added deflocculant. In general, slurry used to prepare dense green bodies must process low viscosity, high solids content, and good dispersion. Therefore, slurries with the characteristics listed

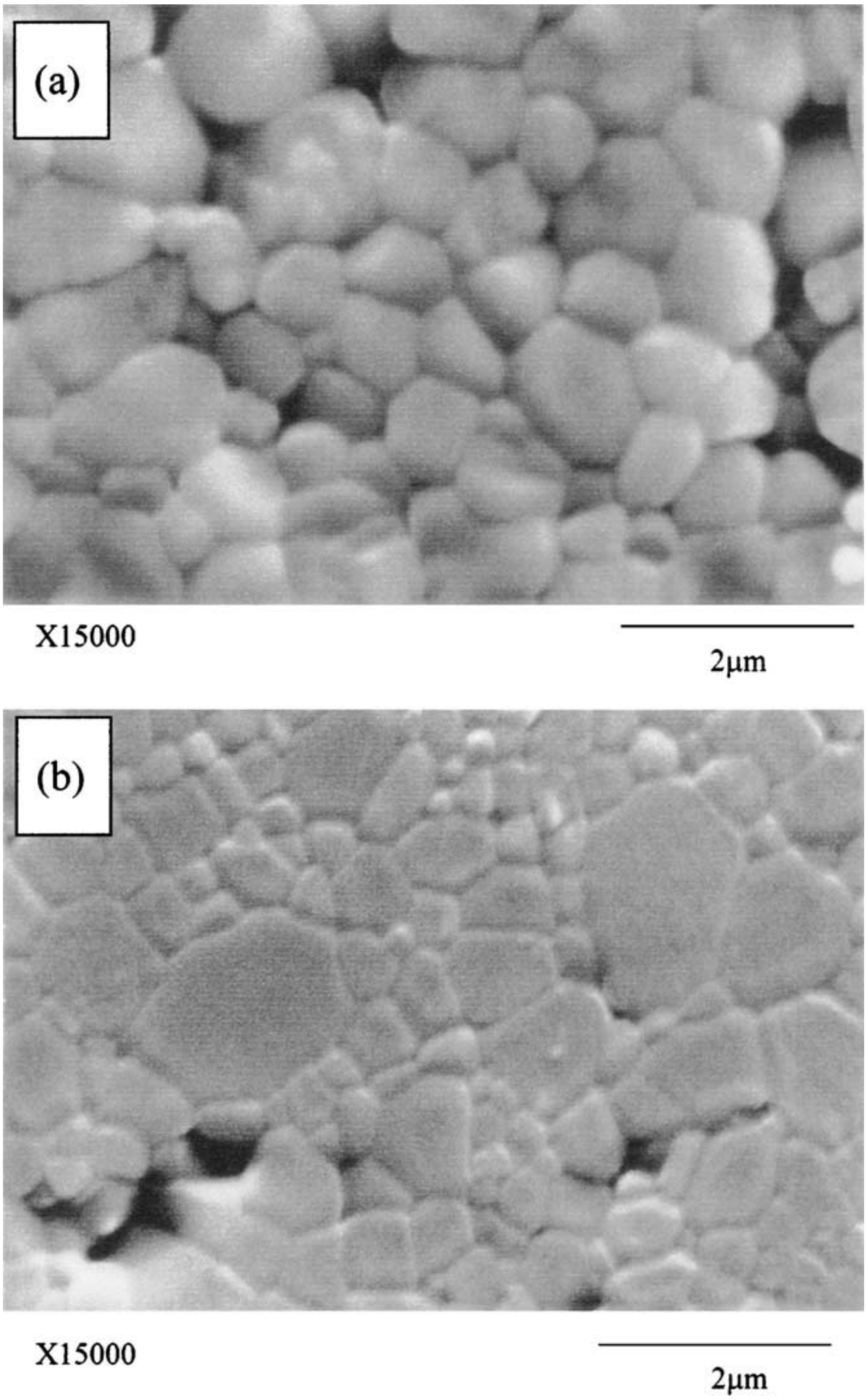


Figure 7 Microstructures of the samples sintered at 1350°C for 2 h under vacuum after washing calcined bodies with HCl and (b) unwashing calcined bodies with HCl.

in Table I were chosen for slip casting in the present study.

Contamination penetrated into green compacts after slip casting using the gypsum mold was analyzed with a mapping method and EDX apparatus. Fig. 2 shows the results of the calcium-mapping measurements. Form the result of a calcium mapping measurement for the Al_2O_3 bodies of non-calcination, and at 500, 700 and 800°C, it was found that calcium component of non-calcinad and calcined compacts at 500°C was existed as a lump and the component was decreased with increasing the calcination temperature. The melting point and the boiling point of calcium are 848 and 1487°C, respectively. Thus the calcining at 800°C is not able to remove calcium from green bodies. However, the calcium component was decreased with increasing the temperature in spite of being not able to remove the contamination by calcinig. It is considered that calcium component is penetrated into the green bodies. Fig. 3 shows EDX spectra of the compacts produced by slip casting using gypsum molds. Fig. 3a–d are the EDX spectra of the green bodies, the bodies calcined at 500, 700 and 800°C, respectively. The gypsum components (Ca, SO_4) on the green bodies were observed as the peaks of CaK (3.6 keV) and SK (2.3 keV). Calcium and sulfate components were existed on the surface of the green bodies prepared by slip casting using gypsum molds. The calcium and sulfur peaks were decreased with increasing the calcination temperature. It is considered that the gypsum

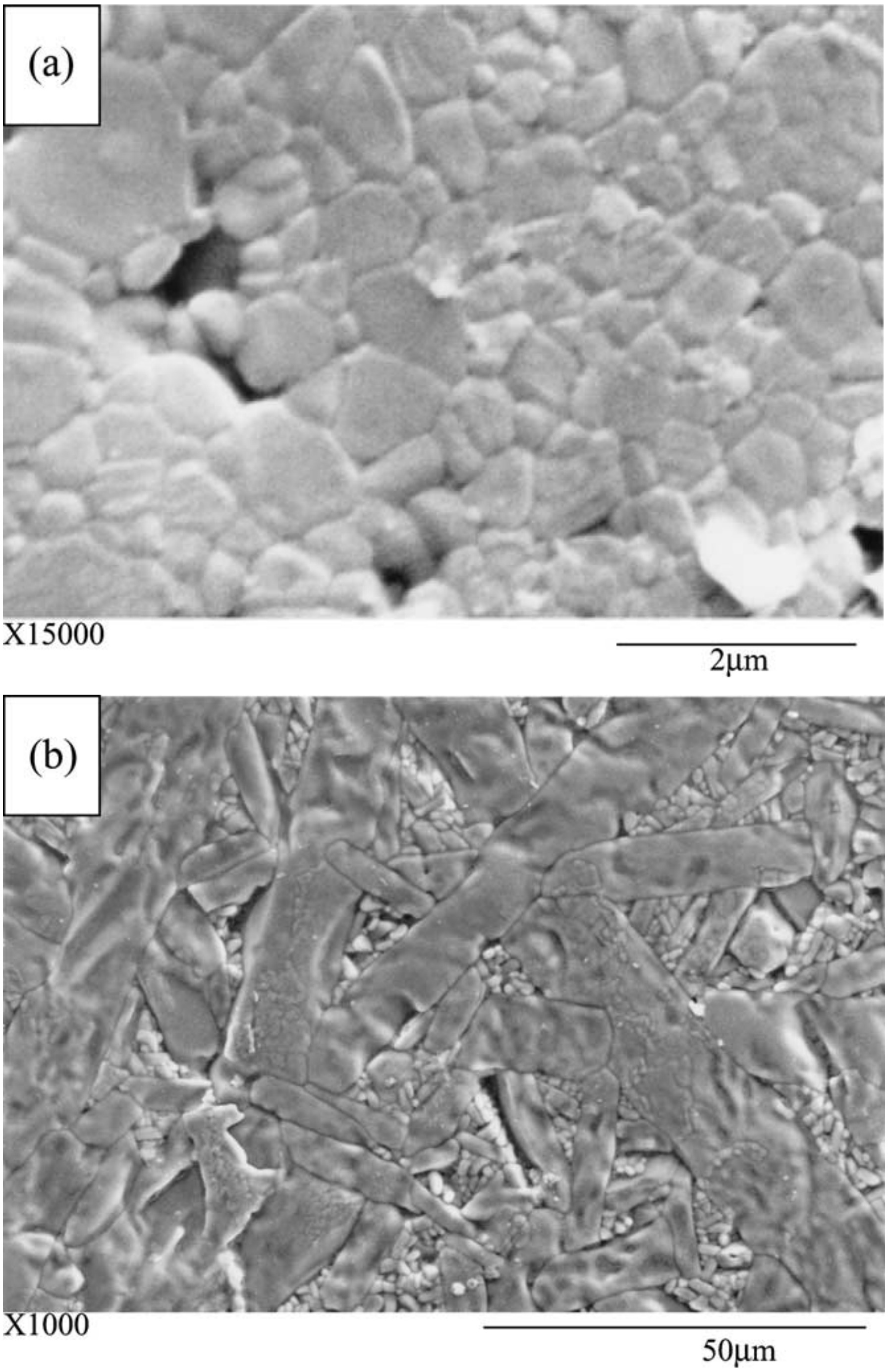


Figure 8 SEM photographs of the grain growth of samples sintered at 1350, 1450, and 1550°C in air after unwashing calcined bodies with HCl (*Continued.*)

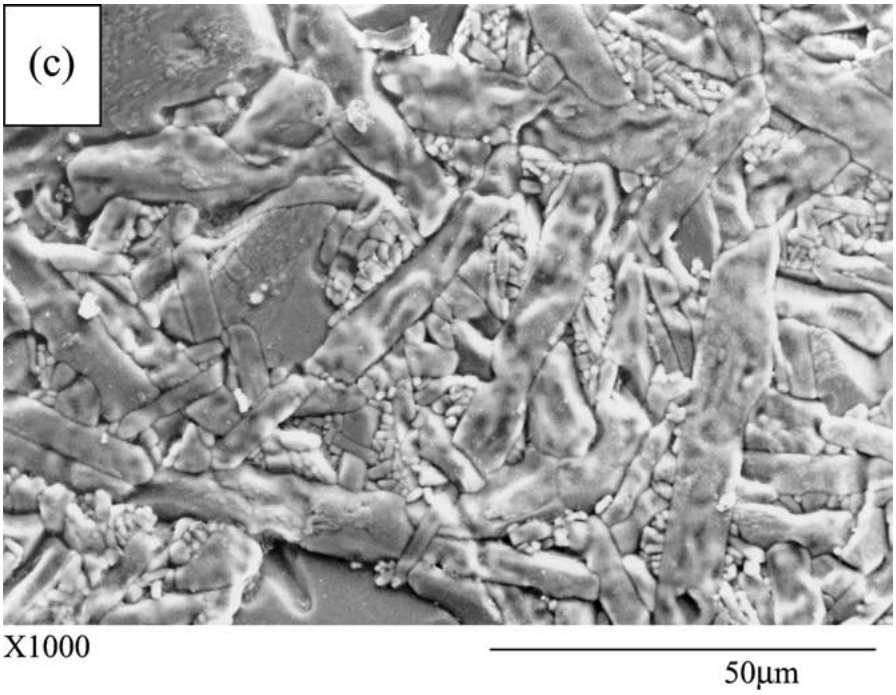


Figure 8 (*Continued.*)

components are penetrated into the green bodies. Fig. 4a–c are the EDX spectra of the green body, the body calcined at 800°C, and the body after washing the calcined body with HCl, respectively. The intensities of the gypsum components were decreased by calcining at 800°C. However, the calcining at 800°C is not able to remove $CaSO_4$ from the green bodies. On the other hand, the peaks of the gypsum components in the body after washing the calcined body with HCl were not observed. Thus, the contamination penetrated into the green bodies could be removed by the HCl-wash. Washing the green bodies with HCl ionized the $CaSO_4$ and removed it from the green body, according to the following reaction.

$$\begin{aligned} CaSO_4(s) + HCl(l) &\rightarrow Ca^{2+}(l) + Cl^{-}(l) \\ &+ H^{+}(l) + SO_4^{2-}(l) \end{aligned} \quad (1)$$

Fig. 5 shows the relationship between the keeping time and relative density of samples sintered at 1350°C under vacuum when the baking rate was 100°C/h. Samples were prepared from HCl-washed compacts using slurry with 80 wt% Al_2O_3 contents. When the keeping time at 1350°C was 1, 2, and 5 hours, the relative densities were 99.2 ± 0.16, 99.5 ± 0.16, and

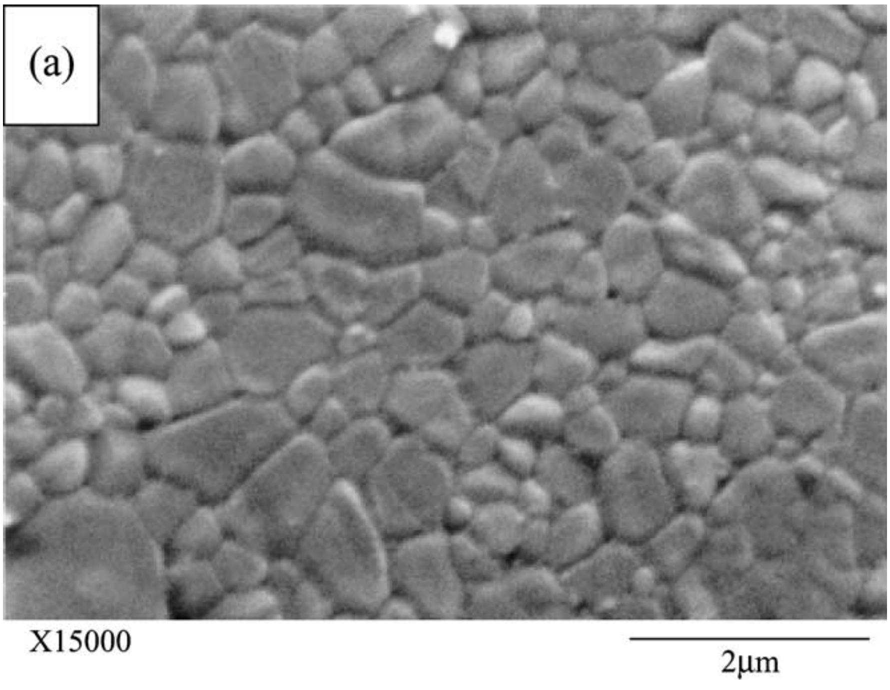


Figure 9 SEM photographs of the grain growth of samples sintered at 1350, 1450, and 1550°C after washing calcined bodies with HCl. (*Continued.*)

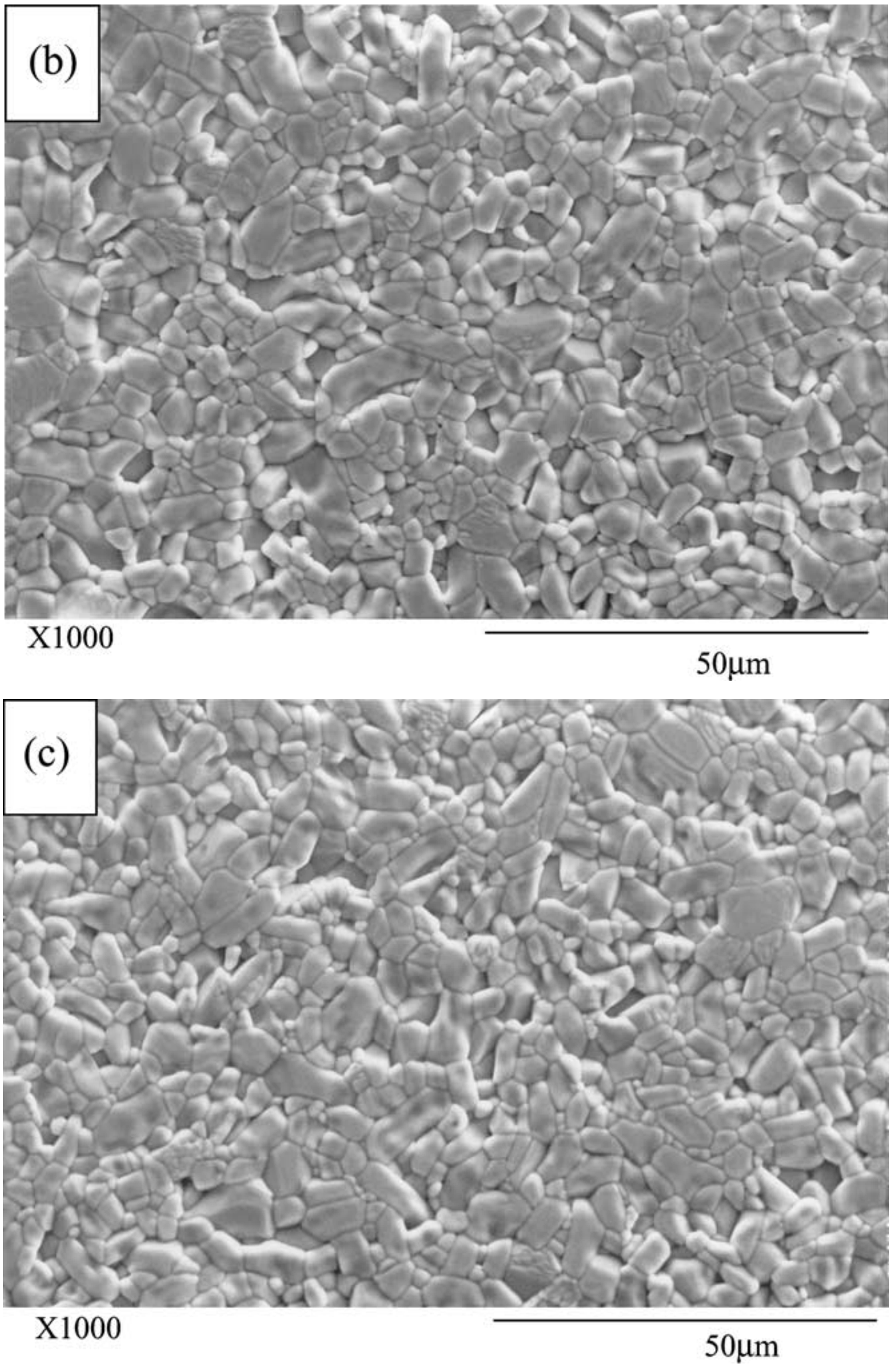


Figure 9 (*Continued.*)

99.1 ± 0.14%. The relative density was highest when the keeping time was 2 hours. Fig. 6 shows the relationship between the baking rate and relative density for samples sintered at 1350°C for 2 hours under vacuum. Samples were prepared from HCl-washed compacts using slurry with 80 wt% Al_2O_3 contents. When the baking rate was 50, 100, and 200°C/h, the relative densities were 98.5 ± 0.15, 99.5 ± 0.16, and 99.4 ± 0.16%, respectively. The relative density was highest when the baking rate was 100°C/h. In general, it is known that transmittance of translucent ceramics is higher as decreasing porosity and forming homogeneous grains [8, 9]. The degradation of the transmittance is caused with the scattering of the pore, grain boundaries, and refraction produced by anomalous grain growth. Thus, a high-density body is needed to gain the translucent ceramics. The Al_2O_3 green bodies sintered by the conditions of the baking keeping time 2 hours and the baking rate 100°C/h showed the highest density.

Fig. 7 shows the microstructures of the bodies sintered at 1350°C for 2 h under vacuum after (a) washing the calcined bodies with HCl and (b) unwashig the calcined bodies with HCl. The grain size of the unwashed bodies ranged from ∼0.2 to 2 μm. On the other hand, the grain size of the sintered bodies after washing the calcined bodies with HCl was about 1 μm. Grain in the washed samples grew homogeneously. These results suggest that grain growth was influenced by $CaSO_4$that had penetrated into the green bodies from the gypsum molds. Fig. 8 shows microstructures of the grain growth of samples sintered at (a) 1350, (b) 1450, and

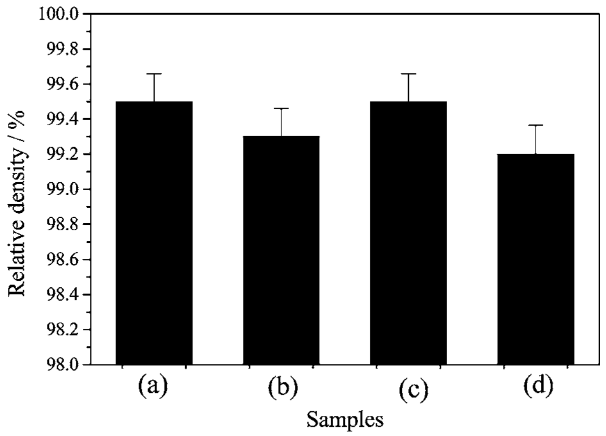


Figure 10 Relative densities of the samples sintered at 1350°C for 2 h under vacuum after washing calcined bodies with HCl ((a), (c)) and unwashing calcined bodies with HCl ((b), (d)). The (a) and (b) samples are the bodies prepared by slip casting using slurry of 80 wt% Al_2O_3. The (c) and (d) samples are the bodies prepared by slip casting using slurry of 70 wt% Al_2O_3.

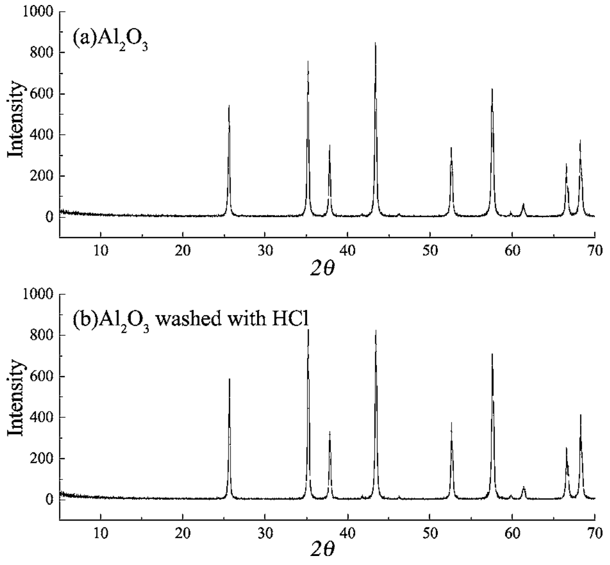


Figure 11 XRD patterns of Al_2O_3 powder unwashed with (a) HCl and washed with (b) HCl.

(c) 1550°C after unwashing the bodies with HCl. As increasing the sintering temperature, the anomalous of the grain growth became bigger. Fig. 9 shows microstructures of samples sintered at (a) 1350, (b) 1450, and (c) 1550°C after washing the bodies with HCl. Grains in the HCl-washed bodies grew homogeneously, compared with that in the HCl-unwashed bodies. These results suggest that grain growth was influenced by $CaSO_4$. Grain growths in the sintered bodies become homogeneous by removing gypsum components with HCl. The abnormal grain growths are not caused.

Fig. 10a–d shows the relative densities of the bodies sintered at 1350°C for 2 h under vacuum after washing the bodies with HCl (Fig. 10a and c) and without washing the bodies with HCl (Fig. 10b and d). Samples were prepared from HCl-washed and unwashed bodies using slurries with 80 wt% and 70 wt% Al_2O_3 contents. The relative densities of the sintered bodies of the calcined bodies, which were produced by 80 wt% and 70 wt% Al_2O_3 contents, with the HCl-wash were 99.5 ± 0.16 and $99.5 \pm 0.16\%$, respectively. On the other hand, the relative densities of the sintered bodies of the calcined bodies, which were produced by 80 wt% and 70 wt% Al_2O_3 slurries, without the HCl-wash were 99.3 ± 0.16 and $99.2 \pm 0.17\%$, respectively. Thus, the relative densities of the HCl-washed bodies were higher than those of unwashed bodies. Fig. 11 shows X-ray patterns of Al_2O_3 powders without HCl-wash (a) and with HCl-wash (b). X-ray patterns of Al_2O_3 powders without HCl-wash were agreed with those of Al_2O_3 powders with HCl-wash. It was considered that the Al_2O_3 powders were not inferenced by HCl-wash. The difference in relative densities between the washed and the unwashed bodies was attributed to anomalous grain growth caused by $CaSO_4$ impurities.

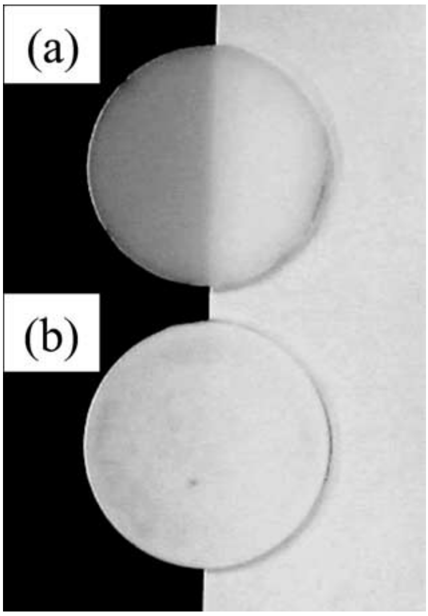


Figure 12 Photographs of the bodies sintered at 1350°C for 2 h under vacuum after washing calcined bodies with HCl and unwashing calcined bodies with HCl. The thickness was 1 mm.

Fig. 12 shows photographs of the sintered bodies of (a) HCl-washed and (b) HCl-unwashed bodies. The unwashed compact was white and opaque. On the other hand, the body treated with HCl allows the background to pass through. As shown in Fig. 4, the gypsum components are present in body of (b) sample and absent in the body of (a) sample by treating with HCl. The effect of grain growth on transmittance has been researched elsewhere [19]. Coble [20] revealed that control of abnormal grain growth is important for transmittance, because more scattering and refraction occur between discrete grain boundaries with abnormal grain growth than with normal grain growth. As shown in Fig. 7, the grain growths in the sintered bodies with HCl-wash were homogeneous and the grain growths in the sintered bodies without HCl-wash were heterogeneous. Therefore, it is considered that the samples with HCl-wash showed translucency and samples without HCl-wash did not show translucency. These results indicate that treatment with HCl after slip casting using gypsum molds resulted in Al_2O_3 bodies with transmittance properties.

Fig. 13 shows the relationship between transmittance and wavelength from 300 to 900 nm. Fig. 13a and b

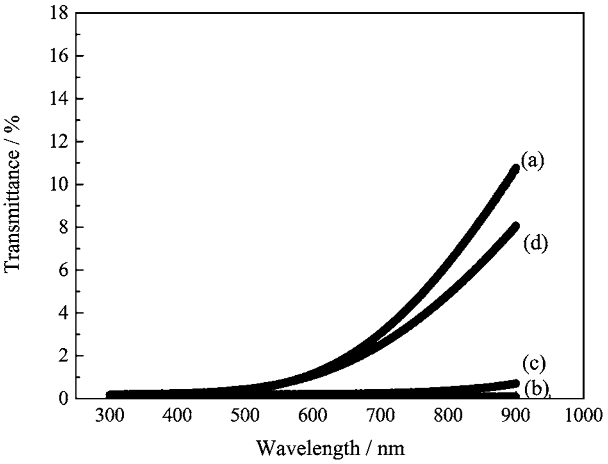


Figure 13 Relationship between wavelength and transmittance from 300 to 900 nm. The thickness was 1 mm. (a): the sintered Al_2O_3 body with HCl-wash (solid content of 80 wt% Al_2O_3), (b): the sintered Al_2O_3 body without HCl (solid content of 80 wt% Al_2O_3), (c): the sintered Al_2O_3 body with HCl-wash (solid content of 70 wt% Al_2O_3), and (d): the sintered Al_2O_3 body prepared by using a synthetic resin mold (solid content of 80 wt% Al_2O_3).

show the spectrum curve of the sintered bodies after washing the calcined bodies, which were prepared by slip casting of 80 wt% Al_2O_3 slurries, with HCl and without HCl, respectively. Fig. 13c shows the spectrum curve of the sintered body after washing the calcined body, which was prepared by slip casting of 70 wt% Al_2O_3 slurry, with HCl. As a comparison, Fig. 13d shows the spectrum curve of the sintered body, which was prepared by using a synthetic resin mold [4] to non-contaminate Ca and SO_4 components, at 1350°C for 2 hours under vacuum. The transmittance was appeared to non-contaminate gypsum components. No transmittance occurred in the HCl-untreated sample (Fig. 13b), whereas transmittance was present in the HCl-treated samples beyond 420 nm in the visible region. The transmittance values of the HCl-washed sample (Fig. 13a), which was prepared by slip casting using 80 wt% Al_2O_3 slurry, increased from 0 to 12% as the wavelength increased from 300 to 900 nm. Acid treatment after slip casting using gypsum molds may offer a means of achieving transmittance in Al_2O_3 ceramics. However, the transmittance values of the sample (Fig. 13c), which was prepared by slip casting of 70 wt% Al_2O_3 slurry, was very small. Thus, it is suggested that high solids content of slurry is important to obtain a good substance.

4. Conclusion

Translucent Al_2O_3 ceramics were prepared from in the present by slip casting using a gypsum mold when gypsum impurities ($CaSO_4$) were removed from the calcined bodies with HCl-wash. The present results demonstrated that acid treatment after slip casting using a gypsum mold might successfully produce transmittance in Al_2O_3 ceramics. Characteristics of translucent Al_2O_3 produced by slip casting method using gypsum molds.

1. Relative densities of the sintered Al_2O_3 ceramics after washing the green bodies with HCl were higher than that of HCl-unwashed bodies.
2. Grains in HCl-washed bodies grew homogeneously. Grains in HCl-unwashed bodies grew heterogeneously.
3. No transmittance was found in the HCl-untreated samples. In contrast, the samples with HCl-wash exhibited transmittance. Acid treatment after slip casting using gypsum molds may offer a means of achieving transmittance in Al_2O_3 ceramics.
4. The solids content of slurry exerted the influence on the transmittance.

References

1. M. P. ALBANO and L. B. GARRIDO, *J. Amer. Ceram. Soc.* **81** (1998) 837.
2. T. SHIONO and K. NODA, *J. Mater. Sci.* **32** (1997) 2665.
3. J. M. F. FRERREIRA and H. M. M. DIZ, *J. Eur. Ceram. Soc.* **10** (1992) 59.
4. F. NUNES, A. G. LAMAS, M. ALMEIDA and H. M. M. DIZ, *J. Mater. Sci.* **27** (1992) 6662.
5. A. J. RUYS and C. C. SORRELL, *Am. Ceram. Soc. Bull.* **69** (1990) 828.
6. K-S. CHOU and L-J. LEE, *J. Amer. Ceram. Soc.* **72** (1989) 1622.
7. C-D. LI, K. MANCINI and G. C. ROBINSON, *Am. Ceram. Soc. Bull.* **73** (1994) 70.
8. M. TORIYAMA, A. RAVAGRIOLI, A. KRAJEWSKI, C. GALASSI, E. RONCARI and A. PIANCASTELLI, *J. Mater. Sci.* **30** (1995) 3216.
9. U. SENTURK and M. TIMUCIN, *ibid.* **33** (1998) 1881.
10. P. A. SMITH, *J. Amer. Ceram Soc.* **78** (1995) 809.
11. H. MIZUTA, K. ODA, Y. SHIBASAKI, M. MAEDA, M. MACHIDA and K. OHSHIMA, *ibid.* **75** (1992) 469.
12. R. L. COBLE, U.S. Patent no. 3026210 (1962).
13. Y. HOTTA, T. BANNO, S. SANO, A. TSUZUKI and K. ODA, *J. Ceram. Soc. Japan* **108** (2000) 1030.
14. H. MIZUTA, Y. SHIBASAKI, S. SAKAI, M. KATAGIRI and H. FUJIMOTO, *Funtai oyobi Funmatsu Yakin* **35** (1988) 619.
15. H. MIZUTA, Y. SHIBASAKI, M. MAEDA, S. SAKAI, M. ITOH and K. OHSHIMA, *Rep. Gov. Ind. Res. Inst., Nagoya* **39** (1990) 25.
16. H. MIZUTA, K. ODA, M. MAEDA, Y. SHIBASAKI, M. MACHIDA and K. OHSHIMA, *ibid.* **39** (1990) 284.
17. S. SANO, T. BANNO, M. MAEDA, K. ODA and Y. SHIBASAKI, *J. Ceram. Soc. Japan* **104** (1996) 984.
18. Y. KONDO, Y. HASHIZUKA, M. NAKAHARA and K. YOKOTA, *ibid.* **101** (1993) 928.
19. J. G. J. PEELEN, *The Brit. Ceram. Soc.* (1975).
20. N. GRIMM, *Am. Ceram. Soc. Bull.* **50** (1971) 962.

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