

Comparison of hot-corrosion behavior of Al_2O_3 , Lu_2O_3 and their silicates

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The hot-corrosion behavior of Al_2O_3 , Lu_2O_3 , mullite and $\text{Lu}_2\text{Si}_2\text{O}_7$ phases were examined at 1500 °C. In the case of Lu_2O_3 , no phase change was observed and no anisotropic corrosion occurred. In the case of the $\text{Lu}_2\text{Si}_2\text{O}_7$ phase, anisotropic corrosion was observed. The $\text{Lu}_2\text{Si}_2\text{O}_7$ crystal grains were well sustained to the hot-corrosion, however, the sodium element diffused though the boundary phase and anomalous grain growth occurred. On the other hand, in the case of Al_2O_3 , the grains at the bulk surface corroded anisotropically. The corroded grain had a characteristic morphology as terrace field. In the case of mullite, the surface of the bulk was decomposed to the Al_2O_3 phase and the silica component was completely removed from the bulk surface. The sodium ions diffused though the sample during the corrosion test.

Key words: hot corrosion, silicates, mullite, Al_2O_3 .

Introduction

Recently silicon nitride ceramics for high temperature applications which possess high strength and high fracture toughness high enough for application in gas turbine components have been developed [1, 2]. However, silicon nitride easily oxidizes by oxygen and/or water vapor and the silica formed is easily corroded by water vapor in the actual combustion field at high temperatures [3-5]. Furthermore, it is well known that the water vapor corrosion of the silica phase is accelerated by the existence of alkali elements [6, 7]. Because the formation free energy change of NaOH according to equation (1) is negative from room temperature to 2000 K, the formation of NaOH is a spontaneous reaction when water and sodium oxide coexist [8].



The mechanism for the acceleration of silica corrosion by water vapor is believed to be due to the fact that the OH^- ion acts as catalysis [6].

Detailed alkali corrosion, the so called hot corrosion of non-oxide ceramics at high temperatures has been studied by Fox and Jacobson [9, 10]. They reported that non-oxide ceramics oxidize and a sodium silicate phase is formed on the surface of the substrate. A parabolic weight gain behavior was observed during

the hot corrosion. Li et al., examined alkali corrosion behavior of silicon nitride ceramics with various oxide coatings those were coated by a sol-gel method [11]. The weights of the samples increased during the corrosion test and the substrates were oxidized.

When considering using silicon nitride as a gas turbine component, an EBC (Environmental Barrier Coating) system is needed to protect the non-oxide ceramic components from oxidation, water vapor corrosion and alkali corrosion in the combustion environment. Simultaneously, the EBC system must be sustained under gas turbine conditions. Because the thermal expansion coefficients of silicon-based non-oxide ceramics are low, silicate compounds with low thermal expansion coefficients such as $\text{Ln}_2\text{Si}_2\text{O}_7$ (Ln=rare earth elements) and mullite are candidates for EBC materials. However, hot corrosion mechanisms for such monolithic oxides have not been studied as yet.

Hence, in this paper, the sodium corrosion behavior of polycrystalline bulk $\text{Lu}_2\text{Si}_2\text{O}_7$ and mullite at 1500 °C were studied in comparison with the corrosion behavior of Al_2O_3 , mullite and Lu_2O_3 .

Experimental Procedures

High purity Lu_2O_3 (99.99% purity, Shin-Etsu Chemical Co. Ltd., 4 μm particle size), Al_2O_3 (99.99% purity with 0.001% sodium, High Purity Chemicals Co. Ltd.) and SiO_2 (99.99% purity, High Purity Chemicals Co. Ltd., 0.8 μm particle size) powders were used as the starting materials. These powders in a stoichiometric molar ratio ($\text{Lu}_2\text{O}_3:\text{SiO}_2=1:2$ for $\text{Lu}_2\text{Si}_2\text{O}_7$, $\text{Al}_2\text{O}_3:\text{SiO}_2=3:2$ for mullite) were mixed in an agate mortar and

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were sintered at 1600 °C for 3 hours in an Ar atmosphere under an applied load of 20 MPa. The samples were cut into 3×4×2 mm³ test pieces.

Al₂O₃ bulk was obtained from Kyocera, Japan (A-480S, Kyocera Co. Ltd.) and was used for the alumina corrosion test. Lu₂O₃ bulk was prepared from high purity Lu₂O₃ powder. Sintering of Lu₂O₃ was performed at 1500 °C for 24 hours in air.

The samples surfaces were polished and dip coated with NaHCO₃. The samples were then heated at 1500 °C for 5 hours with heating and cooling rates of 200 K/h. Moreover, the Lu₂Si₂O₇ sample was packed inside NaHCO₃ powder in a platinum crucible and then, heated at 1500 °C for 5 hours.

Phase identification was performed by an X-ray diffraction method and the surface structures were examined by scanning electron microscopy (SEM). X-ray diffraction data were collected by a step scan method with a step width, 0.02°, and counting time, 3 s. The chemical composition of the phases was determined by energy dispersive X-ray (EDX) analysis.

Results and Discussion

Corrosion behavior of Al₂O₃

The purity of this sample was 99.7%. Other additive oxides are known. Figures 1(a) and (b) show the X-ray diffraction patterns of the sample before and after the corrosion test. Only the corundum phase can be recognized in both patterns. However, the relative intensities of some peaks were changed during the corrosion test. The relative intensity of the 116 peak increased and the 012 peak decreased. This fact suggests that the corrosion of the Al₂O₃ surface occurred anisotropically like the water vapor corrosion of TiO₂ or Al₂TiO₅ [12, 13].

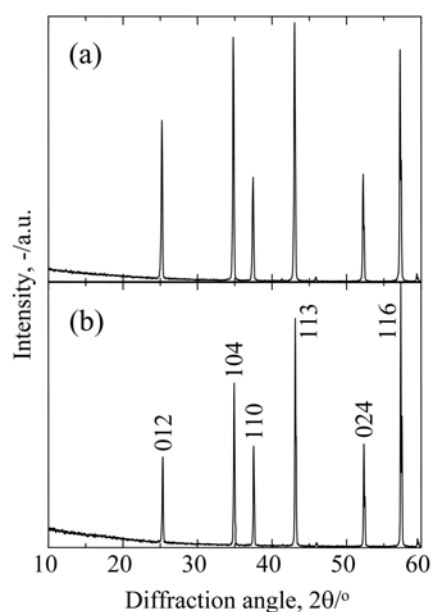


Fig. 1. X-ray diffraction patterns of Al₂O₃ samples (a) before and (b) after the corrosion test.

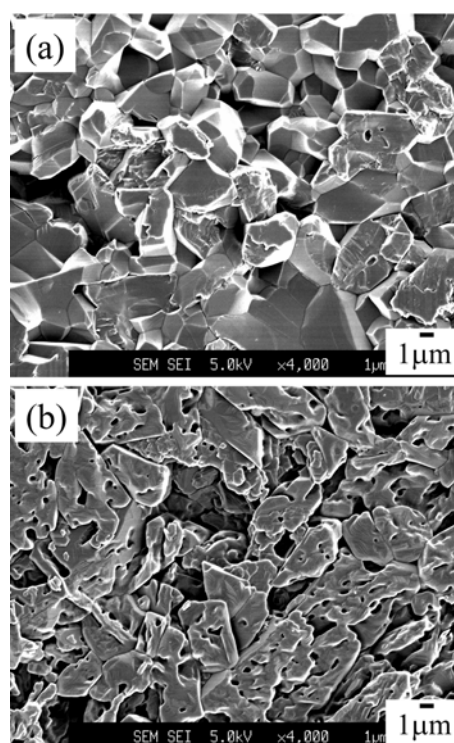


Fig. 2. SEM images of Al₂O₃ surfaces (a) before and (b) after the test.

Figures 2(a) and (b) show the SEM images of the sample surface before and after the test. It can be seen that a porous surface is formed after the test. Figure 3 shows a high magnification SEM image of a part of Figure 2(b). A terrace field like morphology [12, 13] is generated on the surface of each grain. The sidewall of the terrace, indicated by arrows, is corroded hardly and a sponge-like surface consisting of nano-holes is generated. In some places, enclosed by circles, the nano-holes lie on a line and the terrace fields have begun to form.

In the NaAlO₂-Al₂O₃ binary system, there is a eutectic point at 1410 °C. Thus, it is considered that the Al₂O₃ bulk surface first melts down during the corrosion test by reacting with sodium oxide. As the

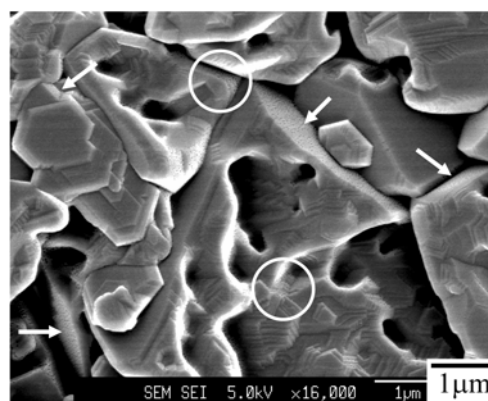


Fig. 3. High magnification SEM image of Al₂O₃ surface after the test.

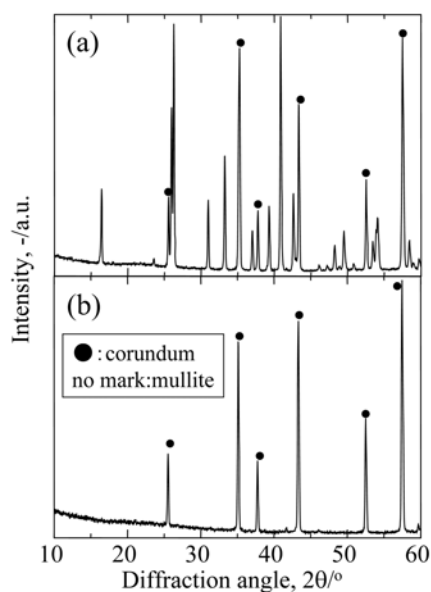


Fig. 4. X-ray diffraction patterns of mullite samples (a) before and (b) after corrosion test.

formation free energy of aluminum hydroxide is lower than that of silicon hydroxide at 1500°C [8], it is considered that the alumina component of the sodium aluminate is removed by moisture.

From these results, it is clearly seen that (1) the Al_2O_3 bulk easily corrodes by alkali attack at 1500°C and (2) the corrosion occurs anisotropically.

Corrosion behavior of mullite

Figures 4(a) and (b) show X-ray diffraction patterns of the sample before and after corrosion test. As bulk mullite in this study was sintered in a graphite crucible, a small amount of the Al_2O_3 phase was formed [14] as shown in Fig. 4(a). However, the sample surface consisted of the corundum phase after the test as shown in Fig. 4(b).

Figures 5(a) and (b) show SEM images of the surface after the test. Figure 5(b) is a high magnification image of 5(a). Many deposited phases were observed on the surface. From EDX analysis, the deposited phase consisted of a silica-rich mullite composition with sodium. The sample the before test was used as a reference and the X-ray intensity ratio for Al and Si peaks of the reference sample was assumed to be exactly 6:2. On the other hand, the composition of the sample surface surrounded by the rectangle and marked “A” in Figure 5(b) is of a silica-poor mullite composition. The concentration of silica in area “B” is smaller than that of area A. In Fig. 5(b), some steps can be observed as indicated by arrows. Whole of the sample surface contained sodium element.

Figures 6(a) and (b) show a cross section of the sample after the test. Many cavities were generated under the bulk surface. Figure 6(b) is a high magnification image of a cavity. The composition of Al:Si in

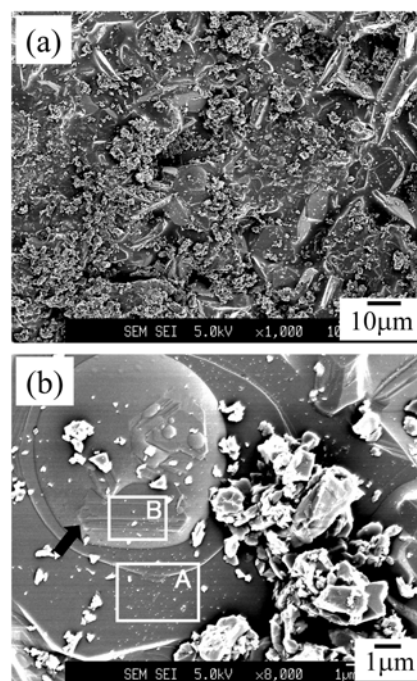


Fig. 5. SEM images of the mullite surface after the test. (b) denotes a high magnification image of (a).

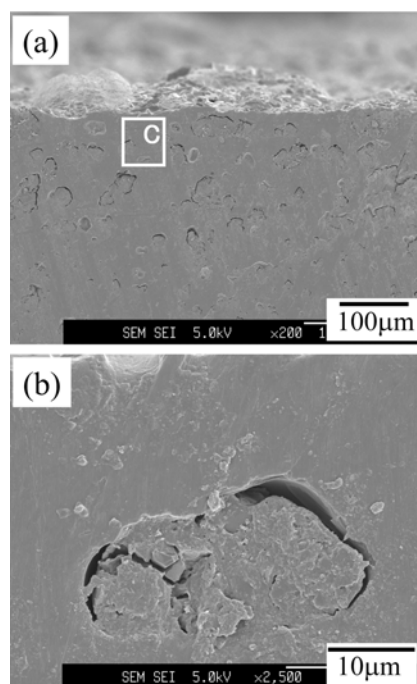


Fig. 6. SEM images of the cross section. (b) denote high magnification image of (a).

area “C” of Fig. 6(a) is almost the same as that of the sample before test. However, sodium ions could be detected in this area. On the other hand, the composition of the particle in the cavity is a silica-poor mullite composition. Sodium was also detected from the particle.

The X-ray diffraction pattern of the sample surface

after the test (Fig. 4(b)) shows the corundum phase. However, when looking at the cross sectional microstructure, the chemical composition of the grains near the surface (Fig. 6(a)) is almost the same as that of the sample before test. Thus, it is recognized that the decomposition of mullite occurs only near the bulk surface. Because the relative intensities of the corundum phase in Fig. 4(b) are very close to that of Fig. 1(b), it can be considered that the corundum phase formed is also corroded by a similar corrosion mechanism of the Al_2O_3 phase as mentioned above.

Corrosion behavior of Lu_2O_3

From the X-ray diffraction patterns of the samples before and after corrosion test, it is recognized that no phase changes occurred during the corrosion test. Figures 7(a) and (b) show the sample surfaces before and after test. During the corrosion test, grain growth occurred. However, a large difference in the surface microstructure can not be observed.

From these results, it is recognized that the Lu_2O_3 phase sustained well to alkali corrosion at 1500 °C.

Corrosion behavior of $\text{Lu}_2\text{Si}_2\text{O}_7$

High density polycrystalline bulk $\text{Lu}_2\text{Si}_2\text{O}_7$ was successfully prepared by a hot pressing method. Because the nominal composition of the $\text{Lu}_2\text{O}_3\text{:SiO}_2$ was exactly 1:2, the Lu_2SiO_5 phase was formed as a secondary phase due to the formation of boundary silica [15]. Thus, $\text{Lu}_2\text{Si}_2\text{O}_7$ bulk examined here contains a small amount of Lu_2SiO_5 phase as a secondary phase and corresponding amount of boundary silica.

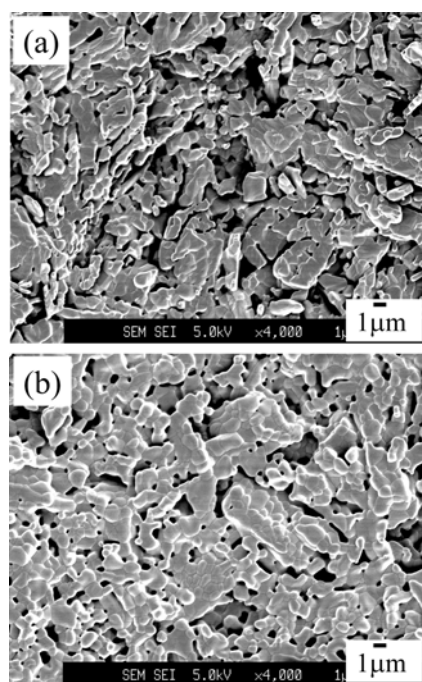


Fig. 7. SEM images of Lu_2O_3 surface (a) before and (b) after the test.

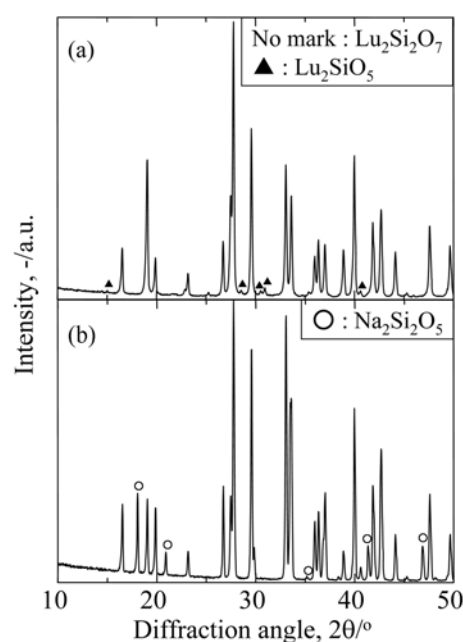


Fig. 8. X-ray diffraction patterns of $\text{Lu}_2\text{Si}_2\text{O}_7$ samples (a) before and (b) after test.

Figures 8(a) and (b) show the X-ray diffraction patterns of the samples before and after test. Some peaks marked by white circles in Fig. 8(b) appeared after the corrosion test. These peaks were identified as from sodium silicate phases. The peaks for the Lu_2SiO_5 phase, indicated by triangles in Fig. 8(a), completely disappeared after the corrosion test as shown in Fig. 8(b). The relative intensities of $\text{Lu}_2\text{Si}_2\text{O}_7$ peaks changed during the corrosion test.

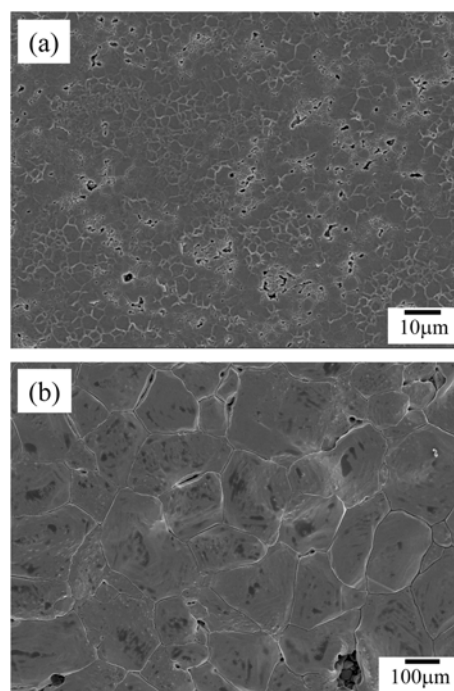


Fig. 9. SEM images of the $\text{Lu}_2\text{Si}_2\text{O}_7$ bulk surfaces (a) before and (b) after corrosion test.

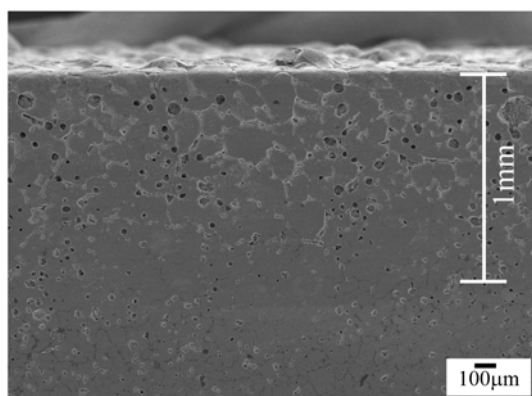


Fig. 10. SEM image of a cross section.

Figures 9(a) and (b) show SEM images of the sample surface before and after the corrosion test. The grains after the corrosion test are at least 50 times larger than that of the sample before the test. Also faceted shape grains can be observed in Fig. 9(a). No sodium ions could be detected from the $\text{Lu}_2\text{Si}_2\text{O}_7$ crystal grains after the corrosion test.

Figure 10 shows a cross sectional view of the sample after the corrosion test. A boundary phase to a 1 mm depth was completely removed. Also large cavities were generated in these areas. The composition of the crystal grains near the surface was close to that of $\text{Lu}_2\text{Si}_2\text{O}_7$, where the as-sintered sample was used as a reference. The composition of the sample before the test was assumed to $\text{Lu}:\text{Si}=1:1$ because the nominal composition of the $\text{Lu}_2\text{O}_3:\text{SiO}_2$ ratio was exactly 1:2. Below, around 1mm deep, the boundary phase can be seen as a dark image. The boundary phase consisted of silica with the sodium element.

Figure 11 shows the sample surface after the corrosion test performed by packing with NaHCO_3 powder. Faceted $\text{Lu}_2\text{Si}_2\text{O}_7$ crystallites were clearly observed.

From these results, the hot corrosion mechanism of bulk $\text{Lu}_2\text{Si}_2\text{O}_7$ includes (1) the formation of sodium silicate $\text{Na}_2\text{Si}_2\text{O}_5$, (2) the removal or escape of Lu_2SiO_5 phase, (3) the escape of the $\text{Lu}_2\text{Si}_2\text{O}_7$ phase into sodium silicate, (4) the elimination of the boundary phase near the surface and (5) the formation of large cavities.

$\text{Lu}_2\text{Si}_2\text{O}_7$ crystal grains resisted the alkali attack well, however, sodium oxide easily reacts with the boundary silica and sodium silicate that have low melting points which were formed.

Conclusions

The hot corrosion behavior of Al_2O_3 , Lu_2O_3 , mullite and $\text{Lu}_2\text{Si}_2\text{O}_7$ were examined. By comparing the corrosion mechanisms for these samples, the corrosion

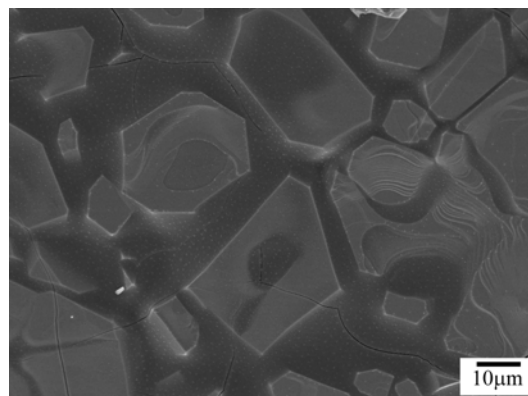


Fig. 11. SEM image of a $\text{Lu}_2\text{Si}_2\text{O}_7$ after the corrosion test performed packed in NaHCO_3 powder.

resistance abilities of silicates were low compared to that of the component oxides. The mullite phase easily reacted with sodium oxide and the sodium element easily diffused into the mullite phase. On the other hand, the corrosion resistance ability of the $\text{Lu}_2\text{Si}_2\text{O}_7$ phase is high compared to that of mullite, however, the boundary silica easily reacted with sodium oxide and formed a low melting compound, sodium silicate, at the boundary. Because the boundary phase melted at below 1500°C , the anomalous grain growth occurred.

References

1. S.M. Wiederhorn and M.K. Ferber, *Current Opinion in Solid State and Materials Science* 5 (2001) 311-316.
2. H.J. Choi, J.G. Lee, and Y.W. Kim, *J. Mater. Sci.* 32 (1997) 1937-1942.
3. I. Yuri and T. Hisamatsu, *Proc. 2003 ASME TURBO EXPO, Power for Land, Sea and Air*, GT2003-38886.
4. E.J. Opila, *J. Am. Ceram. Soc.* 86 (2003) 1238-48.
5. S. Ueno, D.D. Jayaseelan, and T. Ohji, *Int. J. Applied Ceram. Technology* 1 (2004) 362-373.
6. P.K. Iler, *The Chemistry of Silica*, A Wiley-Interscience Publication, New York (1979).
7. E. Opila, *J. Am. Ceram. Soc.* 78 (1995) 1107-1110.
8. JANAF thermochemical table.
9. D.S. Fox and N.S. Jacobson, *J. Am. Ceram. Soc.* 71 (1988) 128-138.
10. N.S. Jacobson and D.S. Fox, *J. Am. Ceram. Soc.* 71 (1988) 139-148.
11. T.K. Li, D.A. Hirschfeld, and J.J. Brown, *J. Mater. Sci.* 32 (1997) 4455-4461.
12. S. Ueno, D. Doni Jayaseelan, N. Kondo, T. Ohji, and S. Kanzaki, *Mater. Trans.* 45 (2004) 281-283.
13. S. Ueno, D.D. Jayaseelan, N. Kondo, T. Ohji, and S. Kanzaki, *J. Ceram. Soc. Japan* 111 (2003) 859-861.
14. R.F. Davis, I.A. Aksay, and J.A. Pask, *J. Am. Ceram. Soc.* 55 (1972) 98-101.
15. F. Monteverde and G. Celotti, *J. Euro. Ceram. Soc.* 19 (1999) 2021-2026.