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Low-temperature reaction-sintering of mullite ceramics with an Y_2O_3 addition

Jihong She *, Peter Mechnich, Martin Schmücker, Hartmut Schneider

Institute of Materials Research, German Aerospace Center (DLR), 51147 Köln, Germany

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Abstract

Mullite ceramics were fabricated at relatively low temperatures from powder mixtures of α-Al_2O_3 and quartz, with an Y_2O_3 addition. The mullitization process was analyzed by X-ray diffraction. The densification behavior was investigated as a function of the Y_2O_3 content, sintering temperature and holding time as well as mullite seeds. It has been shown that mullitization occurs via a nucleation and growth mechanism within an yttrious aluminosilicate glass, but lattice and grain-boundary diffusion becomes important during the densification process. Moreover, the incorporation of mullite seeds was observed to enhance both mullitization and densification. At 1400°C for 5 h or 1450°C for 2 h, 15 mol% Y_2O_3-doped and 5 mol% mullite-seeded specimens can be sintered to almost full density. © 2001 Elsevier Science Ltd and Techna S.r.l. All rights reserved.

Keywords: A. Sintering; D. Mullite

1. Introduction

Reaction sintering of Al_2O_3–SiO_2 mixtures is a conventional method to produce mullite ceramics. As demonstrated by Rodrigo and Boch [1], the reaction sintering behavior is determined by two processes: mullitization and densification. It has been shown [2,3] that an earlier formation of mullite retards the densification process. This suggests that densification prior to mullitization might be the best route to achieve high densities. Therefore, the use of less reactive reactants such as α-Al_2O_3 and amorphous silica should be advantageous. For instance, with the utilization of amorphous silica-coated α-Al_2O_3 powders, an almost fully dense state has been observed at temperatures as low as ~1300°C [4,5]. However, a relatively high temperature of 1600°C is needed to complete the mullitization reaction.

The objective of the present work was to fabricate dense mullite ceramics from the powder mixtures of α-alumina and quartz at moderate sintering temperatures. For this purpose, Y_2O_3 was used as sintering additive. To determine the mullitization behavior of the Al_2O_3–SiO_2 mixtures in the presence of Y_2O_3, the phase development during the reaction-sintering process was evaluated by X-ray diffraction (XRD). Moreover, the effects of Y_2O_3 content, sintering temperature and holding time as well as mullite seeds on densification and microstructure were investigated.

2. Experimental procedure

The starting powders were α-Al_2O_3 (>99.95%, Martoxid CS-400/M, Martinswerk GmbH, Bergheim, Germany), quartz (>99.7%, 795-10/1, Novacite, Germany), and Y_2O_3 (>99.9%, HCST 4469, H. C. Starck, Berlin, Germany), which had an average particle size of 0.3, 0.3 and 0.2 μm, respectively. The molar ratio of Al_2O_3, SiO_2 and Y_2O_3 was taken as $3(100-x)$ $2(100-x)$ x, with values of $x = 5$, 10 and 15. The powder mixtures were ball milled in water with Si_3N_4 balls at 300 rpm for 2 h to increase homogeneity. Green compacts were prepared by die-pressing at a 100-MPa pressure. Reaction sintering was performed in air using a one-step heating cycle in a box furnace, with a heating rate of 10°C/min. Bulk density and open porosity were determined by the

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* Corresponding author at present address: Synergy Ceramics Laboratory, National Industrial Research Institute of Nagoya (NIRIN), Cooperative Research Center for Advanced Technology, Shimo-Shidami, Moriyama-ku, Nagoya 463-8687, Japan.

E-mail address: jhshe@nirin.go.jp (J. She).

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Archimedes method with distilled water as the liquid medium. Phase analysis was conducted by XRD using a computer-controlled diffractometer (D-5000, Siemens, Karlsruhe, Germany) with CuK_α radiation. Microstructures were investigated by scanning electron microscopy (SEM).

3. Results and discussion

Fig. 1 shows the XRD patterns of 10 mol% Y_2O_3-doped specimens, which were heated at a rate of 10°C/min to various temperatures in the range of 1050-1400°C and then quenched in air to room temperature. Clearly, no reaction occurs at 1050C, with the evidence that the specimen contains the same phases as present in the green state. After heating to 1100°C, some Y_2SiO_5 forms due to the reaction between yttria and quartz $Y_2O_3+SiO_2 \rightarrow Y_2SiO_5$. As the temperature is further increased to 1150°C, Y_2SiO_5 reacts with quartz to form $Y_2Si_2O_7$: $Y_2SiO_5+SiO_2 \rightarrow Y_2Si_2O_7$. Note that the conversion is not complete until 1200°C for Y_2O_3 to Y_2SiO_5 and 1250°C for Y_2SiO_5 to $Y_2Si_2O_7$. On the other hand, the transformation of quartz to cristobalite takes place at 1200°C, and the transformation increases with increasing temperature. At a temperature of 1325°C, such a transformation is completed, as evidenced by the disappearance of the quartz peaks in the XRD pattern. When the specimen is heated to 1350°C, a considerable amount of mullite has formed. At 1375°C, the mullite reaction is nearly complete, with only a trace of unreacted cristobalite. At 1400°C, a further mullitization occurs, as indicated by a decreased intensity of the cristobalite (101) peak at $2\theta=21.9°$.

Additionally, it is worth to note in Fig. 1(b) that no yttrious phase could be detected by XRD at temperatures between 1325 and 1375°C. This is probably due to the formation of a yttrious glass. According to the metastable corundum–cristobalite diagram [6], a eutectic aluminosilicate glass may form at temperatures above ~1260°C. When the temperature is increased to 1300°C, some $Y_2Si_2O_7$ dissolves into the aluminosilicate glass, giving rise to a decreased amount of the $Y_2Si_2O_7$ phase. This is consistent with the XRD results in Fig. 1 that the intensities of the $Y_2Si_2O_7$ peaks are lower at 1300 than 1250°C. The dissolution of $Y_2Si_2O_7$ would decrease the viscosity of the aluminosilicate glass. This, in turn, accelerates the dissolution of $Y_2Si_2O_7$. At 1325°C, $Y_2Si_2O_7$ dissolves completely into the aluminosilicate glass, leading to the disappearance of the $Y_2Si_2O_7$ peaks in the XRD pattern.

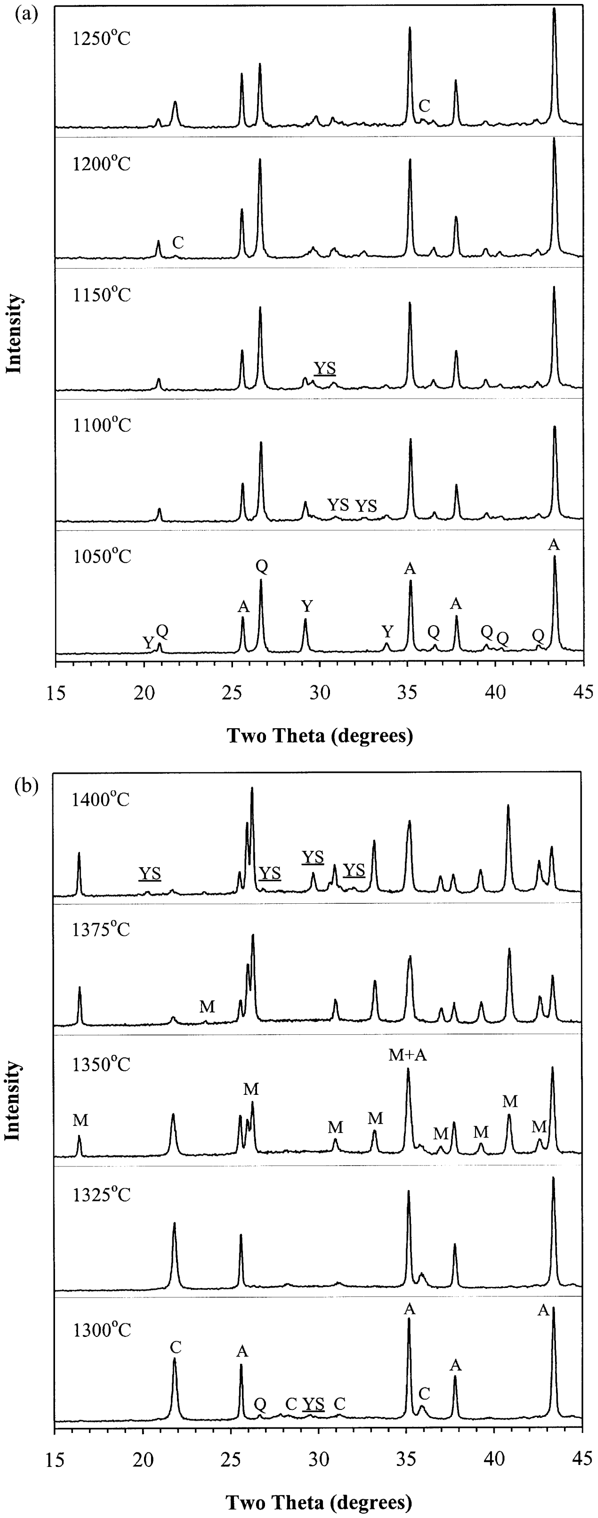

Fig. 1. XRD patterns of 10 mol% Y_2O_3-doped specimens after heating to different temperatures in the range of (a) 1050–1250°C and (b) 1300–1400°C without a hold (A is α-Al_2O_3, C is cristobalite, M is mullite, Q is quartz, Y is Y_2O_3, YS is Y_2SiO_5, and $\underline{YS}$ is $Y_2Si_2O_7$).

Although some investigations [7,8] have shown that the formation of mullite in the Al_2O_3–SiO_2 mixtures is due to a direct reaction between alumina and silica through a diffusion-controlled process, it is not the case in the present work, because extensive mullitization takes place at temperatures as low as 1350°C. Based on the work of Wei and Halloran [9,10], Sundaresan and Aksay [11] have conclusively established that low-temperature mullitization occurs by a nucleation and growth mechanism within an aluminosilicate glass. In this work, the dominant mechanism of mullite formation is believed to be nucleation and growth in an yttrious aluminosilicate glass. As mentioned above, such a glass has extensively formed at 1325°C. Due to the low viscosity of the yttrious glass, alumina particles dissolve rapidly. When the silicate glass is saturated with alumina, mullite nucleates in a very short time [11]. Subsequently, mullite grows as alumina particles dissolve continuously in the glass. On the other hand, the concentration of the yttrious silicate glass increases with the growth of mullite grains due to the consumption of the siliceous phase. When the yttrious glass reaches the $Y_2Si_2O_7$ composition, precipitation occurs, leading to the formation of the crystalline $Y_2Si_2O_7$ phase. This is confirmed by the XRD results in Fig. 1(b) that the $Y_2Si_2O_7$ peaks appear in the specimen after heating to 1400°C.

Based on the proposed mechanism of nucleation and growth, it is likely that the growth rate of mullite grains is controlled by the dissolution of alumina particles in the yttrious silicate glass [11]. Thus, the mullitization behavior should be related to the amount of yttria addition. As can be seen in Fig. 2, the mullitization reaction is incomplete for a 5 mol% Y_2O_3-doped specimen, which exhibits a notable amount of cristobalite and α-alumina. In contrast, no cristobalite is present in 10 and 15 mol% Y_2O_3-doped specimens, indicating that mullitization is essentially completed. Note, the degree of mullitization is higher in 15 mol% Y_2O_3-doped specimen, as indicated by a relatively low intensity of the α-alumina peaks. The presence of excess alumina in the specimens is due to the fact that a part of SiO_2 was consumed due to the formation of $Y_2Si_2O_7$. By increasing the SiO_2/Al_2O_3 ratio in the initial powder composition, it should be possible to obtain a mullite ceramic without any residual alumina.

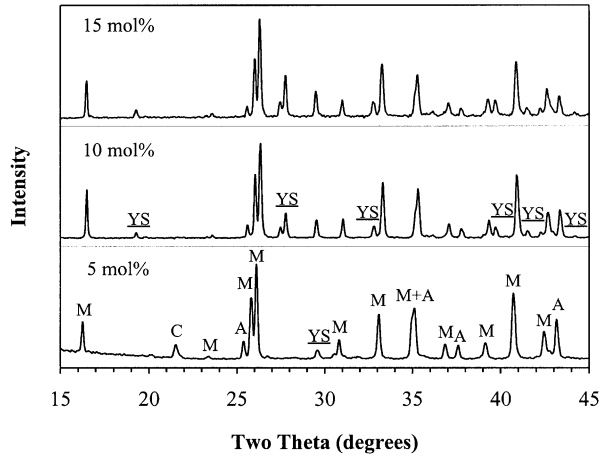

Fig. 2. XRD patterns of the RSM specimens with different Y_2O_3 additions, which were sintered at 1400C for 2 h (A is α-Al_2O_3, C is cristobalite, M is mullite, and $\underline{YS}$ is $Y_2Si_2O_7$).

Fig. 3 shows the effect of Y_2O_3 addition on bulk density and open porosity for the reaction-sintered mullite (RSM) ceramics, which were heated at 1400°C for 2 h. As shown, the density increases and the porosity decreases with the increase in the Y_2O_3 content. This can be explained on the basis of the nucleation and growth mechanism for mullite formation. It has been demonstrated [5,12] that mullite nuclei form only at a limited number of sites within the aluminosilicate glass. In this case, each grain may grow to a relatively large size until it collides with other growing grains, leaving some voids at the multigrain junctions. Such voids can be filled with the yttrious silicate glass. Since the amount of the yttrious glass correlates directly to the addition of yttria, the residual porosity decreases as the yttria content increases. However, the open porosity is still up to ~16% for a 15 mol% Y_2O_3-doped RSM specimen. This means that a further increase in the yttria content is required to completely fill the void space with the yttrious glass.

Fig. 4 is an SEM micrograph of a 15 mol% Y_2O_3-doped RSM ceramic, which was sintered at 1400°C for 2

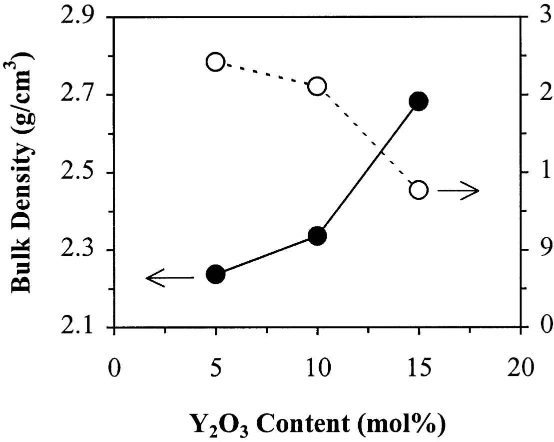

Fig. 3. Bulk density and open porosity versus Y_2O_3 content for the RSM ceramics after sintering at 1400°C for 2 h.

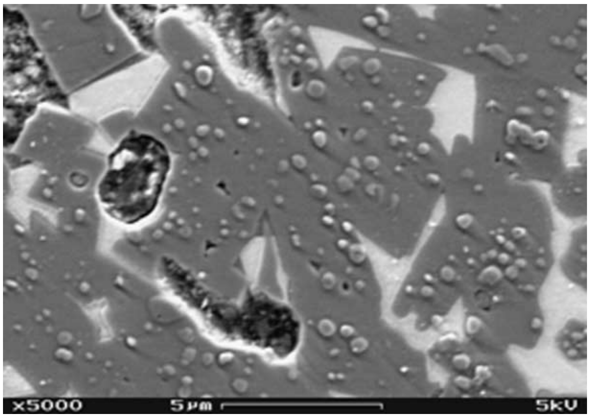

Fig. 4. Microstructure of a 15 mol% Y_2O_3-doped RSM specimen, which was sintered at 1400°C for 2 h.

h. In light of the energy-dispersive spectroscopy and the XRD pattern, the white and gray phases are $Y_2Si_2O_7$ and mullite, while the light-gray phase corresponds to α-alumina. As can be seen, the mullite grain sizes are in the range of 2-4 μm, approximately an order of magnitude larger than the starting particles. This is in agreement with nucleation of mullite at a relatively low number of sites. In addition, the excessive growth of mullite nuclei through the yttrious silicate glass may also cause the entrapment of some alumina particles within the mullite grains. As shown in Fig. 4, a noticeable amount of small rounded alumina particles are present at the intragranular locations. Moreover, the elongated appearance of mullite grains is also consistent with the growth of mullite in an yttrious silicate glass, because the presence of a glassy phase is one of the necessary conditions for the growth of anisotropic mullite grains, especially in the Al-rich composition [13]. On the other hand, it can be observed in Fig. 4 that some large pores are distributed at the multigrain junctions. Again, this agrees well with the proposed mechanism.

Based on the above discussion, the dominant mechanism of mullite formation should be nucleation and growth in an yttrious silicate glass. However, the conventional sintering mechanisms such as lattice diffusion and/or grain-boundary diffusion would become important after the crystallization of the yttrious glass. This may account for the results in Fig. 5 that the porosity in 15 mol% Y_2O_3-doped RSM specimens decreases only from ~16 to ~14.5% with an increase in the holding time from 2 to 10 h at 1400°C. As indicated earlier, large mullite grains develop during the mullitization process due to a relatively low number of mullite growth sites. In this case, the residual pores are difficult to remove by extending the sintering time because of the low lattice and grain-boundary diffusion coefficients for mullite [4].

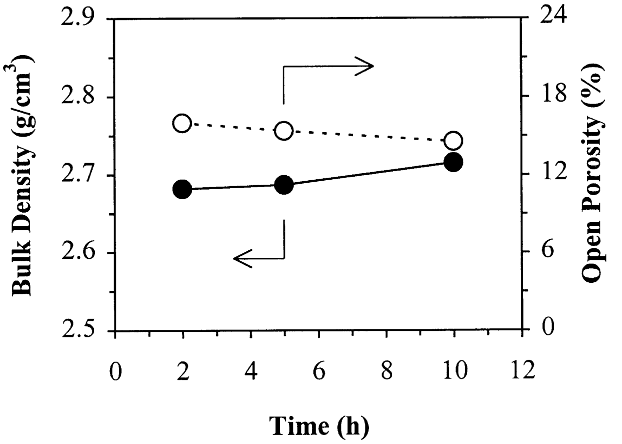

Fig. 5. Bulk density and open porosity as a function of sintering time at 1400°C for 15 mol% Y_2O_3-doped RSM ceramics.

It has been reported [5,12,14,15] that crystalline mullite seeds are highly effective as mullite growth sites. If a high number of mullite growth sites are provided by the seeds, each mullite grain would undergo less growth before it contacts with other growing grains. Hence, a smaller mullite grain size is expected by the incorporation of fine mullite particles into the initial powder

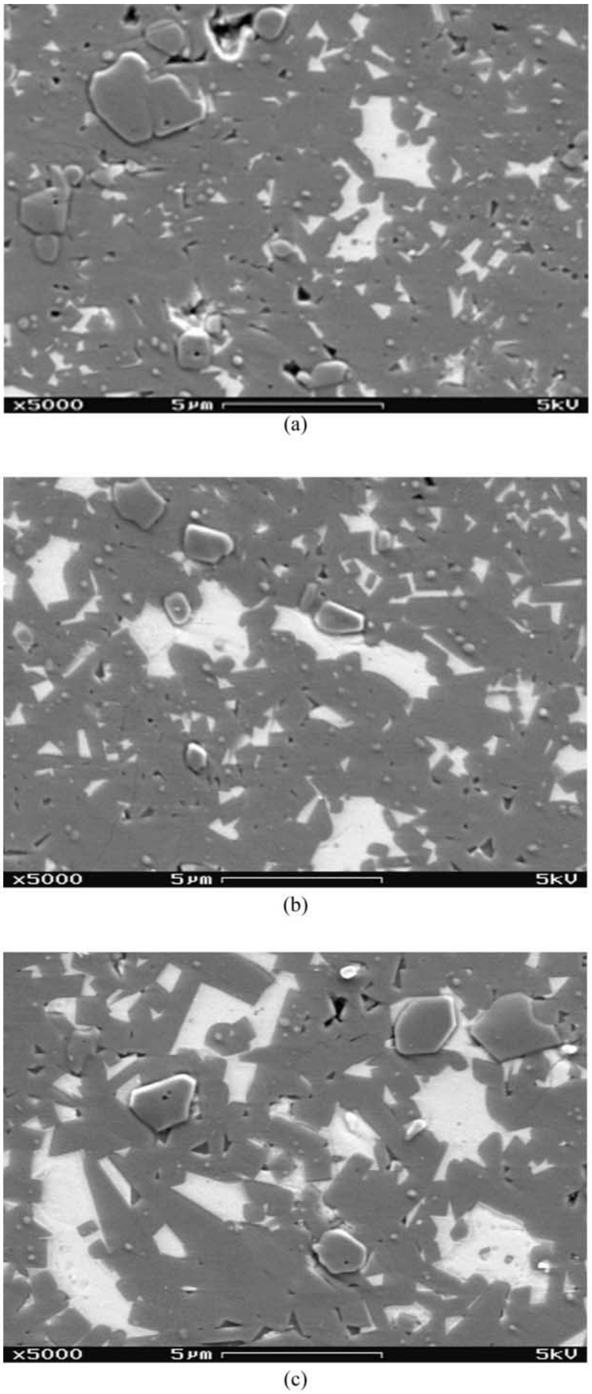

Fig. 6. Typical microstructures of 15 mol% Y_2O_3-doped and 5 mol% mullite-seeded RSM ceramics after sintering at 1400°C for (a) 2 h, (b) 5 h and (c) 10 h.

mixtures. For this consideration, a commercially available aluminosilicate precursor (Siral II, Condea Chemie, Hamburg, Germany) was used as the mullite seeds after crystallization at 1400°C for 5 h. It is evident from the SEM micrographs in Figs. 4 and 6(a) that the seeded specimen has a considerably smaller mullite grain size than the unseeded specimen. Moreover, the seeded specimen exhibits a relatively dense microstructure. This should be attributed to the development of smaller mullite grains in the mullitization process. In addition, it is interesting that the "trapped" alumina particles within mullite grains are much smaller in the seeded specimen. This suggests that mullitization can be enhanced by the addition of mullite seeds. Fig. 6(b) shows the microstructure of the seeded specimen after sintering at 1400°C for 5 h. Although some small pores can be occasionally observed at the intergranular locations, the specimen is almost fully densified. An additional increase in the sintering time from 5 to 10 h does not significantly affect the microstructure, as shown in Fig. 6(c). These observations agree well with the results of the density measurements in Fig. 7.

Fig. 8 shows the XRD pattern of a 15 mol% Y_2O_3-doped and 5 mol% mullite-seeded RBM specimen after sintering at 1400°C for 2 h. As shown, the specimen contains mullite, alumina and $Y_2Si_2O_7$. This is consistent with the microstructural observations in Fig. 6(a). When the sintering time was extended to 5 h or even to 10 h, no significant changes were observed in the XRD patterns, except for a little increase in the intensity of the $Y_2Si_2O_7$ peaks. This indicates that the mullitization reaction is almost complete in the specimens after a 2 h holding at 1400°C.

Fig. 9 shows the bulk density and open porosity of the seeded and unseeded specimens, which were sintered at three different temperatures of 1350, 1400 and 1450°C for 2 h. As can be seen, the density increases and the porosity decreases with the sintering temperature. This can be understood, because the lattice and grain-boundary diffusion becomes faster at higher temperatures. Fig. 10 shows the microstructure of the seeded specimen after sintering at 1450°C for 2 h. Evidently, the specimen has essentially the same microstructure as

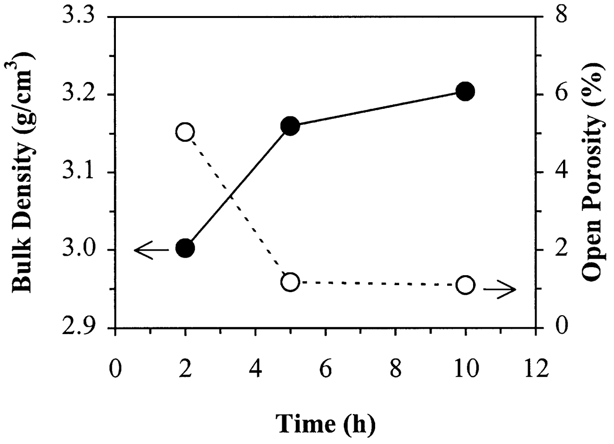

Fig. 7. Bulk density and open porosity as a function of sintering time at 1400°C for 15 mol% Y_2O_3-doped and 5 mol% mullite-seeded RSM ceramics.

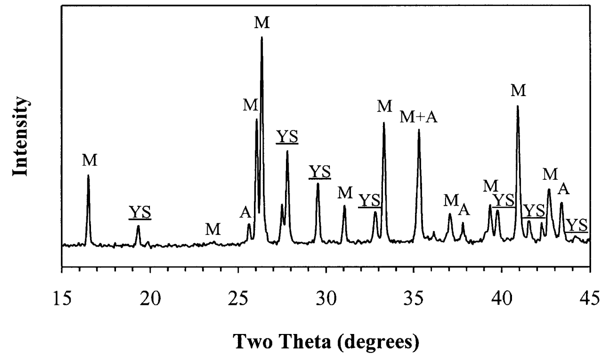

Fig. 8. XRD pattern of a 15 mol% Y_2O_3-doped and 5 mol% mullite-seeded RSM specimen after sintering at 1400°C for 2 h (A is α-alumina, M is mullite, and <u>YS</u> is $Y_2Si_2O_7$).

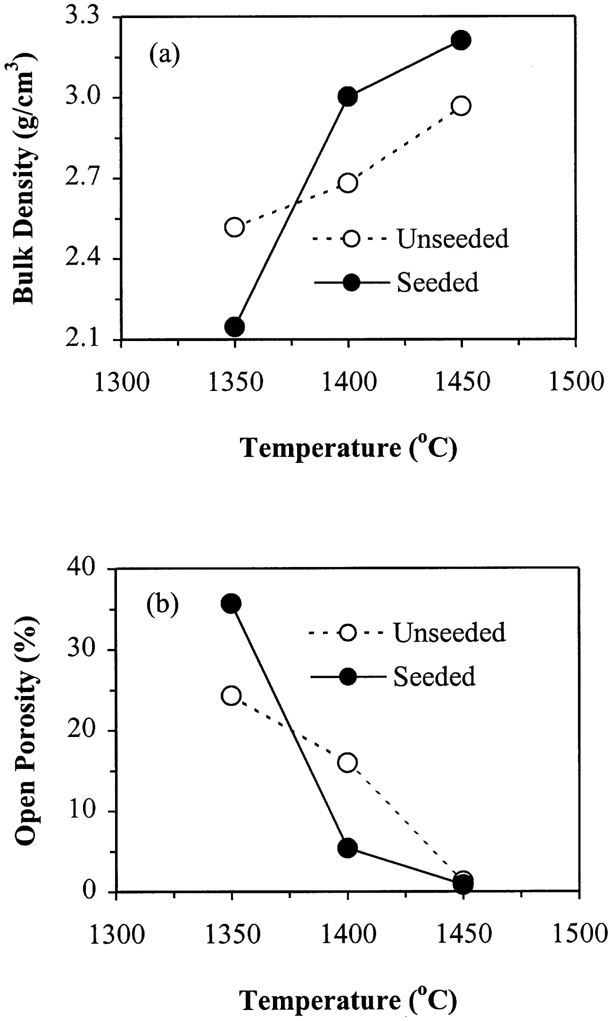

Fig. 9. Variation of (a) bulk density and (b) open porosity with sintering temperature for seeded and unseeded specimens.

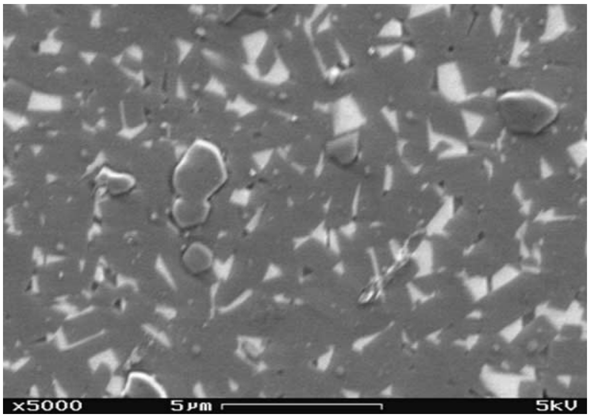

Fig. 10. SEM micrograph of a 15 mol% Y_2O_3-doped and 5 mol% mullite-seeded RSM specimen after sintering at 1450°C for 2 h.

observed in Fig. 6(c). Since the mullite grains have an elongated morphology, an improved toughness and an increased reliability are expected for the RSM ceramics. Also, the mechanical properties should be maintained at elevated temperature, because no glassy phase was observed in the final products.

4. Conclusions

The conventional reaction-bonding technique was employed to fabricate high-density mullite ceramics at moderate temperatures from powder mixtures of α-Al_2O_3 and quartz, with an Y_2O_3 addition. The XRD results indicate that mullite forms by a nucleation and growth mechanism within an yttrious aluminosilicate glass. At the later stages of the RSM process, the lattice and grain-boundary diffusions become more important for densification. This necessitates the incorporation of mullite seeds to achieve a higher sintered density. With 15 mol% Y_2O_3 and 5 mol% seeds, the specimens can be sintered to an almost fully dense state at 1400°C for 5 h or 1450°C for 2 h. Due to the presence of elongated mullite grains and the absence of glassy phases in the final products, a good mechanical behavior is expected.

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