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Effect of alkaline-earth oxides on phase formation and morphology development of mullite ceramics

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Abstract

The effect of alkaline-earth oxides, including MgO, CaO, SrO and BaO, on the phase formation and morphology development of mullite ($3Al_2O_3{\cdot}2SiO_2$) ceramics from oxide mixtures activated by a high-energy ball milling process, were investigated. Different alkaline-earth oxides demonstrated different influences on the mullitization behavior and morphology/microstructure development of the mullite ceramics. Mullitization temperature increased as the additives were from MgO to BaO. Well developed mullite whiskers were formed in the MgO doped group, while grains with normal shapes were observed in the cases of CaO, SrO and BaO. The dependence of both mullite formation temperature and morphology development on the kinds of alkaline-earth oxides were explained in terms of the mullitization mechanism of dissolution–precipitation.

Keywords: D. Mullite; D. Alkaline-earth oxide; Anisotropic grain growth; Mullitization

1. Introduction

Many attractive mechanical and thermal properties of mullite ($3Al_2O_3{\cdot}2SiO_2$) make it a promising engineering material [1–4]. Mullite powders were conventionally prepared via the solid-state reaction with oxide precursors. Due to the relatively low interdiffusion rates of Si^{4+} and Al^{3+} within the mullite lattice, the kinetics of mullitization by reaction thus depend strongly on the precursor mixing [5]. Therefore, the mullite phase formation temperature of the solid-state reaction between Al_2O_3 and SiO_2 (quartz) particles can be as high as 1600 °C. Various strategies have been developed to reduce the mullite phase formation temperature. For example, mullite can be formed at 1400–1500 °C using α-Al_2O_3 particles coated with amorphous sol–gel silica [6]. If nanosized γ-Al_2O_3 particles are used, the mullitization temperature can be further decreased to 1300 °C [7]. Sol–gel process is another way to produce mullite at low temperatures. During this process, the precursors are mixed at atomic level so that mullite formation can be greatly enhanced. The mullitization temperature is usually 900–1200 °C [8–10]. The disadvantages of the sol–gel process, as well as the coating method, include their complicated experimental procedure, expensive precursor chemicals used and small quantity of production. It would be desired to develop alternative processes to prepare mullite ceramic in an effective way.

High-energy ball milling process, which was designed to produce oxide-dispersed metallic composites [11] and subsequently mechanical alloying [12], has been applied to the preparation of ceramic materials [13–15]. Some compounds can be directly synthesized via the high-energy ball milling. For example, lead zirconate titanate ($PbZr_{1-x}Ti_xO_3$ or PZT) can be obtained from oxide mixture of PbO, ZrO_2 and TiO_2 powders by high-energy ball milling for a certain period of time, depending on the milling media and milling parameters used [13]. Other materials, such as $BaTiO_3$ [14] and $MgAl_2O_4$ [15] can be prepared from the high-energy ball milled precursors at much lower temperatures compared to their unmilled counterparts. The enhancement in the phase formation ability of these materials is attributed to the refined precursors as a result of the high-energy ball milling process. The refined precursors allow for the direct reactions during the milling process or the subsequent low temperature treatment.

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We initially intended to employ the high-energy ball milling for low temperature fabrication of mullite ceramics. However, dense mullite ceramics could not be derived from the high-energy ball milled precursor oxides. Instead, mullite whiskers were obtained [16]. We also found that the mullitization behavior and the dimension of the mullite whiskers could be modified by the addition of other oxides [17]. Various oxides have already been investigated. In the present study, we report the effect of alkaline-earth oxides on the mullitization behavior and morphology/microstructure development of the Al_2O_3–quartz mixtures activated by a high-energy ball milling process. It is interesting to find that mullite whiskers were only available in the case of MgO, while the addition of CaO, SrO and BaO led to dense mullite ceramics with much less anisotropic grains. These observations were explained by the dissolution–precipitation mechanism.

2. Experimental

Commercially available SiO_2 (Quartz, 99 + % purity, Aldrich Chemical Company Inc., USA), Al_2O_3 (>99% purity, Aldrich Chemical Company Inc., USA), MgO, CaO, $SrCO_3$ and $BaCO_3$ powders were used as the starting materials. The nominal composition was $(3Al_2O_3{\cdot}2SiO_2)_{0.9}(MO)_{0.1}$ (M: Mg, Ca, Sr and Ba). The powders were first mixed by the conventional milling process, using ZrO_2 media. The mixed powders were then activated by a high-energy ball milling. The milling operation was carried out using a Retsch PM400 type planetary ball milling system in air at room temperature for 5 h. A 250 ml tungsten carbide vial and 100 tungsten carbide balls with diameter of 10 mm were used as a milling medium at a milling speed of 200 rpm. The ball-to-powder weight ratio was about 40:1. The milled powders were pressed uniaxially into pellets of 10 mm diameter, at a pressure of 50 MPa. The green pellets were then sintered in a Carbolite RHF 1600 type furnace in air for 4 h at temperatures from 1000 to 1500 °C at heating and cooling rate of 10 °C/min.

X-ray diffraction (XRD) analysis of the powders and sintered samples was performed using a Rigaku ultima + type diffractometer (XRD) with Cu Kα radiation. Densification behavior of the green pellets was recorded using a Setaram Setsys 16/18 type dilatometer at a heating rate of 10 °C/min in air atmosphere. The microstructure of the sintered samples was examined using a JEOL JSM-6340F type field emission scanning electronic microscope (FESEM). The density of

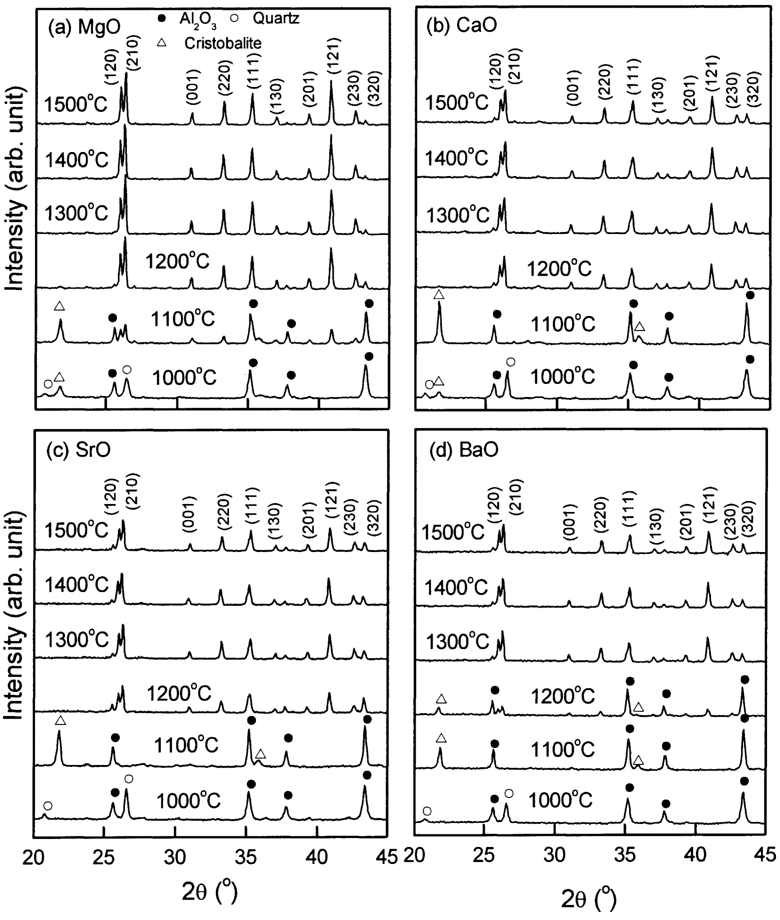

Fig. 1. XRD patterns of the alkaline-earth oxide doped mixtures sintered at different temperatures for 4 h.

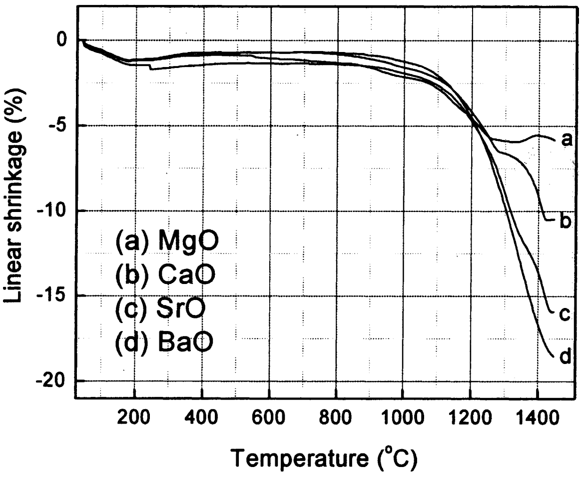

Fig. 2. Densification behavior of the alkaline-earth oxide doped mixtures.

the mullite ceramics was measured by a Mirage MD-200S type electronic densimeter using water as the liquid media.

3. Results and discussion

Fig. 1 shows the XRD patterns of the alkaline-earth oxide-doped samples sintered at different temperatures. The four groups have similar XRD patterns after sintering at 1000 °C, where Al_2O_3 and quartz are major phases. For MgO and CaO, a small peak at $2\theta \approx 21.69^\circ$ is detected by the XRD measurement. This peak corresponds to cristobalite, meaning that a phase transformation from quartz to cristobalite occurred during the sintering process at this temperature. No cristobalite is observed in the samples with SrO and BaO, which means that the presence

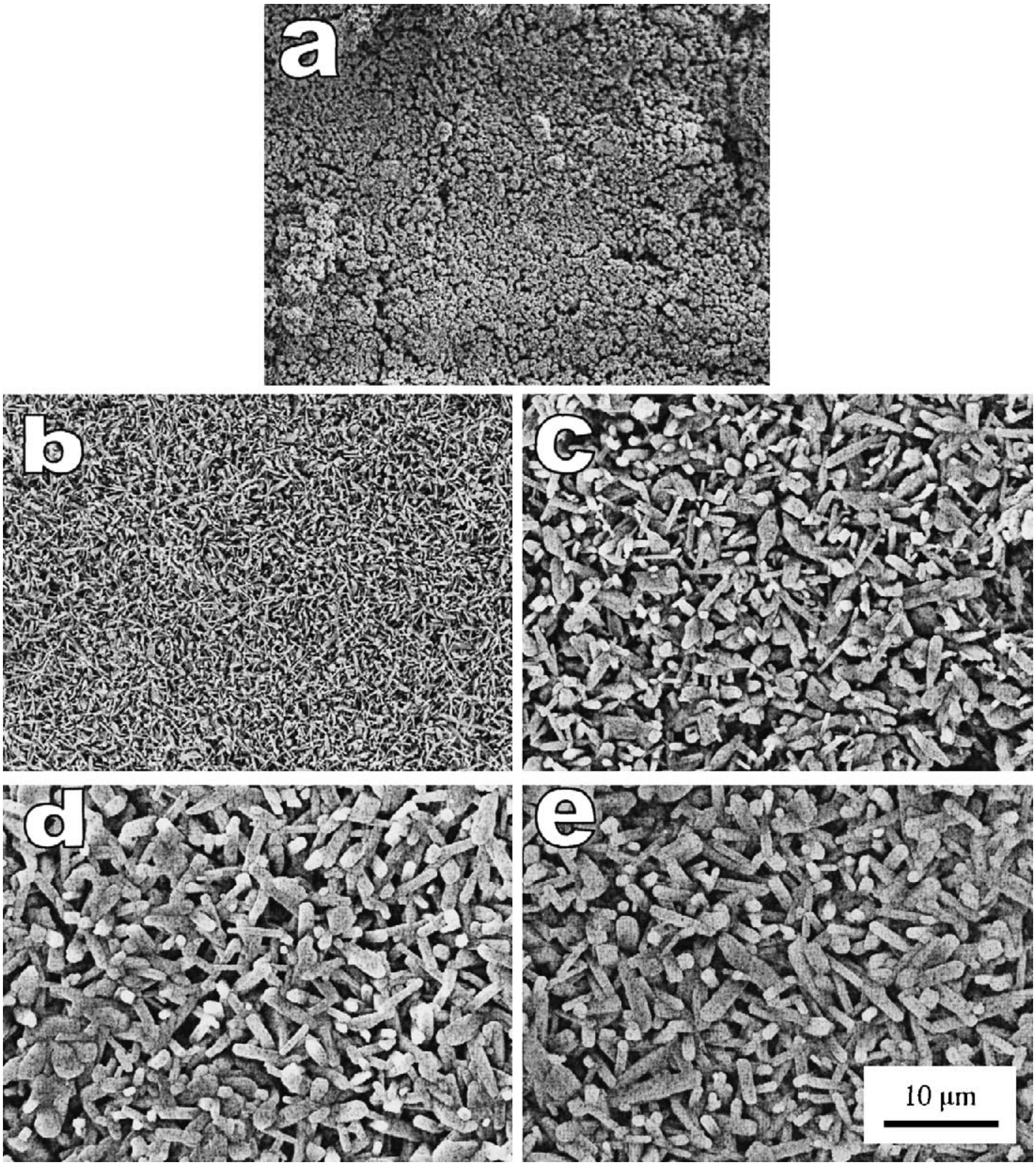

Fig. 3. SEM images of the MgO-doped samples sintered for 4 h at: (a) 1100 °C, (b) 1200 °C, (c) 1300 °C, (d) 1400 °C and (e) 1500 °C.

of SrO and BaO inhibited the quartz to cristobalite phase transition. After sintering at 1100 °C, mullite phase appears in the MgO-doped group, although the peaks coming from Al_2O_3 and cristobalite are still pretty strong. However, no mullite is formed in other three groups at this temperature. It is also noted that the phase transformation from quartz to cristobalite is already complete. As the sintering temperature increases to 1200 °C, mullitization is almost complete in the MgO-doped group, while mullite is already the major phase in the CaO and SrO-doped samples. However, mullite is still a minor phase in the BaO group. The mullitization temperature of the MgO-doped group is almost the same as that of the undoped Al_2O_3–quartz system with the high-energy ball milling, whereas the mullitization temperature of the BaO sample is very close to that of the undoped system without milling. Our previous study showed that high-energy ball milling reduced the mullitization temperature of Al_2O_3–quartz by ~200 °C. Therefore, these observations indicate that CaO, SrO and BaO have a negative effect on the mullite phase formation and the degree of this effect is in the order of CaO $<$ SrO $<$ BaO. The XRD patterns of all the samples sintered at 1300 °C or above are almost the same.

The densification behaviors of the four alkaline-earth oxide doped samples are shown in Fig. 2. The densification is not significant below 1200 °C and the densification characteristics of the four samples are very similar. However, significant difference can be observed above 1200 °C. Almost no densification is observed for the MgO sample. The maximum linear shrinkages of the CaO, SrO and BaO doped samples are ~10.5, ~15.9 and ~18.5%, respectively.

Fig. 3 shows the SEM images of the MgO-doped samples sintered at different temperatures. The 1000 °C-sintered sample consists of equiaxed grains. Mullite phase is not formed at this temperature. Whiskers can be readily observed in the MgO-sample sintered at 1100 °C. The mullite whiskers continue growing with increasing sintering temperature. Selected SEM images of the 1400 °C-sintered samples doped with CaO, SrO and BaO are shown in Fig. 4. In contrast to the MgO group, samples doped with these three alkaline-earth oxides do not demonstrate obvious anisotropic grain growth. Instead, dense mullite ceramics are achieved. This is also confirmed by the measured density of the sintered samples as shown in Fig. 5. The fact that the density of the BaO-doped samples is higher than the theoretic density of mullite is mainly due to the high density of BaO.

It has been widely accepted that mullite phase formation in Al_2O_3–SiO_2 binary system is governed by the dissolution–precipitation mechanism [7]. During the sintering process in Al_2O_3–SiO_2 systems, a silica-rich liquid-like layer is formed at relatively low temperature, in which Al_2O_3 component dissolves. Mullite nuclei crystallize as the Al_2O_3 concentration reaches a critical level. This liquid-like layer also serves as a sintering aid to promote densification of the sintered samples, which is known as the viscous transient flow sintering. If mullite phase is formed before densification, whiskers can be obtained. This is because mullite grains have a strong tendency of anisotropic growth as the grain growth is underway under an unconstrained environment. Otherwise, dense mullite ceramics with equiaxed grains will be the final products. In the conventional solid-state reaction processing for the preparation of mullite ceramics, mullite phase formation in the oxide precursors required very high temperatures [5]. This is mainly because commercial Al_2O_3 and SiO_2 (quartz) consist of very large particles, so that the dissolution of Al_2O_3 was very difficult. This in turn led to a mullitization after the occurrence of densification [6,7]. In this case, mullite grains could not grow anistropically, and thus mullite whiskers were unavailable. High-energy ball milling can reduce the particles of oxide precursors to

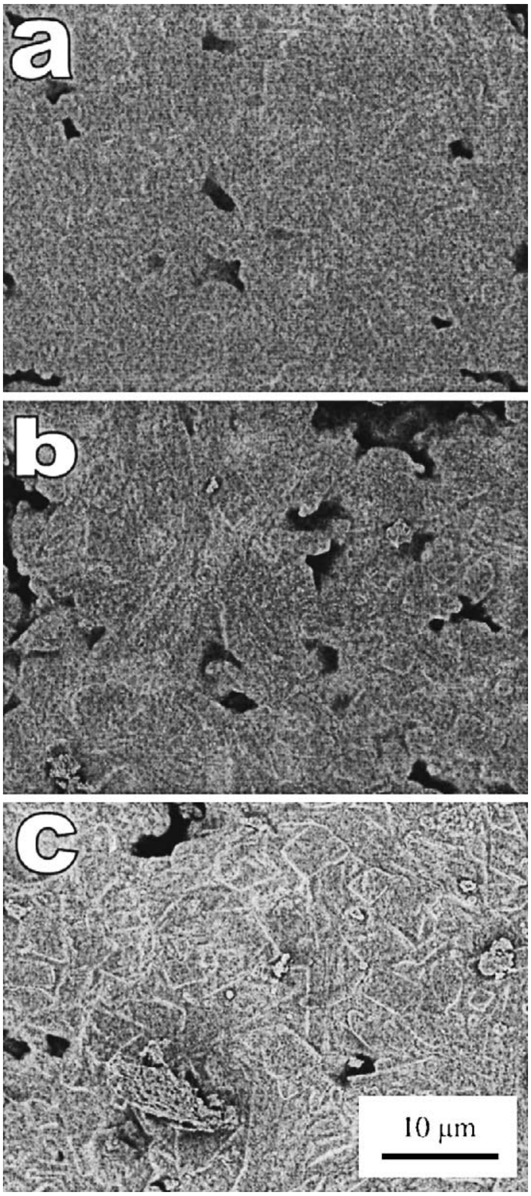

Fig. 4. SEM images of the doped samples sintered at 1400 °C for 4 h: (a) CaO, (b) SrO and (c) BaO.

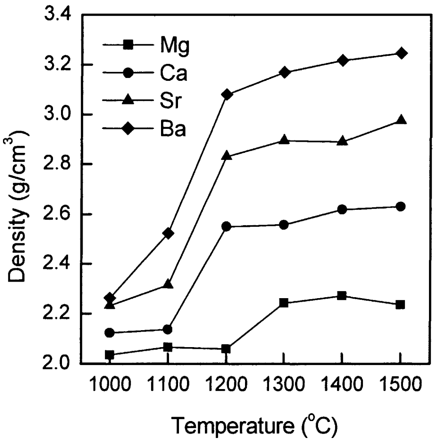

Fig. 5. Relative density of the alkaline-earth oxide doped mixtures as a function of sintering temperature.

nanometer scale. The refined precursors have very high reactivity, leading to mullitization at a temperature lower than that of densification. So mullite whiskers can be obtained. It is, therefore, suggested that alkaline-earth oxides alter the characteristics of the SiO_2-rich liquid-like phase in different ways. MgO and BaO are two extreme cases, between which are CaO and SrO. The $MgO–Al_2O_3–SiO_2$ system is similar to the high-energy ball milled $Al_2O_3–SiO_2$, while the $BaO–Al_2O_3–SiO_2$ sample demonstrates a mullitization behavior like the pure mixture of $Al_2O_3–SiO_2$ without milling. Further work is needed to clarify these effects of the alkaline-earth oxides.

4. Conclusions

The mullitization behavior and morphology development of the MgO-group was similar to its undoped counterpart, where low temperature mullitization and formation of whiskers were observed. The mullitization temperature increased from CaO to SrO and BaO. In contrast to MgO, CaO, SrO and BaO led to dense mullite ceramics without the presence of significant anisotropic grain growth. The effect of alkaline-earth oxides on both the mullite formation temperature and mullite morphology were qualitatively explained by the dissolution–precipitation mechanism.

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