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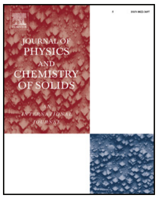

Phase formation and microstructure evolution in mullite ceramics synthesized from mechanochemically activated oxide powders doped with Cr_2O_3

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ABSTRACT

In this study, we investigated the influence of Cr_2O_3 on phase formation and microstructure evolution in mullite ceramics. We also explored the mechanochemical effects of high-energy milling with stainless steel and tungsten carbide. X-ray diffraction and scanning electronic microscopy analyses showed that the introduction of Cr_2O_3 had a negative effect on the formation of mullite. As the Cr_2O_3 content increased from 5 mol% to 20 mol%, the initial formation temperature for mullite increased from 1300 °C to 1500 °C. The negative effect of Cr_2O_3 on the formation and growth of mullite can be mitigated by mechanochemically activating the precursor mixture via high-energy ball milling.

1. Introduction

Due to their high mechanical strength, excellent thermal shock resistance, high creep resistance, low thermal conductivity, and high-temperature stability [1,2], mullite-based ceramics are considered ideal candidates for use in traditional refractory industries [3,4]. Recent studies indicate that mullite ceramics also have promising applications in the microelectronics [5–7] and optical [8–10] industries due to their low dielectric constant, excellent electrical insulation, small birefringence, and excellent infrared transmission capability. Moreover, it has been shown that the mechanical and thermal performance of mullite ceramics can be enhanced greatly by exploiting the interlocking behavior of mullite whiskers via anisotropic grain growth [11]. However, the formation of mullite whiskers requires strict conditions in terms of both the composition and synthetic process. Classical theory predicts that the growth of mullite whiskers is based on a vapor-solid reaction [12–15], so dopants that can generate or decompose into gases are required in the precursor materials. The commonly used dopants include AlF_3 [13,15], CF_4 [14], and $AlCl_3$ [16]. Unfortunately, the gases formed due to the presence of these additives at high temperatures are known to be carcinogens [17]. In order to address the problem of toxic gases, Kong et al. developed a new method for synthesizing mullite whiskers from mechanochemically activated precursors but without requiring harmful dopants [18–20]. Subsequently, the effects of various oxide additives on phase formation and grain growth in mullite with this method were comprehensively studied. These oxides include Fe_2O_3 [21,22], CoO [21,22], NiO [21,22], CuO [23], B_2O_3 [24], Bi_2O_3 [25], Sb_2O_3 [25], Y_2O_3 [26], La_2O_3 [26], SnO_2 [25], TiO_2 [27], CeO_2 [26], V_2O_5 [28], Nb_2O_5 [28], Ta_2O_5 [28], and WO_3 [29].

Cr_2O_3 is a non-environmental friendly oxide and it is generally not suitable for use as an additive to tailor the properties of materials. However, it is very difficult to avoid the unpredictable contamination of raw materials during industrial production. Quartz sand and bauxite are the main raw materials used for the production of mullite ceramics but they are often contaminated by Cr_2O_3 in Hunan, Jiangxi, and other regions of China [30]. Therefore, it is important to study the effects of

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Cr_2O_3 on mullite ceramics and suitable measures for improving their industrial production.

However, the effects of Cr_2O_3 on the formation of mullite and its crystal structure remain unclear. Mitra et al. showed that Cr_2O_3 had a positive effect on the formation of mullite [31], whereas Chandra suggested that Cr_2O_3 suppressed grain growth in mullite [32]. Mitra et al. stated that Cr^{3+} does not enter the mullite lattice but that it can coexist in an amorphous matrix [31], whereas Murthy indicated that Cr^{3+} can be incorporated in the mullite structure up to 8–10 wt% Cr_2O_3 by substituting in the Al^{3+} sites [33]. Another study showed that the maximum content of Cr_2O_3 in the mullite structure can be up to 12 wt% [34]. The synthesis conditions were different in these studies but their conflicting conclusions still need to be explained.

In this study, we aimed to clarify the influence of Cr_2O_3 on phase formation and microstructural development in mullite ceramics where the Cr_2O_3 contents were up to 20 mol%. Furthermore, we examined the effects of mechanochemical activation by using two types of milling media (stainless steel and tungsten carbide) for comparison.

2. Experimental procedure

Commercially available SiO_2 (quartz, 99+% purity, Aldrich Chemical Company Inc., USA), Al_2O_2 (99+% purity, Aldrich Chemical Company Inc., USA), and Cr_2O_3 (99.9+% purity, Aldrich Chemical Company Inc., USA) powders were used as the starting materials. The nominal composition was $(3Al_2O_3{\cdot}2SiO_2)_{1-x}$ $(Cr_2O_3)_x$ (x = 0, 0.05, 0.10, and 0.20), which corresponded to Cr_2O_3 contents of 0, 1.4, 2.0, and 4.1 wt%, respectively. The starting powders were mixed thoroughly and the mixtures were then divided into three groups. The first group was not subjected to high-energy milling. The other two groups were activated by high-energy ball milling for 10 h with stainless steel and tungsten carbide media. High-energy milling with stainless steel media was conducted using a Fritsch Pulverisette 5 planetary ball milling machine, whereas that with tungsten carbide media was performed using a Retsch PM400 type planetary milling system. In both cases, a 250 mL vial was used containing 100 balls with a diameter of 10 mm. Milling was conducted at 200 rpm, with a ball-to-powder weight ratio of about 40:1 for the tungsten carbide media and 20:1 for the stainless steel media.

All of the batch powders were pressed uniaxially at a pressure of 50 MPa into pellets with a diameter of 10 mm. The green pellets were sintered in a Carbolite RHF 1600 type furnace in the air for 4 h. Sintering was conducted at temperatures from 1000 °C to 1500 °C, with heating and cooling rates of 10 °C/min. X-ray diffraction (XRD) analyses of the powders and sintered products were performed using a Rigaku (Tokyo, Japan) ultima + type diffractometer with Cu Kα radiation. The microstructure and grain morphology of the sintered samples without surface chemical treatment were examined using a JEOL (Tokyo, Japan) JSM-6340 F type field emission scanning electronic microscope (SEM).

3. Results and discussion

3.1. Phase formation by mullite

3.1.1. Mullite ceramics derived from unmilled mixtures

Fig. 1 shows the XRD patterns obtained for the ceramic samples produced from unmilled mixtures containing 5 mol% Cr_2O_3, which were sintered at different temperatures. Al_2O_3, quartz, cristobalite, and mullite phases were observed in these samples. No peaks attributable to WC or WO_3 were observed in the XRD patterns, although the precursor mixtures were milled with WC for 10 h, thereby indicating that high-energy ball milling had no obvious effects on the phase compositions of the mullite ceramics, as shown in our previous studies [35–38]. Moreover, Jiang et al. found that the contamination by WC was sufficiently low even when the raw materials were milled for more than 100 h [39,40]. After sintering at temperatures ranging from 1000 °C to 1200 °C, only Al_2O_3, quartz, and cristobalite phases were identified. As the sintering temperature increased, the peak intensity of Al_2O_3 remained basically unchanged, whereas those for quartz and cristobalite decreased and increased, respectively, thereby indicating that the quartz gradually transformed into cristobalite as the temperature increased. When the sintering temperature reached 1300 °C, the mullite crystalline phase began to appear and the peaks for quartz were entirely absent. In addition, the peak intensities for Al_2O_3 and cristobalite also decreased gradually. As the sintering temperature increased further, the peak intensity for mullite was gradually enhanced. However, the Al_2O_3 and cristobalite phases were still present in the samples even when the sintering temperature was as high as 1500 °C, thereby suggesting that the formation of the mullite phase was not yet complete. It should be noted that no peaks for Cr_2O_3 were observed in any of the samples. These results are essentially the same as our previous observations based on mullite ceramics without any dopants [18] and they suggest that small amounts of Cr_2O_3 had no significant effects on phase formation in mullite.

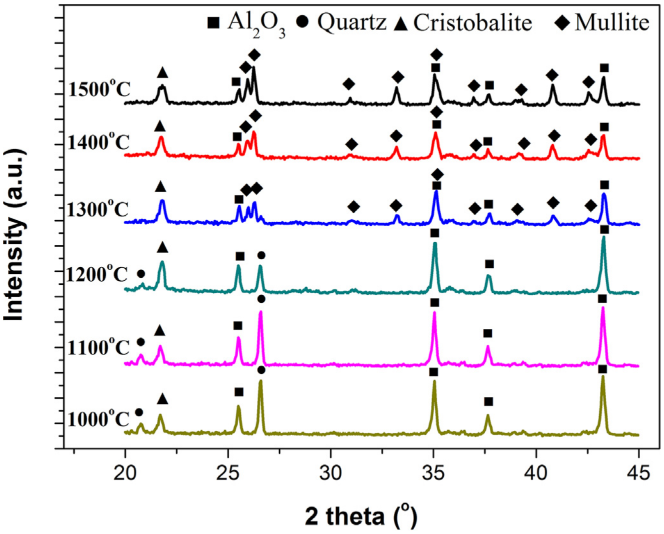

Fig. 1. XRD patterns obtained for the unmilled mixture with 5 mol% Cr_2O_3 and sintered at different temperatures.

3.1.2. Mullite ceramics derived from the mixtures activated with stainless steel medium

Fig. 2 shows the XRD patterns obtained for the ceramic samples sintered at different temperatures, where the raw material mixture contained 5 mol% Cr_2O_3 and it was milled with the stainless steel medium for 10 h. The phase evolution was similar to that for the unmilled mixtures, but several significant differences can be highlighted. First, only quartz and Al_2O_3 were found in the sample after sintering at 1000 °C. In addition, the peaks for quartz were obviously weaker and some minor characteristic peaks disappeared. According to the basic theories of mechanochemical activation, amorphization of some raw materials is inevitable because of the severe plastic deformation and fracturing of the milled powders [41]. Due to its rather low density and hardness, quartz is first transformed into an amorphous structure according to many previous studies [19,20,23,29,42].

Bettermann et al. showed that the phase transition sequence for amorphous SiO_2 in most cases follows the order of amorphous silica, cristobalite, keatite, and quartz, whereas the direct transition of amorphous silica into quartz is rarely observed [43]. Thus, in our study, the transformation of quartz into an amorphous structure was not complete and a small amount of quartz was still retained in the mixture. Therefore, the peak intensity for quartz was clearly decreased. Second, the quartz phase gradually transformed into cristobalite as the