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Journal of the European Ceramic Society 23 (2003) 2257–2264
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Growth of mullite whiskers in mechanochemically activated oxides doped with WO_3

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Received 5 September 2002; received in revised form 17 January 2003; accepted 24 January 2003

Abstract

The effect of WO_3 on mullite formation and mullite whisker morphology, in oxide mixtures activated by a high-energy ball milling process, was investigated. Differential thermal analysis (DTA) measurement indicated that WO_3 enhanced the mullite phase formation, with mullitization temperature of 951 °C, 921 °C and 835 °C for the samples doped with 5, 10 and 20 mol% WO_3, respectively. However, the presence of WO_3 had an undesired effect on the whisker morphology. A decrease in the length of mullite whisker was observed with increasing WO_3 content. The effect of WO_3 on the mullite phase formation temperature, as well as the whisker morphology, was explained using a dissolution-precipitation mechanism.

Keywords: Anisotropy; Grain growth; Milling; Mullite; Whiskers

1. Introduction

Mullite has been extensively investigated as an engineering material in the last decades because of its good mechanical strength, excellent thermal shock and high creep resistance, low thermal conductivity and high-temperature stability.[1–4] Mullite powders were conventionally synthesized via the solid-state reaction processing, which usually required a high calcination temperature (>1500 °C). Mullite powders synthesized in this way had poor sinterability. In order to lower the synthesis temperature, many chemical routes were developed to prepare ultrafine mullite powders. Successful methods included sol-gel, co-precipitation, and spray pyrolysis.[5–9] Although these chemical methods can promote mullitization at temperatures of 900–1300 °C, they still have inevitable disadvantages. For example, in the sol-gel synthesis with alkoxides as starting materials, experimental parameters in the processing such as pH value, water-to-alkoxide ratio, catalyst concentration and reaction temperature must be carefully controlled to promote simultaneous reaction and homogeneous copolymerization, because the hydrolysis of silicon alkoxide was relatively slower than aluminum.[6] In this respect, alternative processing for the preparation of mullite material is still of great interest.

In our earlier work, attempt was made to improve the mullite formation from oxide precursors (Al_2O_3 and SiO_2) using a high-energy ball milling process. It was because of the fact that high-energy ball milling could greatly reduce the grain/particle size of the starting materials (Al_2O_3 and SiO_2), thus dense mullite ceramics were expected to be fabricated at lower temperature. On the other hand, oxides are much cheaper than the chemicals required by the chemical processing routes. So, high-energy ball milling is a cost-effective technique to fabricate mullite ceramics. The results showed that the mullite formation temperature was lowered by nearly 300 °C, but the sample had a very low density (~70% of mullite theoretical density).[10] The low density of the sintered product was due to the fact that the milled powder resulted in mullite whiskers rather than equiaxed mullite grains. It was due to expansion of the samples as the whisker is formed.[11]

Fabrication of mullite whisker is highly desired because it is an important candidate to achieve reinforced mullite ceramics. Due to its anisotropic structure,

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doi:10.1016/S0955-2219(03)00083-9

mullite grain has a strong tendency to grow anisotropically as long as the mullite formation occurs without constraints. A number of methods have been developed to produce mullite whiskers. Vapor-solid reaction process is one of the most successful techniques to synthesize mullite whiskers. In this method, a mixture of xerogel or silica gel and aluminum fluoride or hydrogen fluoride was calcined at high temperatures (900–1600 °C) and mullite anisotropically grew from the mixtures due to the unconstrained environment.[12–14] However, due to the gaseous phases involved, the reaction sequence was very complex and control of the reaction system was difficult. Similarly, needlelike mullite could be obtained by firing kaolin minerals at temperatures ranging from 1400 to 1600 °C in a sulfate flux.[15] To obtain phase pure mullite, the reacted product must be washed repeatedly to remove the salt species. Preparation of mullite whiskers was also possible from aluminum hydroxide-silica gel with erbia doping,[16] where the pellet sample surface was fully covered by mullite whiskers, while small grains in the bulk were much less anisotropic. Similar results were observed by using lanthanum doping.[17] Anisotropic grain growth of mullite was reported by Messing et al., by doping with B_2O_3 or TiO_2.[18,19] But the formation temperature was higher than 1600 °C. Compared to the methods reported in the literature, preparation of mullite whiskers via the high-energy ball milling process is relatively easier.

In this paper, we report the effect of WO_3 on the mullite phase formation and whisker morphology in the oxide mixtures activated by a high-energy ball milling process. It was found that the addition of WO_3 demonstrated a positive effect on the mullite formation and a negative effect on the whisker morphology.

2. Experimental procedure

Commercially available precipitated SiO_2 (Laboratory reagent, BDH Chemicals Ltd Poole, England), Al_2O_3 (99 + % purity, Aldrich Chemical Company Inc., USA) and WO_3 (>99% purity, MERCK, Damstadt, Germany) powders were used as the starting materials with a nominal composition of $(3Al_2O_3{\cdot}2SiO_2)_{1-x}(WO_3)_x$ with $x = 0.05$, 0.10 and 0.20, corresponding to WO_3 weight percentage of about 2.8, 5.8 and 12%, respectively. Before the application of high-energy ball milling, all samples were thoroughly mixed via conventional ball milling, using ZrO_2 vials and balls. The high-energy ball milling was conducted using a Retsch PM400 type planetary ball milling system in air for 5 h. A 250 ml tungsten carbide vial and 100 tungsten carbide balls with diameter of 10 mm were used as the milling medium at a milling speed of 200 rpm, with a ball-to-powder weight ratio of about 40:1. The milled powders were then pressed uniaxially into pellets of 10 mm diameter, at a pressure of 50 MPa. The green pellets were sintered in a Carbolite RHF 1600 type furnace in air for 4 hour at temperatures from 1000 to 1500 °C at heating and cooling rate of 10 °C/min.

X-ray diffraction analysis was performed using a Rigaku (Tokyo, Japan) ultima + type diffractometer (XRD) with CuK_α radiation. The average particle size was estimated on the basis of the Brunauer–Emmett–Teller (BET) specific surface area (Model ASAP 2000) using nitrogen as the absorption gas. The density of the mullite ceramics was measured by a Mirage MD-200S (ALFA Mirage Co. Ltd., Japan) type electronic densimeter using water as the liquid media. The microstructure and the whisker morphology of the sintered samples were examined using a Jeol JSM-6340F (Tokyo, Japan) type field emission scanning electronic microscope (FESEM). Both cross-section and surface of the sintered samples were examined. Dimensional parameters (length and width) of the mullite whiskers were estimated from the SEM images.

3. Results and discussion

Fig. 1 shows the XRD patterns of the milled powders doped with different WO_3 levels. The dominant phase in the milled samples is Al_2O_3. The reduced and broadened diffraction peaks indicate that Al_2O_3 has been greatly refined as a result of the high-energy ball milling. Due to its amorphous state, no silica phase is observed in the XRD patterns. No peaks can be clearly attributed to

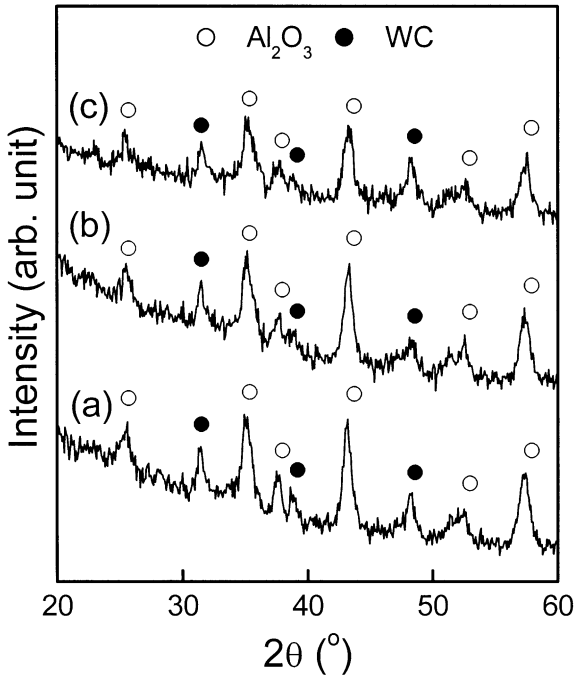

Fig. 1. XRD patterns of the milled samples with different level of WO_3: (a) 5 mol%, (b) 10 mol% and (c) 20 mol%.

WO_3 even in the samples with 20 mol% WO_3, which is most likely due to the fact that its diffraction peaks are too weak to be detected by the XRD measurement. A trace of tungsten carbide (WC) appears in the XRD patterns, which comes from the milling media due to the abrasion caused by the high-energy ball milling. As discussed in,[10] the quantity of the WC contamination is actually very small. The relatively strong diffraction peaks are due to good crystallinity. As discussed later, the WC contamination will not interfere with the influence of WO_3 on the mullite phase formation behavior and whisker morphology. The refinement of the starting materials was also confirmed by the BET measurement. Particle size distribution of the sample with 5 mol% WO_3, before and after milling, is shown in Fig. 2. Similar results were obtained for the samples with higher WO_3 contents. It is clearly noticed that the particle size was greatly reduced and the size distribution was largely narrowed, as a consequence of the high-energy ball milling.

Fig. 3 shows the DTA curves of the milled samples with different concentration of WO_3. Two distinct exothermic peaks are observed in each DAT curve. The peak at 853, 854 and 855 °C is attributed to the crystallization of cristobalite from the amorphous silica, while that at 951, 912 and 835 °C corresponds to the mullite phase formation. It indicates that the addition of WO_3 into the mixture of Al_2O_3 and SiO_2 is helpful to the mullite phase formation.

XRD patterns of the 5 mol% WO_3 doped mixture sintered at different temperatures are shown in Fig. 4. After sintering at 1000 °C for 4 h, mullite is already formed although appearing as a minority. The dominant phase is still Al_2O_3 and SiO_2. As the sintering temperature increases to 1100 °C, mullite phase becomes dominant, with Al_2O_3 and cristobalite appearing as

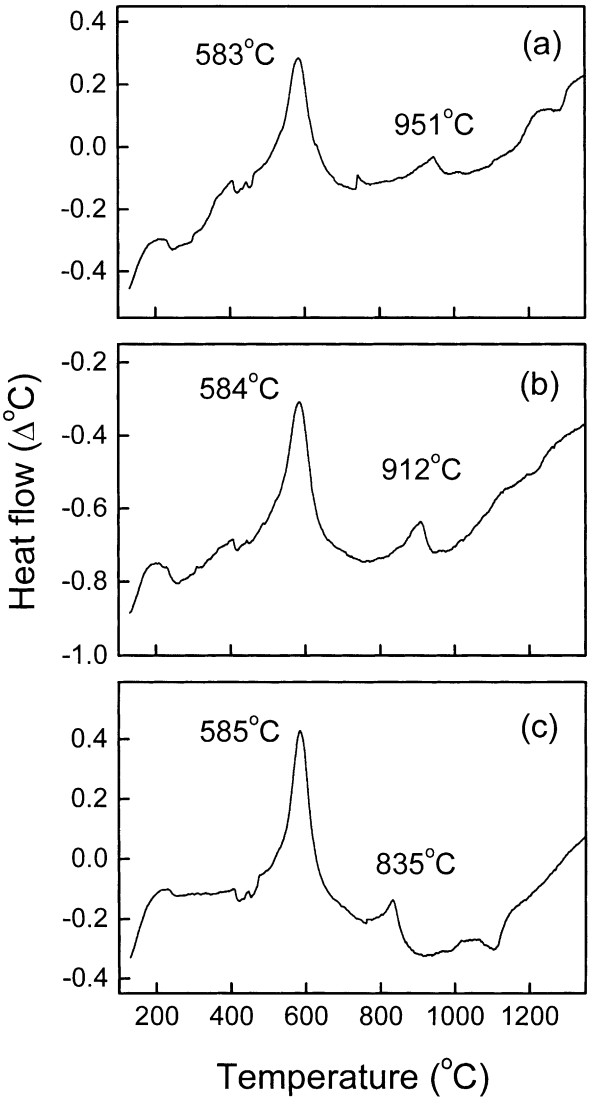

Fig. 3. DTA curves of the milled samples with different level of WO_3: (a) 5 mol%, (b) 10 mol% and (c) 20 mol%.

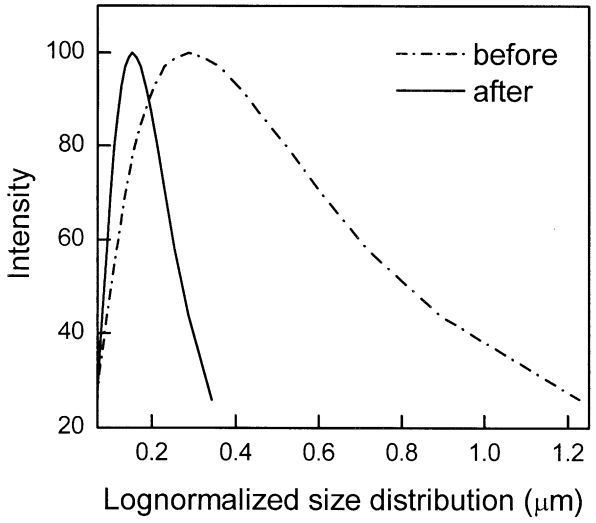

Fig. 2. Particle size distribution of the milled powder with 5 mol% WO_3.

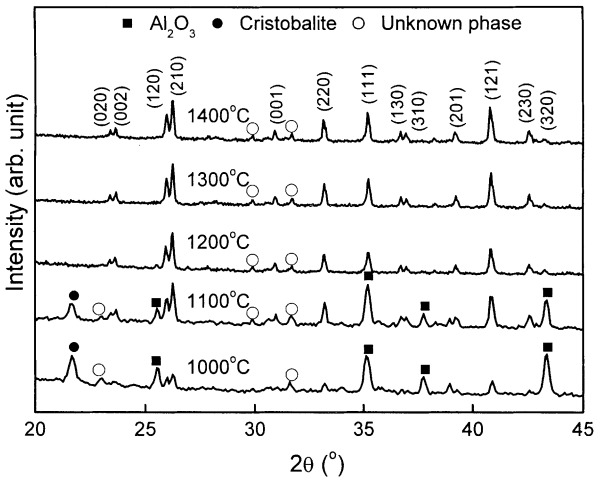

Fig. 4. XRD patterns of the 5 mol%-WO_3-doped sample sintered at different temperatures.

minorities. Almost single phase mullite is achieved after sintering at 1200 °C. No significant change is observed as the sintering temperature increases further. Similar results are observed in the samples doped with 10 and 20 mol% WO_3 (not shown here), with mullite phase temperature being lower than in the 5 mol% WO_3 doped sample. This result is in good agreement with that of the DTA analysis. Some minority phases are also detected by the XRD measurement, which cannot be identified.

In addition to the effect on the mullite phase formation temperature, WO_3 also has an effect on the mullite morphology. Well-developed mullite whiskers were formed in all the three WO_3-doped samples. Whiskers are usually of regular shapes and single-crystal characteristics, with a relatively large aspect ratio (length over width), while anisotropic grains are those that have smaller aspect ratio and more irregular shapes.[12,13,18,19]

SEM images of the sintered samples with different WO_3 contents are shown in Figs. 5–7. Fig. 5 shows that mullite whiskers are already formed in the sample sintered at 1000 °C, although sphere grains are still observed. At this temperature, the dominant phase is Al_2O_3 and SiO_2, with mullite appearing as a minority (Fig. 4). After sintering at 1100 °C, whiskers are totally formed and mullite phase becomes dominant at the same time. Similar results are observed in the samples doped with 10 and 20 mol% WO_3 (Figs. 6 and 7). This observation implies that once the mullite phase is formed, it appears as whiskers.

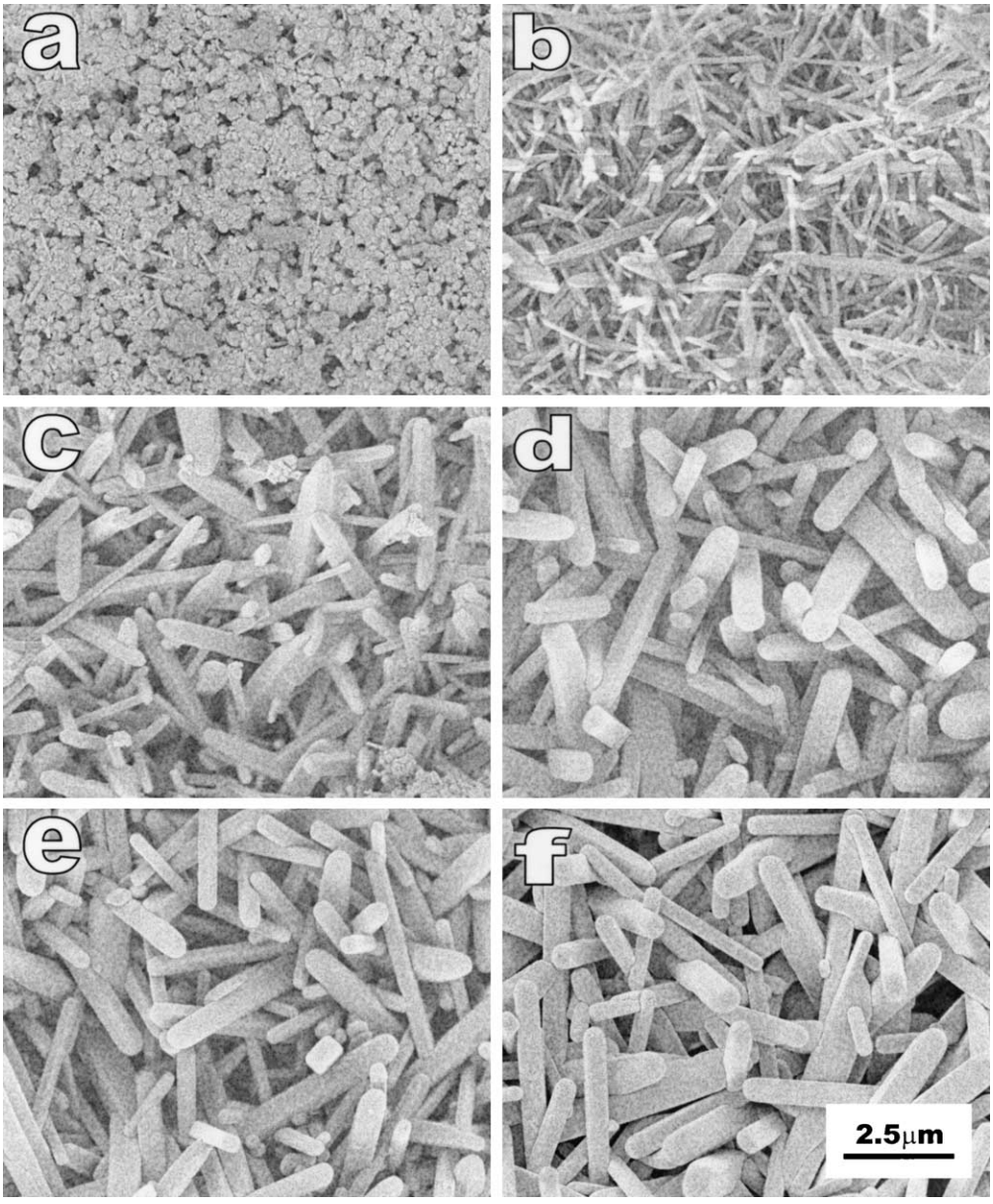

Fig. 5. SEM images of the 5 mol% WO_3 doped sample sintered at different temperatures: (a) 1000 °C, (b) 1100 °C, (c) 1200 °C, (d) 1300 °C, (e) 1400 °C and (d) 1500 °C.

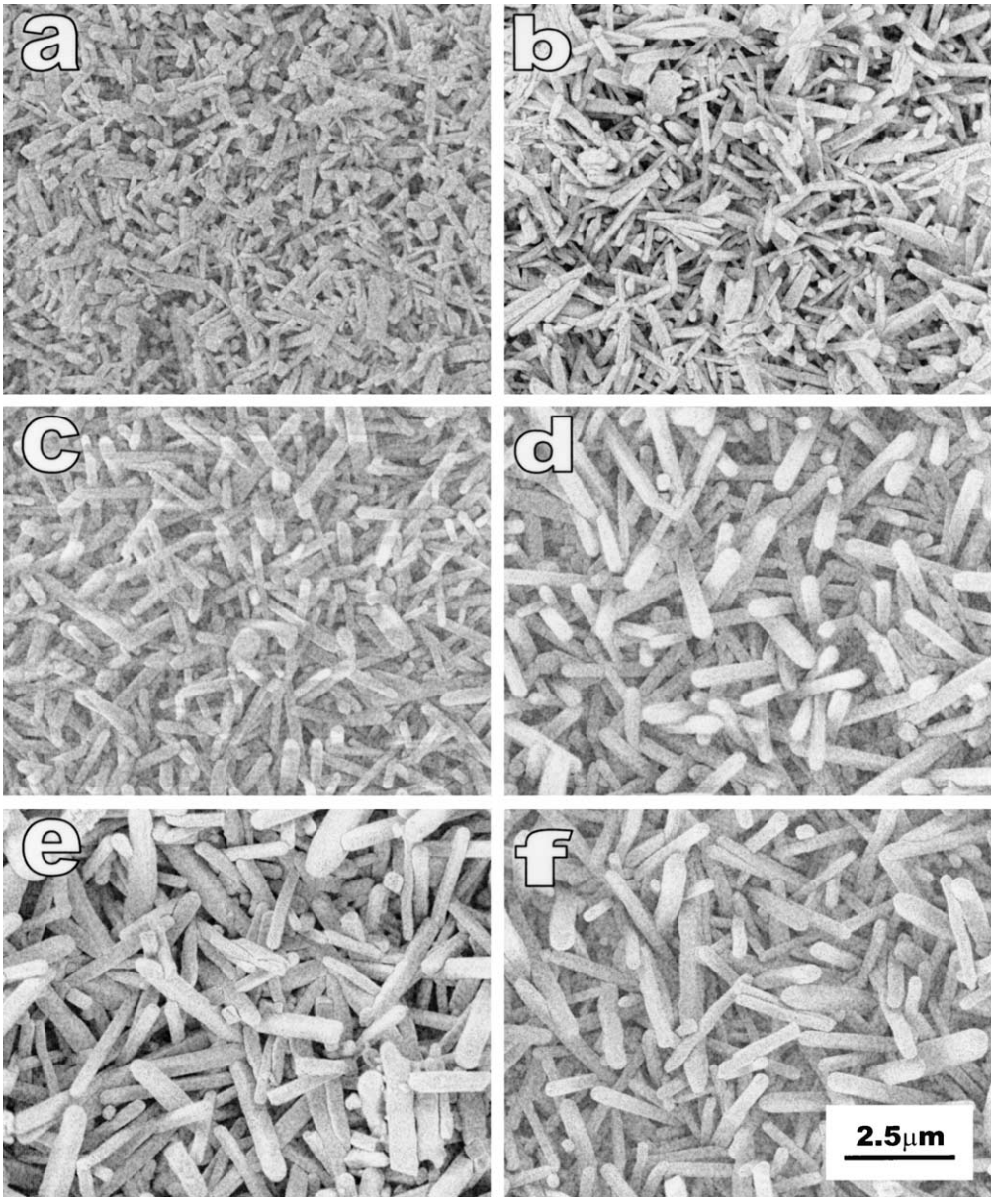

Fig. 6. SEM images of the 10 mol% WO_3 doped sample sintered at different temperatures: (a) 1000 °C, (b) 1100 °C, (c) 1200 °C, (d) 1300 °C, (e) 1400 °C and (f) 1500 °C.

In the sample doped with 5 mol% WO_3, it is noticed that whiskers formed at 1100 °C have a length of ~3 μm and a thickness of ~0.2 μm, with an aspect ratio of 15. Several thick whiskers are found in the matrix consisting primarily of the thinner ones. As the sintering temperature increases to 1200 °C, the number of thick whiskers greatly increases, while the thinner ones become less, which implies that the former grows at the expense of the latter. The size distribution of the mullite whiskers becomes narrow as the sintering temperature further increases to 1300 °C. Only slight increase in the dimensions of the mullite whiskers is observed at temperature higher than 1400 °C, and stopped at a certain temperature (critical size). The whisker growth in the sample doped with 10 and 20 mol% WO_3 follows a similar pattern, with the whisker growth stopping at 1300 °C. However, with increase in WO_3 content, the whiskers become shorter, indicating that the addition of WO_3 has a negative effect on the mullite whisker growth.

Both cross-section and surface of the sintered samples were examined by the SEM measurement. Since it is much easier to have a good image on samples' surface, all the SEM results are surface images. However, the surface images were totally representative of the interior of the sintered bulks. This is confirmed by the cross-sectional SEM images of the 5 mol%-doped samples sintered at different temperatures, as shown in Fig. 8. It indicates that the mullite whiskers grew throughout the bulk of the sintered samples, where some broken whiskers were caused by sample preparation.

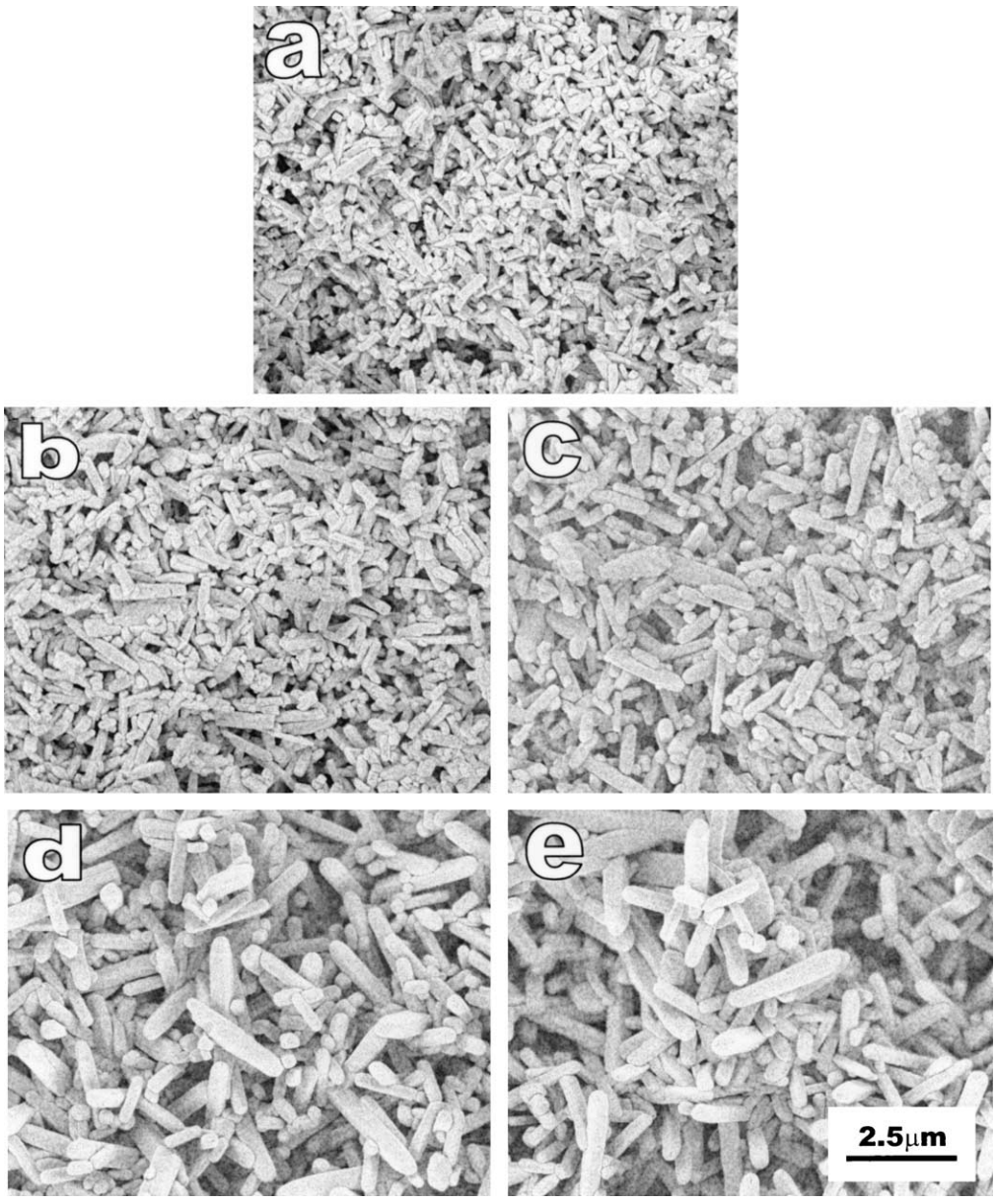

Fig. 7. SEM images of the 20 mol% WO_3 doped sample sintered at different temperatures: (a) 1000 °C, (b) 1100 °C, (c) 1200 °C, (d) 1300 °C and (e) 1400 °C.

The effect of WO_3 on the mullitization temperature, as well as the morphology of the mullite whiskers, can be explained according to the dissolution-precipitation mechanism.[20] It has been reported that mullite formation in diphasic aluminosilicate gels or in reaction sintering couples of quartz and Al_2O_3 is controlled by dissolution-precipitation reactions, where a SiO_2-rich liquid phase is formed at a certain temperature and Al_2O_3 species then dissolve in the liquid phase.[20] As the Al_2O_3 concentration reaches a critical value, random mullite nucleation occurs. The dissolution velocity of Al_2O_3 into the SiO_2 liquid is, therefore, the rate-limiting step for mullite nucleation and crystal growth. Factors that enhance the formation of the SiO_2-rich liquid phase and promote the dissolution of Al_2O_3 into the liquid phase will be helpful to lower the mullitization temperature. In our earlier work, mullite phase was formed from a milled Al_2O_3 and SiO_2 mixture without any doping at a temperature of about 300 °C lower than that in unmilled mixture.[10] The lowered mullitization temperature was attributed to the fact that the starting oxides were greatly refined by the high-energy ball milling process. Due to the low mullitization temperature, mullite grains grew without occurrence of densification. Therefore, the mullite grains grew under an unconstrained environment. As a result, formation of mullite whiskers in this case was possible.

The reduced temperature of mullite phase formation due to the addition of WO_3 in the present work can be explained in a similar manner. It is well known that

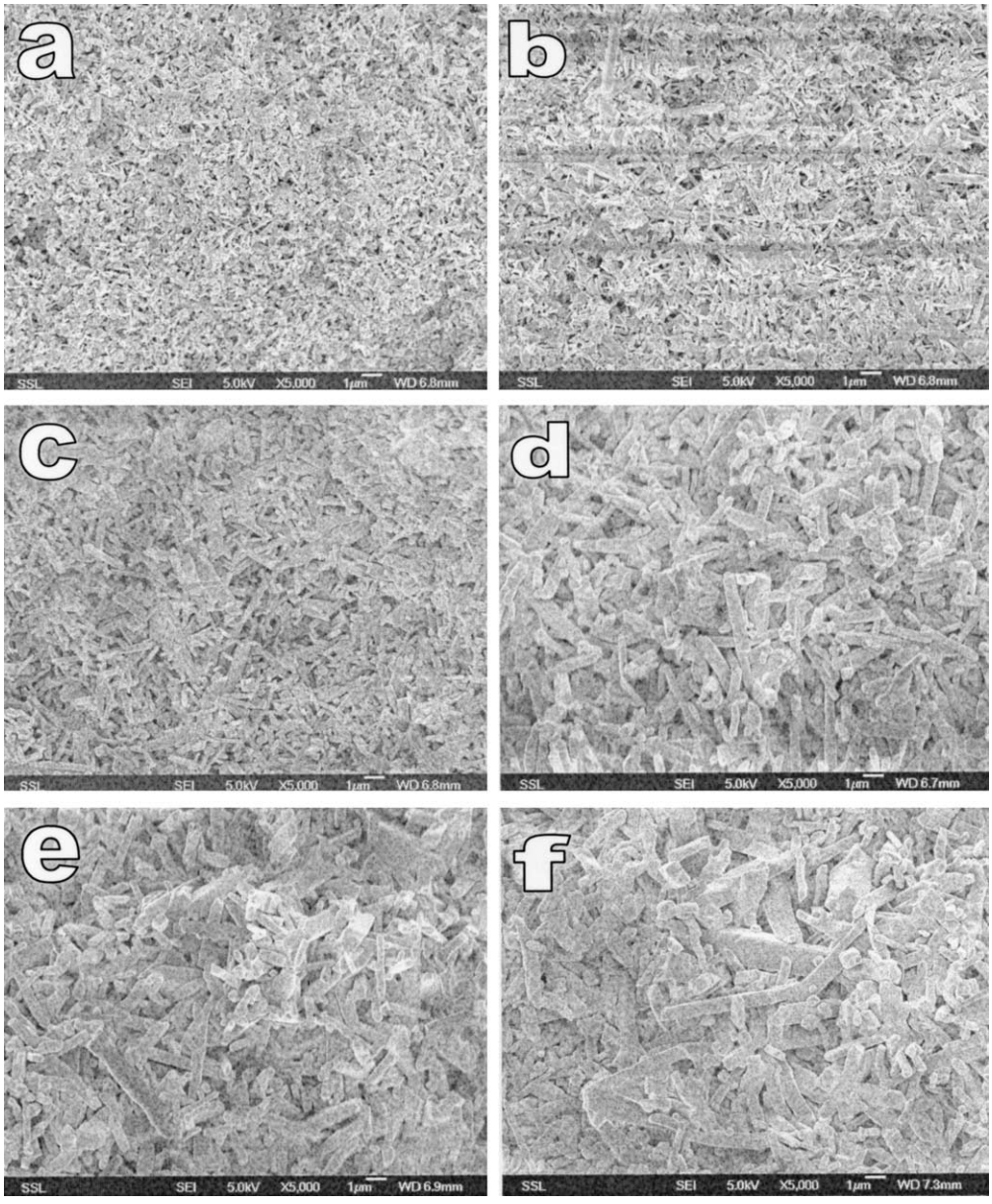

Fig. 8. Cross-sectional SEM image of the 5 mol%-doped sample sintered at different temperatures: (a) 1000 °C, (b) 1100 °C, (c) 1200 °C, (d) 1300 °C, (e) 1400 °C and (f) 1500 °C for 4 h.

mullite phase formation is related not only to the characteristics of the starting materials, but also to the addition of other compounds. For example, the viscosity of the SiO_2-rich liquid phase can be decreased by several orders of magnitude through adding glass-forming oxides, such as B_2O_3 and P_2O_5.[18,19] The reduction in viscosity of the liquid phase is favorable to mullite phase formation. It is reasonable to assume that WO_3 acted as heterogeneous centers where mullite nucleation could be induced at lower temperature, leading to lower mullitization temperature. The higher the WO_3 content, the larger the number of nucleation centers. Therefore, mullite formation temperature decreases with increasing WO_3 content. At the same time, the increased number of mullite nucleation centers was responsible for the shorter whiskers.

4. Conclusions

Mullite whiskers were produced from oxide mixtures activated by the high-energy ball milling process. The addition of WO_3 into the Al_2O_3 and SiO_2 system enhanced the mullite phase formation by lowering the mullitization temperature from 951, to 921 and 835 °C, as the WO_3 content was increased from 5 to 10 and 20 mol%. The dimension of the mullite whisker was reduced with increasing WO_3 content. The effect of WO_3 on the mullite phase formation temperature and

the whisker morphology was believed to be attributed to its effect on the characteristics of the SiO_2-rich liquid phase.

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