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Anisotropic grain growth of mullite in high-energy ball milled powders doped with transition metal oxides

L.B. Kong[a,*], T.S. Zhang[b], J. Ma[b], F. Boey[b]

[a]*Temasek Laboratories, National University of Singapore, 10 Kent Ridge Crescent, Singapore 119260, Singapore*
[b]*School of Materials Engineering, Nanyang Technological University, Nanyang Avenue, Singapore 639798, Singapore*

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Abstract

Dense mullite ceramics with anisotropic grains were derived from the high-energy ball milled mixtures of Al_2O_3 and amorphous silica with the presence of transition metal oxides ($FeO_{1.5}$, CoO and NiO). The mullitization and grain growth behavior of the unmilled mixture without the addition of the transition metal oxides and the undoped system of Al_2O_3 and amorphous silica with and without milling were also investigated and compared. The mullitization temperature was about 1200 °C in the milled systems, 100 °C lower than that required by the conventional solid-state reaction process. The lowered mullitization temperature, as well as the anisotropic grain growth, was attributed to the refined structure of the oxide powders, as a result of the high-energy ball milling. The experimental results have been explained by a dissolution-precipitation mechanism.

Keywords: Anisotrophy; Grain growth; Milling; Mullite

1. Introduction

Anisotropic grain growth has been found to be of great significance in the development of materials with self-reinforcing microstructure. Silicon nitride (Si_3N_4) is a good example showing how the mechanical properties of a polycrystalline ceramic can be improved by optimizing anisotropic grain growth.[1–3] However, due to its relatively low oxidation resistance, Si_3N_4 has shown its disadvantage for high temperature applications.[4] In this respect, development of oxide based ceramics with similar self-reinforcing microstructure is therefore highly desired.

Mullite is a promising candidate of oxide ceramics due to its good mechanical strength, excellent thermal shock and high creep resistance, low thermal conductivity and high-temperature stability.[5–7] Reinforced mullite ceramics have been produced by introducing mullite whiskers, which were derived from a mixture of xerogel, silica gel and aluminum fluoride via the solid-vapor reaction process.[8,9] The introduction of mullite whiskers makes the processing relatively complicated and great care is required to prevent the whiskers from breaking. Therefore, fabrication of reinforced mullite ceramics, via in situ anisotropic grain growth, is more feasible in comparison to whisker-reinforcement.

It is well known that, mullite prepared in the absence of a liquid phase invariably led to an equiaxial microstructure, whereas the formation of anisotropic grains required the presence of a liquid phase.[10,11] According to the Al_2O_3–SiO_2 phase diagrams,[12–14] a liquid phase can be formed in a silica-rich composition at above the eutectic temperature (1590±10 °C). Anisotropic grain growth was reported in single phase mullite ceramics above 1750 °C,[10] which was attributed to the formation of the eutectic phase at this temperature. The presence of other phases was also possible to activate anisotropic grain growth of mullite. For example, dopants such as B_2O_3 and TiO_2 have been shown to reduce the viscosity of the liquid phase and to decrease the mullite phase formation temperature, leading to anisotropic grain growth.[4,11] However, fairly rapid anisotropic grain growth was only observed at temperature above 1600 °C.[11]

In this paper, a simple process for anisotropic grain growth of mullite will be presented. The in situ anisotropic grain growth was observed in oxide powders

* Corresponding author. Tel.: +65-687-46910.
E-mail address: tslklb@nus.edu.sg (L.B. Kong).

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activated by a high-energy ball milling process. The most significant aspect of this process is that the anisotropic grain growth occurred at a temperature much lower than those required by the conventional solid-state reaction process[10] and oxides-doped aluminosilicate gels.[11] The effect of transition metal oxides ($FeO_{1.5}$, CoO and NiO) on the temperature of mullite phase formation and dimensions of the mullite grains, will be discussed. In addition, mullite phase formation and microstructural development, of the powders for pure mullite with and without milling and the unmilled powders doped with the transition metal oxides, will also be presented for comparisons.

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), Fe_2O_3 (>99% purity, MERCK, Damstadt, Germany), CoO (99.99% purity, Aldrich Chemical Company Inc., USA) and NiO (99 + % purity, Aldrich Chemical Company Inc., USA) powders were used as the starting materials. Before high-energy ball milling, the starting powders were thoroughly mixed via the conventional milling process, using ZrO_2 vial and balls. Mixture of Al_2O_3 and silica without any dopants was also investigated as a comparison. In the case of transition oxide doping, the sample composition was $(3Al_2O_3{\cdot}2SiO_2)_{0.9}(MO_y)_{0.1}$ ($MO_y = FeO_{1.5}$, CoO and NiO), corresponding to a transition metal oxide weight concentration of about 2%. Both the undoped and doped mixtures were divided into two groups. One group was milled via the high-energy ball milling and another was not. The milling operation was carried out for 5 h using a Fritsch Pulverisette 5 planetary high-energy ball milling machine. A 250 ml stainless steel vial and 100 stainless steel balls with diameter of 10 mm were used as the

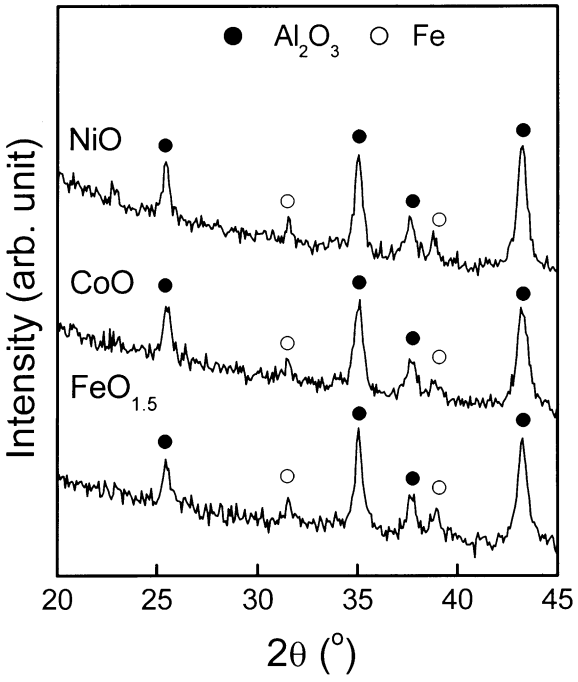

Fig. 1. XRD patterns of the mixed powders.

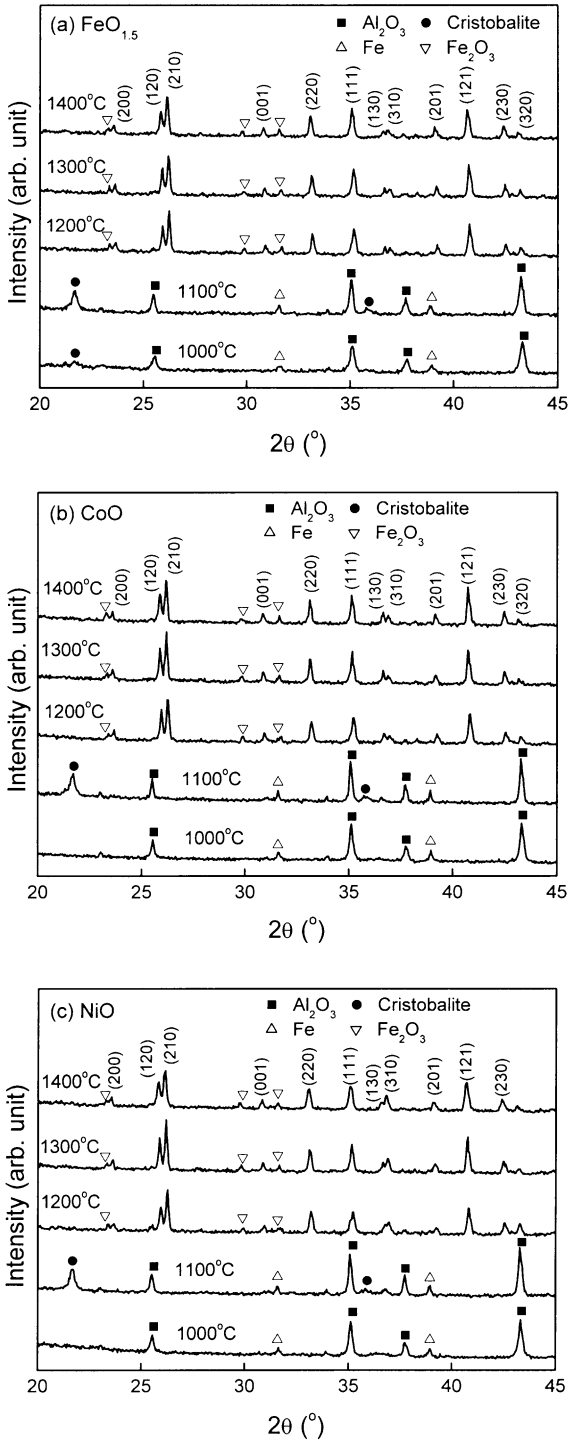

Fig. 2. XRD patterns of the milled mixtures doped with the transition metaal oxides sintered at different temperatures.

milling medium. The milling speed was 200 rpm, with a ball-to-powder weight ratio of about 20:1.

All milled and unmilled 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 h. The sintering was conducted at temperature from 1000 to 1400 °C, at heating and cooling rate of 10 °C/min.

X-ray diffraction analysis of the powders 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. Thermal analysis was conducted using a Setaram Labsys™ type TG-DTA/DSC system (Caluire, France) in nitrogen gas flow. 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 medium. The microstructure and grain morphology of the sintered samples were examined using a Jeol (Tokyo, Japan) JSM-6340F type field emission scanning electronic microscope (FESEM). The anisotropic parameters (length and thickness) of the mullite grains were estimated from the SEM images.

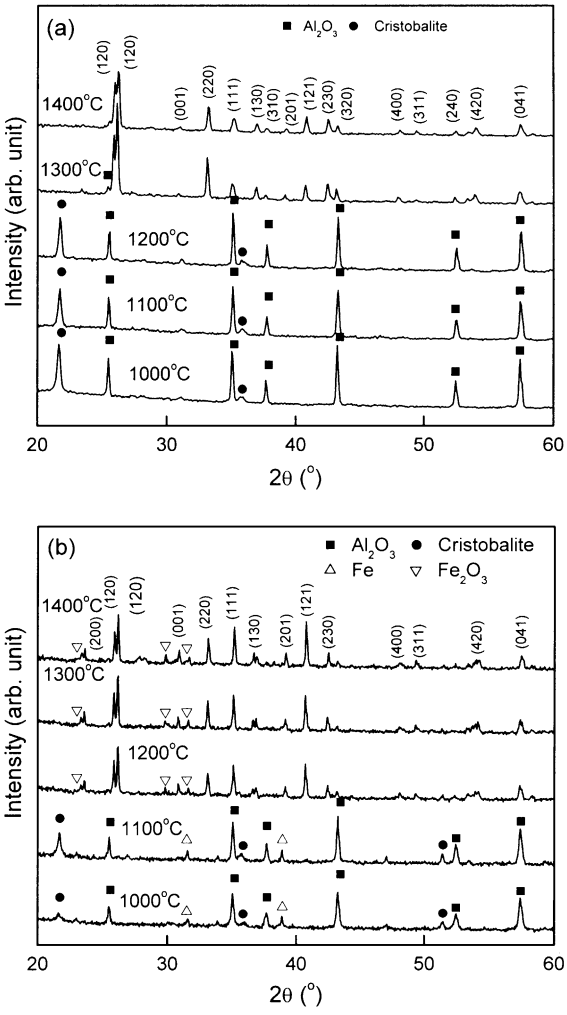

Fig. 3. XRD patterns of the undoped mixtures of Al_2O_3 and silica for pure mullite sintered at different temperatures: (a) unmilled and (b) milled for 5 h.

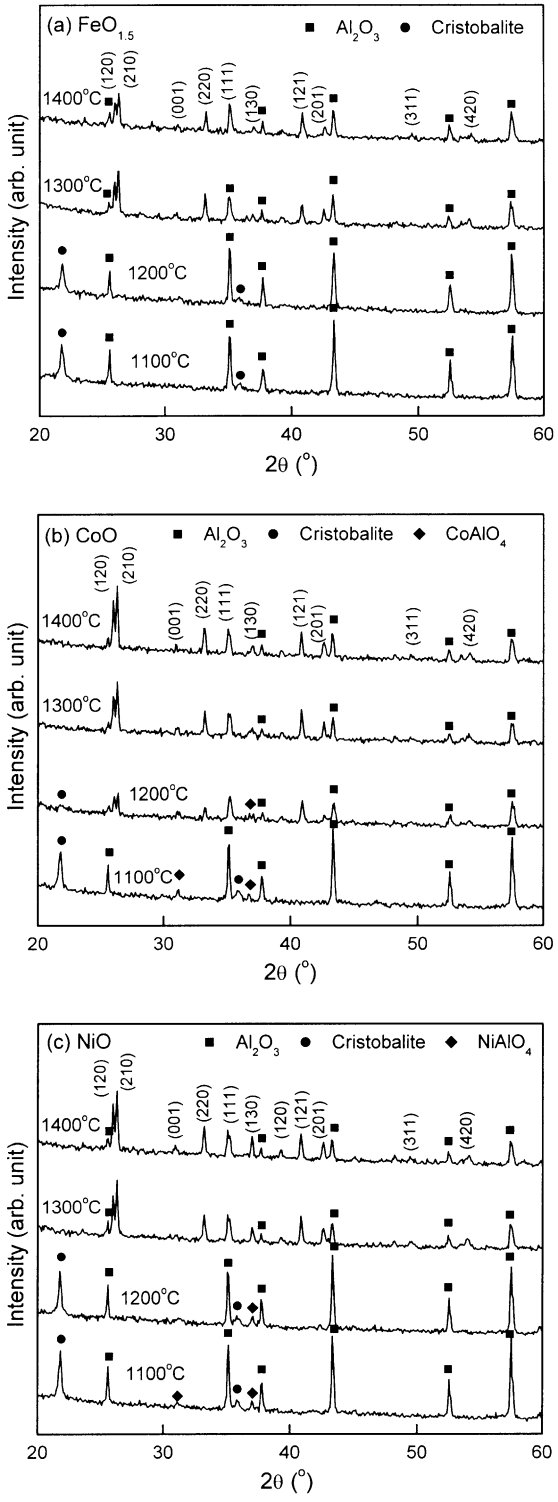

Fig. 4. XRD pattern of the unmilled mixtures doped with the transition metal oxides sintered at different temperatures.

3. Results and discussion

Fig. 1 shows the XRD patterns of the powders milled for 5 h using a high-energy ball milling with stainless steel vial and balls. The diffraction peaks of Al_2O_3 are greatly reduced and broadened compared to those in the unmilled samples, indicating refinement of the powders as a result of the high-energy ball milling. A trace of Fe is observed as a minor phase, which was from the milling media due to strong collision during the milling process. No silica phase is detected by the XRD measurement because of its amorphous state. It is also noticed that no reaction happened during the milling process. All transition metal oxides ($FeO_{1.5}$, CoO and NiO) are also not detected by the XRD measurement, which is due mainly to their low concentration. However, the effect of the transition metal oxides on the phase formation and microtructural development of mullite ceramics is clearly presented by the experimental results which will be shown later.

XRD patterns of the milled powders, sintered at different temperatures, are shown in Fig. 2. Similar patterns are observed in all three groups. In the samples sintered at 1000 °C for 4 h, the dominant phase is Al_2O_3. As the sintering temperature increases to 1100 °C, besides Al_2O_3, cristobalite is detected by the XRD measurement, which was crystallized from the amorphous silica. After sintering for four hours at 1200 °C, almost single

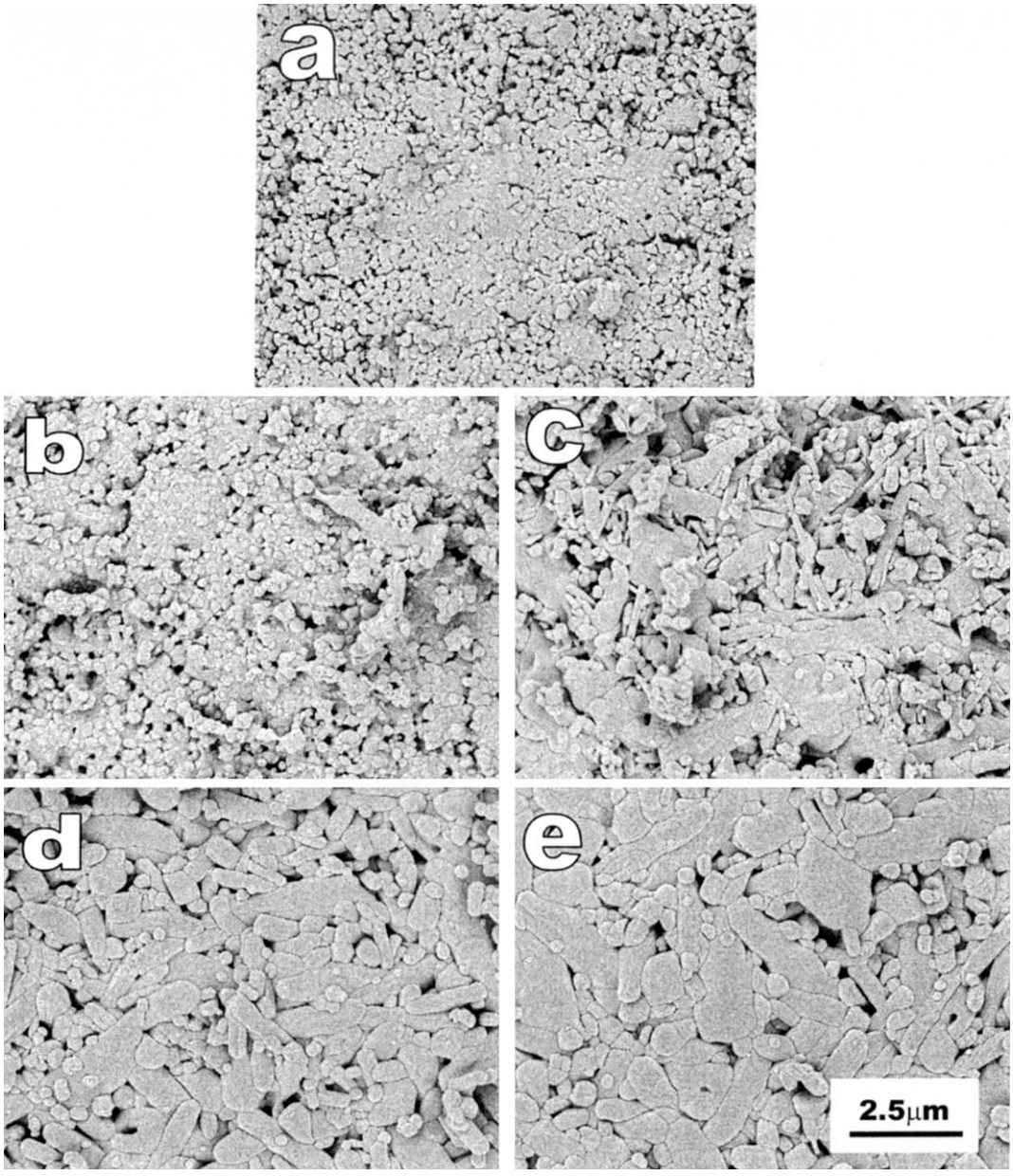

Fig. 5. SEM images of the $FeO_{1.5}$-doped mixture sintered at different temperatures: (a) 1000 °C, (b) 1100 °C, (c) 1200 °C, (d) 1300 °C and (e) 1400 °C.

phase mullite is formed. This temperature, at which mullite can be formed in the present work, is nearly 100 °C lower than that required by the conventional solid-state reaction process.[15] It is also necessary to point out that although formation of $NiAl_2O_4$ spinel was reported as mullite crystallized from aluminosilicate gels with NiO,[16] it is very hard to identify MAl_2O_4 (M = Co and Ni) in the present work. This is probably due to the fact that the concentration of the transition metal oxides in this work is much lower than that reported in the literature.[16] The iron contamination coming from the milling media was stable at 1100 °C and oxidized into Fe_2O_3 at 1200 °C. Similar result was observed in the sample without the addition of the transition metal oxides, as can be seen later.

To show clearly the effect of the high-energy ball milling and the addition of the transition metal oxides on the phase formation of mullite, the unmilled and milled mixture of Al_2O_3 and silica without the addition of the transition metal oxides and unmilled powders with the transition oxides, were also investigated. Their XRD patterns are shown in Figs. 3 and 4, respectively. Fig. 3(a) demonstrates that mullite phase formation occurred at 1300 °C in the mixture of Al_2O_3 and silica which was not milled by the high-energy ball milling process, while mullitization took place at 1200 °C after

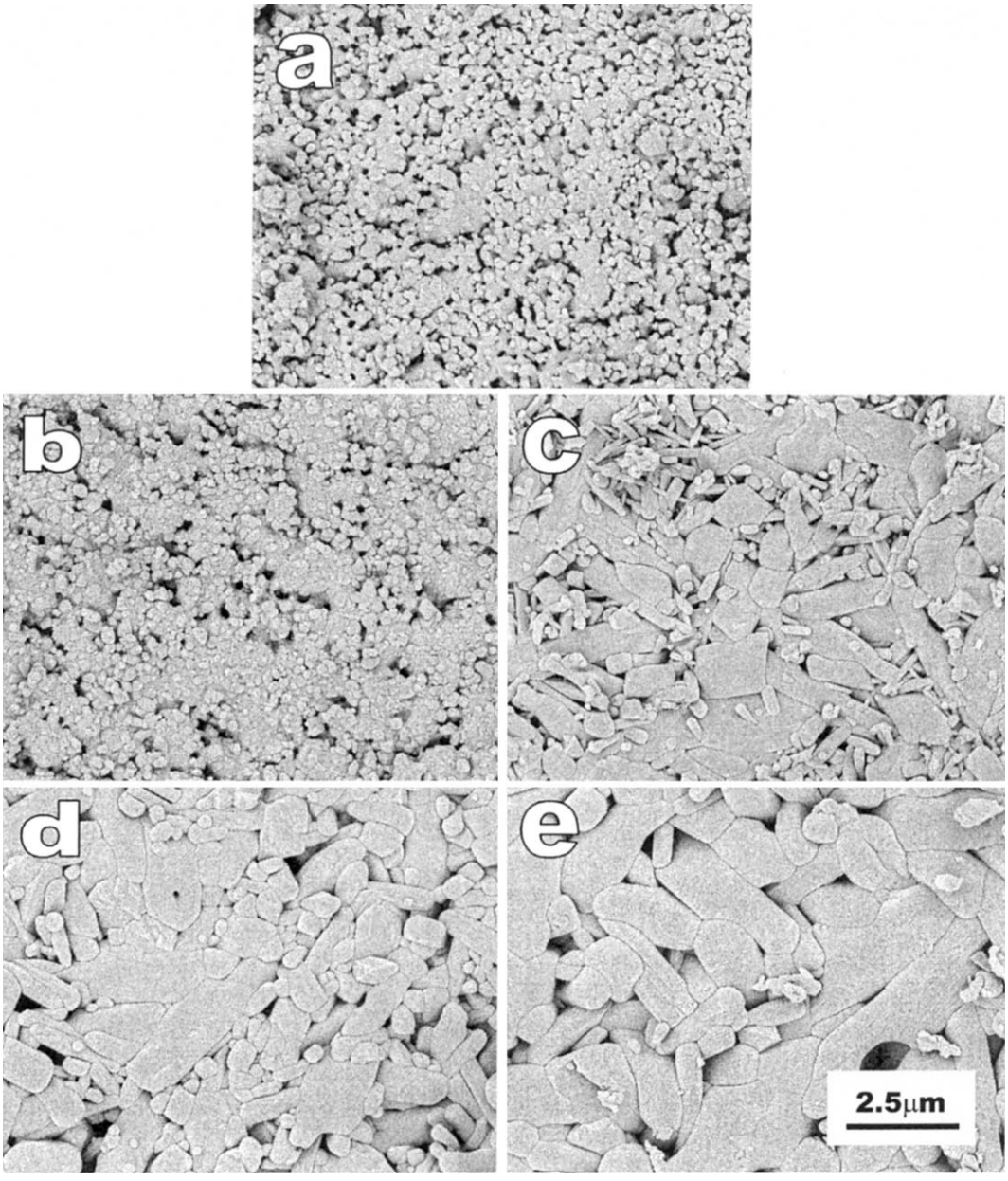

Fig. 6. SEM images of the CoO-doped mixture sintered at different temperatures: (a) 1000 °C, (b) 1100 °C, (c) 1200 °C, (d) 1300 °C and (e) 1400 °C.

the mixture was milled for 5 h (Fig. 3b). For the doped powders which were not subjected to high-energy ball milling, mullite phase formation temperature was also 1300 °C in the case of $FeO_{1.5}$ and NiO doping, while the occurrence of mullitization already took place at 1200 °C in the sample doped with CoO. This observation means that $FeO_{1.5}$ and NiO show almost no influence on the mullite phase formation, while CoO has a positive effect on the mullitization behavior. In addition, a trace of $CoAl_2O_4$ and $NiAl_2O_4$ was detected by the XRD measurement, in the case of CoO and NiO doping. It is different from that observed in the milled samples, where spinel phase was not detected.

SEM images of the sintered samples are shown in Figs. 5–7. Anisotropic grain growth is observed in all the three systems. Fig. 5 indicates that the sample sintered at 1000 and 1100 °C comprises equiaxed grains, while that sintered at 1200 °C is of anisotropic grains. The grain dimension increases as the sintering temperature is further increased. As compared to the XRD patterns shown in Fig. 3(a), it is found that as long as mullite phase is formed, the anisotropic grain growth occurred. The anisotropic parameters of the mullite grains estimated from the SEM images are listed in Table 1, with grain dimension increasing from $FeO_{1.5}$ to CoO and NiO.

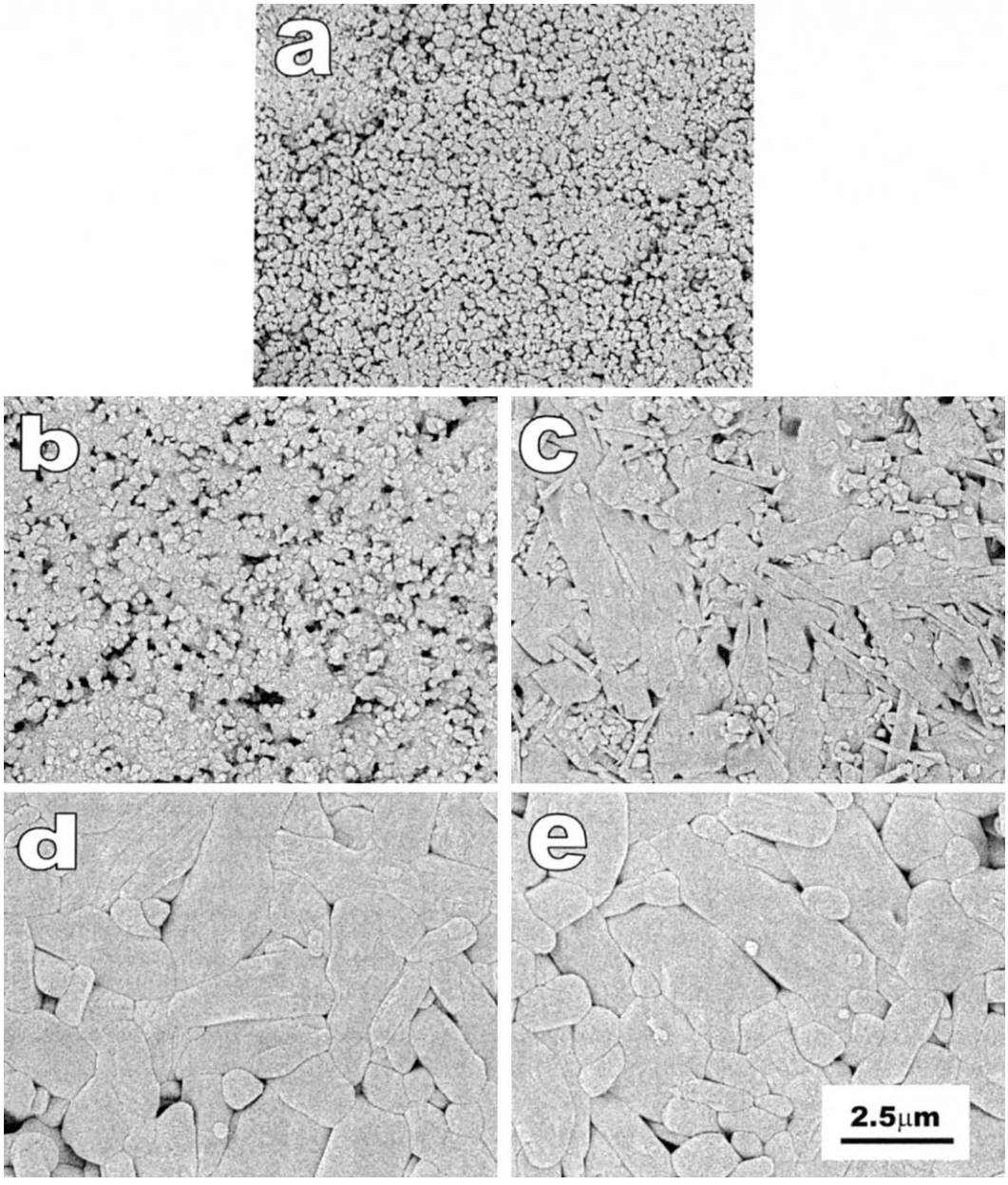

Fig. 7. SEM images of the NiO-doped mixture sintered at different temperatures: (a) 1000 °C, (b) 1100 °C, (c) 1200 °C, (d) 1300 °C and (e) 1400 °C.

Table 1
Dimension parameters of the mullite whiskers derived from the milled powders

Dopant	Sintering temperature (°C)	Length (μm)	Thickness (μm)	Aspect ratio
$FeO_{1.5}$	1200	2.1±0.8	0.5±0.2	4.2
	1300	3.6±1.2	0.7±0.4	5.1
	1400	4.7±2.2	1.2±0.8	3.9
CoO	1200	2.3±0.5	0.6±0.2	3.8
	1300	3.1±0.9	0.8±0.5	3.9
	1400	5.2±1.1	1.4±0.7	3.7
NiO	1200	2.8±0.5	0.6±0.3	4.7
	1300	4.9±0.9	1.5±0.7	3.3
	1400	6.2±1.1	2.1±0.9	2.9

Figs. 8 and 9 show the SEM images of the undoped mixture of Al_2O_3 and silica without and with high-energy ball milling, sintered at 1100–1400 °C for 4 h. It is demonstrated that the sample without the transition metal oxides and high-energy ball milling is characterized by equiaxed grains. No anisotropic grain growth is observed in this case. The relative density of the unmilled sample indicated that very high density can be achieved after sintering at 1100 °C, while almost fully dense (>95% of the theoretical density, 3.17 g/cm^3) samples have been obtained at 1200 °C,[25] at which, however, mullite phase was not yet formed [Fig. 3(a)]. Mullite formation is only observed at 1300 °C, which means that the densification occurred before mullitization. The densification of the unmilled mixture before the mullite formation has been explained by the transient viscous sintering theory.[11,17]

In the mixture that was milled for 5 h, totally different grain growth behavior is observed. As shown in Fig. 9, the mixture sintered at 1000 and 1100 °C have only equiaxed grains. By comparing with Fig. 3(b), one can find that mullite phase was not formed below 1100 °C. However, well-developed mullite whiskers are observed in the sample sintered at 1200 °C, at which mullitization has completed. The dimension of the mullite whiskers increases with increasing sintering temperature.

Fig. 10 shows selected SEM images of the doped samples derived from the powders that were not milled. Similar to the undoped and unmilled sample, only normal equiaxed grains are observed, which means that the addition of the transition metal oxides is not the direct cause of the anisotropic grain growth. Instead, it is the high-energy ball milling that makes it possible to achieve mullite ceramics with anisotropic microstructures. However, the presence of the transition metal oxides affected the microstructures of the mullite ceramics derived from the milled powders (Figs. 5–7).

From the above experimental results, following conclusions can be easily arrived. The high-energy ball milling reduced the mullite formation temperature by about 100 °C in the mixture of Al_2O_3 and silica without

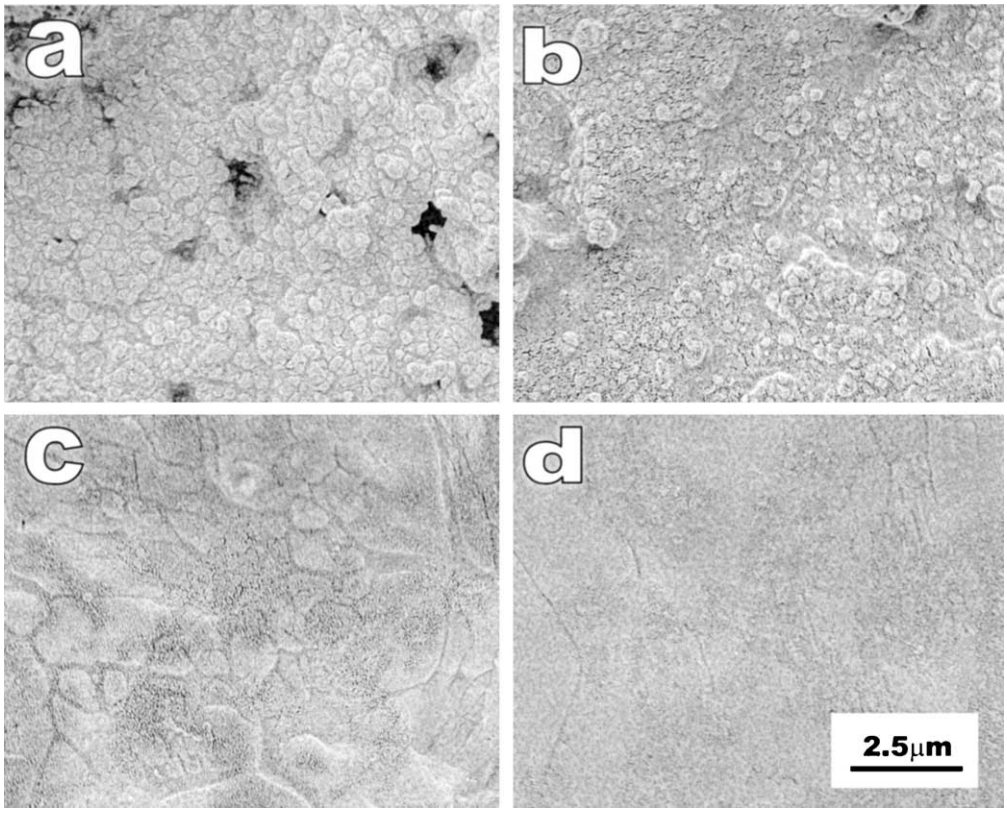

Fig. 8. SEM images of unmilled mixture of Al_2O_3 and silica for pure mullite sintered at: (a) 1100 °C, (b) 1200 °C, (c) 1300 °C and (d) 1400 °C.

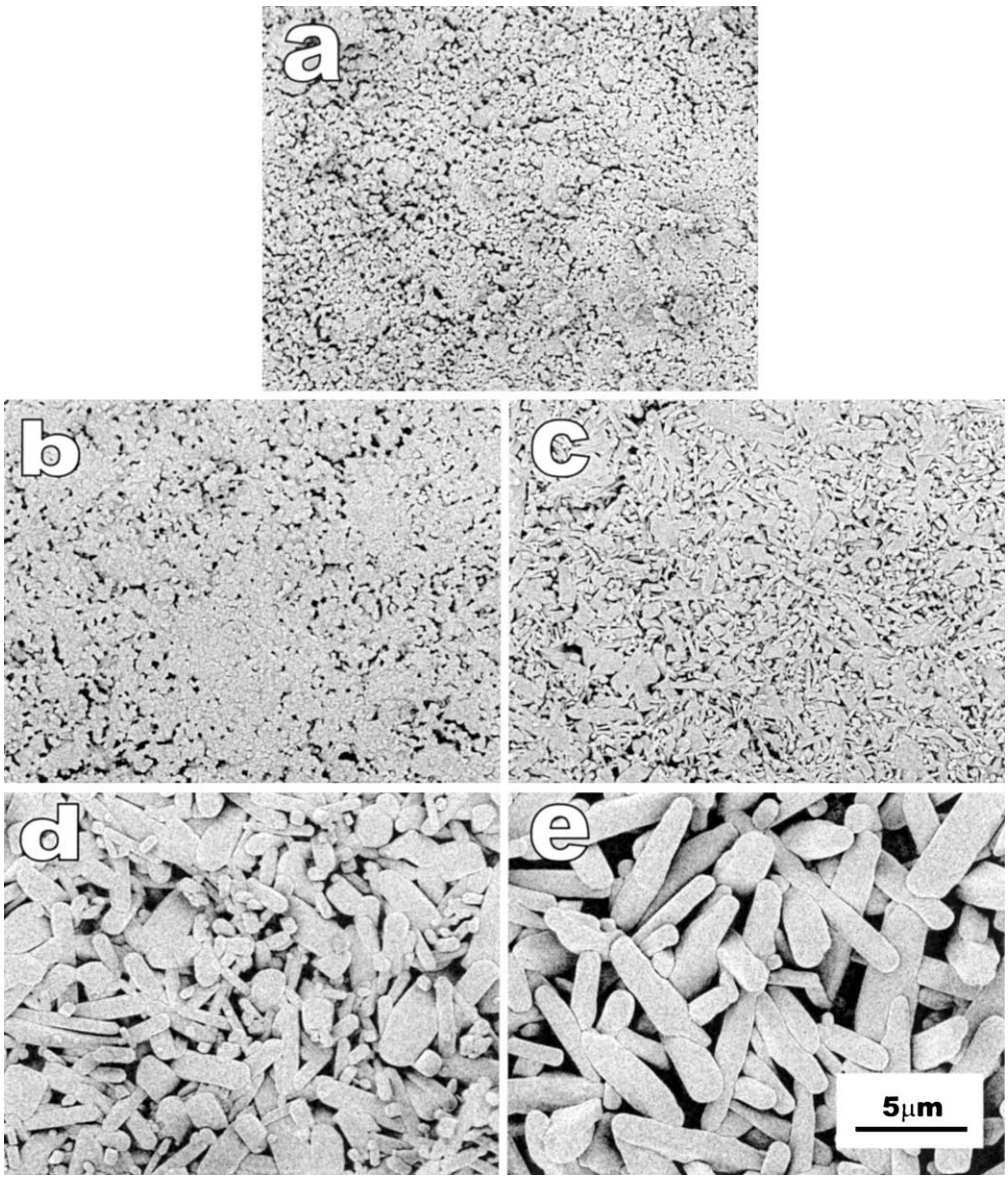

Fig. 9. SEM images of the milled mixture of Al_2O_3 and silica for pure mullite sintered at: (a) 1100 °C, (b) 1200 °C, (c) 1300 °C and (d) 1400 °C.

the addition of transition metal oxides. The unmilled sample experienced densification before the mullite phase formation and possessed normal equiaxed grains, while the milled powder did not densify due to the formation of the mullite whiskers. The addition of CoO reduced the mullitization temperature, while $FeO_{1.5}$ and NiO have no such effect. Dense mullite ceramics with anisotropic grains were derived from the milled samples doped with transition metal oxides, while only normal grains were observed in the doped mixtures without high-energy ball milling.

Mullite phase formation in diphasic aluminosilicate gels or in reaction sintering couples of quartz and Al_2O_3 is controlled by dissolution-precipitation reactions, where Al_2O_3 species dissolve in the SiO_2-rich liquid phase.[18] As the concentration of Al_2O_3 reaches a critical level, random mullite nucleation will be induced in the bulk of the liquid phase. The dissolution velocity of Al_2O_3 into the SiO_2 liquid is, therefore, the rate-limiting step for mullite nucleation and crystal growth. Al_2O_3 dissolution velocity is dependent on the viscosity of the liquid phase as well as on the particle size of Al_2O_3. Mullite phase formation is related to both the formation ability of the SiO_2-rich liquid phase and the dissolution velocity of the Al_2O_3 into the liquid phase.

High-energy ball milling or mechanochemical processing, which was initially invented for ceramic strengthened alloys,[18] has been used to synthesize a wide range of nano-sized ceramic powders including ZrO_2,[19] YBCO superconductors,[20] ferrites[21] and ferroelectrics.[22] This technique is superior to both the conventional solid-state reaction and the wet-chemistry-based processing routes for several reasons, such as the use of low-cost and widely available oxides as starting materials, low

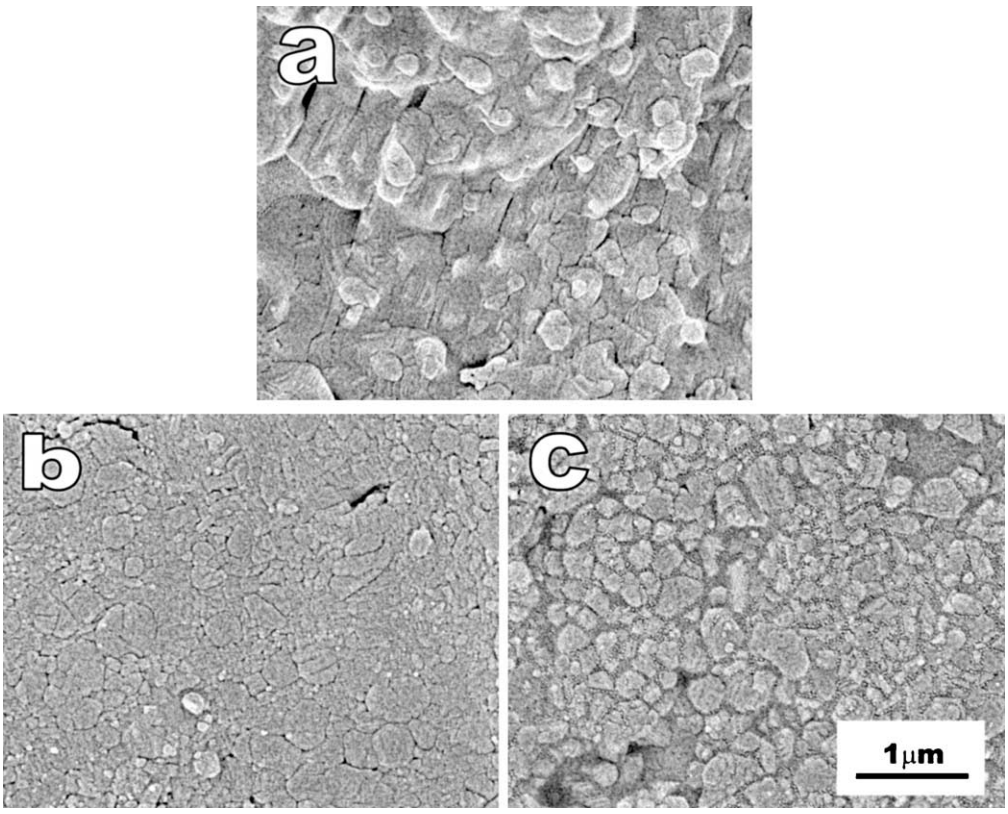

Fig. 10. SEM images of the unmilled mixtures sintered at 1400 °C: (a) $FeO_{1.5}$, (b) CoO and (c) NiO.

operating temperature and simple facility requirement. Besides its success in the synthesis of nano-sized powders, high-energy ball milling has also been employed to modify starting materials in order to reduce phase formation temperature. For example, the reaction between commercial $BaCO_3$ and TiO_2 to $BaTiO_3$ usually required a calcination temperature of higher than 1000 °C. After milling $BaCO_3$ and TiO_2 for 10 h, $BaTiO_3$ can be formed at temperature as low as 800 °C.[23] The reduced calcination temperature was attributed to the refined $BaCO_3$ and TiO_2 powders.

In the present work, since the oxide mixtures were milled by the high-energy ball milling process, the particle size of the starting materials was greatly reduced. As a result, the liquid phase is formed at lower temperature and the dissolution velocity of Al_2O_3 into the liquid is higher, as compared to the unmilled powders, both of which are favorable to low mullitization temperature. This explanation is supported by the particle size distribution of the mixture with and without milling. Fig. 11 shows the size distribution of the mixture of Al_2O_3 and silica before and after the milling. Both reduced particle size and narrowed size distribution as a result of the high energy ball milling are observed. Similar result was obtained in the samples doped with the transition metal oxides.

Mullite has an orthorhombic structure with lattice parameters $a = 7.5456$ Å, $b = 7.6968$ Å and $c = 2.8842$ Å (JCPDS No. 15-776). Due to its anisotropic structure, mullite has a strong tendency to grow anisotropically if the grain growth occurs under an unrestrictive environment.[8] This is the reason why whiskers or needlelike mullite can be formed easily during vapor-solid synthesis[8] or in melten salt flux.[5] In the conventional solid-state reaction process and most chemical processing routes, sample densification occurred before mullite formation via a

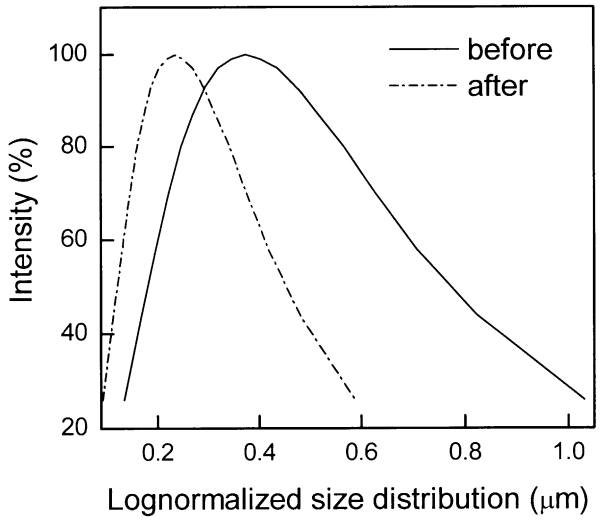

Fig. 11. Particle size distribution of the mixture of Al_2O_3 and silica before and after the high-energy ball milling.

transient viscous flow sintering.[10,11,17] It is, therefore, difficult for mullite grains to grow anisotropically under the constrained environment. As discussed in the introduction, to achieve anisotropic grain growth, high temperature (>1590 °C, the eutectic temperature) is required.[10,11] In comparison, our milled powders had a very low mullitization temperature, which offered an environment where anisotropic grain growth was possible, that is, the mullite phase formation occurred before the samples densified. Further work is underway to clarify this hypothesis.

The effect of transition metal oxides on the dimension of the anisotropic mullite grains can be closely related to their effect on the viscosity of the SiO_2-rich liquid phase. A number of dopants such as transition metal oxides, B_2O_3 and TiO_2 have been reported to promote anisotropic grain growth in mullite, which was attributed to the fact that the oxides reduced the glass viscosity and thus increased the mobility of diffusing species.[4,11]

The advantage of anisotropic grain growth of mullite in the milled oxides is that it happens at a temperature which is significantly lower than that observed in conventional sintered mullite ceramics[10] and doped aluminosilicate gels.[11] Furthermore, it is possible to fabricate in situ reinforced mullite ceramics by introducing the milled powders into the conventional solid-state reaction system. The volume fraction of the anisotropic grain growth can be controlled by adjusting the amount of the milled powder addition. Related works are underway and will be reported separately.[24]

4. Conclusions

The high-energy ball milling reduced the mullite formation temperature by about 100 °C and led to the formation of mullite whiskers, in the mixture of Al_2O_3 and silica. The addition of the transition metal oxides ($FeO_{1.5}$, CoO and NiO), combined with the high-energy ball milling process, produced dense mullite ceramics with anisotropic microstructures. The lowered mullite formation temperature was attributed to the refinement of the oxides as a result of the high-energy ball milling. The anisotropic grain growth of mullite was due to the fact that mullite phase was formed before densification. The effect of the transition metal oxides on the dimension and morphology of the mullite grains might be due to the different roles they played during the formation of the formation of the SiO_2-rich liquid phase, which means the transition metal oxides can be used to control the microstructure of the anisotropic mullite ceramics.

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