

The influences of fluorine and chlorine ions on the formation of nanostructure forsterite during mechanical activation of talc and periclase

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The effects of mechanical activation of a powder mixture of basic talc and periclase on the reaction rate of the formation of the forsterite structure were studied in the absence and presence of fluorine and chlorine ions. Mechanical activation with fluorine/chlorine ions caused the formation of a series of intermediate transition compounds in an explosive reaction that enhanced the forsterite fabrication rate. Fluorine/chlorine ions were released from the system by hydrolysis. Single-phase nanocrystalline forsterite powder was successfully synthesized by 1 h of mechanical activation with subsequent annealing at 1000 and 1200 °C for 1 h in the presence of fluorine ions. In the presence of chlorine ions, single-phase forsterite powder was obtained after 1 h of mechanical activation with subsequent annealing at 1200 °C for 1 h, but the crystallite size of this sample was larger than 100 nm. In the absence of these ions, forsterite can be fabricated by 5 h of mechanical activation with subsequent annealing at 1000 °C for 1 h.

Key words: Mechanical activation, Forsterite, Nanostructure materials, Fluorine ions, Chlorine ions.

Introduction

Forsterite is a crystalline magnesium silicate with the chemical formula Mg_2SiO_4 . It is used in electronic ceramics, ceramic-metal seals, refractories and cements due to its low thermal expansion, low dielectric permittivity, high melting point (1890 °C), good chemical stability and excellent insulation properties even at high temperatures [1-4].

Different methods have been utilized to synthesize forsterite ceramic, including the solid state reaction of MgO and SiO_2 [1], bauxite and MgCO_3 [5], and also by various sol-gel methods [6, 7]. The solid state reaction of MgO and SiO_2 is a sluggish reaction due to the relatively low diffusivity of the compounds formed. Therefore, pure forsterite can not be obtained and metastable phases such as enstatite (MgSiO_3) may be formed because of its faster kinetics [8]. The presence of enstatite (MgSiO_3) in forsterite refractories can be detrimental to the high temperature properties and the behavior of the material because enstatite dissociates into forsterite and a SiO_2 -rich liquid at 1557 °C [9]. To avoid the formation of these phases, thermal treatments up to 1200-1600 °C are required [10].

Although, Kiss *et al.* [11] investigated the positive effect of fluorine ions on the formation of the forsterite structure, they could not fabricate single-phase nanocrystalline forsterite powder by this route. As it is recognized that the formation of the forsterite structure is a sluggish process, the aim of this paper is to synthesize single-phase nano-

crystalline forsterite powder from a mixture of basic talc and periclase (MgO) by mechanical activation in the presence and absence of fluorine and chlorine ions.

Experimental Procedure

Sample preparation

The raw materials used in this study include talc ($\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$) (98% purity), periclase (98% purity), ammonium fluoride (NH_4F) (98% purity) and ammonium chloride (NH_4Cl) (98% purity) all of them from the Merck company. Three mixtures were prepared to study the reaction of forsterite formation. The first mixture was prepared by mixing periclase and talc powders with a molar ratio of 5 : 1 to obtain stoichiometric forsterite. To evaluate the effect of fluorine ions on the forsterite reaction rate, the second mixture was prepared on the basis of the previous starting materials containing NH_4F powder. The powders of $\text{MgO} : \text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2 : \text{NH}_4\text{F}$ with a stoichiometric composition of forsterite were weighed with molar ratios of 5 : 1 : 2. The third mixture was prepared to be the same as mixture 2 but NH_4Cl powder was used instead of NH_4F powder. The mixtures were milled in a planetary ball mill (Fritsch P7 type) under ambient conditions. The milling media consisted of a hardened steel vial with five 20 mm diameter balls (each ball was 32.5 g weight). In all milling runs the ball-to-powder weight ratio was 10 : 1 and the rotational speed of the main disc was set at 500 rpm. After milling for 5 minutes, 1 and 5 h, heat treatments were carried out at 1000 and 1200 °C for 1 hour.

Characterization of forsterite powder

The microstructure of specimens was observed with

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a Philips XL30 scanning electron microscope (SEM). The crystalline phases of specimens were determined by X-ray diffractometry (Philips X'PERT MPD diffractometer, XRD with Cu K α radiation ($\lambda = 0.154056$ nm) and a Ni filter. The scanning range of the samples was from 20 to 80°, with a scanning speed of 0.04°s⁻¹. The accelerating voltage and current were 20 kV and 30 mA, respectively. The crystallite size of forsterite powder was determined by the Williamson–Hall equation [12]:

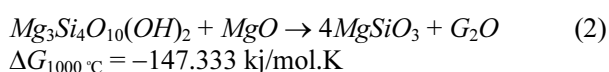
$$\beta \cos \theta = \frac{0.9\lambda}{D} + \varepsilon \sin \theta \quad (1)$$

where β is the full-width at half maximum intensity, λ is the wavelength of the X-rays used ($\lambda = 0.154056$ nm), D is the average crystallite size, θ is the Bragg angle, and ε is the residual strain in the powder.

Results and Discussion

XRD phase analysis

X-ray diffraction patterns of mixture 1 (talc and periclase) samples which were mechanically activated for 5 minutes, 1 and 5 h and then annealed at 1000 and 1200 °C for 1 h are shown in Figs. 1(a) and (b), respectively. As can be seen, in the sample milled for 5 minutes the XRD peaks of talc disappeared and enstatite and MgO peaks appeared on the XRD trace after subsequent annealing at 1000 °C for 1 h. At this stage, enstatite could be formed according to the following equation:



By increasing the milling time to 1 h, the XRD peaks of the enstatite phase vanished after subsequent annealing. It can be concluded that the enstatite produced reacts with the remaining MgO and produces forsterite according to the following equation:



As can be seen in the X-ray diffraction patterns, the peaks of enstatite and MgO disappeared and forsterite was formed after 5 h milling time.

In contrast to Fig. 1(a), for the samples milled for 5 minutes and 1 h, the fraction of the forsterite phase in Fig. 1(b) increased enormously after subsequent annealing at 1200 °C for 1 h while the fraction of periclase and enstatite phases reduced. As can be seen in Fig. 1(b), for the sample milled for 5 h just the forsterite phase could be detected in the XRD pattern after subsequent annealing. With an increase in the annealing temperature, the intensity of forsterite peaks increased as a result of the better crystallinity of the forsterite powder and the recovery of internal strain and growth of the crystallite size [8].

Figs. 1(c) and (d) show the X-ray diffraction patterns of milled powder of mixture 2 (talc and periclase containing ammonium fluoride, NH₄F) samples for 5 minutes, 1 and

5 h milling with subsequent annealing at 1000 and 1200 °C, respectively. Ball milling of mixture 2 affected the mechanism of forsterite formation and increased the rate of reactions. As seen in Fig. 1(c) (in comparison to Fig. 1(a)), in the presence of fluorine ions, the fraction of the forsterite phase increased and fluorine ions increased the rate of reactions. The XRD results (Fig. 1(c)) showed that a single phase forsterite powder was obtained after 1 h milling with subsequent annealing at 1000 °C for 1 h. By increasing the temperature to 1200 °C (Fig. 1(d)), no compositional changes of the powder were observed, except that the peak intensity of the forsterite phase increased as a result of increasing the crystallinity of the forsterite powder produced. Kiss *et al.* [11] studied the formation mechanism of forsterite in the presence of fluorine ions. They reported the production of MgF₂ in the MgO–SiO₂–SiF₄ system. The presence of fluorine ions caused the formation of a series of more complex compounds [12] such as (Mg₂SiO₄)₄–Mg (F,OH)₂ (clinohumite) during mechanical activation which in turn, increased the rate of reactions. Clinohumite is a compound of the humite group which can be fabricated during a mechanical activation process. Clinohumite as a transition product affected the mechanism of the formation of forsterite and increased the rate of formation reactions of forsterite. In the present study, single-phase forsterite powder could be fully fabricated after 1 h ball milling with subsequent annealing at 1000 °C for 1 h. In the absence of fluorine ions (mixture 1), forsterite could be fabricated by 5 h of mechanical activation with subsequent annealing at 1000 °C for 1 h.

X-ray diffraction patterns of mixture 3 (talc and periclase containing ammonium chloride, NH₄Cl) sample powders which were mechanically activated for 5 minutes, 1 and 5 h and then annealed at 1000 and 1200 °C for 1 h are shown in Figs. 1(e) and (f), respectively. As can be seen, mechanical activation with chlorine ions enhances the forsterite formation in a basic talc–MgO mixture at a lower temperature. Detailed analysis of the change of the MgO diffraction line intensities, as one of the possible parameters for describing the reaction advance, showed that a prolonged activation time speeded up the reaction in the three mixtures. The faster disappearance of MgO diffraction lines in mixture 2 than in mixture 3 is a consequence of the additional positive effect of fluorine ions on the reaction rate. While the processes in mixture 1 are in accordance with our expectations, the processes in mixtures 2 and 3 are much more complicated due to the presence of fluorine and chlorine ions.

The X-ray diffraction analysis of mixture 2 (Fig. 1(c)) shows the disappearance of MgO diffraction peaks after 1 h milling and subsequent annealing at 1000 °C for 1 h, while the diffraction peaks of MgO disappear at a much lower rate in mixture 3 and the MgO peaks disappear after 1 h milling and subsequent annealing at 1200 °C for 1 h (Fig. 1(f)).

The expected beneficial effect of mechanical activation on the forsterite reaction during subsequent thermal treatment

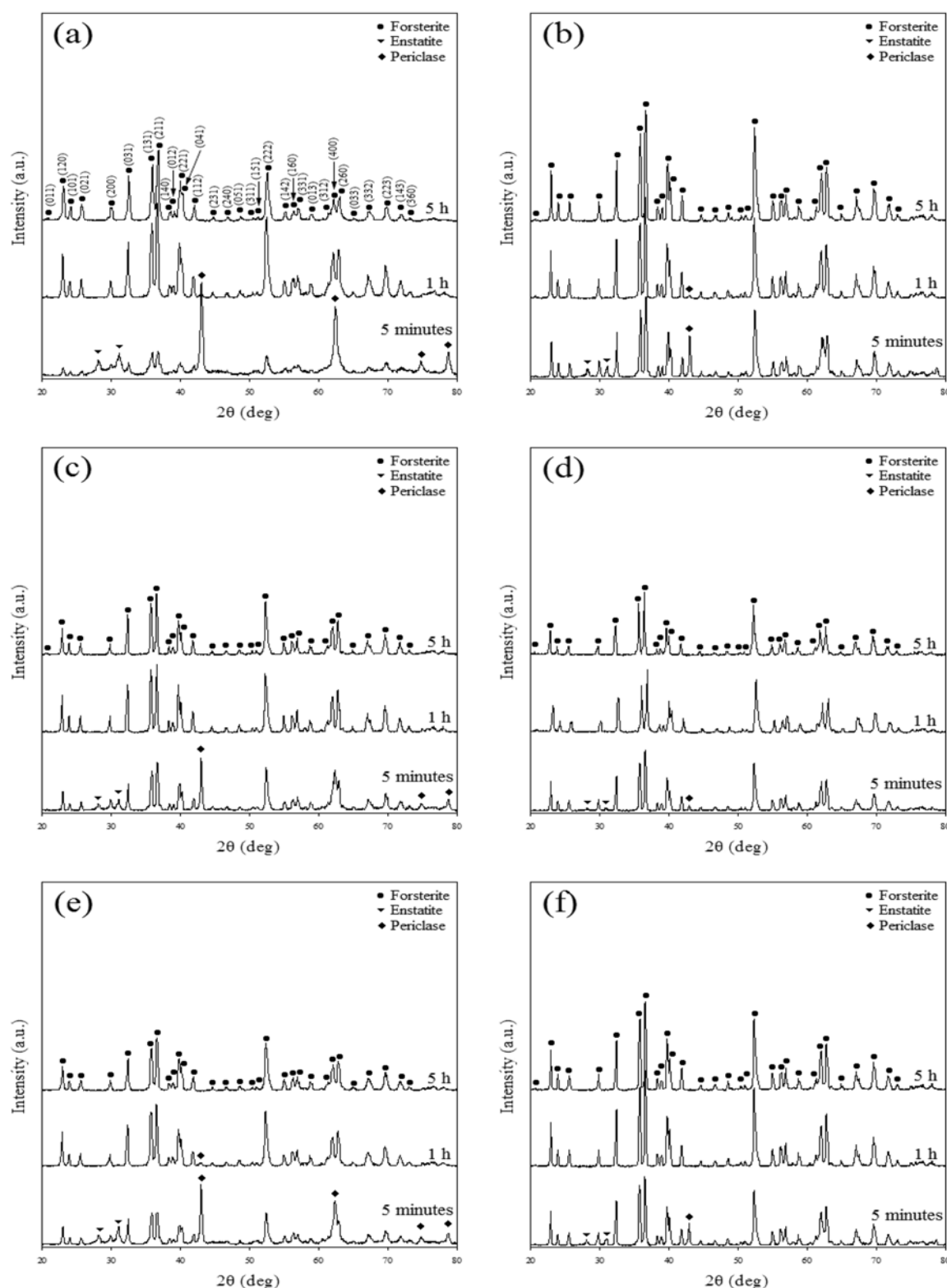


Fig. 1. XRD patterns of the powders obtained from (a and b) mixture 1, (c and d) mixture 2, and (e and f) mixture 3 after mechanical activation for various periods of time with subsequent annealing at (a, c, and e) 1000 °C and (b, d, and f) 1200 °C for 1 h.

is, therefore, different in nature with mixtures 1, 2 and 3. The beneficial effect of mechanical activation with mixture 1 without fluorine and chlorine ions is, first of all, expected

through an increase of the contact surface area of reacting phases as a consequence of an intense reduction of the particle size, which is very important in the case of diffusion-

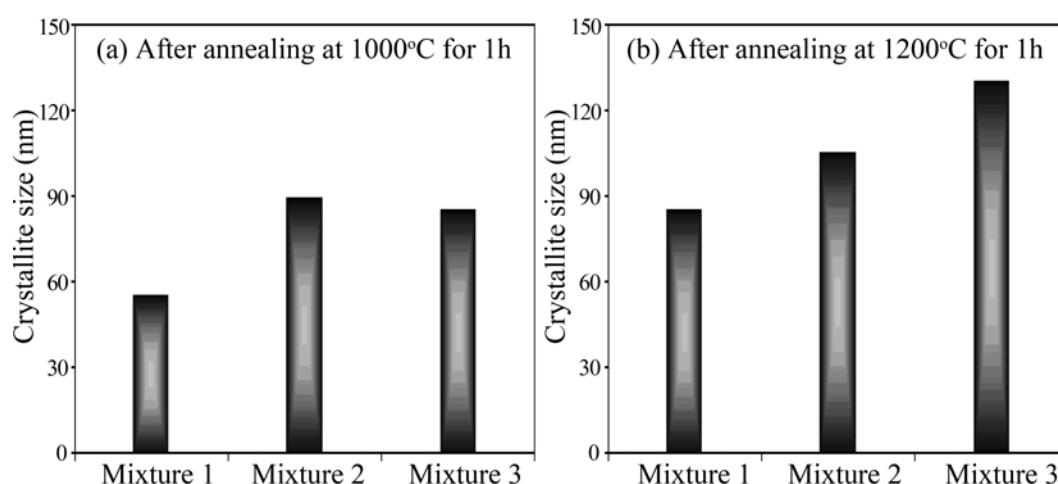


Fig. 2. The crystallite sizes of the forsterite powders obtained from mixtures 1, 2 and 3 after 1 h mechanical activation with subsequent annealing at (a) 1000 and (b) 1200 °C for 1 h.

controlled reactions. With mixtures 2 and 3, however, besides an increased contact area of the reacting phases during activation, an additional effect of existing fluorine and chlorine ions can be expected.

Kiss *et al.* [11] have reported that the loss of ions is in the form of hydrates. During the thermal treatment, the system is open and water vapor from the surroundings or the hydration water of talc becomes an active reactant and allows the slow hydrolysis of MgF_2 from group compounds [11].

The crystallite sizes of the forsterite powders obtained from the three mixtures after 1 h mechanical activation and heat treatment at 1000 and 1200 °C for 1 h are shown in Figs. 2(a) and (b), respectively. The crystallite sizes of mixtures 2 and 3 are larger than mixture 1 at the two different annealing temperatures because of the formation of crystallite phases during mechanical activation which act as nuclei for the other phases which will be formed during the subsequent heat treatment which finally increased the rate of reactions and the crystallite size. As can be seen in Figs. 2(a), 1(c) and 1(e), single phase nanocrystalline forsterite powder with a crystallite size of about 90 nm can be successfully synthesized after 1 h milling and subsequent annealing at 1000 °C for 1 h in mixture 2, while in mixture 3 beside the forsterite phase, the MgO phase was seen in the XRD patterns. With an increase in the annealing temperature up to 1200 °C (Fig. 2(b)), single phase forsterite powder could be obtained in both mixtures 2 and 3, but the crystallite size of mixture 3 was not less than 100 nm. The XRD results of mixture 2 showed that mechanical activation with fluorine ions can produce pure nanocrystalline forsterite powder after 1 h of annealing at 1000 and 1200 °C.

Thermal analysis

TG and DSC curves of mixture 1 (talc + MgO) powder, after 1 h mechanical activation are shown in Fig. 3. The

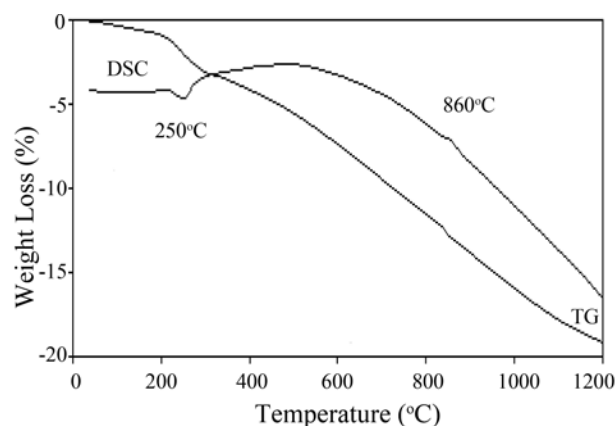


Fig. 3. TG and DSC curves of mixture 1 (talc + MgO) powder, after 1 h mechanical activation.

weight loss of ball milled powder occurred in two main stages. The first stage below 300 °C was about 4% due to loss of hydration water. The second stage, between 300–1200 °C (about 15%) was due to the loss of structural water of talc [13]. DSC traces exhibited one endothermic peak at about 250 °C and one exothermic peak at 860 °C. The endothermic peak can be attributed to the dehydration of powders and the exothermic peak can be ascribed to the formation of the forsterite structure [8].

Fig. 4 shows the TG and DSC curves of mixture 2 (talc + MgO + NH_4F powders), after 1 h mechanical activation. As can be seen, a weight loss of powder up to 3.5% could be recognized below 200 °C, due to the liberation of hydration water. A second stage of weight loss occurred between 200 and 500 °C (about 2%) due to the removal of residual organic substances and fluorine ions in the form of HF [11]. A third stage of weight loss occurred from 500 up to 1200 °C due to the liberation of the structural water of talc [13]. As can be seen in Fig. 4, a small endothermic peak was observed around 85 °C which

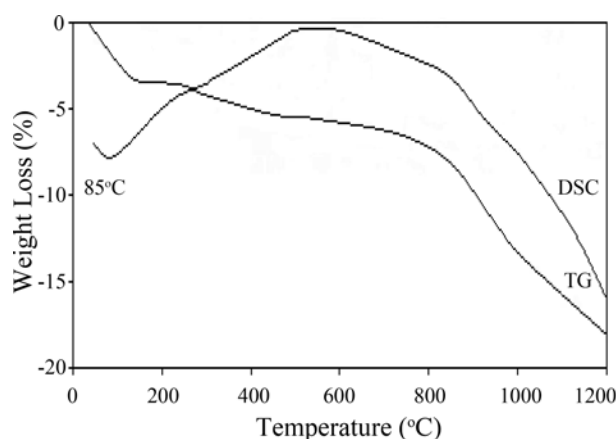


Fig. 4. TG and DSC curves of mixture 2 (talc + MgO + F ion) powder, after 1 h mechanical activation.

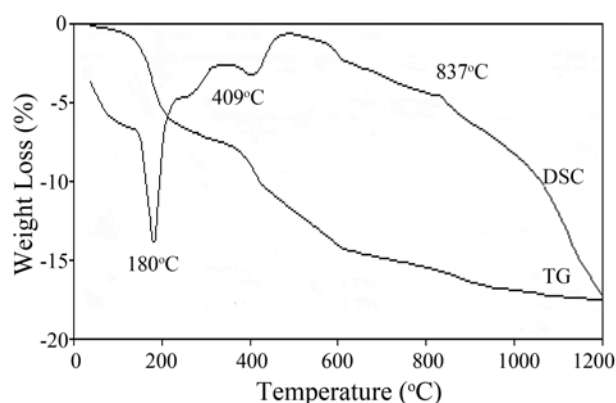


Fig. 5. TG and DSC curves of mixture 2 (talc + MgO + Cl ions) powder, after 1 h mechanical activation.

can be attributed to the liberation of hydration water. No further endo/exothermic peak was observed in the DSC curve indicating that the formation of forsterite could occur during ball milling with a new mechanism.

Fig. 5 shows the TG and DSC curves of mixture 3 (talc + MgO + NH_4Cl powders) powder, after 1 h mechanical activation. As can be seen, the weight loss occurred in three main stages. The first stage (about 7% weight loss) occurred below 300 °C and is probably due to the removal of hydration water. The next stage (between 300 and 650 °C, about 7% weight loss) was caused by removal of organic material. The third stage of weight loss occurred between 650 and 1200 °C due to the liberation of the structural water of talc [13]. As can be seen in the DSC curve two strong endothermic peaks and one small exothermic peak can be observed at 180, 409 and 837 °C which can be attributed to the liberation of hydration water, organic material and crystallization of the forsterite structure, respectively.

Microstructure evolution

SEM micrographs of the forsterite powders obtained from mixtures 2 and 3 after 1 h milling and subsequent annealing at 1200 °C for 1 h are shown in Fig. 6(a) and

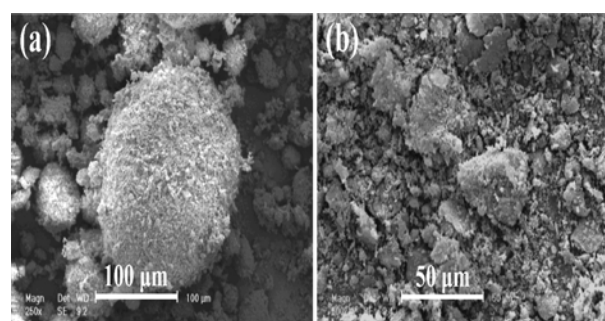


Fig. 6. SEM micrographs of the powders obtained after 1 h mechanical activation with subsequent annealing at 1200 °C for 1 h from (a) mixture 2 and (b) mixture 3.

(b), respectively. As can be seen, the forsterite powder particles obtained from mixture 2 (Fig. 6(a)) had a uniform and spherical shape and was composed of small and highly agglomerated particles. Due to the liberation of fluorine ions during mechanical activation (before annealing) in mixture 2, large agglomerates (about 100 μm) could be detected in this sample. The agglomerate size of the forsterite powder obtained from mixture 2 was smaller than 100 μm. By contrast, as can be seen in Fig. 6(b), the agglomerate size of the forsterite powder obtained from mixture 3 was smaller than 50 μm. This could be attributed to the liberation of volatile materials after the subsequent annealing. This phenomenon affected the morphology of the powder obtained from mixture 3 after the subsequent annealing, which in turn caused the agglomerates to be crushed during the annealing. The agglomerates of the forsterite powder obtained from mixture 3 had a fuzzy shape and its agglomerate size was smaller than that of mixture 2.

Conclusion

Mechanical activation of talc and periclase with fluorine/chlorine ions enhanced the formation rate of forsterite. Gaseous decomposition products of $\text{NH}_4\text{F}/\text{NH}_4\text{Cl}$ leave the system during ball milling and partially during the initial period of the thermal treatment. On the basis of the results obtained, pure nanocrystalline forsterite was synthesized by 1 h of mechanical activation and annealing at 1000 and 1200 °C for 1 h in the presence of fluorine ions. The forsterite powder obtained from mixture 3 (containing NH_4Cl) had a crystallite size larger than 100 nm. In the absence of fluorine and chlorine ions, forsterite powder could be fabricated by 5 h of mechanical activation with subsequent annealing at 1000 °C for 1 h.

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