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Synthesis and characterization of Bi_3NbTiO_9 powders prepared by molten salt method

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ABSTRACT

Bi_3NbTiO_9 powders were obtained by the molten salt synthesis method. The influence of the calcinations temperature, holding time, salt species and amount on the crystallization habit and morphology of Bi_3NbTiO_9 powders was studied. Under the same processing conditions, the Bi_3NbTiO_9 powders synthesized from KCl generally showed a lower crystallization temperature and smaller particle size than those synthesized using NaCl as salt. Furthermore, the salt content showed a strong influence on the particle size of the synthesized Bi_3NbTiO_9 powders. The particle size of Bi_3NbTiO_9 powders prepared in NaCl sulfate flux increased as the mole ratio of the sulfate salts to Bi_3NbTiO_9 was increased. Compared with the calcinations temperature the influence of holding time on the particle size was not obvious although the prolonged holding time could improve the particle morphology greatly.

1. Introduction

Bismuth titanate niobate, Bi_3TiNbO_9, a typical Aurivillius oxide, consists of $(Bi_2O_2)^{2+}$ layers between which perovskite-like layers $(BiTiNbO_7)^{2-}$ are inserted. In the $BiTiNbO_7$ units, Ti/Nb ions are surrounded by oxygen octahedra, which are corner shared to form O–Ti/Nb–O linear chains, while Bi ions occupy the spaces in the framework of Ti/NbO_6 octahedra.

Bi_3NbTiO_9 was discovered by Aurivillius in 1949. Subbarao and Newnham showed it to be a ferroelectric with the highest known Curie point in the BLSF family at that time of 940 °C. So it is one of the promising candidates for high temperature piezoelectric applications [1].

Molten salt synthesis (MSS) is a suitable method for synthesizing oxide powders with anisotropic particle morphologies, and has been widely used to form ferrites, PZT, $(Pb_{0.97}La_{0.02})(Zr_{0.66}Sn_{0.27}Ti_{0.07})O_3$ and $SrTiO_3$ powders [2–5]. However, there are limited reports on Bi_3TiNbO_9 compound prepared by molten salt method.

In this paper, the synthesis of plate-like Bi_3TiNbO_9 by MSS method was studied. The effects of the calcinations temperature, holding time, salt species and salt content on the formation process and morphology of the Bi_3TiNbO_9 platelets were investigated.

2. Experimental procedure

In the present study commercial ceramic powders of Bi_2O_3, TiO_2, Nb_2O_5 were used as the raw materials. A powder mixture of these raw materials according to the stoichiometric ratio of Bi_3TiNbO_9 was prepared as a reactant. The prepared reactant and the used salt were mixed and ball-milled in an ethanol medium. After ball milling, the obtained slurry was dried at 80 °C to remove the ethanol. Heat treatment was then carried out at different temperatures for different holding time in a muffle furnace. After heat treatment, the products were washed using hot deionized water to remove the residual salt. The products were then dried and characterized using an X-ray diffractometer (XRD, D/max-RB, Japan) for phase composition and a scanning electron microscopy (SEM, Model SM-450, Japan) for particle morphology.

3. Results and discussion

3.1. Influence of the salt species

KCl and NaCl were chosen as solvent, respectively. The ratio of the prepared reactant to solvent was 2:1. Fig. 1 showed the XRD patterns of the Bi_3TiNbO_9 powders obtained through the molten salt method. The precursor mixed with KCl was fully converted to crystalline Bi_3TiNbO_9 after being heated to 800 °C. In contrast, the precursor mixed with NaCl only partially crystallized to Bi_3TiNbO_9 at the same temperature. This suggested KCl could reduce the crystallization temperature more effectively than NaCl.

Fig. 2 showed the SEM images of Bi_3TiNbO_9 powders fabricated using different salt species. Fig. 2(a) revealed the Bi_3TiNbO_9 powders in NaCl–KCl flux were quadrate-like morphology. Comparing Fig. 2(b) with (c), it should be noted that the powders synthesized using KCl as salt were fine although they were accompanied by a few of coarse particles. This was probably due to that a low-melting

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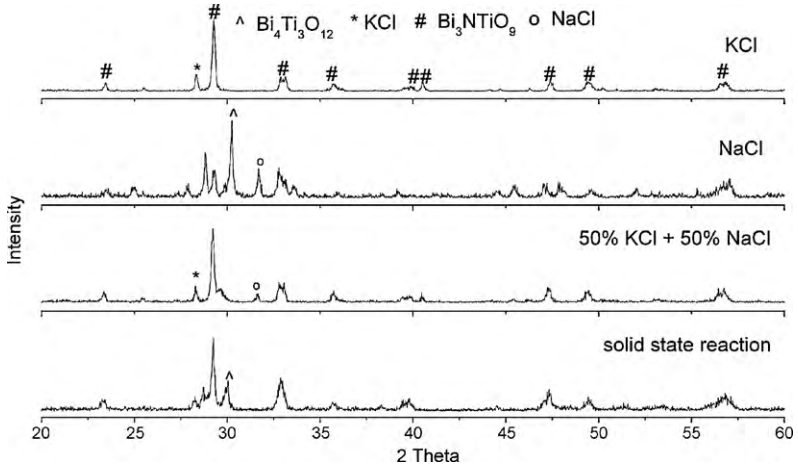

Fig. 1. XRD of Bi_3TiNbO_9 powders from precursors with different salt species calcined at 800 °C.

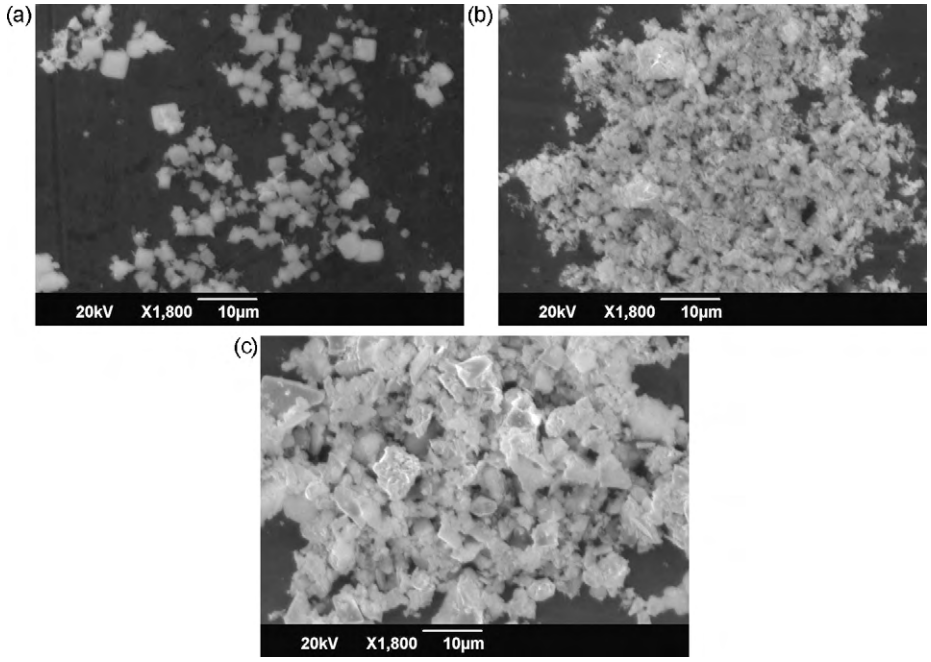

Fig. 2. SEM micrographs of Bi_3TiNbO_9 powders from precursors with different salt species calcined at 800 °C (a) 50%NaCl and 50%KCl; (b) 100% KCl; and (c) 100%NaCl.

point salt could cause a higher nucleation rate at the same temperature. The eutectic point of NaCl–KCl is 650 °C, lower than that of NaCl (801 °C) and KCl (771 °C). As for low-melting point salt, the reactants could achieve an effective dissolution and transport and well distribute in the flux. In the following precipitation or diffusion process higher nucleation rate resulted in small particles. However, for high-melting point salt, its initial period of reaction was usually accompanied with an Ostwald ripening mechanism: the growth of big particles by the dissolving consumption of small particles and unavoidably led to individual particle growth [6].

3.2. Influence of the sulfate content

In order to reveal the influence of the sulfate content upon Bi_3TiNbO_9 powders formation various mole ratios of salt to the prepared reactant were chosen from 1:3 to 6:1. NaCl was used as a solvent.

Fig. 3 showed the XRD patterns of Bi_3TiNbO_9 powders synthesized under different conditions. It was easily observed that in the case of our investigations, apart from the diffraction peaks of BNT

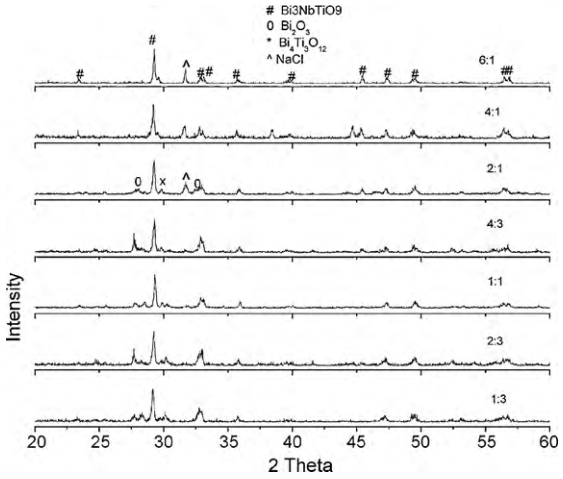

Fig. 3. XRD of the Bi_3TiNbO_9 powders prepared at 900 °C for 2 h in NaCl sulfate flux at different mole ratios.

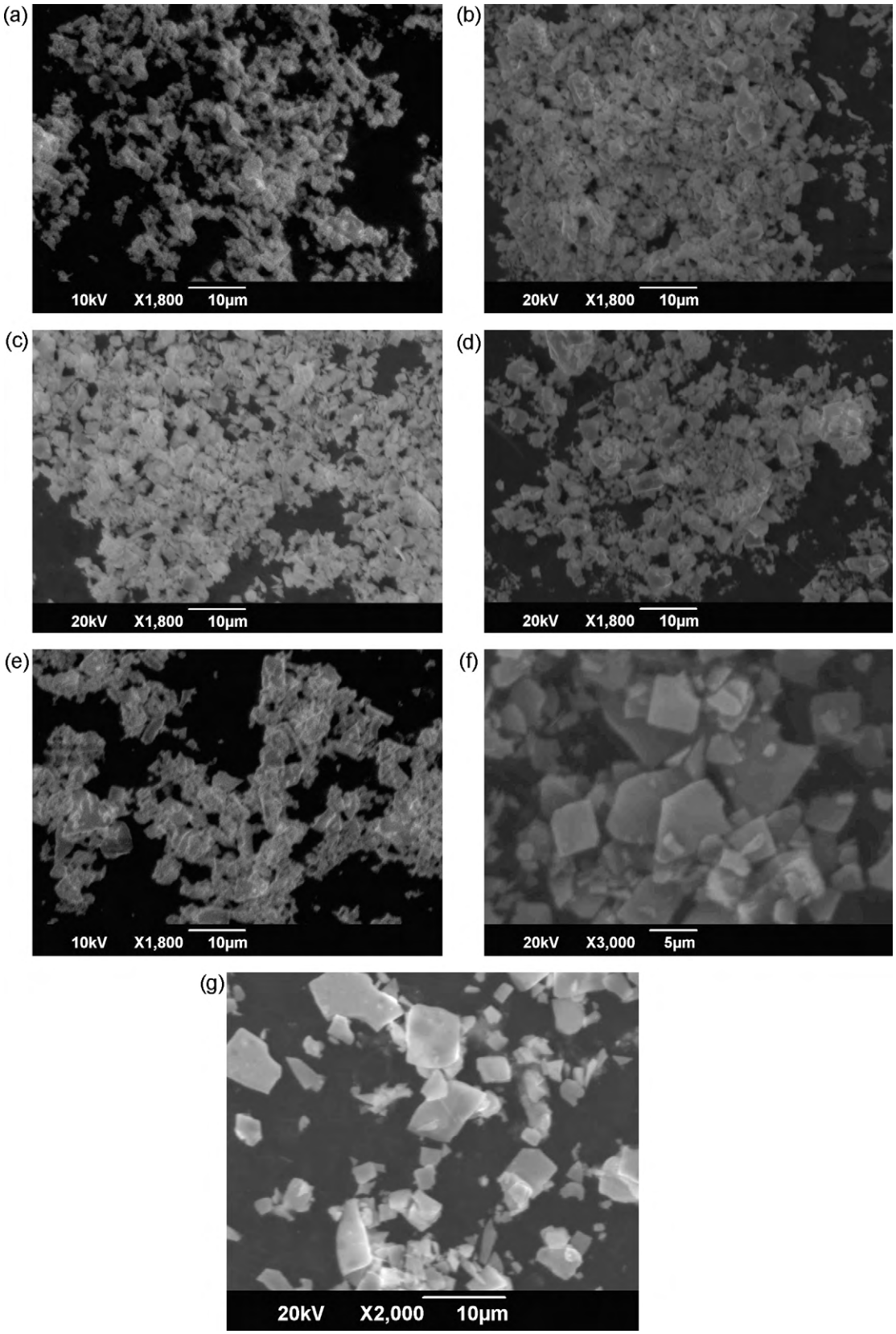

Fig. 4. SEM micrographs of the Bi_3TiNbO_9 powders prepared at 900 °C for 2 h in NaCl sulfate flux at different mole ratios (a) 1:3; (b) 2:3; (c) 1:1; (d) 4:3; (e) 2:1; (f) 4:1; and (g) 6:1.

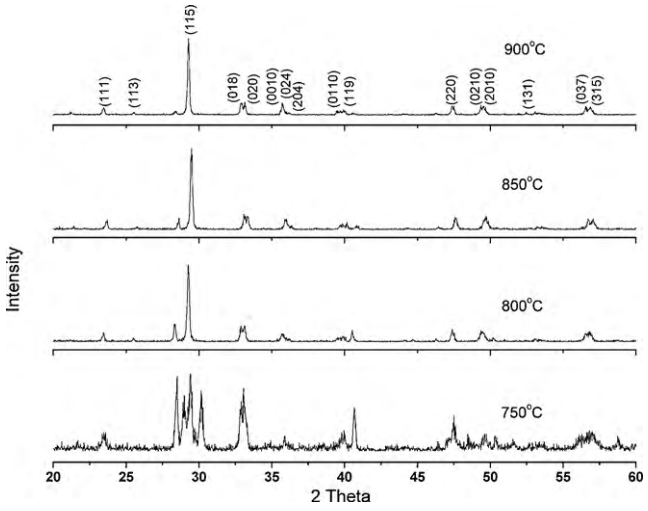

Fig. 5. XRD patterns of Bi_3TiNbO_9 powders calcined at different temperatures while KCl was used as a solvent.

compound, additional peaks of Bi_2O_3 and $Bi_4Ti_3O_{12}$ were detected when the mole ratio was below 2:1. However, with increasing the amount of salt, especially as the mole ratio was higher than 4:1, the peaks of Bi_2O_3 and $Bi_4Ti_3O_{12}$ were found to disappear. This phenomenon suggested that the sulfate content played an important role in the development of Bi_3TiNbO_9 particle crystallization. It was reported that shorter calcinations time or lower soaking temperature than the melting point of the used salts led to impurities during MSS [7,2]. In the present experiment, the calcinations temperature was 900 °C, higher than 801 °C (the melting point of NaCl) and the holding time was 2 h. So the above conclusions did not work in our studies. This suggested that the increased ratio might change either the melt viscosity or the solubility of Bi_3TiNbO_9 in the melt, which

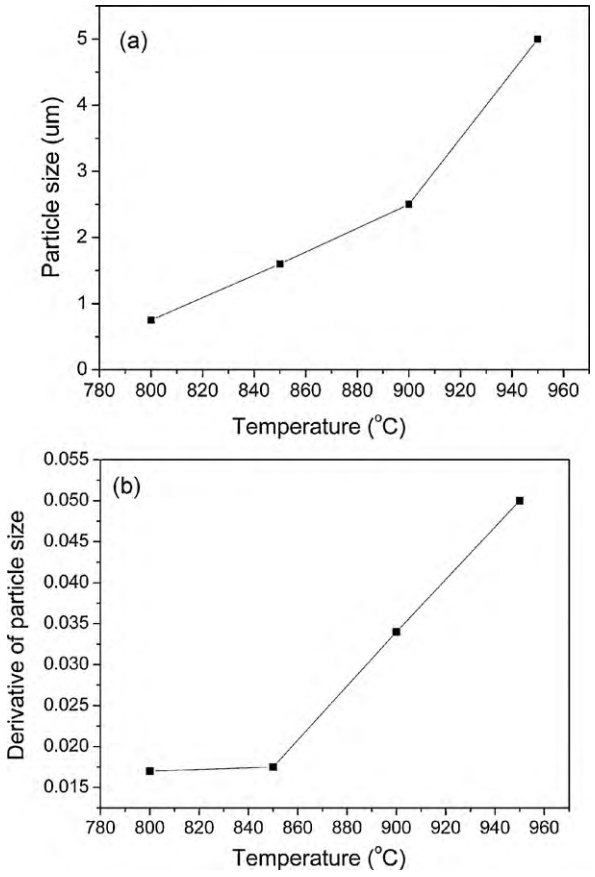

Fig. 7. (a) The dependence of the averaged particle size on the synthesized temperatures; (b) differential data of (a).

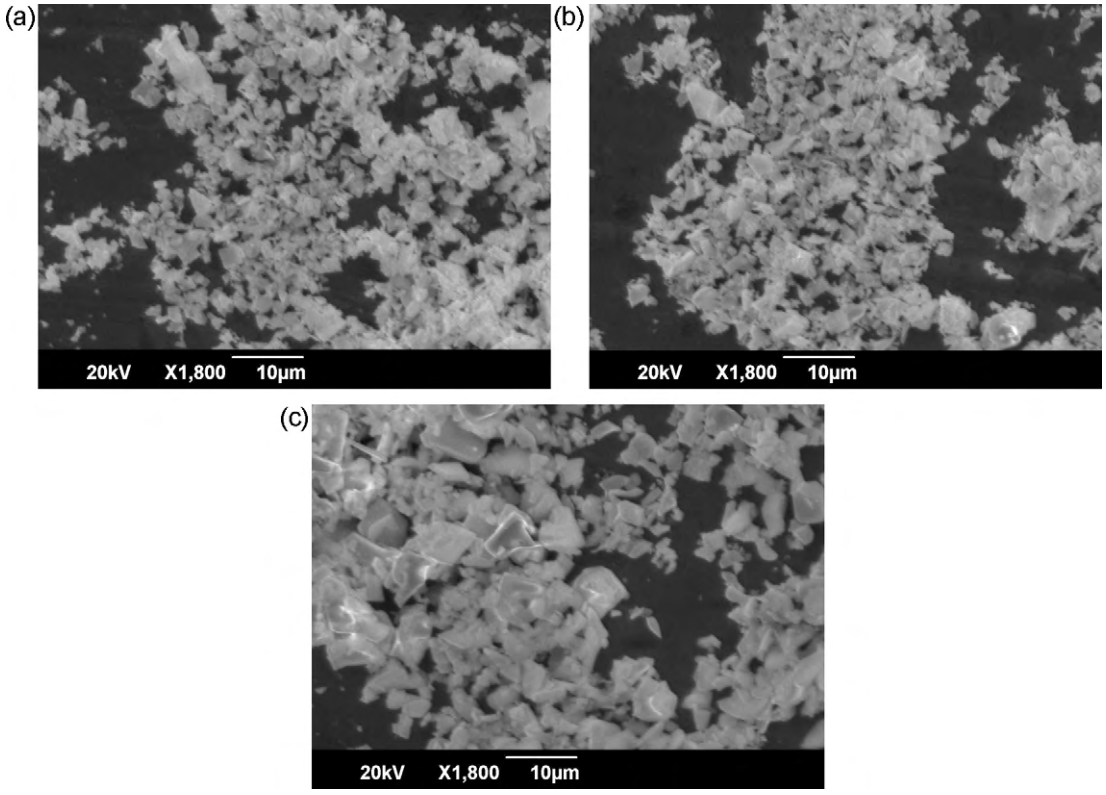

Fig. 6. SEM of the Bi_3TiNbO_9 powders synthesized at different temperatures (a) 850 °C; (b) 900 °C; and (c) 950 °C.

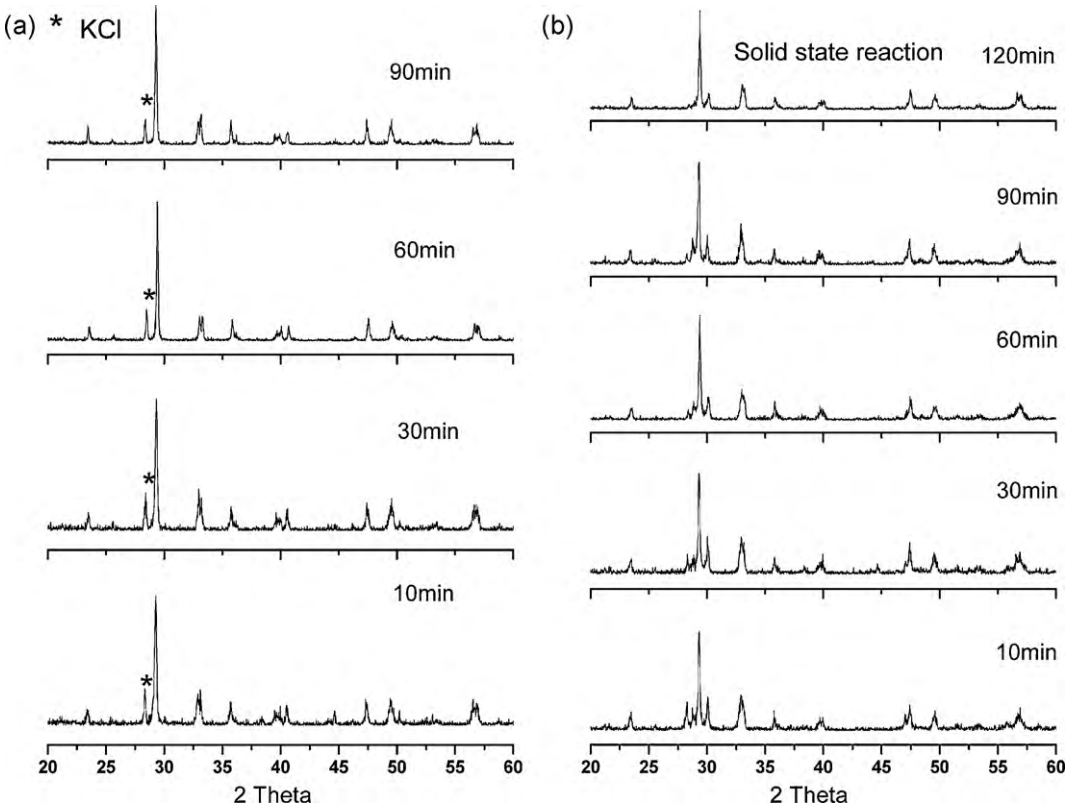

Fig. 8. XRD patterns of the Bi_3TiNbO_9 powders calcinated for different time at 850 °C (a) molten salt method; (b) solid-state reaction.

further contributed to the uniformly distribution of the reactant in the melt.

Fig. 4 showed the SEM micrographs of the Bi_3TiNbO_9 powders synthesized under different conditions. The particle size of the Bi_3TiNbO_9 powder showed a strong dependence on the mole ratio (*M*) of the sulfate salts to Bi_3TiNbO_9. The Bi_3TiNbO_9 particles increased with increasing salt contents. Especially the powders dispersed well and most of them become quadrate as the *M* value was beyond 2:1. This phenomenon was ascribed to the increases in the formation rate and the particle growth space with increasing sulfate salt contents [3].

3.3. Effect of the calcinations temperature

The XRD patterns of the powders synthesized at different temperatures for 2 h were shown in Fig. 5. Some unidentified impurities were found to be present in the powders at 750 °C. A further increase in temperature to 800 °C resulted in a pure Bi_3TiNbO_9 phase. It was reported that conventional solid-state synthesis of Bi_3TiNbO_9 was virtually impossible at a temperature <900 °C. Moreover, Bi_2O_3 with different crystal structures and $Bi_4Ti_3O_{12}$ phase were reported to present with formation of pure Bi_3TiNbO_9 [8]. However, this was not found in KCl flux. Fig. 5 indicated the increased synthesizing temperature could significantly increase the amount of single Bi_3TiNbO_9 phase without any other compounds or intermediate phases.

Fig. 6 showed the SEM photographs of Bi_3TiNbO_9 powders synthesized at different temperatures. With increasing temperature, the degree of crystalline was improved. The Bi_3TiNbO_9 particles grew larger and more plate-like, due to the preferential growth of the low-interfacial energy surface planes of Bi_3TiNbO_9 particles. In addition, because of the consumption of fine Bi_3TiNbO_9 particles by the large ones, just as described previously, the particle size distribution of Bi_3TiNbO_9 powder synthesized at high temperature became more uniform. Especially Fig. 6 implied the Bi_3TiNbO_9 particles grew very quickly when the synthesized temperature was high than 900 °C.

Fig. 7 showed the dependence of Bi_3TiNbO_9 particles size on the calcinations temperatures. The particle size increased with increasing temperature. Fig. 7(b) showed the particle growth rate was not sensitive to temperature below 850 °C. However, when temperature was higher than 850 °C the growth rate was found to increase almost linearly with temperature. This result was consistent with the observations in Fig. 6. It is generally believed that the particle morphology is initially dominated by the nucleation process and later growth process during the MS synthesis [6]. The nucleation process depends on the difference of dissolution rates between the reacting oxides in the molten salt. Particle growth can be initiated by an interfacial reaction controlled mechanism or diffusion controlled mechanism. So two distinct regions found in Fig. 7(b) indicated two different growth stages. Below 850 °C the nucleation process was probably faster than the particle growth process and the rate of particle growth was delayed in comparison with nucleation. The particles grew finer. However, when the temperature was higher than 850 °C the growth process became dominant leading to large particle size. The above observations indicated the synthesizing temperature could significantly influence the growth rate and morphology of the Bi_3TiNbO_9 particles.

3.4. Effect of the holding time

As the kinetics of the solid-phase synthesis reaction depended on both the synthesis temperature and holding time the dependence of the X-ray diffraction patterns on the holding time was collected in Fig. 8. The holding time was carried out within the range from 10 min to 12 h at the constant temperature of 850 °C while KCl was used as salt. For comparison Bi_3TiNbO_9 powders were prepared by solid-state reaction (SSR) and the dependence

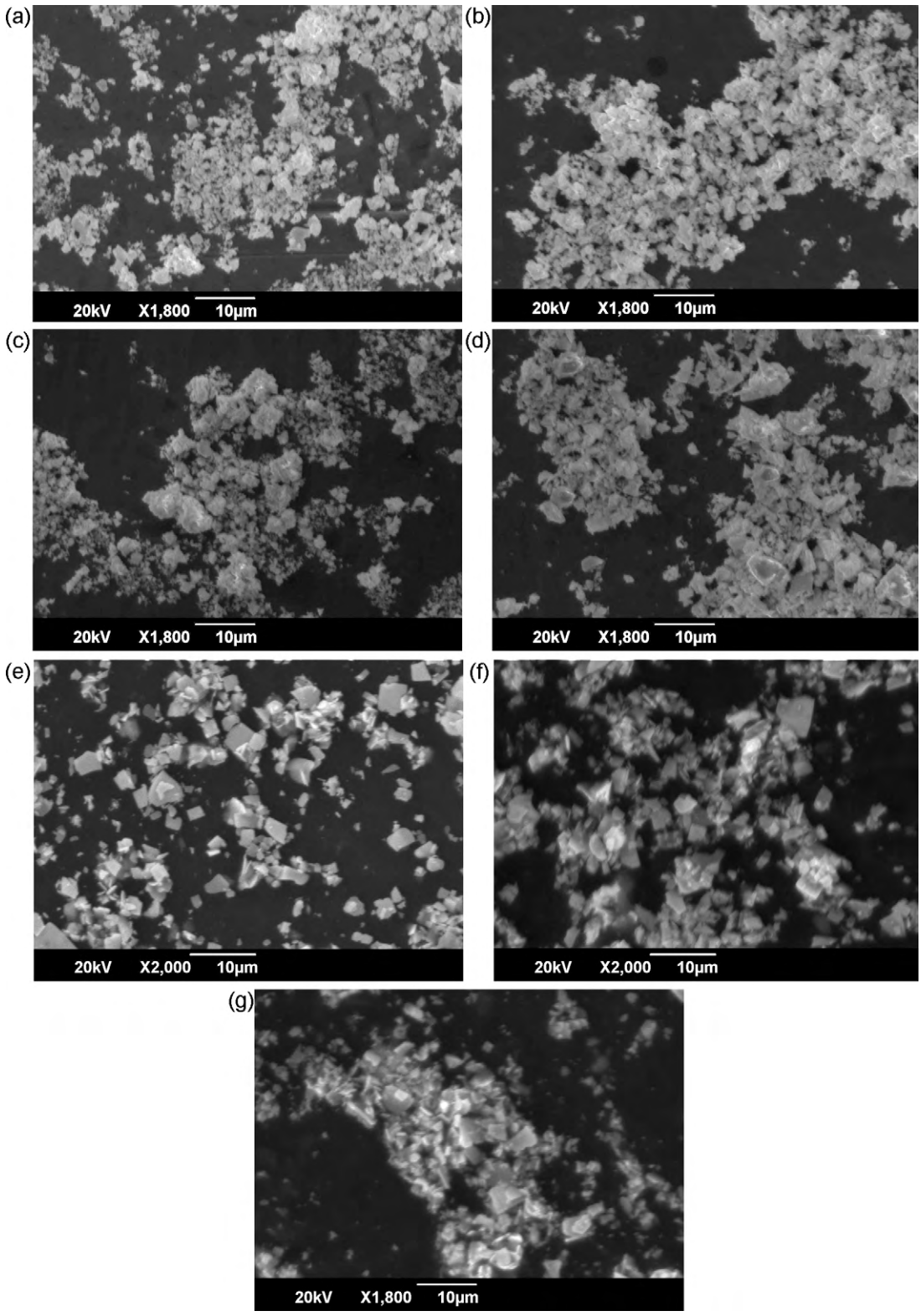

Fig. 9. SEM results of the Bi_3TiNbO_9 powders calcinated at 850 °C for different time. (a) 10 min; (b) 30 min; (c) 1 h; (d) 1.5 h; (e) 4 h; (f) 8 h; and (g) 12 h.

of its XRD patterns on time duration was also presented in Fig. 8.

All of the samples in Fig. 8(a) exhibited a similar XRD pattern in spite of different time durations. Pure Bi_3TiNbO_9 phase could be obtained within 10 min in KCl flux. However, in the case of solid-state method, the XRD results showed that the calcinations time longer than 2 h were necessary for the formation of pure Bi_3TiNbO_9 phase at 850 °C. These implied that the molten salt could accelerate the kinetics at lower temperature and facilitate the formation of Bi_3TiNbO_9, which was reported to be attributed to the enhanced diffusion coefficients in the molten chloride liquid phase compared to that in the solid-state [9].

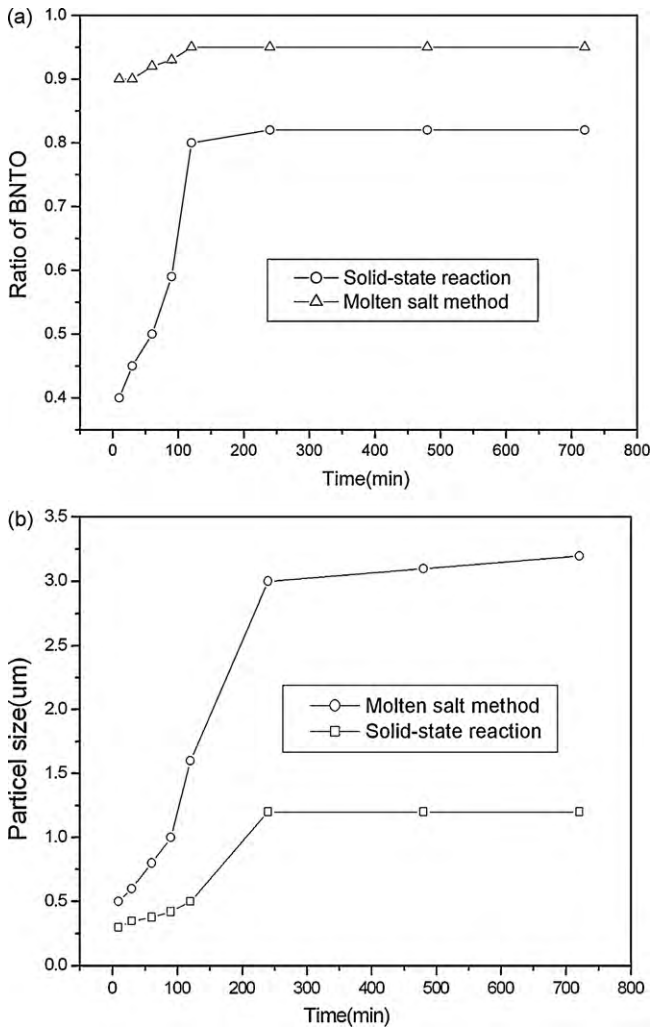

Fig. 10. (a) Dependence of ratio of Bi_3TiNbO_9 phase on the calcinations time; (b) dependence of the corresponding particle size on the calcinations time.

Fig. 9 showed the SEM results of the Bi_3TiNbO_9 powders calcinated at 850 °C for different time. The powders were agglomerated and irregular in shape when the holding time was less than 2 h. However, with further increased time beyond 4 h, the powders started to exhibit plate-like particles.

Variations in the average particle size and calculated ratio of the Bi_3TiNbO_9 phase as a function of holding time were shown in Fig. 10. For quantifying the ratio of the Bi_3TiNbO_9 phase, the following equation was used:

$$\text{ratio}\,(\%) = \frac{\sum I_{\text{BNTO}(hkl)}}{\sum I_{(hkl)}}$$

where $I_{\text{BNTO}(hkl)}$ were the intensities of the diffraction peaks of Bi_3TiNbO_9.

One could see in Fig. 10 that, no matter for MSS or SSR, the particle size increased rapidly at short annealing time and then continued to grow at a very low rate. At longer calcinations time, the particle size exhibited a leveling-off trend and approached a limiting particle size. However, the dependence of volume fraction Bi_3TiNbO_9 on the holding time was different. The amount of Bi_3TiNbO_9 in MSS remained remarkably stable within 12 h while that of SSR increased obviously with the prolonged time within 4 h.This was probably attributed to lower crystalline temperature of MSS, which led to a mass transformation of Bi_3TiNbO_9 at temperature lower than 850 °C.

4. Conclusions

Compared with NaCl, KCl could reduce the crystallization temperature effectively. Using KCl as solvent with the ratio of the prepared reactant to solvent 2:1, Bi_3NbTiO_9 could be synthesized at 800 °C without other intermediate phases. The increased sulfate salt contents increased the synthesis rate and the particle growth space leading to the easy formation of plate-like shape Bi3NbTiO9. Both the calcinations temperature and holding time improved the particle morphology greatly. However, their influence on the particle growth was different.

Acknowledgements

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