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Effect of salt species on characterization of Bi_3NbTiO_9 powders prepared by molten salt method

Bao-rang Li [a,*], Xing-tao Liu [b], Peng-lei Chen [a], Yang-sheng Zheng [a]

[a] *National Engineering Laboratory for Biomass Power Generation Equipment, North China Electric Power University, Beijing 102206, China*

[b] *Tsing-hua University, Beijing 100084, China*

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Abstract

The carbonates, chloride and sulphate salts were chosen as fluxes to synthesize Bi_3NbTiO_9 (BNTO) powders at low temperature by the molten salt synthesis (MSS) method and the influence of salt species on the formation and powder characteristics of BNTO was investigated in this paper. The results showed that for the sulphate flux the formed particle size was the largest among all the used salts, but the fastest particle growth rate was found in the carbonates flux. Investigations on morphology characteristics of powders showed the plate-like powders with smaller particle size were synthesized in the chloride flux, but the powders obtained in the sulphate flux were shown to be irregular blocks in shape. Further studies indicated the salt content had a strong influence on crystallization of BNTO from the chloride flux.

Keywords: Bi_3NbTiO_9; A. Powders: solid state reaction; D. Perovskites

1. Introduction

Bismuth layer-structured ferroelectrics (BLSF) are the common acronym for the Aurivilius phase materials that are ferroelectric. In recent years, BLSF have been given much attention because some materials, such as $SrBi_2Ta_2O_9$ and $Bi_4Ti_3O_{12}$, are excellent candidate materials for nonvolatile ferroelectric random access memory (FRAM) applications. Compared with the widely used PZT ceramics with perovskite structure, BLSF ceramics are characterized by high Curie points, low dielectric constants, low dielectric losses, low aging, high dielectric breakdown strengths, strong anisotropic electromechanical coupling factors and low temperature coefficients of resonant frequency [1].

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 [2]. So far, most of the reported studies of BNTO have been concentrated on its crystal structure and electric properties while the used powders were mainly prepared by the conventional method [1,3,4].

Molten-salt synthesis is one of the simplest methods to obtain oxide powders with anisotropic morphology at a relatively low temperature for a shorter soaking time, in which the molten salt was used as a reaction aid. So it is widely used to synthesize anisotropic morphology particles [5–10]. Requirements for selecting the salt in MSS are follows: (i) the melting point of any given salt must be appropriately low compared to the formation temperature of the main phase; (ii) the solubility of a salt must be sufficient to be eliminated by simple washing step; (iii) there must be no undesirable reaction between salt and constituent oxides.

There are many experimental parameters in the MSS, which influence the resulting powder characteristics and the reaction kinetics. Besides the usual factors such as the synthesis temperature and time, changes in type of salt can induce a huge difference in powder characteristics because they are responsible for the reaction and growth environments. Therefore, the selection of salt is critical in obtaining desirable powder characteristics.

Recently it was reported that Bi_3NbTiO_9 template particles had been prepared by MSS successfully [11,12]. However, to our knowledge, no studies related to the influence of salt species

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[*] Corresponding author. Tel.: +86 13581926096/010 61772355; fax: +86 010 61772177.

E-mail address: libr@ncepu.edu.cn (B.-r. Li).

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on BNTO powder characterization by MSS were reported. So in this paper, BNTO powders were first prepared in various salt fluxes and then the effects of the salt species on the powder characterization were analyzed.

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 BNTO was prepared as a reactant and KCl, NaCl, K_2CO_3 and K_2SO_4 were chosen as solvent respectively. The prepared reactant and the solvent were mixed in a mol ratio of 2:1 and ball-milled for 12 h in an ethanol medium. After ball milling, the obtained slurry was dried at 80 °C for 6 h to remove the ethanol. Heat treatment was then carried out in the temperature range of 750–950 °C for 2 h in a muffle furnace. After heat treatment, the powders were washed using hot deionized water to remove the residual salt. The obtained powders were then dried at 120 °C and characterized.

The powders were identified using an X-ray diffracto-meter (XRD, Model D8 Advance, Bruker, Germany) for phase composition and a scanning electron microscopy (SEM, Model JSM-5800, JEOL, Japan) for particle morphology. Different thermal analysis (DTA) and thermo-gravimetric analysis (TG) were carried out at a heating rate of 5 °C min^{-1}.

For quantifying the ratio of the BNTO phase, the following equation was used:

$$\text{ratio}\,(\%) = \frac{\sum I_{\mathrm{BNTO}(h\,k\,l)}}{\sum I_{(h\,k\,l)}}$$

where $I_{\mathrm{BNTO}(h\,k\,l)}$ is the intensities of the diffraction peaks of Bi_3NbTiO_9.

3. Results and discussion

3.1. DTA–TG

DTA–TG curves for precursors with various species of salts are illustrated in Fig. 1. It was easily found from Fig. 1 that the curves of KCl and NaCl were shown to be very similar. The endothermic peaks at 660 and 746 °C were caused by the mixture melting. The precursors were transformed into liquid phase at these temperatures. BNTO phase started to synthesize at 700 °C in KCl flux, but it was approached to 800 °C in NaCl. The endothermic peaks at about 918 and 943 °C in the DTA, companied with a dramatic weight loss, were due to the total formation of BNTO phase, implying that suitable synthesis temperature is below 1000 °C in chloride fluxes.

The DTA curve of K_2CO_3 was shown to be a little complex. Its corresponding TG curve showed a typically multiple decomposition of precursor. The first endothermic peak at 85.91 °C in DTA, corresponding to about 5% weight loss, was probably due to the dehydration of free water and disappeared solvent, which was formed during the milling process using ethanol. The endothermic peaks of 644.9 and 684.24 °C were attributed to possible phase transition and the mixture melting. The formation of BNTO perovskite phase started at 758.75 °C. Fig. 1 indicated product with BNTO as the main phase could be obtained at 1000 °C in K_2CO_3.

The first endothermic peak in the DTA curve of K_2SO_4 was around 583.55 °C, which corresponded to the possible phase transition of the salt to liquid phase and the intermediate product formation. BNTO phase started to form at about 725 °C, which was a little lower than K_2CO_3. However, its followed endothermic peaks with temperature increasing were shown to be very broad indicating the prolonged formation process.

3.2. XRD

X-ray diffraction patterns (XRD) of BNTO powders obtained from different salts are shown in Fig. 2. For comparison, XRD of BNTO powders prepared by the solid state reaction method (SSR) is also included in Fig. 2. The other samples, except in the cases of KCl and K_2SO_4, were observed to consist of BNTO and un-reacted oxides such as Bi_2O_3 and secondary phase $Bi_4Ti_3O_{12}$ in various degrees. As shown in Fig. 2, the impurity content in carbonates and sodium chlorides was higher than those in SSR.

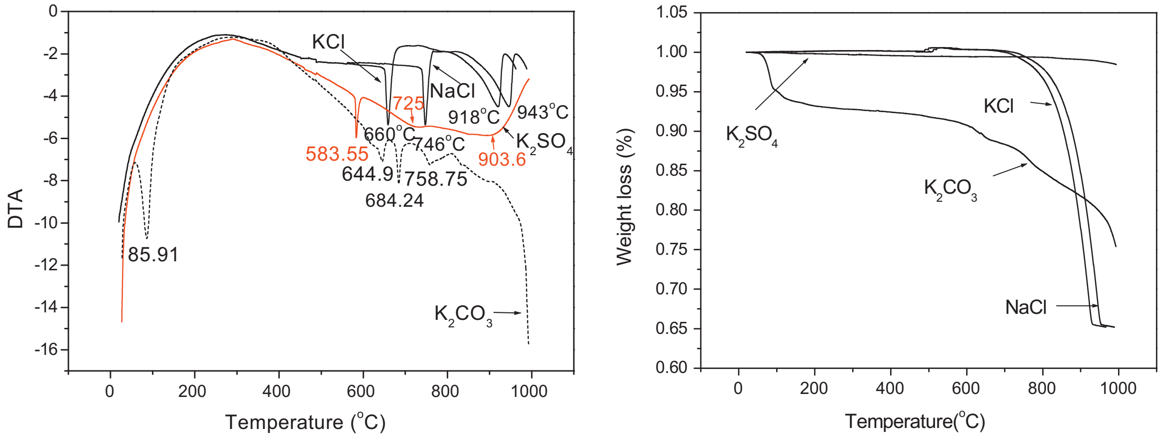

Fig. 1. DTA and TG curves of the precursors from various species of salt.

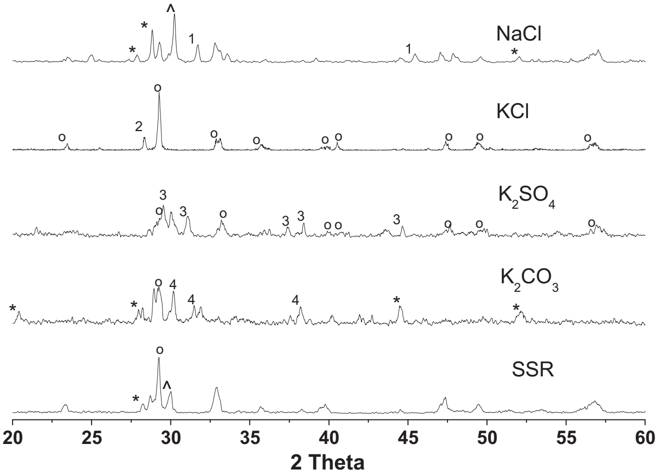

Fig. 2. XRD patterns of BNTO powders synthesized at 800 °C. 1: NaCl; 2: KCl; 3: K_2SO_4; 4: K_2CO_3; ^: $Bi_4Ti_3O_{12}$; *: Bi_2O_3; o: BNTO; SSR: solid-state reaction.

It was reported that the conventional solid-state synthesis of BNTO is virtually impossible at a temperature <900 °C because Bi_2O_3 with different crystal structures and $Bi_4Ti_3O_{12}$ phase were reported to present with formation of pure BNTO [2]. This result was consistent to our investigations. Further studies on sodium chloride flux implied impurities presented with BNTO phase during synthesis process had close relations with variation in molar ratio between the prepared reactant and salts amount. As the ratio of salt to the prepared reactant was increased beyond 4:1, the typical diffraction peaks of perovskite BNTO appeared and no impurity was detected. This illustrated the impurities found in our studies were produced from lower ratio of salt to the prepared reactant [11]. Compared with KCl flux, the XRD peaks from K_2SO_4 flux were relative wide, implying that the precursors were not completely transformed into crystals, which was in accordance with the observation of DTA. The above results indicated the chlorides flux is more suitable to synthesize BNTO powders than K_2SO_4 and K_2CO_3.

3.3. Phase transformation

Fig. 3 shows the dependence of XRD patterns of BNTO powders on temperatures. Fig. 4 is the variation in BNTO phase content with synthesis temperature according to the processing salt types. Compared with SSR method, the MSS was shown to be more effective in promoting the reaction of BNTO. The low transformation ratio of NaCl, shown in Fig. 4, was attributed to lower ratio of salt to the prepared reactant. It was also easily found from Fig. 4 that K_2CO_3 differed from the other salt fluxes in its influences on BNTO phase transformation. Its corresponding curve showed BNTO phase content tended to increase first and then decrease sharply as the temperature increased. This might have close relations with low melting point of Bi_2O_3 and thermal decompose of carbonate [13]. Another phenomenon shown in Fig. 4 was that almost 90% perovskite phase was obtained within a relatively narrow temperature range of 700–800 °C. This indicated compared with other salts, relatively high transformation rate of BNTO could be achieved at low temperature in K_2CO_3.

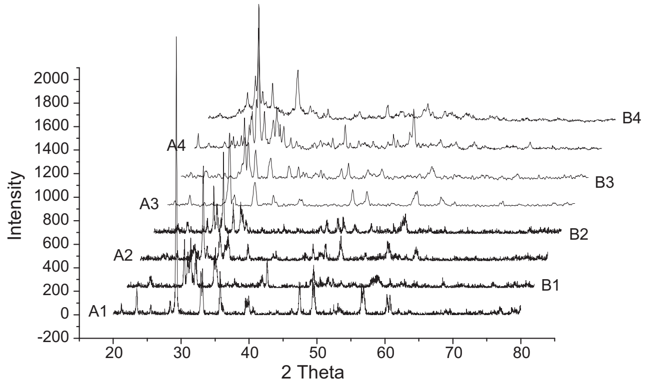

Fig. 3. XRD patterns of BNTO powders synthesized at various temperatures. KCl: A1 900 °C, B1 750 °C; NaCl: A2 900 °C, B2 750 °C; K_2SO_4: A3 900 °C, B3 750 °C; K_2CO_3: A4 900 °C, B4 750 °C.

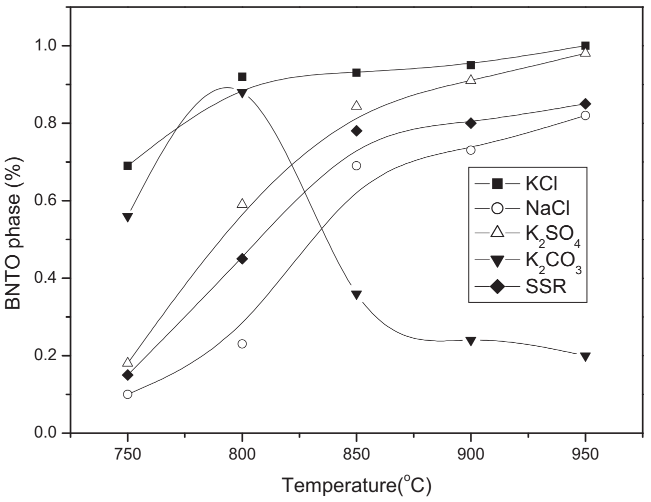

Fig. 4. Variations in BNTO phase as a function of calcination temperature.

3.4. Particle size

Fig. 5 shows scanning electron micrographs of BNTO powders synthesized at 800 °C in different salt fluxes. It was easily found from Fig. 5 that salt species affected the morphology characteristics of powders greatly. Relatively small-sized particles with a uniform distribution were obtained in carbonates flux. The average particle size was about 1 μm. This was associated with the fast reaction rate, which had been discussed in Fig. 4. So the smaller particle size in carbonates might result from high nucleation and fast reaction rate achieved at relatively low temperature.

In comparison with chloride flux, the sulphate MSS powders had a relatively larger particle size. Its average particle size was about 20 μm while in chloride flux it was only 5–6 μm at 800 °C. In addition, the BNTO particle shape showed a strong dependence on the salt species. The particles in chloride and carbonates flux grew more plate-like and the typical quadrate-like morphology was obtained in KCl. However, in the case of sulphates, the faceting of particles was not found to be

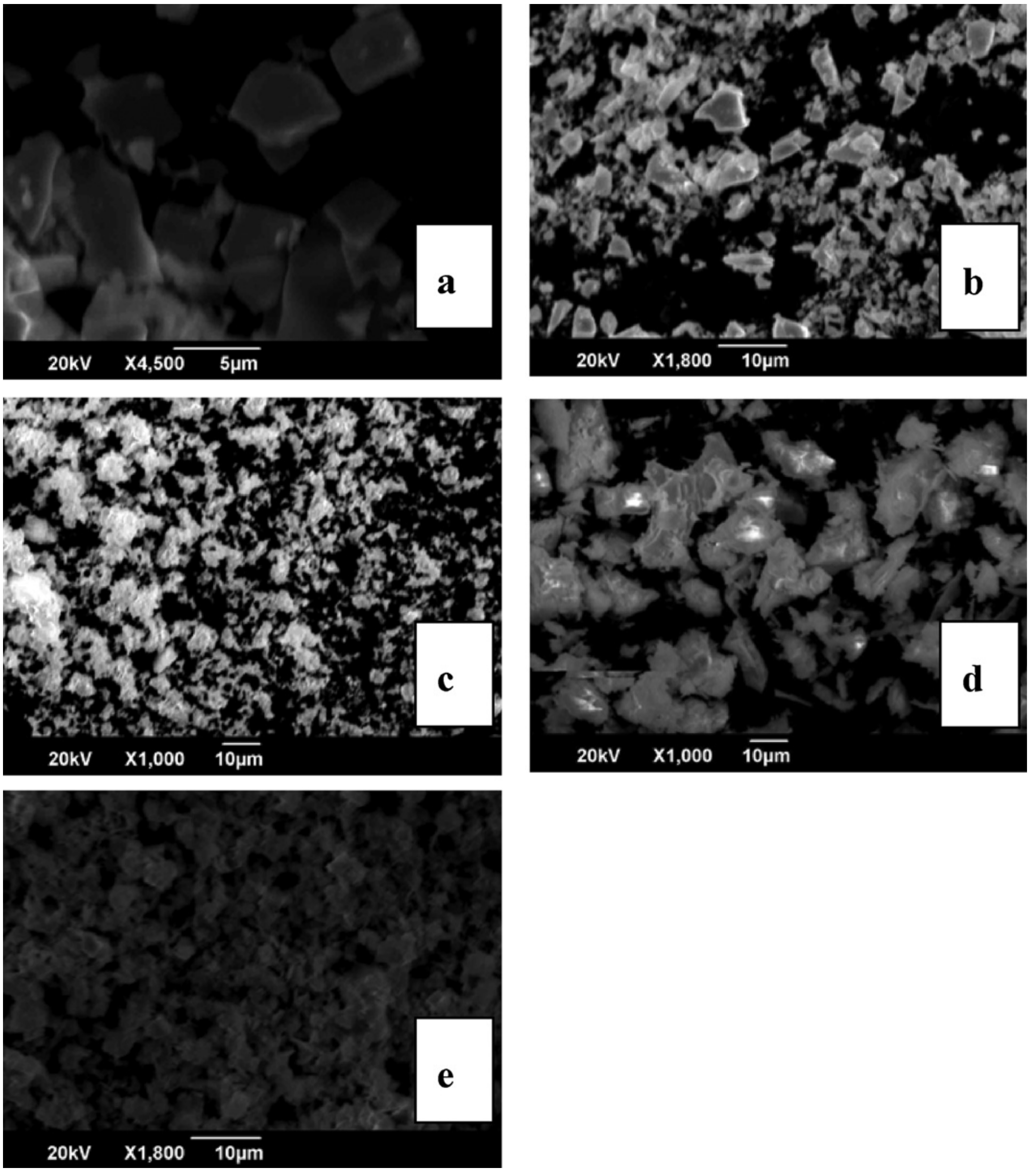

Fig. 5. Scanning electron micrographs of powders synthesized at 800 °C for BNTO (a) KCl; (b) NaCl; (c) K_2CO_3; (d) K_2SO_4; (e) SSR.

predominant and powders were mainly composed of irregular blocks.

There are many factors which influence the morphological characteristics of BNTO phase. Besides the experimental parameters such as the temperature, time, relative amount of salt, etc., under the same conditions, anion size and solubility effect, induced by changes in types of salt, were reported to be responsible for the reaction rate and further contributed to the change of particle size and shape. So the morphological difference of BNTO powders caused by the salt species could be explained by the differences in the anion sizes of the salts and the solubility of the constituent oxides in the salt fluxes. The similar results were also found in the literatures by Ki Hyun Yoon, in which the crystallographic constraints given by the different sizes of the anions were regarded to be the main reasons for morphological difference. Compared with the chloride ions, the sulphate ions were larger. When Cl^- and SO_4^{2-} ions move freely in the flux, it was suggested the growth of the BNTO particles between the large sulphate ions progressed more rapidly than between the smaller chloride ions [14,15].

Fig. 6(a) shows the temperature dependence of the average particle size. The particle size increased with temperature increasing in spite of different salt species. Fig. 6 (b) shows the particle growth rate under different conditions. Except carbonates, all the rest curves tended to be level. This indicated BNTO particles had the fastest growth rate in carbonates especially when the temperature was higher than 800 °C. The particle growth behavior with temperature for different salt species can be represented by the following equation:

$$D^2 = k(t - t_o)\exp\left(-\frac{E}{RT}\right)$$

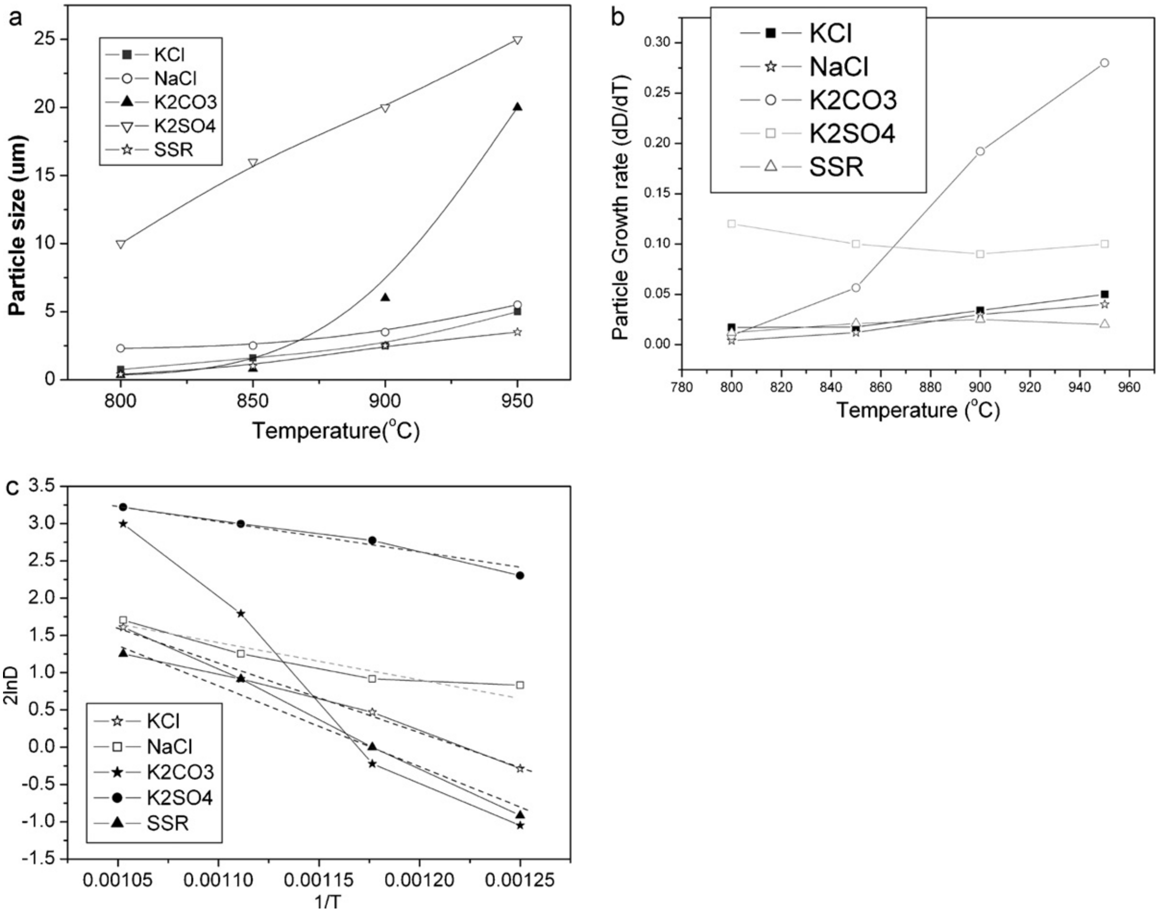

Fig. 6. (a) Dependence of BNTO particle size on the calcination temperature; (b) particle growth rate of BNTO; (c) plots of 2 ln D (D: the average particle size) vs. $1/T$.

where D is the average particle size at time t, k is the rate constant, E is the activation energy for particle growth, R is the gas constant and T is the fire temperature. The Arrhenius dependence of BNTO particles on the formation temperatures is depicted in Fig. 6(c). The activation energy for particle growth could be calculated from the plot of 2 ln D versus $1/T$. So the slopes of the dashed line indicated the average activation energies for particles growth. The corresponding results are shown in Table 1.

It was easily found from Fig. 6(c) and Table 1 there were two distinct regions for K_2CO_3 while no big difference in activation energy was found for the rest lines. This implied the growth process of BNTO in K_2CO_3 might undergo a possible transition when the temperature was increased higher than 850 °C.

The MMS mechanism was a two-step process consisting of particle nucleation and subsequent growth. The nucleation process depended on the difference of dissolution rates between the reacting oxides in the molten salt. The fast-dissolving component was transported to the outer surface of the low-dissolving component and nucleated on the surface of the latter. This process was mainly controlled by diffusion and happened at relative low temperature. So lower temperature was a possible facility for nucleation in K_2CO_3 and its nucleation rate was faster than the particle growth rate. The delayed particle growth led to smaller particle size.

With an increase in temperature, the solubility of oxides in K_2CO_3 flux increased, which accelerated the atom diffusion process. On the other hand, the formed small particles also started to contact and merge with each other. Under these conditions, the synthesis process underwent a transition from a diffusion control mechanism to an interfacial reaction controlled mechanism, which led to a fast growth rate and faceted shapes formation.

Table 1
The average activation energy of BNTO under different conditions.

Salt species	KCl	NaCl	K_2SO_4	SSR	K_2CO_3	
					<850 °C	>850 °C
The average activation energy (KJ/mol)	78.86	36.2	38.09	90.16	98.18	205.85

4. Conclusions

BNTO powders have been prepared by the molten salt method and the influences of the salt species on the morphology characteristics of powders were investigated. The results indicated the salt species had a significant effect on the particle size and morphology. BNTO powders synthesized from K_2SO_4 flux had relatively larger particle size with irregular shapes. In the case of K_2CO_3, the particle growth process underwent a transition from a diffusion mechanism to an interfacial reaction mechanism with temperature increasing, which led to the fast growth rate when temperature was beyond 800 °C. Compared with K_2CO_3 and K_2SO_4 fluxes, the plate-like BNTO powders were found to be easily synthesized at relatively low temperature in chloride.

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