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Synthesis, sintering, and characterization of BNT perovskite powders prepared by the solution combustion method

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Abstract

Pure $Bi_{0.5}Na_{0.5}TiO_3$ powders have been successfully synthesized by a single-step solution combustion technology using urea as fuel and metal (Bi and Na) nitrates as reactants. The phase structure and morphology of the as-prepared product were examined by X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FT-IR) and scanning electron microscopy (SEM). Effects of reaction parameters including fuel to oxidizers ratio and ignition temperature on the phase formation and morphology evolution were investigated. XRD shows that a single perovskite BNT phase is formed at the ignition temperature of 600 °C with fuel to oxidizers ratio of 2.0. Well-dispersed powders with the average particle size of 200 nm are obtained after milling for 24 h. BNT ceramics can be well densified at 1140 °C for 2 h with average grain size about 2 μm and show evidence of relaxor ferroelectric behaviors with diffuse phase transition and frequency dispersion.

Keywords: Dielectric properties; Bismuth sodium titanate; Ceramic; Solution combustion

1. Introduction

Lead zirconium titanate (PZT) based ceramics are high-performance piezoelectric materials, which are widely used in sensors, actuators, transducers and other electronic devices [1–3]. However, owing to the high volatility of element Pb during synthesis and sintering process, the preparation and the application of lead-based ceramics would caused serious lead pollution and instability of the compositions [4,5]. Therefore, it is necessary to develop environment-friendly lead-free piezoelectric ceramics.

Bismuth sodium titanate $Na_{0.5}Bi_{0.5}TiO_3$ (abbreviated as BNT) is a typical lead-free piezoelectric material with remnant polarization (P_r) of 38 $\mu C/cm^2$, Curie temperature (T_c) of 320 °C and coercive field (E_c) of 73 Kv/cm at room temperature [6,7]. It has been considered to be one of the most excellent lead-free ferroelectric materials [8,9]. It is well known that sintering and piezoelectric properties of ceramics are closely related to their powders. Therefore, it is important to produce powders with desired particle size and morphology. BNT powders have been synthesized by solid state reaction [10,11], sol–gel technique [12–15], hydrothermal method [16,17] and mechanochemical synthesis [18]. However, these techniques require a high temperature, a long processing period, repeated heat treatment or costly reagents. Recently, solution combustion synthesis is attracting much attention because of its low temperature, relatively inexpensive feedstock and simplicity. However, there are few reports on BNT and BNT-based piezoelectric materials by solution combustion synthesis. Samikhya Joshi [19] prepared BNT–-$BiFeO_3$ composite powders through citrate–nitrate solution combustion route. He used citric acid as a fuel and obtained amorphous powders after combustion. A further calcination step was needed to promote BNT phase formation. In this work, we synthesized BNT powders with single perovskite phase by the solution combustion synthesis method in a single step. The effects of reaction parameters including ignition temperature and fuel to oxidizers ratio on phase formation and morphology evolution of the product are investigated.

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2. Experimental

2.1. Synthesis

BNT powders were prepared by the solution combustion synthesis method. Tetrabutyl titanate ($Ti(C_4H_9O_4)_4$, 98%), bismuth nitrate pentahydrate ($Bi(NO_3)_3 \cdot 5H_2O$, AR) and sodium nitrate ($NaNO_3$, AR) were used as starting materials. $Ti(C_4H_9O_4)_4$ was added into distilled water to get a white precipitation. The precipitation was washed with distilled water and then dissolved in HNO_3 to get a clear $TiO(NO_3)_2$ solution.

Metal nitrates and urea were employed as oxidizers and a reducer, respectively. The stoichiometry composition of the redox mixture was calculated according to the method of Jain et al. [20]. To calculate fuel to oxidizers ratio, the elements were assigned formal valences as follows: Na = +1, Bi = +3, Ti = +4, C = +4, H = +1, O = −2 and N = 0. For complete combustion reaction, the fuel to oxidizers ratio, φ, should be equal to 1.0 theoretically. Accordingly, the overall reaction could be given as below:

$$Bi(NO_3)_3 \cdot 5H_2O + NaNO_3 + 2\ TiO(NO_3)_2 + 6.67\ CO(NH_2)_2 = 2\ Bi_{0.5}Na_{0.5}TiO_3 + 6.67\ CO_2 + 10.67\ N_2 + 13.34H_2O$$

The molar ratio of the reactants taken is 1: 1: 2: 6.67 of $Bi(NO_3)_3 \cdot 5H_2O$: $NaNO_3$: $TiO(NO_3)_2$: $CO(NH_2)_2$.

The appropriate amounts of reactants were mixed in a glass beaker to get a clear solution. Then the mixture solution was introduced into a muffle furnace preheated to a proper temperature. Within a few minutes, the solution boiled and was ignited to produce a self-propagating flame. Finally, a white powder was obtained.

The combusted powders were ground in a planetary ball mill for 24 h and then pressed at 20 MPa to form disc specimens with a diameter of 15 mm and a thickness of ~1.5 mm. The disc specimens were sintered at 1140 °C for 2 h to get ceramics.

2.2. Characterization

The phase of the powders was analyzed by the X-ray diffractometer (Netherlands, X′Pert PRO) with a Cu Kα radiation ($\lambda = 1.5406$ Å) at 40 kV tube voltage and 40 mA tube voltage current in a 2θ ranging from 10° to 90°. Scanning electronic microscopy (FEI, Sirion 200) was used to investigate the microstructures. The Infrared (IR) spectra of the powders were recorded in the range of 400–4000 cm^{-1} on a Fourier Transform Infrared (FT-IR) spectrometer (Thermo-Nicolet Avatar 370) by the KBr pellet method. The density of ceramics was determined by the Archimedes method in distilled water. The sintered samples were polished and covered with silver paste as the electrode for the dielectric measurement. Multi-frequency LCR meters (Agilent, HP4294) was used to measure dielectric permittivity as a function of temperature and frequency. Measurements were taken from 100 Hz to 10 kHz in the temperature range of 25 °C to 450 °C with a heating rate of 2 °C/min.

3. Results and discussion

3.1. Effects of fuel to oxidizers ratio

Fuels and fuel to oxidizers ratio play very important roles in the properties of the synthesized powders including phases, crystallite size, morphology and specific surface area. Fig. 1 shows the XRD patterns of powders prepared at different φ values at an ignition temperature of 600 °C. The obtained powder was amorphous at $\varphi = 1.0$. When φ was increased to 1.5, BNT perovskite phase was formed and a small amount of $Bi_2Ti_2O_7$ phase was also observed. With the value of φ further increasing to 2.0, the diffraction intensity of BNT phase increased and that of $Bi_2Ti_2O_7$ phase disappeared. All the diffraction peaks can be indexed to the standard patterns of the rhombohedral $Na_{0.5}Bi_{0.5}TiO_3$ (JCPDS No. 36-0340), which agree well with the reported values [21]. The chemical compositions of this powder were analyzed by ICP-AES. The results are listed in Table 1. It indicated that the mole ratio was 1.000:0.993:2.002 for Bi:Na:Ti. The chemical composition is almost the same to the theoretical chemical compositions of BNT, which is 1:1:2 for Bi:Na:Ti. The FT-IR spectra of the powders are shown in Fig. 2. The weak peak at 1639 cm^{-1} and the band around 3453 cm^{-1} could be attributed

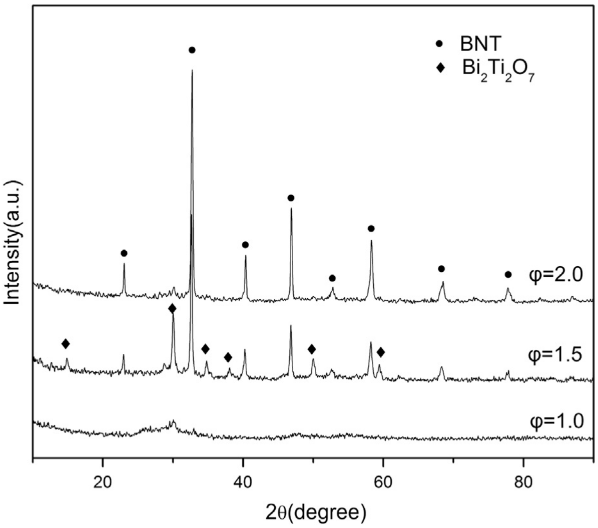

Fig. 1. XRD patterns of as-prepared powders with different φ ignited at 600 °C.

Table 1
Element compositions of the powders determined by ICP-AES

Element	Analytical line (nm)	Content (mg/L)
Bi	223.061	19.99
Na	589.592	2.181
Ti	334.940	9.172

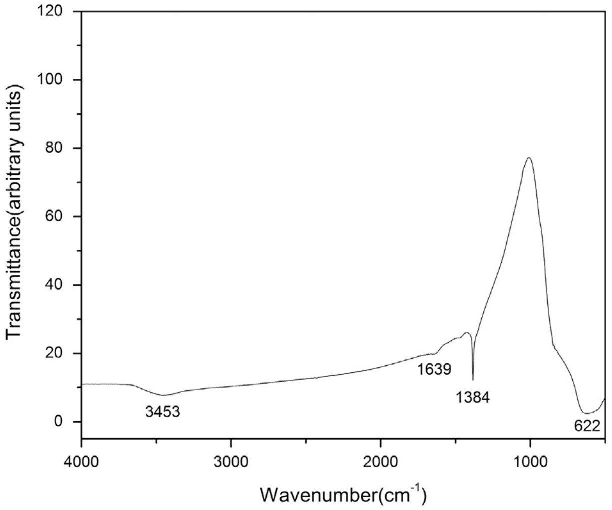

Fig. 2. The infrared spectrum of the powders at $\varphi=2$ with an ignition temperature of 600 °C.

to the stretching and bending mode of H_2O from the air. The sharp and intensive peak at 1390 cm^{-1} was due to the presence of nitrate. A large band appeared around 600 cm^{-1}, which could be attributed to the characteristic vibration of Ti–O octahedron and indicated the formation of the perovskite phase. Those above results confirm that a pure BNT phase was prepared by the solution combustion synthesis method at 600 °C and $\varphi=2.0$.

The overall chemical equation of combustion reaction at different values of φ can be represented as:

$$Bi(NO_3)_3\cdot 5H_2O + NaNO_3 + 2\ TiO(NO_3)_2 + (6.67+x)\ CO(NH_2)_2 + 1.5x\ O_2 = 2Bi_{0.5}Na_{0.5}TiO_3 + (6.67+x)\ CO_2 + (10.67+x)\ N_2 + (13.34+2x)\ H_2O \tag{1}$$

The enthalpy of combustion and the adiabatic flame temperature as a function of fuel amounts can be approximately calculated using the following equations [22]:

$$\Delta H = \left(\sum n\Delta H_p\right) - \left(\sum n\Delta H_r\right) = -\int_{T_0}^{T_f} \left(\sum nC_p\right) dT \tag{2}$$

and

$$T_f = \frac{T_0 + (\Delta H_r - \Delta H_p)}{C_p} \tag{3}$$

where ΔH_r and ΔH_p are the enthalpies of formation of the reactants and products, respectively; T_f is the adiabatic flame temperature, T_0 is 298 K and C_p is the molar heat capacity of products at constant pressure. The related thermodynamic datas are listed in Table 2 [23].

It can be calculated that T_f will increase continuously with the increase of x. According to the different values of fuel to oxidizers ratio, Mukasyan et. al have summarized three different ways in combustion synthesis reaction: 1. Smoldering Combustion Synthesis (SCS); 2. Volume Combustion Synthesis (VCS); 3. Self-propagating High-temperature Synthesis (SHS) [24]. These three methods can be clarified by visual observation and have different maximum temperatures during reaction. The SCS mode is characterized by relatively slow, essentially flameless reaction with the lowest maximum temperature and the formation of an amorphous product. The VCS mode includes an extremely fast (explosion-type) reaction with the highest maximum temperature. The reaction proceeding in SHS mode initiates locally and propagates as a combustion wave in a self-sustained manner through the solution. In our experiment, because of heat conduction and radiation to the outside, the actual maximum temperatures were much lower than the calculated adiabatic flame temperature, so the reaction proceeded at $\varphi=1.0$ was SCS mode and incompleted. When φ was equal to 1.5, the addition of excessive fuel could cause a higher T_f due to the exothermal combustion reaction of urea with oxygen, so the reaction temperature increased and the reaction converted from SCS mode to SHS mode. When the value of φ increased to 2.0, ΔH was more negative than that of $\varphi=1.5$, so T_f would be higher and the reaction was VCS mode.

Table 2
Relevant thermodynamic data

Compound	ΔH_f° (25 °C) (kJ/mol)
$CO(NH_2)_2$ (s)	−79.71
H_2O (g)	−59.796
CO_2 (g)	−94.051
N_2 (g)	0
O_2 (g)	0

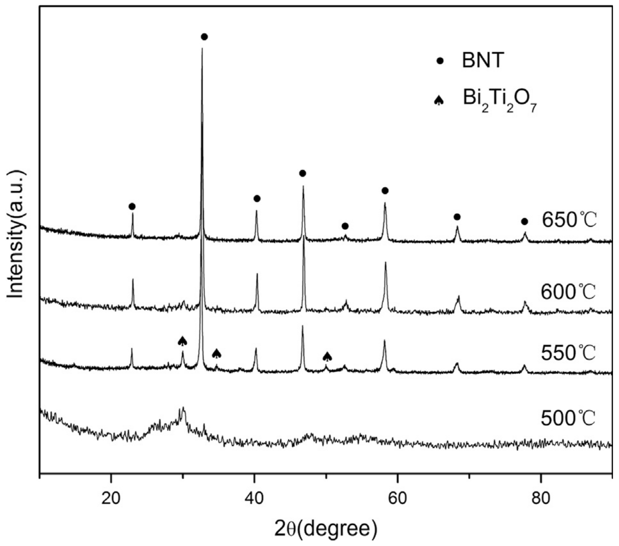

Fig. 3. XRD patterns of as-prepared powders ignited at different temperatures.

3.2. *Effects of ignition temperature*

The XRD patterns of the as-prepared powders calcined at different ignition temperatures are shown in Fig. 3. All these products were synthesized at $\varphi=2.0$. When the ignition temperature was 500 °C, the powders exhibited typical patterns of amorphous phase. The characteristic diffraction peaks of BNT phase began to appear as the ignition temperature increased to 550 °C. However, the corresponding diffraction peaks were low and some peaks of $Bi_2Ti_2O_7$ phase were also found in the product. The intensity of the diffraction peaks of BNT increased and the diffraction peaks of impurities $Bi_2Ti_2O_7$ disappeared gradually at higher ignition temperature. The $Bi_2Ti_2O_7$ pyrochlore phase easily formed at lower calcination temperature. And it could transform to BNT perovskite phase completely at higher temperature [25]. In our experiment, pure BNT phase could be obtained at ignition temperature of 600 °C, which was approximately 200 °C lower than those prepared by conventional solid state method [10].

Fig. 4 shows the SEM images of as-prepared powders ignited at different temperatures. There was a clear dependence of the grain size on the ignition temperature. The particles synthesized at 550 °C were rather small in size (1 μm or less) and spherical in shape (Fig. 4a). When the ignition temperature increased, the size of the particles became bigger (~5 μm) and the morphology was uniform quasi-spherical (Fig. 4b). Further

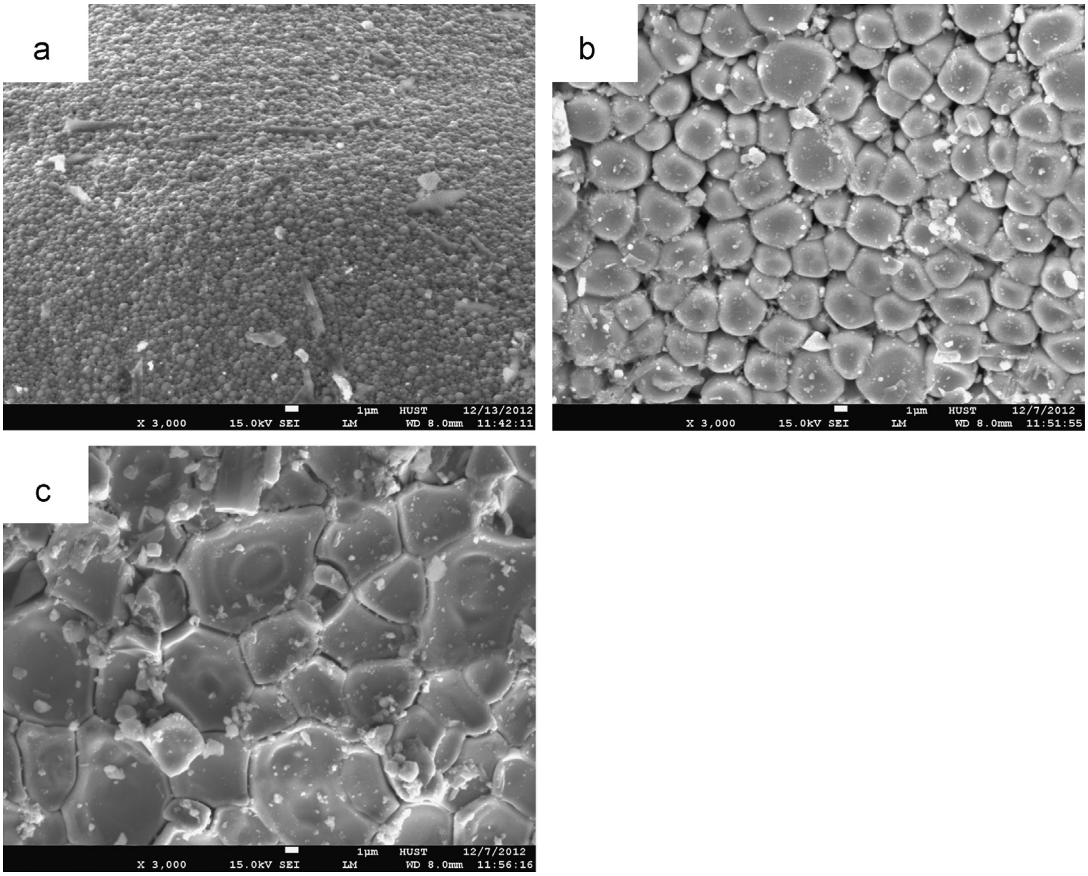

Fig. 4. SEM images of as-prepared powders ignited at different temperatures (a) 550 °C (b) 600 °C (c) 650 °C.

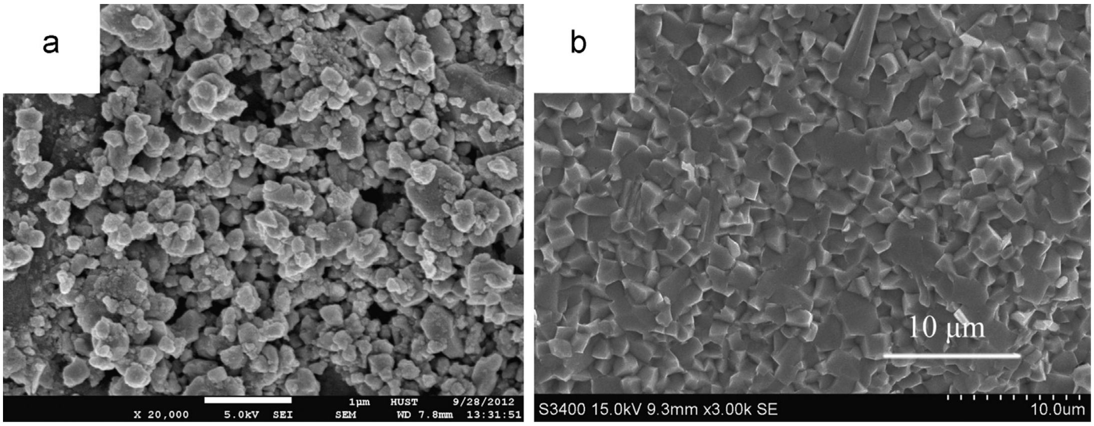

Fig. 5. SEM images of the BNT powders with ball milling for 24 h (a) and fracture surface of ceramic sintered at 1140 °C for 2 h (b).

increasing the temperature to 650 °C, the products were aggregated seriously and irregular polygonal crystallites with an average size of 10 μm were observed (Fig. 4c).

3.3. Microstructure and dielectric properties of BNT ceramics

The BNT powder prepared at $\varphi=2.0$ and 600 °C were ball milled for 24 h to obtain uniform and fine particles. Fig. 5a shows a SEM image of BNT powders after ball milling. The crystalline particles were well dispersed and about 200 nm in size. The as-prepared powders were pressed at 20 MPa and then sintered at 1140 °C for 2 h to get dense ceramics. The bulk density of the ceramic reached above 96% of the theoretical density (5.994 g/cm^3). A SEM photograph of the fractured surface of ceramic is presented in Fig. 5b. The ceramic showed an intergranular fracture with some transgranular fracture. The sizes of uniformly distributed grains were about 2 μm.

The temperature dependence of dielectric constant measured at different frequencies (100 Hz, 1 kHz and 10 kHz) is shown in Fig. 6. It can be clearly seen that two abnormal dielectric peaks existed, which was caused by the phase transitions from ferroelectric to anti-ferroelectric ($T_d=215$ °C) and from anti-ferroelectric to paraelectric phase ($T_m=350$ °C). On the other hand, ε_r showed a very strong dependence on frequency below T_d, and then the dependence became weaker between T_d and T_m. The dependence became obvious again above T_m, which was agreed with previous reports of BNT-based lead-free ceramics system [26–28]. The relaxor behaviors can be explained by local compositional fluctuation theory [29]. The A- or B-site sublattice of ABO_3 perovskite unit cell is occupied randomly by different ions, forming numerous chemical microregions with distinctive composition of the A- or B-site cations. Each microregion possesses its own Curie temperature (T_c), leading to relaxor characteristics. In our work, the coexistence of Na^+ and Bi^{3+} ions in the A-site induced a relaxor ferroelectric behavior, which was also proved by Saïd et al. [14].

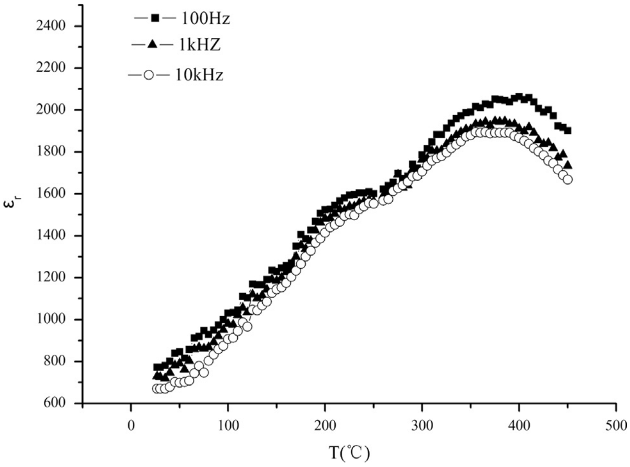

Fig. 6. Temperature dependence of the relative permittivity for BNT ceramic at different frequencies.

4. Conclusions

Bismuth sodium titanate has been successfully synthesized via a single step solution combustion method. The fuel to oxidizers ratio (φ) and ignition temperature have significant impacts on the phase of produced powders. The obtained powder was amorphous at $\varphi=1.0$ or low temperature (500 °C). A single perovskite BNT phase was formed at the ignition temperature of 600 °C with $\varphi=2.0$. The size of the particles was about 5 μm and the morphology was uniform quasi-spherical. Well-dispersed powders (about 200 nm) were produced after milling for 24 h. Dense BNT ceramics with average grain size about 2 μm were obtained by sintering the green pellet at 1140 °C for 2 h. The ceramic showed evidence of relaxor ferroelectrics with diffuse phase transition and frequency dispersion. The temperature of ferroelectric-antiferroelectric phase transition was ~215 °C (T_d) and the antiferroelectric-paraelectric phase transition at ~350 °C (T_m).

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