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Synthesis and characterization of $Bi_{1/2}Na_{1/2}TiO_3$ nanopowders by pyrogenation-with-sugar-protection method

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ABSTRACT

This study developed a method, pyrogenation-with-sugar-protection, to prepare $Bi_{1/2}Na_{1/2}TiO_3$ nanopowders at a temperature as low as 500 °C. In this method, the process of agglomeration is controlled and the excessive grain growth is avoided. Studies by X-ray diffraction, scanning electron microscopy and transmission electron microscopy (TEM) indicate that the powders are well crystallized, chemically stoichiometric and ~50 nm in diameter. It is a universal method to prepare various oxide nanopowders without calcination at a high temperature. The dense ceramics with grain size lower than 1 μm can be obtained sintering at 1150 °C using the powder prepared by this method and the piezoelectric and dielectric properties of them were also investigated.

1. Introduction

Lead-based piezoelectric ceramics, represented by $PbTiO_3$–$PbZrO_3$ (abbreviated as PZT) and PZT-based multi-system, are widely applied in electronic and microelectronic devices due to their excellent piezoelectric properties. However, the toxicity of lead oxide and its high vapor pressure during sintering processing cause a serious ecological problem. To reduce and eliminate lead pollution, much attention has been paid to lead-free piezoelectric ceramics. It is necessary to develop ceramics with excellent piezoelectric properties that should be "lead-free at last"[1].

$Bi_{1/2}Na_{1/2}TiO_3$ (BNT) is considered as an excellent lead-free piezoelectric ceramic candidate [2]. With a perovskite structure of rhombohedral symmetry at room temperature [5–7], it shows strong ferroelectric property with a relatively high Curie temperature of 320 °C and a large remnant polarization (~38 μC cm^{-2}) [3,4,8–10]. Compared with PZT, BNT possess high anisotropic electro-mechanical coupling property with the coupling constant K_p = 16.5–25.5% in plane direction and $K_t \geq 48\%$ in thickness direction, high frequency constant (which equals the product of resonance frequency and the dimension in the resonance direction) $N_t \geq 2550$ Hz m and lower dielectric constant $\varepsilon_T^{33} = 290$–524 [11] that just meet the demand on ultrasonic application. Therefore, BNT-based ceramics show a great prospect not only for environment protection but also for various applications.

Because of the poor sintering property of the pure BNT-based ceramics and the comparatively low piezoelectric constant $d_{33} < 100$ pC N^{-1} [11], much research focuses on the improvement of piezoelectric properties through A-site or B-site substitution in perovskite BNT. However, little research has been done on the synthesis of BNT-base powders. High calcination temperature and repeated grinding are needed for the conventional solid-state method. Hence, a method with relatively low temperature and simplicity is attractive for the preparation of high-quality BNT-based lead-free piezoelectric ceramics.

2. Experimental procedure

2.1. Preparation

The starting materials for the synthesis include analytical reagent $Bi(NO_3)_3{\cdot}5H_2O$, $NaNO_3$, $Ti(OBu)_4$, glycerol, NH_4NO_3 and cane sugar (saccharose). The synthesis process may be divided into three steps. The first step was to prepare a base solution. The base solution was prepared by dissolving $Bi(NO_3)_3{\cdot}5H_2O$ (9.7014 g) and $NaNO_3$ (1.6998 g) and $Ti(OBu)_4$ (13.614 g, dissolved in absolute alcohol) into glycerol. The solution concentration is for the composition of BNT, for other compositions the solution concentration is changed accordingly. The second step was to prepare a sugar-protecting precursor. By adding sugar (21.6 g) and NH_4NO_3 (1.6008 g) to the base solution (60 °C) under intensive stirring, a sugar-containing solution was obtained. The solution was then dried at 180 °C for 24 h to allow the reaction of dehydration and carbonization to take place. In the third step, the sugar-protecting precursor was calcined from 300 to 900 °C. Accordingly powders of $Bi_{1/2}Na_{1/2}TiO_3$ with different grain sizes were obtained.

The powders calcined at 500 °C were pressed into disks with 10 mm in diameter and 1 mm in thickness, then sintered in a box furnace at 1150 °C for 3 h. The bulk density of the sintered samples was measured by the Archimedes method (dewatering method).

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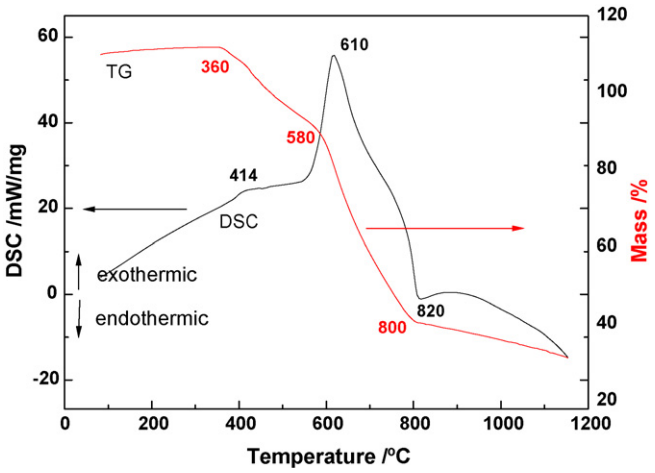

Fig. 1. Results of TG–DSC of the sugar-protecting precursor.

2.2. Characterization

The process of crystallization was characterized by DSC analysis and thermogravimetric analysis (TG). Powder X-ray diffraction (XRD, Rigaku D/max-RB, Japan) analysis was carried out to examine the phase identification and structure of the thermally treated samples. The particle size and morphology of the calcined powders were determined by transmission electron microscopy (TEM, Hitachi H-800, Japan). The microstructure of the sintered sample was examined by field emission scanning electron microscopy (FE-SEM, JEOL JSM-6301F, Japan).

On the both surfaces of the sintered ceramic disk, silver electrodes were prepared by painting and firing silver paste. Such Ag/BNT/Ag samples were used in the ferroelectric tests.

3. Results and discussion

The TG–DSC analysis gives some information about the process of crystallization. Fig. 1 shows the weight loss and DSC of the sugar-protecting precursor powders as a function of temperature. From 360 to about 580 °C, there is a weight loss of ~10%. Such weight loss is mainly due to the decomposition of the inorganic compound and consequently the formation of BNT nano-particle. The DSC peak in the curve shows only a shoulder at about 414 °C due to the complicated chemical process including the reaction between carbon and the inorganic substances, the pyrogenation of the inorganic substances, and the crystallization of the BNT. In this complicated process, the oxidation of carbon by the nitrate and the crystallization of the consequently formed oxide are assumed to be an exothermic reaction, while the pyrogenation of the inorganic substances is considered as an endothermic reaction. Such difference attributed to the shoulder in the DSC curve at about 414 °C. From 580 to ~800 °C, another weight loss as much as 50% is observed, which is mainly caused by the oxidation and elimination of the carbon network by the atmosphere, with a corresponding exothermic peak at 610 °C shown. The slow weight loss above 800 °C is attributed to the volatilization of Bi_2O_3, with the endothermic peak at about 820 °C.

X-ray diffraction was performed to characterize the crystallinity and phase of the powders. Fig. 2 shows the XRD patterns of BNT powders calcined at different temperatures. The scan was done with the scanning speed of 6° min^{-1}. The pattern of powders calcined at 300 °C appears to be mainly Na_4TiO_4, although small intensity of BNT peak is also found. Thus, BNT is not well formed according to our designing. When calcined above 500 °C, the pattern shows that BNT becomes main phase. The crystal structure of BNT powders is classified as rhombohedral perovskite and it does not change with calcining temperature. All other peaks are identified as from perovskite BNT except for one small peak at

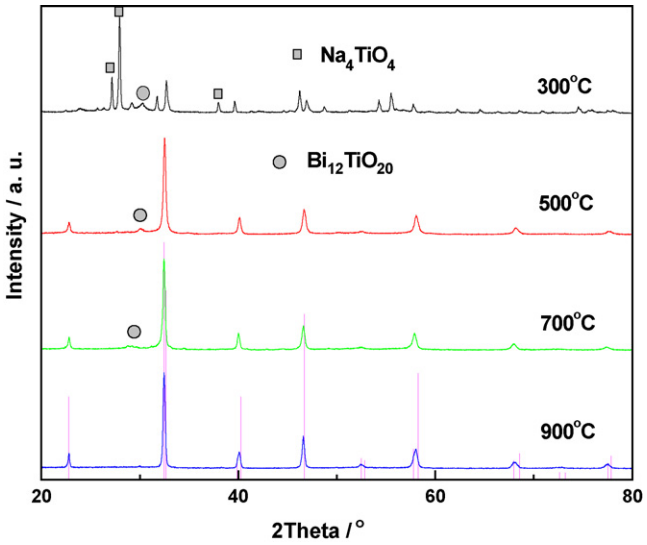

Fig. 2. XRD patterns of BNT powders calcined at different temperatures.

about 29° which is caused by the diffraction of $Bi_{12}TiO_{20}$. And this small peak disappeared when the calcining temperature is raised to 900 °C. Therefore, crystallization happens at a temperature as low as 300 °C, while heat treatment at a temperature above 500 °C has helped to get purer BNT powder. Considering the fact that the rise of calcining temperature leads to the agglomeration of BNT particles, the calcining temperature 500 °C is applied for fabrication of the ceramics in this study.

To form a network of carbon, sugar plays an important role in the reaction and its mole content according to Bi^{3+} ion in the system strongly influences the configuration of obtained BNT powder, which is shown in Fig. 3. With the mole fraction of sugar to Bi^{3+} ion rising from 1:1 to 6:1, better crystallized perovskite BNT powder are obtained, with a smaller peak intensity caused by impurity (marked as peaks A and B in the pattern). To clearly show such effect, the ratio of intensity of peaks A and B to one of BNT standard peak (marked as C) with different sugar content is shown in Fig. 4. It is clearly

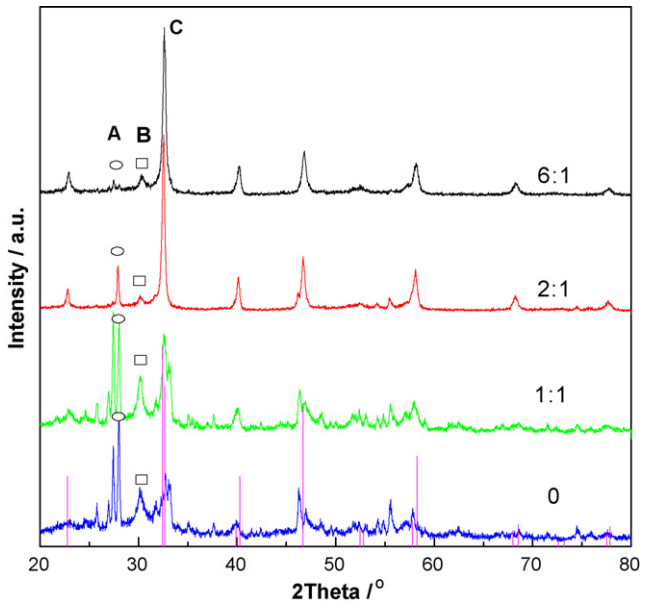

Fig. 3. XRD patterns of BNT powders with different sugar content.