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Pyroelectric, ferroelectric, piezoelectric and dielectric properties of $Na_{0.5}Bi_{0.5}TiO_3$ ceramic prepared by sol-gel method

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ABSTRACT

Sodium bismuth titanate (BNT) nanopowder of molar composition 50/50 ($Na_{0.5}Bi_{0.5}TiO_3$) was prepared by a sol-gel processing method. The structure and microstructure of the precursor gel as well as the ferroelectric, pyroelectric, dielectric and piezoelectric properties of the BNT were studied. BNT crystallized in the rhombohedra perovskites structure $Na_{0.5}Bi_{0.5}TiO_3$ was obtained from the precursor gel by heating at 700 °C for 2 h in air. The BNT ceramic at 1100 °C sintering temperature present high crystallinity, good dielectric properties at 1 kHz ($\varepsilon'=885$, tan $\delta=0.03$, $T_c=370$ °C), piezoelectric properties ($k_{33}=0.39$, $c_{33}=105$ GPa, $e_{33}=12.6$ C/m^2, $d_{33}=120$ pC/N), high remnant polarization ($P_r=47$ μC/cm^2) and pyroelectric coefficient ($p=707$ μC/m^2 K) and low coercive field ($E_c=55$ kV/cm). Hence, the BNT prepared by sol-gel method could be used for silicon based memory device application where a low synthesis temperature is a key requirement.

1. Introduction

Sodium bismuth titanate, $Na_{0.5}Bi_{0.5}TiO_3$ (BNT) is considered to be an excellent alternative candidate for lead-free piezoelectric ceramics and shows strong ferroelectric properties [1]. BNT ceramic has a perovskite ABO_3 structure, large remnant polarization, $P_r=38$ μC/cm^2 at room temperature and high Curie temperature ($T_c=320$ °C) [2], compared with that of commercial lead ferroelectric material (lead zicronate titanate, PZT) which has $P_r=31$ μC/cm^2 and $T_c=490$ °C [3]. However, BNT has a relatively high coercive field ($E_c=73$ kV/cm) which causes poling difficulty [2] and electrical conduction due to oxygen vacancies [4].

Conventional solid state reaction method is used frequently for the synthesis of BNT ceramics. However, this technique usually results in larger particle size [5] and the formation of secondary $Bi_2Ti_2O_7$ phase is unavoidable [6]. Moreover, it is difficult to maintain a chemical homogeneity of the obtained powders using the conventional solid state method since the reaction among the solid powders of starting materials is heterogeneous [7]. As for to date, many authors have developed alternative methods to replace the conventional solid state method such as sol-gel using either citrate and steric acid as a solvent [2,6,7]. Piezoelectricity can be enhance by decreasing the domain size of a ceramic [8,9] and the domain size can be decreased by reducing the grain size of the ceramic [10,11]. BNT ceramic made by sol gel method produces nanoscale particle size and it has also been reported that such samples required lower electric field for poling and exhibits the higher piezoelectric properties [12].

There are substantial reports on BNT prepared by sol-gel method [12–14]. However, the electrical properties of the sample are rarely analyzed and discussed especially on the pyroelectric properties and the piezoelectric resonance of the BNT. In this study, the structure and electrical properties such as pyroelectric, piezoelectric resonance and ferroelectric properties of BNT ceramic synthesized by the sol gel method were thoroughly examined.

2. Experimental

Anhydrous sodium acetate (CH_3COONa, 99.95%), bismuth (III) acetate ($(CH_3COO)_3Bi$, 99.99+%) and titanium (IV) butoxide ($Ti[O(CH_2)CH_3]_4$, 97%) were selected as raw materials. 2-methoxyethanol and glacial acetic acid were used as the solvent and the chelating agent, respectively. A stoichiometry amount of sodium acetate was diluted in 2-methoxyethanol and bismuth (III) acetate in glacial acetic acid and deionized water separately. Thenceforth, both solutions were mixed together and stirred for 15 min and subsequently; titanium (IV) butoxide was added slowly. Finally, stabilizing agent (acetyl acetone) was added into the mixture and stirred at 70 °C for another 15 min to produce homogeneous and clear yellowish sol. The BNT sol was dried in an oven at 100 °C for 24 h and calcined at 700 °C for 2 h. Dried sol was ground in a mortar to get fine BNT powders. Finally, BNT powder was pressed

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into disk at 12 tones for 10 min to obtain a 13 mm diameter and ~0.7 mm thick pellet, followed by sintering at 900 °C, 1000 °C, 1100 °C and 1200 °C for 6 h in air.

Thermal behavior and the decomposition of BNT gel were obtained through thermo gravimetric analysis (TG) and differential thermal analysis (DTA Q500 V20). The phase and crystal structure of BNT at different sintering temperature were examined by X-ray diffractometer (Siemens D500). The particle size and morphology of BNT pellets were investigated by high-resolution transmission electron microscopy, HRTEM (JEOL-JSM-7600F) and field electron scanning electron microscopy, FESEM (JEOL-JSM-7600F). The dielectric properties and piezoelectric resonance were measured using Impedance Analyzer (Agilent 4294A). The ferroelectric hysteresis loop was measured using Precision LC Analyzer at room temperature. Prior to the pyroelectric and piezoelectric measurements, the samples were poled by applying a dc electric field. Poling is a process where a dc electric field higher than the coercive field, E_c is applied to a multi domain ferroelectric to acquire a net remnant polarization, P_r. The E_c is in general minimum near the Curie temperature, T_c or depolarization temperature, T_d. The sintered BNT ceramic pellets were poled in a silicone oil bath at a temperature of 200 °C (near to the depolarization temperature, T_d) with an applied dc field varying between 40 kV/cm to 55 kV/cm for 30 min and field-cooled to room temperature [15]. The pyroelectric coefficient of the poled BNT samples was measured using quasi-static method. Triangular temperature waveforms with five different heating rates were applied to the samples and the resultant short-circuited pyroelectric current was measured. The triangular waveform range was generated using LakeShore temperature controller and the pyroelectric current, I_p was measured using a Keithly 617 electrometer.

3. Result and discussion

3.1. Thermogravimetric analysis

Fig. 1 shows the results of TG and DTA curves of the dried xerogel of BNT. The decomposition pathway of the xerogel was divided into three stages. The first stage of the weight loss (temperature ranging from 25 to 110 °C) corresponds to the removal of adsorbed water on the surface of xerogel. The second stage of the decomposition occurs between 110 and ~270 °C, showing a high exothermic peak with a weight loss of 74% and a high crystallization temperature. In this range, some water, carbon dioxide and acetone are decomposed from the products of oxidation

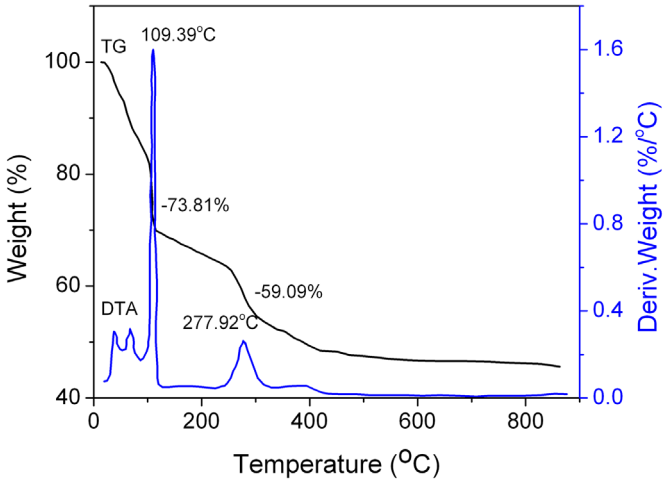

Fig. 1. TG and DTA curves of NBT dried xerogel.

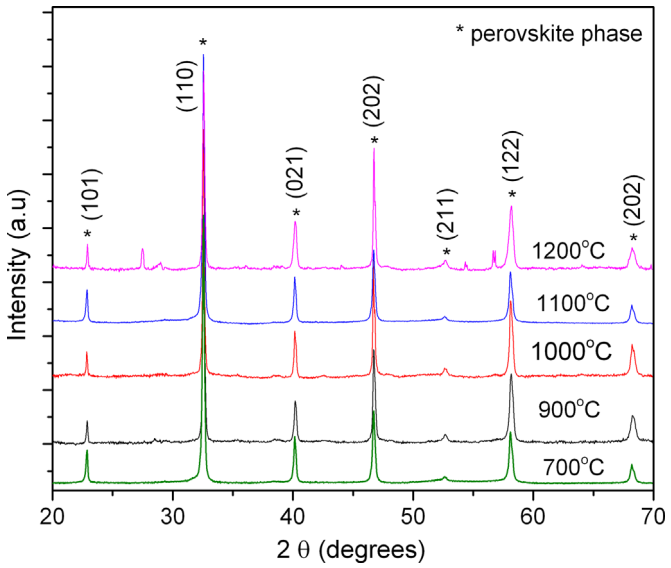

Fig. 2. XRD of BNT powder calcined at 700 °C and sintered pellets at 900 °C, 1000 °C, 1100 °C and 1200 °C.

process and it is mainly due to the evaporation of organic solvent. In the temperature range of 270 °C to 800 °C, carbon dioxide was decomposed [13]. The exothermic peak shows melting temperature at 278 °C and the weight loss ended at around 500 °C. No further weight loss or peak observed above 600 °C in the TG or DTA curves, indicating a complete decomposition of xerogel. The residue of the xerogel is 46%.

3.2. XRD analysis

XRD pattern of BNT powder calcined at 700 °C for two hours is shown in Fig. 2. The observed sharp and high intensity XRD peaks indicate that the calcination temperature of 700 °C produced $Na_{0.5}Bi_{0.5}TiO_3$ rhombohedral perovskites crystal structure [16]. Sintering the ceramic pellets at temperatures of 900 °C, 1000 °C, 1100 °C and 1200 °C increased the crystallinity of the calcined powder. The crystallinity increased up to 1100 °C while above 1200 °C crystallinity decreased and small peaks of a secondary phase appeared. Higher sintering temperature may cause the volatilization of A-site element from BNT, which can cause the oxygen vacancies induce the secondary phase. The secondary phase can be avoided by using an excess of volatile Na and Bi precursors [17] or by using an oxygen atmosphere in combustion [18].

3.2.1. Determination of crystallite size by Scherrer analysis

The XRD result can be used to evaluate the peak broadening with crystallite size and lattice strain. The breadth of the Bragg peak is a combination of both instrument- and sample-effects. The instrumental corrected broadening β_{hkl} corresponding to the diffraction peak of BNT was estimated using the relation:

$$\beta_{hkl} = \left[(\beta_{hkl})^2 \text{measured} - (\beta)^2 \text{instrumental} \right] \quad (1)$$

The crystallite size, D of the BNT nanoparticles was determined by X-ray line broadening method using Scherrer equation [19].

$$D = \frac{k\lambda}{\beta_{hkl}\cos\theta_{hkl}} \quad (2)$$

where, D is the crystallite size in nanometers, λ is the wavelength of the radiation (1.54060 Å for CuKα radiation), k is the shape factor ($k = 0.89$), β_{hkl} is the broadening of the *hkl* diffraction peak at half-maximum intensity (in radians) and θ_{hkl} is the Bragg