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Sol-gel combustion synthesis of $Bi_{0.5}Na_{0.5}TiO_3$–ZrO_2 ceramic composite

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Bismuth sodium zirconium titanate, belonging to a new class of ceramic composite powders, was prepared by the sol-gel combustion technique. A yellow precipitate was obtained by slow evaporation of precursor solution at 90 °C for 2 h. The final composition of powder is $Bi_{0.5}Na_{0.5}TiO_3/ZrO_2$. Small, elongated particles of uniform size and shape were identified with an atomic force microscope. The X-ray diffraction pattern confirms that the final powder is composite in nature and consists of a very distinct phase of bismuth titanate, sodium bismuth titanate and zirconia. The electric permittivity for the samples sintered at 1050 °C is about 640 at 50 Hz.

Keywords: *sol-gel combustion; composite; XRD; FTIR; AFM; electric permittivity*

1. Introduction

Due to their wide range of applications such as touch sensors for micromanipulation in microbiology [1], piezoelectric transformers and actuators [2–4], lead zirconium titanate (PZT) piezoelectric ceramics are considered as an important candidate material in electronic industries [5–7]. But, the worldwide restriction on hazardous substances limits the use of lead. A large quantity of lead based piezoelectric, ferroelectric and electrostrictive materials such as $PbZrO_3$–$PbTiO_3$ (PZT) [8–10] and $Pb(Mg_{1/3}Nb_{2/3})O_3$–$PbTiO_3$ (PMN–PT) [11, 12], are produced every year. Due to the toxicity of lead based ceramics, alternative lead free materials are highly preferred in the electronic industry. For two decades, great effort has been made to find high performance lead free materials. For instance, $(Bi_{0.5}Na_{0.5})TiO_3$ (BNT) [13, 14], $Bi_4Ti_3O_{12}$ (BT) [15–18], $SrBi_2Ta_2O_9$ [19, 20] and $BaTiO_3$ [21] based systems have been extensively studied. However, the remnant polarization and electrostrictive properties of these lead

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free materials are still far inferior to the lead-containing materials currently in use. By varying the chemical composition, dielectric and piezoelectric properties of lead free ceramics can be altered. Such materials attract much attention as actuators in electronic applications. Extensive studies, in multiple directions, have been made on lead free piezoelectric ceramics by the research community such as the synthesis of pure ceramics, ceramic–ceramic composites and ceramic polymer composite by various techniques, such as the sol-gel method [22–24], coprecipitation [25, 26], solid state reaction [25] and high temperature deposition technique. Above all, bismuth sodium titanate, $Bi_{0.5}Na_{0.5}TiO_3$ (BNT), is considered to be an excellent alternative candidate as a lead free piezoelectric ceramics. BNT is a ferroelectric ceramics with a remnant polarization of 38 μC/cm^2, Curie temperature (T_c) of 320 °C and a coercive field (E_c) of 73 kV/cm at room temperature. However, although bismuth sodium titanate (BNT) is considered to be a good alternate material to PZT ceramics, it has the drawback of having a strong coercive field (E_c) that causes problems in the poling process.

It is known that zirconia is one of the key materials for engineering and electronics. By doping a small amount of zirconia, the properties of the matrix material can be altered. It has been demonstrated that by doping 0.05 mol % of zirconia, $BaTiO_3$ ceramics showed a fairly satisfactory piezoelectric response, with a d_{33} value of 236 pC/N at room temperature [27]. From this viewpoint, the present work aims to synthesise lead free ferroelectric ceramic, bismuth sodium zirconium titanate (BNZT), by self-propagating combustion synthesis; this involves the exothermic reaction between metal nitrates and an organic fuel, typically ethanol, methanol, urea, or glycine. The thermal behaviour of the dried gel was analyzed by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). An X-ray diffractometer (XRD) was used to evaluate the phase formation of the calcined powder. Fourier transform infrared spectroscopy (FTIR) was used to identify tvarious functional groups. The particle morphology and size was obtained by an atomic force microscopic study (AFM).

2. Experimental

Solutions of bismuth nitrate, sodium nitrate, zirconium oxychloride and titanium isopropoxide were used as starting materials. Three separate solutions were prepared and mixed together for combustion synthesis. A stable solution of titanium isopropoxide ($TiC_{12}H_{28}O_4$) was obtained by mixing $TiC_{12}H_{28}O_4$ with acetyl acetone and 2-isoproponal (solution 1). The nominal amount of zirconium oxychloride ($ZrOCl_2 \cdot 8H_2O$) was dissolved in methanol (solution 2). Solution 3 was prepared by dissolving bismuth nitrate with acetic acid and HNO_3. The required amount of sodium nitrate was added to solution 3. After preparation, all three solutions were mixed together under stirring, which yielded a firebrick coloured viscous sol. The sol was slowly evaporated under stirring at 90 °C. After 2 h, a foam-like precipitate formed, due to the exother-

mic reaction between the metal nitrates and organic fuel. The precipitate was combusted at 400 °C. The final calcination was carried out at 700 °C for 3 h to produce $Bi_{05}Na_{05}TiO_3ZrO_2$ composite powder. The calcined powder was ground in a planetary mill in order to obtain fine particles.

3. Results and discussion

The X-ray diffraction pattern (Fig. 1) for the bismuth sodium zirconium titanate (BNZT) composite calcined at 700 °C shows the formation of mixed phases. Characteristic peaks corresponding to monoclinic $BiTi_3O_{12}$ crystals (JCPDS File No. 80 -2143) were recordered at 14.61°, 24.35°, 29.40°, 30.06°, 34.08°, 48.99°, 49.89° and 53.26°. The formation of $mZrO_2$ and $BiTiO_3$ was confirmed by the peaks at 28.09° and 33.56°, respectively. The reflections by rhombohedral BNT crystal planes (JCPDS File No.36-0340) were predicted to be at 32.48°, 40.5°and 58.26° with lower intensities. Since no powder diffraction data is available for the BNZT composite, the phase formation was analyzed by comparing the existing powder diffraction data files for BNT, BT and ZrO_2

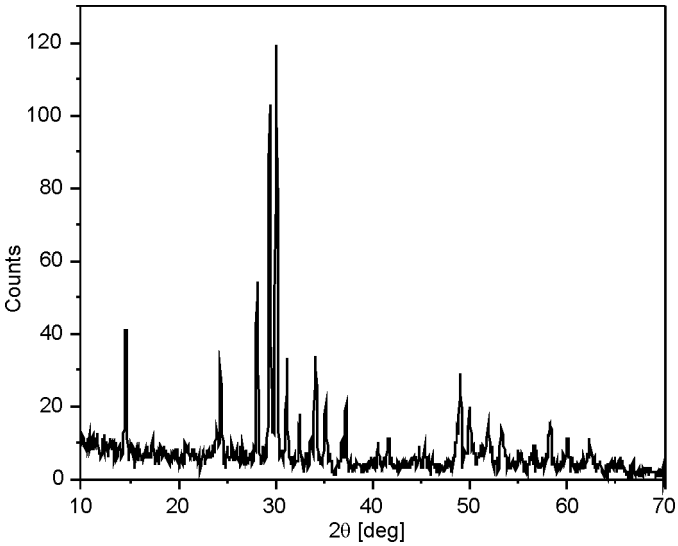

Fig. 1. X-ray diffraction pattern of BNZT composite

The FTIR spectrum of BNZT composite gel is shown in Fig. 2. Three absorption bands corresponding to N–H stretching modes were observed at 3184.3, 1355.9 and 1309.6 cm^{-1}. The vibration at 1384.8 cm^{-1} indicates the presence of nitrate, and the absorption band around 1541 cm^{-1} is due to NO_2 vibration. The strong and sharp absorption bands at 894.9 cm^{-1} and 812 cm^{-1} were recorded as being related to ν(Zr–O) $+\delta$(O–C=O).

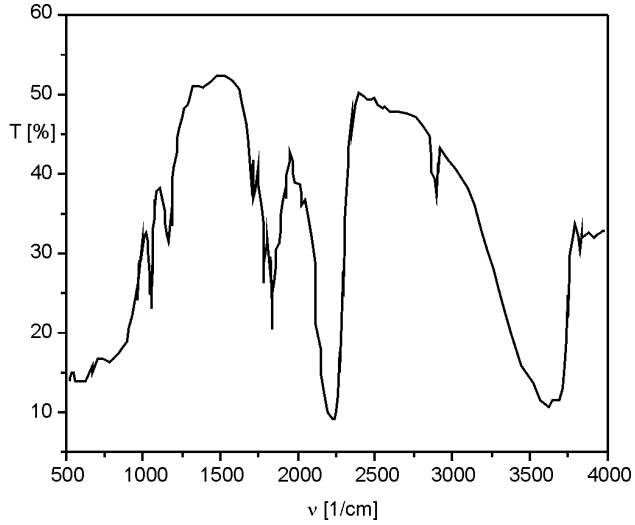

Fig. 2. FTIR spectrum of BNZT gel dried at 100 °C

The DSC (Fig. 3) shows various decomposition stages of BNZT gel with respect to temperature. An endothermic peak at 149 °C is due to removal of adsorbed water, and a broad exothermic peak between 225 °C to 400 °C is due to the burn out of oxalate and nitrates from the amorphous gel. A small exothermic peak around 470 °C may be related to the crystallization of zirconium oxalate gel into zirconia. A small exothermic peak between 520 °C to 600 °C is due to the formation of sodium bismuth titanate phase. From the TGA analysis, a major weight loss of 29 % was predicted, and the overall yield was calculated to be about 38 % of the starting materials.

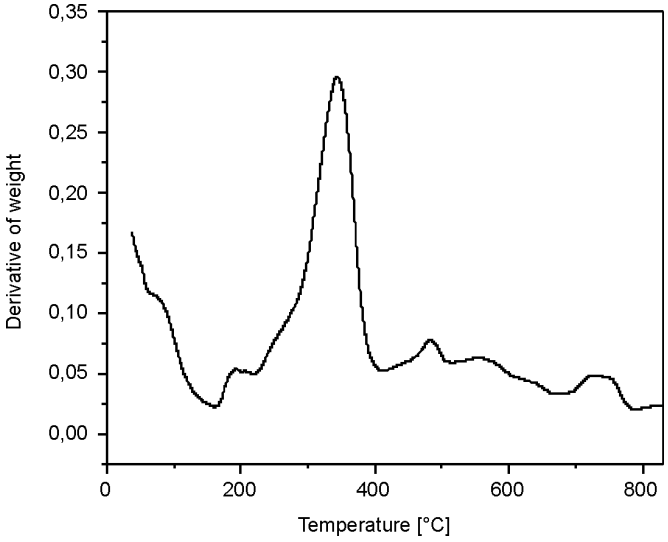

Fig. 3. DSC of BNZT composite

For the AFM study, the particles were deposited on a Si wafer. Before deposition, the wafer was thoroughly cleaned with a mixed aqueous solution of HNO_3 and H_2SO_4. The BNZT powder was dispersed in acetone and dip coated on the Si wafer. AFM images were taken with a silicon cantilever, with the force constant of 0.02 N/m and the tip height of 10–15 μm in a contact mode. Figure 4 shows the AFM image of BNZT particles having uniform size and shape. After data fitting, line profiles were taken to calculate the size of individual BNZT particles. The particles were not spherical in shape, rather they were elongated. The width and length of a BNZT particle was measured to be 170 nm and 550 nm, respectively.

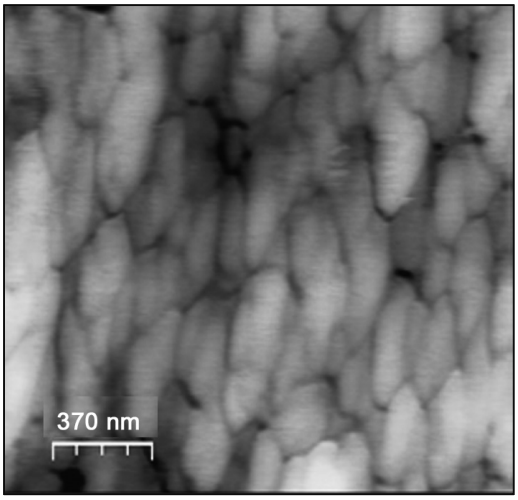

Fig. 4. AFM image of BNZT composite powder

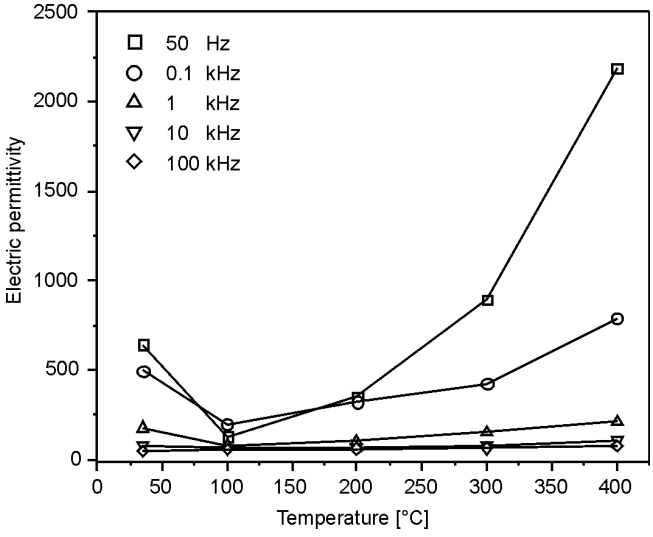

Fig. 5. Temperature dependence of the electric permittivity

Figure 5 shows the temperature dependence of the electric permittivity. In the higher frequency range (1–100 kHz), the electric permittivity (ranging from 75 to 211) is more or less temperature independent and does not increase much for temperatures below 400 °C. But, at lower frequencies (50–100 Hz), the change of the electric permittivity is significant, and attains a maximum value of 2200 at 400 °C. The electric permittivity for pure BNT is 400 at room temperature and 1800 at 400 °C for 100 kHz [28]. For BNT thin film, the electric permittivity was measured to be 300 [29]. Zhu et al. measured the electric permittivity of potassium bismuth titanate to be 536 [30].

Therefore, in the higher frequency range, the zirconia doped BNT has a lower electric permittivity compared with pure BNT. The electric permittivity for the considered composite was measured to be 46 at room temperature and 75 at 400 °C, at 100 kHz. But, in the lower frequency range, the considered BNZT composite has much higher electric permittivity of 640 at room temperature and 2200 at 400 °C at 50 Hz.

4. Conclusions

The X-ray diffraction analysis of the calcined powder indicated that the addition of zirconia suppresses the predominant reflection peak at 32.48° corresponding to BNT phase. The final powder shows a mixed phase which confirms the formation of composite between BNT and ZrO_2. The reason why the measured electric permittivity, at higher frequencies is lower than the expected value may be because the ionic radius of Zr^{4+} is higher than that of Ti^{4+}. For equal molar mixing of ZrO_2 and BNT, zirconium exceeds the stabilization limits and reduces the polarization attributable to the Ti^{4+} ion, and hence the electric permittivity is reduced to a low value. The relaxation temperature of the considered composite was not predicted to lie below 400 °C. Therefore, heavy zirconia doping suppresses the formation of BNT phase and reduces the dielectric permittivity, increasing the relaxation temperature. The ferroelectric property of the considered material is under investigation.

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