

Phase, microstructure and dielectric properties of $0.94\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3\text{--}0.06\text{BaTiO}_3$ ceramics prepared by sol-gel technique

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$0.94\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3\text{--}0.06\text{BaTiO}_3$ ceramics were fabricated by sol-gel technique. The XRD results revealed the formation of a single phase perovskite structured $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3\text{--BaTiO}_3$ at 600 °C. The SEM images showed dense microstructure and the optimum density of the ceramics sintered at 1100 °C was 5.2 g/cm³. The saturation polarization (P_s) was found to be increased with increasing temperature while the remnant polarization (P_r) was found to be increased gradually and then decreased abruptly near 85 °C, which could be attributed to the phase transformation. The coercive electric field (E_c) was found to be decreased gradually with increasing temperature. The maximum value of dielectric constant (ϵ_r) at room temperature was 800 and dielectric loss at 1 MHz was 0.07.

Keywords: lead free; perovskite; sol-gel; FT-IR; ferroelectrics

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1. Introduction

Perovskite structured lead zirconate titanate (PZT) based compositions have excellent piezoelectric and ferroelectric properties but one of the limitations of these lead containing ceramics is the environmental concern over the applications of these materials and therefore researchers are in search of lead-free and environmentally friendly electroceramics with efficient ferroelectric properties. $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ (BNT) is a lead-free ferroelectric material first reported by Smolenskii *et al.* [1] in 1960. BNT has a perovskite (ABO_3) structure in which the positive A site is shared by Na^+ and Bi^{+3} ions while Ti^{+4} ion occupy B site. BNT has a large remnant polarization (P_r) of 38 $\mu\text{C}/\text{cm}^2$, a large coercive field (E_c) of 73 kV/cm at room temperature and high Curie temperature (T_c) of 320 °C [2, 3]. BNT undergoes two thermally-induced structural phase transitions from ferroelectric rhombohedral to antiferroelectric tetragonal phase at 200 °C and from antiferro-

electric tetragonal phase to paraelectric cubic phase at 320 °C [4]. The drawbacks of BNT are its high leakage current which exists during poling process due to its relatively high electrical conductivity and the large coercive field (E_c) [5]. To improve the ferroelectric properties of BNT, different additives like BaTiO_3 [6], $(\text{Bi}_{0.5}\text{K}_{0.5})\text{TiO}_3$ [7], PbTiO_3 [8], BiFeO_3 [9], $\text{Ba}(\text{Cu}_{0.5}\text{W}_{0.5})\text{O}_3$ [10] and $\text{Bi}_{0.5}\text{K}_{0.5}\text{TiO}_3\text{--BaTiO}_3$ [11] have been doped.

In this study, $0.94\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3\text{--}0.06\text{BaTiO}_3$ ceramics were synthesized by low temperature processing, sol-gel technique. Sol-gel technique is relatively better method comparing with other methods for ceramics fabrication because using sol-gel method, fine powders can be obtained after calcination, the stoichiometry can be controlled and the phase purity can be achieved easily at relatively low temperature. The phase and microstructure of the samples were analyzed using different techniques. The temperature dependent ferroelectric properties were measured and dielectric properties of sintered ceramics were investigated at relatively high frequencies.

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2. Experimental procedure

Bismuth acetate ($\text{Bi}(\text{CH}_3\text{COO})_3$) (>99.99 % Aldrich), sodium acetate ($\text{Na}(\text{CH}_3\text{COO})$) (>99 % reagent Sigma-Aldrich) and barium acetate ($\text{Ba}(\text{CH}_3\text{COO})_2$) (>99 % reagent ACS Sigma-Aldrich) were separately dissolved in acetic acid on a hot plate with a magnetic stirrer. Titanium(IV) butoxide ($\text{C}_{16}\text{H}_{36}\text{O}_4\text{Ti}$) (99 % reagent grade Aldrich) was dissolved in ethanol and acetylacetone was added dropwise to this solution in order to stabilize it. These four solutions were mixed in a flask on a hot plate with magnetic stirrer at 75°C and a yellowish colored stable solution was obtained.

The solution was kept on a hot plate with magnetic stirrer at 100°C for 4 hours and as a result a yellowish colored gel was obtained. The gel was dried at 120°C for 24 hours and dark grey colored powders were obtained. The dried gel powders were calcined at 400°C , 600°C and 800°C for 2 hours with heating/cooling rates of $5^\circ\text{C}/\text{min}$. The calcined powders were pressed by uniaxial pressing at 100 MPa in the form of 10 mm diameter ceramic pellets and finally these pellets were sintered at various temperatures with $5^\circ\text{C}/\text{min}$ of heating and cooling rates.

The thermogravimetric and differential thermal analyses (TG/DTA) were carried out at a heating rate of $5^\circ\text{C}/\text{min}$ using thermal analyzer (Perkin Elmer Diamond series, USA). The FT-IR analysis was carried out by using Fourier transform infrared

spectrometer (Perkin-Elmer 1700). The phase and microstructure of samples were analyzed using X-Ray diffractometer (JDX-3532, JEOL, Japan) and scanning electron microscope (SEM) (JSM-5910, JEOL Japan) respectively. The apparent bulk densities of sintered ceramic pellets were measured by densitometer using the Archimedes principle. The temperature dependent ferroelectric properties were measured with a ferroelectric test system (TF Analyzer 2000E, aixACCT). The dielectric properties of the fabricated ceramic pellet sintered at 1100°C were measured with a LCR meter (Agilent 4287A).

3. Results and discussion

The TGA results show that the weight loss occurs in three different steps as shown in Fig. 1. In the temperature range of 28°C to 150°C a weight loss of 7.505 % is assigned to the desorption of chemically and physically adsorbed water which is also indicated by the exothermic peak at the same temperature in the DTA curve. A major weight loss of 22.901 % occurs from 150°C to 495°C due to the decomposition of organic derivatives. The DTA endothermic peak at 390°C indicates the initiation of the solid state reaction. In the third step, 9.888 % weight loss is observed at a slow rate in the temperature range of 495°C to 870°C . The weight loss in the third step is probably due to the transformation of material from an amorphous to a complete crystalline phase consistent with the DTA exothermic peak at 590°C which is not quite obvious.

The FT-IR spectra of the dried gel powders consist mainly of two regions as shown in Fig. 2. The first region corresponds to the absorption bands at 1540 , 1400 and 1329 cm^{-1} , characteristic of the symmetrical vibrations and bending vibrations (in plane) of COO^- groups arising from two types of ligands, acetylacetone and acetic acid. The second region at about 547 cm^{-1} represents the characteristic infrared absorptions of the Ti-O vibration. The sharp peaks at 1540 , 1400 and 1329 cm^{-1} become flat and weaker as the temperature of heat treatment is increased to 400°C and this is attributed to the burning out of the organic derivatives which has been also confirmed by the TGA results. The bands

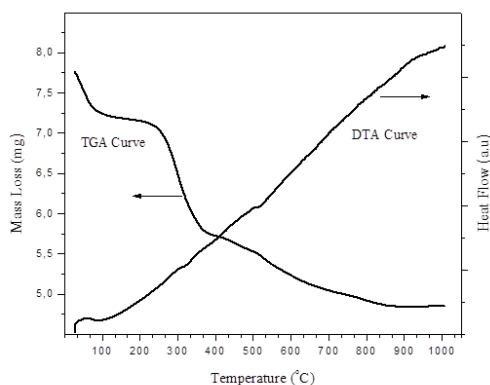


Fig. 1. TG/DTA curves of $0.94\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ - 0.06BaTiO_3 dried gel powders.

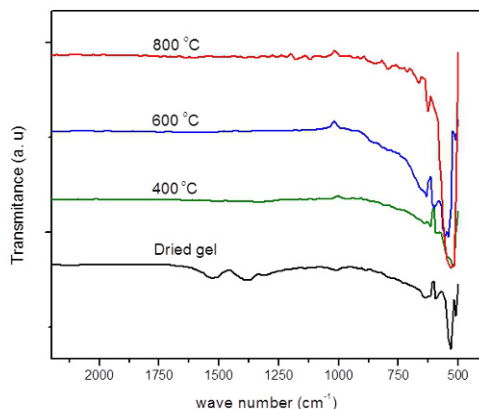


Fig. 2. FT-IR plot of $0.94\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3-0.06\text{BaTiO}_3$ treated at different temperatures.

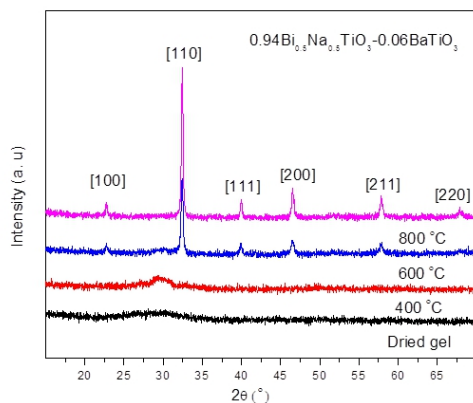


Fig. 3. XRD patterns of $0.94\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3-0.06\text{BaTiO}_3$ heat treated at different temperatures.

at 1540 , 1400 and 1329 cm^{-1} completely disappear as the calcinations temperature is increased to $600\text{ }^\circ\text{C}$. The absorption band of Ti-O vibrations increases with increasing the calcination temperature and approaches its maximum at $800\text{ }^\circ\text{C}$.

The room temperature XRD patterns of the $0.94\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3-0.06\text{BaTiO}_3$ dried gel powders calcined at $400\text{ }^\circ\text{C}$, $600\text{ }^\circ\text{C}$ and $800\text{ }^\circ\text{C}$ are shown in Fig. 3. The dried gels calcined at $600\text{ }^\circ\text{C}$ and $800\text{ }^\circ\text{C}$ reveal a single phase perovskite structured $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3-\text{BaTiO}_3$ (PDF # 89-3109) while the dried gel, heat treated at $400\text{ }^\circ\text{C}$ shows an amorphous structure. The XRD analysis

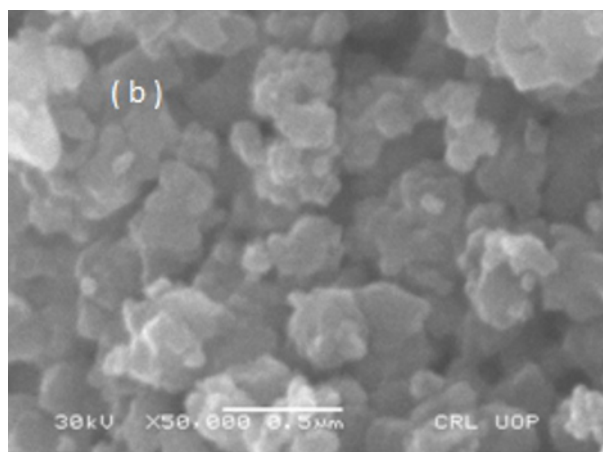
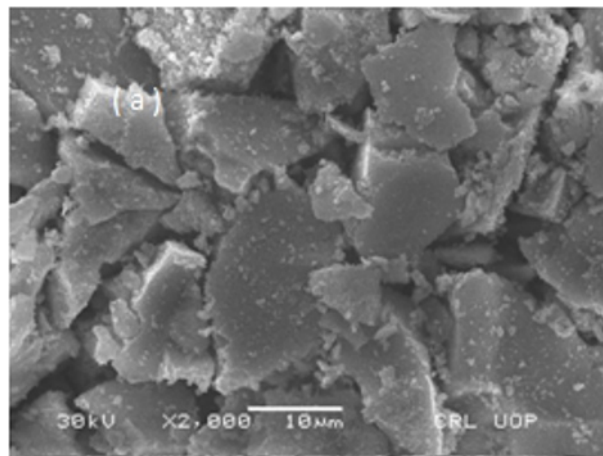


Fig. 4. SEM images of $0.94\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3-0.06\text{BaTiO}_3$ (a) dried gel powder calcined at $800\text{ }^\circ\text{C}$; (b) polished and thermally etched ceramic pellet sintered in air at $1100\text{ }^\circ\text{C}$

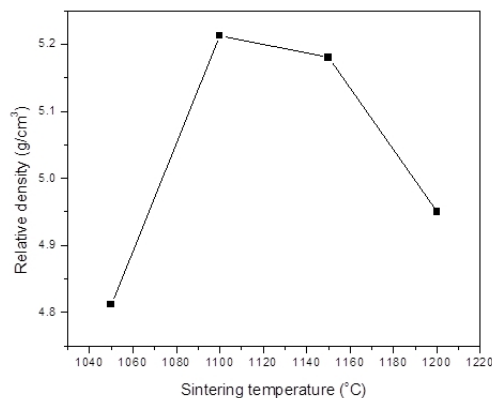


Fig. 5. Relative density as a function of sintering temperature.

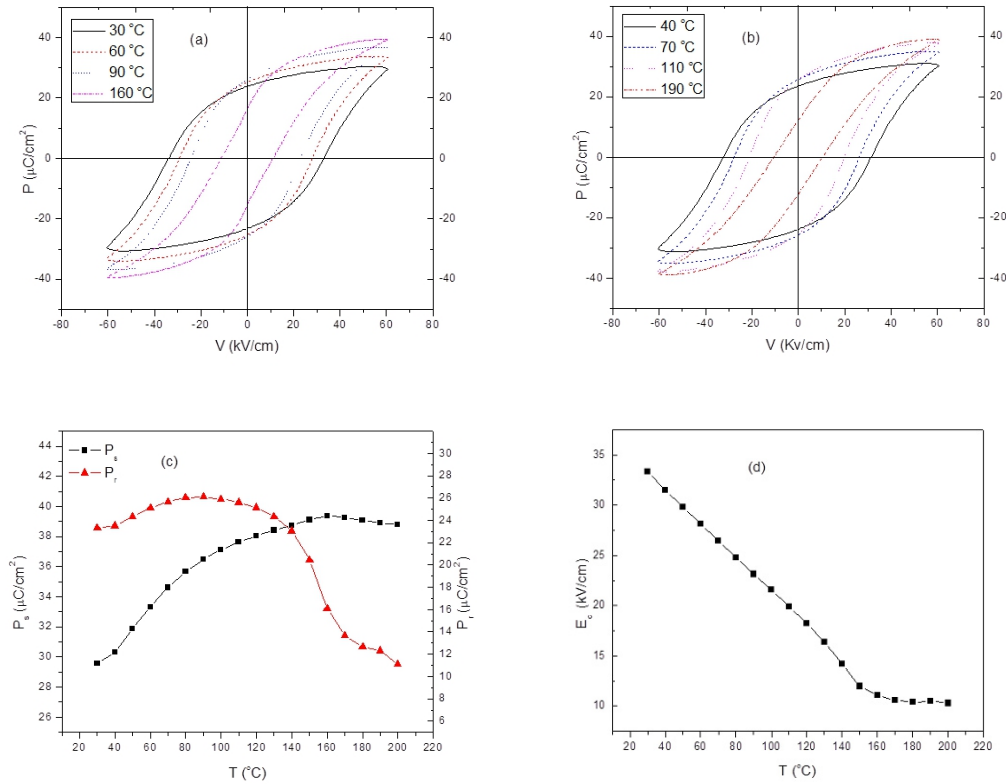


Fig. 6. Temperature dependent ferroelectric properties P-E loops (a, b), P_s and P_r (c) and E_c (d) of $0.94\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3\text{-}0.06\text{BaTiO}_3$ ceramics sintered at $1100\text{ }^{\circ}\text{C}$.

indicates that calcination temperature greater than $400\text{ }^{\circ}\text{C}$ is required to get a crystalline single phase of $0.94\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3\text{-}0.06\text{BaTiO}_3$ ceramics. The crystallinity is found to be increased with increasing the calcination temperature to $800\text{ }^{\circ}\text{C}$. The crystallite size of $0.94\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3\text{-}0.06\text{BaTiO}_3$ powder, calculated from the Scherrer formula using the XRD data, is 38 nm .

The SEM images of the calcined powders and polished, thermally etched ceramic pellet sintered at $1100\text{ }^{\circ}\text{C}$ are shown in Figs. 4(a, b). Fig. 4(a) shows large grains of calcined powders with different sizes. Fig. 4(b) shows a dense microstructure of the sample sintered at $1100\text{ }^{\circ}\text{C}$ with no obvious pore.

The apparent bulk densities of the ceramic samples were measured with a densitometer. Fig. 5 shows the variation of the obtained density with changing the sintering temperature of the samples, from $1050\text{ }^{\circ}\text{C}$ to $1200\text{ }^{\circ}\text{C}$. The optimum density of

the sample sintered at $1100\text{ }^{\circ}\text{C}$ is $5.20\text{ g}/\text{cm}^3$ while the theoretical density of $0.94\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3\text{-}0.06\text{BaTiO}_3$ is $5.98\text{ g}/\text{cm}^3$ [12].

The ferroelectric properties of the sample sintered at $1100\text{ }^{\circ}\text{C}$ are shown in Fig. 6(a – d). The P-E loops, Fig. 6(a, b) of the sample at different temperatures indicates that the loops become slimmer with rising the temperature, showing that the coercive electric field (E_c) is decreasing as it is also indicated in Fig. 6(d) from E_c versus temperature (T) plot. The saturation polarization (P_s), Fig. 6(c) is increased with increasing temperature but some decrease is observed above $170\text{ }^{\circ}\text{C}$, which may be due to the increase of the leakage current at high temperature. The remnant polarization (P_r) at first slightly increases with increasing temperature and then abruptly decreases at the temperatures beyond $85\text{ }^{\circ}\text{C}$. This change may be attributed to the phase transformation from ferroelectric rhombohedral to antiferroelectric tetragonal phase as it was also re-

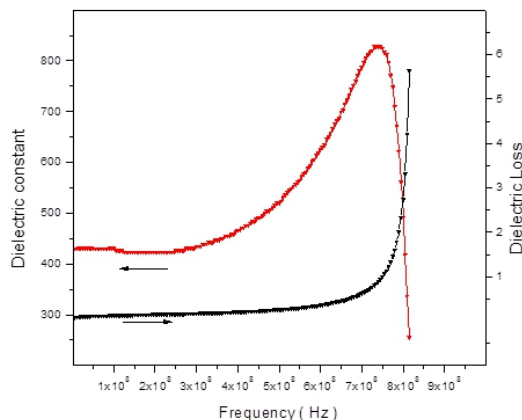


Fig. 7. Frequency dependent dielectric constant (ϵ_r) and dielectric loss ($\tan \sigma$) of $0.94\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ – 0.06BaTiO_3 ceramics sintered at 1100°C .

ported by Zhang *et al.* [13]. The results of the ferroelectric properties are found to be in full agreement with the results reported by Bai *et al.* [14].

The dielectric constant (ϵ_r) and dielectric loss ($\tan \sigma$) of the sample sintered at 1100°C are shown in Fig. 7 as functions of frequency. The dielectric constant (ϵ_r) remains nearly unchanged up to some extent and then increases abruptly to a maximum value of 800 which may indicate a resonance phenomenon at a specific frequency, which is in agreement with the dielectric constant reported by Cernia *et al.* [15]. The dielectric loss at 1 MHz was 0.07 and that reported by Cernia *et al.* [15] is 0.06. The dielectric loss is found to increase rapidly with increasing the frequency.

4. Conclusion

The perovskite structured $0.94\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ – 0.06BaTiO_3 ceramics were fabricated by low temperature sol-gel technique. XRD analysis confirmed the formation of a single phase at 600°C . SEM image of the sample sintered at 1100°C showed a dense and homogenous microstructure. The sintering temperature of the sample fabricated by sol-gel technique was relatively lower

than that obtained by solid state route [6]. The temperature dependent ferroelectric properties indicated a phase transformation from ferroelectric rhombohedral to antiferroelectric tetragonal phase at a temperature near 85°C . The sol-gel derived $0.94\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ – 0.06BaTiO_3 ceramics showed relatively better dielectric properties.

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