Original Article

Structural and dielectric properties of Bi-doped barium strontium titanate nanopowders synthesized by sol–gel method

Abbas Sadeghzadeh Attar\textsuperscript{a,}\textsuperscript{*}, Ehsan Salehi Sichani\textsuperscript{b}, Shahriar Sharafi\textsuperscript{b}

\textsuperscript{a} Department of Metallurgy and Materials Engineering, University of Kashan, Kashan, Iran
\textsuperscript{b} Department of Metallurgy and Materials Engineering, Shahid Bahonar University of Kerman, Kerman, Iran

\begin{abstract}
Nano-crystalline barium strontium titanate, $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$, (BST) powders were synthesized by sol–gel method, and the effects of Bi-doped on the microstructure and dielectric properties of BST powders were investigated. At first, the stable BST sols with optimum molar ratio were prepared and then different precents of bismuth were doped in precursor solutions. The samples, after drying and calcination at 850 $^\circ$C for 2 h, were characterized by TG-DTA, FTIR, XRD, FESEM and LCR meter equipments. The results showed that the crystallite size and lattice parameter changed by increasing doped Bi content of BST. Also, with increasing Bi content from 2 to 4 mol\%, average particle size of BSTB decreased from 40 to 35 nm. The dielectric constant for all samples increased with increasing calcination temperatures and then decreased after Curie temperature. An increase in the dielectric constant was observed up to a maximum of 1040 at a temperature of 80 $^\circ$C for BSTB2 and 910 at 70 $^\circ$C for BSTB4, respectively. The maximum value of dielectric constant and dielectric loss of the Bi-doped BST ceramics decreased with increasing Bi content.
\end{abstract}

\begin{keyword}
Barium strontium titanate \hspace{1cm} Bi-doped \hspace{1cm} Sol–gel process \hspace{1cm} Dielectric properties
\end{keyword}

1. Introduction

As a ferroelectric material, barium strontium titanate has considerably attracted interest of researchers and engineers due to high dielectric permittivity, low optical losses, ferroelectric activity and composition dependent Curie temperature [1]. Because of its perovskite structure, BST has been used as a high voltage capacitor, tunable filter, detector, piezoelectric, sensor, pressure transducer, actuator, optoelectronic device and so on [2,3]. $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ is a continuous solid solution between two traditional ferroelectrics-barium titanate ($\text{BaTiO}_3$) and strontium titanate ($\text{SrTiO}_3$). $\text{BaTiO}_3$ ($T_c = 393$ K) is a prototype ferroelectric, which undergoes a sequence of crystal structure transitions as it switches from ferroelectric to paraelectric phase [4]. $\text{SrTiO}_3$ is an incipient ferroelectric,
i.e., it exhibits quantum ferroelectricity, which means that though it undergoes phase transition at very low temperatures (Tc = 105 K), the quantum effect prevents complete transition to paraelectric phase. Therefore, SrTiO3 exhibits ferroelectric behavior well above its Curie temperature or paraelectric effect well below Curie temperature [5]. The Curie temperature of BST decreases linearly with increasing amounts of Sr in the (Ba, Sr)TiO3 lattice, which enables the ferroelectric/paraelectric transition temperature to be tailored for specific applications by varying Sr content. This kind of flexibility in properties and hence the prospective application range is absent in conventional ferroelectric ceramics. Therefore, depending on Ba:Sr ratio, transition temperature and, hence, electrical and optical properties of the BST show a variation over a broad range [6,7]. The BST ceramic with Ba:Sr ratio of 0.5:0.5 has high relative dielectric permittivity and phase transitions occur at temperatures well below room temperature. Hence, a good trade-off between dielectric permittivity and loss is obtained in which can be ideal for room temperature tunable microwave applications [8]. BST nanostructures have been synthesized by various techniques such as metal-organic decomposition (MOD) [9], sputtering [10], pulsed laser deposition (PLD) [11,12], metal-organic chemical vapor deposition (MOCVD) [13], hydrothermal [14,15] and sol–gel methods [16–18]. Among them, sol–gel process offers important advantages over other techniques due to its simplicity, low cost, excellent composition control, high homogeneity at molecular level, high purity, low processing temperature, feasibility of producing complex materials and easy to dope other elements in a homogenous manner [19]. It is well known that properties of dielectric materials (dielectric constant, dielectric loss and leakage current), including BST nanomaterials, are affected by preparation method, chemical composition, microstructure, type and content of dopant. Some dopant elements are able to modify and improve electrical properties of BST [20]. Particularly, to reduce dielectric loss and leakage-current density, the dopants occupying B site in the ABO3 perovskite structure (Fe2+, Fe3+, Co2+, Co3+, Mn2+, Mn3+, Ni2+, Mg2+, Al3+, Ga3+, In3+, Cr3+ and Sc3+) are used [21]. As a first report, Bi-doped barium strontium titanate (Ba0.5Sr0.5TiO3) nanopowders were synthesized by sol–gel method and the influence of Bi-doped on the microstructural and dielectric properties of prepared ceramics were investigated.

2. Experimental method

2.1. Synthesis procedure

The starting materials to synthesize Bi-doped Ba0.5Sr0.5TiO3 by sol–gel method included barium acetate [Ba(CH3COO)2]; Merck; with normal purity of 99%, strontium acetate [Sr(CH3COO)2]; Merck; with normal purity of 99%), titanium tetraisopropoxide (TTIP; Merck; ≥ 97%) and bismuth nitrate (III) pentahydrate [Bi(NO3)3·5H2O; Aldrich; ≥ 98%) as barium, strontium, titanium and bismuth precursors, respectively. Glacial acetic acid and ethanol were used as the solvent, while acetylacetone (AcAc; Merck; ≥ 99.5%) was used as a chelating agent. All of the starting materials used in the experiment were of analytical grade reagents.

For the preparation of BST sols, the barium and strontium acetates were initially dissolved in acetic acid with molar ratio of 1:1 and stirred at 40 °C for 0.5 h until becoming a transparent and clear solution. Afterward, TTIP was dissolved in absolute ethanol and then acetyl acetone was added to it. In the next step, this solution was added to (Ba, Sr) precursor solution and stirred to form a sol, which contained barium, strontium and titanium. Finally, bismuth nitrate (III) pentahydrate (as dopant precursor with concentration of 2 and 4 mol%) was dissolved in acetic acid and then mixed with BST solution to obtain a stoichiometric and stable Bi-doped BST solution. The 0, 2 and 4 mol% Bi (various amounts of Bi-doped) powders were subsequently abbreviated as BST, BSTB2 and BSTB4, respectively. The prepared sols were dried in a muffle furnace at 100 °C for 5 h to be dehydrated and then were heat-treated up to 650, 750 and 850 °C at rate of 10 °C/min and held for 2 h to obtain the crystalline powders. The calcined powders were isostatically pressed into pellets 10 mm in diameter and average thickness of about 3 mm using a hydraulic press at 100 MPa. The samples were placed into the tube furnace and sintered at temperature of 1300 °C for 2 h at the heating rate of 10 °C/min in an air atmosphere.

2.2. Characterization of nanopowders

Thermal gravimetric analysis (TGA) and differential thermal analysis (DTA) were performed using a Netzsch STA 409 PC Luxx thermal analyzer under air flow with heating rate of 10 °C/min from room temperature to 1000 °C. FTIR spectra of the sol, as-prepared and calcined samples were recorded on a Bruker TENSOR27 spectrophotometer in range of 400–4000 cm⁻¹. The dried powders were mixed with KBr powder and compressed to a thin pellet for infrared examination. The phase identification, crystallite size and lattice parameter of the prepared nanopowders were obtained using a Philips X-ray diffractometer (XRD, model X’Pert-MPD) with CuKα (λ = 1.54056Å) radiation source at 40 kV, 30 mA and scan rate of 10°/min. The microstructure of Bi-doped BST powders were observed by field emission scanning electron microscopy (FESEM, model CamScan MV2300). The chemical compositions of the samples were studied using energy dispersive spectroscopy (EDS). The particle size and morphology of the doped BST nanopowder was also examined by using a transmission electron microscope (TEM, model Philips CM30) operated at 200 kV. The sample for TEM was prepared by dropping the particle suspensions onto a carbon-coated copper grid. Density of pure and doped BST ceramics was obtained by measuring dimensions and dry weight of the samples and calculating from equation $\rho = \frac{4m}{d^2h\pi}$ (where $m$ is the mass, $d$ is the average diameter and $h$ is the height of the sintered samples) [22]. Dielectric measurements were carried out using an LCR meter (model INSTEK LCR-821) at 1, 10, 100 and 1000 kHz frequencies from room temperature to 125 °C. The samples used in the measurement were in the form of silver-electrode discs.

3. Results and discussion

Fig. 1 shows TG and DSC curves of BSTB2 powder in the air flow. An endothermic peak at 91 °C was found in the heating
stage, which was related to the initial weight loss ∼6% and observed in TGA curve up to 180 °C was due to the evaporation of water [23]. The subsequent major weight loss of about 27% was found between 250 °C and 400 °C, accompanied by an exothermic peak at 379 °C, due to decomposition of organic and formation of BaCO₃ phase. Formation of BaCO₃ phase as well as decomposition and combustion of the polymer happened concurrently [24]. The exothermic peak at 476 °C was due to burning of organic carbon groups. The exothermic peak at 585 °C with weight loss of about 7% corresponded to the formation of perovskite and the exothermic peak at 642 °C was associated with the formation temperature of BSTB, which was related to bismuth ions into the perovskite lattice [24] and also could be attributed to the decomposition and burning of residual carbon components. The endothermic peak localized at 800 °C could be attributed to polymorphic transformation of BST material [7].

Fig. 1 – TG-DSC curves of the thermal decomposition of BSTB2 powder.

Fig. 2a–c shows IR spectra of the BSTB2 sol, as-prepared powder and calcined at 850 °C for 2 h, respectively. The broad band around 3400 cm⁻¹ (Fig. 2a) was due to O–H stretching vibrations of the hydroxyls present in the system; it decreased in intensity with heating at 100 °C (Fig. 2b) and disappeared after calcination at 850 °C (Fig. 2c). The extremely low intensity of the bands due to C–H stretching vibrations at 2600–3000 cm⁻¹ testified to the very low content of organic radicals in the samples. These bands completely disappear in the calcined samples at 850 °C. The bands in the region of 1400 cm⁻¹ were attributed to the formation of Ba–O–Ti bond. It can be observed that the absorption bands in the range of 1000–1100 cm⁻¹ can be attributed to the OR groups linked to Ti, such as OCH₃, OCH₂ and OC₃H₇. The two bands at about 500 and 540 cm⁻¹ were of typical Bi–O and Ti–O vibrations, respectively [7], which might be due to the formation of metal oxide bonds as suggested in the XRD results.

Fig. 3 illustrates XRD patterns of BST, BSTB2 and BSTB4 powders calcined at 850 °C for 2 h. It can be seen that (100), (110), (111), (200), (210), (211), (220), (300) and (310) peaks corresponding to the Ba₀.₅Sr₀.₅TiO₃ cubic perovskite structure were present in all patterns (JCPDS card no. 00-039-1395). The full width at half maximum (FWHM) of the peaks and lattice parameter increased with increasing Bi content. This peak broadening might be connected with decreasing crystallite

Fig. 2 – IR spectra of the BSTB2 (a) sol, (b) dry at 100 °C and (c) calcined at 850 °C for 2 h.

Fig. 3 – The XRD patterns of BST, BSTB2 and BSTB4 powders calcined at 850 °C for 2 h.
size by increasing Bi content, implying that Bi\(^{2+}\) ions were entered into the unit cell of the perovskite structure. All these processes happened due to the difference between ionic radius of Bi\(^{3+}\) (0.074 nm) and Ti\(^{4+}\) (0.068 nm). Additionally, undefined diffraction peaks appeared in these patterns, which might be attributed to the formation of BaCO\(_3\), TiO\(_2\) or Bi\(_2\)O\(_3\) as secondary phases due to the excess Bi content [21,24,25]. It is well known that BaCO\(_3\) represents a potential impurity in the BST powders and may negatively affect the properties of the obtained ceramics [26]. Therefore, elimination of carbonates from compound at higher temperatures is necessary.

Crystallite sizes of the BST nanopowders calcined at 850 °C for 2 h were evaluated, as summarized in Table 1. Mean crystallite size of these nanoparticles was estimated using Debye-Scherrer’s equation [27]:

\[
D = \frac{0.89 \lambda}{\beta \cos \theta}
\]

(1)

where D is average crystallite size (nm), \(\lambda\) is wave length of CuK\(_\alpha\) (0.154 nm), \(\beta\) is full width at half maximum intensity (FWHM) in radian and \(\theta\) is Bragg angle.

X-ray diffraction data, depending on the calcination temperature of BSTB2 powder, are shown in Fig. 4. It is evident that all the powders had crystalline structure containing barium strontium titanate phases. It can be seen that, with increase in temperature, the amount of formed carbonate decreased, which was due to burning the remained carbon compounds. Average crystallite size of the calcined samples at 650, 750 and 850 °C estimated using Debye-Scherrer’s equation was 29, 31 and 34 nm, respectively. Full width at half maximum (FWHM) decreased with increasing calcination temperature, which is an indicative of higher crystallinity and larger particle size [16]. It can be seen that crystallite size increases with increasing in temperature. However, higher calcination temperatures caused particle growth and surface area decrease and the powder could be less reactive for sintering.

As described in the experimental section, the BST ceramics with different Bi additions were sintered in air at 1200 °C for 2 h. Table 2 reports the green and sintered bulk density of pure and doped BST ceramics. The density of green samples BST, BSTB2 and BSTB4 is found to be 4.50, 4.65 and 4.82 g/cm\(^3\), respectively. The theoretical density of the Ba\(_{0.5}\)Sr\(_{0.5}\)TiO\(_3\) is approximately 5.52 g/cm\(^3\) based on the XRD lattice parameter analysis [28]. The excellent electrical properties of BST ceramics are affected by many physical features such as grain size, crystalline structure, purity, density, etc. These physical features can be controlled directly by parameters of preparation processing especially sintering conditions. The sintering process promotes not only the densification but also grain growth, which strongly results in dielectric properties [29]. It is well known that it is difficult to prepare fully dense nanostructured ceramics due to a lot of factors, which can have an effect on producing fine-grained materials with high density. It is also strongly influenced by the powder preparation process and powder agglomeration, as well as sintering regime (sintering temperature, time and atmosphere) [30]. Dopants can also have effect on the densification and microstructure of barium strontium titanate [31]. It appears that the increment of Bi content gives an increase in sintered bulk density to reach a maximum value of 5.35 g/cm\(^3\) for 4 mol% due to more density of Bi (9.78 g/cm\(^3\)) than Sr (2.63 g/cm\(^3\)) and Ba (3.51 g/cm\(^3\)). Related results reported by other investigators [32,33] show that the Bi\(_2\)O\(_3\) assists in the densification of the BST dielectrics through liquid-phase sintering.

**Fig. 4** – The XRD patterns of BSTB2 powders calcined at 650, 750 and 850 °C for 2 h.

**Table 1** – Average crystallite size obtained from XRD results for BSTB nanopowders calcined at 850 °C for 2 h.

<table>
<thead>
<tr>
<th>Sample</th>
<th>a (lattice parameter), nm</th>
<th>D (crystallite size), nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>BST</td>
<td>3.9471</td>
<td>35.76</td>
</tr>
<tr>
<td>BSTB2</td>
<td>3.9502</td>
<td>34.28</td>
</tr>
<tr>
<td>BSTB4</td>
<td>3.9538</td>
<td>31.94</td>
</tr>
</tbody>
</table>

**Table 2** – Density value for different specimens of BST (green and sintered at 1300 °C for 2 h).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Density (g/cm(^3))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Green pellets</td>
</tr>
<tr>
<td>BST</td>
<td>4.50</td>
</tr>
<tr>
<td>BSTB2</td>
<td>4.65</td>
</tr>
<tr>
<td>BSTB4</td>
<td>4.82</td>
</tr>
</tbody>
</table>
and shape. To determine the average particle size of the powder, measurements were taken along the diameter of several particles and the average of these measurements was calculated. Based on this method, the average particle size of BSTB2 nanopowder, synthesized by sol–gel method, was about 38 nm, which is in good agreement with that obtained by XRD analysis.

Fig. 7 shows the temperature dependence of dielectric properties for undoped and Bi-doped BST ceramics measured at various frequencies. It is found that the maximum of dielectric constant initially increases with the increasing of temperature and then decreases after a special temperature. Also, the dielectric loss of all samples follows the same trend; they are decreasing with temperature and then increases.

The dielectric behavior shows an increase in dielectric constant up to a maximum of 1040 at a temperature of 80 °C for BSTB2 and 910 at 70 °C for BSTB4, approximately. This special temperature called Curie temperature and is related to structural transition (cubic to tetragonal Tc–T) in BST samples. From the results, there are three important observations. First of all, the maximum value of dielectric constant and dielectric loss decreased with increasing of Bi content. It is well known that the value of the dielectric constant of dielectric ceramics is strongly affected by microstructure, grain structure, and the grain size [21]. As for the last factor, the larger grain size usually results in larger polarization and therefore gives higher value of dielectric constant. The low values of dielectric constant of Bi-doped BST ceramics are due to the fact
that the crystalline size is visibly smaller than that of undoped BST ceramics; this is known as the grain size effect. The second, the temperature $T_{tr}$ corresponding to the maximum value of the dielectric constant, is shifted to lower temperature with the increase of Bi concentration. Some authors [34,35] have connected the lowering of $T_{tr}$ with grain size decrease and this is in agreement with results obtained in our study. The $T_{tr}$ determined at various frequencies for BST, BSTB2 and BSTB4 are 100, 80 and 70 °C, respectively. The last, for the all Bi-doped BST ceramics, the maximum value of dielectric constant is decreased with increasing of the frequency. This phenomenon reveals that BST ceramics with Bi doping have behaved with a typical relaxer behavior [36].

As the ferroelectric transition of Ba$_{1-x}$Sr$_x$TiO$_3$ system accompanies a cubic-to-tetragonal structure transition, the decrease in $T_{tr}$ reveals that Bi doping increases the stability of the cubic structure. According to the study of Gao [37], the oxygen vacancies generate from the BaTiO$_3$ doped with the 3d elements play important role in determining the phase stability. In BSTB ceramics, the Bi ions substituted at Ti$^{4+}$ sites

---

**Fig. 6** – TEM photographs of BSTB2 nanopowder calcined at 850 °C for 2 h.

**Fig. 7** – Values of dielectric constant and dielectric loss at various frequencies plotted as a function of temperature for (a, b) BST; (c, d) BSTB2 and (e, f) BSTB4 ceramics.
are in the Bi$^{2+}$ state, which tends to generate oxygen vacancies and internal dipole required by change neutrality. Such oxygen vacancies are expected to make the cubic structure favorable in energy [38]. Thus, $T_N$ shifts to lower temperature. At the same time, the dielectric loss of BST4 ceramic is lower than that of BSTB2 ceramic. Generally, when Bi$^{2+}$, Mg$^{2+}$, Mn$^{3+}$ ions (act as “B” site acceptor dopants in ABO$_3$ perovskite) substitute Ti$^{4+}$ extrinsic oxygen vacancies are created in order to maintain the charge balance [39]. The acceptor dopants prevent reduction of Ti$^{4+}$ to Ti$^{3+}$ by neutralizing the donor action of the oxygen vacancies. High-temperature calcination in air creates intrinsic oxygen vacancies in BST ceramics. The dopant ion carries an extra negative charge and compensates the positive charge of the oxygen vacancies, as a result, the concentration of free carrier (electrons) are reduced [16]. The decrease in electron concentration leads to lower dielectric loss in Bi-doped BST ceramics. On the other hand, it was suggested that Bi ions were located at off-center positions of Sr$^{2+}$ sites and that strontium vacancies may occur in Bi doped SrTiO$_3$ in order to balance the charge misfit caused by trivalent Bi$^{3+}$ ions diverting divalent Sr$^{2+}$ ions. Off-center Bi$^{3+}$ ions and Bi$^{3+}$–Sr vacancy centers form dipoles and thus set up local electric fields [40]. Similarly, as suggested, the Bi ions substituting for Sr$^{2+}$ ions in Ba$_{0.5}$Sr$_{0.5}$TiO$_3$ solid solution can also be located at off-center positions and A site (strontium and/or barium). Vacancies may also appear to compensate the charge imbalance arising from the substitution of A sites by Bi$^{3+}$ ions.

4. Conclusions

Barium strontium titanate (Ba$_{0.5}$Sr$_{0.5}$TiO$_3$) with doped Bi was successfully prepared via sol–gel method at room temperature. The crystal structure was identified to be cubic from the XRD data and Bi existed in the BST lattice. FESEM and TEM images showed that ultrafine particles of BSTB with average particle size of 35–40 nm could be obtained at 850 °C after holding for 2 h. It was shown that particle size depended on the amount of Bi dopant and decreased with increasing the bismuth concentration. The presence of O–H, C=H, C=O, Ti–O and Bi–O stretching frequencies was confirmed in the dry samples by FTIR spectra, the band of which became sharper and narrower as a result of calcination. The dielectric results showed an increase in dielectric constant up to a maximum of 1040 at a temperature of 80 °C for BSTB2. The maximum value of dielectric constant decreases with increasing of Bi content. The $T_N$ determined at various frequencies for BST, BSTB2 and BSTB4 are 100, 80 and 70 °C, respectively. This showed that the temperature $T_N$ corresponding to the maximum value of the dielectric constant, is shifted to lower temperature with the increase of Bi concentration. Also, the maximum value of dielectric loss is decreased with increasing of the frequency.

Conflicts of interest

The authors declare no conflicts of interest.

References

[12] Sekhar KC, Key SH, Hong KP, Han CS, Yook JM, Kim DS, et al. Thickness–dependent tunable characteristics of (Ba$_{0.5}$Sr$_{0.5}$)$_{0.95}$K$_{0.05}$TiO$_3$ thin films prepared by pulsed laser deposition. Curr Appl Phys 2012;12:654–8.
[38] Kim K-T, Kim C-I. Electrical and dielectric properties of Ce-doped $\text{Ba}_{0.8}\text{Sr}_{0.2}\text{TiO}_3$ thin films. Surf Coat Technol 2006;200:4708–12.