Synthesis and Characterization of Bismuth Doped Barium Titanate
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Abstract: The mixture Ba$_{1-x}$Bi$_{2x/3}$TiO$_3$ was prepared by the standard solid state reaction method. Bi$_2$O$_3$ was added as a dopant to the powder mixture of Barium Carbonate BaCO$_3$ and Titanium Dioxide TiO$_2$ and sintered at 1150°C for five hours. The microstructure, dielectric and electric properties of the mixture have been investigated. The dielectric constant increased with increasing Bi$_2$O$_3$ until it reached the maximum value with 0.6 mol% Bi$_2$O$_3$ additive, and the maximum dielectric loss was found 0.021 for 0.02% Bi$_2$O$_3$ content. The maximum Curie temperature was found 135°C for 0.02, 0.03, 0.04% Bi content. The frequency dependent dielectric constant ($\varepsilon'$) and dielectric loss (tanδ) of the samples at room temperature were collected in the frequency range from 40 Hz to 110MHz.

Keywords: Sintering, Microstructure, SEM, Barium titanate, Bismuth doping, Dielectric property, Electrical Resistivity.

I. Introduction

Barium Titanate is a very important Perovskite crystal in the world of electronics. The crystal structure is a primitive cube, with the Ba-larger cation in the corner, the Ti-smaller cation in the middle of the cube and oxygen, in the centre of the faces edges [1]. Barium Titanate is considered as a Perovskite because of its corner linked oxygen octahedral with a small cation filling the octahedral hole and a large cation filling the dodecahedral hole, so that we can substitute the cations, maintaining the charge balance and keeping the size within the range for particular co-ordination number to improve its physical properties [2]. Its ferroelectric properties are connected with a series of four structural phase transitions having the following sequence upon heating: rhombohedral, orthorhombic, tetragonal and cubic. It has piezoelectric property, so it can be used in the production of transducer. The temperature, at which the phase transition occurs, is known as Curie temperature. Above this temperature, the ferroelectric property does not exist. The higher Tc resembles the wider stable region for Multilayer capacitor. The property of BaTiO$_3$ has been widely investigated for many years. In the previous investigation, M.M. Vjatovicˇ Petrovicˇ et al. synthesized Sb doped BaTiO$_3$. The influence of Sb doping concentration shifts the temperature phase transition peaks to the lower temperatures and broadens $\varepsilon$ –T curves [3]. S. Hao et al. prepared BaTiO$_3$ powders doped with Ag by sol-gel method. The lowest resistivity was found 5.644\(\Omega\)-m [4]. S. Thirumalai et al. synthesized and characterized the microwave assisted BaTiO$_3$ Nanoparticles. They found the tetragonal crystal structure even at lower heating temperature of 1000°C. The particle size is about 20 nm for the microwave heated samples than the conventional heating. The dielectric constant values measured at room temperature was relatively higher than that of the conventionally heated product. The dielectric loss values were also relatively lesser for microwave heated samples [5]. TadasRamoška et al. showed that La doped BaTiO$_3$ gives maximally enhanced dielectric constant at low, room and high temperature phase transition [6]. Barium Titanate has higher sintering Temperature, which is 1300°C. S. Wu et al. investigated Bi doping as a sintering additive, can effectively lower the sintering temperature of BaTiO$_3$ based ceramics from 1300 °C to 1130°C [7]. In this study, we desired to synthesize Bi doped BaTiO$_3$ and analyze its various properties.

II. Materials and Method

A. Experimental Procedure

Polycrystalline samples of BaTiO$_3$ + x wt. % (Bi$_2$O$_3$) (x = 0.01; 0.06) were prepared using a solid state synthesis. The samples were synthesized from an analytically pure barium carbonate BaCO$_3$, titanium oxide TiO$_2$, and bismuth oxide (Bi$_2$O$_3$) [8]. Mixture of the raw materials was ground in ball mill in ethanol for five hours. The materials were dried and calcined at the temperature of 900°C for three hours. The powder was made into disk-like pellets and then sintered at 1150 °C for three hours in a furnace.
B. Ceramics Characterization

The surface morphology of Bi doped BTO ceramics was determined by scanning electron microscopy (SEM, Hitachi S-3400N). In order to measure the dielectric properties, conductive layer of silver paste (Demetron Leipzegrstr.10, Germany) was painted on the polished ceramic samples as the electrodes. The capacitances of the ceramics were determined by a Good Will LCR-814 LCR meter (20mF to 200pF). The frequency dependence of the capacitances and loss were measured by an Agilent 4294A Precision Impedance Analyzer with frequency range 40 Hz to 110 MHz at room temperature. The dielectric constant was calculated from the capacitance using the following equation

\[ \varepsilon = \frac{C d}{\varepsilon_0 A} \]  

where C is the capacitance (F), d the thickness (m), A is the area (m²) and \( \varepsilon_0 = 8.85 \times 10^{-12} \) F m⁻¹.

III. Result and Discussion

A. Surface Morphology

The surface SEM investigations were performed on both Bi doped and undoped Barium Titanate samples. The microstructure consists of inter-granular pores and grains of various sizes. Fig.1 (a) shows fairly uniform micrograph of pure BT sample. Micrograph shows some agglomerations as well as small grains but less porous. In fig.1 (b), the BaTiO₃-based ceramics doped with 0.01 mol% Bi₂O₃ shows similar micro graph like undoped Barium Titanate. As the Bi₂O₃ content is increased, as shown in Fig. 2(c-g), more porous ceramics are revealed and the morphologies show less dense surface. The average grain size of pure BT was 230.68 nm. The maximum grain size was found 458.2 nm for 0.06% Bi doping.

B. Dielectric Properties

Temperature Dependent Dielectric Properties

It is observed from the Table 1 that dielectric constant of BTO ceramics increases significantly with Bi doping. This might be due to the role of conducting Bismuth ions in BaTiO₃ network in the place of Barium ions [2]. In addition, Bi³⁺ substitutes Ba²⁺ in BaTiO₃, so the ion volume of A-site decreases due to the barium vacancy, which makes a bigger active space for Ti⁴⁺. For the increase of electrovalence from +2 to +3 of A-site ion, a residual positive charge appears and the mutual effect between A and B (Ti⁴⁺) sites becomes stronger. Thus the
polarization of Ti$^{4+}$ is enhanced, and then the dielectric constant increase sharply [5]. The Curie temperature $T_c$, which is the transition temperature from ferroelectric to paraelectric phase, was found to be in the range of 125°C to 135°C. Variation of Curie temperature with doping concentration is given in fig. 2. At $T < T_c$, the material becomes spontaneously polarized. At $T > T_c$, the dielectric constant is given by Curie Weiss Law [9],

$$\varepsilon = \frac{C}{(T - T_c)}$$  \hspace{1cm} (2)

Decrease in $T_c$ with Bi doping indicates a partial substitution of Ba$^{2+}$ ions with Bi$^{3+}$ into the perovskite lattice [10].

Table 1 Effect of Bi doping on Dielectric constant, Dielectric Loss and Curie temperature.

<table>
<thead>
<tr>
<th>Sample X%</th>
<th>Dielectric Constant $\varepsilon(T_{room})$</th>
<th>Dielectric Constant $\varepsilon(T_c)$</th>
<th>Dielectric Constant $\varepsilon(frequency)$</th>
<th>Curie Temperature $T_c (^{\circ}C)$</th>
<th>tan$\delta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>12905.3</td>
<td>13013.9</td>
<td>975.81</td>
<td>125</td>
<td>0.012</td>
</tr>
<tr>
<td>0.01</td>
<td>31229.4</td>
<td>31930.2</td>
<td>421.81</td>
<td>125</td>
<td>0.008</td>
</tr>
<tr>
<td>0.02</td>
<td>34727.6</td>
<td>35456.1</td>
<td>120.09</td>
<td>135</td>
<td>0.021</td>
</tr>
<tr>
<td>0.03</td>
<td>42673.0</td>
<td>44085.0</td>
<td>839.71</td>
<td>135</td>
<td>0.011</td>
</tr>
<tr>
<td>0.04</td>
<td>42687.5</td>
<td>44750.0</td>
<td>230.48</td>
<td>135</td>
<td>0.013</td>
</tr>
<tr>
<td>0.05</td>
<td>53014.4</td>
<td>54890.8</td>
<td>539.82</td>
<td>130</td>
<td>0.007</td>
</tr>
<tr>
<td>0.06</td>
<td>67585.5</td>
<td>69694.6</td>
<td>803.49</td>
<td>130</td>
<td>0.009</td>
</tr>
</tbody>
</table>

The energy losses which occur in dielectrics are due to dc conductivity and dipole relaxation. The loss factor (tan$\delta$) is the useful indication of the energy loss as heat [9] From the Table 1, it was found that BT with 0.05% Bi showed less dielectric loss while 0.02% doped BT exhibit greater dielectric loss. So it can be concluded that addition of Bismuth could minimize the dielectric loss (Fig. 3).

**Frequency Dependent Dielectric Properties**

The frequency dependence of the dielectric constant of pure and Bi doped BaTiO$_3$ is given in Table 1. The maximum Dielectric Constant with varying frequency was found 3421.81 for 0.01% doping. And the minimum Dielectric constant was 803.49 for 0.06% doping. Higher values of Dielectric Constant are due to the presence of all different types of polarizations, such as dipolar, atomic ionic and electrical polarization [11].

The frequency dependent dielectric loss is given in fig. 4. The maximum dielectric losses are 0.0256, 0.0319, 0.0326, 0.0486, 0.0494, 0.0577, and 0.0593 for pure and 0.01, 0.02, 0.03, 0.04, 0.05, and 0.06% Bi doped BTO. So dielectric loss factor increases with the increase of Bi doping. The dielectric loss corresponding to frequency is due to the ion jump relaxation, ion vibration-deformation loss and electron polarization loss. The ion jump relaxation between two equivalent ion positions is the main contributor to the dielectric loss at moderate frequencies below 10$^5$ Hz. So, in this case the dielectric loss was found due to the ion relaxation [12].
Table 2 Effect of Bi doping on temperature dependent resistivity.

<table>
<thead>
<tr>
<th>Sample, X%</th>
<th>Resistivity, ρ (Ω-cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>6.77 × 10^7</td>
</tr>
<tr>
<td>0.01</td>
<td>2.98 × 10^7</td>
</tr>
<tr>
<td>0.02</td>
<td>2.19 × 10^7</td>
</tr>
<tr>
<td>0.03</td>
<td>2.06 × 10^7</td>
</tr>
<tr>
<td>0.04</td>
<td>2.00 × 10^7</td>
</tr>
<tr>
<td>0.05</td>
<td>1.65 × 10^7</td>
</tr>
<tr>
<td>0.06</td>
<td>1.86 × 10^7</td>
</tr>
</tbody>
</table>

C. Electric Properties

Temperature Dependent Electrical Resistivity

The temperature dependence of the capacitance and resistivity of pure and Bi doped BaTiO₃ is given in Table 2. The resistivity decreases with the increase of Bi composition, except for x = 0.06 composition. That means that the presence of Bi increases the conductivity of BaTiO₃. So Bismuth infused BTO shows low PTRC behavior. Whereas T. Hashishin et al. observed that Barium Titanate with 0.25 mole% and 0.45 mole% Nd additive shows too high resistivity at room temperature which meet the industrial application [12].

Frequency Dependent Electrical Conductivity

The frequency dependent electrical conductivity is shown in fig. 5. The maximum value of logσ was found 3.623 Scm⁻¹ for 0.05% Bi Doped BTO and the minimum value of logσ was found 1.121 Scm⁻¹ for 0.04% Bi Doped BTO. In the low frequency region the variation of conductivity is due to the polarization effect and in the intermediate frequency plateau region, conductivity is almost frequency independent and is equal to dc conductivity σdc (fig.5). As only high frequency range was accounted in our observation, so these regions are absent as shown in fig. 6. In this frequency range, conductivity increases with the frequency i.e., only dispersive effect is existent [14]. In fact, the frequency dependence of conductivity or universal dynamic response (UDR) of ionic conductivity is related by the simple expression and is given by the Jonscher’s power law,

$$\sigma_{ac} = \sigma_{dc} + A \omega^n$$

Where, the $\sigma_{ac}$ is the ac conductivity, $\sigma_{dc}$ is the limiting zero frequency conductivity, A is the pre-exponential constant $\omega = 2\pi f$ is the angular frequency and n is the power law exponent, where $0 < n < 1$ [14][15].

IV. Conclusion

The present study describes the synthesis of Bi doped barium titanate by solid state reaction method. Bi doping is used to lower the sintering temperature. In this study the sintering temperature was 1150°C. The microstructure development of Bismuth doped barium titanate was fine grained with grains in the range from 230.68 nm for pure to 458.2 nm for 0.06% Bi doped BaTiO₃. The grain size is increasing with the Bi₂O₃ doping. The Temperature dependent resistivity of BaTiO₃ base ceramics doped with Bi decreases with the doping.
concentration. The dielectric constant increases with doping concentration but the dielectric loss increases up to 0.02% doping concentration then decreases for increasing doping concentration. The ac electrical conductivity was found maximum for 0.05% Bi doping. The Dielectric Constant with varying frequency changes with the doping concentration and Bi doping increases the dielectric loss factor.

V. References

[14] P. Muralidharan, Impedence Spectroscopy; Chapter 4; Investigation of Ac conductivity and electrical modulus of LBS, LPBS and LVP samples.

VI. Acknowledgments

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