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Dielectric Characterization of Sn Doped Ferroelectric Compound

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Abstract: $BaBi_4Zr_2Sn_2O_{15}$, a Sn-modified ceramic sample belonging to the oxide family of layered ferroelectrics, is synthesized using the mixed oxide process after firing for calcination at 810 ^oC for 6 hrs. XRD study of the compound exhibits the formation of an orthorhombic single-phase structure at atmospheric temperature. The electrical properties of the sample are investigated in a broad temperature range (30-500 ^oC) and frequency range (100Hz - 10^6Hz). The dielectric properties recommend the transition from ferro to paraelectric state at 410 ^oC which is much more than room temperature. The ac conductivity versus temperature plots obeys the Arrhenius relation and confirm the presence of the mixed type of conductivity process like space charge conductivity created from oxygen ion vacancies, ionic-polaronic conductivity, etc in the sample. Ac conductivity versus frequency spectra is as per Jonscher's Universal Power law.

Keywords: X-ray techniques, dielectrics, electrical conductivity, Ceramics.

1. INTRODUCTION

In the present era, nanoscience and technology bring revolutionary changes in the world of ferroelectrics which is possible due to the

enlightenment of new ideas in materials science as a parental branch. The most challenging aspect of the current condition is simplifying the complex process of developing and fabricating thin-layered compound nanostructures at an affordable cost in a friendly manner [1]. By taking into consideration the synthesis of quality materials, materials science comes to the forefront to a great extent. It plays a vital role in most emerging fields and has various applications like multilayer capacitors, detectors, RAM, memories, displays, sensors, etc. Among all the discovered ferroelectric structural compounds, the perovskite structure is the most fascinating. Perovskite structure has a general chemical formula ABX_3 (for example $BaTiO_3$, $CaTiO_3$), here the anion X is bonded to both the cations A & B of different sizes [2]. This ABO_3 structure can be splitted using thin sheets of intrusive materials such as motif and known as layer perovskite which has interesting multiferroic properties [3]. Layer perovskite structural compounds possess various interesting properties. Barium titanate ($BaTiO_3$) and calcium titanate ($CaTiO_3$) are an example of perovskite structures. According to the Aurivillius phase, the layered perovskite contains $[Ba_2O_2]_2$ ions having n-ABO_3 layers [4]. The electrical properties of layered perovskite are studied by Khokhar and Sreenivas [5]. By changing the temperature, the electrical properties of the material are modified & high resistivity and low dielectric loss ceramics are yielded. J. D. Bobic et al [6] prepared lead-free ceramics $BaBi_4Ti_4O_{15}$ and reported the changes that occur in its properties. Mishra et al studied the Sb modification of Sb on the barium bismuth titanate taking separate concentrations [7]. The variant in the Sb concentrations found variation in structural parameters. Behera et al studied the impact of Zr substitution on layered perovskite of $CaBi_4Ti_4O_{15}$ ceramics [8]. They used a four-layered compound that had been prepared in single-phase form. No research has been done on the impact of the substitution of Sn at Zr site on the structure, microstructure, electrical & dielectric characteristics of $BaBi_4Zr_2Sn_2O_{15}$ compounds, so we are planning to investigate & understand various mechanisms involved in the phase transition, impedance, conductivity etc.

2. METHODOLOGY:

2.1: Materials synthesis:

Polycrystalline sample $BaBi_4Zr_2Sn_2O_{15}$ is prepared using the appropriate stoichiometric ratio of ingredients of highly pure powders chemicals (> 99.9%) of $BaCO_3$(Sarabhai M. Chemicals private limited), Bi_2CO_3 (Central drug House private limited), SnO_2 (Zenith Metalik Alloys Ltd), ZrO_2 (Loba Chemicals private limited). The ingredients were weighed & mixed by a mortar & pestle in air and then in methanol for ~3h each until the formation of fine powders which are then fired in a high-temperature furnace at 790 ^oC in air. The powders obtained are calcined at an optimized temperature and time i.e., 790^oC for 12 h in the presence of air for 12 hrs. Pallets are made by adding polyvinyl alcohol binder with the calcined powder and by a hydraulic press applying 4 MPa pressure. The pellet samples are sintered at 810^oC inside the furnace. Finally, electroding of the pellet is done using highly pure silver paint on either side of the pellet.

2.2: Materials characterization:

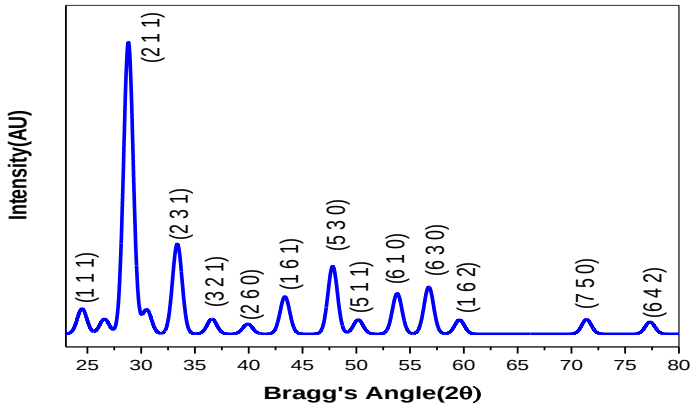
The characterization of the structure of the material is carried out by XRD data analysis obtained by a diffractometer (Rigaku, Miniflex) using CuKα radiations of wavelength 1.54 Å having Bragg's angle 2θ ranging from 20^o to 80^o with scattering rate 3^o/ min. The electrical and dielectric properties of the materials are investigated by using LCR Hi-tester HIOKI-3532-50 in a wide temperature (30 ^{o}- 500 ^oC) and frequency (100Hz-10^6Hz) with a heat rate of 5^oC/min.

3. ANALYSIS OF RESULTS:

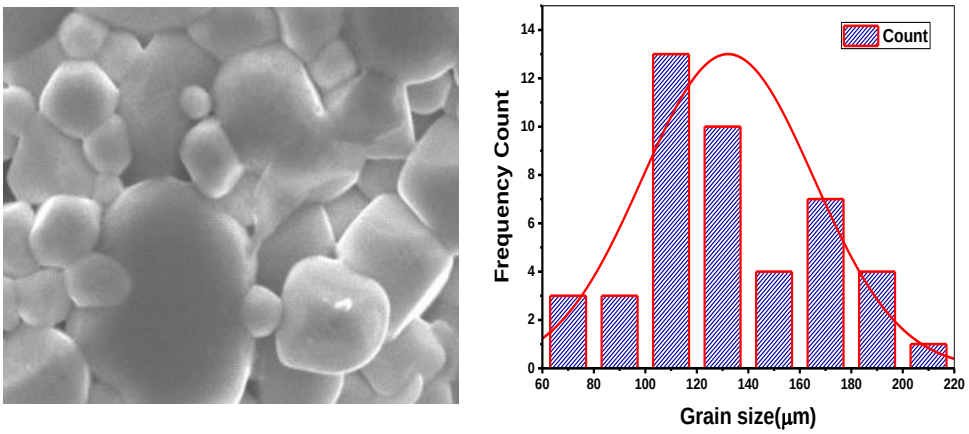
3.1: Structural & microstructural analysis:

The XRD pattern of $BaBi_4Zr_2Sn_2O_{15}$ (BBZS) is shown in Figure 1(a). The development of a new compound is confirmed by the clear and sharp peaks which are noticed to be separated from the patterns of ingredients in Figure 1 (a) [9]. From the literature study, the XRD data at room temperature of the parent compound ($BaBi_4Zr_2Sn_2O_{15}$) is orthorhombic possessing a space group - F2mm [10-12]. It is tough to obtain the specific structure of the complex layered Sn-modified ferroelectric $BaBi_4Zr_2Sn_2O_{15}$ compound due to the presence of a large number of atoms in a unit cell.

The researchers use various methods for the investigation of XRD data which give separate results. As the prepared compound is entirely a newly formed complex compound, so adequate CIF data is inaccessible, for which the exact structure of the crystal cannot be analyzed by the Rietveld refinement method. However, the investigation following other methods by anyone cannot be ruled out but the outcomes of various physical properties obtained must be consistent with the reported one. By use of the software - POWD MULT the structure of the sample is confirmed to be the orthorhombic unit cell [13]. The diffraction maxima are indexed & analyses of the configurations of the cell are examined using the software - POWD. The selection of configurations of the unit cell of the orthorhombic structure are chosen based on the finest matching with observed and calculated inter-planar spacings (d). The parameters of the unit cell are a = 10.2809(42)Å, b = 15.0756(42)Å, c = 4.0171(42)Å (the standard deviations are mentioned in parentheses) and unit cell volume is V = 622.62Å^3. The size of the crystallite (P) of the material is measured by utilizing Scherrer's relation [14] $P_{hkl} = k\lambda / \beta_{1/2}$, $\beta_{1/2}$ is full width at half maximum (FWHM) of the XRD peaks. The normal size of the crystallite of the Figure 1(b, c) represents the SEM of the sintered material indicating its microstructure & surface properties, which confirms the existence of the polycrystalline texture of the sample with the presence of pores and voids.



(a)



(b) (c)

Figure 1. Room temperature (a) XRD, (b) SEM, and (c) Histogram of $BaBi_4Zr_2Sn_2O_{15}$ compound

Table.1. Cell parameters, volume, and crystallite size of the $BaBi_4Zr_2Sn_2O_{15}$ compound

Individual compound	a (Å)	b (Å)	C (Å)	Volume ($Å^3$)	P (nm)
$BaBi_4Zr_2Sn_2O_{15}$	10.2809	15.0756	4.0171	622.62	9.01845

The grains of irregular shape are densely & nonuniformly distributed over the whole surface of the pellet. The grain size is found to be 132.14 microns using Gaussian fit. The grains are of different shapes like cubical and rectangular and a few are smaller & spherical in shape. The size of the grain is much bigger than the crystallite size which confirms that a single grain comprises several crystallites. The same type of microstructure is observed in other similar polycrystalline ceramics of the same family. [7]

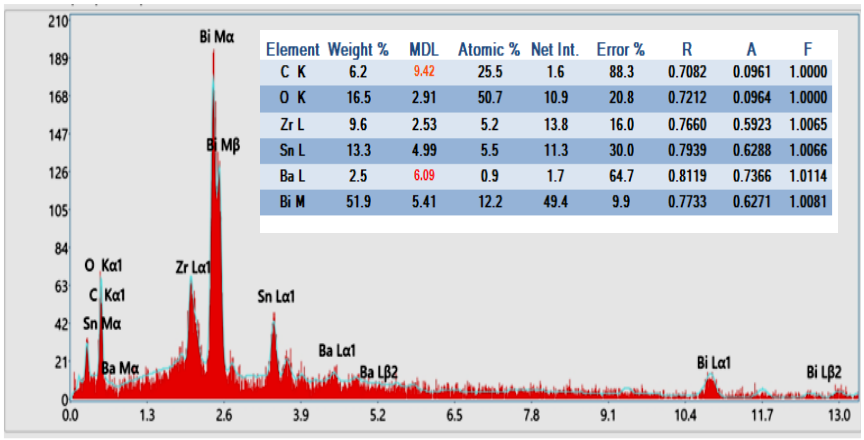


Figure 2. EDX of $BaBi_4Zr_2Sn_2O_{15}$

The EDX of $BaBi_4Zr_2Sn_2O_{15}$ is demonstrated in Figure 2, which provides the atomic percentage and weight of all the ingredient elements on the surface. The peaks in the spectrum of the corresponding elements like barium, bismuth, zirconium, tin, and oxygen are shown in pure form, which is the evidence of purity of synthesis materials in graphic form. The small atomic number of barium relates to the invisibility of weight and the atomic percentage of the spectrum.

3.2 Dielectric (ε_r and tanδ) studies

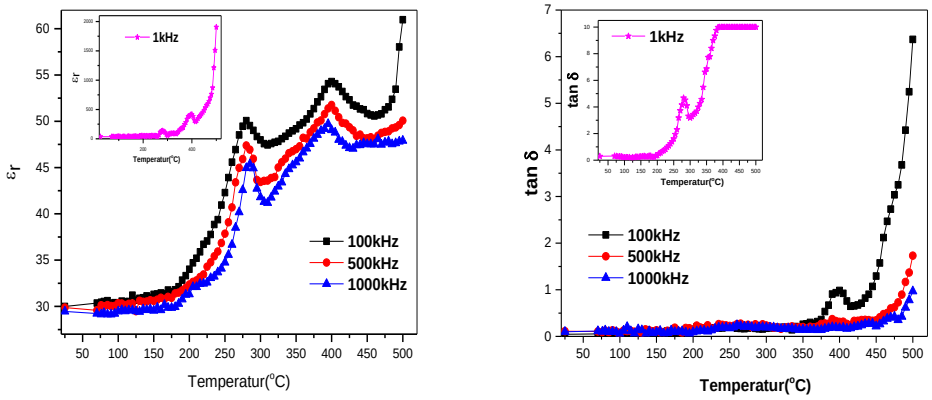


Figure 3. Variation of ε_r (left) and tanδ (right) with temperature of $BaBi_4Sn_4O_{15}$ sample at selected frequencies.

Figure 3. shows the variation of the relative permittivity (ε_r) and tangent loss (tanδ) with temperature for $BaBi_4Zr_2Sn_2O_{15}$ at some of the

frequencies. The graph of (ε_r ~temperature) displays a regular upward movement in (ε_r) with the rise in temperatures, thereafter ascends quickly to Tc=410 ^oC temperature where ε_r is highest (=192.57). Here transition occurred from unstable ferro state to stable paraelectric state. In the high-frequency regime, the Curie condition is obeyed (as in Figure 2), which is due to the presence of all kinds of polarizations in low frequency at all temperatures [8]. The low-temperature peak appeared in the plot in the lower temperature zone because of the structural phase transition [9].

The low dielectric loss (tanδ) indicates that the material shows good ferroelectric behavior. At high temperatures & lower frequencies tanδ is higher showing the improvement in conductivity & lessening the ferroelectric domain walls [10]. The smaller relative permittivity responds to a greater electric field. A diminution in relative permittivity with rising frequency is noticed in this compound.

Loss tangent decreases with frequency, which rises with a rise in temperature till peaks are reached at transition temperature for all frequencies. The hike in loss tangent with temperature confirms the enhancement of electric and ionic conduction for the BBZS sample [11].

3.3 Conductivity study:

The ac conductivity (σ_{ac}) can be measured from the expression given by the formula [12], $\sigma_{ac}=\varepsilon_o\varepsilon_r\omega\tan\delta$. Where, ϵ_o= absolute permittivity, ϵ_r = relative permittivity, ω = angular frequency, and tan δ is the loss tangent. The conductivity ~ temperature plot is shown in Figure 4. It is noticed from the plot that σ_{ac} rises to some temperature with temperature rise, which can be interpreted as the negative temperature coefficient of resistance (NTCR) characteristic of BBZSO compound.

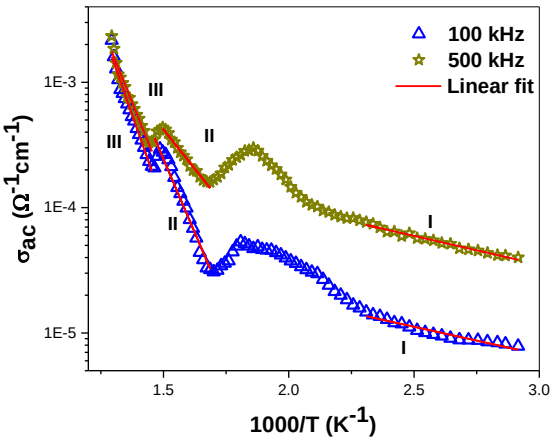


Figure 4. Variation of ac conductivity with inverse absolute temperature of $BaBiZr_2Sn_2O_{15}$

The nature of conductivity is investigated by dividing the plots into three distinct regions both the selected frequencies. At low temperatures and high frequency (500 kHz) the conductivity is observed to be temperature-independent. This kind of variation follows the Arrhenius relation specified below, which allows us to measure the activation energy (Table.2) i.e. $\sigma_{ac} = \sigma_0 \exp(-E_a/K_BT)$, where E_a = activation energy, T= absolute temperature, and K_B = Boltzmann constant.

The disparity in slopes establishes the presence of various mechanisms of conductivity. The merging of both curves into a single master curve at high temperatures confirms the temperature as well as frequency-independent behavior of the conductivity of the sample. For ferroelectrics, experimentally it is confirmed that the activation energies in the range 0.4–0.7 eV for the Arrhenius conduction mechanism is because of localized hoping of oxygen vacancies, whereas that for the range 0.9 – 1.5 eV, the diffusion of doubly ionized oxygen vacancies causes the conduction process. The lower E_a value in lower temperatures suggests that the excitation of the diffused ions can be possible by a smaller amount of energy and the conduction is for localized hoping of oxygen vacancies.

4. CONCLUSIONS:

Polycrystalline sample $BaBi_4Zr_2Sn_2O_{15}$ is synthesized with a suitable stoichiometric ratio following the mixed oxide process. The structure of the sample, confirmed from the XRD study, is an orthorhombic single-phase crystal in nature. The polycrystalline surface is confirmed by SEM study. Phase transition is noticed in the dielectric plot at 370^0C temperature. Comparatively lower dielectric constant at environmental temperature conditions informs that this compound is much more useful for infrared pyroelectric & electro-optic detectors when produced in the form of thin film or single crystal. Impedance study exhibits the existence of an electric relaxation process that is independent of temperature contributed from both grain and grain boundaries. The graphs of frequency-dependent ac-conductivity obey Jonscher's universal power law. The differences in activation energies in various temperature regimes indicate the participation of various conduction phenomena in the material. NTCR behavior observed in conductivity plots indicates that this property of the material can be used for some potential device applications in electronics.

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