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Complex Impedance Analysis of Sb-modified $Li_{0.5}Bi_{0.3}Sb_{0.2}TiO_3$ Ferroelectric Compound

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Abstract: Sb-modified lithium bismuth titanate $Li_{0.5}Bi_{0.3}Sb_{0.2}TiO_3$ is prepared following the mixed oxide method. The formation of the compound with a single-phase orthorhombic crystal structure is approved from the XRD analysis at environmental temperature. The impact of frequency and temperature on complex immittance parameters (impedance and modulus) are analyzed by an impedance analyzer in broad frequencies and temperature ranges. The electrical properties show; (i) the existence of semiconductor-like negative temperature coefficients of resistance behavior, (ii) evidence of electrical relaxation phenomena as a function of temperature, and (iii) the existence of single electrical relaxation ascribed to the existence of grain contribution to the electric properties.

Keywords: X-Ray techniques, Complex-immittance, electrical conductivity, Ceramics.

1. INTRODUCTION

Material science is a multidisciplinary field that involves the properties of matter, which applies to different areas of science and technology. In ferroelectric compounds, electrical polarization is a spontaneous process that can be reversed by reversing the applied field. Ferroelectrics are a group of materials suggested as smart materials because of the simultaneous co-existence of various properties like photosensitive, dielectric, and piezoelectric properties in the same material [1]. Perovskites gain great interest from scientists because it is easy to combine ferroelectricity and ferromagnetism [2, 3]. The perovskite structural family has common chemical formula ABX_3, where A & B sites are filled by cations having various sizes of ion & the X - anion bonds both. After the discovery [4], these compounds show a vital role in materials research. These have applications as sensor and catalyst electrodes & being good applicants for spintronics & memory devices. Perovskite exhibits physical properties like ionic conductivity, superconductivity, and magnetoresistance. Ferroelectricity, & a multitude of dielectric behavior plays a significant role in telecommunication and microelectronics [5]. Mishra et.al researched the Sb-modified barium bismuth titanate with varying concentrations of Sb [6]. A variation in structural parameters was acquired by varying the Sb content. The Sb concentration in the $BaBi_{1/2}Ti_{1/2}O_3$ induced the shifting of phase transition temperature to a higher value along with high temperature diffused phase transition in temperature-dependent relative permittivity graphs. They also observed that the dielectric permittivity and dielectric losses of the Sb substituted lithium bismuth titanate and pure barium bismuth titanate are frequency dependent and grain and grain boundaries effect are observed in the complex impedance spectroscopy. Research being carried out by N Pavlovic, et.al [7] on bismuth titanate-based Nano-powders with varying concentrations of lanthanum or cesium had been prepared using the sol-gel technique. The structural, ferroelectric, and piezoelectric characteristics of lithium and antimony based $K_{0.5}Na_{0.5}NbO_3$ eco-friendly ceramic were studied by Lin et .al [8] and he found that the substitution of Sb decreases improvement in the piezoelectric properties. As lesser work is done in Sb-modified compounds, therefore we are interested in investigating the ferroelectric characteristics of antimony-substituted lithium bismuth titanate i.e. $Li_{0.5}Bi_{0.3}Sb_{0.2}TiO_3$. Sb is chosen as a dopant because of the matching of its ionic radius with bismuth.

2. METHODOLOGY:

2.1: Materials synthesis:

Highly pure (99.9%) oxides and carbonates Bi_2O_3, (Central Drug House private limited), $LiCO_3$ (BRM Enterprises private limited), Sb_2O_3(Loba

Chemicals private limited) TiO_2 (Merck Specialties private limited) are measured in a proper Stoichiometry & are grounded by an agate mortar to obtain homogeneous powder in the air followed by methanol for 3 hours each to synthesize the $Li_{0.5}Bi_{0.3}Sb_{0.2}TiO_3$ perovskite. The powder is then heated at an enhanced temperature (980^{o}C) for 6 hours for calcination in a step of 50^{o}C starting from 650^{o}C. The calcined powders are palletized by a hydraulic press after mixing the binder Polyvinyl alcohol at a uniaxial pressure of 4 MPa. The pellets are then sintered at 990^{o}C for 6h, followed by electroding the surfaces using highly pure conducting silver paint. Then the pallets are kept in the furnace at 150^{o}C for 2 hours to evaporate the moisture if any present in the samples and cooled before taking for measurement.

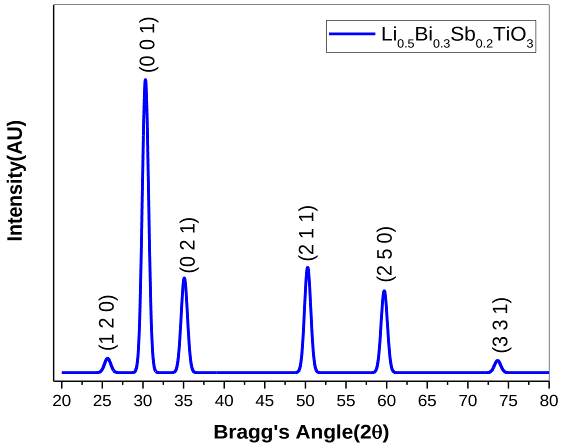
2.2: Materials characterization:

The quality, as well as the formation of the sample $Li_{0.5}Bi_{0.3}Sb_{0.2}TiO_3$ (LBST), are tested by XRD analysis with the help of X-ray powder diffractometer (Rigaku, Miniflex) with CuK_α radiations with wavelength 1.540Å in a broad span of Bragg's angles 2θ ($20^0 \leq 2\theta \leq 80^0$) at 3^0/min scattering rate. The dielectric and impedance behavior are analyzed using the experimental data obtained measurement by a HIOKI-3532-50 LCR Hi-tester in a range of frequency & temperature 100 Hz to 1MHz and 30^{0}C to 500^{0}C respectively in an interval of 5^{0}C/minute.

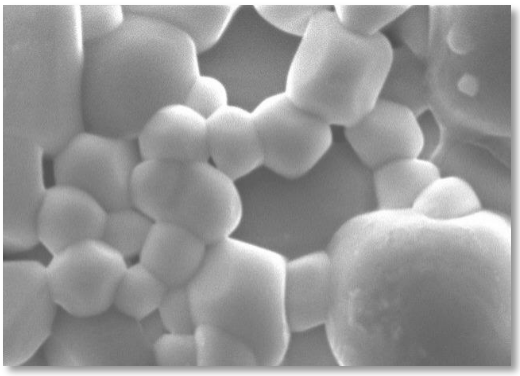
3. ANALYSIS OF RESULTS:

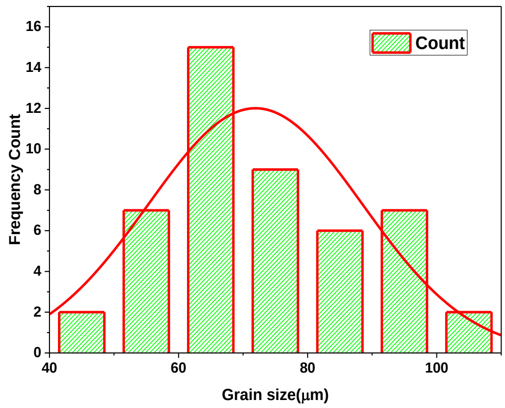
3.1: Structural & microstructural analysis:

XRD study of fired LBST compound informs its crystal structure. Figure 1 represents XRD plots of the compound. XRD patterns are observed to be of different natures in comparison to the constituent oxides, which proves the development of a new compound [9] having a single-phase structure. Scientists follow different software for the XRD data analysis which may give separate results. From the enlisted reflection peaks of the plots (2θ value), lattice parameters, miller indices & volume of the studied compound are acquired by POWD MULT Software [10] based on the best agreement of refined data. The analysis of the data by anyone using separate software giving different results cannot be ruled out, provided the results of different physical properties obtained must agree with the reported one.



(a) XRD





(b) SEM **(c) Histogram**

Figure 1. (a) XRD, (b) SEM & (c) histogram of $Li_{0.5}Bi_{0.3}Sb_{0.2}TiO_3$ at room temperature

The Literature study reveals the presence of a tetragonal structure of parent lithium bismuth titanate (LBT) at environmental temperature as reported by some authors, while according to other authors, the LBT compound shows the orthorhombic structure [11, 12]. Based on the best agreement among the calculated and observed data of interplanar spacing (d), where the standard deviation $\Delta d = d_{obs} - d_{cal}$ is minimum, it is confirmed that the sample has an orthorhombic crystal system at environmental conditions. The primitive cell parameters of the orthorhombic unit cell and volume are a = 4.7146 Å, b = 10.2649 Å, c = 2.9477 Å V = 142.65 Å^3 respectively. The particle size of the sintered pallets is estimated from peak broadening of XRD peaks by applying Scherer's equations $P = k\lambda/\beta_{1/2}\cos\theta_{hkl}$ [13], where the constant k has a value 0.89, wavelength (λ) is 1.54 Å & $\beta_{1/2}$ is the width of reflection peak at half maxima. The crystallite size is calculated by taking the average of data taken and the value is ~ 9.7999 nm. The microstructure of the sample is observed to have grains of irregular shape. Uniform distribution of grains is noticed on the entire surface (Fig 1(b and c)) with grain sizes ~ 69.552 µm for LBST.

Figure 2 demonstrates EDX information which supports the weight and atomic percentage of all the constituent elements on the surface. The spectral peaks of the constituent elements namely lithium, bismuth, antimony, titanium, and oxygen are demonstrated without any impurity. It exhibits graphic evidence of the purity of prepared samples. However, the small atomic number of lithium corresponds to invisibility in weight and atomic percentage of the spectra.

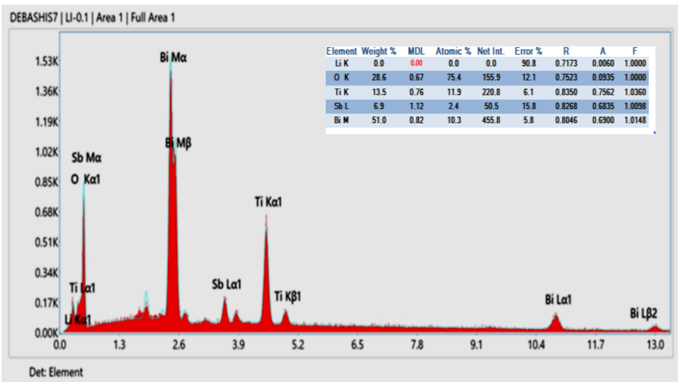


Figure 2. EDX of $Li_{0.5}Bi_{0.3}Sb_{0.2}TiO_3$

3.2 Impedance analysis:

CIS (Complex immittance spectroscopy explains the most reliable procedure to explain the electric behavior of the systems that include several intensely combined processes. It makes it easier to differentiate bulk (intra-grain) and bulk-interface (inter-grain) influences in the transport behavior of the system.

Z' ~Z" (complex impedance spectrum) plot of LBST at a series chosen temperature is shown in Figure 3 for both high and low temperatures. At all temperature regions, single semi-circular arcs are observed in the spectrum suggesting the electric responses are due to bulk activities within the material. This response is equivalent to a parallel RC circuit.

The decrease in resistivity is confirmed by the shifting of the point of interception of the arcs toward the origin of the complex plot on the real axis. This reducing nature of the resistance of the sample is supported by the bulk conduction with increasing temperature [13].

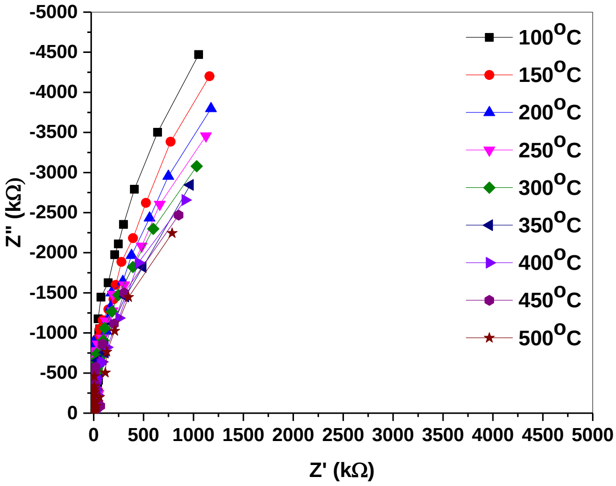
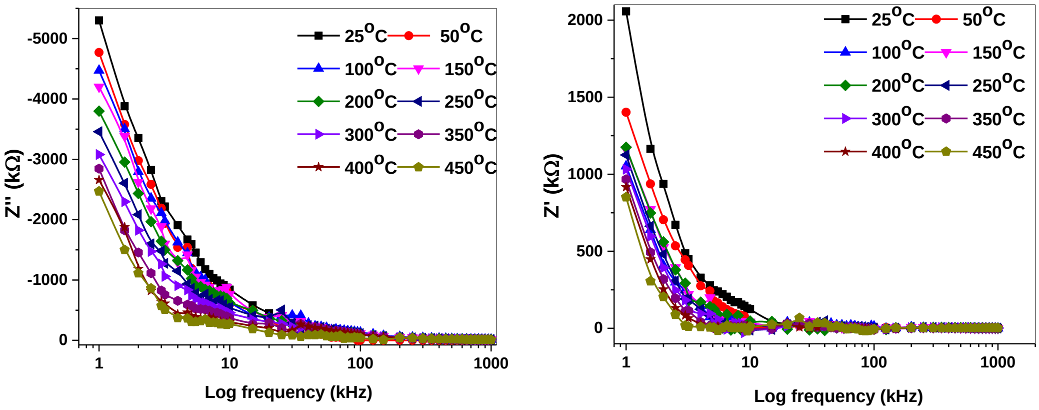


Figure 3. Nyquist plots of $Li_{0.5}Bi_{0.3}Sb_{0.2}TiO_3$ at different temperatures

The loss spectra or frequency-dependent Z″ of $Li_{0.5}Bi_{0.3}Sb_{0.2}TiO_3$ at various temperatures is as in Figure.4 (a). Dispersion of curves at low-frequency regions for all the temperatures suggests the presence of space charges like ions, vacancies, electrons, etc. The Z″ value decreases with the increase in frequency and merges at higher frequencies showing both frequency and temperature-independent nature. The merging of the dispersion curves at higher frequencies is because of the liberation of space charges.



(a) **(b)**

Figure.4. Frequency-dependent Z" (a) and Z' graphs (b) of $Li_{0.5}Bi_{0.3}Sb_{0.2}TiO_3$ at different temperatures

The Z′~frequency plots at various temperatures (25–500^{0}C) are shown in Figure 4 (b). At low frequency, the figure shows a spike-like response at almost all temperatures, and also dispersion spreads in the high-frequency regime with temperature rise. The values of Z' are observed to be decreasing with a rise in temperature showing NTCR behavior. The Z' value rises to a large extent both at low and high temperatures.

4. CONCLUSIONS:

$Li_{0.5}Bi_{0.3}Sb_{0.2}TiO_3$ sample is prepared following a mixed oxide reaction process. The formation of a single-phase orthorhombic compound is confirmed by XRD analysis. The low value of the loss tangent implies good ferroelectric material. The frequency dependence ac conductivity plots completely follow Jonscher's universal power law. In Z' ~Z" for all temperature region, single semi-circular arcs are observed in the spectrum suggesting the electric responses is due to bulk activities within the material. NTCR behavior noticed in material implies that this can be a better choice for some prospective electronics device applications.

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