

Synthesis, Structural and Electrical Properties of $\text{Ba}_{0.5}\text{Bi}_{0.5}\text{Ti}_{0.5}\text{Fe}_{0.2}\text{Mn}_{0.3}\text{O}_3$ Compound

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Abstract: A $\text{Ba}_{0.5}\text{Bi}_{0.5}\text{Ti}_{0.5}\text{Fe}_{0.2}\text{Mn}_{0.3}\text{O}_3$, a single-phase ceramic is successfully prepared following Mixed Oxide Process and the formation of the compound is confirmed from X-Ray diffraction. The surface morphology of the ceramic sample is examined using scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDX). EDX analysis confirms the elemental composition of the sample, indicating the presence of all the constituent elements, including barium (Ba), bismuth (Bi), titanium (Ti), iron (Fe), manganese (Mn), and oxygen (O), in both weight and atomic percentages. The dielectric and ac-conductivity properties of the material are studied across a wide frequency range (1kHz to 1MHz) and temperature range (25°C to 500°C). The material shows Maxwell-Wagner-type dielectric dispersion, which is often linked to the heterogeneous nature of the material, and a thermally activated relaxation mechanism, indicating that the dielectric properties of the sample are influenced by temperature. The dielectric and conductivity properties supports the semiconducting nature of the material, suggesting that it could be useful in electronic and energy storage applications. Lastly, the material demonstrates a high dielectric constant and low tangent loss, which indicate that the material is suitable for capacitors, sensors, and actuators.

Keywords: Dielectric, Capacitors, AC-conductivity, Sensors.

1. INTRODUCTION

Materials scientists have made some amazing achievements in understanding new preparation techniques and different properties of various materials. Smart materials are well known as materials that sense an external stimulus such as sensors and actuating a controlled response (actuators). These materials can be categorised as electrostrictive materials, piezoelectric materials, magnetostrictive materials and optical fibres etc. having fixed set of properties. These materials can alter their properties in several ways to achieve the requirements in device applications. Ferroics have special attention among various smart materials.

Generally, ferroics in physics is related to ferroelectric, ferromagnetic and ferroelastic ordering [1]. Ferroelectrics are a class of polar dielectric materials that possess at least two equilibrium orientations of the spontaneous polarization vector in the absence of an external electric field, and in which the polarization may be switched between those orientations by means of an electric field [2]. Perovskite material is the most widely studied ferroelectrics. Its simplest structure is cubic, which is the high temperature form for many mixed oxides of ABO_3 type, where A is a large radius cation, which occupies the empty sites between oxygen octahedra, while B is a small radius cation, which occupies the center of the octahedron, formed by O_2^- ions. $BiFeO_3$ is one of the early perovskites, having simultaneous ferroelectric and magnetic properties due to the polarizability of Bi^{3+} , and the presence of Fe^{3+} with uncompensated spin [3]. $BaTiO_3$ is the most investigated ferroelectric material, which discloses many aspects of ferroelectricity. Since its Discovery in 1940s, Barium titanate has been an exciting material due to chemically and mechanically stable nature and shows ferroelectricity at and above room temperature [4]. The bismuth based layered perovskite structures are discovered by B. Aurivillius (1949) [5]. Enhanced Electrical and Magnetic Properties of Samarium (Sm) doped Multiferroic Bismuth Ferrite (BFO) Ceramics is done by H. Hemanta Singh & H. Basanta Kumar Sharma. Samarium (Sm) doped modified bismuth ferrite samples $Bi_{1-x}Sm_xFeO_3$ are prepared by sol-gel technique. They studied that the X-ray diffraction patterns confirm the formation of the pure phase rhombohedral structure of bismuth ferrite and the dielectric constant (ϵ) and loss tangent ($\tan \delta$) shows the large frequency dispersion at low frequency. Sm substitution of Bi improves the saturation magnetization and magneto-dielectric coefficients [6]. So, we are interested to prepare, work and investigate the structure, microstructure, electrical and ferroelectric characteristics of $Ba_{0.5}Bi_{0.5}Ti_{0.5}Fe_{0.2}Mn_{0.3}O_3$ for a better understanding of various mechanisms in them at phase transition.

2. METHODOLOGY

2.1. Material synthesis

The empirical formula of the compound $Ba_{0.5}Bi_{0.5}Ti_{0.5}Fe_{0.2}Mn_{0.3}O_3$ (BBTFMO) is prepared by mixed oxide process [7]. Ingredients like highly-pure ingredients of carbonates and oxides (>99.9%); Barium carbonate $BaCO_3$ (M/S Sarabhai M. chemicals private limited), Bismuth oxide Bi_2O_3 (Central drug house private limited), Fe_2O_3 (Durga Bondchem Pvt. Ltd), Mn_2O_3 (Global Adsorbents Pvt.

Ltd), Titanium dioxide TiO_2 (Merck Specialities Pvt. Ltd) are weighted according to stoichiometric molecular mass ratio by a digital balance. All the constituents are mixed and grinded by a mortar and pestle in air and then in methanol medium for about 3h each till the formation of a homogeneous mixture. After that the mixture is heated in a furnace for 6h at 950°C for calcination. The obtained material is then re-grinded thoroughly by mixing polyvinyl alcohol (a binder) and made pellets by applying a uniaxial pressure, $4 \times 10^6 \text{Pa}$ with the help of a hydraulic press. The pellets are sintered at 975°C for 5h in a furnace at higher temperature.

2.2. Materials characterization

The material structure is studied using XRD data obtained from X-ray powder diffractometer (Rigaku, Miniflex) applying CuK_α radiation of wavelength 1.54\AA in a broad span of Bragg's angle 2Θ ranging from 20° to 80° with a scattering rate $3^\circ/\text{min}$. Dielectric property of the sample is analysed using data from electrical measurement of the sintered and electrode sample with help of a HIOKI-3532-50 LCR Hi-tester within the frequency range of 1kHz to 1000kHz and temperature range 30°C to 500°C with a heat rate of $5^\circ\text{C}/\text{min}$.

3. RESULTS AND DISCUSSION

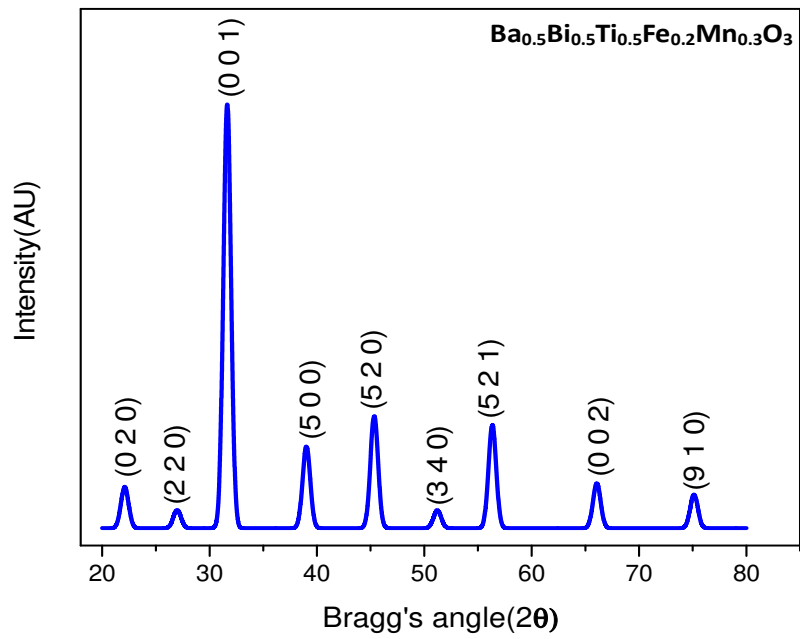
3.1. Structure and microstructure studies

A new orthorhombic single-phase compound $\text{Ba}_{0.5}\text{Bi}_{0.5}\text{Ti}_{0.5}\text{Fe}_{0.2}\text{Mn}_{0.3}\text{O}_3$ which is checked from the XRD data analysis is as in Fig1. The patterns obtained from the XRD data are separate from the constituent oxides and carbonates indicating the development of a new compound [8]. According to the literature review [9–11], the parent compound $\text{Ba}_{0.5}\text{Bi}_{0.5}\text{Ti}_{0.5}\text{Fe}_{0.5}\text{O}_3$ crystallizes in an orthorhombic structure having space group $F2\text{mm}$. The unit cell parameters, inter-planar spacings are calculated from the XRD data; the volume and the cell parameters of the material are found by use of a software-POWD MULT [12]. The best agreement among calculated and observed data of inter-planar space (d) ($\Delta_d = d_{\text{obs}} - d_{\text{cal}} = \text{minimum}$) confirms that the compound possesses orthorhombic structure. A reduction in unit cell volume is observed in Mn- modified BFOBT in comparison to the volume of the parent compound BBTFO. smaller ionic radius of Mn relating to Bi which indicates the potential applications of BBTFMO material as larger surface area with smallest volume which is important for devices applications in nano-research. The crystallite size was estimated using the X-ray peak broadening method as per Scherer's relation [13]

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$$P = k\lambda/\beta_{1/2}\cos\Theta_{hkl}$$

here, $k=0.89$ is a constant, $\lambda=1.54\text{\AA}$, $\beta_{1/2}$ breadth of the reflection peak at half maximum.



(a)-XRD

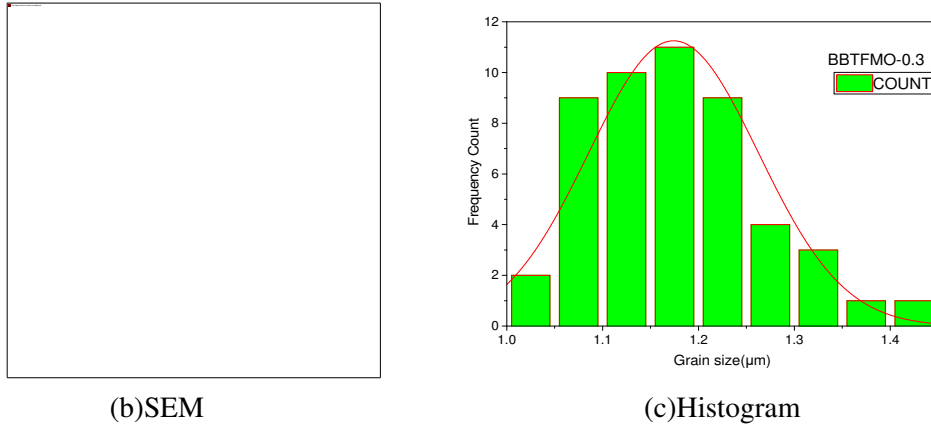


Fig1.shows X-ray diffraction pattern, SEM, Histogram data of $Ba_{0.5}Bi_{0.5}Ti_{0.5}Fe_{0.2}Mn_{0.3}O_3$

The SEM image shows a dense microstructure with rounded to polyhedral grains that are closely packed and well-connected indicating effective densification during synthesis. From the SEM analysis size of most grains fall within 10-12 μm , with an average size of approximately 11 μm . The histogram exhibits a near-gaussian distribution, confirming uniform grain growth without abnormal coarsening.

The EDX of the compound is demonstrated in Fig2, which shows the atomic percentage and weight of all the constituent elements on the surface. The peaks of the spectrum of the corresponding elements such as barium, bismuth, titanium, iron and oxygen are shown with purity which is the evidence of the prepared materials in graphic form. Barium having smaller atomic number relays to the invisibility of weight and atomic percentage of the spectrum.

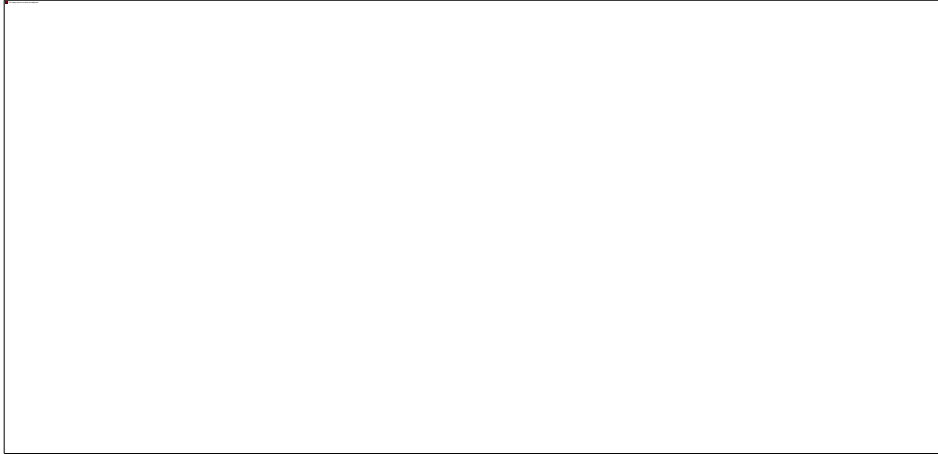


Fig2. EDX of Ba_{0.5}Bi_{0.5}Ti_{0.5}Fe_{0.2}Mn_{0.3}O₃

Element	Weight %	MDL	Atomic %	Net Int.	Error %	R	A	F
O K	22.1	1.61	65.5	48.5	14.3	0.7495	0.1124	1.0000
Ti K	9.7	1.86	9.6	56.8	10.5	0.8324	0.8012	1.0464
Mn K	6.	1.63	5.4	25.2	17.8	0.8506	0.8365	1.0579
Fe K	4.5	1.37	3.8	17.5	19.3	0.8571	0.8594	1.0663
Ba L	22.3	5.95	7.7	48.5	14.0	0.8383	0.8103	1.0131
Bi M	35.2	2.35	8.0	98.6	9.3	0.8018	0.6442	1.0179

3.2 Dielectric study

The variation of relative permittivity (ϵ_r) and loss tangent ($\tan\delta$) with temperature of Ba_{0.5}Bi_{0.5}Ti_{0.5}Fe_{0.2}Mn_{0.3}O₃ are as shown in fig.3.

The temperature- ϵ_r plot demonstrates a slow and gradual enhancement of ϵ_r with temperature up to 300⁰c and then rises rapidly up to the transition temperature (T_c) 460⁰c representing the change of ferro to paraelectric phase. ϵ_r becomes maximum at this transition temperature, which reduces on further temperature rise. The value of relative permittivity at peak is high in low-frequency regions, signifies the existence of several kinds of polarizations [14,15]. A low-loss tangent ($\tan\delta$) at a low- temperature regime is a sign of better ferroelectric compound. Higher $\tan\delta$ is observed towards high temperatures, which is because of the enhancement of conductivity and reducing the impact of ferroelectric domain wall in high temperature regime [16].

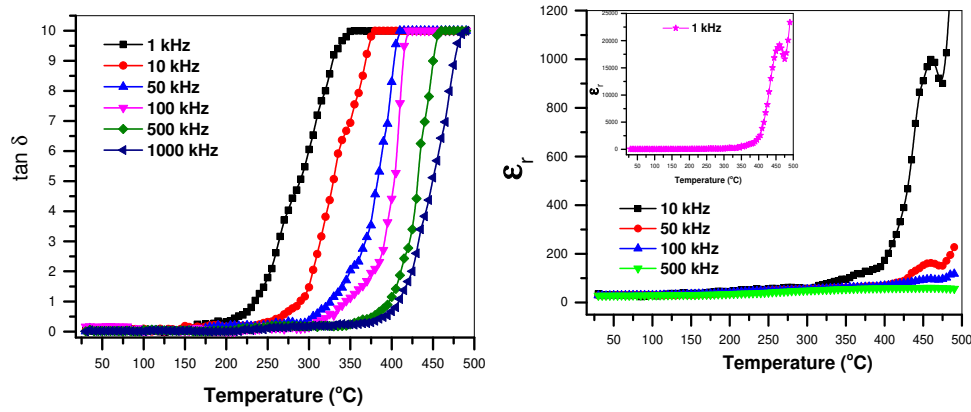


Fig 3. Plots of temperature versus ϵ_r (left) and temperature versus $\tan\delta$ (right) of $\text{Ba}_{0.5}\text{Bi}_{0.5}\text{Ti}_{0.5}\text{Fe}_{0.2}\text{Mn}_{0.3}\text{O}_3$ compound at particular frequencies

3.3. Conductivity analysis

The variation of ac conductivity is shown in Fig4. With the rise in temperature, σ_{ac} rises up to certain temperatures which is observed from the graph, exhibiting negative temperature coefficient of resistance (NTCR) behaviour most common in semiconductors, thereafter becomes temperature independent. Based on different slopes of the graph, the temperature range is divided into three separate zones such as lower, intermediate, and higher temperature regions. For two selected frequencies in BBTFM O material, σ_{ac} is nearly temperature independent at lower temperature for all frequencies. It seems to be independent of frequency at higher temperatures. This type of variation obeys Arrhenius relation which is

$$\sigma_{ac} = \sigma_0 \exp(-E_a/K_B T),$$

[here, T =absolute temperature, E_a =activation energy, and K_B =Boltzmann constant]. The amount of E_a is calculated from Arrhenius relation. Different values of the slopes indicate different conduction mechanism. At higher temperatures both the plots merge in to a single master curve suggesting the temperature and frequency independent nature of conduction mechanism. Low value of E_a in lower temperatures suggests that only small amount of energy is needed for the excitation of the ions.

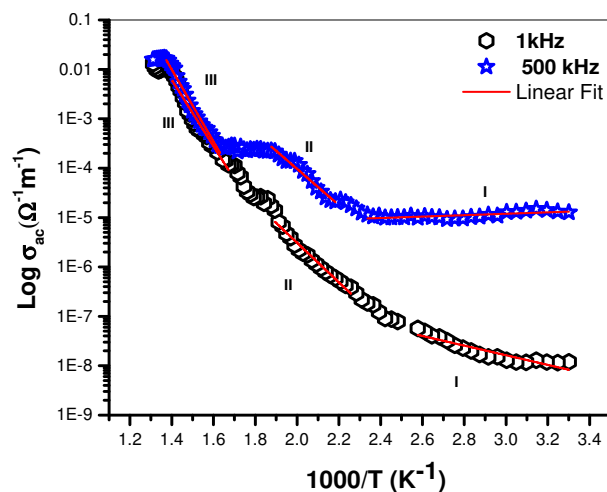


Fig4. Variation of ac conductivity with temperature of the compound $\text{Ba}_{0.5}\text{Bi}_{0.5}\text{Ti}_{0.5}\text{Fe}_{0.2}\text{Mn}_{0.3}\text{O}_3$

4. CONCLUSIONS

The $\text{Ba}_{0.5}\text{Bi}_{0.5}\text{Ti}_{0.5}\text{Fe}_{0.2}\text{Mn}_{0.3}\text{O}_3$ ceramic is prepared using mixed oxide process. From XRD analysis, it is observed that the structure of compound is single-phase and orthorhombic. The frequency independent phase transition is noticed at 460°C , specifies that the material is non-relaxor type ferroelectric. The thermal variation of σ_{ac} exhibits alteration of slope at transition temperature. Merging of the two plots is noticed towards higher temperature because of the rise of intrinsic conductivity and frequency independent nature of the sample.

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