

Studies on Structural and Electrical Characteristics of (Co / Ti) Modified Bismuth Ferrite

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Abstract: The polycrystalline sample of $\text{Bi}(\text{Co}_{0.35}\text{Ti}_{0.35}\text{Fe}_{0.30})\text{O}_3$ ceramic has been synthesized using high temperature solid-state reaction technique. A preliminary X-ray diffraction analysis (at room temperature) suggests that the compound possesses orthorhombic structure. Average particles size is calculated to be about 29 nm. Surface morphologies of the sintered samples were recorded by a scanning electron microscope (SEM). It reveals the uniform distribution of grains on the surfaces of the sample. The dielectric analysis for dielectric parameters, dielectric constant and tangent loss, has been analyzed at various temperature (RT – 773 K) and frequency (1 kHz – 1 MHz) ranges. However, no phase transition is observed for $\text{Bi}(\text{Co}_{0.35}\text{Ti}_{0.35}\text{Fe}_{0.30})\text{O}_3$ ceramic in the above experimental temperature range. Analysis of the frequency dependence of the real and imaginary impedance shows the existence of non-Debye type of relaxation in the material.

Key Words: Solid State Reaction, XRD, SEM. Dielectric Constant.

1. Introduction

Nowadays the multiferroic materials are considered as an attracting and promising deal due to a wide range of scientific and industrial applications in data storage devices, spintronic devices, sensors, actuators and multiple stage memories^{1, 2}. The materials having simultaneously more than one or more ferroic order properties namely ferroelectricity, ferromagnetism and ferroelasticity in the same phase, known as multiferroic materials³. A lot of discovered and well-studied multiferroic materials are namely YMnO_3 , TbMnO_3 , BiMnO_3 and BiFeO_3 having interesting features. Among them multiferroics family, BiFeO_3 (BFO) is found to be very useful material because of having its high Neel temperature 653 K and Curie temperature 1103 K⁴. In BFO, it has antiferromagnetic G-type spin configuration along the $[1\ 1\ 1]_c$ or $[001]_h$ directions in its pseudocubic or rhombohedral symmetry at room temperature with $R3c$ point group⁵. In this material, the

ferroelectric and ferromagnetic nature are mainly arises due to the 6s lone pair electrons in A-site of Bi^{+3} ions and partially filled d-orbital in B-site of Fe^{+3} ions respectively⁶.

Moreover, BFO shows high leakage current density on account of the presence of impurities, defects or nonstoichiometry nature. However, its potential applications are affected. To reduce its high leakage current and enhances its utility various approaches has already been performed based on the substitution of Co, Er, Ba by bismuth (A-site) and Sm, Co, Ti by iron (B-site) materials⁷⁻⁹. Currently, the scientific communities are focusing on the progress of lead-free multiferroic materials due to its environmental friendly nature and possible promising applications. That's why, an attempt has to be made to synthesize new lead-free $\text{Bi}(\text{Co}_{0.35}\text{Ti}_{0.35}\text{Fe}_{0.30})\text{O}_3$ environmental friendly multiferroic material via a simple solvent-free solid state reaction approach. Based on the above approach and literature survey suggests not much works have been reported so far.

2. Experimental

The polycrystalline sample of a chemical composition; $\text{Bi}(\text{Co}_{0.35}\text{Ti}_{0.35}\text{Fe}_{0.30})\text{O}_3$ was prepared by the conventional solid state reaction (SSR) technique. The starting reagents were using high-purity (>99.5%) oxides such as; bismuth oxide [Bi_2O_3], cobalt oxide [CoO], titanium oxide [TiO_2] and iron oxide [Fe_2O_3] mixed in a suitable stoichiometric ratio. These ingredients were first thoroughly mixed by using agate mortar and pestle in dry medium (air) for 8h, and then in wet medium (methanol) for 10h. The homogeneous mixture of the ingredients was calcined at an optimized temperature (750 °C) and time (6h). At room temperature, the formation of single phase of calcined powder of $\text{Bi}(\text{Co}_{0.35}\text{Ti}_{0.35}\text{Fe}_{0.30})\text{O}_3$ were studied from experimental data collected by powder X-ray diffraction (Rigaku Diffractometer, Japan) with $\text{CuK}\alpha$ radiation ($\lambda = 0.15405 \text{ nm}$) in a wide range of Bragg angles ($20^\circ \leq 2\theta \leq 70^\circ$) at a scan speed of 2° min^{-1} . The micro-structural characteristics of the sintered sample were investigated by using scanning electron microscope (SEM, Carl Zeiss).

The calcined powder of the prepared material was cold pressed into circular disc-shaped pellets were prepared (10 mm diameter and 1-2 mm thickness). The prepared pellets were then sintered at an optimized temperature of 800 °C for 6 h in air atmosphere. The capacitance, dielectric constant, loss tangent and other parameters were measured as a function of temperature (25-500 °C) over a wide range of frequency (1 kHz -1 MHz)

using a computer-interfaced phase sensitive meter (N4L PSM-1735) and a laboratory-fabricated sample holder.

3. Results and Discussion

Fig.1 shows the XRD pattern of as-prepared compound at room temperature. The XRD pattern (i.e., peak position and intensity), which is different from those of its ingredients, clearly shows the formation of a new compound. The calculated value of tolerance factor $T(f)$ for $\text{Bi}(\text{Co}_{0.35}\text{Ti}_{0.35}\text{Fe}_{0.30})\text{O}_3$ compound is 0.83 which confirm a deviation from ideal perovskite structure ($t=1$). A standard 'POWDMULT' computer programme was used to index all the peaks in all crystal systems. Based on the best agreement between observed (obs.) and calculated (cal.) inter planar spacing d [(i.e., $\sum \Delta d = d_{(\text{obs.})} - d_{(\text{cal.})} = \text{minimum}$)], unit cell parameters of $\text{Bi}(\text{Co}_{0.35}\text{Ti}_{0.35}\text{Fe}_{0.30})\text{O}_3$ sample, the compound were determined and hence system was found to be orthorhombic crystal structure. The least-squares refinement sub-routine parameters of the compound are; $a=36.1275\text{\AA}$, $b=8.1214\text{\AA}$, $c=3.5105\text{\AA}$, (with ± 0.0016 as minimum standard deviation) and volume $V=1172.31\text{ \AA}^3$. By using strong reflection peak (11, 1 0) of XRD pattern, the crystallite size of the samples was calculated and average crystallite size of the compound was found to be 29 nm. Fig.2 exhibits the room temperature scanning electron (SEM) micrograph of $\text{Bi}(\text{Co}_{0.35}\text{Ti}_{0.35}\text{Fe}_{0.30})\text{O}_3$ ceramic sintered pellet. The grains are of different shape and size indicating the existence of polycrystalline microstructure. They are of unequal sizes but with distinct grain boundaries. The average grain size is estimated to be $2.2\text{ }\mu\text{m}$.

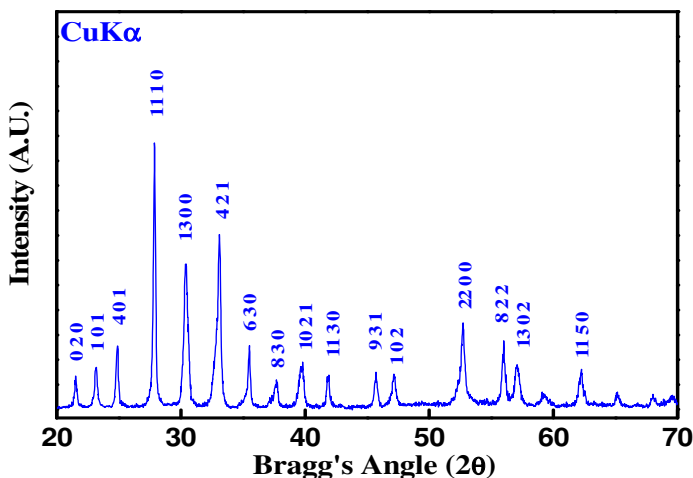


Figure 1: Powder X-ray diffraction pattern for $\text{Bi}(\text{Co}_{0.35}\text{Ti}_{0.35}\text{Fe}_{0.30})\text{O}_3$ compound at room temperature

Fig.3 (a-b) shows the temperature dependence (RT-773 K) of the relative dielectric constant (ϵ_r) and corresponding loss tangent ($\tan \delta$) at various frequencies (1 kHz - 1 MHz) for sintered pellet. It is observed that, the dielectric dispersion curves possess strongly temperature and frequency dependent dielectric constant for sintered pellet. For all the frequencies, the relative dielectric constant increases linearly with rise in temperature but dielectric parameters (ϵ_r and $\tan \delta$) decrease on increasing frequency, which is a general characteristic of dielectric materials. The value of ϵ_r increases with temperature and decrease with frequency. The increase of ϵ_r with temperature may be due to the electron-phonon interaction. However, no phase transition is observed in the experimental temperature range of (RT–500 °C). In addition, the value of dielectric loss ($\tan \delta$) increases smoothly initially but after the temperature increases, the loss increases sharply. The nature of variation of $\tan \delta$ with temperature is same as that of ϵ_r (i.e., the value of $\tan \delta$ gradually increases on increasing temperature). Generally, $\tan \delta$ has very high value in low-frequency and high-temperatures range in Fe-containing compounds which decrease rapidly with rise in frequency.

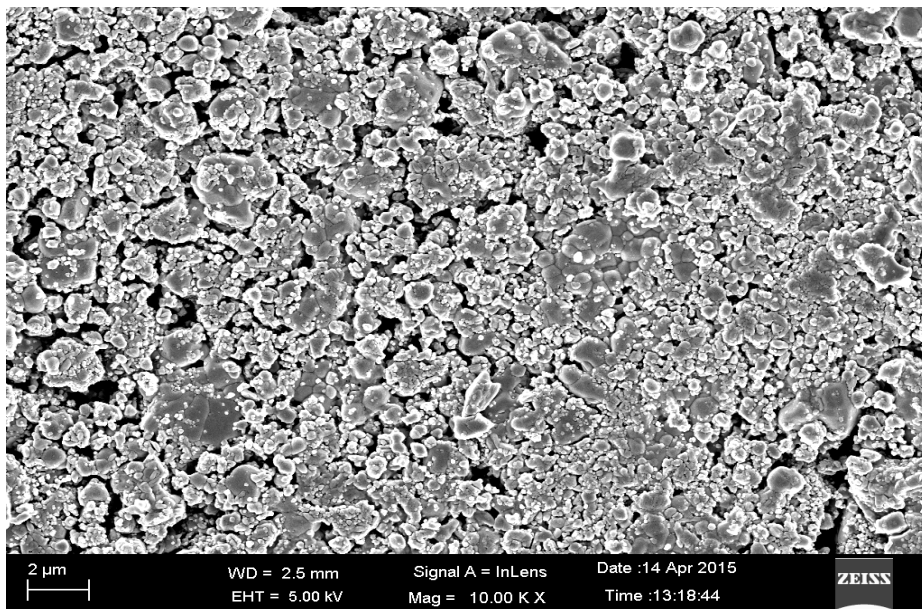


Figure 2: FE-SEM micrograph of $\text{Bi}(\text{Co}_{0.35}\text{Ti}_{0.35}\text{Fe}_{0.30})\text{O}_3$ ceramic at room temperature

4. Conclusions

The polycrystalline solid solution of $\text{Bi}(\text{Co}_{0.35}\text{Ti}_{0.35}\text{Fe}_{0.30})\text{O}_3$ was synthesized using a standard high temperature solid-state reaction technique.

The $\text{Bi}(\text{Co}_{0.35}\text{Ti}_{0.35}\text{Fe}_{0.30})\text{O}_3$ belonging to solid solution have been elaborated and their structural and dielectric properties were investigated. It is important to note that impurities phase formation has been suppressed in the present samples. The structural analysis of the compound using XRD spectra revealed the formation of single phase at room temperature with a orthorhombic structure. The crystallite size of the material was calculated using Scherrer's formula and found to be about 29nm.

Dielectric study reveals that the both dielectric parameters increase with temperature whereas they decrease with frequency. The value of dielectric constant and tangent loss increases with increase in space charge polarization. It may be due to some defects in the material.

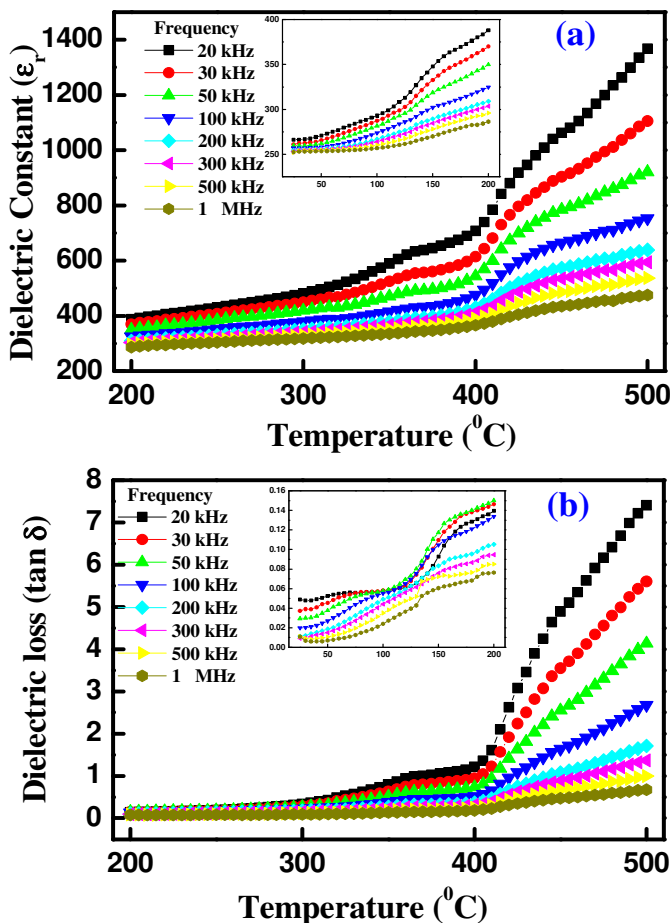


Figure 3 (a-b): Variation of relative dielectric constant (ϵ_r) and dielectric loss ($\tan \delta$) for $\text{Bi}(\text{Co}_{0.35}\text{Ti}_{0.35}\text{Fe}_{0.30})\text{O}_3$ compound as a function of temperature at different frequencies

References

1. Y. Wang, Q. Jiang, H. He and C. W. Nan, Multiferroic BiFeO₃ thin films prepared via a simple sol-gel method. *Appl. Phys. Lett.*, 88:142503 (2006) 1-3.
2. S. K. Pradhan and B. K. Roul, Electrical behaviour of high resistivity Ce-doped BiFeO₃ multiferroic, *Physica B*, **407** (2012) 2527-2532.
3. D. H. Wang, W. C. Goh, M. Ning and C. K. Ong, *Appl. Phys. Lett.*, 88, 212907 (2006).
4. A. Kumar, N. M. Murari and R. S. Katiyar, Probing the ferroelectric phase transition in sol-gel-derived polycrystalline bismuth ferrite thin films, *J. Raman Spectrosc.*, **39** (2008) 1262–1267.
5. J. M. Moreau, C. Michel, R. Gerson and W. J. James, *J. Phys. Chem. Solids*, 32, 1315 (1971).
6. S. Pattanayak, R. N. P. Choudhary, P. R. Das and S. R. Shannigrahi, Dysubstitution on structural, electrical and, magnetic properties of multiferroic BiFeO₃ ceramics, *Ceram. Int.*, **40** (2014) 7983–7991.
7. V. S. Puli, A. Kumar, N. Panwar, I. C. Panwar and R. S. Katiyar, Transition metal modified BiFeO₃ with improved magnetization and linear magneto-electric coupling, *J. Alloy. Compd.*, **509** (2011) 8223–8227.
8. W. Mao, X. Li, Y. Li, X. Wang, Y. Wang, Y. Ma, X. Feng, T. Yang and J. Yang, Structural phase transition and multiferroic properties of single-phase Bi_{1-x}Er_xFe_{0.95}Co_{0.05}O₃, *Mater. Lett.*, **97** (2013) 56–58.
9. H. Deng, M. Zhang, Z. Hu, Q. Xie, Q. Zhong, J. Wei and H. Yan, *J. Alloy, Compd.*, **582** (2014) 273–276.
10. B. D. Cullity, *Elements of X-Ray Diffraction, second ed.*, Addison-Wesley, Publishing Company Inc., Reading, MA, USA, 1978.