

Study of Structural and Dielectric Properties of Nb⁵⁺ Doped Bi_{0.80}Ca_{0.20}FeO₃ Ceramic

Sandhaya Jangra, Sujata Sanghi, Ashish Agarwal and Manisha Rangi

Department of Physics

Guru Jambheshwar University of Science & Technology

Hisar (India)

Email: sndh17@gmail.com

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Abstract: A Ca²⁺ and Nb⁵⁺ modified Bi_{0.80}Ca_{0.20}Fe_{0.98}Nb_{0.02}O₃ system have been fabricated via solid-state route. The phase transitional behavior, temperature and frequency dependent dielectric properties were investigated for the understanding of the effect of co-substitution. X-ray diffraction and Rietveld refinement confirmed the phase transformation from rhombohedral symmetry. The synthesized perovskite structure has combined effect of rhombohedral and orthorhombic phase. The electric behavior of proposed sample was analyzed by impedance spectroscopy over a wide range of frequency 1 Hz-7 MHz. The combined effect of temperature and frequency revealed that dielectric parameters gradually increased with temperature and reduced with a rise in frequency. The frequency dependent dielectric analysis reflects that ϵ' and $\tan \delta$ possess dispersion at lower frequency range. The studies of ac conductivity reflected that system obeys Jonscher's universal power law. Temperature-dependent behavior of frequency exponent 's' recommends that correlated barrier hopping (CBH) model is appropriate for describing conduction mechanism in the present system.

Keywords: Multiferroics, Rietveld Refinement, Dielectric properties.

1. Introduction

There has been remarkable research interest in the field of multiferroic due to the existence of more than one ferroic orders (ferroelectric, ferromagnetic and ferroelastic) simultaneously¹. As the result, they are considered as a potential candidate in the field of device fabrication². Among the class of multiferroics, BiFeO₃³ is one of the most studied materials due to its properties favourable in practical application. BiFeO₃

belongs to the ABO_3 perovskite structure with rhombohedral symmetry (R3c space group)³. It possesses a high value of Curie temperature ($\text{TC} \approx 1100 \text{ K}$) and Neel temperature ($\text{TN} \approx 640 \text{ K}$)⁴. Unfortunately, the material also has some major problems including difficulty in formation of pure phase, high leakage current and its basic antiferromagnetic nature⁵. These limitations hold back the use of BFO in practical applications. As polarization in BiFeO_3 is controlled by a $6s^2$ lone pair of A site ion (i.e. Bi^{3+}) and magnetization is prescribed by the magnetic character of B site ion (i.e. Fe^{3+}) respectively^{6, 3}. So, in order to overcome these constraints of BFO in practical use the possible way is modification at A and B site to enhance physical properties. Enhancement in multiferroic properties obtained by several reporters by substituting divalent ion and higher valance ion at A and B site respectively⁷. Therefore, we in this present work we have investigated the effect of Ca^{2+} and Nb^{5+} co-substitution on structural and dielectric properties of BiFeO_3 .

2. Experimental

Polycrystalline sample with composition $\text{Bi}_{0.80}\text{Ca}_{0.20}\text{Fe}_{0.98}\text{Nb}_{0.02}\text{O}_3$ (BCFN2) was prepared by Bi_2O_3 , CaCO_3 , Fe_2O_3 and Nb_2O_5 ($\geq 98\%$ purity) reagents by solid state route. All these reagents were taken in a stoichiometric ratio and mixed in mortar pestle for 2 hr. The formation of the compacted mixture was obtained firstly by calcination at 773 K then sintering at 1083 K. The crystal structural analysis was performed on Rigaku Miniflex Diffractometer-II with radiation source $\text{Cu-K}\alpha$ ($\lambda=1.54 \text{ \AA}$). XRD pattern was studied in diffraction angle range ($10^\circ \leq 2\theta \leq 80^\circ$) with a slow scanning rate $2^\circ/\text{min}$. The XRD data was further studied by Rietveld refinement using FullProf program. The dielectric analysis was performed on Newton's 4th Ltd. 1735 impedance/gain-phase analyzer over a wide frequency range 10 Hz -7 MHz. For collecting dielectric data calcined powder was converted pellet form with a diameter of 10 mm and thickness 1 mm. Such disk shape pellet then sintered and aim of making it electrode is achieved by painting its faces with silver paste.

3. Results and discussion

3.1 Structural analysis

Fig. 1 display room temperature X-ray diffraction pattern for $\text{Bi}_{0.80}\text{Ca}_{0.20}\text{Fe}_{0.98}\text{Nb}_{0.02}\text{O}_3$ sample. It shows that substitution at A and B

site is able to prevent the origin of impurity phases that generally occurred in pure BiFeO₃⁸. As reported by several research groups that 20% Ca substitution is not able to transform basic rhombohedral symmetry of BiFeO₃^{8,9}.

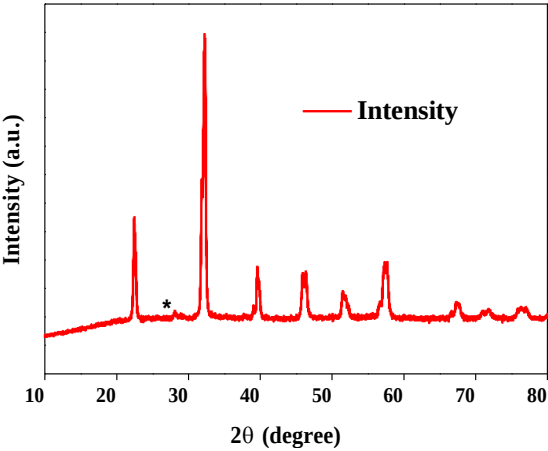


Figure 1: X-ray diffraction pattern for Bi_{0.80}Ca_{0.20}Fe_{0.98}Nb_{0.02}O₃ ceramic in diffraction angle 10° - 80°.

In our study, detailed investigation for crystal structure obtained by Rietveld refinement using Fullprof program. Refinement results confirmed suggested the best-fitted peaks were obtained by taking mixed phase (rhombohedral + orthorhombic) into account.

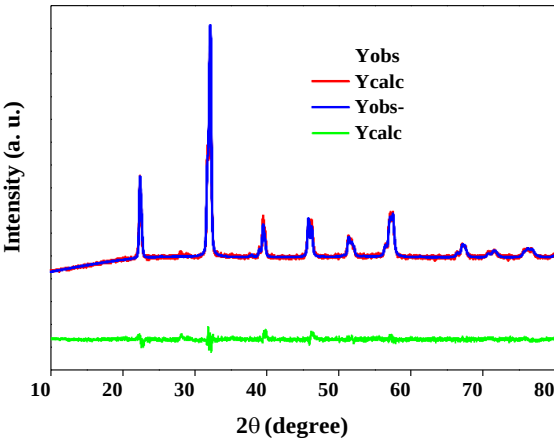


Figure 2: Rietveld refined XRD pattern for Bi_{0.80}Ca_{0.20}Fe_{0.98}Nb_{0.02}O₃ ceramic.

Fig.2 shows the Rietveld refined XRD pattern comprising observed, calculated intensities with their difference. The refined structural parameters such as profile and lattice parameters along with R factors were listed in Table 1. The fitting of observed and calculated XRD data is relatively good based on reflection of the low value of R factor (R_w and R_{wp}) and goodness of fit parameter (χ^2). The tolerance factor determines that the perovskite with highly symmetric cubic structure accomplish unity value. The disparity from unity corresponds to distortion from cubic structure. For BCFN2 sample, tolerance factor is 0.8874 which is less than unity and support deviation from cubic structure^{9, 10}.

Table 1 Lattice and profile parameters extracted from Rietveld refined XRD data.

Sample	Crystal structure	Lattice parameters	Atomic positions (x, y, z)	R-factors (%)
BCFN2	Rhombohedral (R3c)	a=5.567 Å	Bi/Ca (0, 0, 0.220)	$R_w=3.96$
		c=13.829 Å	Fe/Nb (0, 0, -0.002)	$R_{wp}=5.11$
		V =371.22 Å ³	O (0.848,0.633,0.429)	$\chi^2 =2.80$
	Orthorhombic (Pbnm)	a=5.557 Å	Bi/Ca (-0.011,0.003, 0.250)	
		b=5.531 Å	Fe/Nb (0, 0.5, 0)	
		c=7.827 Å	O1 (0.596, 0.006, 0.25)	
		V=240.651 Å ³	O2 (0.452, 0.192, 0.180)	

3.2 Dielectric analysis

Fig. 3 represents temperature dependence of real part of dielectric constant (ϵ') and $\tan \delta$ (in inset) for BCFN2 is at a variable frequency range (10 kHz, 100 kHz and 1 MHz) respectively. The value of dielectric constant is adequately constant at lower temperature range and after that increases sharply with temperature caused by thermally induced hopping conduction³. The observed variation with frequency is that both dielectric parameters were decreased with temperature. An abrupt increase in $\tan \delta$ is observed at higher temperatures range may be due to defects like oxygen vacancies and distribution of thermally activated charge carrier. However, at higher temperatures conductivity begin to dominate which in turn, increase in $\tan \delta^2$.

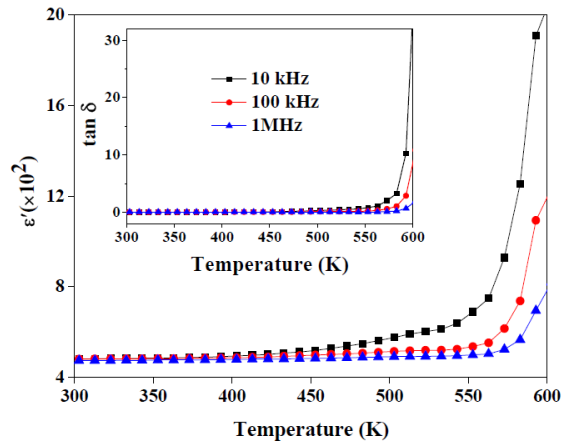


Figure 3: Variation of dielectric constant & $\tan \delta$ with temperatures at 10 kHz, 100 kHz & 1 MH.

The variation of dielectric constant (ϵ') and loss tangent ($\tan \delta$) in (inset) with frequencies at selected temperatures is shown in Fig. 4. At lower frequency, both shows dispersion type behavior similar to the previous reports of BFO and doped BFO^{3, 11}. At lower frequency the main cause of dispersive behavior is the conductivity generated due to oxygen vacancy in modified BiFeO₃ ceramics. However, total polarization contributed due to a different type of polarization such as electronic, atomic and ionic, dipolar and interfacial polarization. All these types of polarization play an active role in the different frequency range. Dipolar polarization contributes in the frequency range of 10^3 - 10^6 Hz (i.e. Infrared frequency range). Whereas, interfacial polarization contribute up to frequency a range $\approx 10^3$ Hz. Therefore, at lower frequency range the value of ϵ' is large and reduced with a rise in frequency¹².

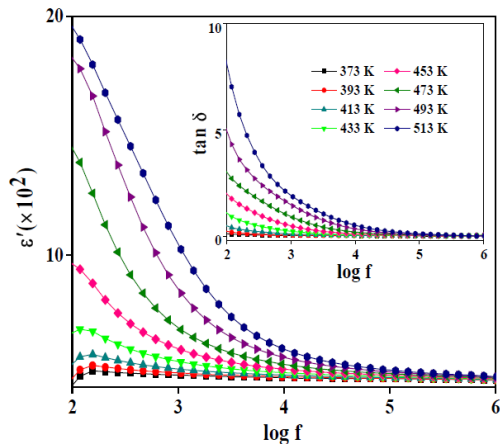


Figure 4: Frequency dependent behavior of dielectric constant & $\tan \delta$ at different temperatures

Fig. 5 illustrates the variation of ac conductivity with frequency at different temperatures. It is observed that variation of ac conductivity with frequency obey Jonscher's universal power law described by the relation $\sigma(\omega) = \sigma_{dc} + A\omega^s$, where $\sigma(\omega)$ is ac conductivity, σ_{dc} is frequency independent part of conductivity i.e. dc conductivity, A and s thermally activated quantities. The term $A\omega^s$ is an empirical expression for illustrating the transport properties of polarons, ions and electrons. At elevated temperatures, dc conductivity region magnitude of conductivity increases confirmed the negative temperature coefficient of resistance (NTCR) behavior of materials¹³. The value of dc conductivity, A and s were extracted by non-linear curve fitting. A good agreement is obtained between solid line (observed data) and dotted line (calculated data). Fig. 6 represents the variation of 's' with the rise in temperatures further analysis of which provide information about the conduction mechanism attributed to the material. Decreasing trend of frequency exponent 's' with the rise in temperature is correlated with CBH model⁹.

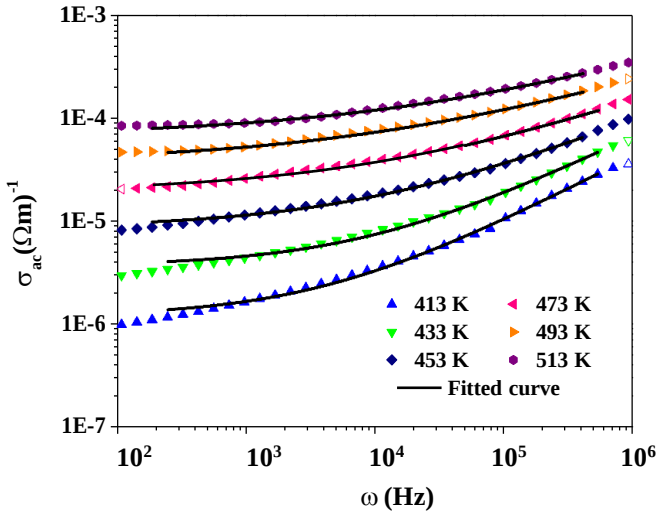


Figure 5: Ac conductivity variations at different temperatures

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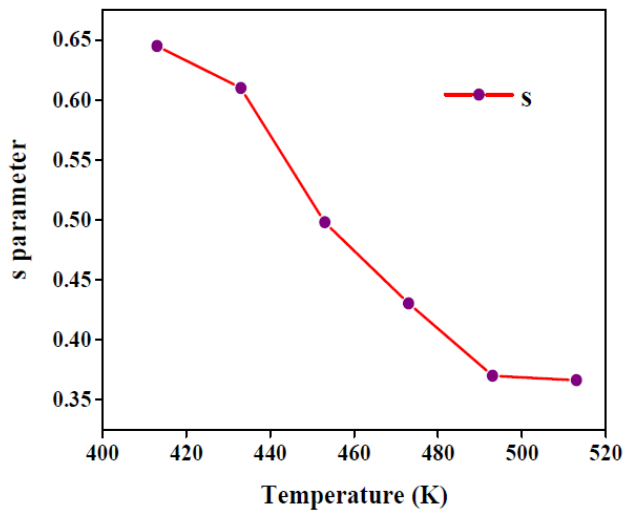


Figure 6: Variation of frequency exponent ‘s’ with temperatures.

4. Conclusion

The polycrystalline material Bi_{0.80}Ca_{0.20}Fe_{0.98}Nb_{0.02}O₃ was prepared by solid-state reaction technique. The basic structural analysis was performed on X-ray diffraction and Rietveld refinement. The refinement results confirmed that perovskite materials stabilized in mixed space group of rhombohedral symmetry (R3c space group) and orthorhombic (Pbnm space group). Ca and Nb co-doping in bismuth ferrite is quite successful in diminishing the secondary phases. We also observed the remarkable enhancement in the dielectric constant and losses with the rise in temperatures. Dielectric parameters show strong dispersion type behavior at lower frequency range and fairly constant at a higher frequency. The conductivity analysis confirmed that sample obeys Jonscher’s power law. It is found that conductivity increases with rising in temperatures indicated the existence of negative temperature coefficient of resistance (NTCR) in the material. The variation of ‘s’ with temperatures suggests that attributed mechanism in prepared ceramic is CBH model.

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