IOSR Journal of Applied Physics (IOSR-JAP)
e-ISSN: 2278-4861.Volume 18, Issue 4 Ser. 1 (Jul. – Aug. 2026), PP 41-45
www.iosrjournals.org

Improvement in Magneto-Dielectric Properties of Multiferroic $BiFeO_3$ by Gd (+3) Substitution

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Abstract : *$BiFeO_3$ is well known for its multiferroic properties at room temperature. Magnetoelectric coupling makes this material useful for spintronic applications. Herein, we present the study of change in structural, magnetic and dielectric properties of polycrystalline $BiFeO_3$ with Gd substitution at room temperature. The solution combustion method is used for our samples preparation. Crystal structures are analyzed by using X–ray diffraction technique with the help of reitveld refinement. Raman spectroscopy is used to study their bonding environment and structural changes. Dielectric studies indicate improvement in the value of dielectric constant and reduction in dielectric losses after Gd substitution. Temperature dependence study of dielectric constant, provides signature of magnetoelectric coupling. An increase in remanent magnetization observed in Magnetic studies shows its potential usefulness in data storage systems.*

Keywords - *$BiFeO_3$ polycrystalline material, solution combustion method of synthesis, structural, magnetic and dielectric properties.*

Date of Submission: 10-08-2026 Date of Acceptance: 22-08-2026

I. INTRODUCTION

Multiferroic materials have attracted the great attention of researchers due to their potential applications in data storage devices, magnetic recording media, sensors, and actuators. The importance of these materials lies in exhibiting more than one ferroic order parameter simultaneously in a single phase. The strong coupling between these multiferroic ordered parameters leads to a new family of devices whose properties can be modified by both electric and magnetic fields. [1]. Despite this, one of the most attractive applications of these materials is in spintronic devices, which arise as a result of coupling between ferroelectric and (anti-) ferromagnetic ordered parameters, whereby these offer the advantage to use both the charge as well as spin to alter their properties [2, 3].

Bismuth ferrite $BiFeO_3$ (BFO) is a well-known multiferroic material which shows antiferromagnetic, ferromagnetic and ferroelastic ordered parameters well above room temperature. BFO is a rhomboedral G-type antiferromagnet with a Neel temperature T_N~ 370 ˚C [4] which shows ferroelectric polarization of 100 μC/cm^2 along the [111] c direction of the pseudocubic structure [5] with a very high Curie temperature T_C~820 ˚C [6]. Similarly, huge polarization values with linear magnetoelectric coupling between the two orders has been observed experimentally [7], allowing an electric control of the BFO antiferromagnetic state [8]. BFO also allows altering its electric and magnetic properties by suitable substitution of ions either at the Bi (A) or at the Fe (B) site. Several attempts have been made by researchers to study the effect of both A and B site substitutions. Various ions have been tried for suitable substitution during synthesis to improve its properties [9]

Improvement in magnetic behaviour has been well observed by the suitable substitution at Bi and Fe sites. The literature confirms that substitution of the Fe site by transition metal ions can induce spontaneous magnetization at a lower temperature [10, 11], whereas substitution at the Bi site results in a rise in the magnetization value, but at the cost of lowering the saturation electric polarization [12–15]. Here, in this communication, we will discuss the effect of Gd^{3+}substitution on structural, magnetic and dielectric properties at the Bi site of the $BiFeO_3$ crystal.

II. EXPERIMENTAL DETAILS

All commercially available reagents and anhydrous solvents were used without further purification. The samples with chemical composition $BiFeO_3$ (BFO) and $Bi_{0.95}Gd_{0.05}FeO_3$ (BGFO) were synthesized by the solution combustion technique. The precursor was prepared by dissolving metal nitrates and L–alanine (fuel) in 2-methoxyethanolin stoichiometric proportions. An excess of 5 wt% Bi was added to the solution to proportions.

An excess of 5 wt% Bi was added to the solution to compensate some unavoidable bismuth oxide loss during the thermal treatment. The obtained powder was calcined at 400 ˚C for 30 minutes to remove undesired organic compounds whereas further calcination at 850 ˚C for 30 minutes was carried out to form the crystalline phase. The powder was then pressed to form pellets for dielectric measurements. These pellets were finally calcined at 850 ˚C for 30 minutes which were further utilized for dielectric measurements by forming silver contacts on its both flat surfaces. The dielectric measurements were carried out with Wayne Kerr 6500B impedance analyzer in the frequency range 100Hz to 1MHz. The magnetic measurement was carried out using a Micro-sense vibrating sample magnetometer (VSM).

III. RESULTS AND DISCUSSION

Figure 1 shows the XRD spectra of powdered BFO and BGFO recorded using Philips X'pert powder diffractometer with Cu $K\alpha_1$ radiation ($k_{\alpha 1}$ = 1.54056 Å). The crystal structure of both materials was refined taking R3c symmetric hexagonal unit cell. The peaks in the vicinity of 2θ = 28° were not overlapped by simulated pattern, as these belong to impurity phases often noticed with BFO and are responsible for degrading its multiferroic properties. The best fit to the observed XRD data was found with the cell parameters $a = b = 5.572$, $c = 13.855$; $\alpha = \beta = 90$˚and $\gamma = 120$˚in the case of BFO, whereas $a = b = 5.568$, $c = 13.827$; $\alpha = \beta = 90$˚and $\gamma = 120$˚for BGFO. Further, it has been observed that the cell volume of BFO (372.597 $Å^3$) has been reduced to 371.318 $Å^3$ after Gd^{3+} substitution. This change in cell volume may be attributed to the small ionic radius of Gd^{3+} as compared to Bi^{3+} and also the difference between Bi – O and Gd – O bond strengths, which is 343 ± 6 kJ/mol for Bi – O and 719 ±10 kJ/mol for the Gd – O bond. Such a decrease in the cell volume has been well observed in the literature for the same system [16]. Next, it has also been found that Gd substitution has significantly decreased undesired secondary phase content of BFO. This reduction is due to stabilization of perovskite lattice and suppression of Bismuth volatilization.

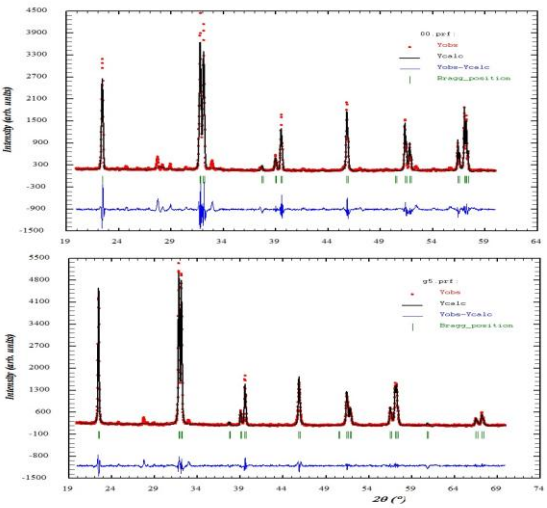

Fig. 1: Powdered X-ray diffraction pattern of as prepared BFO and BGFO at room temperature.

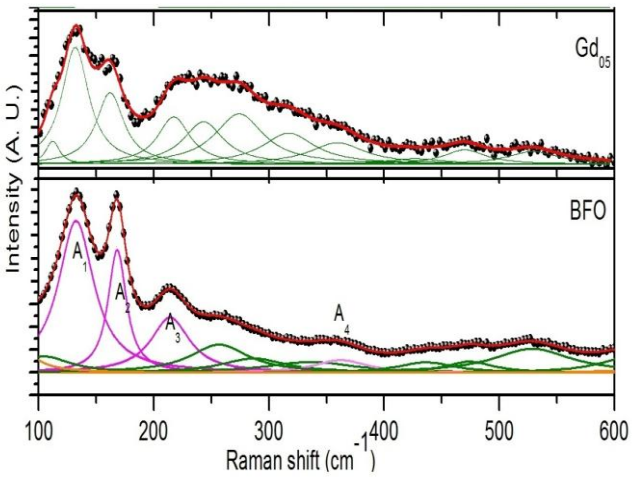

Fig. 2: Raman spectra of BFO and BGFO.

Raman scattering is a quite sensitive technique to observe small changes in atomic displacement and hence can provide valuable information about Raman modes entering after Gd substitution. Therefore, to investigate further changes produced by Gd substitution on lattice properties, structural phase transitions, and spin-phonon coupling of $BiFeO_3$ Raman scattering has been studied for both our samples. Fig. 2 shows Raman spectra for the samples BFO and BGFO. To analyze the samples, each spectrum was resolved into individual Lorentzian components and the peak position of each component was determined. The position of each peak describes the natural frequency (cm^{-1}) of each active Raman mode. The mode frequency of each Raman-active mode was assigned according to irreducible representation: $\Gamma = 4A1 + 9E$**.** In our case, we have observed four A modes (A_1, A_2, A_3, and A_4) and seven E modes. The natural frequency of these active modes are found to be in good agreement with the reported one [**16**].The six characteristic modes, i.e., E_1, A_1, A_2, A_3, A_4, and E_2, observed at 104, 132, 168, 214, 362, and 257 $cm^{-1,}$ respectively are resulting from stereochemical activity of the Bi lone pair for BFO. These modes are found to shift towards higher wave numbers in the case of BGFO, which indicates that the dopant Gd has entered into the Bi site of BFO. Such a shift is attributed to the doping by the ion having relatively light mass [17]. Further, it is also clear from the figure that these peaks became relaxed and

show relatively low intensity in the case of BGFO, which may be due to the change in its cell volume as observed in our XRD studies. The decrease in cell volume is likely responsible for the decline in stereochemical activity of the Bi lone pair.

Fig. 3 represents the frequency response of dielectric constant (ε′) of both the compounds. The BGFO shows a much larger value of dielectric constant, which is almost more than twice the value of BFO. The inset of Fig. 2 shows the variation of dielectric loss (tan δ) with frequency. It has been found that Gd substitution has not only helped in reducing the dielectric loss but also maintained it at almost a constant value, which is desirable from the technological point of view [18]. Experimental results [19] have suggested that defects and impurities in energy levels, in particular, oxygen vacancies and the presence of Fe^{2+} ions, have been proved to be the main cause of high leakage current in BFO [19–23]. Therefore, the frequency response of tan δ has indicated the reduction of impurities which confirms the XRD results. The large value of dielectric constant at low frequencies could be explained by the phenomenon of dipole relaxation, wherein at low frequencies the dipoles are able to follow the frequencies of the applied field.

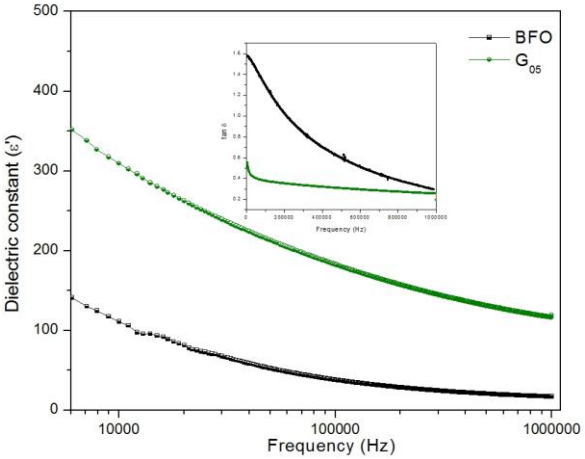

Fig. 3: Variation of dielectric constant with respect to frequency. (Inset shows variation of tanδ with frequency).

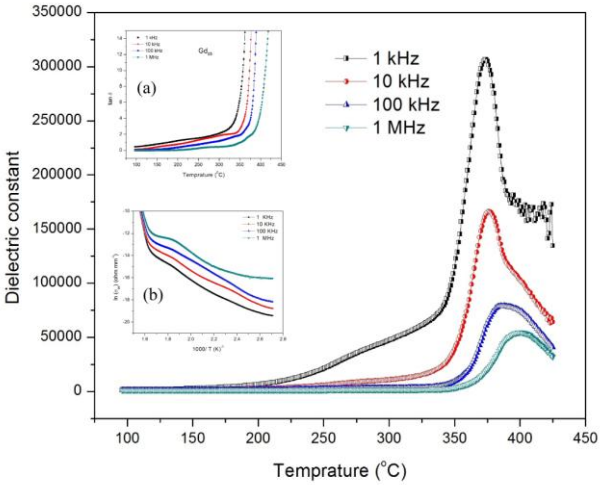

Fig. 4: Variation of dielectric constant with temperature for BGFO at different frequencies Inset (a) variation of tanδ with temperature and inset (b) change in $\ln\sigma_{ac}$ with change in temperature.

The temperature dependence of dielectric constant of BGFO is presented in Fig. 4. A dielectric anomaly is observed in the vicinity of 380 ˚C. This anomaly results from the vanishing magnetic order in the system and its transition to a paramagnetic state which confirms magnetoelectric (ME) coupling [24-26].When the temperature is higher than 320˚C, *ε ′*and *tanδ* become significantly higher (inset (a) fig 4). These high-temperature dielectric properties are apparently due to conduction loss. The inset (b) of fig. 4 represents the variation of ac conductivity (σ_{ac}) with temperature. The a.c. conductivity of these samples was calculated using the relation $\sigma_{ac} = \varepsilon_0\, \omega\, \varepsilon'\, \tan\delta$. In the low temperature region, σ_{ac} was relatively small and increased slowly with temperature. In contrast, σ_{ac} increases rapidly with temperature when it is higher than 350˚C. The rapid increase of σ_{ac} with temperature sets a limit for the application of this ceramic. The change in ac conductivity may be attributed to a change in the conduction mechanism. In the low-temperature region, conduction is due to short-range charge movement whereas the mechanism at higher temperatures is long-range movement of charge carriers.

The magnetic field response of both samples was measured up to a field of 20 kOe, as reproduced in Fig. 5. As a result of the antiferromagnetic nature, BFO and BGFO show small values of magnetic moment ~ 0.12 emu/g and ~ 0.20 emu/g respectively at 20 kOe. Significant increase in M_r and H_c values from 0.0027 emu/g to 0.004 emu/g and 207 Oe to 277 Oe respectively for BFO has been found after doping. Increase in the magnetic moment value with Gd substitution can be attributed to the following two factors: the collapse of the space-modulated spin structure of BFO [12-15] and magnetic contribution arising from magnetically active Gd^{3+} ions [27]. High M_r helps to provide stronger readback signal whereas high H_C ensures stability of data without getting corrupted for decades thus shows potential usefulness of material for practical applications.

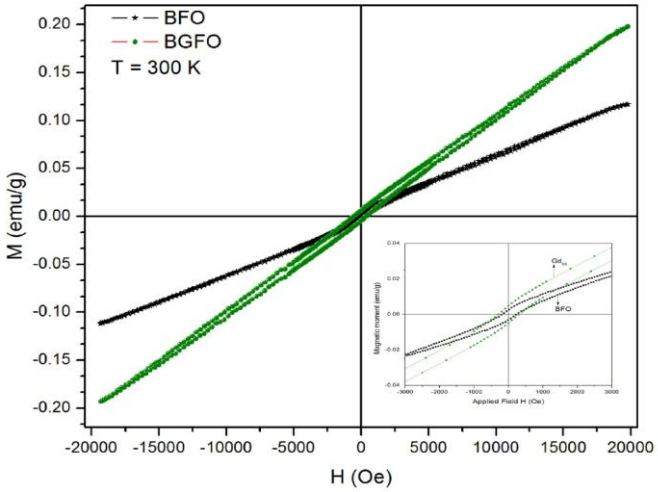

Fig. 5: Variation of magnetic moment with magnetic field for BFO and BGFO at room temperature.

IV. CONCLUSIONS

In the present work, we have found that A-site substitution in BFO by Gd^{3+} stabilized the crystal structure. The dielectric loss for the substituted sample became almost independent of frequency, which is essential technical requirement of designing sensors and capacitors. The Gd ion has also contributed to improving the magnetic character of antiferromagnetic BFO. Furthermore the sign of magneto-electric coupling has also been observed in the temperature dependence of dielectric constant. These improvements in magneto-dielectric properties of multiferroic $BiFeO_3$ by Gd (+3) substitution are quite useful in practical engineering uses.

Acknowledgements

The author Ashish. Gautam is thankful to University Grant Commission, Govt. of India, for providing research fellowship (UGC-SAP) and Defence Research Development Organisation (DRDO) for providing grant No. ERIP/ER/0703665/M/01/1044. Research facility provided by SAIF Chandigarh is highly acknowledged.

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