ISSN: 2633-4828 Vol. 4 No.1, June, 2022

International Journal of Applied Engineering & Technology

STRUCTURAL ANALYSIS, DIELECTRIC STUDIES, AND FERROELECTRIC-FERROMAGNETIC COUPLING OF SAMARIUM-DOPED BARIUM TITANATE AND COBALT FERRITE COMPOSITES

Showket Ahmad Bhat[*], **Ab Mateen Tantray and M. Ikram**
Department. of Physics, NIT Srinagar, J&K 190006, India
*showketbht7@gmail.com

ABSTRACT

To examine the composites' magnetization behavior, temperature-dependent magnetic measurements were made. Experiments involving field cooling and zero field cooling revealed that the magnetization rise with field cooling and fell with zero field cooling. The observed behaviour was explained by the alignment of spins in the direction of the magnetic field and the thermal agitation at high temperatures that breaks magnetic couplings. Dielectric investigations were performed on particulate composites of (1-x)SmBT-xSmCF, and the results showed a high dielectric constant (εr) and temperature-dependent behavior. The observation of an increase in εr with temperature was ascribed to the hopping mechanism between Fe3+→Fe2+ and Sm3+→Sm2+ ions. Nonetheless, the structural transition was the cause of the drop in εr below the Curie point. The critical temperature (Tc) and dielectric constant (εr) increased with the addition of the SmCF phase, and this increase was ascribed to denser structures and improved electron mobility. Dielectric loss (tanδ) decreased for the composite materials, with peak values found close to the Curie temperatures. This thorough investigation advances knowledge of the composites' structural, magnetic, dielectric, and chemical properties.

Keywords: Magnetic properties, dielectric properties, hysteresis loops, domain structures, temperature-dependent magnetization.

INTRODUCTION

The capacity of artificial multiferroic composites to combine multiple ferroic orders to exhibit distinct functional features has attracted a lot of attention in recent years. Because these composites are designed to combine the benefits of several ferroic features into a single material system, they are incredibly adaptable and can be used in a wide range of applications, such as memory devices, actuators, and sensors. Of all the connection schemes used in the fabrication of these composites, the 0-3 particulate approach is the most straightforward and effective. In contrast to alternative techniques like 2-2 laminated and 1-3 fiber rod composites, the 0-3 particulate approach is accessible and economical for large-scale production because it doesn't require complicated equipment.

A broad range of ferroic and magneto-dielectric properties are possible in the 0-3 particle composites due to the embedding of ferroelectric and ferrimagnetic phases inside a matrix, which results in multiferroic behavior. The interaction between the implanted particles and the surrounding matrix results in improved coupling between the ferroelectric and ferromagnetic orders, which gives rise to unique properties of these composites. This coupling allows magnetic properties to be controlled by an electric field and vice versa, which is essential for the development of advanced multiferroic devices [1-3].

The structural, magnetic, dielectric, and ferroelectric-ferromagnetic coupling characteristics of these composites are all thoroughly examined. Through the utilization of methods like temperature-dependent magnetization investigations, X-ray photoelectron spectroscopy, and Raman spectroscopy, scientists can acquire more profound comprehension of the fundamental principles that dictate the actions of these materials. Optimizing the performance of multiferroic composites and customizing them for particular purposes require an understanding of this.

The design of next-generation multiferroic devices could be completely changed by the creation of novel 0-3 particulate composites with improved properties, opening up new possibilities in fields like energy harvesting, spintronics, and multifunctional materials, provided this field of study continues to progress. By examining the complex interactions between structure, magnetism, and dielectric characteristics in samarium-doped barium titanate and cobalt ferrite composites, this work seeks to add to the expanding body of knowledge and pave the way for future advancements in multiferroic materials.[3-6]

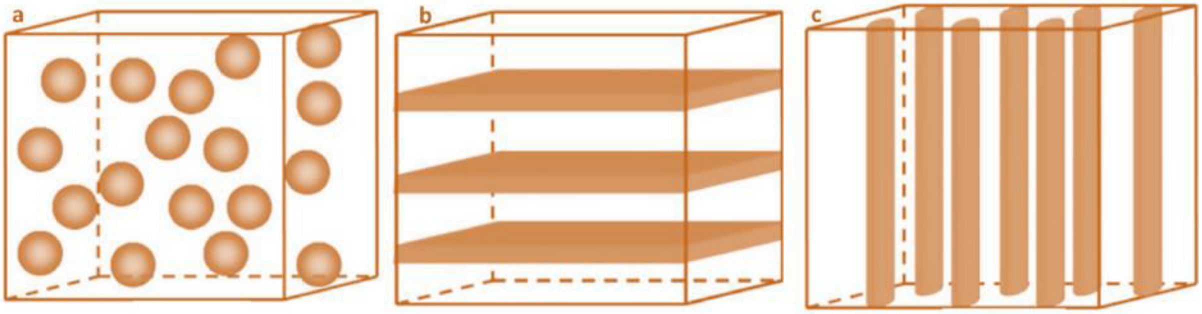

Fig.1: Diagrammatic representation of three bulk composites with three common connection schemes: (a) 0–3 particulate composite, (b) 2–2 laminate composite, and (c) 1–3 fiber/rod composite.

A popular strategy for enhancing the ferroic characteristics of multiferroic composites is to maximize the transfer of strain between the electric and magnetic phases. A ferroelectric phase with low leakage currents and a magnetic phase with a high magnetic moment and magnetostriction can be chosen to accomplish this. By strengthening the magneto electric (ME) response at the boundary interface, this approach can improve the composite material's ME performance. The direct ME effect, which measures the ratio of polarization (P) produced by an applied magnetic field (H), is a measure of the ME responsiveness of these composites.

$$\alpha_H = \frac{\partial P}{\partial H} \cong \varepsilon_o \varepsilon_r \left(\frac{\partial E}{\partial H}\right) \qquad 1$$

As, $$P = \varepsilon_o \chi E = \varepsilon_o(\varepsilon_r - 1)E = \varepsilon_o \varepsilon_r E \qquad for\ \varepsilon_r \gg 1 \qquad 2$$

where ε_o and ε_o are, respectively, the relative permittivity of the medium and the dielectric permittivity of the object. Since E =V/t, where V is the voltage and t are the thickness, the following relationship for the magnetically generated magnetoelectric effect is discovered

$$\alpha_H = \frac{\partial P}{\partial H} \cong \varepsilon_o \varepsilon_r \left(\frac{\partial E}{\partial H}\right) = \frac{\varepsilon_o \varepsilon_r}{t}\left(\frac{\partial V}{\partial H}\right) = \alpha_H^V \varepsilon_o \varepsilon_r \qquad 3$$

where α_H^V is the magnetoelectric coefficient, which is defined as:

$$\alpha_H^V = \frac{\partial E}{\partial H} = \frac{1}{t}\left(\frac{\partial V}{\partial H}\right) \qquad 4$$

The voltage magneto-electric coefficient (α) is the key parameter used in evaluating experimental data and designing various multiferroic-based applications [6-8].

Studying the structural characterizations of composite materials like barium titanate-cobalt ferrite (BaTiO3-CoFe2O4) has shown relationships between interfacial stress, vacancies, and the ferroelectric structure's reduction of tetragonal distortion. According to these results, BCZT85-CFO15 composites may be a viable option for the development of lead-free materials with improved magnetoelectric (ME) coupling at room temperature. Specifically, it was discovered that the ME coupling coefficient for BCZT85-CFO15 was roughly 6.03 ps/m. Subsequent studies have shown that synthesising (1-x)BaTiO3–(x) CoFe1.8Zn0.2O4 using the solid-state reaction method, where x = 10, 20, 30, and 40 weight percentages, results in an increase in the morphology and dielectric constant as the ferrite fraction rises. Furthermore, a sequence of materials with different concentrations of (1-x)(Ba0.8Ca0.2TiO3)–x(Co0.6Zn0.4Fe2O4) were created using a wet chemical process. It was discovered that the measured leakage current values in all samples agreed with the Ohmic conduction mechanism. The saturation magnetization (Ms), which peaked at x = 0.04, rose together with the ferrite content.

The solid-state reaction approach was used in the current investigation to create the composite materials (1-x)Ba0.5Sm0.5TiO3 - x Co0.5Sm0.5Fe2O4 (where x = 0.02, 0.04, and 0.06). The objective of this study was to examine these composite materials' structural, magnetic, temperature-dependent dielectric, and magnetoelectric (ME) coupling characteristics. The findings pave the way for future applications in lead-free multiferroic devices by providing a better knowledge of how changing the composition influences the multiferroic behavior and ME coupling in samarium-doped barium titanate and cobalt ferrite composites.

Magnetic Studies

The ferrimagnetic behavior of the SmBT phase and its particulate composites [(1-x)SmBT-xSmCF (0.02,0.04,0.06)] at room temperature is confirmed by the saturated M-H loops in Figure 3, and the corresponding parameters are displayed in Table 1. All of the SmBT-SmCF composites and the pure SmBT phase show the typical hysteresis loops, indicating that there is exchange interaction between spins with different orientations within domains. As the proportion of the magnetic SmCF ferromagnetic phase increases in the composites, the exchange interactions between different spins become stronger, resulting in an increase in saturation magnetization(M_s) and magnetic moments (μ). This trend is in accordance with the mass ratios of the SmBT phase used in the synthesis, the remnant magnetization (M_r) in the composites also exhibits this same behavior. This gives us reassurance that the ferroelectric SmBT phase limitations prevent the bulk numbers of spins from being orientated in the field direction. One potential explanation for the increased magnetoelectric response is that this causes strain inside the composites[8-12].

The study of domain structures of the SmBT phase and its composites were analyzed by calculating the square-ness ratios (M_r/M_s). The results showed that all the samples SmBT as well as its composites have multi-domain structure as the value of ($M_r/M_s<0.5$). The small values of M_r/M_s in the samples may be attributed to the magnetic domains pinning effect, which is caused by the SmBT ferroelectric phase by blocking the spins from orienting in the field direction. In order to compute the magneto-crystalline anisotropy for such confined magnetic multi-domains, we used the Law of Approach to Saturation (LAS)[13-14].

$$M = M_s\left(1+\frac{b}{H^2}\right)+cH \qquad 5$$

The b/H^2 term in the equation is related to the magneto-crystalline anisotropy, which is a measure of the energy difference between different orientations of a magnetic moment within a crystal lattice. This term is dependent on the crystal structure and the atomic magnetic moments within the lattice. The cH term is referred to as a paramagnetic-like term and is associated with the high field magnetization. This term is related to the susceptibility of the material to an applied magnetic field and the alignment of the atomic magnetic moments within the material.

$$b = \frac{8}{105}\left(\frac{K^2}{\mu_0^2 M_s^2}\right) \Rightarrow K = \mu_0 M_s\sqrt{\frac{105b}{8}} \qquad 6$$

Where μ_o (permeability of free space) = 4π x 10^{-7} H/m, K is the magneto-crystalline anisotropy constant which is measure of the energy difference between the easy axis and the hard axis of a ferromagnetic material. The magneto-crystalline anisotropy constant (K) increases with the increase in ferrite concentration in Sm-based ternary (SmBT) composites. This is due to the increase in Co^{2+} ions in the composites, which results in stronger exchange interactions between Co^{2+} and Fe^{3+} ions. These interactions lead to an increase in the alignment of the magnetic moments, leading to an increase in K [15]. The magnetic moment(μ_{exp}) experimentally is also calculated by the expression [16].

$$\mu_{exp} = \frac{M_w . M_s}{5585} \qquad 7$$

Where M_w is molecular weight of samples.

Table 1: Various parameters of magnetic studies of particulate multiferroic composite of SmBT-XSmCF(X=0.02,0.04,0.06)

Conc. X	M_s(emu/g)	M_r(emu/g)	M_s/M_r	H_c(Oe)	K(J/m^3)
X=0.02	37.69	3.41	0.072	510.47	0.394
X=0.04	84.27	7.82	0.069	521.44	1.129
X=0.06	141. 65	12.48	0.067	527.31	2.190

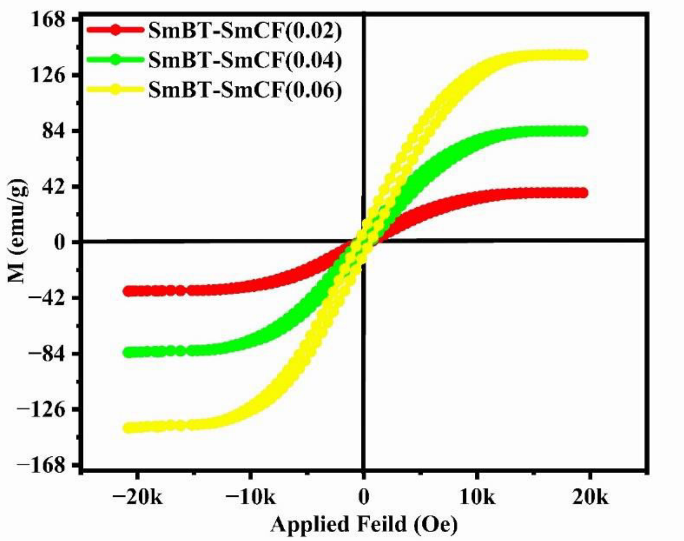

Figure 2: M-H loop of particulate multiferroic composite of (1-x)$Ba_{0.5}Sm_{0.5}TiO_3$–$xCo_{0.5}Sm_{0.5}Fe_2O_3$ (x=0.0,0.02,0.04,0.06).

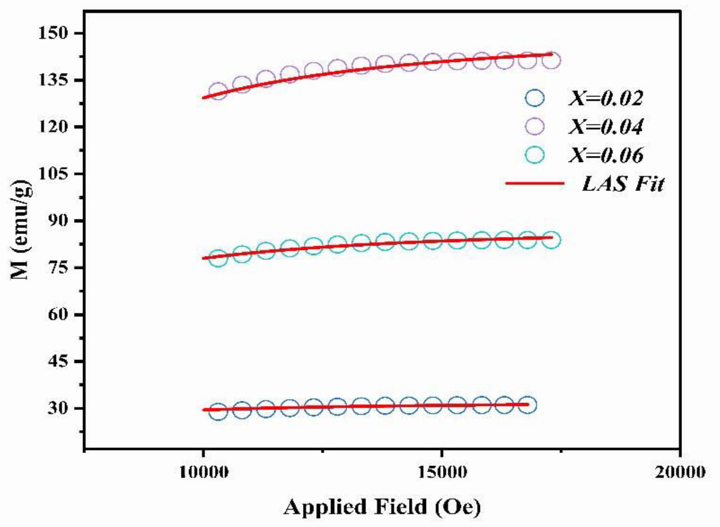

Figure 3: LAS approach of particulate multiferroic composite of (1-x)$Ba_{0.5}Sm_{0.5}TiO_3$–$xCo_{0.5}Sm_{0.5}Fe_2O_3$,(x=0.02, 0.04, 0.06)

Dielectric Studies

The dielectric constant (ε_r) and dielectric loss (tanδ) of the sintered pellets of thickness'd' and area 'A' were evaluated relations 10 and 11 respectively

$$\varepsilon_r = \frac{C_p d}{\varepsilon_0 A} \qquad 7$$

$$Tan\delta = \frac{\varepsilon}{\varepsilon_r} \quad 8$$

where 'C$_p$' stands for capacitance and ε is the imaginary portion of the dielectric function, which is $\varepsilon^* = \varepsilon_r + i\varepsilon$.

Temperature Dependent Dielectric Properties and Curie Weiss Behavior

Figure 7 shows the fluctuation of dielectric constant ε_r for particulate composites (1-X)SmBT-xSmCF(x=0.0,0.02,0.04,0.06) with temperature (100-400 K) at a frequency of 10 kHz. All of the composites exhibit a high value of ε_r as a result of the samarium doping [17], and their behavior is remarkably comparable to that of previous composites made of $BaTiO_3$ and $CoFe_2O_4$ [17-21]. Since the process of electron hopping between ($Fe^{3+} \leftrightarrow Fe^{2+}$ and $Sm^{3+} \leftrightarrow Sm^{2+}$) ions is temperature sensitive, an increase in ε_r with temperature is noticeable. Dielectric polarization rises as a result of the hopping mechanism, which is a temperature-dependent phenomenon. Beyond Curie temperatures, a dramatic decrease in the dielectric constant is seen because the structural transition from the non-centrosymmetric tetragonal phase to the centrosymmetric orthogonal phase cancels the net dipole moment owing to the deformed domain structure [21-23]. Comparing composites to published $BaTiO_3$, the Curie temperature (T_c) is lower. The observed reduction in dielectric constant (ε_r) may be ascribed to the dopant ions presence impeding the migration of Ti^{4+} ions in the core area. In composites, when the SmCF phase concentration rises, the internal stress that SmCF grains creates on SmBT grains causes a modest increase in the critical temperature (T_c). The increase in dielectric constant (ε_r) in composites containing the SmCF phase, that can increase in electron hopping between $Fe^{3+} \leftrightarrow Fe^{2+}$ and $Sm^{3+} \leftrightarrow Sm^{2+}$ ions. Smaller grains provide a compact and dense structure in the composite material, which facilitates interfacial polarisation and results in higher dielectric constants [23-25]. Additionally, the reduction in bond and hopping lengths positively corresponds with the increase in electron hopping brought on by the SmCF phase. We analyzed and thoroughly describe the lengths of the octahedral (B_{oct}) and tetrahedral (B_{tet}) bonds. Similar calculations were made for the hopping distances between neighboring ions occupying octahedral and tetrahedral sites [26]. From SmBT-SmCF(0.02) to SmBT-SmCF(0.06), an increase in Curie temperature is seen in the composites Larger grain size and constrained ferroelectric domains are responsible for this rise in internal tensions. The Curie temperature of SmBT was considerably influenced by Sm^{3+} among all the replaced rare earth ions. The change of Tc has been shown to be larger for composites. Compared to their lower concentrations, rare earth ion concentrations had a substantial impact on Curie temperature. Since there is more electron interaction between the octahedral and tetrahedral sites when the hopping duration is shorter, polarisation is thus increased.

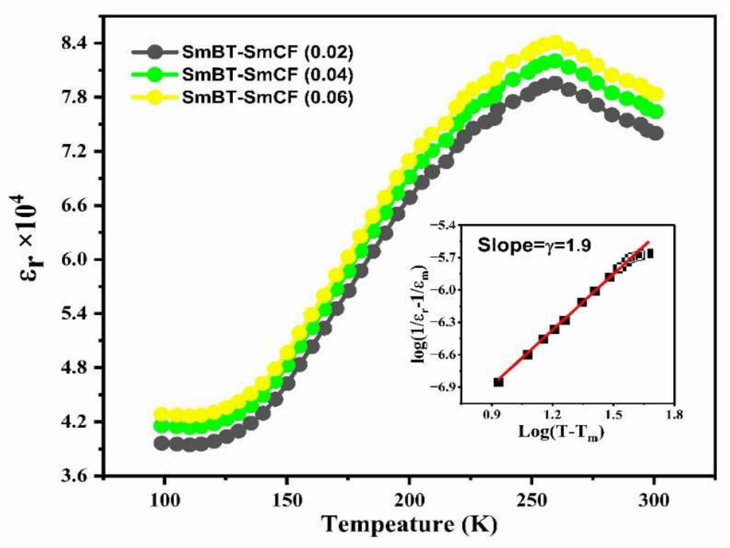

Figure 4: Temperature dependent dielectric constant (ε_r) of (1-x) $Ba_{0.5}Sm_{0.5}TiO_3$-x$Co_{0.5}Sm_{0.5}Fe_2O_3$ (x =0.02, 0.04, 0.06) and insets shows the ε_r of $Ba_{0.5}Sm_{0.5}TiO_3$ and Curie Weiss Behavior.

CONCLUSION

Temperature-dependent magnetic experiments demonstrated that the processes of zero field cooling and field cooling had an impact on the magnetization behavior. Understanding the ferroelectric-ferromagnetic coupling in these composites requires an understanding of the association between the concentration of the non-magnetic SmBT phase and the Curie temperature (Tc), which suggests a reduction in magnetic linkages.

Dielectric analyses of the (1-X)SmBT-xSmCF particulate composites showed interesting temperature-dependent behavior and improved dielectric characteristics. According to the conductivity analysis, the SmCF phase improved the connection between the ferroelectric and magnetic phases and greatly increased the conductivity of the composites. All things considered, our research advances our knowledge of multiferroic composites and their possible use in advanced materials. The foundation for future research and development in the field of multiferroics is laid by this work, which presents chances to produce materials with improved multifunctional qualities.

ACKNOWLEDGEMENT

The Central Research Facility Centre (CRFC) of the National Institute of Technology (NIT), Srinagar is highly regarded for its provision of instrumentation facilities. The authors further expresses gratitude for the financial support provided by the Ministry of Human Resources Development (MHRD).

Declaration of Competing Interest

The authors state that they have no financial conflicts of interest or personal ties that could have influenced the research presented in this study.

Author Contributions:

Showket Ahmad Bhat: Conceptualization, Methodology, Experimentation, Validation, Formal Analysis and Writing Original Draft

Ab Mateen Tantray: Experimentation, Validation, Formal Analysis and Writing Original Draft.

Prof. M Ikram: Conceptualization, Resource, Visualization, Validation, Supervision, and Revision

Data Availability: All data generated or analyzed during this study are included in this article.

REFERENCES

[1] E. C. Devi and S. D. Singh, “Understanding low-temperature magnetization curves with law of approach to saturation in Co0.5Zn0.5Fe2O4,” J. Mater. Sci. Mater. Electron., vol. 33, no. 29, pp. 22751–22758, 2022, doi: 10.1007/s10854-022-09042-7.

[2] P. N. Anantharamaiah and P. A. Joy, “Effect of co-substitution of Co2+ and V5+ for Fe3+ on the magnetic properties of CoFe2O4,” Phys. B Condens. Matter, vol. 554, pp. 107–113, 2019, doi: 10.1016/j.physb.2018.11.031.

[3] S. A. Mazen, N. I. Abu-Elsaad, and A. E. Khadour, “A comparative study of the structural and magnetic properties for Zn2+ and Ge4+ ions substituted nickel ferrites,” J. Magn. Magn. Mater., vol. 491, p. 165562, 2019, doi: 10.1016/j.jmmm.2019.165562.

[4] C. V. Ramana, Y. D. Kolekar, K. Kamala Bharathi, B. Sinha, and K. Ghosh, “Correlation between structural, magnetic, and dielectric properties of manganese substituted cobalt ferrite,” J. Appl. Phys., vol. 114, no. 18, 2013, doi: 10.1063/1.4827416.

[5] A. Franco, F. L. A. MacHado, and V. S. Zapf, “Magnetic properties of nanoparticles of cobalt ferrite at high magnetic field,” J. Appl. Phys., vol. 110, no. 5, 2011, doi: 10.1063/1.3626931.

[6] M. Ganguly, S. K. Rout, W. S. Woo, C. W. Ahn, and I. W. Kim, “Characterization of A-site deficient samarium doped barium titanate,” Phys. B Condens. Matter, vol. 411, pp. 26–34, 2013, doi: 10.1016/j.physb.2012.11.006.

[7] S. Basu, K. R. Babu, and R. N. P. Choudhary, “Studies on the piezoelectric and magnetostrictive phase distribution in lead zirconate titanate-cobalt iron oxide composites,” Mater. Chem. Phys., vol. 132, no. 2–3, pp. 570–580, 2012, doi: 10.1016/j.matchemphys.2011.11.071.

[8] P. Pahuja, R. K. Kotnala, and R. P. Tandon, “Effect of rare earth substitution on properties of barium strontium titanate ceramic and its multiferroic composite with nickel cobalt ferrite,” J. Alloys Compd., vol. 617, pp. 140–148, 2014, doi: 10.1016/j.jallcom.2014.07.204.

[9] R. Clarke and J. C. Burfoot, “The diffuse phase transition in potassium strontium niobate,” Ferroelectrics, vol. 8, no. 1, pp. 505–506, Jan. 1974, doi: 10.1080/00150197408234141.

[10] Z. Yu and C. Ang, “Maxwell-Wagner polarization in ceramic composites BaTiO3-(Ni0.3Zn0.7)Fe2.1O 4,” J. Appl. Phys., vol. 91, no. 2, pp. 794–797, 2002, doi: 10.1063/1.1421033.

[11] I. G. Austin and N. F. Mott, “Polarons in Crystalline and Non-crystalline Materials,” Adv. Phys., vol. 18, no. 71, pp. 41–102, 1969, doi: 10.1080/00018736900101267.

[12] E. J. W. Verwey and J. H. de Boer, “Cation arrangement in a few oxides with crystal structures of the spinel type,” Recl. des Trav. Chim. des Pays-Bas, vol. 55, no. 6, pp. 531–540, 1936, doi: 10.1002/recl.19360550608.

[13] R. S. Devan, Y. D. Kolekar, and B. K. Chougule, “Effect of cobalt substitution on the properties of nickel-copper ferrite,” J. Phys. Condens. Matter, vol. 18, no. 43, pp. 9809–9821, 2006, doi: 10.1088/0953-8984/18/43/004.

[14] K. K. Bharathi, G. Markandeyulu, and C. V. Ramana, “Impedance Spectroscopic Characterization of Sm and Ho Doped Ni Ferrites,” J. Electrochem. Soc., vol. 158, no. 3, p. G71, 2011, doi: 10.1149/1.3534800.

[15] C. P. Zhao, F. Fang, and W. Yang, “A dual-peak phenomenon of magnetoelectric coupling in laminated Terfenol-D/PZT/Terfenol-D composites,” Smart Mater. Struct., vol. 19, no. 12, p. 125004, Dec. 2010, doi: 10.1088/0964-1726/19/12/125004.

[16] S. Chakraborty and S. K. Mandal, “Magnetoelectric Zn0.2Co0.8Fe2O4-PbZr0.58Ti0.42O3 nanocomposite for bistable memory and magnetic field sensor applications,” J. Magn. Magn. Mater., vol. 491, no. May, p. 165573, Dec. 2019, doi: 10.1016/j.jmmm.2019.165573.

[17] M. Etier et al., “Magnetoelectric coupling on multiferroic cobalt ferrite-barium titanate ceramic composites with different connectivity schemes,” Acta Mater., vol. 90, pp. 1–9, 2015, doi: 10.1016/j.actamat.2015.02.032.

[18] R. Gao, Z. Wang, G. Chen, X. Deng, W. Cai, and C. Fu, “Influence of core size on the multiferroic properties of CoFe2O4@BaTiO3 core shell structured composites,” Ceram. Int., vol. 44, no. xxxx, pp. S84–S87, 2018, doi: 10.1016/j.ceramint.2018.08.234.

[19] Kavita Verma, M. K. Shamim, S. Kumar, and S. Sharma, “Role of ferrite phase on the structural, ferroelectric and magnetic properties of (1-x) BCT-x CZFO composites,” Mater. Chem. Phys., vol. 255, no. November 2019, p. 123284, 2020, doi: 10.1016/j.matchemphys.2020.123284.

[20] S.Shankar, O. P. Thakur, and M. Jayasimhadri, “Conductivity behavior and impedance studies in BaTiO3–CoFe2O4 magnetoelectric composites,” Mater. Chem. Phys., vol. 234, pp. 110–121, Aug. 2019, doi: 10.1016/j.matchemphys.2019.05.095.

[21] Z. Yao et al., “Structure and dielectric behavior of Nd-doped BaTiO3 perovskites,” Mater. Chem. Phys., vol. 109, no. 2–3, pp. 475–481, Jun. 2008, doi: 10.1016/j.matchemphys.2007.12.019.

[22] I. Coondoo, N. Panwar, H. Amor, V. E. Ramana, and A. Kholkin, “, ¶ Indrani Coondoo, ‡ , † Neeraj Panwar, § Harvey Amor ın, ¶ Venkata Eskilla Ramana,” vol. 3135, pp. 3127–3135, 2015, doi: 10.1111/jace.13713.

[23] W. B. White and B. A. D. Anoelis, “Interpretation of the vibrational spectra of spinels,” vol. 25, no. 1964, 1967, doi: https://doi.org/10.1016/0584-8539(67)80023-0.

[24] Y. Shen et al., “The enhanced magnetodielectric interaction of (1 - X)BaTiO 3-xCoFe2O4 multiferroic composites,” J. Mater. Chem. C, vol. 2, no. 14, pp. 2545–2551, 2014, doi: 10.1039/c4tc00008k.

[25] G. Lawes and G. Srinivasan, “Introduction to magnetoelectric coupling and multiferroic films,” J. Phys. D. Appl. Phys., vol. 44, no. 24, 2011, doi: 10.1088/0022-3727/44/24/243001.

[26] J. Ma, J. Hu, Z. Li, and C. W. Nan, “Recent progress in multiferroic magnetoelectric composites: From bulk to thin films,” Adv. Mater., vol. 23, no. 9, pp. 1062–1087, 2011, doi: 10.1002/adma.201003636.