

Synthesis and Characterization of Cr³⁺ doped BiFe_{1-x}Cr_xO₃ Multiferroic Ceramics

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Received: 02 January 2023 **Published:** 30 June 2023

Abstract:

The main purpose of this work is to evaluate the multiferroic properties of cerium-doped bismuth ferrite BiFe_{1-x}Cr_xO₃ ($x = 0.0, 0.01, 0.03, 0.05, 0.07, 0.10, 0.20,$ and 0.30) at the sintering temperature of 750°C. The Cr-doped bismuth ferrite was synthesized by the conventional solid reaction method. XRD technique was used to analyse the phase structure for calcined powders, and the rhombohedral phase was observed in pure BiFe_{1-x}Cr_xO₃. Furthermore, XRD results showed a single-phase (BFOCr) ceramic with all concentrations. The confirmation of FTIR results also revealed the single-phase structure of the prepared material. In order to better understand the thermal breakdown characteristics of the calcinated powder and the distribution of pure and Cr-doped BiFeO₃ phases, thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed. The dielectric properties of all samples were investigated; the dielectric constant was decreased with increasing frequency for samples 3%, 5% and 7% at room temperature. However, the samples 1%, 10%, 20% and 30% materials exhibited small changes with the relative permittivity and frequency. The proposed ceramic materials may be used for high-frequency devices.

Keywords: Bismuth ferrite, Chromium oxide, Multiferroic Ceramic, Relative Permittivity, Rhombohedral phase.

DOI Number: <https://10.52700/jn.v4i1.69>

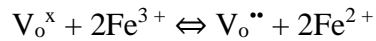
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1. Introduction

Multiferroic materials are a significant family of materials with several functions that combine various ferroic features, including ferroelectricity, ferromagnetism, and ferroelasticity [1]. Development of single-phase multiferroics is still challenging because it is difficult to maintain at room temperature with large polarization and magnetization and to develop strong coupling between them. Therefore, those compounds which have combine both ferroelectric and magnetic materials, which may be in mixtures or in layers, with interfaces coupling, are more noticeable and providing a way to produce multiferroicity [2]. Multiferroics materials are not only famous for their physical properties, but they have a lot of applications as magnetic field sensors, switches, actuators, or memory devices [3]. These devices incorporate multiple-state memory components that store information using electric and magnetic polarizations, allowing for electrical and magnetic data writing and reading [1]. BiFeO₃ (BFO), the first multiferroic material, demonstrates ferroelectricity at high Curie temperatures (TC=830 °C) and antiferromagnetic below the Néel temperature (TN=370 °C). It has a disproportionate to the lattice long-range cycloidal spin configuration with a wavelength of 62 nm[4,5]. Despite having such useful functionalities, BFO has few device applications since there are several urgent issues that need to be fixed. The ferroic transition temperatures (TC and TN), weak magnetic properties, poor magnetoelectric coupling coefficients, and high leakage current differ significantly [6]. Doped or replaced BFO have recently received considerable attention [7-8] as researchers throughout the world try to enhance the magnetic features without losing its ferroelectric qualities [9]. B-site cation substitution is critical in BFO because the doping or replacement of elements may change the magnetic structure. The procedure is challenging, however, and calls for answers to several problems, such as the instability of Bi ions, the constrained temperature window for BFO synthesis, and the existence of several impurity phases.

However, in different applications, BiFeO₃ (BFO) play a vital role; still, on another side, it has some drawbacks, such as high leakage current, large dielectric loss (occurs due to oxygen vacancy), valence fluctuation of Fe ions at room temperature and non-stoichiometry [10], which need to be resolved. At room temperature, a higher leakage current in bismuth ferrite hinders the measurement of the ferroelectric properties of BFO. And this problem of higher leakage creates more difficulties in studying the electrical properties of bismuth ferrite and applications in

electrical devices affected by these types of drawbacks. In BFO materials, oxygen vacancies are the leading cause of the formation of Fe^{2+} ,



where $\text{V}_\text{o}^{\bullet\bullet}$ represents to oxygen vacancy and V_o^\times shows the oxygen position [11]. According to the principle of Le Chatelier [12], the denseness of Fe^{2+} is decreased if the content of Fe^{3+} is reduced. It is observed from previous research that doping of rare-earth ions such as (Nd, Gd, La) in BFO at Bi^{3+} sites or transition-metal-ions such as (Cu, Co and Mn) in BFO at Fe^{3+} sites can reduce the concentration of Fe^{2+} in bismuth ferrite and can control the development of oxygen vacancies [13].

On other side BFO is a challenging compound because it is difficult to optimize sintering temperature and control of geometrical shape and grain size is another challenge. It is considered as a typical material in which doping is quite difficult because of its volatile nature [14]. Here in this work Cr doping in BFO compound creates more curiosity because in previous research less work has been done on this dopant. In this work, dielectric properties have been focused and on various concentrations of dopant, this material will be investigated, and it is expected that doping of Cr in BFO could enhance the properties as compared to pure BFO. Enhanced dielectric properties could be utilized in developing and designing new electronic devices, storage devices such as capacitors or actuators, sensors and other data storage devices. BFO and Cr_2O_3 have traditionally been prepared via the sol-gel approach [15], simple and microwave based hydrothermal procedures [16,17], laser fragmentation [18], quick liquid-phase sintering technology, and various other wet-chemical based methods. In this work, we study the synthesis of $\text{BiFe}_{1-x}\text{Cr}_x\text{O}_3$ where ($0 \leq x \leq 0.50$) multiferroic ceramics by solid state reaction method. However, the solid-state technique has shown to be the most straightforward, repeatable, and economical.

The main objectives of this study are to synthesize the pure BFO and isovalent doping of (Cr^{3+}) in BFO with various concentrations, Optimization of calcination and sintering temperatures of the compounds, Bi volatility in pure BFO and BFOCr formulations and their structural temperature and dielectric properties at various frequencies.

2. Materials and method

The previously described solid-state reaction approach was used to create chromium-doped multiferroic bismuth ferrite $\text{BiFe}_{1-x}\text{Cr}_x\text{O}_3$ ($x = 0.00, 0.03, 0.05, 0.07, 0.10, 0.20, 0.30$). Powders, Bi_2O_3 (Sigma-Aldrich, 1-5 μm 99.99%) Fe_2O_3 (Sigma-Aldrich, 1-5 μm 99.99%), Cr_2O_3 (Sigma-Aldrich, 1-5 μm 99.99%), were kept in the furnace (FNC-BX1200-16L) on 300°C for 5 hours to remove moisture. After completion of drying time, hot powders were weighed according to their stoichiometry, $\text{BiFe}_{0.97}\text{Cr}_{0.03}$, $\text{BiFe}_{0.95}\text{Cr}_{0.05}$, $\text{BiFe}_{0.93}\text{Cr}_{0.07}$, $\text{BiFe}_{0.90}\text{Cr}_{0.10}$, $\text{BiFe}_{0.80}\text{Cr}_{0.20}$, $\text{BiFe}_{0.70}\text{Cr}_{0.30}$, by digital weight measuring instrument. The weighed powders are thoroughly mixed with ethanol in a ball mill (M-1 Desk-Top Planetary Ball Miller) for 1 hr. Milling is carried out to fulfil twofold purposes, one is to reduce the particle size, and another is to mix the raw materials homogeneously. After milling, mixed material was kept in the furnace at 80°C for 6 hours to dry. This mixture was then heated in the furnace to 750°C and calcined for 3 hours holding time. Hydraulic or mechanical press was used to press powder into desired shape at the pressure of ~ 100 to 300 MPa and pellets with a diameter of 8 mm and a thickness of 1.5 mm were made and sintered at 850°C for two hour, holding time, for characterization. Using the Rigaku RINT 2000 and the copper target ($\lambda = 1.54 \text{ \AA}$), the structural characterization was carried out using the x-ray diffraction (XRD) technique. A [Tonghui TH-2826]. LCR Meter was used to measure the dielectric property of samples, and to create electrodes, the silver paste was added to the polished surfaces of the pellets. The FTIR technique was used for all samples to investigate the chemical bonding.

3. Results and discussion

3.1 Structural characterization (XRD)

The structural properties of cerium-doped bismuth ferrite $\text{BiFe}_{1-x}\text{Cr}_x\text{O}_3$ ($x = 0.0, 0.01, 0.03, 0.05, 0.07, 0.10, 0.20, \text{ and } 0.30$) are shown in **Fig.1**. According to card 01-071-2494, most of the peaks in pure BFO show the compound bismuth iron oxide BiFeO_3 and rhombohedral crystal structure with group space of R3c and space group number 161 was observed. Consequently, all diffraction peaks show single-phase crystalline material because no extra peak was observed. It is observed that as the Cr doping increases, several peaks disappear [19]. In 20% and 30%, Cr doped samples show some different patterns than the other doped samples, which may indicate structural change.

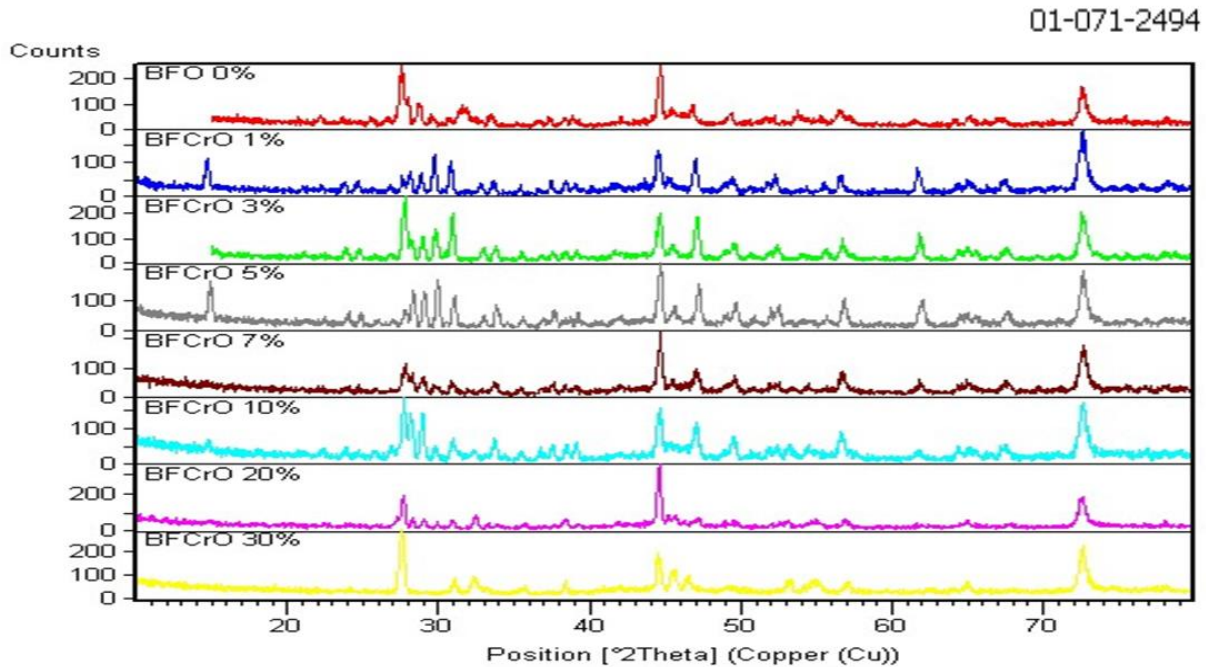


Fig. 1: XRD patterns of Cr-doped bismuth ferrites $\text{BiFe}_{1-x}\text{Cr}_x\text{O}_3$ ($x = 0.0, 0.01, 0.03, 0.05, 0.07, 0.10, 0.20,$ and 0.30)

3.2 Fourier-transform infrared spectroscopy (FTIR)

The absorption spectrum for different Cr-doped samples for FTIR can be seen in **Fig.2**. The absorption band was observed from 365 cm^{-1} to 800 cm^{-1} , indicating metal oxide bands [20]. At near 750 cm^{-1} heavy absorption of the infrared spectrum was observed, and most probably, this band indicate the bond of Fe-O, which may be considered as a group of FeO_6 octahedral in perovskite [21]. It was also observed that as the Cr doping increases, the absorption of infrared spectrum also increases, and 30% doped sample shows high absorption of the infrared radiations.

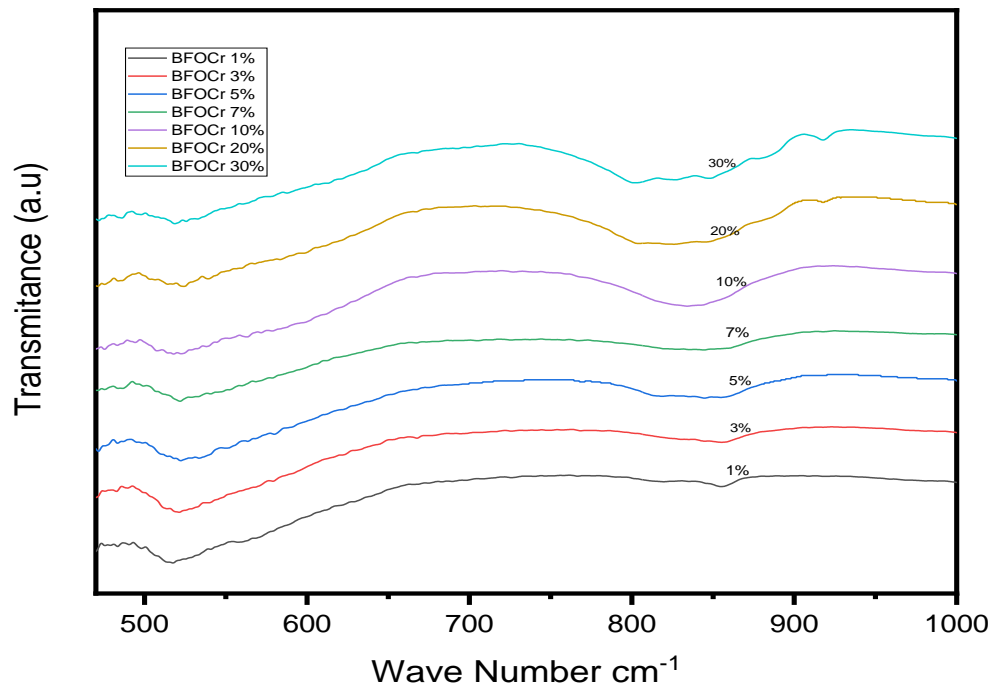


Fig. 2: Shows the FTIR representation of Cr-doped bismuth ferrites $\text{BiFe}_{1-x}\text{Cr}_x\text{O}_3$ ($x = 0.0, 0.01, 0.03, 0.05, 0.07, 0.10, 0.20,$ and 0.30)

3.3 TGA & DSC Analysis.

In all samples, it is observed that some mass is reduced when the temperature increases as shown in **Fig.3**.

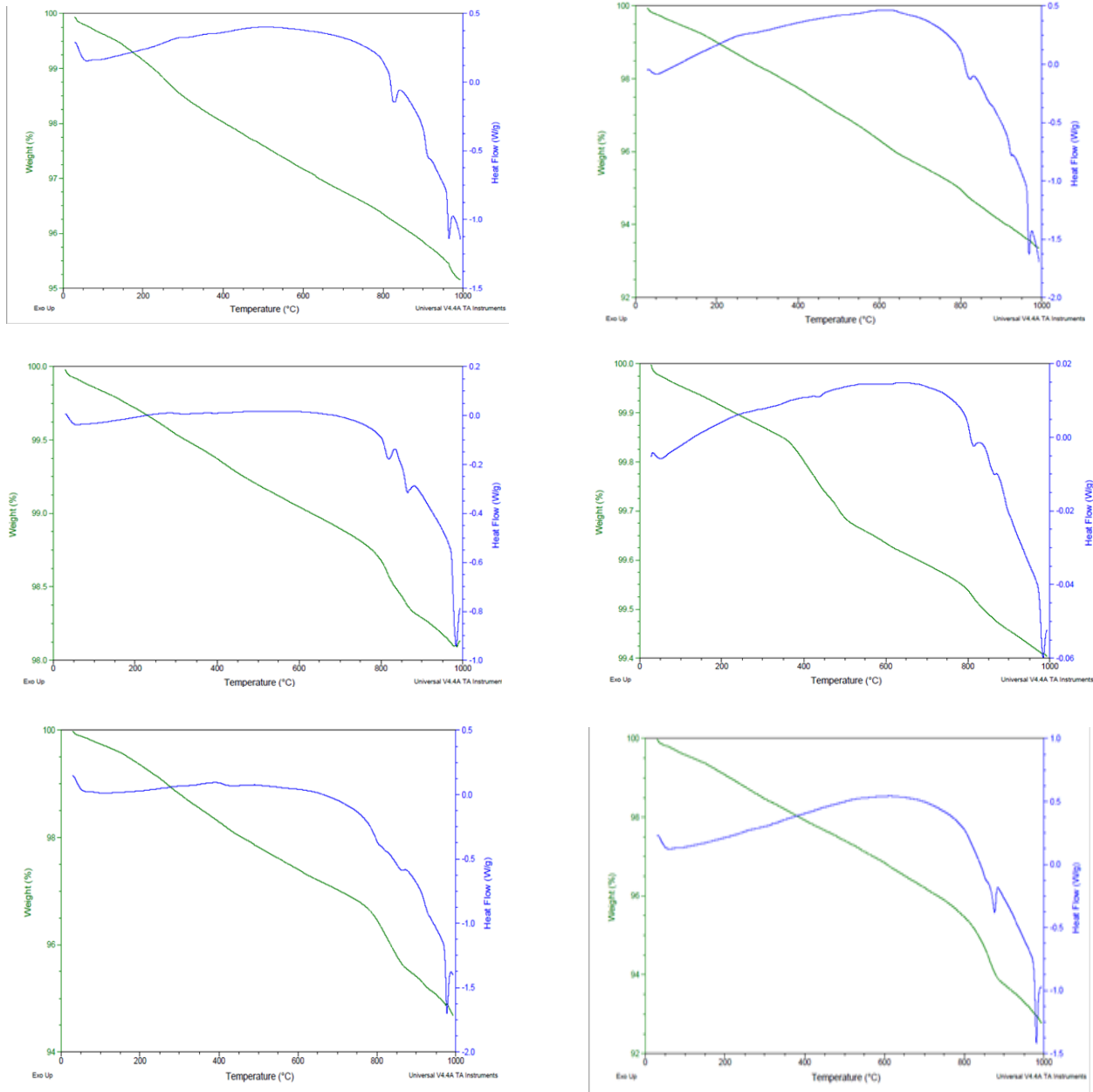


Fig. 3: Shows TGA/DSC of Cr-doped bismuth ferrites $\text{BiFe}_{1-x}\text{Cr}_x\text{O}_3$ ($x = 0.0, 0.01, 0.03, 0.05, 0.07, 0.10, 0.20,$ and 0.30)

The green line represents TGA which indicates that the mass of the sample rapidly decreases as the temperature increases and here could be many reasons for decreased weight of sample, but BFO main reason of mass reduction is its volatile nature it contains bismuth which is consider as volatile material [22]. A minimum mass reduction was observed in 5% and 7% Cr doped samples which are represented in **Table.1**; in these samples minimal volatility occurred.

Table 1: Shows weight loss of Cr-doped bismuth ferrites $\text{BiFe}_{1-x}\text{Cr}_x\text{O}_3$ ($x = 0.0, 0.01, 0.03, 0.05, 0.07, 0.10, 0.20,$ and 0.30)

Dopant %	0%	1%	3%	5%	7%	10%	20%	30%
Loss of weight %	3.6%	6%	6.2%	1.9 %	0.6 %	5.2%	7%	8.2%

3.4 Dielectric Properties

3.4.1 Dielectric Constant

From **Fig. 4.** it was observed in all samples that when the frequency increased, the value of the dielectric constant was decreased, however, from frequency range of 50 KHz, the dielectric constant for all samples, was observed constant. The main reason this phenomenon is motion of dipoles and charge carriers [23]. In previous research, it was also investigated that conductivity produced due to oxygen vacancies, and these oxygen vacancies occurs because of the Bi volatile nature [24]. It is becoming difficult for dipoles to change their position rapidly high oscillating field, which is created by high frequency hence in result, dielectric constant decreases [25]. Initially, at low range frequency of 1KHz the dielectric constant for BFO, $x=0.0$, has value about 36 and other side Cr-doped with 3%, 5% and 7%, shows high dielectric constant. At 1Khz, 5% doped sample gives the highest value 306 of dielectric constant. Meanwhile, 1%, 10%, 20% and 30% doped samples shows variation in dielectric constant but it is observed that value of dielectric constant for 1% doped slightly increase at 1 Khz than it becomes constant and when frequency reached at 4 kHz it decreases drastically however 10%, 20% and 30% have some dielectric constant but with frequency increasing, there is no change observed in these samples and it is observed that as the doping concentration increases the value of dielectric constant increases [26].

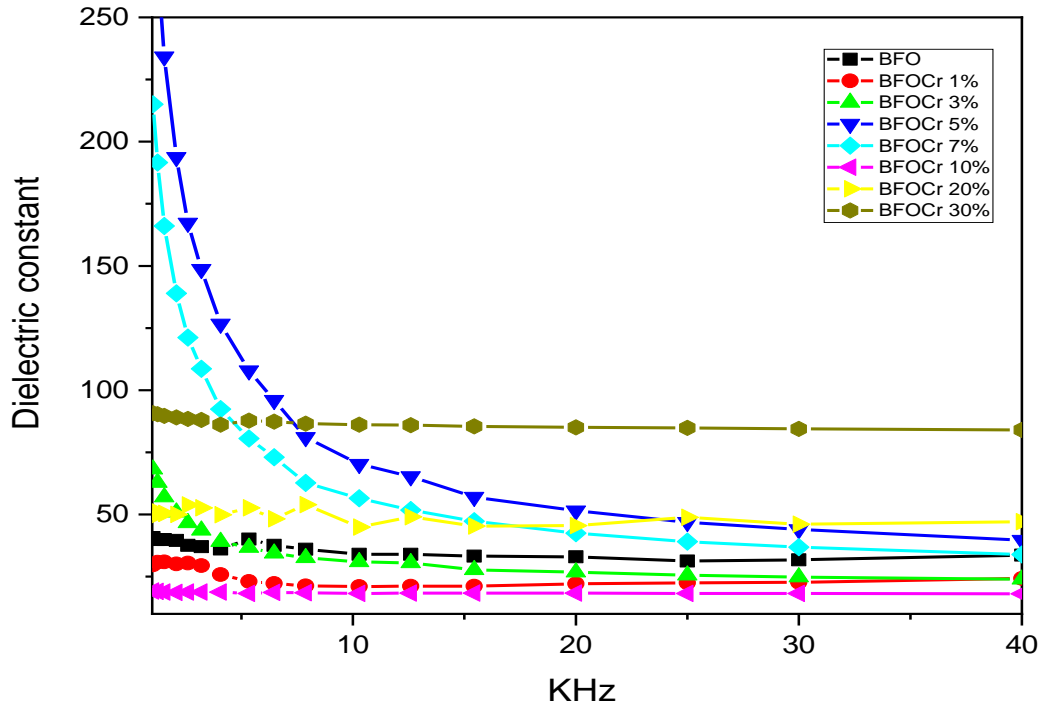


Fig. 4: Shows dielectric constant with Frequency of Cr-doped bismuth ferrites $\text{BiFe}_{1-x}\text{Cr}_x\text{O}_3$ ($x = 0.0, 0.01, 0.03, 0.05, 0.07, 0.10, 0.20,$ and 0.30)

3.4.2 Dielectric Losses

Fig.5. shows the dielectric loss factor (ϵ'') behavior for all samples as a function of frequency. It was observed that all sample contain dielectric losses but BFO $x=0.0$ shows irregular pattern however Cr doped 3%, 5% and 7% shows some resulting dielectric loss. The frequency range from 1kHz to 3 KHz, Cr doped samples 5% and 7% has same value of dielectric loss. Moreover, near about 1.5 however 3% Cr doped sample has a low dielectric loss as compare to 5% and 7% . It is observed that dielectric losses are decreased with the increasing frequency, Moreover, other highly doped samples, 10%, 20%, and 30%, are showing very low losses with the variation in dielectric losses was observed with increased in frequency [27]. Dielectric losses may occur due to different reasons, from previous research it was observed that doping of Cr in BFO, reduces grain size and increased the volume of grain boundaries. It is also investigated as [28] sintering

temperature above 700°C creates oxygen vacancies and in result dielectric losses and electrical conductivity increases. In this work it was observed that dielectric loss increases at lower frequencies and decreases at high frequency [29]. Grain boundaries at low frequency create high resistance and because of high resistance, more losses occurred however fast oscillating electric field produced at high frequency which decreases the losses [30].

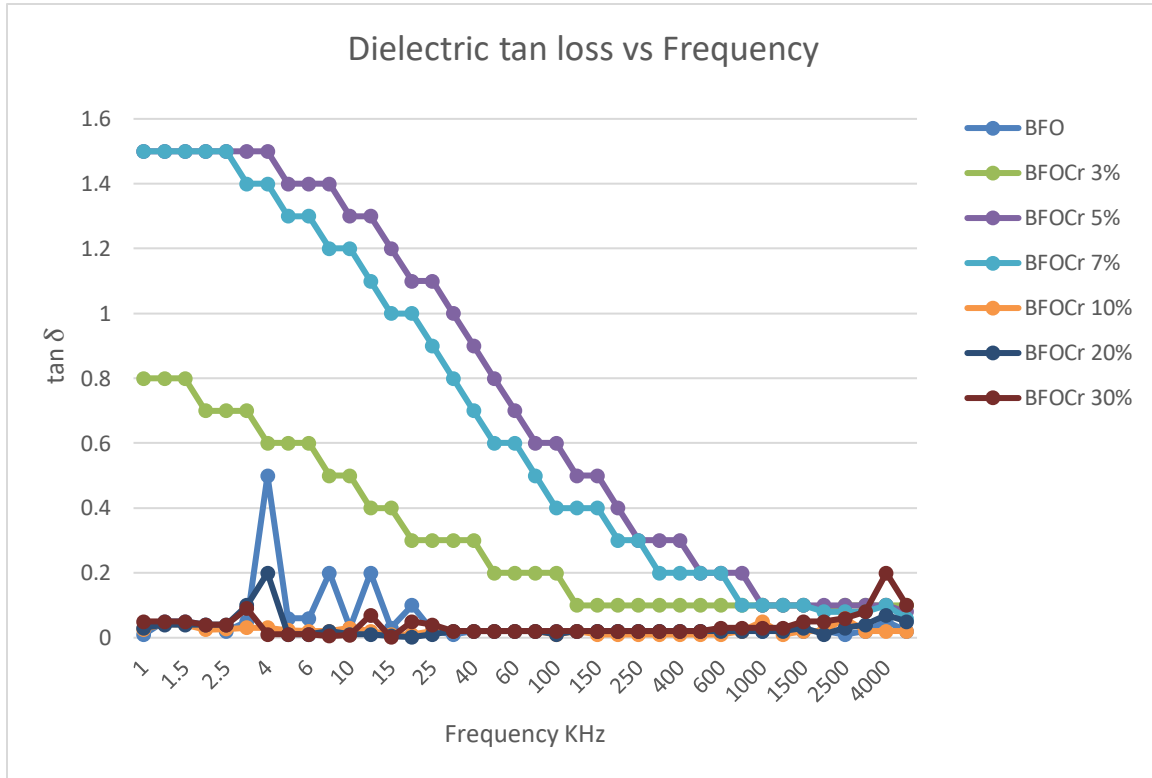


Fig. 5: Dielectric loss of Cr-doped bismuth ferrites $\text{BiFe}_{1-x}\text{Cr}_x\text{O}_3$ ($x = 0.0, 0.01, 0.03, 0.05, 0.07, 0.10, 0.20,$ and 0.30)

4. Conclusion

The purpose of this study was to investigate how doping Cr affected BFO. $\text{BiFe}_{1-x}\text{Cr}_x\text{O}_3$ materials with nominal compositions of ($x = 0.00, 0.01, 0.03, 0.05, 0.07, 0.10, 0.20,$ and 0.30) were created using a traditional solid-state reaction method. For calcined powder, phase analysis by X-ray diffraction (XRD) showed that pure BFO formed a rhombohedral phase. All samples' XRD patterns showed structural deformation after the replacement of Fe with Cr. All samples were subjected to DSC analysis, and it was found that, although heat flow rose initially as temperature climbed for all samples, as the temperature reached 700°C or above, the heat flow substantially decreased as temperature increased. Around 820°C to 870°C, when oxygen and bismuth start to lose their stability, the sample begins to decompose irreversibly chemically. In samples with 5%

and 7% Cr doping, a minimal mass loss was discovered using TGA analysis. For samples 3%, 5%, and 7%, the dielectric constant declined with increasing frequency, whereas for samples 1%, 10%, 20%, and 30%, there was no change in the dielectric constant with increasing frequency. Low dielectric tan loss was seen in samples with Cr doping levels of 1%, 10%, 20%, and 30% compared to pure BFO, and this was caused by space charge polarization. While 3%, 5%, and 7% showed large dielectric losses, as frequency rose, losses reduced.

Acknowledgement

Special thanks from author to Director, Department of Materials Engineering, NED university of engineering and technology, for providing all research facilities.

Conflict of Interest

It can be confirmed that all the authors contributed equally to this manuscript, and no conflict of interest existed between the authors.

References

- [1] Spaldin, N. A., & Fiebig, M. (2005). The renaissance of magnetoelectric multiferroics. *Science*, 309(5733), 391-392.
- [2] Spaldin, N. A., Fiebig, M., & Mostovoy, M. (2008). The toroidal moment in condensed-matter physics and its relation to the magnetoelectric effect. *Journal of Physics: Condensed Matter*, 20(43), 434203.
- [3] Ederer, C., & Spaldin, N. A. (2007). Towards a microscopic theory of toroidal moments in bulk periodic crystals. *Physical Review B*, 76(21), 214404.
- [4] Ramesh, R., & Spaldin, N. A. (2007). Multiferroics: progress and prospects in thin films. *Nature materials*, 6(1), 2129-29. Bibcode:2007NatMa...6...21R. doi:10.1038/nmat1805. ISSN 1476-4660. PMID 17199122.
- [5] Hill, N. A., Bättig, P., & Daul, C. (2002). First principles search for multiferroism in BiCrO₃. *The Journal of Physical Chemistry B*, 106(13), 3383-3388.
- [6] Van Delft, D., & Kes, P. (2010). The discovery of superconductivity. *Physics today*, 63(9), 38-43.

- [7] Neaton, J. B., Ederer, C., Waghmare, U. V., Spaldin, N. A., & Rabe, K. M. (2005). First-principles study of spontaneous polarization in multiferroic Bi Fe O 3. *Physical Review B*, 71(1), 014113.
- [8] Seshadri, R., & Hill, N. A. (2001). Visualizing the role of Bi 6s “lone pairs” in the off-center distortion in ferromagnetic BiMnO3. *Chemistry of materials*, 13(9), 2892-2899.
- [9] Shpanchenko, R. V., Chernaya, V. V., Tsirlin, A. A., Chizhov, P. S., Sklovsky, D. E., Antipov, E. V., ... & Geibel, C. (2004). Synthesis, structure, and properties of new perovskite PbVO3. *Chemistry of materials*, 16(17), 3267-3273.
- [10] Waghmare, U. V., Spaldin, N. A., Kandpal, H. C., & Seshadri, R. (2003). First-principles indicators of metallicity and cation off-centricity in the IV-VI rocksalt chalcogenides of divalent Ge, Sn, and Pb. *Physical Review B*, 67(12), 125111.
- [11] Scott, J. F. (1979). Phase transitions in BaMnF4. *Reports on Progress in Physics*, 42(6), 1055.
- [12] Ederer, C., & Spaldin, N. A. (2006). Origin of ferroelectricity in the multiferroic barium fluorides Ba M F 4: A first principles study. *Physical Review B*, 74(2), 024102.
- [13] Yen, F., Dela Cruz, C., Lorenz, B., Galstyan, E., Sun, Y. Y., Gospodinov, M., & Chu, C. W. (2007). Magnetic phase diagrams of multiferroic hexagonal RMnO3 (R= Er, Yb, Tm, and Ho). *Journal of materials research*, 22(8), 2163-2173.
- [14] Yen, F., Dela Cruz, C. R., Lorenz, B., Sun, Y. Y., Wang, Y. Q., Gospodinov, M. M., & Chu, C. W. (2005). Low-temperature dielectric anomalies in Ho Mn O 3: The complex phase diagram. *Physical Review B*, 71(18), 180407.
- [15] Van Den Brink, J., & Khomskii, D. I. (2008). Multiferroicity due to charge ordering. *Journal of Physics: Condensed Matter*, 20(43), 434217.
- [16] Ikeda, N., Ohsumi, H., Ohwada, K., Ishii, K., Inami, T., Kakurai, K., ... & Kitô, H. (2005). Ferroelectricity from iron valence ordering in the charge-frustrated system LuFe2O4. *Nature*, 436(7054), 1136-1138.
- [17] Mundy, J. A., Brooks, C. M., Holtz, M. E., Moyer, J. A., Das, H., Rébola, A. F., ... & Schlom, D. G. (2016). Atomically engineered ferroic layers yield a room-temperature magnetoelectric multiferroic. *Nature*, 537(7621), 523-527.

- [18] Baettig, P., Ederer, C., & Spaldin, N. A. (2005). First principles study of the multiferroics BiFeO_3 , $\text{Bi}_2\text{FeCrO}_6$, and BiCrO_3 : Structure, polarization, and magnetic ordering temperature. *Physical Review B*, 72(21), 214105.
- [19] Arora, M., & Kumar, M. (2015). Structural, magnetic and optical properties of Ce substituted BiFeO_3 nanoparticles. *Ceramics International*, 41(4), 5705-5712.
- [20] Hussain, G., Ahmed, I., Rehman, A. U., Subhani, M. U., Morley, N., Akhtar, M., ... & Anwar, H. (2022). Study of the role of dysprosium substitution in tuning structural, optical, electrical, dielectric, ferroelectric, and magnetic properties of bismuth ferrite multiferroic. *Journal of Alloys and Compounds*, 919, 165743.
- [21] Srivastav, S. K., & S. Gajbhiye, N. (2012). Low temperature synthesis, structural, optical and magnetic properties of bismuth ferrite nanoparticles. *Journal of the American Ceramic Society*, 95(11), 3678-3682.
- [22] Sharma, P., Diwan, P. K., & Pandey, O. P. (2019). Impact of environment on the kinetics involved in the solid-state synthesis of bismuth ferrite. *Materials Chemistry and Physics*, 233, 171-179.
- [23] Saeed, S., Sadiq, I., Hussain, S., Idrees, M., Sadiq, F., Riaz, S., & Naseem, S. (2020). La^{3+} -substituted β -ferrite: Investigation of structural, dielectric, FTIR and electrical polarization properties. *Journal of Alloys and Compounds*, 831, 154854.
- [24] Chaudhuri, A., & Mandal, K. (2012). Enhancement of ferromagnetic and dielectric properties of lanthanum doped bismuth ferrite nanostructures. *Materials Research Bulletin*, 47(4), 1057-1061.
- [25] Pashchenko, A. V., Liedienov, N. A., Li, Q., Makoed, I. I., Tatarchuk, D. D., Didenko, Y. V., ... & Levchenko, G. G. (2021). Control of dielectric properties in bismuth ferrite multiferroic by compacting pressure. *Materials Chemistry and Physics*, 258, 123925.
- [26] Sreekanth, K., Dhanalakshmi, B., & Madhavaprasad, D. (2022). Typical superparamagnetism with improved electrical properties of nano modified bismuth ferrite multiferroic composites. *Journal of the Indian Chemical Society*, 99(7), 100565.

- [27] Hussain, S., Sadiq, I., Khan, H. M., Idrees, M., Sadiq, F., Shah, A., ... & Naseem, S. (2021). Characterization and curve fittings of Mg²⁺ substituted R-type hexagonal ferrites. *Physica B: Condensed Matter*, 605, 412642.
- [28] Liu, W., & Ren, X. (2009). Large piezoelectric effect in Pb-free ceramics. *Physical review letters*, 103(25), 257602.
- [29] Gupta, R., Singh, S. P., Walia, R., Kumar, V., & Verma, V. (2022). Modification in photovoltaic and photocatalytic properties of bismuth ferrites by tailoring band-gap and ferroelectric properties. *Journal of Alloys and Compounds*, 908, 164602.
- [30] Mansour, S. F., Imam, N. G., Goda, S., & Abdo, M. A. (2020). Constructive coupling between BiFeO₃ and CoFe₂O₄; promising magnetic and dielectric properties. *Journal of Materials Research and Technology*, 9(2), 1434-1446.