

Synthesis and Characterization of Ba^{2+} , La^{3+} and Zr^{4+} Co-Modified Multiferroic BiFeO_3

F Khan¹, S Mondal², H M Usama³, A Sharif⁴, M A Matin⁵

^{1,2,3,4}MME Department, Bangladesh University of Engineering and Technology, Dhaka-1000, Bangladesh

⁵Department of Glass and Ceramics, Bangladesh University of Engineering and Technology, Dhaka-1000, Bangladesh

Abstract : The objective of this research project was to reduce the electrical leakage, enhance the magnetic and electric property as well as to stabilize the BiFeO_3 structure by co-doping La, Ba and Zr. At first the solid state sintering process was done to synthesize the $\text{Bi}_{0.8}\text{La}_x\text{Ba}_{0.2-x}\text{Fe}_{0.95}\text{Zr}_{0.05}\text{O}_3$ (where, $x = 0.05, 0.10, 0.15, 0.20$). X-ray diffraction data revealed a stabilized R_3C structure with the dopants. The amount of zirconia in B-site resulted in the reduction of vacancy which ultimately reduced leakage current. For the higher percentage of Ba^{2+} the oxygen vacancy increased which led to higher leakage current. Thus for increasing the La^{3+} up to 15 mole % with decreasing Ba^{2+} dielectric constant increased. For further addition of La^{3+} (i.e. 20%) the dielectric constant decreased again. From the SEM analysis the coherent grain size was confirmed for the temperature at 950°C . With the increase of La^{3+} and decrease of Ba^{2+} the grain size increased. For the composition with 5% of La^{3+} , the p-loop was found to be satisfactory with the remnant polarization of $0.25 \text{ } (\mu\text{C}/\text{cm}^2)$ and the coercivity of 330V . However the p-e loop for the other compositions was found to be unsatisfactory.

1.Introduction

Multiferroics are multifunctional materials which display more than one ferroic order in the same phase. In recent years, multi-ferroics have been drawing the attention of researchers due to their unique behavior of coupling between two or more properties of ferroelectricity, ferromagnetism and ferroelasticity and also because of their potential technological applications in devices in spintronics, information storage, sensing and actuation. There are many magnetic and ferroelectric materials, there are relatively few multi-ferroic materials. BiFeO_3 (BFO) is perhaps the only material that is both magnetic and a strong ferroelectric at room temperature. Bismuth ferrite is one of the most promising multi-ferroics and at room temperature, bulk BiFeO_3 presents a rhombohedrally distorted perovskite structure belonging to the space group $\text{R}\bar{3}\text{c}$. Compared to other multi-ferroics, BFO exhibits a higher ferroelectric Curie temperature ($T_C \sim 830^\circ\text{C}$) and a high G-type antiferromagnetic ordering ($T_N \sim 370^\circ\text{C}$) temperature. Bulk BiFeO_3 suffers from a high leakage current, thought to be the result of vacancies invariably produced due to the volatility of Bi_2O_3 . High leakage current translates into loss of stored charged. However, it is very difficult to observe the ferromagnetic loop of a bulk BiFeO_3 sample at room temperature due to its low spiral spin modulation which is caused by defects and non-stoichiometry in the bulk BiFeO_3 sample. Hence, it is essential to improve the ferromagnetic properties of BiFeO_3 without much disturbing its ferroelectric properties before its actual use in device application. And the formation of oxygen vacancies induces impurity energy level in the band gap and increases the free carrier density by hopping of electrons to these defect levels. The weak magnetization is attributed to the superimposition of a spiral spin structure on BFO antiferromagnetic order. The main purpose of this research was to determine the effects of Ba and La along with co-modification by Zirconia on bismuth ferrite, with a view to improving its dielectric and magnetic properties. Solid state process was the route of choice at first. Sintering was done at 950°C to obtain coherent grain size. The room temperature magnetization improved remarkably compared to pure BFO after co-modification, more work needs to be done before its implementation in real life applications. The increased amount of Zr^{4+} resulted in the reduction of leakage current. For the higher percentage of Ba^{2+} the oxygen vacancy increased which led to higher leakage current. Thus for increasing the La^{3+} up to 15 mole % with decreasing Ba^{2+} content, dielectric constant increased. For further addition of La^{3+} (i.e. 20%) the dielectric constant decreased again.



2. Experimental

At first, constituent powders were mixed at proper amount depending on the doping level. Next, the mixture was ball milled at 120 rpm in acetone for 18 hrs. Finally, the mixture was pressed into pellets using a hand pressing unit and subsequently sintered. The basic raw materials used are powders of Bi_2O_3 , Fe_2O_3 , La_2O_3 , ZrO_2 and BaCO_3 . These powders were taken according to the target composition of the batch to be prepared. . Four compositions were chosen for this thesis:

- a) $\text{Bi}_{0.8}\text{La}_{0.20}\text{Fe}_{0.95}\text{Zr}_{0.05}\text{O}_3$ b) $\text{Bi}_{0.8}\text{La}_{0.15}\text{Ba}_{0.05}\text{Fe}_{0.95}\text{Zr}_{0.05}\text{O}_3$ c) $\text{Bi}_{0.8}\text{La}_{0.10}\text{Ba}_{0.10}\text{Fe}_{0.95}\text{Zr}_{0.05}\text{O}_3$
d) $\text{Bi}_{0.8}\text{La}_{0.05}\text{Ba}_{0.15}\text{Fe}_{0.95}\text{Zr}_{0.05}\text{O}_3$

Then ball milling was done for proper mixing and homogenization of the raw materials. The powders of different compositions were taken into different high density polyethylene (HDPE) pots serving as the milling chamber. Y_2O_3 stabilized ZrO_2 balls, together with acetone, were used as the grinding medium. All the compositions were milled for 18 hours. Then the dried product was taken into a mortar and grinded to form fine powders. After milling, the mixture taken into suspension in acetone and then carefully extracted into a glass beaker (which was ultrasonically cleaned). The beaker was covered with a perforated aluminum foil and kept in a drier at around 100°C . It was important to keep the mixtures in the drier for a sufficiently long time, so that a completely dry powder mixture was obtained. Then the powder was calcined at 800°C for 2 hours. As we used BaCO_3 , we need to calcine to form BaO . That's why calcination is done. Around 0.6 gm of powder was taken and pressed into disk-like pellets using a manual hydraulic pressing machine. 2 tons of load was applied for 60 seconds. The pressed pellets were then dried in an oven for at least 24 hours to enhance their green strength. Then sintering is done at 950°C to get BiFeO_3 pellet of required composition. Then density measurement, SEM Dielectric properties measurement by impedance analyzer , Ferroelectric properties measurements were done.

3. Results and Discussion

3.1 XRD Analysis:

XRD analyses of the samples were done at room temperature. The diffraction patterns obtained are shown in Figure 1 for $\text{Bi}_{0.8}\text{La}_x\text{Ba}_{0.2-x}\text{Fe}_{0.95}\text{Zr}_{0.05}\text{O}_3$ compositions. All the samples were sintered at 950°C . The pattern of $x = 0.05$ sample showed that BFO structure was indeed formed. The peaks are not identical to pure BFO; there are some differences in peak positions and some split peaks seem to merge upon modification with 20% La. This is in accordance with previous reports [1, 2] and is assumed to be the result of space group modification, i.e. the space group is no longer $R3c$. The diffraction pattern is nearly the same for $x = 0.1$. And there is no identical 2nd phase present in any of the sample

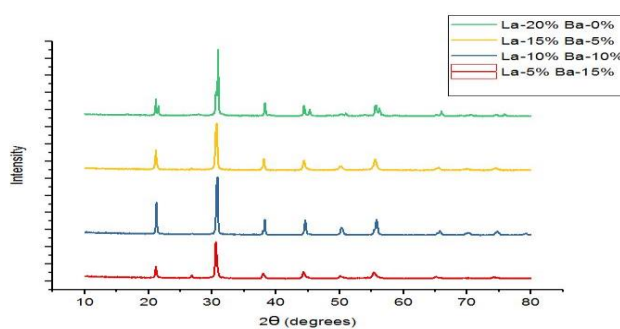


Figure 1 : Room temperature XRD patterns for $\text{Bi}_{0.8}\text{La}_x\text{Ba}_{0.2-x}\text{Fe}_{0.95}\text{Zr}_{0.05}\text{O}_3$ sintered at 950°C .

Figure 2 shows the peak around 29.5-31.5 degrees more closely for different compositions. It can be readily seen that the peak gradually shifts towards higher theta values with increasing La^{3+} content & decreasing Ba^{2+} content. Since the theta value (θ) and the planar spacing (d) for a given peak are related by the equation,

$$\lambda = 2d \sin(\theta)$$

Where λ is the wavelength, it follows that higher theta values correspond to smaller d values, i.e. lattice spacing. So it can be said with increasing La^{3+} content & decreasing Ba^{2+} content results in change of the lattice parameter, and this is expected because differences in ionic size. Looking now at the patterns for La-15% Ba-5% & La-20% Ba-0%, we see that the peak in question is quite prominently split indicating that whatever structural modification was set in by La-substitution. The peaks at this position belong to the [100] family of planes in the pseudo-cubic cell. All six [100] planes have the same d-spacing in cubic and rhombohedral symmetry and so this peak splitting indicates that the symmetry has been lowered to at least tetragonal, possibly even lower.

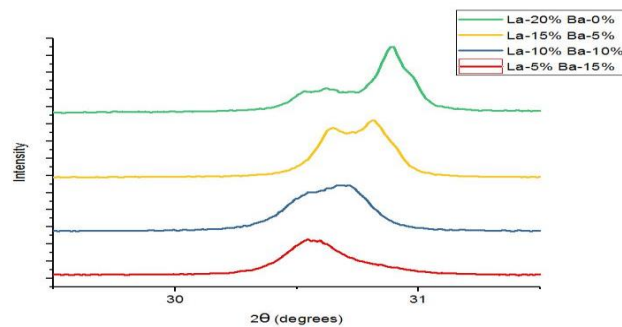


Figure 2 : Change in peak position with increasing La^{3+} content & decreasing Ba^{2+} content

3.2 Microstructure development:

Obtaining dense samples is one of the important parts of the optimization process. The best properties will be obtained for those samples that have both high %TD and desirable grain size. Figure 3 shows that $\text{Bi}_{0.8}\text{La}_{0.05}\text{Ba}_{0.15}\text{Fe}_{0.95}\text{Zr}_{0.05}\text{O}_3$ sintered at 900°C contain large amount of porosity. And average grain size is $\sim 0.2\ \mu\text{m}$. It is evident that densification had not occurred to any respectable degree and higher temperature would be required for obtaining proper microstructure. This situation is improved in the case of sintering at 950°C . Porosity decreases sufficiently and the grain size also increased to $\sim (0.6-0.7)\ \mu\text{m}$. Literature review reveals that the Ba^{2+} ion substitution in BiFeO_3 has a strong grain growth inhibiting effect in the microstructure [20]. Hence, sintering temperature at 950°C is seemed to be optimum for $\text{Bi}_{0.8}\text{La}_{0.05}\text{Ba}_{0.15}\text{Fe}_{0.95}\text{Zr}_{0.05}\text{O}_3$. The %TD and grain size achieved in this temperature range was satisfactory.

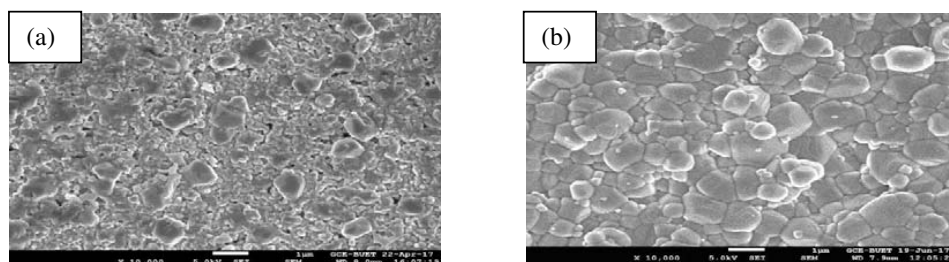


Figure 3: FESEM micrograph of $\text{Bi}_{0.8}\text{La}_{0.05}\text{Ba}_{0.15}\text{Fe}_{0.95}\text{Zr}_{0.05}\text{O}_3$ sintered at (a) 900°C (b) 950°C

Figure 4 shows the micrographs of $\text{Bi}_{0.8}\text{La}_{0.10}\text{Ba}_{0.10}\text{Fe}_{0.95}\text{Zr}_{0.05}\text{O}_3$ sintered at various temperatures. Sintering of $\text{Bi}_{0.8}\text{La}_{0.10}\text{Ba}_{0.10}\text{Fe}_{0.95}\text{Zr}_{0.05}\text{O}_3$ at 850°C shows the similar effect of porosity as obtained in the case of $\text{Bi}_{0.8}\text{La}_{0.05}\text{Ba}_{0.15}\text{Fe}_{0.95}\text{Zr}_{0.05}\text{O}_3$ sample sintered at 900°C . Here sintering is not up to the mark. The situation is improved at 950°C where porosity decreases to a significant amount and grain size increases. Average grain size is found to be $\sim 1\ \mu\text{m}$.

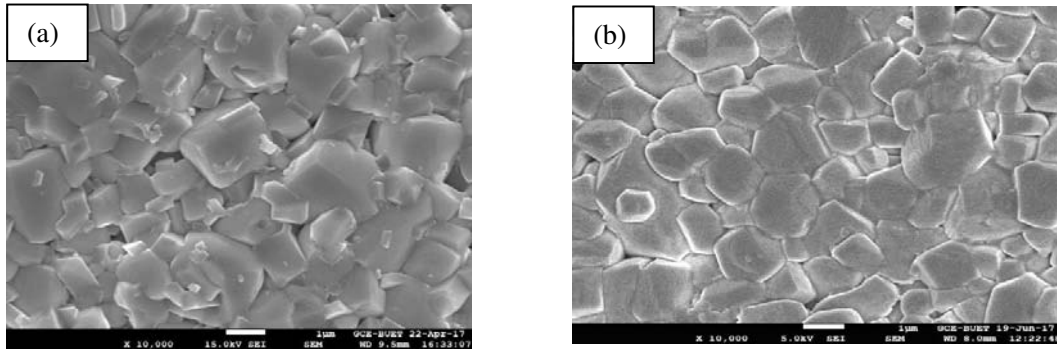


Figure 4: FESEM micrograph of $\text{Bi}_{0.8}\text{La}_{0.10}\text{Ba}_{0.10}\text{Fe}_{0.95}\text{Zr}_{0.05}\text{O}_3$ sintered at (a) 900°C (b) 950°C

$\text{Bi}_{0.8}\text{La}_{0.15}\text{Ba}_{0.05}\text{Fe}_{0.95}\text{Zr}_{0.05}\text{O}_3$ sintered at 900°C shows Figure 5(a) significant amount of porosity which on increasing sintering temperature gives better densification at 950°C. But the grain size here is much larger (~3 µm). And there is some amount of porosity too. Hence, optimum sintering temperature for $\text{Bi}_{0.8}\text{La}_{0.15}\text{Ba}_{0.05}\text{Fe}_{0.95}\text{Zr}_{0.05}\text{O}_3$ should be 950°C.

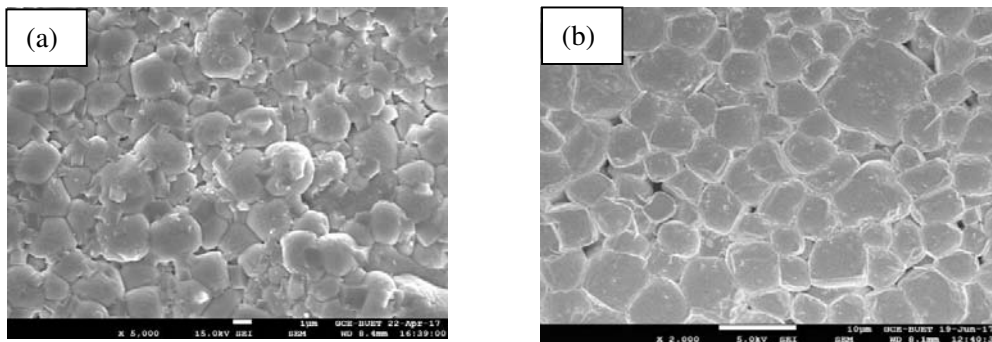


Figure 5: FESEM micrograph of $\text{Bi}_{0.8}\text{La}_{0.15}\text{Ba}_{0.05}\text{Fe}_{0.95}\text{Zr}_{0.05}\text{O}_3$ sintered at (a) 900°C (b) 950°C

Figure 6 shows the micrographs of $\text{Bi}_{0.8}\text{La}_{0.20}\text{Fe}_{0.95}\text{Zr}_{0.05}\text{O}_3$ sintered at various temperatures. Sintering of $\text{Bi}_{0.8}\text{La}_{0.20}\text{Fe}_{0.95}\text{Zr}_{0.05}\text{O}_3$ at 850°C shows the similar effect of porosity as obtained in the case of $\text{Bi}_{0.8}\text{La}_{0.20}\text{Fe}_{0.95}\text{Zr}_{0.05}\text{O}_3$ sample sintered at 900°C. Here sintering is not up to the mark. The situation is improved at 950°C where porosity decreases to a significant amount and grain size increases. Average grain size is found to be ~1 µm.

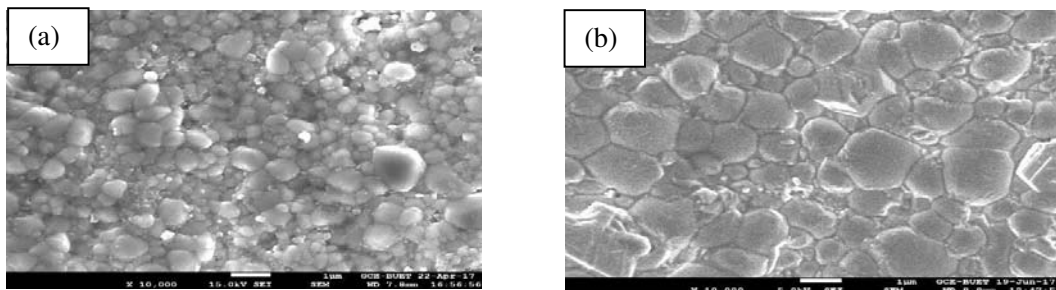


Figure 6: FESEM micrograph of $\text{Bi}_{0.8}\text{La}_{0.20}\text{Fe}_{0.95}\text{Zr}_{0.05}\text{O}_3$ sintered at (a) 900°C (b) 950°C

La and Ba have important effect on grain growth. La and Ba have dissimilar identity regarding the grain growth effect. Generally, the increased amount of La results in the increase of grain size as well as helps grain growth. As when amount of La is increased the round grain transformed to elongated grain and root mean square surface roughness is decreased as well. On the other hand, Ba impedes or retards the grain growth. From the figure for La (5%) & Ba (15%) in 7(a), As the amount of La is less in compared to other compositions available for La, the grain growth increased effect is least and at the same time the increased percentage of Ba results the impede of grain growth. Thus the overall grain size in the microstructure is smallest.

From the figure for La (10%) & Ba (10%) in 7(b), Here the amount of La% is increased which results in the increase of grain size to a small extent compared to the former one. As the amount of Ba is decreased thus retardation characters of Ba decreased thus the combined effect results in increase of grain growth. From the figure for La(15%) & Ba (5%) in 7(c), Here the La% is increased to a further extend which enhances the grain growth characters at the same time the decreased quantity of Ba lowers the impeding characters and their combining effect at this composition results in the increase of grain growth than the previous two compositions.

From the figure for La (20%) & Ba (0%) in 7(d), unusual effect is shown. The aim of our research is the analysis of the combining effect of both Ba & La. When both the dopants are present then it shows simultaneous continuous properties. But when only one of the dopant is used in the absence of another one then completely identical different properties shown which is not the follow of the previous one. Exactly same situation happens in our research. The absence of Ba and the presence of high La% should tend to develop high grain size but the fact from the experiment found that the grain size lowers than the La (15%) & Ba (5%).

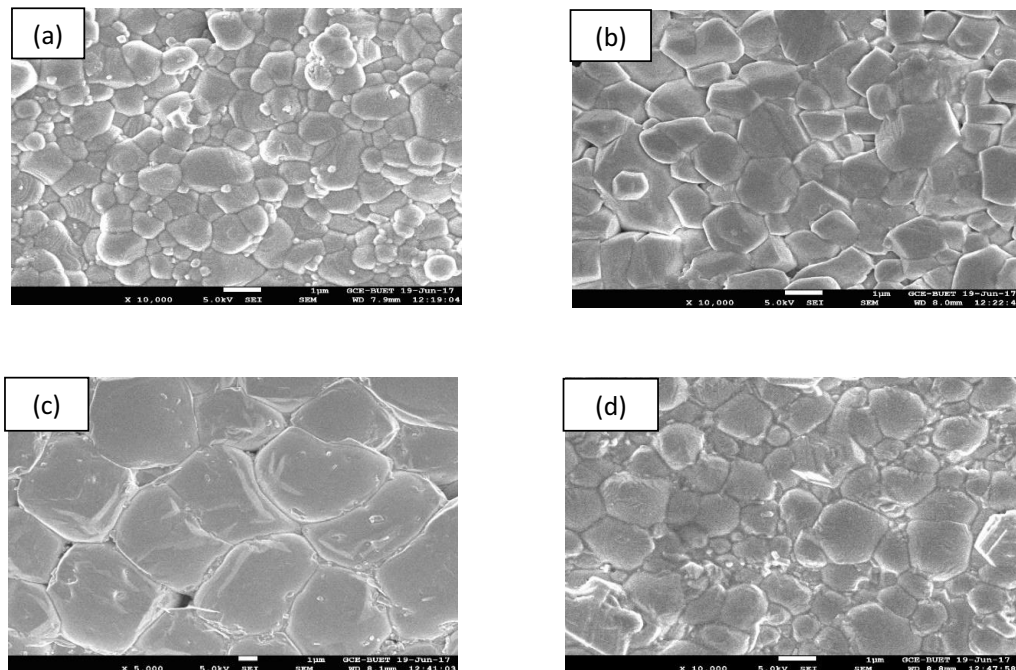


Figure 7: FESEM micrograph of $\text{Bi}_{0.8}\text{La}_x\text{Ba}_{0.2-x}\text{Fe}_{0.95}\text{Zr}_{0.05}\text{O}_3$ sintered at 950°C . (a) $x=0.05$, (b) $x=0.10$, (c) $x=0.15$, (d) $x=0.20$

3.3 Dielectric study:

The dielectric constant measures the polarizability of a medium. Upon application of an electric field, the medium which polarizes more and does not conduct electricity will be the one to show a higher dielectric constant. Already present polarization, if any, of the material does not contribute to the dielectric constant; it is the change in polarization with electric field which contributes. Thus if a material contains dipoles in its structure, but the dipoles do not change direction or change in magnitude appreciably with applied electric field the dielectric constant will be low.

As we know, the crystal structure of bismuth ferrite is non-centrosymmetric, and the unit cell does have a polarization in the pseudo-cubic [111] direction. The ferroelectric nature of the material allows the dipoles to reverse direction in response to an oscillating electric field. At low frequencies these dipoles can follow the electric field and contribute to the dielectric constant. But as the frequency is increased a point is reached where, the dipoles cannot reorient fast enough and so a drop in dielectric constant is expected. In this range only electronic polarization contributes to the dielectric constant.

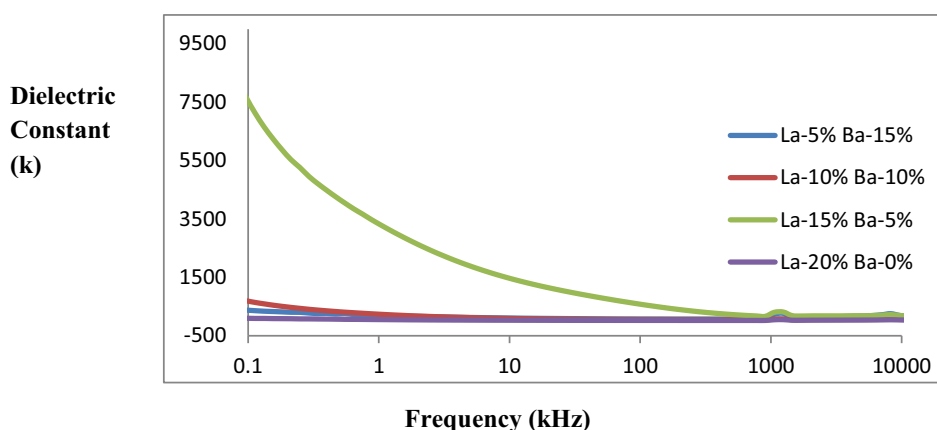


Figure 8: Frequency dependence of dielectric constant for $\text{Bi}_{0.8}\text{La}_x\text{Ba}_{0.2-x}\text{Fe}_{0.95}\text{Zr}_{0.05}\text{O}_3$ sintered at 950°C

Figure 8 shows the variation of dielectric constant of $\text{Bi}_{0.8}\text{La}_x\text{Ba}_{0.2-x}\text{Fe}_{0.95}\text{Zr}_{0.05}\text{O}_3$ with frequency in the range 100 Hz–10 MHz. It was evident that the dielectric constant falls off with increasing frequency, settling to a nearly constant value at high frequencies. The reason behind this phenomenon has been described above. Something that's not explained by the above discussion however, is the abnormally high dielectric constant for BLFO at low frequencies. This can be attributed to Maxwell-Wagner type contribution to the dielectric constant. This effect is related to space charge relaxation at the interface. The space charges can arise due to vacancies in the bismuth or oxygen site i.e. VO_2^+ , VBi^{3-} . These space charges can follow the electric field at low frequencies but do not have enough time to build up at the interface at high frequencies. Thus that contribution steadily decreases as frequency is increased.

At lower frequencies, the net contribution from various polarizations viz. space charges, ionic defects, permanent dipoles, induced atomic and ionic dipoles, contribute dielectric resulting in high values [3]. As frequency increases, different participating mechanisms for dielectric constant decrease gradually and subsequently. In the present scenario, Ba^{2+} substitution in Bi^{3+} ions increases the oxygen vacancy in the lattice of $\text{Bi}_{0.8}\text{Ba}_{0.2}\text{FeO}_3$ resulting in the increase of space charge [4]. Thus, for $\text{Bi}_{0.8}\text{Ba}_{0.2}\text{FeO}_3$ samples at low frequency show a high value of dielectric constant.

The observed dielectric constant decreases rapidly with the frequency, the decrease of dielectric constant with increase in frequency can be explained by a dipole relaxation phenomenon which is due to Maxwell-Wagner type of interfacial polarization contribution [5]. A high dielectric constant value in $\text{Bi}_{0.8}\text{Ba}_{0.2}\text{FeO}_3$ could also be

due to structural distortion in the sample. The Zr^{4+} substitution decreases the oxygen vacancy by charge compensation.

For increasing Ba content, leakage current is increasing. So the dielectric constant is lower. For La-15% Ba-5%, leakage current lower. So, the dielectric constant is highest. But unusual results have been found in only La-20% sample. Here, the effect of Ba is absent. So, the leakage is higher. So, the dielectric constant is lower.

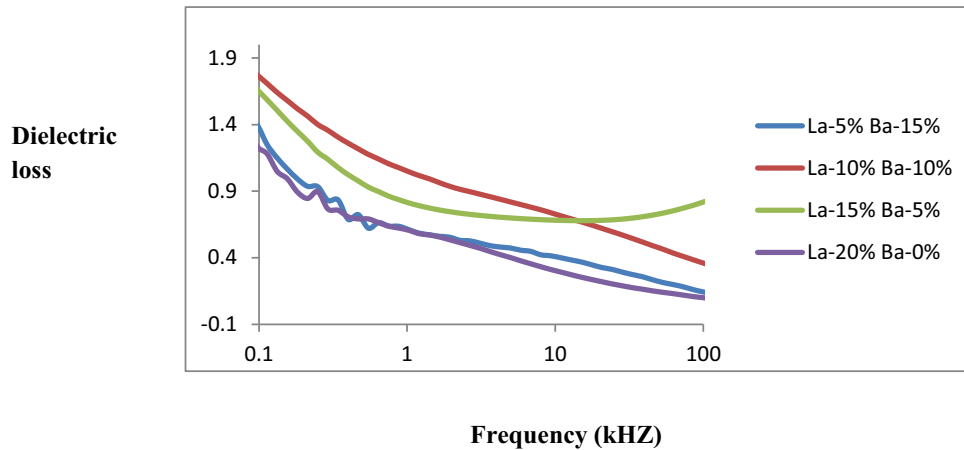


Figure 9: Frequency dependence of dielectric loss (D-factor) for $Bi_{0.8}La_xBa_{0.2-x}Fe_{0.95}Zr_{0.05}O_3$ sintered at $950^\circ C$

Figure 9 represents the frequency dependence of dielectric loss. Here same results have been found in the frequency range of (0.1-100 kHz). We know that higher dielectric loss means higher leakage current. For Ba-0%, dielectric loss is minimum. Increasing Ba content means increasing dielectric loss. But for Ba-15%, dielectric loss is lower for lower frequencies.

3.4 Ferroelectric property analysis

When Ba is doped in the BFO then it results in the creation of oxygen vacancy. As a result of the increase of the oxygen vacancy it generates electrons which ultimately increase leakage current. Thus increased amount of Ba result in the decrease of the remnant polarization. From the composition of La (5%) and Ba (15%) the p-loop found was satisfactory. It gives a decent identical curve on the polarization Vs electric field axes. And from that curve the precise data of remnant polarization and the coercively can be found. The comparison with the other composition cannot be done in our research. As the P-Loop obtained from the other variable compositions is not satisfactory as well as improper. As the P-Loop obtained from other compositions are unsatisfactory, this may happen due to the lack of sample preparation, improper surface area calculations or mishandling during technical operations.

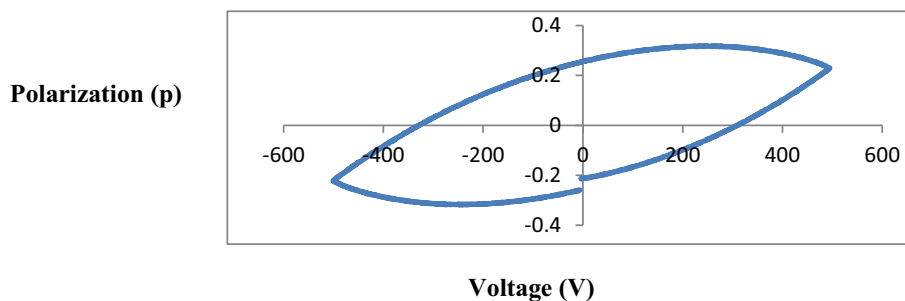


Fig 10: P-E loop for $Bi_{0.8}La_xBa_{0.2-x}Fe_{0.95}Zr_{0.05}O_3$ La-5% Ba-15%

4. Conclusion:

The main purpose of this research was to determine the effects of Ba and La along with co-modification by Zirconia on bismuth ferrite, with a view to improve its dielectric and magnetic properties. Solid state process was the route of choice at first. Sintering was done at 950°C to obtain coherent grain size. The room temperature magnetization improved remarkably compared to pure BFO after co-modification, more work needs to be done before its implementation in real life applications. The followings are in brief the highlighted findings from this research work.

Pure BFO produced by solid state process exhibited less amount impurity which was confirmed by XRD analysis. When dopants were used unknown impurities were not found in the XRD analysis. It also found that with the increase of La^{3+} the grain size increased. $\text{Bi}_{0.8}\text{La}_x\text{Ba}_{0.02-x}\text{FeO}_{0.95}\text{ZrO}_{0.05}$ ($x=0.05, 0.10, 0.15, 0.20$) were successfully produced by solid state methods which was confirmed by XRD analysis that indicated formation of the main BFO structure in all the samples. The increased amount of Zr^{4+} resulted in the reduction of leakage current. For the higher percentage of Ba^{2+} the oxygen vacancy increased which led to higher leakage current. Thus for increasing the La^{3+} up to 15 mole % with decreasing Ba^{2+} content, dielectric constant increased. For further addition of La^{3+} (i.e. 20%) the dielectric constant decreased again. For the compositions with 5% of La^{3+} the p-loop was found to be satisfactory with the remnant polarization of 0.25 ($\mu\text{C}/\text{cm}^2$) and the coercivity of 330V. However the p-loop for the other compositions was found to be unsatisfactory.

5. References:

- [1] H Singh and K L Yadav 2011 *Dielectric, magnetic and magnetoelectric properties of La and Nb codoped bismuth ferrite* Journal of Physics: Condensed Matter vol 23 pp 385901:1-6
- [2] M Cazayous, D Malka, D Lebeugle, D Colson 2007 *Electric field effect on BiFeO_3 single crystal investigated by Raman spectroscopy* Applied Physics Letters vol 91 pp 071910-071910
- [3] Z M Tian, S L Tuan, X L Wang, X F Zheng, S Y Yin, C H Wang and L Liu 2009 *Size effect on magnetic and ferroelectric properties in $\text{Bi}_2\text{Fe}_4\text{O}_9$ multiferroic ceramics* Journal of Applied Physics vol 106 pp 103912:1-4.
- [4] S Cheong and M Mostovoy 2007 *Multiferroic: a magnetic twist for ferroelectricity* Nature Materials vol 6 p 13-20.
- [5] N A Hill 2000 *Why are there so few magnetic ferroelectrics?* Journal of Physical Chemistry vol 104 p 6694-6709.
- [7] C Ederer and N A Spaldin 2005 *Weak ferromagnetism and magnetoelectric coupling in bismuth ferrite* Physics Review B vol 71 pp 060401.
- [8] I Sosnowska, T P Neumaier and E Steichele 1982 *Spiral magnetic ordering in bismuth ferrite* Journal of Physics C: Solid state Physics vol 15 pp 4835.
- [9] Y K Jun and S H Hong 2007 *Dielectric and magnetic properties in Co and Nb-substituted BiFeO_3 ceramics* Solid State Communication vol 144 p 329-333
- [10] M E Lines and A M Glass 2004 *Principles and Applications of Ferroelectrics and Related Materials* Oxford University Press.

Acknowledgements

The authors are thankful to the Department of Materials and Metallurgical Engineering, BUET; the Department of Glass and Ceramics Engineering, BUET.