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Characterization and study of Electrical properties of Lanthanum doped Bismuth Layered Ferroelectrics $La_{0.1}Bi_{3.9}$ Ti_3O_{12} and $La_{0.5}Bi_{3.5}$ Ti_3O_{12}

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Abstract: The present paper explains the Characterization and study of Electrical properties of Lanthanum doped Bismuth Layered Ferroelectrics $La_{0.1}Bi_{3.9}$ Ti_3O_{12} and $La_{0.5}Bi_{3.5}$ $Ti_3O_{12.}$ Theoretically obtained density from X-ray data for $Bi_4Ti_3O_{12}$ was 8.11 gm/cm^3. This shows that the density is decreasing with addition of Lanthanum. In the plot of Temperature Vs Dielectric Constant clear peak was observed at 653^{0}C for $La_{0.1}Bi_{3.9}$ Ti_3O_{12} and 513^{0}C for $La_{0.5}Bi_{3.5}$ Ti_3O_{12}. It is observed that the Curie temperature is decreasing with the addition of Lanthanum. The peak dielectric constant is 2098 for BLT 0.1 and 1088 for BLT 0.5.The Ferroelectric Hysteresis loops were traced at room temperature applying different electric fields.

Key words: $Bi_2O_{2,,}$ X-ray, Lanthanum

1. Introduction

Ferroelectric materials in general have attracted the attention of scientific community because of their application as sensor and actuator material. The materials for either laboratory or commercial use there are many processes, which influence the chemical and physical structure of the product. The selection of raw materials, the fabrication and the heat treatment, are all-important and must be carried out which care. BLSF ceramic bear the represented by the general formula $(Bi_2O_2)^{2+}$ $(A_{n-1}$ B_n $O_{3n+1})^{2-}$In the above formula, A can be a mono, di, trivavelant or a mixture of these for example A=Bi, Sr, Ba, etc. while the smaller but higher charged ions Ti, Nb, Ta,Cr etc can go into the Bsite."m" refers to the no. of perovskite layers between the Bi-O layers. These are several empirical rules concerning these material outlined by Newnham et.al (1971). Some of them are listed below.

The Bismuth ions in the perovskite are readily replaced by a large no. of mono, di, and trivalent cations. The Bismuth oxide layer is almost involite. Ions ranging from sizes as small as Na and Ca as large as Ba and K can be substituted for Bi $^{3+.}$ The octahedral site in bismuth titanate structure lacks the flexibility found in pervoskites.

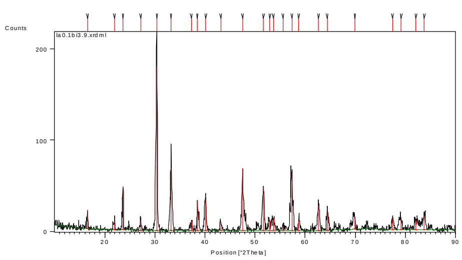
2. Preparation of BIT, $La_{0.1}Bi_{3.9}$ Ti_3O_{12} (BLT 0.1) and $La_{0.5}Bi_{3.5}$ Ti_3O_{12} (BLT 0.5) using solid state sintering method

AR grade La_2O_3 , Bi_2O_3 and TiO_2 are taken in the pure form. The three materials are first weighed according to the stoichiometric formula to obtain **$La_{0.1}Bi_{3.9}$ Ti_3O_{12}** and **$La_{0.5}Bi_{3.5}$ $Ti_3O_{12.}$** Electronic weighing machine with a least count of 0.001g was used for weighing the raw materials. Care taken that no dust or foreign bodies are present while weighing the material. Two samples are kept in dust free boxes

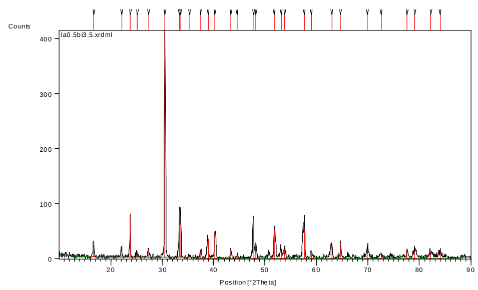
The mixture of raw materials is ground and homogenously mixed using agate mortar and pestle. Mixing the starting materials into a homogeneous mixture is important to get better densities, dielectric and other properties.

3. Characterization of Samples BLT 0.1 AND BLT0.5

3.1.XRD of the Samples BLT 0.1 AND BLT0.5. XRD of the samples are taken. The conditions and the pattern is given below



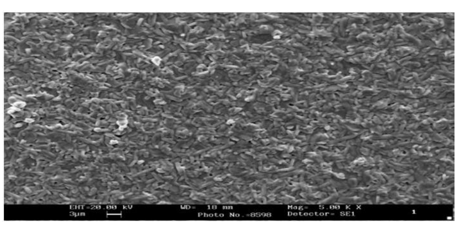
XRD of $La_{0.1}Bi_{3.9}Ti_3O_{12}$



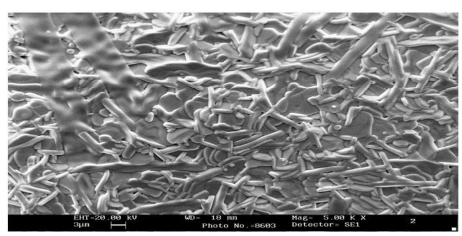
XRD of $La_{0.5}Bi_{3.5}Ti_3O_{12}$

The maximum intensity is observed approximately at 30.40^o of 2θ value for **$La_{0.1}Bi_{3.9}Ti_3O_{12}$** and 30.51^o of 2θ value for **$La_{0.5}Bi_{3.5}Ti_3O_{12}$**, corresponding to [1 1 7] reflection, which is also observed in the parent compound. All peaks in the XRD patterns is found to shift slightly towards lower 2θ values with addition of Lanthanum. This shows gradual change of unit cell dimensions due to the presence of Lanthanum instead of Bismuth.

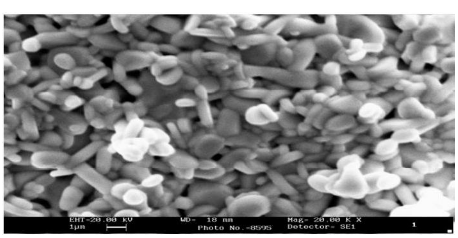
3.2.SEM of the samples:



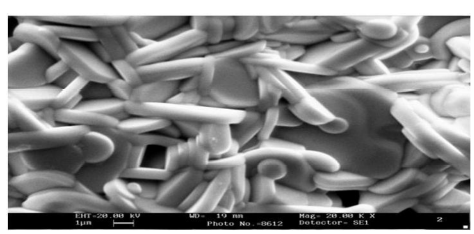
3a. SEM $La_{0.1}Bi_{3.9}Ti_3O_{12}$ at 5x



3b. SEM $La_{0.5}Bi_{3.5}Ti_3O_{12}$ at 5x



3c. SEM $La_{0.1}Bi_{3.9}Ti_3O_{12}$ at 20x



3d. SEM $La_{0.5}Bi_{3.5}Ti_3O_{12}$ at 20x

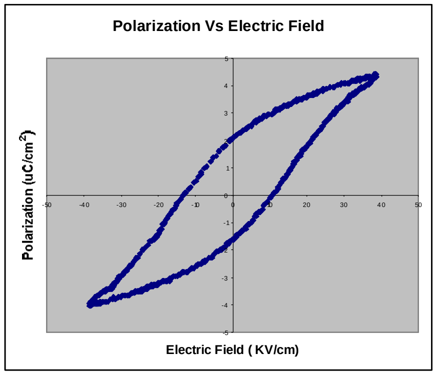
Above Figures 3(a,b,c & d) show the micrographs obtained on the sintered pallets of $La_{0.1}Bi_{3.9}Ti_3O_{12}$ and $La_{0.5}Bi_{3.5}Ti_3O_{12}$. The figures are arranged according to the magnification. Pictures of the two samples with the same magnification are placed together. The Micro structural features are analyzed through SEM of sintered pellet of ceramics prepared. The SEM images show grains in the form of platelets. This orientation is typical of Aurivillius phases and is due to the polycrystalline nature of the samples. Crystal grains are greatly enhanced relative to $Bi_4Ti_3O_{12}$. It also observed that La addition tends to enhance grain growth.

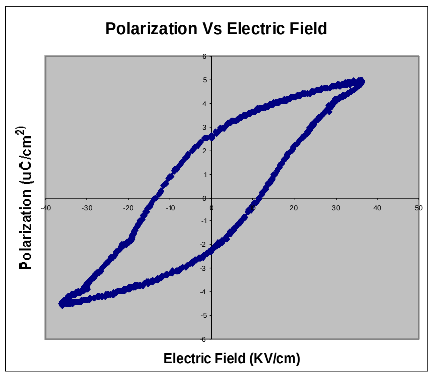
3.3. DENSITY MEASUREMENTS:

Density of the samples was found to be 7.27 gm/cm^3 for $La_{0.1}Bi_{3.9}Ti_3O_{12}$ and 6.55 gm/cm^3 for $La_{0.5}Bi_{3.5}Ti_3O_{12}$. Theoretically obtained density from X-ray data for $Bi_4Ti_3O_{12}$ was 8.11 gm/cm^3 (JCPDS Powder Diffraction file, Inorganic Phases by International Centre for diffraction data (1999). This shows that the density is decreasing with addition of Lanthanum.

4. Electrical properties of BLT0.1 and BLT0.5

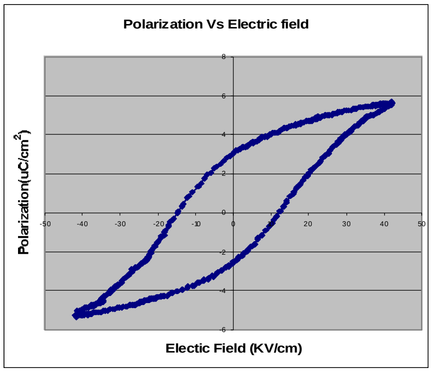
a)P-E for different Electric fields BLT 0.1





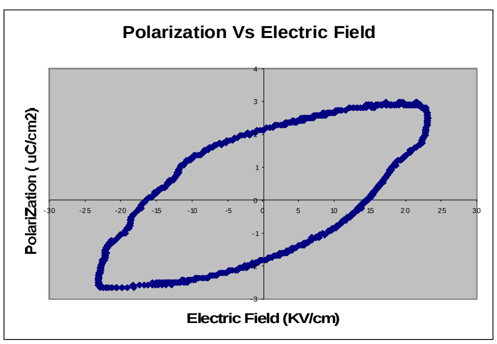
4a.Electric field = 36.044 KV/cm
4b. Electric field = 38.436 KV/cm

S.No	Saturation electric field KV/cm	Remanent Polarization µC/cm^2	Coercive field KV/cm
1	36.044	1.853	11.905
2	38.436	2.462	12.443
3	41.944	2.777	13.520

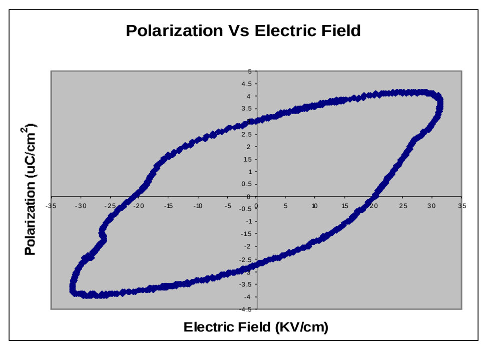


4c.Electric field = 41.944 KV/cm Remanent Polarization & Coercive field for different Electric fields

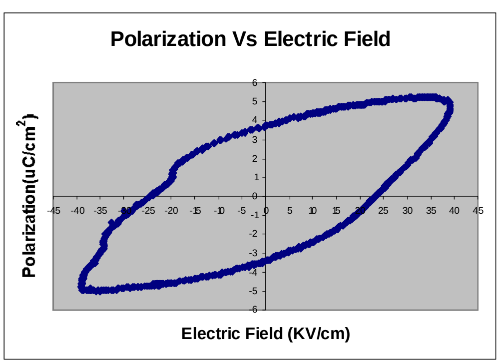
b)P-E for different Electric fields BLT 0.5



4e. Electric field = 23.098 KV/cm



4f.Electric field = 31.390 KV/cm



S.No	Saturation elec tric field KV/cm	Remanent Polarization $\mu C/cm^2$	Coercive field KV/cm
1	23.098	1.982	15.525
2	31.390	2.874	21.454
3	39.084	3.561	23.816

4g. Electric field = 39.084KV/cm
Remanent Polarization & Coercive field for different Electric fields

By measuring of the polarization as a function of the applied electric field (hysteresis loop). This type of loop is similar to the magnetic loop (magnetization Vs magnetic field). The instrument utilized for this measurement is based a Sawyer-Tower circuit that consist of two serially connected components, a ferroelectric capacitor (metal-ferroelectric-metal) "CF" and a linear capacitor "C0", being C0>> CF where an applied voltage of an appropriate wave and an amplitude results in polarization switching of the ferroelectric obtaining a hysteresis loop.It is observed that remanent polarization and coercive field increased with increase in the applied electric field. Here also it is observed that remanent polarization and coercive field decreased with increase in the concentration La.

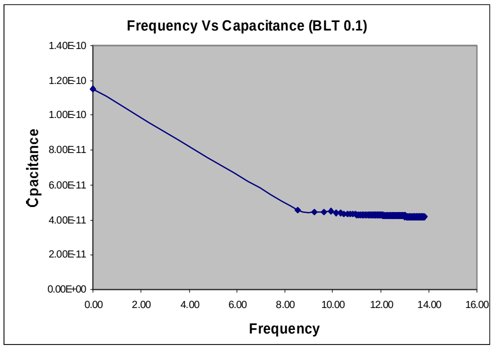
The data and P-E loops for both samples $La_{0.1}Bi_{3.9}Ti_3O_{12}$ and $La_{0.5}Bi_{3.5}Ti_3O_{12}$ are taken for different applied electric fields. The hysteresis loops are plotted (Figure 4(a-g)). Tables show the variation of remanent Polarization and Coercive field values at different fields for BLT 0.1 and BLT 0.5. It is observed that remanent polarization and coercive field increased with increase in the applied electric field. From the P-E studies, it is observed that there is an increase in the remanent polarization and coercive field with increase in the concentration of Lanthanum. This shows that the substitution of Lanthanum in place of Bismuth has affected the polarization phenomenon. The presence of larger ionic radii ions has resulted in the increase in the remanent polarization and coercive field. This result is in consistent with the results reported by **Haixue Yan et al. (2000)**.

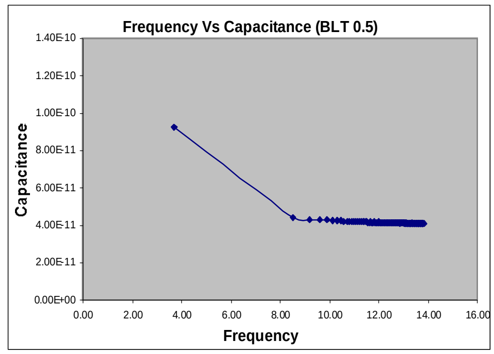
5. Variation of Capacitance with and frequency

Variation of capacitance with frequency is obtained at room temperature from the Impedance analyzer; It is measured using AUTOLAB PGSTAT 30 low frequency impedance analyzer. Measurements are done in the frequency range of 1Hz to1MHz at room temperature. It is observed that the capacitance has decreased with increase in frequency initially and becomes constant. The results are presented in Figures 5a and 5b

6. Variation of Impedance with Frequency

A great deal of additional information comes out of studying electrical properties over a wide range of frequencies. Polycrystalline materials exhibit a wide variety of frequency dependent properties. The figures (6a&6b) show a strong frequency dependence of impedance values.

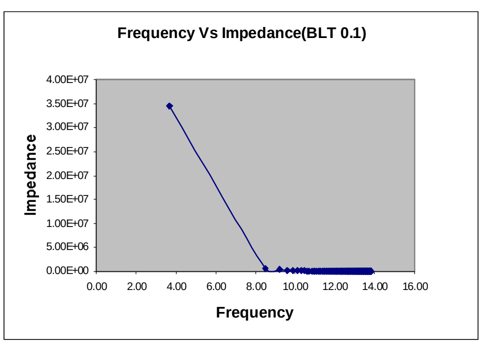




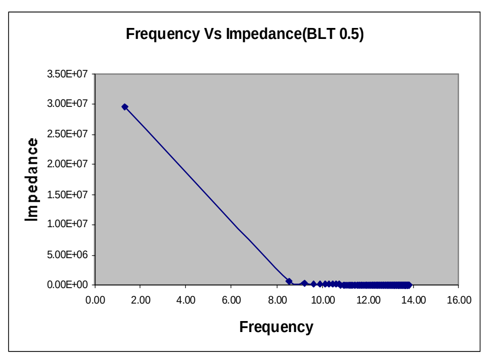
5a.Frequency Vs Capacitance for BLT 0.1 5b.Frequency Vs Capacitance for BLT 0.5

Impedance in a frequency range of 1Hz to 1MHz is measured at room temperature using Impedance analyzer. The impedance has decreased with increase in frequency for both BLT 0.1 and BLT 0.5.The result are presented in Figures 6a & 6b

From the data obtained, the large values of impedance at low frequencies may be due to defect concentration and hence a consequent increase in the space charge polarization. A large decrease of impedance with increase of frequency also indicates the presence of space charge polarization in three samples (**Rao and Suryanarayana Rao 1971**)



6a.Frequency Vs Impedance for BLT 0.1



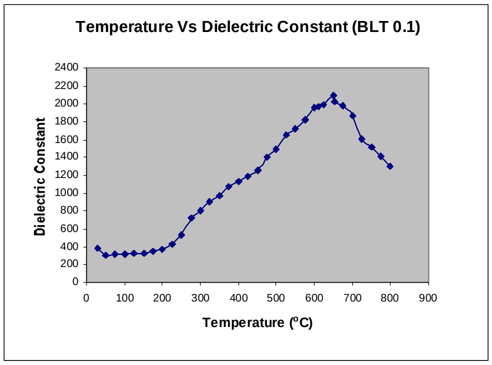
6b.Frequency Vs Impedance for BLT 0.5

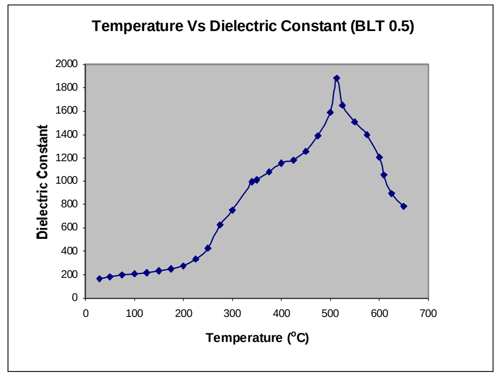
Above studies show that the variation of Impedance and Dielectric constant with frequency are in resemblance of data for BIT. It shows that the Ferroelecric properties are not destroyed by doping Lanthanum into BIT.

The study of the electrical properties of BLT 0.1 and BLT 0.5 has given us the clear idea that with the doping of the lanthanum into BLT has enhanced the ferroelectric properties making them suitable for memory applications. The preparation methods adopted are very simple and cost effective. These methods can be used in bulk production.

7.Dielectric properties of BLT

Temperature Vs Dielectric Constant for BLT 0.1





7a.**Temperature Vs Dielectric Constant for BLT 0.1** **7b. Temperature Vs Dielectric Constant for BLT 0.5**

Ferroelectric in nature. The T_c was found to decrease with increase in Lanthanum content in BIT. It is evident from the results that the Curie temperature is decreasing with the increase in the Lanthanum doping percentage. Such a decrease in Tc of La modified bismuth layer-structured ferroelectric ceramics has been observed in previous research (**T. Takeneka et al.**(**1980**)). It is reported to be due to decrease in the lattice distortion.

The maximum dielectric constant is found to be 2098 for BLT 0.1 and 1880 for BLT 0.5.the dielectric constant is found to reduce with increase of Lanthanum content

8. Conclusion

Two samples $La_{0.1}Bi_{3.9}$ Ti_3O_{12} and $La_{0.5}$ $Bi_{3.5}$ Ti_3O_{12} are prepared by solid state sintering method. The sampled are sintered at 1000°C for 3hours. The samples are characterized by X-ray diffraction and showed single phase formation.All peaks in the XRD patterns are found to shift slightly towards lower 2θ values with addition of Lanthanum. This shows gradual change of unit cell dimensions due to the presence of Lanthanum instead of Bismuth.Scanning Electron Micrograph showed needle like morphology. The orientation of samples is typical of Aurivillius phases and is due to the Polycrystalline nature of the samples. Crystal grains are greatly enhanced relative to $Bi_4Ti_3O_{12}$ (BIT). It also observed that Lanthanum addition tends to enhance grain growth. The grain size is found to be 2-3 µm in case of $La_{0.1}Bi_{3.9}$ Ti_3O_{12} and 4-5 µm in $La_{0.5}Bi_{3.5}$ Ti_3O_{12}. Density of the samples is found to be 7.27 gm/cm^3 for $La_{0.1}Bi_{3.5}$ Ti_3O_{12} and 6.55 gm/cm^3 for $La_{0.5}Bi_{3.5}$ Ti_3O_{12}. Theoretically obtained density from X-ray data for $Bi_4Ti_3O_{12}$ was 8.11 gm/cm^3. This shows that the density is decreasing with addition of Lanthanum. In the plot of Temperature Vs Dielectric Constant clear peak was observed at 653^{0}C for $La_{0.1}Bi_{3.9}$ Ti_3O_{12} and 513^{0}C for $La_{0.5}Bi_{3.5}$ Ti_3O_{12}. It is observed that the Curie temperature is decreasing with the addition of Lanthanum. The peak dielectric constant is 2098 for BLT 0.1 and 1088 for BLT 0.5.The Ferroelectric Hysteresis loops were traced at room temperature applying different electric fields. It is observed that remanent polarization and coercive field increased with increase in the applied electric field. From the P-E studies, it is observed that there is an increase in the remanent polarization and coercive field with increase in the concentration of Lanthanum in BIT. This shows that the substitution of Lanthanum in place of Bismuth has affected the polarization phenomenon. The maximum field applied for BLT 0.1 is 40.794 KV / cm and for BLT 0.5 is 39.084 KV / cm The maximum remanent polarization for the BLT 0.1 is 2.339 µC/cm and for BLT 0.5 is 3.561µC/cm presence of larger ionic radii ions has resulted in the increase in the remanent polarization and coercive field. Variation of capacitance with frequency is obtained at room temperature from the impedance analyzer. It is observed that the capacitance has decreased with increase in frequency initially and becomes constant.Impedance Vs frequency values are measured at room temperature using impedance analyzer. The frequency range is 1Hz to 1MHz. The impedance has decreased with increase in frequency for both BLT 0.1 and BLT 0.5.

References:

Barranco A.P., Gutierrez-Amador M.P., Huanasto A. and Valenzuela R., Appl. Phys. Letters 73 (14), 2039 (1998)

Cole K.S and Cole R.H., J. Chem. Phys 9, 341 (1941)

Elliot S.R., Physics of Amorphous Materials, 2nd Edition (Longman, London, 1990).

Gupta V and Mansingh A., Phys. Rev. B 49, 1989 (1994)

Haberey F and Wijn H.P.G., Phys. Status Solid, 26, 1, 231 (1968)

Iguchi E., and Mochizuki S., J. Appl. Phys., 96, 3889 (2004).

Ishida Y., Natsuo M and Yamafuji K., Kolloid-Z, 200, 48 (1964)

James A.R., Balaji S. and Krupanidhi S.B., Maters Sci Engg, B64, 149 (1999)

James A.R., Kumar G.S., Suryanarayana S.V. and Bhimasankaram T., Ferroelectrics, 216, 11 (1996)

Jonscher A.K., Nature 267, 673 (1977)

Jonscher A.K.., Dielectric relaxation in solids (Chelsea Dielectric press, London, 1983).