

# Dielectric and Impedance Spectroscopy of Samarium and Lanthanum Doped Barium Titanate at Room Temperature

Sukhleen Bindra Narang, Dalveer Kaur, Kunal Pubby

**Abstract**—Dielectric ceramic samples in the BaO-Re<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> ternary system were synthesized with structural formula Ba<sub>2-x</sub>Re<sub>4+2x/3</sub>Ti<sub>8</sub>O<sub>24</sub> where Re= rare earth metal and Re= Sm and La where x varies from 0.0 to 0.6 with step size 0.1. Polycrystalline samples were prepared by the conventional solid state reaction technique. The dielectric, electrical and impedance analysis of all the samples in the frequency range 1KHz- 1MHz at room temperature (25°C) have been done to get the understanding of electrical conduction and dielectric relaxation and their correlation. Dielectric response of the samples at lower frequencies shows dielectric dispersion while at higher frequencies it shows dielectric relaxation. The ac conductivity is well fitted by the Jonscher law. The spectroscopic data in the impedance plane confirms the existence of grain contribution to the relaxation. All the properties are found out to be function of frequency as well as the amount of substitution.

**Keywords**—Dielectric ceramics, Dielectric constant, Loss tangent, AC conductivity, Impedance spectroscopy.

## I. INTRODUCTION

IN the past three-four decades, various dielectric properties of ceramic materials are being successfully exploited in the design and fabrication of devices and fabrication of devices having importance in consumer and military electronics, communication systems, power transmission and computers depending upon their suitability. The ceramic materials industry is the basis of many other industries. For example: abrasives are used in machine-tool and automobile industries, glass ceramics are used in architectural, electronic and electrical industries and many more. Newly designed devices essentially incorporate these materials because of their useful chemical, electrical, optical, dielectric, mechanical, thermal and structural properties. For better electrical ceramics like Barium titanate (BaTiO<sub>3</sub>), Strontium titanate (SrTiO<sub>3</sub>), Barium Strontium Titanate, lead zirconate, tantalite, niobates, it was found that good dielectric and structural performances are obtained if a number of additives are added in a specific manner [1]-[3]. Substituting the lanthanides to Barium titanate is of great significance in the modern electronic industry. So,

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rare earth metals samarium and lanthanum are intentionally doped in varying composition to the parental barium titanate material [4]-[6]. In our previous work, we made ceramics with structural formula of Ba<sub>6-3x</sub>Re<sub>8+2x</sub>Ti<sub>18</sub>O<sub>54</sub> with Re= Sm and La and studied their properties in detail [7]-[9]. The synthesized materials having high dielectric constant can be used in dielectric resonators, filters, antennas in the field of microwave telecommunication and satellite broadcasting system. Continuing that chain of work, we have made two series with different structural formula.

The dielectric properties of dielectric materials are intrinsic properties indicated by complex dielectric constant:  $\epsilon'' = \epsilon' - j\epsilon''$ , where  $\epsilon'$  represents the real part i.e. permittivity and  $\epsilon''$  represents the losses. The dielectric parameters are generally dependent on the frequency of applied field, density, temperature, material structure, composition etc. [10], [11]. The electrical properties are often represented in terms of complex impedance or ac conductivity. Impedance analysis is a process of display of the impedance data in different formalism to provide us maximum information about the materials. The display of results in the form of semi-circles is attributed to relaxation phenomenon due to various reasons like grains, grain boundary or electrode. This study helps us to understand their individual contribution to the overall electrical properties [12].

In this research paper, we are reporting the frequency and composition dependence of dielectric, electrical and impedance parameters of Ba<sub>2-x</sub>Re<sub>4+2x/3</sub>Ti<sub>8</sub>O<sub>24</sub> with x= 0.0-0.6 and Re= Sm and La in the frequency range 1 KHz – 1MHz at room temperature (25°C).

## II. EXPERIMENTAL

The target materials of Ba<sub>2-x</sub>Re<sub>4+2x/3</sub>Ti<sub>8</sub>O<sub>24</sub> structural formula were prepared by conventional mixed oxide route method (ceramic method) from the raw materials: Ba<sub>2</sub>CO<sub>3</sub>, Sm<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub>. After weighing, these materials were mechanically grounded for about 12 hours by agate mortar with methanol. After that, the process of calcinations was done at 1100°C for 2 h. Then the materials were re-grounded for 12 hours and mixed with 3% solution of polyvinyl alcohol to provide strength and brittleness. This step was followed by re-shaping of samples into pallets of cylindrical shape of 14mm in diameter and 4.5mm in thickness under a load of 98 KN. The sintering was done in air at 1300°C for 6 hours. Finally the samples were cooled down to room temperature at the cooling rate of 200°C/hour. The samples were polished with fine

emery paper to make the surfaces flat, smooth and parallel for electrical measurements. Silver paint was applied on both sides of samples before measurement. Capacitance, Loss-factor and Conductance were measured in frequency range 1 KHz- 1 MHz using Wayne Kerr 6500B Precision Impedance Analyzer in conjunction with a Wayne Kerr sample holder Model no. TF-1000 model with an AC signal (1V).

### III. RESULTS AND DISCUSSION

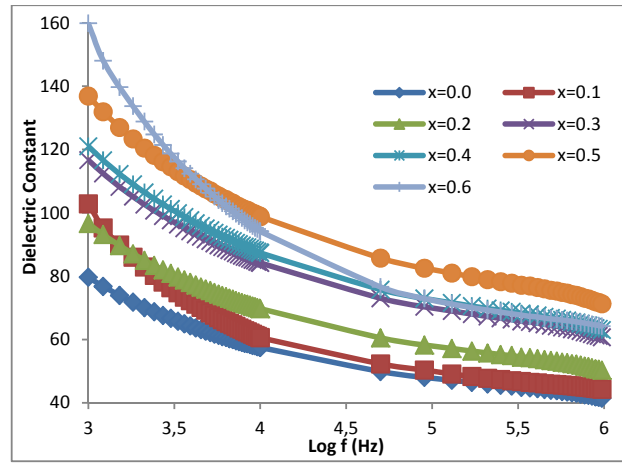
#### A. Dielectric Constant

The study of dielectric properties with frequency gives a good knowledge about the distribution of electric field in the system and field induced perturbations [13]. Figs. 1 (a) and (b) show the behavior of dielectric constant of both series. The phenomenon of dielectric dispersion is observed in all samples that is the normal behavior of dielectrics [14], [15]. There are two different clearly distinguishable regions of dispersion in  $\epsilon_r$  spectra. In first region above 1 KHz, a decrease is observed in lower frequency range that can be explained on the basis of dielectric relaxation. At lower frequencies ( $\omega \ll 1/\tau$ ), dipoles follow the field and dielectric constant is equal to its value at static field. The high value of permittivity at low frequencies may be due to the space charge polarization at the grain boundaries. In second region, almost constant value of permittivity is observed. As the frequency increases, dipoles begin to lag behind the field as the field is reversed before the dipoles respond. At the characteristic frequency, the value of permittivity drops showing the relaxation. At still higher frequencies, dipoles don't follow the field and the value becomes as that at infinite frequency [16], [17]. The following equation can be used to quantify the dielectric dispersion by estimating the parameter  $\alpha$  [18]:

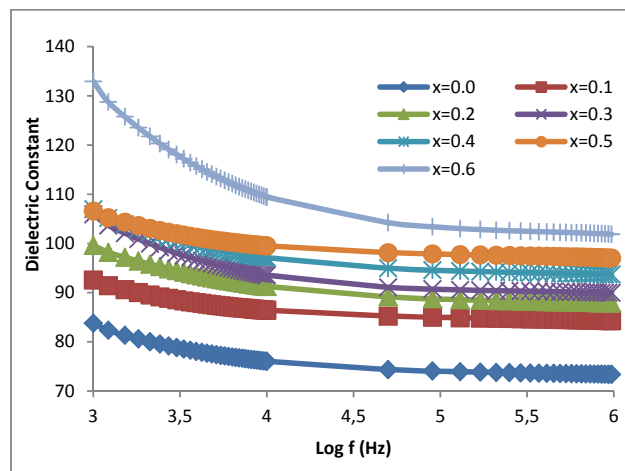
$$\epsilon' = \epsilon_0 - \alpha \log f$$

where,  $\epsilon'$  is the dielectric constant,  $\epsilon_0$  is its value at static field and  $\alpha$  is the slope of the curve.

The compositional variation of permittivity is also demonstrated in Figs. 1 (a) and (b). Increasing the doping concentration induces many compensation mechanisms like electric compensation, B-site compensation and oxide vacancy compensation [19], [20]. These processes induce strong polarization under the external field. In terms of orientation polarization formation, high-valence ions can substitute low valence-ions such as trivalent  $\text{Ba}^{2+}$  ions are replaced by  $\text{Sm}^{3+}$  and  $\text{La}^{3+}$  ions to act as extrinsic acceptor [21]. Therefore, some defects may be introduced because of the different valences of doped ions. Substitution of bivalent ions by trivalent bring effective positive charge. At higher doping levels, the defects generated due to loose of oxygen traces in sintering process, due to Coulomb's attraction [22] and cause a change in the orientation of dipoles [23]. This may results in increase of permittivity.



(a)



(b)

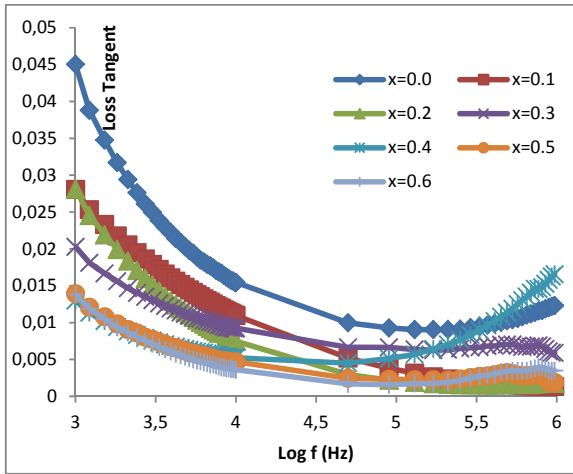
Fig. 1 Variation of permittivity with frequency for different compositions of (a)  $\text{Ba}_{2-x}\text{Sm}_{4+2x/3}\text{Ti}_8\text{O}_{24}$  (b)  $\text{Ba}_{2-x}\text{La}_{4+2x/3}\text{Ti}_8\text{O}_{24}$  at room temperature

#### B. Loss Tangent Analysis

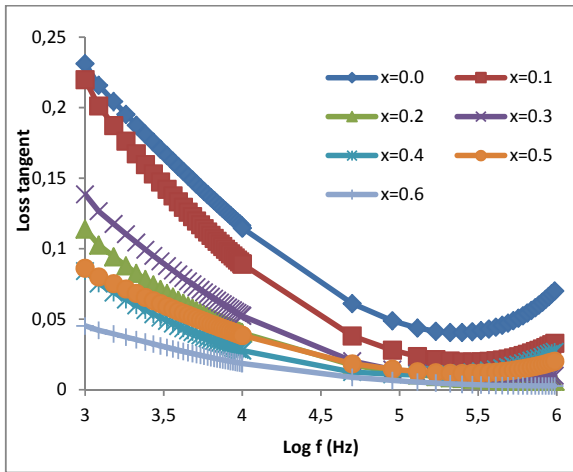
The compositional decrease in value of loss tangent may be attributed to the fact that the loss tangent varies in direct proportion to the internal strain observed in both series [24], [25]. The internal strain is attributed to the generation of vacancies by the substitution of  $3\text{Ba}^{2+}$  by  $2\text{Re}^{3+}$  in the crystal structure. As we increase the concentration, more vacancies are generated in A1-sites by the substitution. Therefore, the internal strain in the crystal structure reduces and the losses decrease.

The frequency dependence of loss tangent, shown in Figs. 2 (a) and (b) is quite proportional to that of dielectric constant. At lower frequencies, conduction losses become more dominant, so the loss tangent remains high [26]. This could be explained taking ion hopping frequency between two ion positions into account. The maximum energy loss occurs for a frequency equal to the hopping frequency. When applied

frequency is higher than hopping frequency, the atoms do not have an opportunity to hop at all and hence losses are small.



(a)



(b)

Fig. 2 Variation of loss tangent with frequency for different compositions of (a)  $Ba_{2-x}Sm_{4+2x/3}Ti_8O_{24}$  (b)  $Ba_{2-x}La_{4+2x/3}Ti_8O_{24}$  at room temperature

C. AC Conductivity Analysis

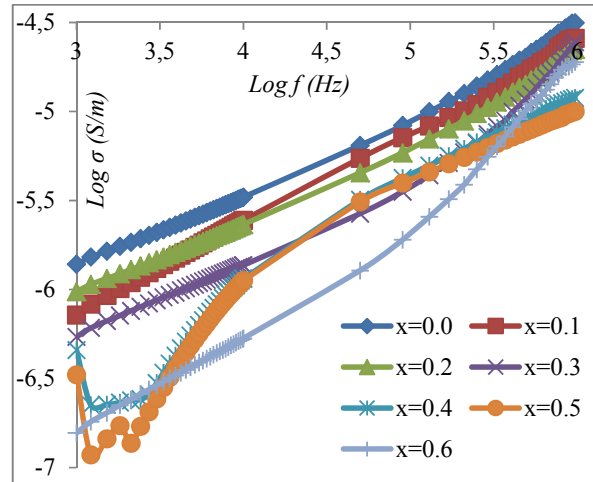
The electrical conductivity in dielectrics is mainly because of hopping of electrons between ions of the same element present in more than one valence state [27]. The charges may migrate under the influence of the field and result in conductivity [28]. In our research, the ac conductivity may be attributed to formation of  $Ti^{3+}$  ions that are formed due to partial reduction of  $Ti^{4+}$  ions during the sintering process. So, the decrease in ac conductivity with composition might be due to lesser formation of  $Ti^{3+}$  ions.

The plots in Fig. 3 show that the conductivity increases with frequency. The patterns observed show some particular features like dispersion throughout the frequency range, low frequency plateau and high frequency dispersion with changing slope. The frequency of change of slope is known as

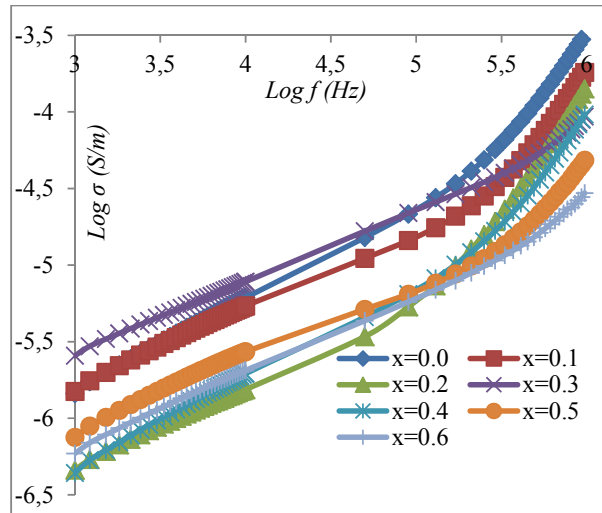
hopping frequency [29]. Pollak has shown that conductivity of dielectrics is an increasing function of frequency in case of conduction by hopping [30]. The behavior at lower frequencies indicates long range movement of mobile charge carriers [31]. This pattern suggests that electrical conduction in the material take place via hopping mechanism governed by Johnscher's universal power law [32]-[34]:

$$\sigma_{ac} = \sigma_{dc} + A\omega^n$$

where n is the frequency exponent ( $0 < n < 1$ ); A and n are thermally activated quantities [35].



(a)



(b)

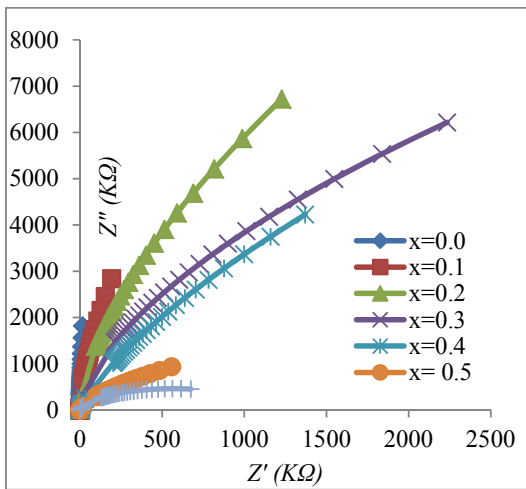
Fig. 3 Variation of AC Conductivity with frequency for different compositions of (a)  $Ba_{2-x}Sm_{4+2x/3}Ti_8O_{24}$  (b)  $Ba_{2-x}La_{4+2x/3}Ti_8O_{24}$  at room temperature

D. Impedance Analysis

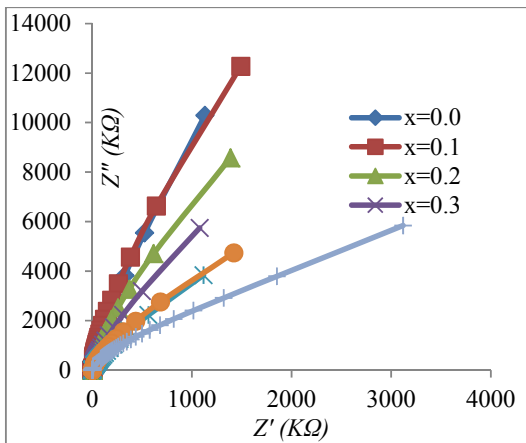
The complex impedance formalism allows us to distinguish between the contribution of intra-grain (bulk), inter-grain

(grain boundary) and the electrode process towards conduction [36]. We have plotted the Nyquist plot for different samples at room temperature. The single semi-circular arcs in the plots indicate that transport properties of the material arise due to the bulk conduction mechanism [37]. No residual semicircle at low frequency may be attributed to the absence of contact or electrode effects. The intercept of the semi-circular arc on x-axis gives us an estimate of the bulk resistance of the material. All the samples deviate from ideal Debye type relaxation [12] and appear to follow non-Debye type of relaxation. The impedance spectra of Figs. 4 (a) and (b) show a single semi-circular arc in the complex plane and can be interpreted by means of an equivalent circuit constituting a resistor (C) and capacitor in parallel combination [38].

frequency region and a saturated response in higher frequencies. This behavior suggests about the mixed nature of polarization in dielectrics. The merger of  $Z'$  at higher frequencies for all the compositions suggests a possibility of the release of the space charge that results in lowering of barrier properties [35].



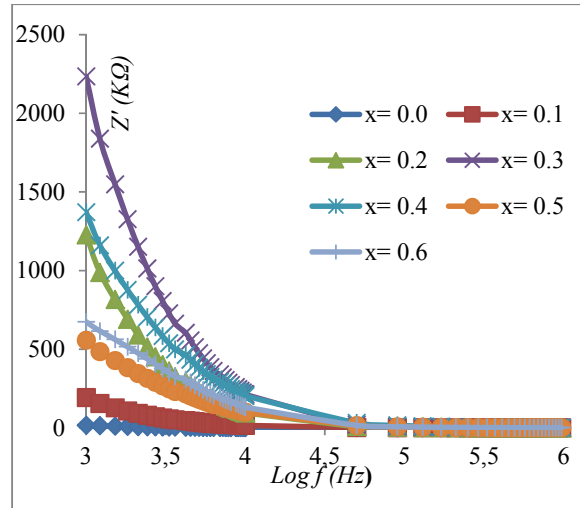
(a)



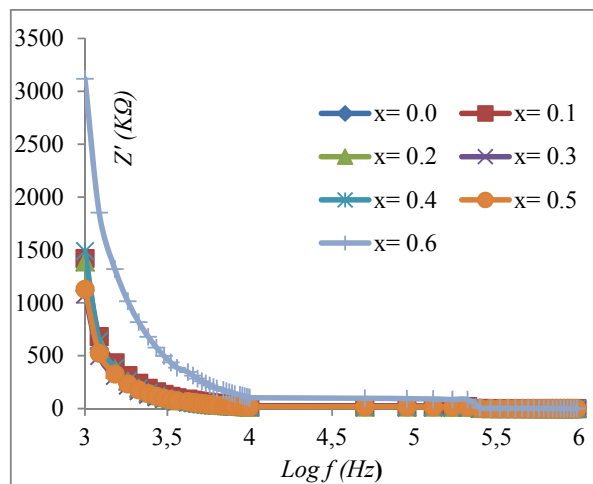
(b)

Fig. 4 Cole-Cole plots for various compositions of (a)  $Ba_{2-x}Sm_{4+2x/3}Ti_8O_{24}$  (b)  $Ba_{2-x}La_{4+2x/3}Ti_8O_{24}$  at room temperature

Figs. 5 and 6 demonstrate the variation of real part ( $Z'$ ) and imaginary part ( $Z''$ ) of impedance as a function of logarithmic frequency for different compositions of both series. The variation observed shows the sigmoidal variation in the lower

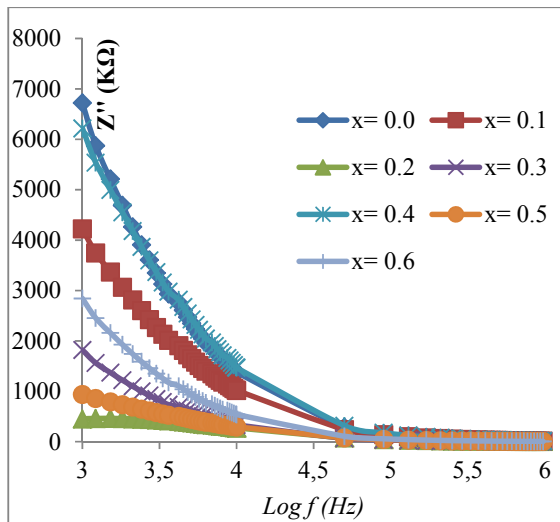


(a)

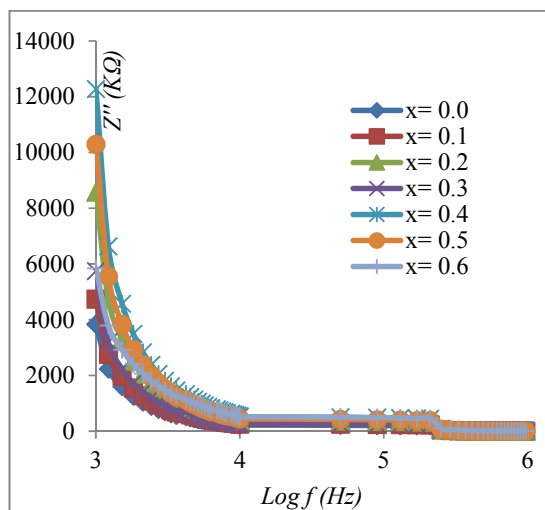


(b)

Fig. 5 Variation of  $Z'$  with frequency for various compositions of (a)  $Ba_{2-x}Sm_{4+2x/3}Ti_8O_{24}$  (b)  $Ba_{2-x}La_{4+2x/3}Ti_8O_{24}$  at room temperature



(a)



(b)

Fig. 6 Variation of  $Z''$  with frequency for various compositions of (a)  $Ba_{2-x}Sm_{4+2x/3}Ti_8O_{24}$  (b)  $Ba_{2-x}La_{4+2x/3}Ti_8O_{24}$  at room temperature

#### IV. CONCLUSION

In summary, complex ceramics prepared with doping of samarium and lanthanum in barium titanate depict the dispersion in dielectric properties, which is explained in the light of space-charge polarization. Both permittivity and loss tangent show relaxation phenomenon at lower frequencies and become almost constant at higher frequencies. The frequency depending electrical data is studied in the framework of conductivity formalism. The ac conductivity is found to follow power law. Impedance analysis is done to have knowledge of dielectric relaxation in the samples. Complex impedance analysis indicates the strong dependence of electrical properties on the frequency of applied field. The single semi-circular arcs are well modeled in term of parallel combination of resistance and capacitance.

#### REFERENCES

- [1] D. Berlincourt, *J. Acoust. Soc. Am.*, 1992, vol. 91, pp. 3034-3040.
- [2] F. Zimmermann, M. Voigts, W. Menesklou and E.I. Tiffée, *J. Eur. Ceram. Soc.*, 2004, vol. 24, pp. 1729-1733.
- [3] A. Tkach and P.M. Vilarinho, *Bol. Soc. Esp. ceram.*, 2008, vol. 47, pp. 238-241.
- [4] S. Bindra Narang, D. Kaur, K.S. Thind, *J. Ceram. Process. Res.*, 2005, vol. 7(1), pp. 31-36.
- [5] O. P. Thakur, C. Parkash, D. K. Aggarwal, *J. Ceram. Process. Res.*, 2002, vol. 3(2), pp. 75-79.
- [6] M. Aparna, T. Bhimasankaram, S. V. Suryanarayana, G. Prasad and G.S. Kumar, *Bull. Mater. Sci.*, 2001, vol. 24, pp. 497-504.
- [7] S. Bindra Narang, D. Kaur D and K.S. Thind, *J. Ceram. Process. Res.*, 2009, vol. 10(5), pp. 595-599.
- [8] S. BindraNarang, D. Kaur and K. Singh, *Ceram. Int.*, 2007, vol. 33(2), pp. 249-253.
- [9] S. Bindra Narang, D. Kaur and S. Bahel, *Mate. Lett.*, 2006, vol. 60, pp. 3179-3182.
- [10] A.K. Bansal, P.J. Singh, K.S. Sharma, *J. Pure Ap. Phy.*, 2001, vol.39, pp. 799-803.
- [11] S.O. Nelson, *Bull. Entomol. Soc. Am.*, 1993, vol. 19(3), pp 157-163.
- [12] N.K. Singh, Pritam Kumar, A. Kumar and S. Sharma, *J. Engg. Tech. Res.*, 2012, vol. 4(6), pp 104-113.
- [13] Makram Megdiche, Carine Perrin-pellegrino and Mohamed Gargouri, *J. Alloys Compd.*, 2014, vol.584, pp.209-215.
- [14] H.V. Alexandru, C. Berbecaru, A. Ioachim, M.I. Toascen, L. Nedelcu and D. Ghetu, *Mater. Sci. Engg. B*, 2004, vol.109, pp.152-159.
- [15] H. Ohsato, T. Ohhashi, S. Nishigaki, T. Okuda, K. Sumiya and S. Suzuki, *Jpn. J. Appl. Phys.*, 1993, vol.32, pp.4323-4326.
- [16] Sujoy Saha, Sadhan Chanda, Alo Dutta and T.P. Sinha, *Mater. Res. Bull.*, 2013, vol.48, pp.4917-4923.
- [17] S. Bindra Narang and D. Kaur, *Integr. Ferroelectr.*, 2009, vol.105(1), pp.87-88.
- [18] E. Buixaderas, D. Nuzhnyy, P. Vanek, I. Gragora, J. Petzelt, V. Porokhonsky, L. Jin, D. Damjanovic, *Phase. Transit.*, 2010, vol.83 (10-11), pp. 917.
- [19] C. Machhi, A. Samoza, A. Dupasquier, A. Lopez and M. Castro, *J. Phys.: Condens. Matter.*, 2001, vol.13, pp. 5717.
- [20] N.S. Hari, T. R. N. Kutty, *J. Mater. Sci.*, 1998, vol.33, pp.3275.
- [21] R.K. Dwivedi, D. Kumar, O. Parkash, *J. Mater. Sci.*, 2001, vol.36, pp.3641.
- [22] I. Burn, *J. Neirman, Mater. Sci.* 1982, vol.17, pp. 3510.
- [23] Yin-Lai Chai, Chi-Shiung His, Yiu-Tingand Lin and Yee-Shin Chang, *J. Alloys Compd.*, 2014, vol. 588, pp. 248-253.
- [24] H. Ohsato, *J. Euro. Ceram. Soc.*, 2001, vol.21, pp. 2703-2711.
- [25] H. Ohsato, *J. Ceram. Soc. Jpn.*, 2005, vol.113(11), pp. 703-711.
- [26] M.T. Sebastian, *Dielectric Materials for Wireless Communication*, Elsevier, New York, 2008.
- [27] H. Rahmouni, M. Nouiri, R. Jemai, N. Kallel, F. Rzigua, A. Selmi, K. Khirouni, S. Alaya, *J. Magn. Magn. Mater.*, 2007, vol. 316, pp. 23.
- [28] S. Khadhraoui, A. Triki, S. Heini, S. Zemni and M. Oumezzine, *J. Alloys Compd.*, 2013, vol. 574, pp. 290-298.
- [29] K. Srinivas, P. Sarah, S.V. Suryanarayana, *Bull. Mater. Sci.*, 2013, vol. 26(2), pp. 247-253.
- [30] M. Pollak, in: *Proceedings of the International Conference on Physics of Semiconductors*, Exeter, 1962 pp. 86.
- [31] S.K. Rout, Ali Hussain, J.S. Lee, I.W. Kim, S.I. Woo, *J. Alloys Compd.*, 2009, vol. 477, pp. 706-711.
- [32] A.K. Jonescher, *Nature*, 1977, vol. 267, pp. 673-679.
- [33] A. K. Jonescher, *Dielectric Relaxation in Solids*, Chelsea Dielectric Press, London 1983.
- [34] A.K. Jonescher, *Universal Relaxation Law*, Chelsea Dielectric Press, London 1996.
- [35] N. Zidi, A. Chaouchi, S. d'Astorg, M. Rguti, C. Courtois, *J. Alloys Compd.*, 2014, vol. 590, pp. 557-564.
- [36] N.K. Singh, Pritam Kumar, Radheshyam Rai, Anderi L. Kholkin, *Adv. Mater. Lett.*, 2012, vol. 3(4), pp. 315-320.
- [37] J.R. Macdonald, *Impedance spectroscopy emphasizing solid materials and system*, Wiley, New York, 1987.
- [38] Paramjeet Singh, Asish Agarwal, Sujata Sanghi, Navneet Singh and Satish Khansa, *Physica B*, 2014, vol. 436, pp. 64-73.