International Journal of Advance Research in Science and Engineering
Volume No.06, Special Issue No.(02), December 2017
www.ijarse.com
IJARSE
ISSN: 2319-8354

Crystal Structure and Dielectric Properties of La and Cr Modified $BaTiO_3$ Ceramic

Arvind Kumar[1*] and Vijayeta Pal[2]

[1]*G. L. Bajaj Institute of technology and management, Greater Noida- India*

[2]*Defence Materials and Stores Research and Development Establishment, Kanpur-208013, India*

ABSTRACT

In this paper, we report the dielectric behavior of a few compositions with $x \leq 0.12$ *in the system* $Ba_{1-x}La_xTi_{1-x}Cr_xO_3$,. *All the compositions have shown solid solution formation. At room temperature, crystal structure is tetragonal for compositions with* $x \leq 0.08$ *and cubic for* $x = 0.12$. *Lattice parameters of these compositions have been calculated. The dielectric measurements have been made over the temperature range 77K – 450K at different frequency 1, 10 & 100 kHz. Dielectric plots in doped systems have shown ferroelectric diffused phase transitions for* $x \leq 0.04$. *Origin of relaxor behavior for compositions* $x \geq 0.04$ *in Cr doped system is observed. Switching of diffused ferroelectric transition to relaxor type behavior has been found to occur with increasing x in BLTC system. Occurrence of one broad peak for x = 0.04 and 0.08 in BLTC may be attributed to the long range effect of Cr in place of Ti in the lattice of* TiO_6 *octahedra which suppresses spontaneous polarization effectively in high temperature ferroelectric phase.*

***Keywords:* Ferroelectric transition, Diffuse phase transition, Dielectric behavior, Crystal structure etc.**

I. INTRODUCTION

Most of the ceramic capacitors at present time have compositions based on $BaTiO_3$, which is a well known ferroelectric material. Pure or undoped $BaTiO_3$ shows marked changes in the values of dielectric constant particularly near its Curie temperature. This is an desirable feature for its use as a thermally stable capacitor material. Its properties are modified by a wide variety of substitutions at A site and B site independently or simultaneously [1]. These substitutions can be isovalent or heterovalent. Extensive research work on the effect of isovalent substitution on dielectric properties and phase transition temperature of $BaTiO_3$ has been done for the last few decades. The theory of the shifting of the transition temperature on isovalent substitution is well established by Von Hipple [2].

The heterovalent substitutions at A or B sites cause charge imbalance and in turn lead to creation of vacancies in A or B or oxygen sub-lattice. It is reported that for small concentration of La^{3+} substituted at Ba^{2+} sites, the charge neutrality is maintained by electronic compensation in accordance with $Ba^{2+}_{1-x} La^{3+}_{x}Ti^{4+}_{1-x}Ti^{3+}_{x}O_3$. However for larger concentration of La^{3+} ions, charge compensation occurs by vacancies on Ba-sites [3] which is described as $Ba_{1-x}La_{2x/3}(V_{Ba}^{''})_{x/4}O_3$. The type of defects vacancies as represented by the formula Ba_{1-x} $La_xTi_{1-x/}4Ti_{1-x/4}(V_{Ti}^{''''})_{x/4}O_3$. The type of defects produced depend on the distance between the impurity atoms and defects generated [4]. The earlier investigations on the solid solubility limit of La^{3+} and Nd^{3+} in $BaTiO_3$ implied that donor charge compensation may depend on the ratio (Ba+La)/Ti of the starting materials [5] When there is simultaneous substitution of La^{3+} at Ba^{2+} sites and Fe^{3+} at Ti^{4+} sites in equivalent amounts then it is expected that the charge compensation is maintained internally without requiring the creation of defects and hence the slid solutions are termed as valence compensated solid solutions. In the last few years, attempts have been made to synthesize and study such type of valence compensated solid solutions [6-9]. Compensations with $x \leq 0.05$ in the system in the system Ba_{1-x} $La_xTi_{1-x}M_xO_3$ (M = Co or Ni) exhibit interesting dielectric properties in these materials in the temperature range 300 – 500K [10].

In view of the above, it was considered worthwhile to investigate analogous valence compensated $Ba_{1-x}La_xTi_{1-x}Cr_xO_3$ (BLTC) perovskite systems. Simultaneous substitution of with lanthanum in equal concentration is expected to maintain change neutrality without creating defects if a Cr exits entirely in the trivalent state. Hence the substitutions of these off-valent ions are expected influence the phase transition temperatures in $BaTiO_3$ similar to the isovalent substations under above mentioned conditions. The effect on independent substitutions i.e. lanthanum and chromium on the dielectric behavior of $BaTiO_3$ has been studied earlier. No report is available as yet on the dielectric and electrical behavior of these systems with simultaneous hetrovalent substitutions in equal concentration. We have limited these studies $x \leq 0.08$ because of interest in dielectric properties.

1.2 Experimental Details

La and Cr Modified $BaTiO_3$ ceramics with $x = 0.02$, 0.04 and 0.08 were prepared by solid state reaction method. High-purity AR-grade $BaCO_3$ (99.9%), La_2O_3 (99.0%), TiO_2 ((97%) and Cr_2O_3 (99.0%). The powders of required amount of compositions were thoroughly grinded in a ball mill for 6 h in the presence of acetone. The grinded powers were dried in a dust-free atmosphere and then calcined at 900°C for 10 h. The calcined powders again ball milled to break the agglomerates. Powders obtained after ball milling were compacted into circular discs at a load of 7 kN. The circular pellets were sintered in a crucible at 1000°C for 10 h. The face of circular sintered pellet were painted using high-purity silver paste the pellets were fired at 400°C for 1 h. Powder X-ray diffraction (XRD) patterns were recorded using a Rigaku X-ray diffractometer with a CuKα radiation. Microstructures of all specimens were studied using field-emission scanning electron microscopy (FE-SEM, Quanta 200 FEG). The surfaces of pellets were coated with gold for the FE-SEM studies. The dielectric constant (ε_r) and tangent loss ($\tan\delta$) of the ceramic specimens were studied as a function of temperature using a HIOKI-LCR (model3532-50) meter in a PID-controlled heating chamber.

II. RESULTS AND DISCUSSION

2.1 Crystal Structure and Microstructure

Attempts were made to synthesize compositions with x = 0.02, 0.04, and 0.08, by solid state ceramic method. Powder x-ray diffraction patterns of these samples were recorded using Cu - $K_{\alpha 1}$ radiation. Compositions with $x \leq 0.08$ have shown the absence of characteristic lines of constituent oxides in their diffraction patterns, which show that the samples with $x \leq 0.08$ are single – phase solid solutions. X-ray diffraction data of the compositions with $x \leq 0.05$ have been indexed on the basis of a tetragonal structure similar to undoped $BaTiO_3$ while for x = 0.10 and 0.15, the data have been indexed on the basis of cubic structure [not shown here]. Lattice parameters, determined by least square fitted of the XRD data, are given in Table – l. The tetragonality (c/a ratio) decreases with increasing x. The theoretical densities have been calculated from the molecular weight and volume of the unit call. Scanning electron micrographs of the polished and chemically etched surface were taken using scanning electron microscope. The grain sizes, calculated by the line intercept method, for sample x = 0.01 is 1μm while for all other samples, it is less than 1μm. Low grain size in these materials may be ascribed to segregation of the dopant ions at the grain boundaries which inhibit the growth in these samples [11].

2.2 Dielectric Behavior

Plots of relative dielectric constant ϵ_r and dissipation factor, D at 75, 275,475 KHz versus temperature for x = 0.02, 0.04, and 0.08 are shown in fig.1 respectively. In pure $BaTiO_3$, it is noted from ϵ_r vs T plots that dielectric anomalies occur at 394K, 283K and 112K these temperatures are very close to the temperatures reported for the transition from cubic to tetragonal, tetragonal to orthorhombic to rhombohedral respectively in undoped $BaLaTiO_3$ [1]. ϵ_r vs T for x=0.02, shown in fig. 1 show the presence of dielectric anomalies at 377K and 275K. These anomalies correspond to cubic to tetragonal and tetragonal to orthorhombic transition in this composition. This is confirmed by the hysterisis loop measurements, which show that this composition is ferroelectric at room temperature (Not shown here). The temperature of the anomaly at 377K does not change with frequency. Corresponding anomalies are observed in D vs T plots also which occur at the same temperature. As we increase the doping concentration of x in $BaTIO_3$ the peak is shift in lower temperature side. The effect of higher doping concentration (x= 0.08) is that the frequency independent dielectric constant becomes frequency dependent.

It is also marked from dielectric graph that the compositions exhibit broad dielectric peak at phase transition temperature, which confirms that samples show dielectric relaxation. The diffuseness behavior of ceramic systems may be explained on the basis of micro-heterogeneities presence in the materials. The micro-heterogeneities take place due to accidental occupation of ions at A and B sites. Such a heterogeneous allocation of ions leads to different relaxation time in different regions in the sample [12-13]. The degree of diffuseness can be calculated with the help of inverse of dielectric constant ($1/\varepsilon_r$) with temperature as proposed by Uchino and Namura [14] at room temperature.

$$1/\varepsilon_r = 1/\varepsilon_{\max} + C^{-1}(T - T_C)^{\gamma} \qquad (1)$$

where C = 2 $\varepsilon_{\max}\delta^2$ and $\varepsilon_{\max}$ are dielectric constant at T_C and δ indicate deviation from Curie Weiss temperature and γ is the degree of diffuseness of the phase transition . If the value of γ = 1, materials are called normal ferroelectrics. However for 1 < γ < 2, they are known as relaxor ferroelectrics, and γ = 2 is known for diffuse phase transition. From figure it is clear that as the value of x increases, γ increases and BLTC becomes disordered in nature. This suggests that the nanoscopic heterogeneity might be present in the sample,which have different local Curie temperatures. So it can be concluded that the sample exhibit relaxor properties with values of γ varying from1.28 to 1.43.

IV. FIGURES AND TABLES

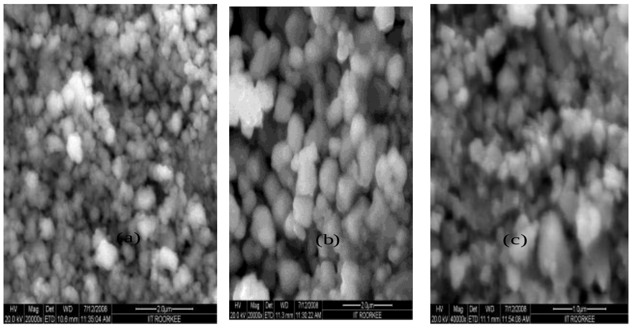

Figure 1: Microstructures of thermally etched samples for compositions x = (a) 0.02, (b) 0.04 and (c) 0.08 in the system $Ba_{1-x}La_xTi_{1-x}Cr_xO_3$

Table 1: Structure, lattice parameters, Unit cell Volume, percentage porosity and average grain size for various compositions (x) in the system $Ba_{1-x}La_xTi_{1-x}Cr_xO_3$.

Composition (X)	Lattice parameters			c/a	Crystal Structure
	a (Å)	b (Å)	c (Å)		
X = 0.02	3.9990	3.9990	4.0173	1.0045	Tetragonal
X = 0.04	3.9955	3.9955	4.0007	1.0013	Tetragonal
X = 0.08	3.9933	3.9933	3.9884	1.0009	Tetragonal

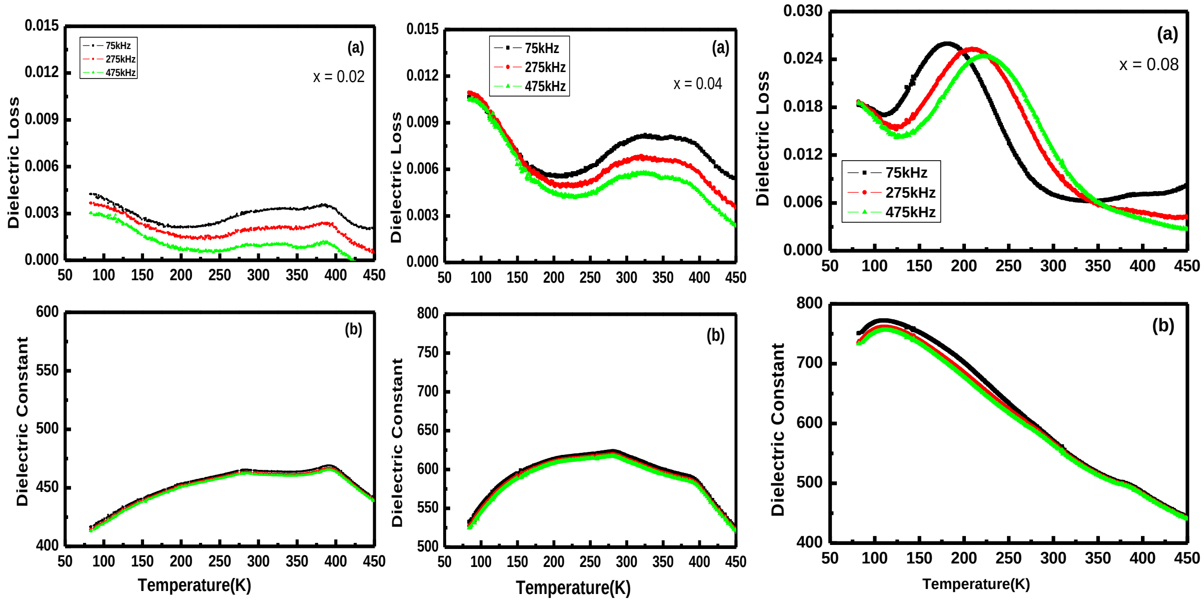

Figure 2. Variation of (a) Dielectric loss and (b) Dielectric constant with temperature forBa$_{1-x}$La$_x$Ti$_{1-x}$Cr$_x$O$_{3.}$

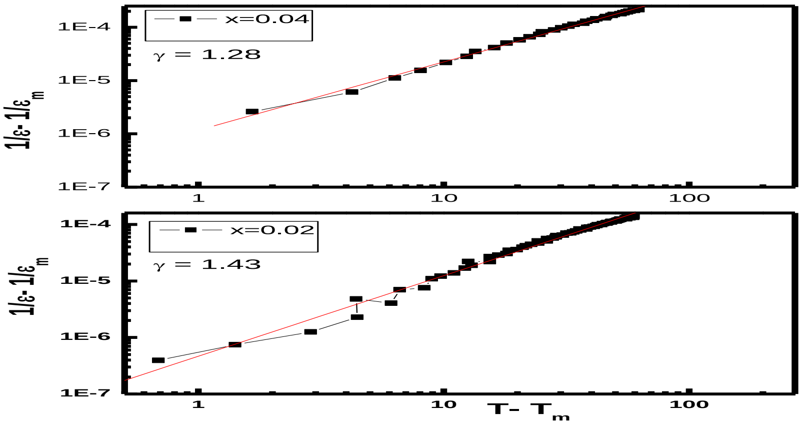

Figure 3. Plots of ln(1/Ɛ$_r$-1/Ɛ$_{max}$) vs ln(T-T$_C$) for x = 0.02 and 0.04 for Ba$_{1-x}$La$_x$Ti$_{1-x}$Cr$_x$O$_3$

V. CONCLUSION

The XRD data collected at room temperature are single phase in nature. From XRD pattern it is clear that compositions are tetragonal at room temperature. The average grain size in these compositions is < 1µm. When the lanthanum and chromium are substituted in BTO the paraelectric to ferroelectric transition temperature does not seem to change. It has been investigated that the value of dielectric constant at transition temperature decreases significantly. However the peak position is independent of frequency at low compositions for x = 0.02 and 0.04. For x =0.08, the peak position is weakly frequency dependent in nature. The composition x = 0.02 and 0.04 are diffuse in nature with values (γ) 1.43 and 1.28. The value of diffuse phase constant is decreases with increasing x value.

REFERENCES

[1] B. Jaffe, W. R. Cook Jr., and H. Jaffe., Piezoelectric ceramics, Journal of Sound and Vibration, 20(4),1971,562-563.

[2] B. Matthias, and Von Hippel A. Domain structure and dielectric response of barium titanate single crystal, Japanese Journal of Applied Physics, 34,1995, 5328–31.

[3] M. M. Nasrallah, H. U. Anderson, A. K. Agarwal, and B. F. Flandermeyer, Oxygen activity dependence of the defect structure of La-doped $BaTiO_3$, Journal of Materials Science, 19 (10), 1984, 3159–3165.

[4] J. F. Fernández, A. C. Caballero, P. Durán, and C. Moure, Improving sintering behaviour of $BaTiO_3$ by small doping additions, Journal of Materials Science, 31(4), 1996, 975–981.

[5] Ko *Takada,* Chang E, and Smyth DM, Equilibrium Conductivity for Er Doped $BaTiO_3$, Japanese Journal of Applied Physics, 26,1987, 42-45.

[6] Vijayeta Pal, A. Kumar, O .P. Thakur, R.K. Dwivedi, N Eswara Prasad, Preparation, microstructure and relaxor ferroelectric characteristics of BLNT–BCT lead-free piezoceramics, Journal of Alloys and Compounds , 714, 2007, 725-735.

[7] Arvind Kumar and S. K. Mishra, Dielectric, piezoelectric, and ferroelectric properties of lanthanum-modified PZTFN ceramics International Journal of Minerals, Metallurgy, and Materials, 21(10), 2014, 1019–1027.

[8] V Pal, OP Thakur, and RK Dwivedi, Effect of co-substitution of La/Li on structure, microstructure, dielectric and piezoelectric behavior of $Bi_{0.50}Na_{0.50}TiO_3$ ceramics, Indian Journal of Physics, 89(2), 2015, 123-130.

[9]Shail Upadhyay, Om Parkash, Devendra Kumar, Preparation and characterization of barium stannate $BaSnO_3$, Journal of Materials Science Letters, 16,1997, 330–1332.

[10] Om Parkash, Devendra Kumar, R. K. Dwivedi, K. K. Srivastava, Prakash Singh, and Sindhu Singh, Effect of simultaneous substitution of La and Mn on dielectric behavior of barium titanate ceramic, Journal of Materials Science, 42,2007, 5490–549.

[10] S Singh, P Singh, O Parkash,a nd D. Kumar, Structural and relaxor behavior of $(Ba_{1-x}La_x)(Ti_{0.85}Sn_{0.15})O_3$ ceramics obtained by solid state reaction, 493(1–2), 2010, 522-528

[12] L. E. Cross, Relaxor – Ferroelectrics. Ferroelectrics,76, 1987, 241-267.

[13] G. A. Smolenskii and A. I. Agranovskaya, Dielectric polarization of a number of complex Compounds, Soviet Physics, Solid State,1, 1959, 1429-1437.

[14] K. Uchino and S. Nomura, Critical Exponents of the Dielectric Constants in Diffused Phase Transition Crystals, Ferroelectrics Letter, 44 (3), 1982, 55-61.