

Effect of Barium Titanate on the parameters of unit cell and electrical properties of



A. H. GHIYA* and B. H. GHIYA**

*Department of Chemistry, Bhalerao Science college Saoner, Dist. Nagpur, 441107 (M.S.), (INDIA)
Mobile No. 922804793 E-mail addresses : ghiyaajit@gmail.com
and ghiyaarjun@yahoo.com

**Department of Physics, L.A.D. College Shankar Nagar Square, Nagpur (M.S.) (INDIA)
Email address-jaiswalbhim@gmail.com.

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Abstract

Structural characteristic and electrical properties of new type of perovskites with formula $\text{Ba}_x [\text{Dy}_{0.25} \text{Li}_{0.25} \text{Be}_{0.50}]_{1-x} \text{TiO}_3$ ($0 \leq x \leq 1$) are prepared and investigated. The new perovskite $\text{Dy}_{0.25} \text{Li}_{0.25} \text{Be}_{0.50} \text{TiO}_3$ crystallizes with orthorhombic distorted perovskite structure, while $\text{Ba}_x [\text{Dy}_{0.25} \text{Li}_{0.25} \text{Be}_{0.50}]_{1-x} \text{TiO}_3$ ($0 \leq x \leq 1$) crystallizes with tetragonal distorted perovskite structure. Because of high melting points of oxides used here, samples are usually prepared by pressing and sintering powder. The anomaly in the relationship between electrical conductivity and dopant concentration in BaTiO_3 is related to obstruction of grain growth during sintering. Above a certain dopant concentration the microstructure remains fine grained, thus resulting in the suppression of electrical conductivity due to existence of barrier layers. The concentration of Ba vacancies is added by the dopant concentration, and by the partial pressure of oxygen PTC type BaTiO_3 ceramics were prepared and analyzed. The electrical properties of the composition in the series $\text{Ba}_x [\text{Dy}_{0.25} \text{Li}_{0.25} \text{Be}_{0.50}]_{1-x} \text{TiO}_3$ ($0 \leq x \leq 1$) are reported. A probable mechanism for the conduction in these compounds is also proposed.

Key words : X-ray diffraction, perovskite, orthorhombic, tetragonal, tolerance factor, barium titanate. PTC.

1 Introduction

The most common Perovskite structure is a simple cubic cell with one ABX_3 formula

unit per unit cell. In this case the A ions are at the corners of the unit cell with the B ions at the centre and the negative ions occupying the face centered position. The atomic arrangement in this structure was first found for the minerals

Perovskite CaTiO_3 but H.D. Megaw¹ found it to be orthorhombic though it retained the name Pervoskite. The BaTiO_3 has ideal Perovskite structure. For BaTiO_3 , the new structure was worked out using x-ray by Danner *et al.*² using neutron diffraction analysis as tetragonal with a & $b = 3.99\text{\AA}$ & $c = 4.04\text{\AA}$. The structure becomes orthorhombic³⁻⁵ below 0°C , with $a = 5.682\text{\AA}$, $b = 5.669\text{\AA}$ and $c = 3.99\text{\AA}$. The unit cell contain two formula units and Ti atoms is displaced from its symmetrical position by 0.06\AA . In order to have contact between the A, B & O ions of Perovskite structure, $R_A + R_O$ should equal to $t \sqrt{2(R_B + R_O)}$ where R_A , R_B & R_O are the ionic radii of A, B, O ions respectively and t is the tolerance factor. Goldschmidt⁶ has shown that the cubic perovskite structure is stable only if a tolerance factor 't' define by $R_A + R_O = t \sqrt{2(R_B + R_O)}$, has an approximate range $0.8 \leq t \leq 0.9$ and somewhat larger range for distorted Perovskite structure. Crystal growth for Perovskite, which was earlier a relatively narrow field of material science, has now been identified as a thrust area among the major areas of science and technology. This become true after the discovery of novel materials which bridge the gap between technology and human life, Perovskite crystals find applications in electronics, lasers, communication devices⁷⁻⁸, thermal imaging, pyroelectric detectors⁹, x-ray spectroscopy¹⁰⁻¹¹, etc. The dielectric properties of Perovskite structure $\text{K}_{1-x}\text{Na}_x\text{NbO}_3$ for some of the composition has been extensively studied at high temperature¹². Verway *et al.*¹³ describe a new type of semiconductor, which contain a fraction of ions of different valency without a simultaneous formation of an ionic vacancy or interstitial. Most of the Perovskites

are known to possess high electrical resistivities which make them useful as dielectric materials. Plot of log resistivity ($\log \sigma$) Vs $1/T$ usually produce a straight line from which the activation energy (ΔE) is obtained. In a plot of $\log \sigma$ Vs $1/T$ for $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ it was observed that below the curie-temperature (T_c) a minimum in $\log \sigma$ occurs and above T_c , a much lower resistance is obtained.

2 Method

All the required compounds were kept in a vacuum oven maintained at 120°C for 4-6 hours and then were kept in desiccator. As rare earth oxides are very costly, only about 1.5 to 2.0 grams of the mixture in each case was prepared. The desired oxide constituent was weighed accurately on an electronic single pan balance in a weighing bottle, the mixed powder was then transferred into an agate mortar. The mixture was then grounded finely in a mortar for one hour, using acetone to ensure effective mixing of all the constituents. The 5% solution of polyvinyl acetate in acetone was then treated with this finely rounded mixture, about 2-3 ml of the binder solution per gram of the powder was found to give well molded pellets. The semisolid plastic like mass containing the binder was moulded in a die specially fabricated for this purpose. The die is extra advantageous because vacuum is created and maintained inside when the pellets are being pressed the pellets formation not only improved the compressibility of the powder to a large extent but also avoided the air trapped during the moulding process. A vacuum of 10^{-2} mm of mercury was maintained while pellets formation by applying a pressure of 3000 Kg cm^{-2} . The pellets were prepared on a Carver Laboratory press fitted with a

calibration gauge. The size of the pellets were normally of 12 mm diameter. The binder from the pellets was first evaporated by slow heating in air upto 300°C for one hour, after which the temperature of the furnace was raised gradually to 900°C for 12 hours and latter to a sintering temperature of 1300°C for five hours. The samples were furnace cooled to room temperature in air. The two faces of each pellet (As Prepared by method describe earlier) were coated with a thin layer of conducting colloidal silver paste (A.R.grade) and allow to dry in air at room temperature. These were then heated in a furnace at 500°C. for two hours, and then slowly cooled to room tempreture. These are tested for any short circuiting or discontinuity in faces.

3 Characterization :

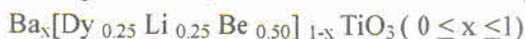
The X-ray diffractometer from Philiphs Holand (model psr / 9/..II) was used for recording the x-ray diffraction patterns of the sintered pellets so prepared. The pellets were grounded to 300 mesh and diffraction patterns were taken by using Cu-K α radiations ($\lambda = 1.54056\text{\AA}$) filtered through Ni/Zr foils. The

instrument is well calibrated with silicon standard samples and the lines obtained are matching with the standard lines. At room temperature some composition exhibit the orthorhombic symmetry while other shows tetragonal symmetry. The sub-cell parameters were obtained using the auto -X computer software and were compatible with those earlier for ceramics¹⁴⁻¹⁶, thus indexing was done for new compositions. For measuring resistance of the order of 10^5 to 10^{12} ohms, conductivity bridge was used.

4 Results and discussion

Pure $\text{Dy}_{0.25}\text{Li}_{0.25}\text{Be}_{0.50}\text{TiO}_3$ with the orthorhombic structure with $a=5.4331\text{\AA}$, $b = 5.9953\text{\AA}$ and $c = 7.5927\text{\AA}$, the pure compound has a tolerance factor (t) 0.693 so that the structure could be visualized as orthorhombic distortion of the cubic perovskite structure. This observation agrees with that of schreider *et al.* (1961) who placed a lower limit of 0.702 for the rare-earth mixed and that of Keith and Roy (1954) who placed a lower limit of 0.707 for the perovskite structures of the $\text{A}^2\text{-B}^4\text{-O}_3$ type. Table 1 shows the variation in unit cell para-meters values of system.

Table 1. Unit cell parameters, tolerance factor and density values of



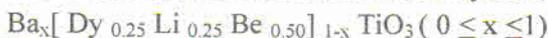
Composition	Symmetry	a	b	c	c/a	b/a
		A°				
$\text{Dy}_{0.25}\text{Li}_{0.25}\text{Be}_{0.50}\text{TiO}_3$	O	5.4331	5.9953	7.5927	1.3874	1.095
$\text{Ba}_{0.15}\text{Dy}_{0.25}\text{Li}_{0.25}\text{Be}_{0.50}\text{TiO}_3$	O	5.3765	5.7979	7.3094	1.3595	1.078
$\text{Ba}_{0.30}\text{Dy}_{0.25}\text{Li}_{0.25}\text{Be}_{0.50}\text{TiO}_3$	O	5.4263	5.8037	6.9829	1.2868	1.069
$\text{Ba}_{0.45}\text{Dy}_{0.25}\text{Li}_{0.25}\text{Be}_{0.50}\text{TiO}_3$	O	6.5330	5.7331	7.0198	1.2689	1.036
$\text{Ba}_{0.60}\text{Dy}_{0.25}\text{Li}_{0.25}\text{Be}_{0.50}\text{TiO}_3$	T	4.0222	4.0222	4.2442	1.0551	1.000
$\text{Ba}_{0.80}\text{Dy}_{0.25}\text{Li}_{0.25}\text{Be}_{0.50}\text{TiO}_3$	T	4.0219	4.0219	4.1972	1.0435	1.000
BaTiO_3	T	3.9820	3.9820	4.0358	1.0328	1.000

O= Orthorhombic T= Tetragonal

Table 2 shows the inter ionic distances for samples calculated by the method suggested by Yakel¹⁷ and the radius sums (R_A+R_O) for different compositions and differences (δ) between the theoretical and observed distances. The relative ' δ ' values indicate small inter ionic distances between oxygen ions and Ti^{+4}

ions, these values probably reflect partial covalent bond character and can be seen to increase with increasing Ba^{+2} % mole concentration. It can be seen from table that the δ_1 values indicate the co-valent character of the B-O bonds exhibit regular decrease with Ba^{+2} concentration.

Table 2. Inter ionic distances calculated by Yakel's method and difference between theoretical and observed distances for system



Composition	$(R_A+R_B) (O-A)_{obs}$		δ_2	$(R_B-R_O) (O-B)_{obs}$		δ
	A°	A°		A°	A°	
$Dy_{0.25} Li_{0.25} Be_{0.50} TiO_3$	1.967	2.224	0.257	2.005	1.573	-0.432
$Ba_{0.15} Dy_{0.25} Li_{0.25} Be_{0.50} TiO_3$	2.081	2.159	0.078	2.005	1.526	-0.479
$Ba_{0.30} Dy_{0.25} Li_{0.25} Be_{0.50} TiO_3$	2.197	2.134	-0.063	2.005	1.508	-0.497
$Ba_{0.45} Dy_{0.25} Li_{0.25} Be_{0.50} TiO_3$	2.312	2.142	-0.170	2.005	1.515	-0.490
$Ba_{0.60} Dy_{0.25} Li_{0.25} Be_{0.50} TiO_3$	2.748	1.447	-0.301	2.005	1.023	-0.982
$Ba_{0.80} Dy_{0.25} Li_{0.25} Be_{0.50} TiO_3$	2.649	1.442	-1.207	2.005	1.019	-0.986

$$\delta_2 = (O-A) - (R_A+R_B) A^\circ \quad \text{and} \quad \delta_1 = (O-B)_{obs} - (R_B+R_O) A^\circ$$

The 't' values for perovskite on other hand show (table 3) an increase with Ba^{+2} addition from 0.693 to 0.934 which indicates an orthorhombic distortion decreases and the end members show tetragonal symmetry.

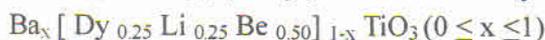
Table 3. Tolerance factor values of $Ba_x [Dy_{0.25} Li_{0.25} Be_{0.50}]_{1-x} TiO_3 \quad (0 \leq x \leq 1)$

Composition	R_A	R_B	R_O	t
	A°			
$Dy_{0.25} Li_{0.25} Be_{0.50} TiO_3$	0.567	0.605	1.400	0.693
$Ba_{0.15} Dy_{0.25} Li_{0.25} Be_{0.50} TiO_3$	0.681	0.605	1.400	0.733
$Ba_{0.30} Dy_{0.25} Li_{0.25} Be_{0.50} TiO_3$	0.797	0.605	1.400	0.774
$Ba_{0.45} Dy_{0.25} Li_{0.25} Be_{0.50} TiO_3$	0.912	0.605	1.400	0.815
$Ba_{0.60} Dy_{0.25} Li_{0.25} Be_{0.50} TiO_3$	1.348	0.605	1.400	0.969
$Ba_{0.80} Dy_{0.25} Li_{0.25} Be_{0.50} TiO_3$	1.249	0.605	1.400	0.934

t = Tolerance factor

From Table 4 it is clear that measured density values (D_M) suggest four formula unit per unit cell ($Z=4$) for first four compositions and one for remaining compositions.

Table 4. D_M and D_{cal} (X-ray) values for the system



Composition	D_M	D_{cal} (x-ray)	Z
	g.ml ⁻¹		
$\text{Dy}_{0.25}\text{Li}_{0.25}\text{Be}_{0.50}\text{TiO}_3$	5.36	5.70	4
$\text{Ba}_{0.15}\text{Dy}_{0.25}\text{Li}_{0.25}\text{Be}_{0.50}\text{TiO}_3$	5.47	5.56	4
$\text{Ba}_{0.30}\text{Dy}_{0.25}\text{Li}_{0.25}\text{Be}_{0.50}\text{TiO}_3$	5.83	5.94	4
$\text{Ba}_{0.45}\text{Dy}_{0.25}\text{Li}_{0.25}\text{Be}_{0.50}\text{TiO}_3$	5.85	6.00	4
$\text{Ba}_{0.60}\text{Dy}_{0.25}\text{Li}_{0.25}\text{Be}_{0.50}\text{TiO}_3$	4.74	4.87	1
$\text{Ba}_{0.80}\text{Dy}_{0.25}\text{Li}_{0.25}\text{Be}_{0.50}\text{TiO}_3$	5.36	5.54	1

Z indicate formula unit per unit cell

It can be seen that the orthorhombic strain ($b/a = 1.095$) present in the pure phase did not disappear but decreases by the addition of 15 mol % BaTiO_3 since the tolerance factor values of the composition increases to 0.733. The c/a value goes on decreasing as the Ba^{2+} concentration increases in contrast to the normal increase in tetragonality (c/a) with increase in size of the ion ($\text{Ba}^{2+} = 1.32 \text{ \AA}$, $\text{Dy}^{3+} = 0.908 \text{ \AA}$, $\text{Li}^+ = 0.60 \text{ \AA}$, $\text{Be}^{2+} = 0.30 \text{ \AA}$) this discrepancy could be understood by comparing the t value of different composition in the series.

It is also seen that there is an increase in the value of t with increase in Ba^{2+} concentration so that the structure gradually changes to that of the perovskite lattice, where the tetragonality (c/a) is nearly 1.0328 for pure BaTiO_3 . This may be ascribed to the polarization of the constituent ions (Roberts 1949, 1951)

which might play an important, role in determining the symmetry formed by a given perovskite structure as shown in figure 1.

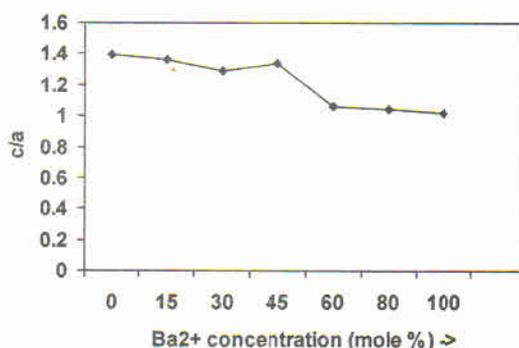
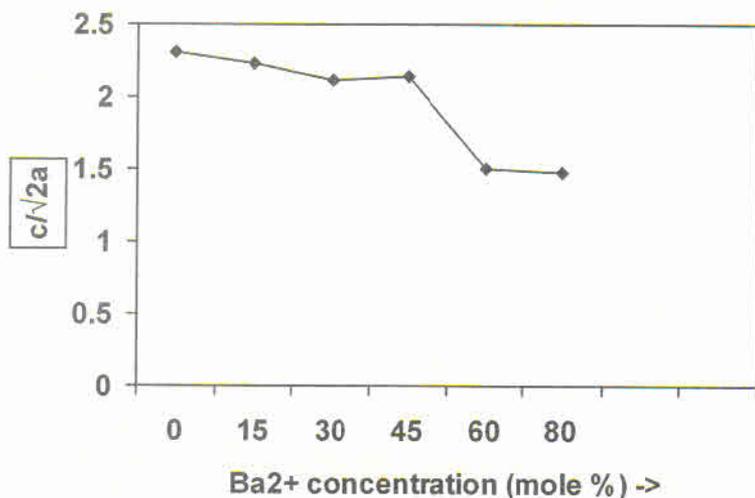


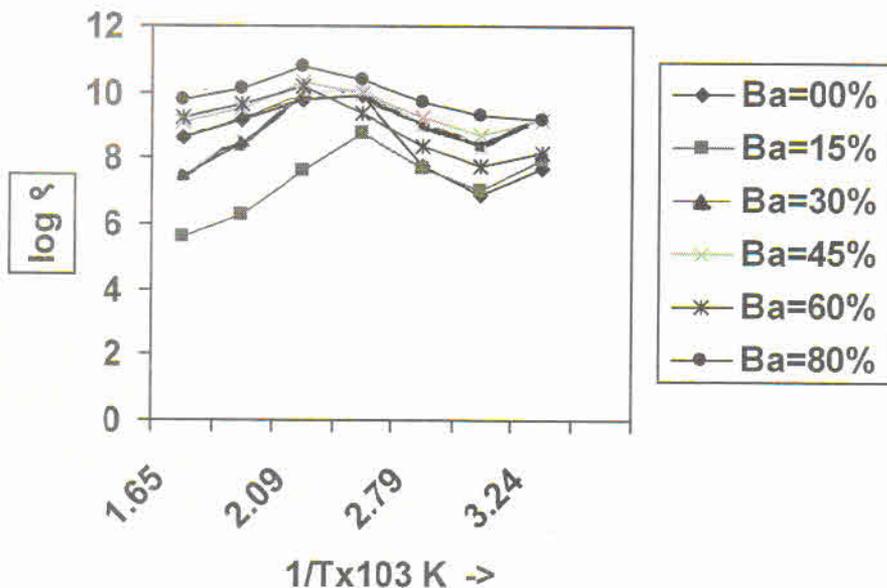
Fig. 1. c/a Vs Ba^{2+} conc. of $\text{Ba}_x(\text{Dy}_{0.25}\text{Li}_{0.25}\text{Be}_{0.50})_{1-x}\text{TiO}_3 (0 \leq x \leq 1)$

From Fig. 2 i.e. the plot of $c/\sqrt{2a}$ Vs Ba^{2+} concentration (conductivity) it indicates that behavior is reminiscent of the structural changes.

Fig. 2. $c/\sqrt{2a}$ Vs Ba^{2+} conc. of $Ba_x(Dy_{0.25}Li_{0.25}Be_{0.50})_{1-x}TiO_3$ ($0 \leq x \leq 1$)

The variation of $\log \epsilon$ Vs $1/T$ Fig. 3 shows that the resistivity (range 0.40×10^6 to 6.34×10^{10} ohm/cm) first increases with temperature passes through a maximum and then

again decreases indicating conductivity first decreases, goes to minimum and again shoot up.

Fig. 3. $\log \epsilon$ Vs $1/T \times 10^3$ K for the system $Ba_x(Dy_{0.25}Li_{0.25}Be_{0.50})_{1-x}TiO_3$ ($0 \leq x \leq 1$)

The temperature (Tr at which maximum resistivity occurred varies from system to system. It is also seen that in the pure phase the Tr value goes on decreasing with the increase in the ionic radius except La system. The highest resistivity (65.97×10^9 ohm/cm) is seen for $\text{Ba}_{0.80}\text{Dy}_{0.25}\text{Li}_{0.25}\text{Be}_{0.50}\text{TiO}_3$ and lowest resistivity value (46.30×10^{10} ohm/cm) for $\text{La}_{0.25}\text{Li}_{0.25}\text{Be}_{0.50}\text{TiO}_3$ composition but pure BaTiO_3 have highest value of resistivity (6.8×10^{10} ohm/cm).

5 Conclusion

The pure phase ($x=0$) was not crystallize with the orthorhombic distorted perovskite structure. The stability limit of the perovskite structure in terms of the tolerance factor 't' is given by

$$t = \frac{R_A + R_O}{\sqrt{2}(R_B + R_O)}$$

Where R_A , R_B and R_O denote the ionic radius of the A, B and O ions respectively. The minimum value for the tolerance factor 't' is found to be 0.693 as compared to 0.780 reported by Schneider *et al.* The orthorhombic distortion b/a in these compounds disappeared with the addition of more than 80 mole % BaTiO_3 . The c/a and b/a both exhibit a linear increase with decreasing radius of Ln^{+3} ion indicating thereby that the strain in the lattice increases with decrease in size of the A (Ln^{+3} , Li^+) ion. This has been ascribed to the partial covalent character of the cation-oxygen bond and also to the lanthanide contraction. Since Ba^{+2} ($r=1.42\text{Å}$) is larger in size than Ln^{+3} ,

Li^+ and Be^{+2} ion (size range 0.90-0.810Å for La-Y) this has been explain in terms of i) polarizability of ions at the A site, ii) the covalent character of the A-O bond which increases with the increasing BaTiO_3 incorporation in the series. For pure phases, the Tr goes on decreasing as the radius of the Ln^{+3} ion decreases. This has been ascribed to the decrease in the covalent character of the Ln-O bond down the rare earth series. The conduction in these compounds have been explained in terms of a band transport mechanism through the anion exchange given by



the conduction being 'n' type in the low symmetry and 'p' type in the high symmetry form. The transition from 'n' type to 'p' type is explain on the basis of the changes over from the electron hoping mechanism at the $\text{Ti}^{+4} \rightarrow \text{Ti}^{+3}$ site to a positive hole migration ($\text{O}^{2-} \rightarrow \text{O}^{-1}$) in high temperature region.

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