Indian J. Phys. **72A** (4), 337–341 (1998)

NOTE

IJP A
- an international journal

Structural and dielectric studies on lanthanum modified $Ba_2LiNb_5O_{15}$

K Sambasiva Rao, K Koteswara Rao, T N V K V Prasad
and M Rajeswara Rao
Solid State Physics Laboratory, Department of Physics, Andhra University, Visakhapatnam-530 003, India

Received 5 September 1997, accepted 17 April 1998

Abstract : Present paper describes the ceramic preparative conditions and the effect of lanthanum (La) on structure and dielectric properties of $Ba_2LiNb_5O_{15}$ (BLN). The materials have been sintered at 1150°C. The low sintering temperature in these compositions attribute to the presence of lithium. Unit cell parameters obtained from XRD studies indicate an orthorhombic structure. Curie temperature of BLN has been found to decrease with La-content

Keywords : $Ba_2LiNb_5O_{15}$, structure, dielectric properties

PACS Nos. : 77.22.–d, 61.66.Fx

One of the most important and numerous groups of ferroelectrics is the family of oxygen-octahedra crystals. The ease of these crystals is a combination of oxygen-octahedra centres and voids of which other ions are located. One of the family members of oxygen octahedra ferroelectrics belongs to the distorted potassium tungsten bronze (TB) structure. The standing representatives of this group are single crystal solid solutions, barium strontium niobate (SBN), barium sodium niobate (BNN), barium silver niobate (BAN) and barium lithium niobate (BLN) [1–4]. The greatest interest in these materials are due to their optical non-linearity and device applications [5–7].

A useful non-linear optical crystal [4], barium lithium niobate, $Ba_4Li_2Nb_{10}O_{30}$ belongs to TB structure with a point group 4 mm. The BLN has phase transition temperature at 586°C. The transition in BLN is first order. It has no microtwinning at room temperature unlike BNN.

However, studies on ceramic materials of lanthanum doped BLN is still not widely found. The present communication describes the preparation, characterization and dielectric studies on lanthanum (La) doped and undoped BLN.

Raw materials used for the preparation of ceramic samples are of reagent grade, $BaCO_3$, Li_2CO_3, La_2O_3 and Nb_2O_5. The constituent carbonates and oxides were weighed to yield the following compositions and mixed well in an agate motor and pestle and calcined at 875°C for 6 hours. This procedure was repeated twice to give more homogeneous, single phase materials and then sintered at 1150°C for 4 hours. The compositions are

$Ba_4Li_2Nb_{10}O_{30}$	BLN,
$Ba_{3.8}Li_{2.1}La_{0.1}Nb_{10}O_{30}$	0.1 La-BLN,
$Ba_{3.6}Li_{2.2}La_{0.2}Nb_{10}O_{30}$	0.2 La-BLN,
$Ba_{3.4}Li_{2.3}La_{0.3}Nb_{10}O_{30}$	0.3 La-BLN.

Lattice constants are determined by the powder method on X-ray powder diffractometer, available at RSIC, Nagpur University, Nagpur, India, using CuK_α radiation. Dielectric constant has been measured at 1 KHZ using a digital LCR meter type VLCR-6. Silver paste, fired on the surface of the well sintered ceramic specimens cured at 600°C was used to form the electrodes.

The compositions are sintered at low temperature due to the presence of lithium and gives liquid phase sintering. The XRD patterns obtained on BLN have been nicely matched with JCPD [8]. Figure 1 indicates the XRD pattern on BLN. Also, it is found that XRD

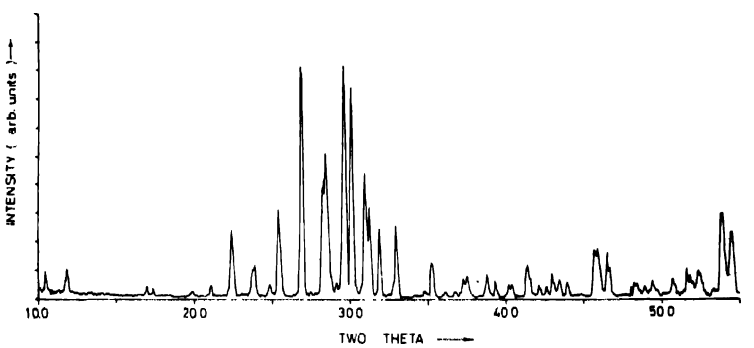

Figure 1. XRD pattern of $Ba_4Li_2Nb_{10}O_{30}$.

peaks are single phase belonging to orthorhombic structure [9]. XRD peaks on BLN have been indexed in Table 1. It is observed that the values of d-spacing observed (d_{obs}) and calculated (d_{cal}) are very much closer. It shows that the assignment of Miller indices h, k, l, values are correct.

The computed lattice parameters are a = 10.194 Å, b = 14.874 Å and c = 7.928 Å, which agrees well with literature values [8] a = 10.197 Å, b = 14.882 Å and c = 7.942 Å. Substitution of La-in BLN does not affect the orthorhombic structure of BLN. Table 2 shows the lattice constants of BLN and lanthanum doped BLN.

Table 1. XRD data on BLN.

d_{obs}	d_{cal}				I/I_0 (%)
5.0895	5.0970	2	0	0	3
4.1962	4.2044	2	2	0	5
3.9574	3.9640	0	0	2	29
3.7140	3.7187	0	4	0	12
3.5807	3.5856	1	1	2	5
3.4966	3.4982	0	2	2	37
3.3074	3.3127	3	1	0	100
3.1250	3.1291	2	0	2	60
3.0075	3.0621	2	1	2	99
2.9626	2.9625	1	3	2	88
2.8840	2.8842	2	2	2	52
2.8543	2.8558	1	5	0	35
2.8005	2.8029	3	3	0	28
2.7127	2.7127	0	4	2	31
2.5477	2.5485	4	0	0	11
2.4797	2.4791	0	6	0	2
2.4115	2.4109	4	2	0	7
2.3922	2.3943	2	4	2	9
2.3178	2.3171	1	5	2	9
2.2888	2.8886	3	3	2	6
2.2389	2.2383	3	5	0	5
2.2279	2.2294	2	6	0	4
2.1438	2.1437	4	0	2	5
2.1187	2.1218	4	1	2	4
2.1031	2.1022	4	4	0	10
2.0797	2.0802	1	7	0	6
2.0600	2.0598	4	2	2	5
1.9834	1.9820	0	0	4	20
1.9493	1.9491	3	5	2	19
1.8810	1.8856	5	3	0	4
1.8593	1.8593	0	8	0	4
1.8430	1.8420	1	7	2	5
1.7984	1.8017	3	7	0	7
1.7683	1.7615	5	2	2	12
1.7442	1.7467	2	8	0	10
1.7027	1.7028	5	3	2	33
1.7022	1.6990	6	0	0	36
1.6832	1.6833	0	8	2	27

Table 2. XRD and dielectric data.

Comps	Lattice parameters Å			Dielectric data			
		b	*c*	K_{RT}	K_{TC}	T_d°C	T_c°C
BLN	10.194	14 874	7.928	380	1110	610	600
0 1 La-BLN	10.189	14 878	7 932	243	5620	470	478
0 2 La-BLN	10 180	14 888	7 962	159	1607	410	390
0 3 La-BLN	10 182	14 904	7 969	185	3329	--	290

Variation of dielectric constant with temperature of BLN and lanthanum doped BLN have been shown in Figure 2. On the basis of the Lyddane-Sachs-Teller (LST) relation [10], Fröhlich [11] predicted that the static dielectric constant of oxygen octahedra ferroelectrics would go to infinity, when the frequency of the lowest transverse optical

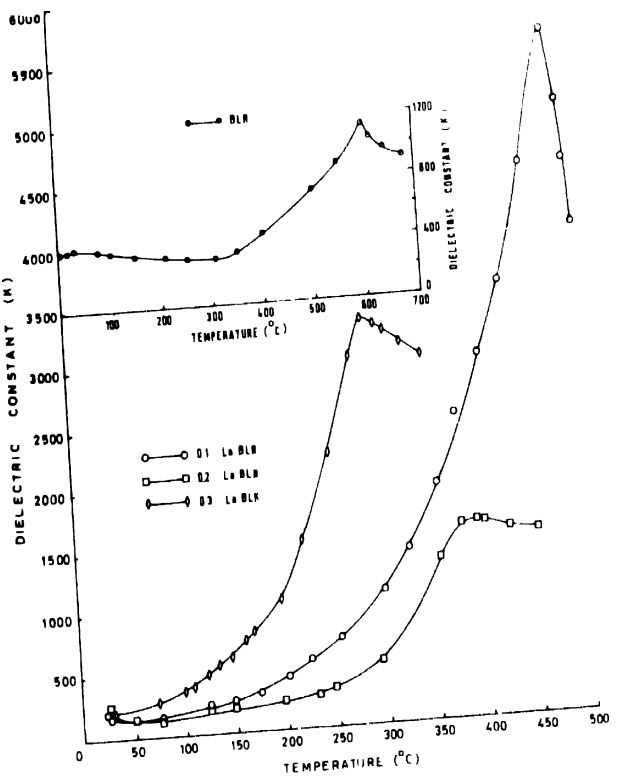

Figure 2. Variation of dielectric constant with temperature of BLN and La BLN

mode goes to zero. Also, the behaviour of static dielectric constant of ferroelectric material [illegible] Weiss law

where C is Curie constant. T_c is the transition temperature. Therefore, as the temperature of the sample approaches transition temperature T_c, the static dielectric constant goes to a maximum value. It is evident that a maximum dielectric constants (K_{T_c}) of 1110 has been observed at 600°C in BLN indicating of its transition temperature (T_c). The observed T_c is very much close to reported value of 586°C [4]. Also, substitution of La-in BLN affects the T_c, which decreases with increase of La-content from 600 to 290°C. The Curie temperature obtained on BLN from differential thermal analysis (DTA) peak temperature of exotherm (T_d) is 610°C, close to experimental value 600°C. The Curie temperatures (T_d) obtained from DTA on 0.1 La-BLN and 0.2 La-BLN are 470°C and 410°C, closed to 478 and 390°C obtained from dielectric measurements. The room temperature dielectric constant (K_{RT}) of La-doped BLN indicates a decrease with increase of La. But, there is no systematic variation. This decrease of K_{RT} may be due to increase in T_c. Similar behaviour has been reported in rare earth modified BNN and BAN ceramics [12,13]. The Curie Weiss law has been obeyed in all the materials and Curie constant (C) in each composition has been computed and found to be of the order of 10^5 K, closed to reported value [4]. It has been observed that the variation of Curie constant with the dopant concentration is very small. The value C is the evidence that the materials belong to oxygen octahedra. The dielectric data is given in Table 2.

It has been concluded that the materials are sintered at a low temperature which may be due to the presence of lithium. Substitution of La affects the T_c, K_{RT} and K_{T_c} of BLN but not structure of BLN. The value of C, 10^5 K indicates that the materials belong to oxygen octahedra.

Acknowledgment

One of the authors, K S Rao is grateful to the Council of Scientific & Industrial Research (CSIR), New Delhi, India, for their financial support.

References

[1] W A Bonner, J R Carruthers and H M O Bryan *Mater. Res. Bull.* **5** 243 (1970)

[2] R R Neurgaonkar, W K Cory and J R Oliver *J. Cryst. Growth* **84** 629 (1987)

[3] Tokuko Sugai and Masanobu Wada *Japan J. Appl. Phys.* **13** 8 (1974)

[4] Hitoshi Hirano, Hunuhiko Takeir and Shigenao Koide *Jpn. J. Appl. Phys.* **9** 580 (1970)

[5] J E Geusic, H J Levinstein, J J Rubin, S Singh and L G Van Uitert *Appl. Phys. Lett.* **11** 269 (1967)

[6] J E Geusic, H J Levinstein, S Singh, R G Smith and L G Van Uitert *Appl. Phys. Lett.* **12** 306 (1968)

[7] R G Smith, J E Geusic, H J Levinstein, J J Rubin, S Singh and L G Van Uitert *Appl. Phys. Lett.* **12** 308 (1968)

[8] JCPDS 27 1215 (1977)

[9] M Matthes *J. Cryst. Growth* **15** 157 (1972)

[10] R H Lyddane, R G Sachs and E Teller *Phys. Rev.* **59** 673 (1941)

[11] H Frohlich *Theory of Dielectrics* (Oxford: Clarendon) (1949)