Effect of Certain Modifier Oxides on Physical and Thermoluminescence Properties of Antimony-Borate Glasses

C. Laxmikanth[1], Ayinalem Gashaw[1], Kassa Belachew[1], Eyob Belew Ababa[2]
[1]Department of Physics, Wollo University, Dessie, Ethiopia.
[2]Department of Materials Science and Engineering, Adama Science and Technology University, Ethiopia.

Abstract- Glasses with composition of 10MO-40Sb_2O_3-50B_2O_3 (where MO = ZnO, CdO, CaO, and BaO) were prepared by melt quenching method. Various physical parameters of these glass materials were calculated and presented. Amorphous nature of these materials was confirmed from XRD and DTA studies. Various stability factors were calculated and presented from DTA analysis; from the results, the stability of the glass network is observed to decrease with increase in ionic radii of modifier ion from ZnSB to BaSB glass with increase in ionic radii of the modifier ion. IR spectral analysis of these glasses exhibited several symmetrical and asymmetrical bands due to borate, antimonite, and zinc structural units; with increase in ionic radii of modifier ions in the glass matrix, it has been observed that the intensity of BO_3 (asymmetrical) band increased at the expense of BO_4 & ν_1-Sb_2O_3 (symmetrical) band, with shifting of its meta-centre towards lower frequency, which suggests an increase in degree of disorder in the glass network from ZnSB to BaSB glass with an increase in ionic radii of the modifier ion. From TL analysis, the intensity of the glow peak is found to increase from ZnSB to BaSB glass in an increasing order of ionic radii of modifier ions; further, the studies suggest that BaSB glass can be used more effectively in radiation dosimetric applications.

Index Terms- Antimony-borate glasses, glass forming ability parameter, IR studies, thermoluminescence, trap depth parameters, radiation dosimetry.

I. INTRODUCTION

Among the various oxide glasses, borate glasses have attracted much attention because of their electrochemical and optical applications, namely as solid-state lasers, optical waveguides and luminescent materials. Borate glass is a particularly suitable optical material because of its high transparency, relatively low melting point, high thermal stability, different coordination numbers and good rare earth ions solubility [1]. Borate glasses, in particular, have been the subject of numerous infra-red studies due to their structural peculiarities [2-5]. In pure B_2O_3 glass structure most of the boron is involved in B_3O_6 (boroxol) ring. Addition of modifier breaks boroxol ring and thereby produced BO_3 and BO_4 units [6-9]. In addition, modifier also changes the physical properties along with structural modifications. The heavy metal oxide based glasses like Sb_2O_3 glasses have attracted extensive investigation in recent years because of their potential applications in non-linear optics and broad band optical amplifiers [10-15]. Further, these glasses are known due to their significant transmission potential in the infrared region and have large refractive index when compared with the conventional borate and silicate glasses [16-17]. Most of the studies available on Sb_2O_3 glasses are on the understanding of their structural aspects by X-ray and neutron diffraction studies [20-23]. Very few studies are available on electrical properties of these glasses [24, 26] and most of them are restricted to the d. c. conductivity measurements. The antimony-borate based glasses are of scientific and technological interest. Starting from the pioneer study by Imaoka et al [27], the binary Sb_2O_3–B_2O_3 glasses have been a subject for structural investigations because Sb_2O_3–B_2O_3 glasses have been considered as promising materials for nonlinear optical applications. There were several attempts made to improve the physical characteristics of these glasses to a considerable extent, by the addition of different modifier metal. Among the four modifier oxides chosen to mix in the present glass system, viz., ZnO, CdO, CaO, and BaO; ZnO is expected to shorten the time taken for solidification of glasses during the quenching process. Both ZnO and Cd are thermally stable and appreciably covalent in character [28]. CaO and BaO are chosen for investigation purpose (as the difference in their ionic radii is more). Also, glasses containing heavy metal oxides such as BaO found applications in plasma displays, gamma ray radiation shields [29], and so forth in addition to exhibiting good chemical durability and higher refractive indices. Addition of CaO and BaO to borate network stabilizes the glasses [29]. In view of these, it is felt worthwhile to have some understanding on the effect these different modifiers over the various physical structures and thermoluminescence properties of Sb_2O_3-B_2O_3 glasses.

II. EXPERIMENTAL

In the present study, the glasses were prepared by the melt-quenching technique. The starting materials Sb_2O_3, $Na_2B_4O_7.10H_2O$, ZnO, CdO, CaO, and BaO that used for the preparation of the present glass systems were with analar grade (larger than 99.9% purity). The chemicals with appropriate weight fractions used in preparation of glass samples were presented in Table 1.

Table 1: Shows the specific composition of MO-Sb_2O_3-B_2O_3 glasses.

Sample	SB wt.%	ZnSB wt.%	CdSB wt.%	CaSB wt.%	BaSB wt.%
Sb_2O_3	40	40	40	40	40
B_2O_3	60	50	50	50	50
ZnO	-	10	-	-	-
CdO	-	-	10	-	-
CaO	-	-	-	10	-
BaO	-	-	-	-	10

III. RESULTS AND DISCUSSION

A. Physical Parameters

The density d of the glasses was determined by the standard principle of Archimedes' using o-xylene (99.99% pure) as the buoyant liquid. The refractive index n_d of the optically polished glasses was measured using sodium vapour lamp λ = 589.3 nm on a precession Abbe's refractometer. The molar volume, V_M, of the glass samples was calculated by using the formula, $V_M = \frac{\bar{M}}{d}$. From the measured values of density, average molecular weight, and refractive index, and molar volume are calculated and presented in Table 2.

Table 2. Physical parameters Sb_2O_3-B_2O_3 based glasses with different modifier oxides.

Physical Parameters	SB	ZnSB	CdSB	CaSB	BaSB
Average molecular weight, $\bar{M}$	202.100	195.375	194.533	195.336	195.972
Density, d (g/cm^3)	2.630	3.823	5.678	2.912	3.986
Molar volume, V_M	23.449	23.398	23.379	23.338	23.283
Refractive index, n_d	1.586	1.572	1.588	1.590	1.595

B. XRD Studies

Fig.1 presents x-ray diffraction patterns for pure and MO-Sb_2O_3-B_2O_3 glasses. XRD patterns of powder form of these glasses were recorded at room temperature by using shimadzu x-ray diffractometer; model XRD-7000 S in 2θ ranges from 10° - 80°. All samples exhibited broad peaks with no any sharp peak, which is an indicative of glassy nature of the prepared materials.

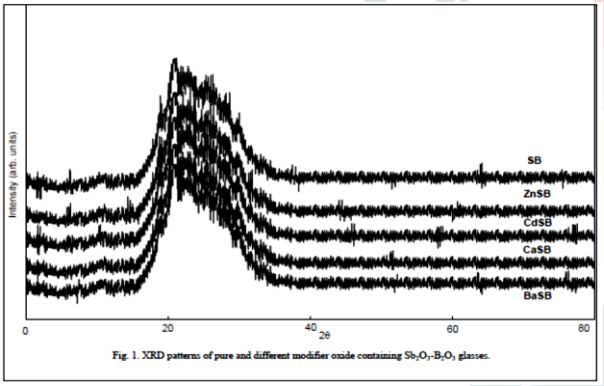

Fig. 1. XRD patterns of pure and different modifier oxide containing Sb_2O_3-B_2O_3 glasses.

C. DTA Studies

Differential Thermal Analysis (DTA) traces for the prepared glass materials were recorded by shimadzu differential thermal gravimetry (DTG) of model DTG-60H with a heating rate of 10 ℃ per minute. Fig. 2 presents DTA traces of pure and MO-Sb_2O_3-B_2O_3 glasses recorded in the temperature range 30-700 ℃.

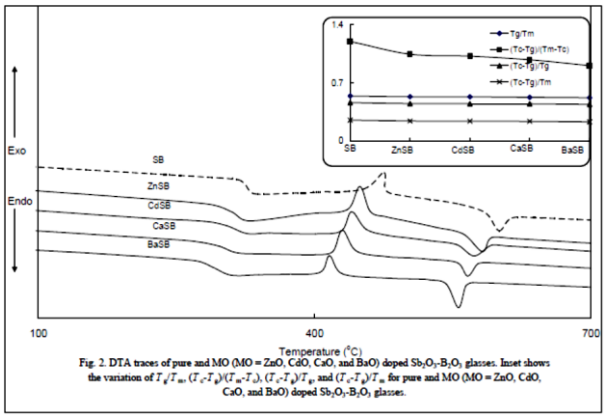

Fig. 2. DTA traces of pure and MO (MO = ZnO, CdO, CaO, and BaO) doped Sb_2O_3-B_2O_3 glasses. Inset shows the variation of T_g/T_m, $(T_c-T_g)/(T_m-T_c)$, $(T_c-T_g)/T_g$, and $(T_c-T_g)/T_m$ for pure and MO (MO = ZnO, CdO, CaO, and BaO) doped Sb_2O_3-B_2O_3 glasses.

The traces show an inflection due to the glass transition temperature T_g in the region from 289 to 325 °C followed by a well-defined exothermic effect due to crystallization temperature T_c between 416 to 479 ℃ and melting temperature T_m due to endothermic effect ranging from 556 to 600 ℃ (Table 3). Presence of single transition temperature T_g indicates homogeneity of the glass. At still higher temperatures an exothermic peak T_c due to the crystal growth followed by an endothermic effect due to re-melting of the glass symbolized by T_m are observed. From the measured values of T_g, T_c and T_m, the parameters (T_c-T_g), T_g/T_m, $(T_c-T_g)/T_m$ and glass forming ability parameter known as Hruby's parameter $K_{gl} = (T_c-T_g)/(T_m-T_c)$, which give the information on the stability of the glass against divetrification [30, 33] are evaluated and presented in Table 3.

Among all modifier containing glasses, the highest value of these parameters are observed for ZnSB glass (inset of Fig. 2) indicating its relatively high glass forming ability.

Table 3. Summary of data on differential thermal analysis of glasses.

Glass	T_g (°C)	T_c (°C)	T_m (°C)	T_g/T_m	$(T_c-T_g)/(T_m-T_c)$	$(T_c-T_g)/T_g$	$(T_c-T_g)/T_m$	$(T_c-T_g)/(T_m-T_c)$
SB	325	475	600	0.542	1.200	0.462	0.250	1.200
ZnSB	310	449	582	0.533	1.045	0.448	0.239	1.045
CdSB	304	440	573	0.530	1.023	0.447	0.237	1.022
CaSB	297	430	566	0.525	0.978	0.448	0.235	0.978
BaSB	289	416	556	0.520	0.907	0.439	0.228	0.907

D. IR Studies

IR spectra of these glasses were recorded by using a Perkin Elmer Spectrometer in the wave number range 400-4400 cm^{-1} with a resolution of 4 cm^{-1} by KBr pellet method. Fig. 3 presents the room temperature recordings of IR spectra of MO-Sb_2O_3-B_2O_3 glasses.

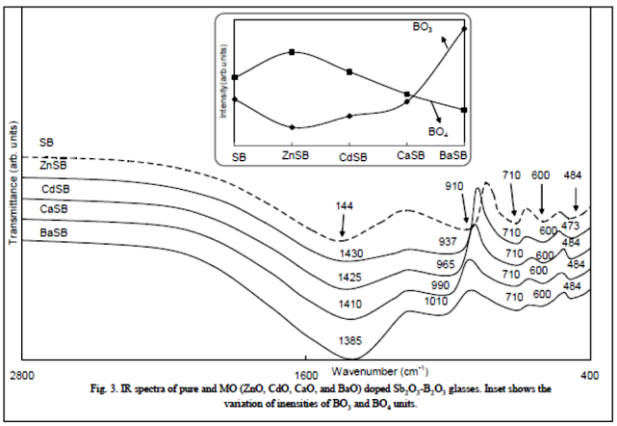

Fig. 3. IR spectra of pure and MO (ZnO, CdO, CaO, and BaO) doped Sb_2O_3-B_2O_3 glasses. Inset shows the variation of inensities of BO_3 and BO_4 units.

The spectra of these glasses exhibited the following several bands due to borate, antimonite and zinc structural units.

(i) A fixed band due to doubly degenerate bending vibrations (ν_4) of Sb_2O_3 at 484 cm^{-1} for all glasses except for ZnSB glass was observed; however, for ZnSB glass a combined band due to ν_4-Sb_2O_3 and ZnO_4 tetrahedral vibrational units was observed at 473 cm^{-1}.

(ii) A fixed band due to symmetric bending vibrations (ν_2) of Sb_2O_3 at 600 $cm^{-1}$is observed for all glasses.

(iii) A combined fixed band due to bending of B-O-B linkages and doubly degenerate stretching vibrations (ν_3) of Sb_2O_3 is observed for all glasses at 710 cm^{-1}.

(iv) A combined band (Band 1) due to B-O band stretching of the tetrahedral BO_4 units and symmetric stretching vibrations (ν_1) of Sb_2O_3 are observed for all glasses in the range 910-1010 cm^{-1}.

(v) A band (Band 2) due to asymmetric stretching relaxation of the B-O of trigonal BO_3 units was observed in the range 1385-1445 cm^{-1} for all glasses.

The data on various band positions from the IR spectra of these glasses was presented in Table 4.

Table 4. Summary of data on the positions of the bands in IR of Sb_2O_3-B_2O_3 based glasses.

Glass	BO_3 (cm^{-1}) (band 2)	BO_4 & ν_1-Sb_2O_3 (cm^{-1}) (band 1)	B–O & ν_3-Sb_2O_3 (cm^{-1})	ν_2-Sb_2O_3 (cm^{-1})	ν_4-Sb_2O_3 /ZnO_4 (cm^{-1})
SB	1445	910	710	600	484
ZnSB	1430	937	710	600	473
CdSB	1425	965	710	600	484
CaSB	1410	990	710	600	484
BaSB	1385	1010	710	600	484

From the IR spectra of these glasses, with increase in ionic radii of the modifier ion in the glass matrix (Zn^{2+} = 0.74 Å, Cd^{2+} = 0.95 Å, Ca^{2+} = 1 Å and Ba^{2+} = 1.35 Å), it is observed that the intensity of band 2 (asymmetrical band) increases at the expense of the intensity of band 1 (responsible for network formation) with shifting its meta-centre towards lower wave number side. However, there is no any change in band positions and intensities of other observed bands in the spectra. These observations obviously suggest that there is an increase in disorder in the glass network with increase in ionic radii of the modifier ion in it.

E. Thermoluminescence (TL) Studies

Fig. 4 shows the thermoluminescence glow curves of x-ray irradiated MO-Sb_2O_3-B_2O_3 glasses at room temperature; recorded by using NUCLEONIX-TL setup (Nucleonix Pvt. Ltd., Hyderabad).

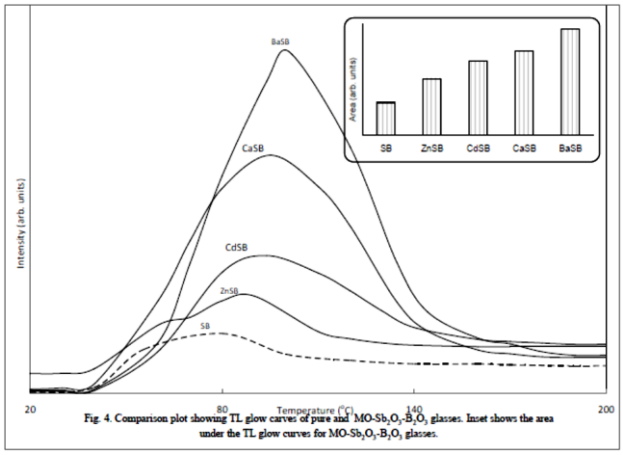

Fig. 4. Comparison plot showing TL glow curves of pure and MO-Sb_2O_3-B_2O_3 glasses. Inset shows the area under the TL glow curves for MO-Sb_2O_3-B_2O_3 glasses.

TL curve of SB (pure) glass has exhibited a broad glow peak centred at 353 K. With the introduction of modifier oxides in to the glass matrix, the intensity of the glow peak is found to increase (substantial increase in the TL light output (inset of Fig. 4)) with the shifting of the glow peak curve towards higher temperatures.

The observed glow curve of these samples are similar to those reported in recent years by many researchers [21, 22, 36-37]. The action of x-ray irradiation on glasses is to produce secondary electrons from the sites where they are in a stable state and have an excess energy. Such electrons may traverse in the glass network depending upon their energy and the composition of the glass and are finally be trapped, thus forming colour centres (or alternatively they may form excitons with energy states in the forbidden gap). The trapping sites may be the metal ions, which constitute the glass structure, ions of admixtures to the main composition, and the structural defects due to impurities in the glass. Thus this process leads to the formation of (i) boron electron centres, (ii) non-bridging oxygen hole centres, and (iii) boron oxygen hole centres. During the heating process for recording the TL light output, the electrons that were captured by metal ions are liberated and later trapped by holes in the recombination centre giving out TL light output as shown in the Fig. 5.

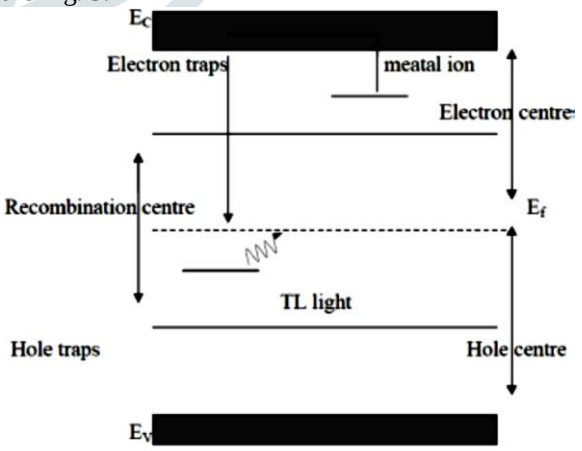

Fig. 5. A proposed TL mechanism for MO-Sb_2O_3-B_2O_3glasses.

The highest TL light output is observed for BaSB glass among all other modifier containing glass networks. When modifier ion of larger ionic radii (Ba^{2+}) is introduced in to the glass network, there will be creation of relatively large number of NBOs and this will possibly produce greater structural defects as mentioned earlier. These defects act as trapping centres to form more number of colour centres, which in turn responsible for more thermoluminescence light output.

Finally, thermoluminescence studies of different modifier oxide containing Sb_2O_3-B_2O_3 glasses suggest that BaSB glass can be used more effectively in radiation dosimetry since they exhibit high TL light output in high temperature region. The trap depth parameters for the glow peaks of MO-Sb_2O_3-B_2O_3 glasses were computed by using Chen's formulae [38].

$$E_\tau = 1.52\left(\frac{kT_m^2}{\tau}\right) - 1.58(2kT_m) \quad (1)$$

$$E_\delta = 0.978\left(\frac{kT_m^2}{\delta}\right) \quad (2)$$

In the above equations k is Boltzmann constant, $\tau = T_m - T_1$, $\delta = T_2 - T_m$, $\mu = \delta/(T_2 - T_1)$; where T_m is the glow peak temperature, T_1 (rising end) and T_2 (falling end) are the temperatures at the half widths of the glow peaks. The summary of the data on thermoluminescence peaks with corresponding activation energies and the trap depths are evaluated and furnished in Table 5.

Table 5. Data on various trap depth parameters of MO-Sb_2O_3-B_2O_3 glasses.

Glass	T_m (K)	τ (K) = T_m-T_1	δ (K) = T_2-T_m	E_τ (eV)	E_δ (eV)	μ
SB	353	25	30	0.549	0.345	0.545
ZnSB	363	30	40	0.470	0.273	0.551
CdSB	367	39	51	0.348	0.219	0.567
CaSB	368	42	58	0.318	0.194	0.580
BaSB	374	45	67	0.301	0.173	0.598

CONCLUSIONS

The summary of main conclusions drawn from various studies on MO-Sb_2O_3-B_2O_3 (where, MO = ZnO, CdO, CaO and BaO) glasses is presented below:

1. DTA studies of these glasses showed that the Hruby's parameter, K_{gl}, is found to decrease with increase in ionic radii of modifier ion; the K_{gl} parameter is found to be highest for ZnSB glass and lowest for BaSB glass among all other modifier containing glasses. This is an indicative of relatively high glass forming ability for ZnSB glass among all other glasses.
2. IR spectra of these glasses presented several band positions due to borate, antimonite, and zinc structural units. With the increase of ionic radii of modifier ions in the glass matrix, it is observed that the intensity of band 2 (asymmetrical bands) increased at the expense of band 1 (BO_4 units) with shifting of its meta-centre towards lower frequency, which is an indicative of relatively high disorder in BaSB glass among all other glasses.
3. The thermoluminescence spectra of these glasses exhibited a single TL glow curve. With the increase of modifier ion radii in the glass matrix, the intensity of the glow peak is found to increase with shifting of its glow peak towards higher temperatures. The highest TL light output is observed for BaSB glass among all other glasses. These results from the thermoluminescence analysis suggest that BaSB glass can be used more effectively in radiation dosimetric applications.

REFERENCES

[1] S. Balaji, P. Abdul Azeem, and P. R. Reddy, Phys. B, 394 (2007) 62.
[2] L. D. Pye, V. D. Fré- chette and N. J. Kreidl, Eds., Borate Glasses: Applic., Plenum Press, New York, 1978, p. 259.
[3] I. Kashif, H. Farouk, A. S. Aly, and A. M. Sanad, Phy. & Chem. of Glasses, 32/2 (1991) 77-78.
[4] A. C. Hannon, D. I. Grimley, R. A. Hulme, A. C. Wright, and R. N. Sinclair, J. Non-Cryst. Solids, 177/1 (1994) 299-316.
[5] D. L. Griscom, Borate Glasses: Applic., Plenum Press, New York, (1978) 11.
[6] W. Soppe, C. van der Marel, W. F. van Gunsteren, and H. W. den Hartog, J. Non-Cryst. Solids, 103 (1988) 201.
[7] T. F. Soules, J. Chem. Phys., 73 (1980) 4032.
[8] A. H. T. Suyoshi Honma, Ryuji Sato, Takayuki Komatsu,Vesselin Dimitrov and Yasuhiko Benino, J. Non-Cryst.Solids, 272 (2000) 1.
[9] H. W. den Hartog and Verhoef J. Non-Cryst. Solids, 182 (1995) 235
[10] J. L. Ribeiro, Marcel Poulain, Michel Poulain, and Y. Messaddeq Gael Poirier, J. Non Cryst. Solids, 284 (2001) 117.
[11] M. Amano, K. Suzuki and H. Sakatha, Journal Mater. Sci., 32 (1997) 4325.
[12] T. Suyoshi Honma, Ryuji Sato, Yasuhiko Benino, Takayuki Komatsu, Vesselin Dimitrov, J. Non-Cryst .Solids 272 (2000) 1.
[13] E. Fargin, A. Berthereau, A. Ducasse, and P. Segonds J. Non-Cryst. Solids, 203 (1996) 96.
[14] A. Mori, K. Y. Ohishi, Y. Nishida, Oikawa, and S. Sudo, Proc. Of Optical Fibre Commun. Conf., 97 (1997).
[15] D. Kumar and D. Chakravorty, J. Phys., 15 (1982) 305.
[16] B.V.R. Chowdari and S. K. Akhter, Sol. State Ionics, 25 (1987) 109.
[17] W. H. Dumbaugh, Phys. Chem. Glasses, 19 (1978) 121.
[18] R. P. Tandon and S. Hotchandani, Physics. Stat. Sol., 185 (2001) 453.
[19] V. Sudarsan, S. K. Kulshreshtha, J. Non-Cryst. Solids, 286 (2001) 99.
[20] Ling Zan, Jiashen Zhong, and Qirong Luo, J. Non-Cryst.Solids, 256 (1999) 396.
[21] D. Chakraborty, H. Satou, and H. Sakata, J. Appl. Phys., 82 (1997) 5520.
[22] J. D. Lee, Concise Inorganic Chem., Oxford: Blackwell Science, (1996).
[23] G. Pal Singh, and D. P. Singh, J. Molec. Structure, 1012 (2012) 137-140.
[24] H. A. Lorentz, Annal., Phys., 9 (1880) 641.
[25] L. Lorentz and Wiedm. Annal., 11 (1881) 70.
[26] Dietzel A., Glasstech. Ber., 22 (1968) 41.
[27] Hruby, Czech. J. Phys. B 32 (1972) 1187.
[28] G. Le Saout, P. Simon, F. Fayon, A. Blin and Y. Villas, J. Raman. Spectrosc., 33 (2002) 740.
[29] L. Montagne, G. Palavit and G. Mairesse, Phys. Chem. Glasses, 37 (1996) 206.
[20] D. K. Durga and N. Veeraiah, J. Phys. & Chem. of Solids 64 (2003) 133-146.
[31] Y. Cheng, W. Zhongqing, H. Xi, W. Tengyan, and Z. W. Wei, J. Rare Earths 32 (2014) 1154–1161.

[32] J. H. Simmons, C.A. Simmons and R.O choa, Fibre Optics (eds I.D. Aggarwal and G. Lu), Academic Press, London, ch 2 (1991) 1-33.
[33] N. Veeraiah, Physica B 324 (2002) 127.
[34] L. Bih, El. Omari, M. Haddad, J. M. Reau, D. Boudlich, A. Yacoubi, and A. Nadiri, Solid State Ionic., 132 (2000) 71.
[35] B. B. Das, R. Ambika, Chem. Phys. Lett., 370 (2003) 670.
[36] M. Imaoka, H. Hasegawa, and S. Shindo, J. Cer. Soc. Japan, 77 (1969) 263.
[37] Srinivasa Reddy G. Nagarjuna, and N. Veeraiah, J. Alloys & Comp., 438 (2007) 41.
[38] R. Chen, J. Appl. Phys., 40 (1969) 570.