Journal of Alloys and Compounds 503 (2010) 384–388

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

IR, density and DTA studies the effect of replacing Pb_3O_4 by CuO in pseudo-binary $Li_2B_4O_7$–Pb_3O_4 glass system

I. Kashif[a,*], A. Abd El-ghany[b], A. Abd El-Maboud[b], M.A. Elsherbiny[a], A.M. Sanad[a]

[a] Physics Department, Faculty of Science, AL-Azhar University, Nasr City, 11884 Cairo, Egypt
[b] Physics Department, Faculty of Science (Girls), AL-Azhar University, Nasr City, 11884 Cairo, Egypt

ARTICLE INFO

Article history:
Received 27 June 2009
Received in revised form 11 April 2010
Accepted 14 April 2010
Available online 22 April 2010

Keywords:
Oxide glass
Pseudo-binary $Li_2B_4O_7$–Pb_3O_4 glass system
Density
Infrared
Differential thermal analysis

ABSTRACT

Effect of replacement of Pb_3O_4 by CuO on structure and properties of pseudo-binary [75%] $Li_2B_4O_7$–[$25-x$%] Pb_3O_4 glass system, where $x=0$, 5, 10, 15, 20 and 25 mol% CuO, have been investigated. IR spectra of the prepared glasses show that CuO goes into the network and play also a role as a glass modifier. The addition of CuO decreases the formation of tetrahedral groups (BO_4) and increasing the triangle one (BO_3), led to increase the borate non-bridging oxygen (NBO). The observed increase in T_g with CuO reflect increase in bond strength, also the glass-forming ability and stability decrease with increasing CuO reflects the reduction of the network rigidity and loosening of glassy structure. The density and molar volume were discussed in terms of the structural modifications that take place in glass matrix. The distance between Cu and Cu atoms and the polaron radius have been carried for all samples.

1. Introduction

Lead borate glasses are of technological interest owing to their properties such as their low melting temperatures, wide glass formation regions, good radiation shielding properties, and its technological and industrial interests for their use in enamels, photonics, and optoelectronic applications [1–4]. IR spectroscopic work has been carried out in lead borate glasses [5], in which the low frequency IR peaks involving PbO vibrations were observed, indicting the appearance of new bands characteristic of covalent PbO bonds with the increased content of PbO.

The introduction of copper oxide (CuO) into an oxide glass changes the oxide network. CuO has been used as a constituent in several borate and vanadate glasses in order to achieve useful physical properties. Though CuO is not a glass-forming oxide by itself, it can be incorporated in substantial quantities into these glass-forming oxide systems. Many investigators have reported that copper (Cu) may exist in glass network both as a network former and also as a network modifier—forming oxide metals as Cu^+ and Cu^{2+} ions [6–12].

Binary diborate glasses with CuO have been investigated [13]. On the basis of the infrared data, it is proposed that the glass structure corresponds to a network formed by four tightly connected diborate units. Thus, in the glasses of Li_2O–$2B_2O_3$ compositions, the structure of glass consists of different structural groupings. These may be constructed as the basis of BO_4 tetrahedral and triangle BO_3 units. Replacement of $Li_2B_4O_7$ by CuO ions increases the trigonal BO_3 (with one NBO) moieties by converting BO_4-containing groups (with 2 BO_4 units) into ring type metaborate groups as revealed from IR spectra. Also, most of the copper ions act as a network modifier and some ions act as a network former by increasing the copper content. The density increased and, consequently, 89 the molar volume decreased, which is explained by the strong covalent B–O and Cu–O bonds substituting long ionic bonds.

The influence of lead oxide ions on some physical properties and structural changes in lithium diborate glasses has been investigated using differential thermal analysis, density, molar volume and the FT-IR spectra [14]. All the results are presented as a function of x mol% PbO treating the investigated glass samples as pseudo-binary $(100-x)$ $Li_2B_4O_7{\cdot}x$PbO, $x=0$, 5, 15, 25 and so on up to 65 mol%. The FT-IR spectra conclude that, PbO plays the dual role in the glass network, where the major part of PbO is acting as a modifier at PbO ≤ 25 mol% and the remaining of PbO enters as a network former and reversed behaviors at $65 \geq$ PbO > 25 content the major part of PbO acts as a network former. It is shown that molar volumes, the glass transition temperature vary as a function of the mole fraction of PbO in a manner consistent with the above role. Introducing PbO into such glass matrix at the expense of $Li_2B_4O_7$, decrease the number of Li^{2+} and increasing the polymerization of Pb^{2+} in the glass network, At >25 mol% PbO, lead oxide is acted as the network former.

Density of solids is mostly the simplest physical property that can be measured. However, it would be a highly informative property if the structure of the material could be well defined. Density

---

* Corresponding author.
E-mail address: isnham@netscape.net (I. Kashif).

0925-8388/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2010.04.079

data were used to calculate the volumes of structural units present in various types of glass. In alkali borate glasses the volume of BO_3 unit and also that of BO_4 unit change markedly with the glass composition.

In the present work, the effect of replacing Pb_3O_4 by CuO in pseudo-binary $Li_2B_4O_7$–Pb_3O_4 glass system was investigated in order to correlate the structural transformations with the changes in their physical properties. IR spectral analysis, density, molar volume together with DTA measurements were employed in this study.

2. Experimental

Glasses with composition 75 mol% $Li_2B_4O_7$–$(25-x)$ mol% Pb_3O_4–x mol% CuO, where $x = 0$, 5, 10, 15, 20 and 25 mol% were prepared. The used raw materials were all of chemically pure grade and were finally pulverized.

The homogenous mixture was melted in platinum crucible in an electrically programmable heated furnace, type VAF 15/10 lenton thermal design, equipped with automatic temperature controller .The samples were melted up at 1200 °C for 2 h with heating rate 30°C/min, the molten materials stirred several times to ensure the complete homogeneity of the samples then they quenched in air and poured at room temperature.

The IR spectra of the glasses were recorded at room temperature using the KBr technique by FT-IR 5300 Jasco spectrophotometer of Michelson interferometer type in a wave number region between 400 and 1600 cm^{-1}. The density was measured by using the Archimedes method with toluene as an immersion fluid. The molar volume is determined as

$$V_m = \frac{\sum M_i N_i}{d} \quad (cm^3/mol) \tag{1}$$

where M_i is the molecular weight of the component [i], N_i its mole fraction and d is the glass density. A Shimadzu DTA 50 thermal analyzer was used at heating rate of 25 °C/min between 25 and 1000 °C to determine the glass transition temperature.

3. Results and discussion

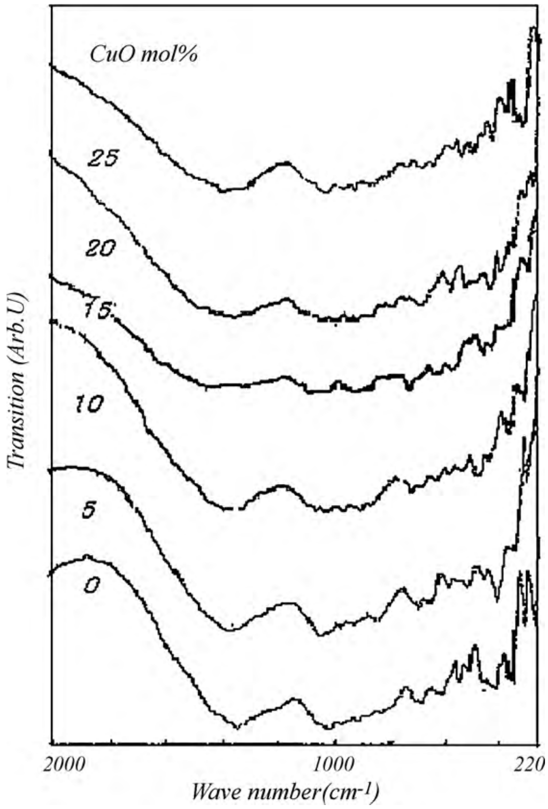

Fig. 1. IR spectra of the glass systems with different copper content mol%.

The fundamental absorption bands of borate glasses are clear at three principal bands the first band which occurs between 800 and 1200 cm^{-1} is due to the B–O bond stretching of tetrahedral BO_4 units. The second band which occurs between 1200 and 1600 cm^{-1} is due to stretching vibration of B–O of trigonal BO_3 units [15,16]. The third band is observed around 700 cm^{-1} is due to the bending of various borate segments [17–19]. Infrared spectra [75 $(Li_2B_4O_7)$–$(25-x)$ Pb_3O_4–x (CuO)] glasses, with $x = 0$, 5, 10, 15, 20 and 25 mol% are shown in Fig. 1.

Infrared spectra collected from lead lithium tetraborate sample (free from copper) shows active peaks around 805, 1050, 1350, 1460 and 1500 cm^{-1} besides bands characteristics of lead oxide at 389, 468, 589 and 620 cm^{-1} characteristics the vibration frequency of lead [19]. The band at 805 $cm^{-1}$is due to the boroxol ring in the borate glass network [20–22]. The band at 1050 cm^{-1} is probably due to the vibration of BO_4 tetrahedra which are present as tetraborate and diborate groups [23,24]. The band at 1350 assigned to the formation of pyroborate groups [25,21], 1460 cm^{-1} attributed to triangle boron oxygen triangle groups [26] and the band at 1500 cm^{-1} attributed to borate arrangements containing BO3 unit only, such as ortho-, meta- and pyroborate groups [27].

Replacement of 5 mol% by CuO caused a band observed at 680, 885, 950, 1336 and 1400 cm^{-1}. The band appears at 680 cm^{-1} is attributed to the B–O–B bond-bending vibrations from pentaborate groups [28,29], the band at 885 cm^{-1} is due to pentaborate units [30], 950 cm^{-1} due to vibrations of structural groups containing BO_4 tetrahedra (orthoborate units) [27], also 950 cm^{-1} attributed to Pb–O bonds [20,31]. The band at 1336 cm^{-1} is due to B–O stretching BO_4 vibrations with one or two non-bridging oxygen atoms [32] and that at 1400 cm^{-1} assigned to BO_3 units with one non-bridging oxygen [8,21,33,34].

For sample containing 10 mol% CuO, besides the bands characteristic vibration of lead and copper oxide, all the above bands shifted to higher wavenumber due to the addition of CuO with strong covalent bond between copper and oxygen Cu–O. The band at 720 cm^{-1} attributed to the vibration of boron atoms in BO_3 units [35]. The band observed at 1390 cm^{-1}attributed to triangle boron oxygen triangle groups [23,36] and the band at 1450 cm^{-1}indicates the presence of the chain-type metaborate groups [21,37].

For sample containing 15 mol% CuO, the band at 1086 cm^{-1} assigned to B–O linkages of BO_4 groups [38], the band at 1283 cm^{-1} due to B–O stretching vibration of metaborate chain and orthoborate [20].

More increasing of copper oxide content (20 mol%) cause a band observed at 1235 cm^{-1} assigned to asymmetric stretching vibration of B–O bonds from orthoborate groups [28] while the one at 1360 cm^{-1} attributed to asymmetric stretching modes of borate triangles BØ3 and BØ2O (Ø representing an oxygen atom bridging two boron atoms and O–NBO) [39].

At higher concentration of copper oxide content (25 mol%), sample free from lead oxide, the band of CuO become sharper and observed at 497 cm^{-1}.

The replacement of PbO by CuO results in progressive spectral changes. This spectrum reveals different structural roles of Pb^{2+} and Cu^{2+} captains. The absorption due to tetrahedral BO_4 decreases relative to that of trigonal BO_3 units with increasing CuO content [17]. That is, increase the number of orthoborate, metaborate and pyroborate groups and decrease the number of diborate and pentaborate groups. The IR spectra can be deconvoluted to the component bands for each one to study the origin of this characteristic infrared symmetry. As an example Fig. 2 represents the deconvolution in Gaussian bands of the spectrum for the glass containing 15 mol% [CuO].

The following method are used in the calculation of the fraction N_4 of the four coordinated boron's in the glass, where N_4 = (concentration of BO_4 tetrahedra)/(concentration of BO_3 triangle + concentration of BO_4 tetrahedra) [40]. The obtained values are shown in Fig. 3 as function of composition.

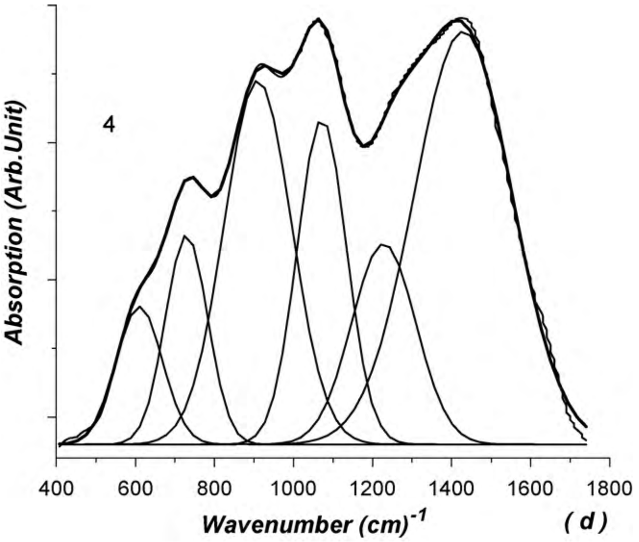

Fig. 2. The deconvolution in Gaussian bands of the spectrum for the glass containing 15 mol% (CuO).

It is clear that the N_4 decreasing by adding copper content. This is agreement with the IR spectroscopy results, which detected decrease of the intensity for four coordinated boron atoms BO_4 (885, 915, 935, 950, 973, 1043 and 1086 cm^{-1}) than that of three coordinated ones BO_3 (1235, 1283, 1350, 1400, 1450 and 1460 cm^{-1}) with increasing copper oxide concentration. The decrease of the BO_4 groups with the replacement of lead oxide by copper oxide depends on the number of oxygen atoms and converted BO_4 to BO_3 groups and form non-bridging oxygen (NBO).

Fig. 4 shows typical differential scanning calorimetric of all glass samples. The curves exhibit an endothermic effect due to glass transition temperature T_g. At still higher temperatures an exothermic peak T_c obtained for all glasses. The appearance of single peak due to the glass transition temperature of all glasses indicates the high homogeneity of the glass prepared [41]. The obtained characteristic temperatures for investigated glasses are summarized in Table 1.

From Table 1 can be seen that T_g, T_c and T_m increase with the increasing of CuO content, this indicates an increase in the structural connectivity by replacing lead ions with high ionic strength Cu^{2+} [1].

The glass transition temperature depends on the oxygen density of the network [42]. Since the oxygen density of the network decreases due to the replacement of lead oxide with copper oxide which led to the compactness of the structure and increasing of the glass transition. A parameter usually employed to estimate the glass stability is the thermal stability ΔT, which is defined by:

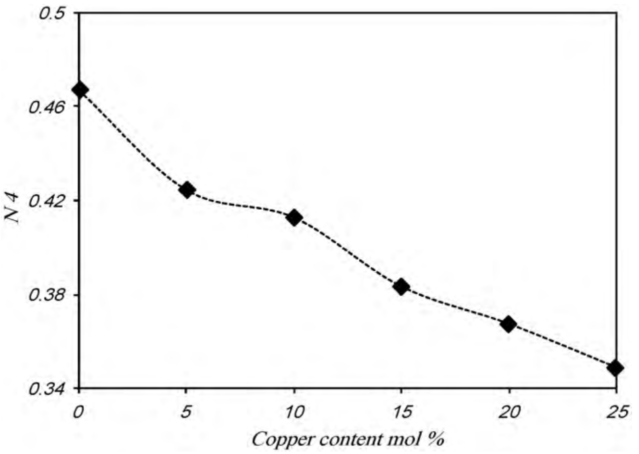

Fig. 3. The fraction N_4 of the four coordinated borons in the glass system.

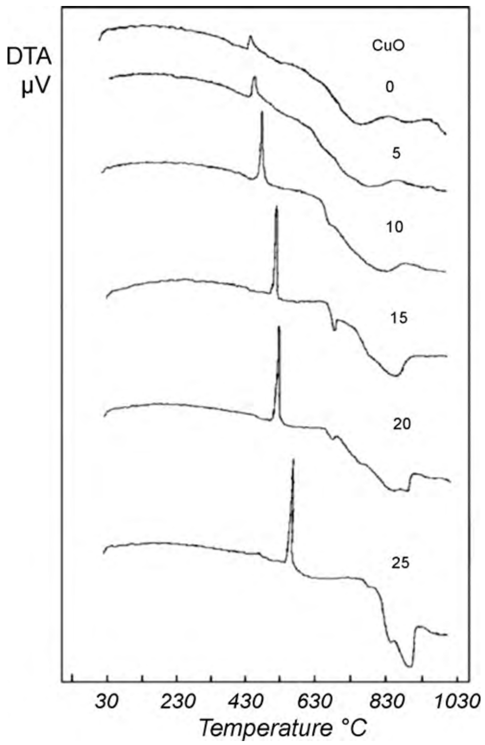

Fig. 4. DTA curves for all the glass samples.

$$\Delta T = T_p - T_g \tag{2}$$

where T_g is the glass transition temperature, T_p is the crystallization temperature. Another parameter introduced by Hruby [43] is the glass-forming ability (K_{gl}) which is defined by the relation:

$$K_{gl} = \frac{T_p - T_g}{T_m - T_p} = \frac{\Delta T}{T_m - T_p} \tag{3}$$

where ΔT: thermal stability, K_{gl}: the glass-forming ability, T_g: glass transition temperature, T_m: melting temperature and T_p: the crystallization temperature.

Glass-forming ability can be determining in order to compare devitrification tendency of the glass. The glass thermal stability parameters ΔT, K_{gl} tabulated in Table 2, show the variation of thermal stability and glass-forming ability with copper content. The decreases of the thermal stability and the glass-forming ability with increasing the copper oxide content suggests high tendency of crystallization with increasing CuO content.

The obtained data of density and molar volume in room temperature are shown in Fig. 5 as a function of CuO content. Fig. 5 indicates that the density decrease from 4.47 to 2.93 g/cm^3 as the copper oxide content increased. The decrease in the density is linked with

Table 1
Glass transition T_g, Crystallization and melting temperatures for all glass samples.

Sample No	T_g (°C)	T_p (°C)	T_m (°C)
1	308	447	758
2	324	457	792
3	370	479	813
4	403	505	822
5	425	522	848
6	481	561	895

Table 2
Glass forming ability and thermal stability for all glass samples.

Sample No	ΔT (°C)	K_g
1	139	0.447
2	133	0.397
3	109	0.326
4	102	0.324
5	97	0.299
6	80	0.241

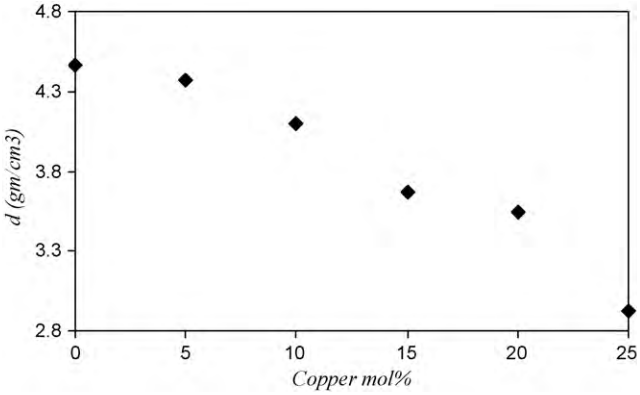

Fig. 5. Variation of the density as a function of copper content mol%.

replacement of high molecular weight of Pb with low molecular weight of Cu modifier.

Since the density depends on [44], the relative sizes of BO_3 and BO_4 unite. The above results show that the copper oxide is introduced as network modifier and former network, the density depends on the composition i.e. CuO occupies interstitial position in the network which led to the decrease of volume (molar volume) as shown in Fig. 6.

The molar volume decreases with increasing copper content, which decreases the homogeneity of the glasses, and this results agreement with the IR and DTA measurements.

According to Austin–Mott model [45] the activation energy is inversely proportional to the polaron radius.

The polaron radius (r_p) can be determined using the relation [46]:

$$r_p = 0.5\left(\frac{\pi}{6N}\right)^{1/3} \text{cm} \tag{4}$$

The average distance "R" between the transition ions Cu–Cu (assuming homogenous distribution of transition ion in glass volume) was calculated as follows [47]:

$$R = \left(\frac{1}{N}\right)^{1/3} \text{cm} \tag{5}$$

where "N" is the concentration of total TMIs (transition metal ions). The copper ion density, N was estimated using the relation [48]:

$$N = 2\left\{\left[\frac{dm}{M}\right]N_A\right\} \text{cm}^{-3} \tag{6}$$

where d is the density of the glass, m is the mole fraction of TM, M is molecular weight of TM and NA is the Avogadro number.

All the calculated parameters of N, r_p and R are shown in Figs. 7–9.

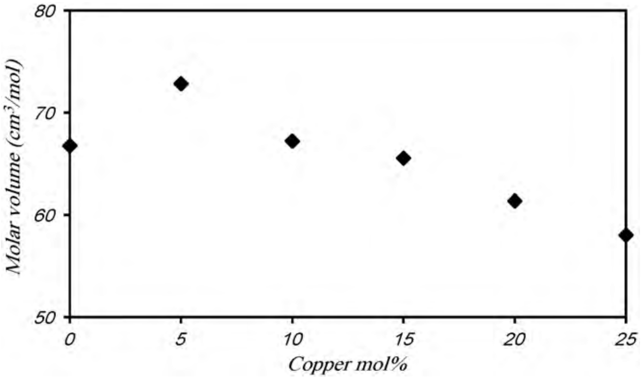

Fig. 6. Variation of molar volume as a function of CuO content mol%.

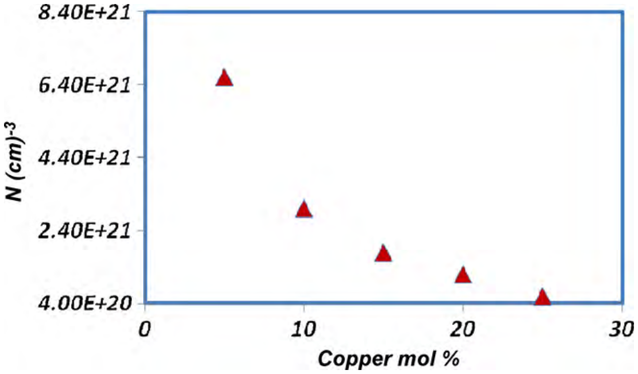

Fig. 7. The concentration of transition metal ions per unit volume as a function of CuO content mol%.

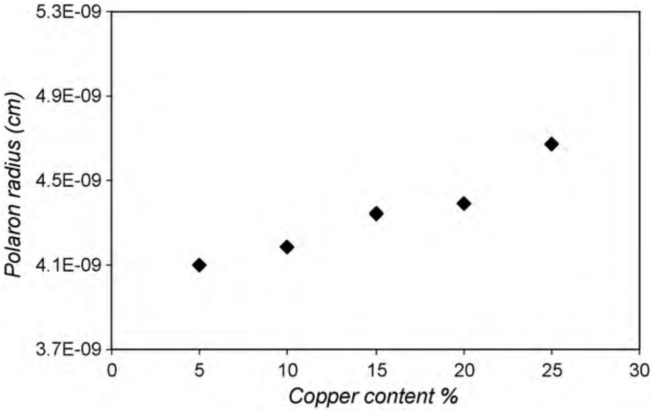

Fig. 8. Polaron radius in each glass systems.

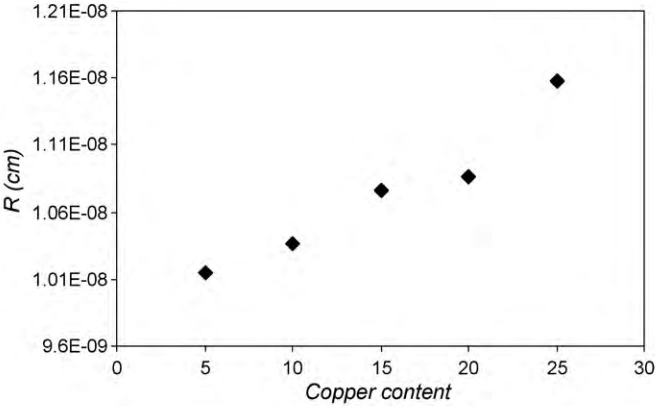

Fig. 9. The space between Cu and Cu atoms in each glass systems.

The values of both R and r_p are increase as the added of copper amount increases. The values of r_p which are found to be smaller than R and greater than the ionic radius of copper (ionic radius of Cu ion is 0.74×10^{-12} cm) indicates that electrons are localized. And the activation energy is decrease as the copper increases.

4. Conclusions

The infrared spectra were recorded over a range (400–1600) to study their structure systematically. The conversion of four coordinated boron (BO_4) to three coordinated (BO_3) took place with the addition of CuO. The increase of CuO content increase the number of orthoborate, metaborate and pyroborate groups and decrease the number of diborate and pentaborate groups. The glass transition temperature (T_g) increase with the addition of CuO content due to the decrease of the density of NBOs in the network. Thermal stability and the glass-forming ability decrease with increasing the copper oxide content. The density and molar volume was discussed in terms of the structural modifications that take place in glass matrix upon replacing PbO by CuO, the density and molar volume of the glass decreases with the network modifying behaviour of CuO. The values of both R and r_p are increase as the added of copper amount increases indicated that the Cu ion enters as former with increase of amount of copper oxide.

References

[1] Y.B. Saddeek, J. Alloys Compd. 467 (2009) 14.
[2] G. Dominiak-Dzik, W. Ryba-Romanowski, J. Pisarska, W.A. Pisarski, J. Lumin. 122–123 (2007) 62.
[3] P. Srivastava, S.B. Rai, D.K. Rai, J. Alloys Compd. 368 (2004) 1.
[4] Joanna Pisarska, Wojciech A. Pisarski, Witold Ryba-Romanowski, Opt. Laser Technol. 42 (2010) 805.
[5] D. Lide, CRC Hand book of Chemistry and Physics, 84th ed., CRC Press, Boca Raton, FL, 2004.
[6] M.M. Smedskjaer, J. Deubener, Y.Z. Yue, Chem. Mater. 21 (2009) 1242.
[7] M.A. Salim, G.D. Khattak, M.S. Hussain, J. Non-Cryst. Solids 185 (1995) 101.
[8] R. Everman, R. Cooper, J. Am. Ceram. Soc. 86 (2003) 487.
[9] A. Thulasiramudu, S. Buddhudu, JQSRT 97 (2006) 181.
[10] G.D. Khattak, A. Mekki, M.A. Gondal, Appl. Surf. Sci. 256 (2010) 3630.
[11] G.D. Khattak, M.A. Salim, L.E. Wenger, A.H. Gilani, J. Non-Cryst. Solids 262 (2000) 66.
[12] A.A. Soliman, Egypt. J. Solids 21 (1998) 2.
[13] I. Kashif, A.A. Soliman, H. Farouk, M. El-Shorpagy, A.M. Sanad, Physica B 403 (2008) 3903.
[14] A.A. Soliman, E.M. Sakr, I. Kashif, Mater. Sci. Eng. B 158 (2009) 30.
[15] A.H. Verhoef, H.W. Den Hartog, J. Non-Cryst. Solids 182 (1995) 221.
[16] E.I. Kamitsos, A.P. Patsis, M.A. Kararkassides, G.D. Chryssikos, J. Non-Cryst. Solids 126 (1990) 52.
[17] N.A. El-Alaily, R.M. Mahamed, J. Nucl. Mater. 303 (2002) 44.
[18] N.A. El-Alaily, R.M. Mohamed, Mater. Sci. Eng. B 98 (2003) 193.
[19] P.S. Gahlot, V.P. Seth, A. Agarwal, S. Sanghi, P. Chand, D.R. Goyal, Physica B 355 (2005) 44.
[20] V. Ramesh Kumar, J.L. Rao, N.O. Gopal, Mater. Res. Bull. 40 (2005) 1256.
[21] R.P. Sreekanth Chakradhar, B. Yasoda, J. Lakshmana Rao, N.O. Gopal, J. Non-Cryst. Solids 352 (2006) 3864.
[22] B.P. Dwivedi, M.H. Rahman, Y. Kumar, B.N. Khanna, J. Phys. Chem. Solids 54 (1993) 621.
[23] Y. Cheng, H. Xiao, W. Guo, Ceram. Int. 34 (2008) 1335.
[24] Y. Cheng, H. Xiao, W. Guo, W. Guo, Ceram. Int. 33 (2007) 1341.
[25] B.N.M. Ramakrishna, J. Non-Cryst. Solids 159 (1993) 1.
[26] R.D. Husung, R.H. Doremus, J. Mater. Res. 25 (1996) 2209.
[27] K. El-Egili, Physica B 325 (2003) 340.
[28] R. Ciceo-Lucacel, I. Ardelean, J. Non-Cryst. Solids 353 (2007) 2020.
[29] A.K. Hassan, L. Borjesson, L.M. Torell, J. Non-Cryst. Solids 172–174 (1994) 154.
[30] D. Maniu, T. Iliescu, I. Ardelean, R. Ciceo-Lucacel, M. Bolboaca, W. Kiefer, Vib. Spectrosc. 29 (2004) 241.
[31] B.G. Rao, H.G. Keshava Sunder, K.J. Rao, J. Chem. Soc. Faraday Trans. 80 (1984) 349.
[32] I. Kashif, A.M. Abo El-Azm, S.S. Gomea, A.M. Sanad, E.E. Assem, Phys. Chem. Glasses 30 (1989) 167.
[33] J.A. Kapoutsis, E.I. Kamitsos, G.D. Chryssikos, H.A. Feller, N. Lower, M. Affatigato, S.A. Feller, Phys. Chem. Glasses 41 (2000) 321.
[34] C.P. Varsamis, E.I. Kamitsos, G.D. Chryssikos, Phys. Rev. B 60 (1999) 3885.
[35] G. El-Damrawi, K. El-Egili, Physica B 299 (2001) 180.
[36] C. Julien, M. Massot, W. Balkanski, A. Krol, W. Nazarewicz, Mater. Sci. Eng. B 3 (1989) 307.
[37] T. Iliescu, S. Simon, D. Maniu, I. Ardelean, J. Mol. Struct. 294 (1992) 201.
[38] H. Farouk, Y.M. Abo-Zeid, M.A. Khaled, I. Kashif, A.M. Sanad, Mater. Sci. 6 (1995) 393.
[39] Z.P. Lu, C.T. Liu, J. Acta Mater. 50 (2002) 3501.
[40] H. Farouk, Aisha A. Solimani, S.A. Aly, H. Zahr El-Deen, I. Kashif, A.M. Sanad, J. Mater. Sci. Eng. B 38 (1996) 217.
[41] F.H. ElBatal, S.Y. Marzouk, N. Nada, S.M. Desouky, Physica B 391 (2007) 88.
[42] G. Lakshminarayana, S. Buddhudu, Spectrochim. Acta A 62 (2005) 364.
[43] A. Hruby, Czech. J. Phys. B22 (1972) 1187.
[44] W. Soppe, F. Aldenkamp, H.W. Den Hartog, J. Non-Cryst. Solids 91 (1987) 351.
[45] I.G. Austin, N.F. Mott, Adv. Phys. 18 (1969) 41.
[46] D. Das, T.K. Kundu, M.K. Dey, S. Chakraborty, D. Chakravorty, Proc. Indian Acad. Sci. (Chem. Sci.) 115 (2003) 341.
[47] Virender Kundu, R.L. Dhiman, A.S. Maan, D.R. Goyal, Adv. Condens. Matter Phys. 2008 (2008) 1.
[48] M. Prashant Kumar, T. Sankarappa, Mater. Sci. Poland 26 (2008) 247.