ISSN : 0974 - 7486

Volume 11 Issue 2



Materials

Science An Indian Journal FUII Paper

MSAIJ, 11(2), 2014 [51-57]

Role of CuO and Li₂O in CuO-Li₂O-B₂O₃ glasses

H.Doweidar¹, G.El-Damaraw¹, S.Abd El-Maksoud¹, M.Nasher^{2*} ¹Glass Research Group, Physics Department, Faculty of Science, Mansoura University, Mansoura 35516, (EGYPT) ²Faculty of Education, Amran University, (YEMEN) E-mail : muneerali2013@gmail.com

ABSTRACT

FTIR spectra of Two CuO- $\text{Li}_2\text{O}-\text{B}_2\text{O}_3$ glass series have been analyzed. There is a decrease in the fraction N_4 of four coordinated boron with increasing the CuO content, at the expense of Li₂O. A new technique has been presented to make use of the N_4 data and follow the change in the fractions of Li₂O and CuO. These fractions change markedly, at different rates, with the glass composition. © 2014 Trade Science Inc. - INDIA

INTRODUCTION

Metal borates are of considerable interest due to their rich structural features and they find extensive industrial use^[1-5].

Copper ions have strong bearing on electrical, optical and magnetic properties of glasses. A large number of interesting studies are available on the environment of copper ion in various inorganic systems^[6,7].

Copper is extensively used in several commercial glasses, such as red glass hematite, aventurine and rubbies. High CuO containing glasses are important because of their semiconducting properties^[8–10] and other potential applications^[11–13]. Copper ions exist in two stable ionic states, the divalent Cu²⁺ and monovalent Cu⁺ ions, and may also exist as a metallic copper^[14].

EXPERIMENTAL TECHNIQUES

Two series of glass, of the formula xCuO.(30x)Li₂O.70B₂O₃ ($0 \le x \le 27.5$) and xCuO.(40x)Li₂O.60B₂O₃ ($0 \le x \le 40$), were prepared using high quality H_3BO_3 , Li_2CO_3 and CuO. The glasses were prepared under normal atmospheric conditions by melting the mixture of raw materials in porcelain crucibles in an electric furnace at a temperature ranged between 950ÚC and 1150ÚC, depending on the glass composition.

The melt was swirled frequently to insure the homogeneity. The melt was poured on steel plates and then pressed by a ceramic plate to form disks of 1to2 mm thickness. The discs were used for the measurement of the electrical conductivity All the obtained samples were visually homogeneous and some of them transparent and the other opaque. The glasses were stored in a desiccator until required.

The amorphous nature of the samples was conûrmed by X-ray diffraction investigations. A Bruker D8 Advance powder XRD was used. It is ûtted with a Vantech Super Speed position sensitive detector and a Cu Ka X-ray tube with a Goebel Mirror. Measurements were made over the range 4° to 80° in 2 θ -scale. X-ray diffraction patterns of all the studied glasses (not shown) show only broad humps typical of amorphous materials.

Full Paper

The FTIR absorption spectra were obtained at room temperature in the range 600–2000 cm⁻¹ using Thermo Nicolet Is 10 spectrometer with a spectral resolution of 4 cm⁻¹. A KBr pellets technique was used where 10 mg of each sample is mixed with 1000 mg of KBr in an agate mortar. From this stock, 200 mg were then pressed into pellets of about 13 mm diameter. The spectrum of each sample represents an average of 32 scans, which was normalized to the spectrum of blank KBr pellet; i.e. a pure KBr spectrum was subtracted from each glass spectrum. Also, the spectra were corrected to the background and dark currents using two- point baseline correction.

RESULT AND DISCUSSION

xCuO·(30-x)Li₂O·70B₂O₃ glasses

Infrared spectra of xCuO·(30-x)Li₂O·70B₂O₃ glasses are shown in Figure (1). The spectra are characteristic for borate glasses modified by alkali or alkaline earth oxides^[15-18].



Figure 1 : Normalized infrared spectra of $xCuO(30-x)Li_2O70B_2O_3$ glasses. Numbers at the plots refer to the concentration of CuO (mol%).

The main features of IR spectra of such glasses are the presence of certain absorption envelopes in the regions ~800-1200 cm⁻¹ and ~1200-1600 cm⁻¹, in addition to a smaller peak centered at 700 cm⁻¹. Bands in the region ~800-1200 cm⁻¹ are generally attributed to B-O stretching vibration of BO₄ units in various borate groups, like pentaborate, triborate and diborate groups^[19-21]. On the other hand, absorption bands in

the region ~1200-1600 cm⁻¹ are related to B-O stretching vibration of trigonal BO₃ units only. The latter are incorporated in various borate groups containing nonbridging oxygen ions such as metaborate, pyroborate and orthoborate groups^[22,23]. The small band at 700 cm⁻¹ is attributed to bending vibration of B-O-B in symmetric BO₃ triangles^[21].

Marked changes are observed in the spectra of xCuO·(30-x)Li₂O·70B₂O₃ glasses (Figure 1). The first one is the decrease in the area under the 800-1200 cm⁻¹ envelope when replacing CuO for Li₂O. This behavior, which reveals a decrease in the concentration of BO₄-containing units. On the other hand, there is an increase of area under the peak centered at 700 cm⁻¹ with increasing CuO content. This reflects an increase in the concentration of symmetric BO₃ units. Both these changes reveal that CuO has lower ability to convert BO₃ units into BO₄ units.

The spectra shown in Figure (1) can be used to get the fraction N_4 of four coordinated boron atoms in the studied glasses. N_4 is the ratio of the concentration of boron atoms in tetrahedral coordination to the total concentration of boron atoms in the glass. It can be calculated by determining the area under the absorption envelopes in the IR spectra. The area under an absorption peak is considered to be proportional to the concentration of structural units emerging it. The deconvolution technique used in^[18,24-26] can be applied to analyze the IR spectra of the studied glasses.

Figure (2) shows that there is a pronounced linear decrease in N_4 when increasing CuO content in xCuO·(30-x)Li₂O·70B₂O₃ glasses. This can mainly be due to the difference in N_4 values of the glasses 30CuO·70B₂O₃ and 30Li₂O·70B₂O₃. The N_4 value of the glass 30Li₂O·70B₂O₃ presented in Figure (2) agrees well with the values obtained by various investigators^[27,28]. Due to the presence of two oxides that can modify the borate network by converting symmetric BO₃ triangles into BO₄ units and forming asymmetric BO₃ units, N_4 of xCuO·(30-x)Li₂O·70B₂O₃ glasses can be expressed by

$$N_4 = N_{4(\text{Li})} + N_{4(\text{Cu})}.$$
(1)

Here, $N_{4(\text{Li})}$ is the part of N_4 that results from modifying the borate network by Li₂O and $N_{4(\text{Cu})}$ is that results from modification by CuO. Since $N_{4(\text{Li})}$ and $N_{4(\text{Cu})}$ depend, respectively, on the content of Li₂O and CuO,



Figure 2 : The fraction N_4 of four coordinated boron atoms as a function of CuO content in xCuO(30-x)Li₂O70B₂O₃ glasses. The symbol (\Box) represents experimental data obtained from deconvoluted infrared spectra. The symbol (\blacklozenge) refers to calculated values obtained from equation (5).

equation (1) can be rewritten as

 $N_4 = f_{Li}C_{Li} + f_{Cu}C_{cu}$ (2) where C_{Li} is the molar fraction of Li₂O in the glass and f_{Li} is a dimensionless factor related to Li₂O. C_{Cu} and f_{Cu} are the corresponding parameters for CuO. The equation of the fitting line of N_4 data in Figure (2) is $N_4 = -0.0057x + 0.3762$ (3)

This equation can be used to get a value of 0.205 for N_4 of the composition 30CuO·70B₂O₃, which devitrifies under the conditions of glass preparation used in the present study.

Equation (2) can be solved simultaneously for two adjacent compositions, using N_4 values from equation (3), to get f_{Li} and f_{Cu} . Figure (3) indicates that f_{Cu} and f_{Li} do not change for all CuO contents, where $f_{Li} = 1.254$ and $f_{\rm Cu} = 0.684$. These values reveal that, in the studied glasses, the contribution of Li_2O to N_4 is mostly twice that of CuO. The constancy of $f_{\rm Li}$ reveals that the composition of the borate matrix modified by Li₂O is independent on the CuO content. This composition might be that of the start glass, i.e. 30Li₂O·70B₂O₃. A similar conclusion can be considered for the borate matrix modified by CuO, which might be $30CuO70B_2O_2$ in all glasses. This leads to assume that the studied xCuO·(30-x)Li₂O·70B₂O₃ glasses can be looked as a mixture of two matrices, each of which contains 70 mol% B₂O₃ regardless the CuO content. It follows that



Figure 3 : Change with CuO content of f_{Li} and f_{Cu} for xCuO(30-x)Li₂O 70B₂O₃ glasses.

 N_4 of a glass of the studied series can be given by $N_4 = N_{4(30\text{Li})}F_{30\text{Li}} + N_{4(30\text{Cu})}F_{30\text{Cu}}$ (4) where $N_{4(30\text{Li})}$ is the N_4 value for $30\text{Li}_2\text{O}\cdot70\text{B}_2\text{O}_3$ matrix and $F_{30\text{Li}}$ is its fraction in the glass. $N_{4(30\text{Cu})}$ and $F_{30\text{Cu}}$ are the corresponding parameters for $30\text{CuO}\cdot70\text{B}_2\text{O}_3$ matrix. Using $N_{4(30\text{Li})} = 0.376$ and $N_{4(30\text{Cu})} = 0.205$ (equation 3), N_4 values of the studied glasses are given by

$$N_{4} = 0.376[(30-x)/30] + 0.205(x/30)$$
 (5)

The symbol (\blacklozenge) in Figure (2) represents N_4 values obtained from equation (5). The agreement with the experimental data supports the assumption that the studied glasses are composed of a mixture of $30\text{Li}_2\text{O}\cdot70\text{B}_2\text{O}_3$ and $30\text{CuO}\cdot70\text{B}_2\text{O}_3$ matrices. The change in N_4 is related to the change in the fraction of each matrix in the glass. In terms of the molar fraction, equation (5) can be reformed to

 $N_4 = (0.376/0.3)[(30-x)/100] + (0.205/0.3)(x/100),$ (5.a) or

$$N_4 = 1.523[(30-x)/100] + 0.683(x/100)$$
 (5.b)

This form is equivalent to equation (2), where $f_{\text{Li}}=1.523$, $C_{\text{Li}}=[(30-x)/100]$, $f_{\text{Cu}}=0.683$, $C_{\text{Cu}}=(x/100)$. As is revealed, the values of f_{Li} and f_{Cu} in equation (3.14b) are the same obtained from solving equation (Figure 2).

From equations (1) and (2) it is concluded that

$$N_{4(\mathrm{Li})} = C_{\mathrm{Li}} f_{\mathrm{Li}} \tag{6}$$

$$N_{4(\mathrm{Cu})} = C_{\mathrm{Cu}} f_{\mathrm{Cu}}.$$

Figure (4) shows a linear decrease in $N_{4(\text{Li})}$ and a linear increase in $N_{4(\text{Cu})}$ when increasing CuO content.



(7)

Full Paper

These are expected features, in the light of the constant values of f_{Li} and f_{Cu} and the decrease in concentration of Li₂O when increasing CuO content. As shown, the magnitude of rate of change in $N_{4(\text{Cu})}$ is lower than that of $N_{4(\text{Li})}$. This is because of the lower value of f_{Cu} with respect to the value of f_{Li} . $N_{4(\text{Li})}$ and $N_{4(\text{Cu})}$ values obtained from equations (6) and (7) can be used to obtain the portions (molar fractions) of Li₂O and CuO that form BO₄ units. These are given as



Figure 4 : Change with CuO content, of the N_4 fractions $(N_{4(\text{Li})} \text{ and } N_{4(\text{Cu})})$ created, respectively, by Li₂O and CuO in xCuO(30-x)Li₂O 70B₂O₃ glasses.

$$C_{\text{Li}(\text{B4})} = N_{4(\text{Li})} C_{\text{B}}$$
and
$$C_{\text{Li}} N_{\text{Li}} C_{\text{B}}$$
(8)

 $C_{\rm Cu(B4)} = N_{\rm 4(Cu)} C_{\rm B}$

In these relations, $C_{\text{Li}(B4)}$ and $C_{\text{Cu}(B4)}$ refer, respectively, to the molar fraction of Li₂O and CuO consumed in the conversion of symmetric BO₃ units to BO₄ tetrahedra. C_{B} is the molar fraction of B₂O₃ in glass. The rest of Li₂O is assumed to form asymmetric BO₃ units (NBOs) and can be given by

$$C_{\mathrm{Li(as)}} = C_{\mathrm{Li}} - C_{\mathrm{Li(B4)}} \tag{10}$$

where $C_{\text{Li(as)}}$ is the molar fraction of Li₂O forming asymmetric BO₃ units. The rest of CuO is would form asymmetric BO₂ units and it can be given by

$$C_{\rm Cu(as)} = C_{\rm Cu} - C_{\rm Cu(B4)} \tag{11}$$

Here $C_{Cu(as)}$ refers to the molar fraction of CuO that forms asymmetric BO₃ units (NBOs). The concentration of residual symmetric BO₃ units ($C_{B(s)}$) can then be obtained as

$$C_{\rm B(s)} = C_{\rm B} \cdot (C_{\rm Li(B4)} + C_{\rm Cu(B4)}) \cdot (C_{\rm Li(as)} + C_{\rm Cu(as)})$$
(12)

Figure (5) presents the dependence on CuO content of the structural species proposed to be in the stud-

ied xCuO·(30-x)Li₂O·70B₂O₃ glasses. There is a linear decrease in $C_{\text{Li(B4)}}$ and $C_{\text{Li(as)}}$ with increasing CuO content, which is attributed to the decrease in concentration of Li₂O content. In addition, there is a linear increase in $C_{\text{Cua(B4)}}$ and $C_{\text{Cu(as)}}$ upon increasing the CuO content. As would be expected, $C_{B(s)}$ does not change with composition because of the constant modifier oxide concentration (30 mol%) in all xCuO(30x)Li₂O \cdot 70B₂O₃ glasses. It is noticed that the magnitude of the rate of change for $C_{\text{Li(B4)}}$ is greater than that for $C_{\text{Cu(B4)}}$, while it is lower for $C_{\text{Li(as)}}$ than for $C_{\text{Cu(as)}}$. Again, these differences are related to the difference in N_{4} values of the glasses 30CuO \cdot 70B₂O₃ and $30 \text{Li}_2 \text{O} \cdot 70 \text{B}_2 \text{O}_3$. The trends of $C_{\text{Li(as)}}$ and $C_{\text{Cu(as)}}$ in Figure (5) refers to the higher ability of CuO to form NBOs in CuO-B₂O₃ glasses than can be done by Li₂O in Li₂O- B_2O_3 glasses.



Figure 5 : Molar fraction of, respectively, Li₂O and CuO that form BO₄ tetrahedra ($C_{Li(B4)}, C_{Cu(B4)}$) and asymmetric BO₃ units ($C_{Li(as)}, C_{Cu(as)}$) as a function of CuO content in *x*CuO(30*x*)Li₂O 70B₂O₃ glasses. $C_{B(s)}$ refers to the molar fraction of symmetric BO₃ units.

xCuO·(40-x)Li₂O·60B₂O₃ glasses

The infrared spectra of xCuO·(40-x)Li₂O·60B₂O₃ glasses are presented in Figure (6). The main features of the spectra resembles those of xCuO·(30-x)Li₂O·70B₂O₃ glasses (Figure 1). There are three marked absorption regions centered at 700, 1000 and 1400 cm⁻¹. The position of the first one seems to be independent of the glass composition. In contrary, There is a shift in the center of the last envelope from 1400 cm⁻¹ for the glass 40Li₂O·60B₂O₃ to 1375 cm⁻¹ for the glass 40CuO·60B₂O₃. The envelope centered at 1000 cm⁻¹ (for the glass 40Li₂O·60B₂O₃) becomes shallower with replacing CuO for Li₂O. Its center can not be identified at the higher CuO contents. bands in the region ~800-1200 cm⁻¹ are related to B-O stretching vibration of BO₄ units in various borate groups, like pentaborate, triborate and diborate groups^[19-21]. The absorption bands in the region ~1200-1600 cm⁻¹ are attributed to B-O stretching vibration of trigonal BO₃ units only. The latter are incorporated in various borate groups^[22,23]. The small band at ~700 cm⁻¹ is assumed to be due bending vibration of B-O-B in symmetric BO₃ triangles^[21].



Figure 6 : Normalized infrared spectra of xCuO(40-x)Li₂O 60B₂O₃ glasses. Numbers at the plots refer to the concentration of CuO (mol%).

The successive decrease of the relative area under the envelope centered at 1000 cm⁻¹ reflects a decrease in the concentration of BO₄ units with increasing CuO content. This is presented in Figure (7) that shows the change of the fraction N_4 of four coordinated boron atoms as a function of CuO content. N_4 values are obtained by applying the deconvolution technique described elsewhere^[24-26]. The linear decrease in N_4 is consistent with the values for the end compositions. The N_4 value of the glass $40\text{Li}_2\text{O}\cdot60\text{B}_2\text{O}_3$ equals to 0.46, which agrees well with literature NMR data^[27,28]. The equation of the fitting line of N_4 data in Figure (7) is $N_4 = -0.0051\text{x} + 0.4768$ (13)

 N_4 data obtained from this relation could be used



Figure 7 : The fraction N_4 of four coordinated boron atoms as a function of CuO content in xCuO'''(40-x)Li₂O'''60B₂O₃ glasses. The symbol (\Box) represents experimental data obtained from deconvoluted infrared spectra. The symbol (\blacklozenge) refers to calculated values obtained from equation (15). The error limit for the experimental data is taken as ±5%. The line is a fitting plot of the experimental data.

to solve equation (2) simultaneously for $f_{\rm Li}$ and $f_{\rm Cu}$. Figure (8) shows that both factors are constant over all the composition change, where $f_{\rm Li} = 1.192$ and $f_{\rm Cu} = 0.682$. The latter is mostly the same for $x{\rm CuO} \cdot (30 - x){\rm Li}_2{\rm O} \cdot 70{\rm B}_2{\rm O}_3$ glasses (= 0.684). On the other hand, $f_{\rm Li}$ is relatively lower than that for $x{\rm CuO} \cdot (30 - x){\rm Li}_2{\rm O} \cdot 70{\rm B}_2{\rm O}_3$ glasses (= 1.254). The lower value of $f_{\rm Li}$ for $x{\rm CuO} \cdot (40 - x){\rm Li}_2{\rm O} \cdot 60{\rm B}_2{\rm O}_3$ glasses can be because the glass $40{\rm Li}_2{\rm O} \cdot 60{\rm B}_2{\rm O}_3$ has the maximum N_4 value among all Li₂O-B₂O₃ glasses^[27,28].

In analogy to equation (4), The fraction of four coordinated boron in xCuO·(40-x)Li₂O·60B₂O₃ glasses



Figure 8 : Change with CuO content of f_{Li} and f_{Cu} for xCuO(40-x)Li₂O 60B₂O₃ glasses.



Full Paper

can be given by

 $N_4 = N_{4(40\text{Li})}F_{40\text{Li}} + N_{4(40\text{Cu})}F_{40\text{Cu}}$ (14) where $N_{4(40\text{Li})}$ is the N_4 value for $40\text{Li}_2\text{O}\cdot60\text{B}_2\text{O}_3$ matrix and $F_{40\text{Li}}$ is its fraction in the glass. $N_{4(40\text{Cu})}$ and $F_{40\text{Cu}}$ are the corresponding parameters for $40\text{CuO}\cdot60\text{B}_2\text{O}_3$ matrix. Equation (13) gives $N_4 = 0.477$ for the glass $40\text{Li}_2\text{O}\cdot60\text{B}_2\text{O}_3$ and 0.273 for the glass $40\text{CuO}\cdot60\text{B}_2\text{O}_3$. These values can be used in equation (14) to calculate N_4 of $x\text{CuO}\cdot(40\text{-}x)\text{Li}_2\text{O}\cdot60\text{B}_2\text{O}_3$ glasses as

 $N_4 = 0.477[(40-x)/40] + 0.273(x/40)$ (15)

The obtained N_4 values, presented in Figure (7), are in good agreement with the experimental values. This agreement indicates that $xCuO\cdot(40-x)Li_2O\cdot60B_2O_3$ glasses can be looked as mixtures of $40Li_2O\cdot60B_2O_3$ and $40CuO\cdot60B_2O_3$ matrices. As equation (15) reveals, x is the sole variable that determines N_4 .

By comparing the last relation with (1), it appears that

 $N_{4(\text{Li})} = 0.477[(40-x)/40]$ (16) and

 $N_{4(Cu)} = 0.273(x/40) \tag{17}$

These relations show that, with increasing x, there would be a linear decrease in $N_{4(\text{Li})}$ and a increase in $N_{4(\text{Cu})}$. These changes are presented in Figure (9), where it is also shown that the magnitude of rate of change in $N_{4(\text{Cu})}$ is lower than that of $N_{4(\text{Li})}$. These effects can be attributed to the lower value of f_{Cu} with respect to f_{Li} and, in turn, the difference in N_4 values of $40\text{Li}_2\text{O}\cdot60\text{B}_2\text{O}_3$ and $40\text{CuO}\cdot60\text{B}_2\text{O}_3$ matrices. Values of $N_{4(\text{Li})}$ and $N_{4(\text{Cu})}$ obtained from equations (16) and (17) can be used to determine the relative concentration of various species in $x\text{CuO}\cdot(40-x)\text{Li}_2\text{O}\cdot60\text{B}_2\text{O}_3$ glasses. In these glasses there are BO₄ and asymmetric BO₃ units linked to Li or Cu ions, in addition to symmetric BO₃ units.

Figure (10) show the molar fraction of these species ($C_{\text{Li(B4)}}$, $C_{\text{Cu(B4)}}$, $C_{\text{Li(as)}}$, $C_{\text{Cu(as)}}$ and $C_{\text{B(s)}}$) as a function of CuO content. These quantities have been obtained from equations (8 – 12), respectively. The general features in Figure (10) resemble those for $x\text{CuO}\cdot(30-x)\text{Li}_2\text{O}\cdot70\text{B}_2\text{O}_3$ glasses (Figure 5). There is a linear decrease in $C_{\text{Li(B4)}}$ and $C_{\text{Li(as)}}$, due the decrease in Li₂O content. In contrary, $C_{\text{Cu(B4)}}$ and $C_{\text{Cu(as)}}$ increase in a linear manner with increasing the concentration.

Materials Science

An Indian Journal



Figure 9 : Change with CuO content, of the N_4 fractions $(N_{4(\text{Li})} \text{ and } N_{4(\text{Cu})})$ created, respectively, by Li₂O and CuO in xCuO(40-x)Li₂O 60B₂O₃ glasses.

tration of CuO. In Figures (10) and (5) $C_{B(s)}$ is independent on CuO content, since it depends on the total concentration of modifier oxide that remains constant in each glass series.



Figure 10 : Molar fraction of, respectively, Li₂O and CuO that form BO₄ tetrahedra ($C_{\text{Li(B4)}}$, $C_{\text{Cu(B4)}}$) and asymmetric BO₃ units ($C_{\text{Li(as)}}$, $C_{\text{Cu(as)}}$) as a function of CuO content in xCuO(40-x)Li₂O 60B₂O₃ glasses. $C_{\text{B(s)}}$ refers to the molar fraction of symmetric BO₃ units.

Figures (10) and (5) indicate that CuO has greater tendency to form asymmetric BO_3 units than Li_2O . In contrast, the latter has higher ability to form BO_4 units.

CONCLUSION

Infrared spectroscopy can be used to get quantitative information about the contribution of both CuO and

57

> Full Paper

 Li_2O to the structure of CuO– Li_2O – B_2O_3 glasses. A decrease in N_4 with increasing CuO content, at the expense of Li_2O , in the studied glasses reveals that CuO has greater tendency to form asymmetric BO_3 units than Li_2O . In contrast, the latter has higher ability to form BO_4 units.

REFRENCES

- [1] C.L.Christ, J.R.Clark; Phys.Chem.Miner, 2, 59 (1977).
- [2] P.C.Burns, J.D.Grice, F.C.Hawthorne; Can.Mineral, 33, 1131 (1995).
- [3] P.C.Burns; Can.Mineral., 33, 1167 (1995).
- [4] J.D.Grice, P.C.Burns, F.C.Hawthorne; Can.Mineral, 37, 731 (1999).
- [5] C.Chen, Y.Wang, B.Wu, K.Wu, W.Zeng, L.Yu; Nature, 373, 322 (1995).
- [6] V.Ravi kumar, N.veeraiah, S.Buddudu; J.de physique, 7, 951 (1997).
- [7] R.V.V.S.N.Ravi Kumar, R.Komatsu, P.S.Rao; Physica B, 334, 398 (2003).
- [8] S.V.G.V.A.Prasad, N.Veeraiah; Phys.status solidi A, 202, 2812 (2005).
- [9] T.Tsuchiya, H.Yamakawa; J.Ceram.Soc.JP, 98, 1083 (1990).
- [10] A.Duran, J.R.Jurado, J.M.F.Navarro; J.Non-Cryst.Solids, 79, 333 (1986).
- [11] P.Znasik, M.Jamnicky; J.Mater.Sci.Lett, 14, 766 (1995).
- [12] C.F.Drake, I.F.Scanlan, I.A.Engel; Phys.Status Solidi, 32, 193 (1969).

- [13] G.R.Moridi, C.A.Horgath; Int.J.Electron, 44, 297 (1978).
- [14] L.S.Rao, M.S.Reddy, D.K.Rao, N.Veeraiah; Solid State Sci, 11, 578 (2009).
- [15] E.I.Kamitsos; Phys.Chem.Glasses, 44, 79 (2003).
- [16] Y.D.Yiannopoulos, G.D.Chryssikos, E.I.Kamitsos; Phys.Chem.Glasses, 42, 164 (2001).
- [17] H.Doweidar, K.El-Igili, S.Abd El-Maksoud; J.Phys.D: Appl.Phys, 33, 2532 (2000).
- [18] H.Doweidar, G.El-Damrawi, E.Mansour, R.E.Fetouh; J.Non-Cryst.Solids, 358, 941 (2012).
- [19] E.I.Kamitsos, M.A.Karakassides, G.D.Chryssikos; J.Phys.Chem, 91, 1073 (1987).
- [20] E.I.Kamitsos, M.A.Karakassides, G.D.Chryssikos; Phys.Chem.Glasses, 28, 203 (1987).
- [21] E.I.Kamitsos, A.P.Patsis, M.A.Karakassides, G.D.Chryssikos; J.Non-Cryst.Solids, 126, 52 (1990).
- [22] B.N.Meera, A.K.Sood, N.Chandrabhas; J.Ramakrishna, J.Non-Cryst.Solids, 126, 224 (1990).
- [23] J.Krogh-Moe; Phys.Chem.Glasses, 6, 46 (1965).
- [24] Y.M.Moustafa, H.Doweidar, G.El-Damrawi; Phys.Chem.Glasses, 35, 104 (1994).
- [25] H.Doweidar, K.El-Egili, G.El-Damrawi, R.M.Ramadan; Phys.Chem.Glasses: Eur.J.Glass Sci.Technol., B49, 271 (2008).
- [26] H.Doweidar, Y.B.Saddeek; J.Non-Cryst.Solids, 356, 1452 (2010).
- [27] P.J.Bray; Inorganic.Chimica.Acta, 289, 158 (1999).
- [28] Vladimir K.Michaelis, Pedro M.Aguiar, Scott Kroeker; J.Non-Cryst.Solids, 353, 2582 (2007).

