Spectroscopic investigations of Cu^{2+} in Li_2O–Na_2O–B_2O_3–Bi_2O_3 glasses

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Abstract. Pure and copper doped glasses with composition, xLi_2O–$(40-x)Na_2O$–$50B_2O_3$–$10Bi_2O_3$, have been prepared over the range $0 \leq x \leq 40$. The electron paramagnetic resonance (EPR) spectra of Cu^{2+} ions of these glasses have been recorded in the X-band at room temperature. Spin Hamiltonian parameters have been calculated. The molecular bonding coefficients, a^2 and b^2, have been calculated by recording the optical absorption spectra in the wavelength range 200–1200 nm. It has been observed that the site symmetry around Cu^{2+} ions is tetragonally distorted octahedral. The density and glass transition temperature variation with alkali content shows non-linear behaviour. The IR studies show that the glassy system contains BO_3 and BO_4 units in the disordered manner.

Keywords. Glass transition temperature; EPR; optical absorption; glasses; bonding parameters.

1. Introduction

Glasses play an important role as both passive and active materials in solid state electronic and ionic devices. These include wave guides, lenses, lasing materials, magneto-optic materials, fast ion conducting materials, optical switching materials and windows. In conventional glasses, metal oxides, such as Na_2O, Li_2O, Ag_2O etc are used as modifiers with network forming oxides like B_2O_3, SiO_2, P_2O_5 etc. Recently, glasses formed with heavy metal ions have received significant attention because of their interesting optical applications. These glasses are better competitors for optical transmission studies due to their long infrared (IR) cut-off (Fu and Yatsuda 1995; Pan and Ghosh 2000). Bismuthate glasses have been studied mainly because of their high non-linear optical susceptibility, higher even in the similar crystalline state of the same compounds (Hall et al 1989; Kityk et al 2003), ability to give rise to the glass ceramic superconductor materials (Komatsu and Matusika 1991) and improved chemical durability. In addition, transition metal oxides are used as colouring agents in glass industry and also to increase the refractive index of the glasses. Recently, Cu^{2+} ion doped glasses have attracted great attention due to their optical properties (Asahara 1997).

Electron paramagnetic resonance (EPR) spectroscopy is an experimental technique capable of obtaining detailed information on some of the structural and dynamic phenomena of a material and to identify site symmetry around transition metal ions in glasses (Imagawa 1968; Griscom

1980). Several studies have been made on the EPR spectra of Cu^{2+} ions in oxide glasses (Bogomolova 1979; Chand et al 1999; Chandrasekhar et al 2002; Agarwal et al 2004). Recently, Murali and Rao (1999), Karthikeyan and Mohan (2003) and Srinivasa Rao et al (2005) studied the EPR and optical absorption spectra of Cu^{2+} ion doped glasses. Ardelean et al (1997, 2005) investigated EPR, magnetic susceptibility and FT–IR studies of Fe^{3+} and Mn^{2+} ions in lead and bismuth based glasses.

Optical absorption of transition metal ions in glasses is another important aspect of this study which gives rise to ligand field absorption energies which sensitively reflect the distortion of the cubic, octahedral and tetrahedral co-ordinations. By correlating the EPR and optical absorption spectral parameters, one can obtain information regarding the bond parameters which will be useful in obtaining information on the metal ligand bond nature in the glasses.

In the present work, an attempt has been made in this direction by doping Cu^{2+} in xLi_2O–$(40-x)Na_2O$–$50B_2O_3$–$10Bi_2O_3$ glasses and the site symmetry was investigated using optical absorption, electron paramagnetic resonance and IR. The values of x were adjusted so that the compositional parameter defined as

$$R = Li_2O/(Li_2O + Na_2O),$$

takes the values of 0, 0·2, 0·4, 0·6, 0·8 and 1.

2. Experimental

Pure and copper (1 mole%) doped glass samples in the present study whose batch compositions are given in table 1, were prepared by the melt quench technique at 1000–

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Table 1. Glass composition, density, molar volume, oxygen packing density and glass transition temperature in the present glass system.

Glass no.	Glass composition	Density (g/cc) (± 0.01)	Molar volume (cc/mole)	Oxygen packing density (g-atom/l)	T_g (°C)
G1	$40Na_2O–50B_2O_3–10Bi_2O_3$	3·57	29·4	74·7	441
G2	$8Li_2O–32Na_2O–50B_2O_3–10Bi_2O_3$	3·31	33·4	65·6	425
G3	$16Li_2O–24Na_2O–50B_2O_3–10Bi_2O_3$	4·03	25·0	87·8	407
G4	$24Li_2O–16Na_2O–50B_2O_3–10Bi_2O_3$	3·94	25·1	87·4	403
G5	$32Li_2O–8Na_2O–50B_2O_3–10Bi_2O_3$	3·71	26·8	81·8	413
G6	$40Li_2O–50B_2O_3–10Bi_2O_3$	3·43	26·6	82·5	415

1150°C depending on the glass composition. The liquids were agitated for 2 h to ensure homogeneous mixture. The clear liquid was quickly cast in a stainless steel mould kept at 200°C and the glasses annealed at the same temperature for a duration of about 14 h.

The amorphous nature of the samples was confirmed by XRD study. The density of the glass samples at room temperature was determined by the Archimedes method. The thermal behaviour of the glass samples was investigated using a differential scanning calorimeter (TA Instruments DSC 2010) with a heating rate of 10°C/min.

The EPR spectra were recorded on powdered glass samples at room temperature using a Bruker ER 200D SRC spectrometer operating in the X-band and employing in a field modulation of 100 kHz. DPPH was used as the standard *g*-marker for the determination of the magnetic field. The room temperature optical absorption spectra in 200–1100 nm region was recorded by using a Shimadzu, Model UV 3100 spectrophotometer. The infrared spectra of the powdered glass samples were recorded at room temperature in the range 400–1400 cm^{-1} using a IR Perkin-Elmer spectrometer. These measurements were made on glass powder dispersed in KBr pellets.

3. Results and discussion

3.1 *Density and transition temperature*

The measured densities of the present glass system along with the evaluated values of molar volume, which is defined as the mean molecular weight of the constituents divided by its measured density and the oxygen packing density which is the ratio of measured density per molecular weight and number of oxygen ions in a formula unit are given in table 1. The DSC thermograms of the glass samples are given in figure 1. The glass transition temperature (T_g) in the present glass system varies from 403–441°C as presented in table 1.

3.2 *EPR spectra*

The room temperature EPR spectra of Cu^{2+} in these glasses is shown in figure 2. The field was scanned between 2000 G and 4400 G. The spectrum was analysed using the spin Hamiltonian.

$$\mathbf{H} = g_\parallel \mathbf{b} H_z S_z + g_\perp \mathbf{b} (H_x S_x + H_y S_y) + A_\parallel I_z S_z + A_\perp (I_x S_x + I_y S_y),$$

where the symbols have their usual meanings (Bleaney *et al* 1955). The hyperfine peak positions are related to the principal values of *g* and *A* tensors by the solutions of the spin Hamiltonian. The parallel hyperfine peaks were resolved in the present glasses, and the perpendicular hyperfine peaks were unresolved. Three hyperfine lines were observed on the parallel features of the spectrum. The changes in the hyperfine linewidths can be attributed to the fluctuations in the coordination sphere surrounding the probe Cu^{2+} ion (Kawazoe *et al* 1978). The values of $g_\parallel$ and $A_\parallel$ were calculated from the spectra and are given in table 2. From the observed $g_\parallel$ and $g_\perp$ values ($g_\parallel > g_\perp$ (2·035) > 2·0023), we can conclude that Cu^{2+} has an octahedral environment elongated along one of the cube axis and the ground state of the Cu^{2+} is $d_{x^2-y^2}$. This configuration satisfies the condition for applying the analysis developed by Maki and McGarvey (1958) and modified by Kivelson and Neiman (1969). The values of $A_\perp$ and $g_\perp$ remain invariant within the interval of uncertainty. $A_\parallel$ and $g_\parallel$ of the samples change in a non-linear manner with the compositional parameter, *R*. These non-linear changes can be attributed to the variation of ligand field around the probe ion.

3.3 *Optical absorption spectra*

The optical absorption spectra of Cu^{2+} ions in these glasses are shown in figure 3. A single absorption band in the near infrared region was observed for all samples. The near infrared band can be identified as *d–d* transition band due to Cu^{2+} ions (Siegel and Lorenc 1966). These transitions can be described in terms of ligand field theory (Bates 1962).

In regular octahedral field, the $3d^9$ configuration would result in a degenerate ground state (^2E_g). In glasses, it is assumed that due to vitreous state disorder, no site is perfectly cubic. Therefore, tetragonal distortions are endemic to the vitreous state which leads to splitting of energy levels. It is observed that the elongated structures are
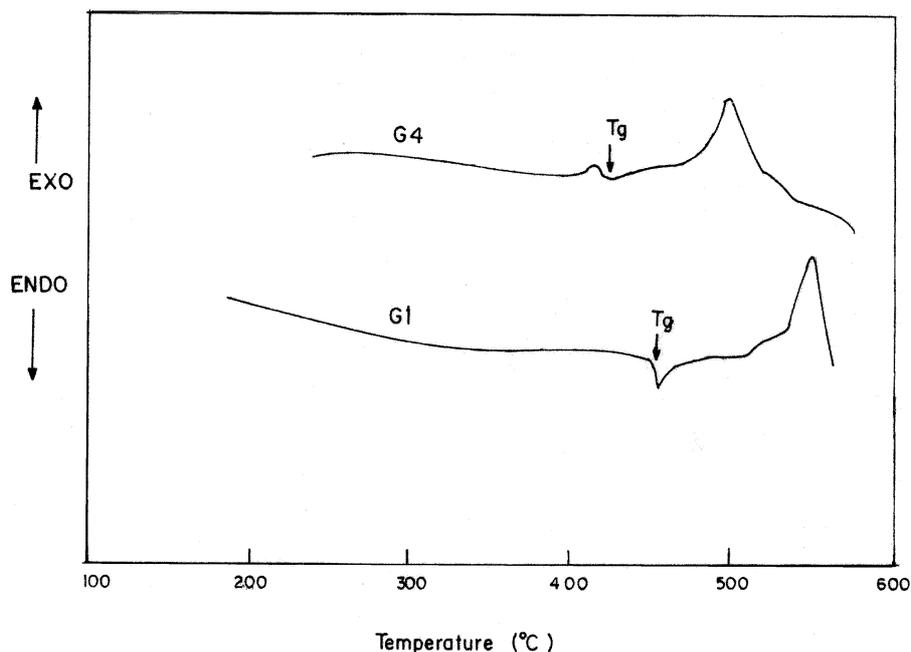
Figure 1. DSC thermograms of xLi$_2$O–$(40-x)$Na$_2$O–50B$_2$O$_3$–10Bi$_2$O$_3$ ($x = 0$ and 24) glasses.
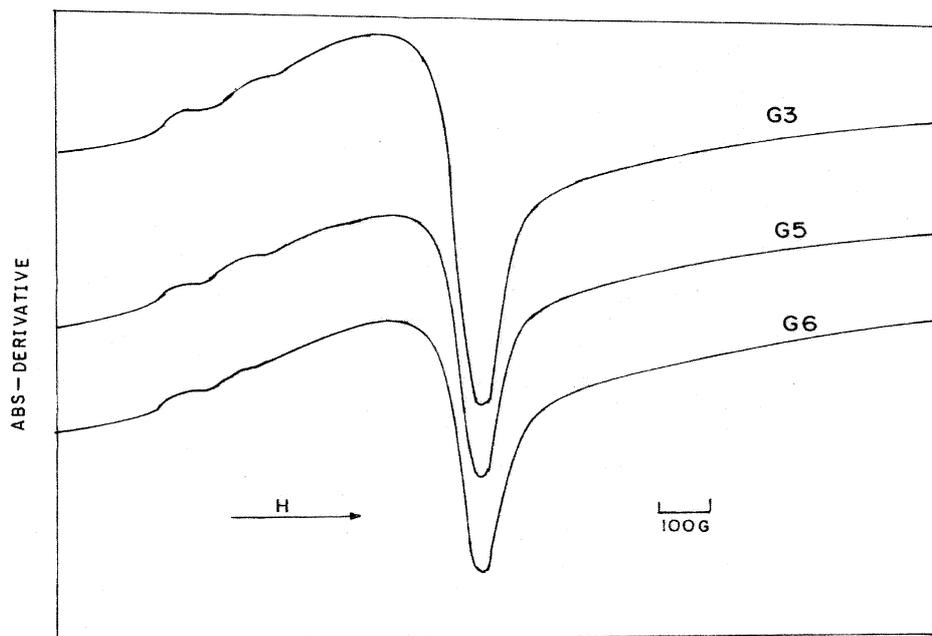
Figure 2. EPR spectra of copper doped xLi$_2$O–$(40-x)$Na$_2$O–50B$_2$O$_3$–10Bi$_2$O$_3$ ($x = 16$, 32 and 40) glasses at room temperature.

usually more energetically favoured than the compressed ones (Jorgensen 1955). Hence, in the present investigation the observed asymmetric band is due to the overlap of $^2B_{1g} \rightarrow {}^2A_{1g}$ and $^2B_{1g} \rightarrow {}^2B_{2g}$ transitions. The peak absorption wavelength varies non-linearly with the compositional parameter. At 40 mole% of alkali oxide content non-bridging oxygen (NBO) anionic groups form and there is a good chance that Cu^{2+} ions will be coordinated by

such non-bridging oxygens which may affect the peak position (Sakka *et al* 1978).

3.4 *Bonding parameters*

To determine the bonding coefficients of Cu^{2+}, one need to know the frequencies from the optical absorption bands,

Table 2. Spin Hamiltonian parameters and bonding coefficient for Cu^{2+} in the present glass system.

Glass system	$g_\parallel$ ($\pm$ 0·002)	$A_\parallel$ (10^{-4} cm^{-1}) ($\pm$ 2)	ΔE_{xy} (cm^{-1})	a^2	b_1^2	Γ_s (%)	Γ_p (%)
G1	2·321	130·0	12,987	0·77	0·80	49·0	40
G2	2·326	135·0	13,850	0·75	0·90	53·4	20
G3	2·329	130·0	13,368	0·74	0·89	55·6	22
G4	2·338	125·0	13,404	0·74	0·92	56·7	16
G5	2·334	135·0	13,333	0·76	0·87	51·2	26
G6	2·329	135·5	13,568	0·76	0·88	52·3	24
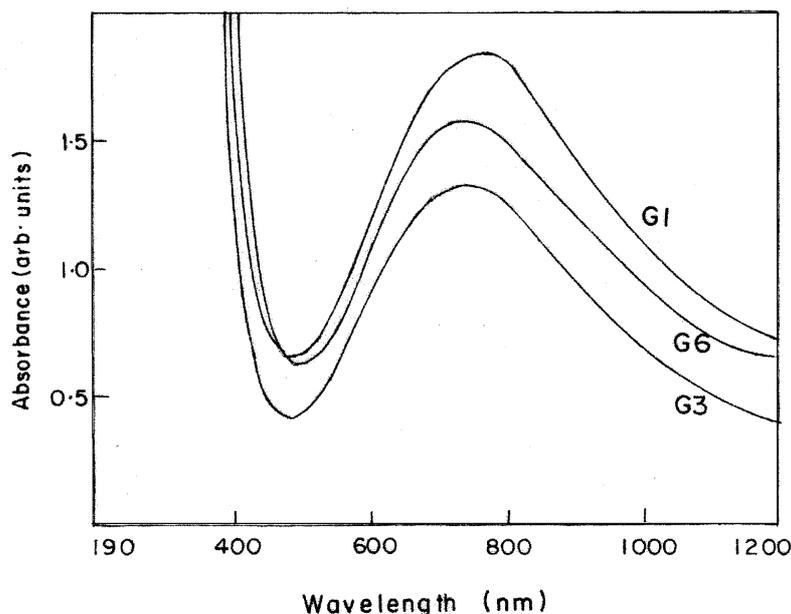
Figure 3. Optical absorption spectra of mixed alkali borobismuthate glasses.

which indicate the ΔE_{xy}. The ΔE_{xy} is the frequency of an intense absorption band in the optical spectrum of Cu^{2+} in a given glass. In the present glass system, the values of ΔE were determined and found to vary with the glass composition.

The bonding coefficients, a^2, b_1^2 and b^2, describe respectively, the in-plane s bonding, in-plane p bonding and out-of-plane p bonding of the Cu^{2+} complex and were evaluated using the following equations (Klonkowski *et al* 1983)

$$a^2 = |A_\parallel/P| + (g_\parallel - 2) + 3/7 \, (g_\perp - 2) + 0·04,$$

$$g_\parallel = 2·0023 \, \{1 - 4 l a^2 b_1^2 / \Delta E_{xy}\},$$

where P is the dipolar hyperfine coupling parameter and l the spin orbit coupling constant for Cu^{2+} ion [$l = -828$ cm^{-1}]. The value of a^2 lie between 0·5 and 1, the limits for pure covalent and ionic bonding, respectively. The values of b^2 may be expected to lie sufficiently close to unity (Kivelson and Lee 1964). The values of a^2 and b_1^2 given in table 2, indicate an intermediate ionic bond for the Cu(II)–O$^-$ in-plane s bonding and the in-plane p bonding. However, the out-of-plane p bonding for the

cupric ion has an invariant covalent component in all the samples within the experimental error.

The normalized covalency of Cu^{2+}–O in-plane bonding of s or p symmetry is expressed by (Kawazoe *et al* 1978)

$$\Gamma_s = 200(1 - S) \, (1 - a^2)/(1 - 2S)\%,$$

and

$$\Gamma_p = 200(1 - b_1^2)\%,$$

where S is the overlap integral ($S_{oxy} = 0·076$).

The normalized covalency (Γ_p) of Cu^{2+}–O bonding of p symmetry indicates the basicity of the oxide ion. We observe that the covalency of the in-plane s bonding (Γ_s) is constant within the experimental error and the covalency of in-plane p bonding (Γ_p) decreases.

3.5 IR spectra

The IR spectra of mixed alkali borobismuthate glasses are shown in figure 4. The structure of borate glasses consists of random network of BO_3 triangles with certain fraction of boroxol rings (Krogh Moe 1965). The vibrational
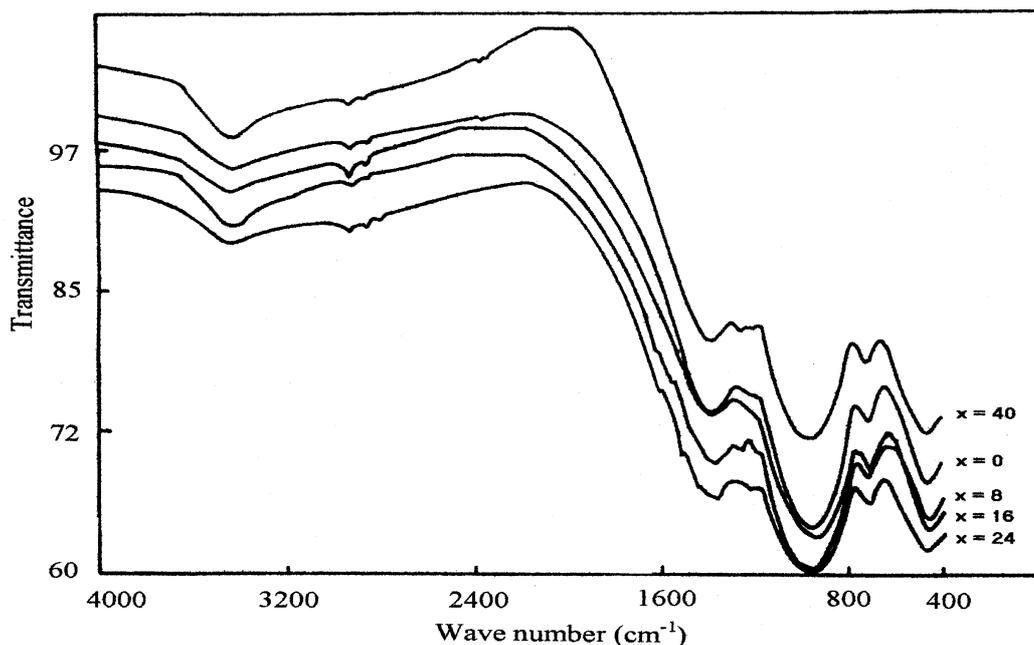
Figure 4.   IR spectra of xLi$_2$O–(40–x)Na$_2$O–50B$_2$O$_3$–10Bi$_2$O$_3$ glasses.

modes of the borate network are mainly active in the three infrared spectral regions. The 1200–1600 cm^{-1} is the first region, which is due to the asymmetric stretching relaxation of B–O bond of trigonal BO$_3$ units. The second region is reclined between 800 and 1200 cm^{-1} and is due to the B–O bond stretching of tetrahedral BO$_4$ units, and the last band around 700 cm^{-1} is due to the bending vibrations of various borate segments (Kamitsos and Karakassides 1989).

Thus, from figure 4, xLi$_2$O–(40–x)Na$_2$O–50B$_2$O$_3$–10Bi$_2$O$_3$ glass system shows two major bands around 950 cm^{-1} and 1376 cm^{-1}. The band around 950 cm^{-1} is attributed to the B–O bond stretching of BO$_4$ containing groups and the band around 1376 cm^{-1} to the diborate groups. The 720 cm^{-1} is assigned to out of plane ring angle bending mode. For $x > 0$ mole%, 1272 cm^{-1} is absent which is attributed to B–O–B linkages between two trigonal BO$_3$ groups and glass network becomes depolymerized. In general, the IR absorption band observed in the region 3200–3600 cm^{-1} is ascribed to hydroxyl or water groups present in the glass. The observations made in the present investigation agree well with the literature values (Kamitsos *et al* 1990).

4.   Conclusions

From the EPR and optical absorption studies discussed above, the following conclusions may be drawn:

(I) An elongated octahedral coordination of Cu^{2+} is observed.

(II) The a^2 values indicate that s bonding is ionic and remains so with the compositional parameter.

(III) The IR spectral analysis confirms the presence of BO$_4$ and diborate local structures in the glass. The glasses show good IR window up to 7 μm due to the presence of heavy metal in the glass.

References

Agarwal A, Seth V P, Gahlot P S, Khasa S and Chand P 2004 *Mater. Chem. Phys.* **85** 215

Ardelean I, Peteanu M, Filip S, Simon V and Gyroffy G 1997 *Solid State Commun.* **102** 341

Ardelean I, Simona Cora, Ciceo Lucacel R and Octavia Hulpus 2005 *Solid State Sci.* **7** 1438

Asahara Y 1997 *Ceram. Int.* **23** 375

Bates T 1962 in *Modern aspects of the vitreous state* (ed.) J D Meckenzie (London: Butterworths) **Vol 2**, p. 195

Bleaney B, Bowers K D and Pryce M H L 1955 *Proc. R. Soc.* **A228** 147

Bogomolova L D 1979 *J. Non-Cryst. Solids* **30** 379

Chand I, Seth V P, Prakash D and Gupta S K 1999 *Phys. Chem. Glasses* **40** 153

Chandrasekhar A V, Ravi Kumar R V S S N, Reddy B J, Reddy Y P and Rao P S 2002 *Glass Technol.* **43** 32

Fu J and Yatsuda H 1995 *Phys. Chem. Glasses* **36** 211

Griscom D L 1980 *J. Non-Cryst. Solids* **40** 211

Hall D, Newhause N, Borrelli N, Dumbaugh W and Weidman D 1989 *J. Appl. Phys. Lett.* **54** 1293

Imagawa H 1968 *Phys. Status Solidi* **30** 469

Jorgensen C K 1955 *Acta Chem. Scand.* **9** 1362

Kamitsos E I and Karakassides M A 1989 *Phys. Chem. Glasses* **30** 19

Kamitsos E I, Patsis A P, Karakassides M A and Chryssikos G D 1990 *J. Non-Cryst. Solids* **126** 52

Karthikeyan B and Mohan S 2003 *Mater. Letts* **57** 3789

Kawazoe H, Hosono H and Kanazawa T 1978 *J. Non-Cryst. Solids* **29** 173

Kityk I V, Imiolek W, Majchrowski A and Michalski E 2003 *Opt. Commun.* **219** 421

Kivelson D and Lee S K 1964 *J. Chem. Phys.* **41** 1896

Kivelson D and Neiman R 1969 *J. Chem. Phys.* **35** 149

Klonkowski A, Frischat G H and Ritchter T 1983 *Phys. Chem. Glasses* **24** 47

Komatsu T and Matusika K 1991 *Thermochim. Acta* **174** 131

Krogh Moe J 1965 *J. Phys. Chem. Glasses* **6** 46

Maki A H and McGarvey B R 1958 *J. Chem. Phys.* **45** 31

Murali A and Rao J L 1999 *J. Phys. Condens. Matter* **11** 7921

Pan A and Ghosh A 2000 *J. Non-Cryst. Solids* **271** 157

Sakka S, Kamiya K and Yoshikawa H 1978 *J. Non-Cryst. Solids* **27** 289

Siegel J and Lorenc J A 1966 *J. Chem. Phys.* **45** 2315

Srinivasa Rao N, Shashidhar Bale, Purnima M, Siva Kumar K and Syed Rahman 2005 *Bull. Mater. Sci.* **28** 589