

Electron spin resonance and optical absorption spectra of Cu^{2+} ions in $\text{Na}_2\text{SO}_4\text{-ZnSO}_4$ glasses

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Electron spin resonance (ESR) and optical absorption spectra of Cu^{2+} ions in $\text{Na}_2\text{SO}_4\text{-ZnSO}_4$ glasses have been studied. The ESR spectra of Cu^{2+} ion-doped glasses exhibited a pronounced peak at $g = 2.07$ and a shallow quadruplet at $g = 2.35$, the latter arising from the hyperfine splitting of g_{\parallel} . ESR spectra of Cu^{2+} ion-doped glasses were also studied by varying the concentration of Cu^{2+} ions, temperature and composition of the glasses. The optical absorption spectra exhibited a broad absorption band in the near infrared region, which is attributed to ${}^2\text{B}_{1g} \rightarrow {}^2\text{B}_{2g}$ transition. By correlating the ESR and optical absorption data, the bonding orbital coefficients α^2 and β_1^2 for Cu^{2+} ions have been evaluated.

1. Introduction

Studies of the bonding characteristics, the coordination and the valence state of transition metal ions in inorganic glasses are very helpful in understanding the structure of glass. Electron spin resonance (ESR) and optical absorption spectra are known to be valuable sources of information with respect to the local environment of some transition elements which are introduced in the vitreous matrix, thus giving a certain knowledge of the structure.

Investigations of the ESR and optical absorption spectra of transition metal ions (Cu^{2+})-doped glasses have been widely studied by various authors in the borate, silicate and phosphate glass systems [1–16]. ESR and optical absorption spectra of paramagnetic ions in $\text{K}_2\text{SO}_4\text{-ZnSO}_4$ glasses [17–23] have been studied by several authors and they have concluded that the paramagnetic ions enter substitutionally at the zinc ion sites which are octahedrally coordinated with six sulphate ions. The formation of other binary alkali zinc sulphate glasses is not known except for Mn^{2+} ion-doped $\text{Na}_2\text{SO}_4\text{-ZnSO}_4$ glasses [24]. In the present investigation, the results of ESR and optical absorption spectra of Cu^{2+} ions in $\text{Na}_2\text{SO}_4\text{-ZnSO}_4$ glasses at room and different temperatures are described. The Cu^{2+} ion provides useful information regarding the structure of its network environment in a glass, because its electronic and ESR spectra are simple.

2. Experimental procedure

Copper-doped glasses were prepared by melting approximate amounts of Analar grade salts, 40 mol % Na_2SO_4 (99.5% purity), 59 mol % $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ (99.5% purity) and 1 mol % $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in an electric furnace in an air atmosphere at about 1173 K for nearly 4 h. The melt was then quenched by pouring it between two polished brass plates. Similarly, $\text{Na}_2\text{SO}_4\text{-ZnSO}_4$ glasses of different compositions

containing different concentrations of Cu^{2+} ions were also prepared.

ESR spectra were recorded on a Jeol-FE1X ESR spectrometer operating in the X-band frequencies, with a field modulation of 100 kHz. The microwave frequency was set at 9.205 GHz and the magnetic field scanned between 2250 and 4250 G. DPPH with $g = 2.0036$ was used as a standard field marker. Care was taken to see that the samples were of the same size and were not exposed to moisture before studying the above properties.

ESR spectra were also recorded at different temperatures (123–423 K). The temperature was varied by using a JES-VT-3A variable temperature controller capable of regulating the temperature from 523–103 K. A temperature stability of ± 1 K was easily obtained by waiting about 0.5 h at the set temperature before recording the spectrum.

Optical absorption spectra were recorded at room and liquid nitrogen temperatures on a Perkin-Elmer 551 spectrophotometer in the wavelength region 700–900 nm. The wave number accuracy for the absorption bands is $\pm 5 \text{ cm}^{-1}$.

3. Results and analysis

No ESR signal was detected for undoped glasses. When Cu^{2+} ions were introduced into the $\text{Na}_2\text{SO}_4\text{-ZnSO}_4$ glasses, all the samples exhibited absorption lines. ESR spectra of Cu^{2+} ions in $\text{Na}_2\text{SO}_4\text{-ZnSO}_4$ glasses at room temperature exhibited a pronounced peak at $g = 2.07 \pm 0.02$ and a broad and shallow quadruplet at $g = 2.35 \pm 0.02$, the latter arising from the splitting of g_{\parallel} [25]. Such spectral features are characteristic of the Cu^{2+} ions present in an axially distorted octahedral sites. Fig. 1 shows a typical ESR spectra of 1 mol % Cu^{2+} ions in $\text{Na}_2\text{SO}_4\text{-ZnSO}_4$ glass at different temperatures.

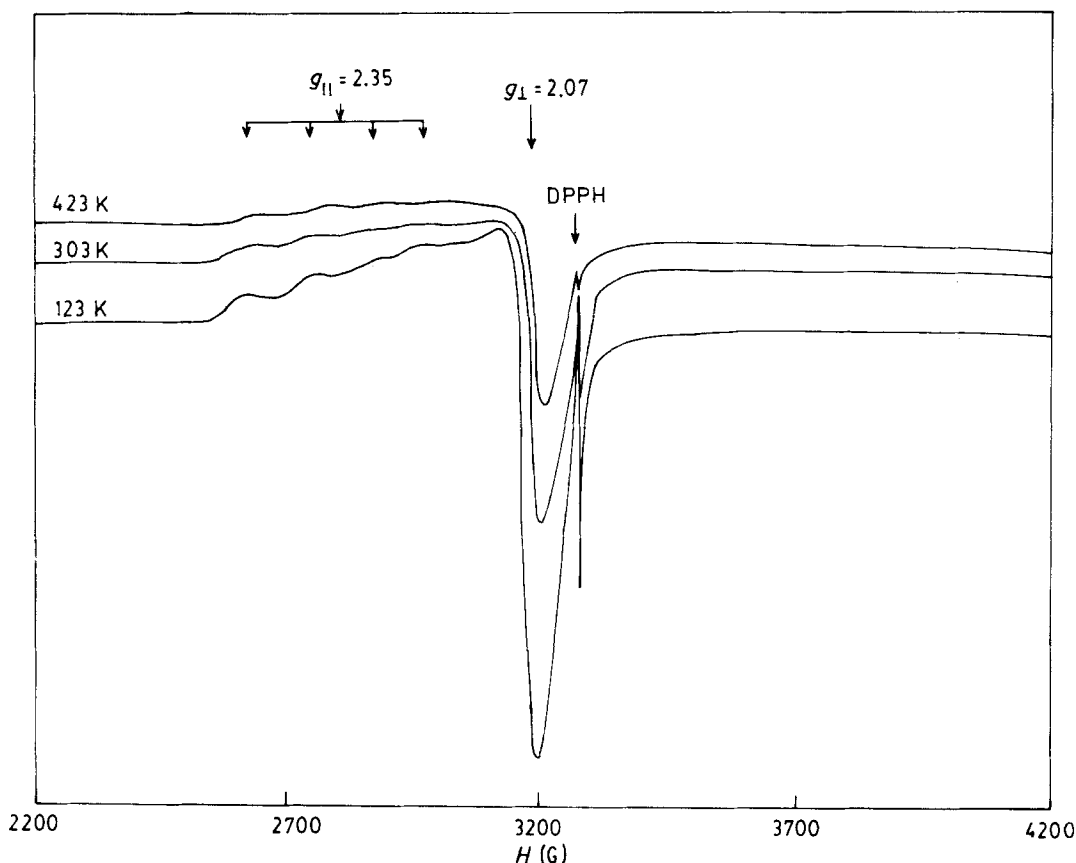


Figure 1 ESR spectra of 1 mol% Cu^{2+} ions in Na_2SO_4 - ZnSO_4 glass at room and different temperatures.

TABLE I Comparison of spin-Hamiltonian parameters of Cu^{2+} ions in various glasses

Serial no.	Glasses	g_{\parallel}	g_{\perp}	A_{\parallel} (10^{-4} cm^{-1})	References
1	$\text{Na}_2\text{O} \cdot \text{SiO}_2$	2.375	2.051	140	[6]
2	$\text{MgO} \cdot \text{P}_2\text{O}_5$	2.417	2.059	109	[10]
	$\text{CaO} \cdot \text{P}_2\text{O}_5$	2.408	2.059	109	
	$\text{SrO} \cdot \text{P}_2\text{O}_5$	2.342	2.063	109	
	$\text{BaO} \cdot \text{P}_2\text{O}_5$	2.408	2.058	108	
3	$\text{ZnO} \cdot \text{P}_2\text{O}_5$	2.415	2.058	109	
	$\text{CdO} \cdot \text{P}_2\text{O}_5$	2.404	2.058	109	[11]
	$\text{PbO} \cdot \text{P}_2\text{O}_5$	2.409	2.062	110	
4	$\text{SrO} \cdot \text{B}_2\text{O}_3$	2.308	2.044	152.7	
5	$\text{ZnO} \cdot \text{B}_2\text{O}_3$	2.321	2.039	159	[16]
	$\text{PbO} \cdot \text{B}_2\text{O}_3$	2.323	2.042	152	
6	K_2SO_4 - ZnSO_4	2.48	2.06	77	
7	K_2SO_4 - ZnSO_4	2.44	2.06	80	[20]
8	K_2SO_4 - ZnSO_4	2.41	2.06	69	[23]
9	Na_2SO_4 - ZnSO_4	2.35	2.07	107	Present work

From the observed ESR spectra, the spin-Hamiltonian parameters have been evaluated [25, 26]. The spin-Hamiltonian parameters reported for various glasses are given in Table I for comparison.

The optical absorption spectra of Cu^{2+} ions in Na_2SO_4 - ZnSO_4 glasses at room temperature and liquid nitrogen temperature are shown in Fig. 2. It may be seen that only one broad absorption band exists in the near-infrared region, both at room and liquid nitrogen temperatures. At room temperature the absorption band is observed at 12345 cm^{-1} . On cooling the sample to liquid nitrogen temperature, a slight blue shift is observed and the band is centred

at 12420 cm^{-1} . This broad band is identified as the $d-d$ transition band corresponding to ${}^2\text{B}_{1g} \rightarrow {}^2\text{B}_{2g}$ transition due to Cu^{2+} ions. The optical absorption bands reported for Cu^{2+} ions in various glasses are given in Table II for comparison.

4. Discussion

The ESR spectra of Cu^{2+} ions in glasses were analysed by using a spin-Hamiltonian:

$$\mathcal{H} = g_{\parallel} \beta H_z S_z + g_{\perp} \beta (H_x S_x + H_y S_y) + A_{\parallel} S_z I_z + A_{\perp} (S_x I_x + S_y I_y) \quad (1)$$

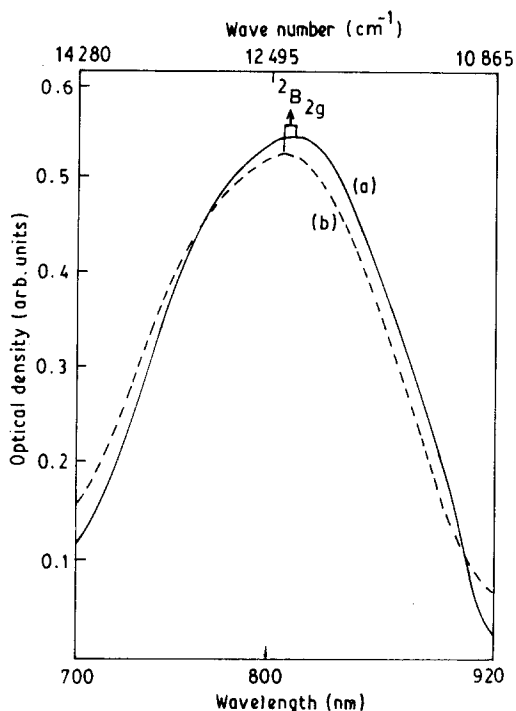


Figure 2 Optical absorption spectra of 1 mol % Cu^{2+} ions in $\text{Na}_2\text{SO}_4\text{-ZnSO}_4$ glass. (a) Room temperature, (b) liquid nitrogen temperature.

where z was taken as the symmetry axis of the individual Cu^{2+} complex. The nuclear quadrupole interaction was neglected.

From the observed ESR spectra, the calculated spin-Hamiltonian parameters were calculated and are shown in Table III. Owing to considerable overlap, it was difficult to estimate the perpendicular component of the hyperfine coupling constant. A broad peak was observed corresponding to which the g_{\perp} value was calculated.

The observed g_{\parallel} and g_{\perp} values ($g_{\parallel} = 2.35$ and $g_{\perp} = 2.07$) are characteristic of the Cu^{2+} ion [31]. Because $g_{\parallel} > g_{\perp} > 2.0023$, we can consider that the ground state for the paramagnetic electron is the $d_{x^2-y^2}$ orbital (${}^2B_{1g}$ state).

ESR signals in glasses show a reasonable concentration dependence. As the Cu^{2+} ion content is increased,

the peak-to-peak height (I) of the resonance line at $g = 2.07$ increased. Fig. 3 shows the concentration dependence of the peak-to-peak height ($I_{g=2.07}$) of the resonance line at $g = 2.07$. Significant changes were observed in the intensity of the ESR spectrum of 1 mol % Cu^{2+} ions in $\text{Na}_2\text{SO}_4\text{-ZnSO}_4$ glasses, when the composition of the glass was changed. Fig. 4 shows the variation of the peak-to-peak height ($I_{g=2.07}$) of the resonance line at $g = 2.07$, as a function of Na_2SO_4 content. As is evident from the figure, as the Na_2SO_4 content increases, the intensity of the resonance line at $g = 2.07$ decreases.

ESR spectra were also recorded at different temperatures (123–423 K), in order to study the temperature dependence of the peak-to-peak height ($I_{g=2.07}$) of the resonance line at $g = 2.07$. Fig. 5 shows the variation of the peak-to-peak height ($I_{g=2.07}$) as a function of temperature for 1 mol % Cu^{2+} ions in $\text{Na}_2\text{SO}_4\text{-ZnSO}_4$ glass. The experimental data are also compared to the Boltzmann factor, i.e. $1/T$, and are shown in Fig. 5. From the figure, it is clear that the peak-to-peak height ($I_{g=2.07}$) of the resonance line at $g = 2.07$ decreased gradually with increasing temperature in proportion to the Boltzmann factor. This fall in intensity with increasing temperature may be attributed to relaxation broadening.

The ESR and optical absorption spectral data can be correlated to evaluate the bonding orbital coefficients as follows [32, 33]

$$g_{\parallel} = 2.0023 \left[1 - \frac{4\lambda\alpha^2\beta_1^2}{E({}^2B_{2g})} \right] \quad (2)$$

$$g_{\perp} = 2.0023 \left[1 - \frac{\lambda\alpha^2\beta^2}{E({}^2E_g)} \right] \quad (3)$$

where λ is the spin-orbit coupling coefficient and the bonding coefficients α^2 , β_1^2 and β^2 ($= 1.00$) characterize, respectively, the in-plane σ bonding, in-plane π bonding and out-of-plane π bonding of the Cu(II) complexes. α^2 given in Equation 2 is the bonding coefficient due to covalency of the σ bonds with the equatorial ligands which measures the electron density delocalized on ligand ions and β_1^2 accounts for the

TABLE II Optical absorption bands reported for Cu^{2+} ions in various glasses at room temperature

System	Energy (cm^{-1})	Assignment	References
Sodium borosilicate	12 340	${}^2B_{1g} \rightarrow {}^2B_{2g}$	[5]
$\text{SrO} \cdot \text{P}_2\text{O}_5$	11 494	${}^2B_{1g} \rightarrow {}^2B_{2g}$	[10]
$\text{Na}_2\text{O} \cdot \text{P}_2\text{O}_5$	11 207	${}^2B_{1g} \rightarrow {}^2B_{2g}$	[13]
$\text{SrO} \cdot \text{B}_2\text{O}_3$	12 820	${}^2B_{1g} \rightarrow {}^2B_{2g}$	[14]
$\text{Ba}_3(\text{PO}_4)_2$	12 000	${}^2B_{1g} \rightarrow {}^2B_{2g}$	[27]
$\text{K}_2\text{SO}_4\text{-ZnSO}_4$	11 270	${}^2B_{1g} \rightarrow {}^2B_{2g}$	[28]
$\text{ZnO} \cdot \text{P}_2\text{O}_5$	12 195	${}^2B_{1g} \rightarrow {}^2B_{2g}$	[29]
$\text{PbO} \cdot \text{P}_2\text{O}_5$	11 628		
$\text{MgO} \cdot \text{P}_2\text{O}_5$	11 905		
$\text{CaO} \cdot \text{P}_2\text{O}_5$	11 765		
$\text{BaO} \cdot \text{P}_2\text{O}_5$	11 628		
$\text{R}_2\text{O} \cdot \text{SiO}_2$ (R = Li, Na, K)	12 500	${}^2B_{1g} \rightarrow {}^2B_{2g}$	[30]
$\text{R}_2\text{O} \cdot \text{B}_2\text{O}_3$ (R = Li, Na, K)	12 500		
$\text{Na}_2\text{O} \cdot \text{B}_2\text{O}_3 \cdot \text{SiO}_2$	12 700		
$\text{Na}_2\text{SO}_4 \cdot \text{ZnSO}_4$	12 340	${}^2B_{1g} \rightarrow {}^2B_{2g}$	Present work

TABLE III Spectral parameters of a Cu^{2+} ion in Na_2SO_4 - ZnSO_4 glass at room and liquid nitrogen temperature

	Room temperature	Liquid nitrogen temperature
g_{\parallel}	2.35 ± 0.02	2.36 ± 0.02
g_{\perp}	2.07 ± 0.02	2.07 ± 0.02
A_{\parallel}	107	113
α^2	0.77	0.77
β_1^2	0.84	0.84

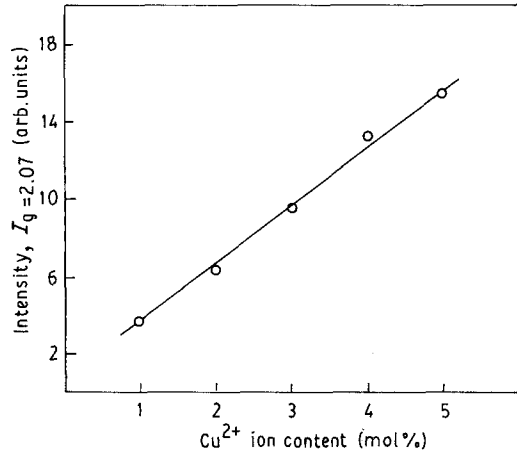


Figure 3 Dependence of the peak-to-peak height, $I_{g=2.07}$, as a function of Cu^{2+} ion content in Na_2SO_4 - ZnSO_4 glasses.

covalency of the π -bonding between ligands and ${}^2\text{B}_{2g}$ excited state. Their values lie between 0.5 and 1, the limits of pure covalent and pure ionic bonding [33]. The value of β^2 may be expected to lie sufficiently close to unity as to be indistinguishable from it in the bonding coefficient calculations [31]. Because only one absorption band was observed corresponding to the transition ${}^2\text{B}_{1g} \rightarrow {}^2\text{B}_{2g}$, the position of the second band was estimated by the approximation [33]

$$E({}^2\text{B}_{1g} \rightarrow {}^2\text{B}_{2g}) = \frac{2k^2\lambda}{2.0023 - g_{\perp}} \quad (4)$$

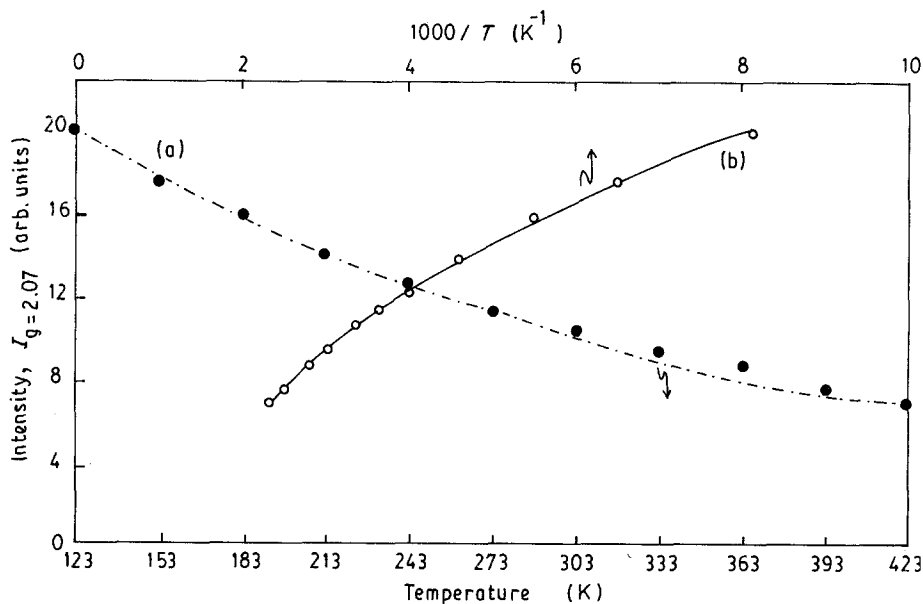


Figure 5 (a) Temperature dependence of the peak-to-peak height, $I_{g=2.07}$, for 1 mol % Cu^{2+} ions in Na_2SO_4 - ZnSO_4 glass. (b) Experimental data compared to the Boltzmann factor, $1/T$.

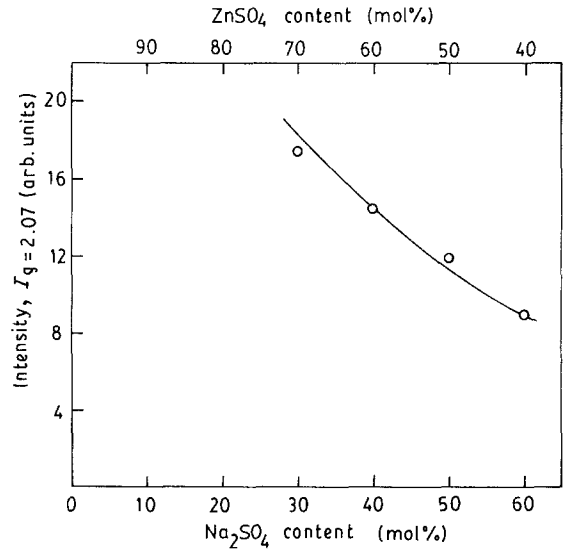


Figure 4 Dependence of the peak-to-peak height, $I_{g=2.07}$, as a function of Na_2SO_4 content in Na_2SO_4 - ZnSO_4 glass.

where k^2 is the orbital reduction factor ($k^2 = 0.77$) and λ is the spin-orbit coupling constant ($= -828 \text{ cm}^{-1}$) [34].

The values of α^2 and β_1^2 obtained in the present work, $\alpha^2 = 0.77$ and $\beta_1^2 = 0.84$, indicate that there is a moderate covalency for the σ bonding and the in-plane π bonding is significantly ionic. These values are comparable to those found for Cu^{2+} ions in various glasses [7, 10, 33].

It may also be noted that the ionic radius of the Cu^{2+} ion is 0.072 nm, which is very close to that of the ionic radius of Zn^{2+} ions, i.e. 0.074 nm. So it is reasonable to assume that the Cu^{2+} ions occupy the zinc ions in these glasses.

5. Conclusion

From the ESR and optical absorption spectra of Cu^{2+} ion-doped Na_2SO_4 - ZnSO_4 glasses, the bonding orbital coefficients α^2 and β_1^2 have been evaluated.

By comparing these copper-doped Na₂SO₄-ZnSO₄ glasses with other glasses, it can be concluded that the Cu²⁺ ions are in tetragonally distorted octahedral sites and they substitute for zinc ions in these glasses.

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References

1. A. PAUL, A. N. TIWARI and G. C. UPRETI, *Phys. Chem. Glasses* **15** (1974) 86.
2. L. D. BOGOMOLOVA, V. A. JACHKIN, V. N. LAZUKIN, T. K. PAVLUSHKINA and V. A. SHMUCKER, *J. Non-Cryst. Solids* **28** (1978) 375.
3. H. HOSONO, H. KAWAZOE and T. KANAZAWA, *ibid.* **34** (1979) 339.
4. J. M. DANCE and J. P. DARNAUDERY, *Solid State Commun.* **39** (1981) 199.
5. SHEN DINGKUN, WANG KAITAI, HUANG XIHUI, CHEN YOUXIN and BAI TINHUA, *J. Non-Cryst. Solids* **52** (1982) 151.
6. L. D. BOGOMOLOVA, A. G. FEDOROV and M. E. KUBRINSKAYA, *ibid.* **54** (1983) 153.
7. L. D. BOGOMOLOVA and V. A. JACHKIN, *ibid.* **58** (1983) 165.
8. I. ARDELEAN, O. COZAR and GH. ILONCA, *ibid.* **68** (1984) 33.
9. RAVISHANKAR HARANI, C. A. HOGARTH and K. A. LOTT, *J. Mater. Sci.* **19** (1984) 1420.
10. A. KLONKOWSKI, *Phys. Chem. Glasses* **26** (1985) 11.
11. *Idem.*, *ibid.* **26** (1985) 31.
12. O. COZAR and I. ARDELEAN, *J. Non-Cryst. Solids* **92** (1987) 278.
13. A. YADAV and V. P. SETH, *J. Mater. Sci.* **22** (1987) 239.
14. V. P. SETH and A. YADAV, *Phys. Chem. Glasses* **28** (1987) 109.
15. A. YADAV, V. P. SETH and PREMCHAND, *J. Mater. Sci. Lett.* **6** (1987) 468.
16. A. YADAV, V. P. SETH and S. K. GUPTA, *J. Non-Cryst. Solids* **101** (1988) 1.
17. J. A. DUFFY and W. J. D. McDONALD, *J. Chem. Soc. A* (1970) 977.
18. P. S. L. NARASIMHAM and K. J. RAO, *Proc. Indian. Acad. Sci.* **A87** (1978) 275.
19. H. G. K. SUNDAR and K. J. RAO, *J. Non-Cryst. Solids* **50** (1982) 137.
20. A. YADAV and V. P. SETH, *Phys. Chem. Glasses* **27** (1986) 182.
21. J. LAKSHMANA RAO, B. SREEDHAR and S. V. J. LAKSHMAN, *J. Non-Cryst. Solids* **105** (1988) 95.
22. J. LAKSHMANA RAO, G. L. NARENDRA, B. SREEDHAR and S. V. J. LAKSHMAN, *Phys. Status Solidi (b)* **153** (1989) 257.
23. J. LAKSHMANA RAO, B. SREEDHAR, M. RAMACHANDRA REDDY and S. V. J. LAKSHMAN, *J. Non-Cryst. Solids* **111** (1989) 228.
24. J. LAKSHMANA RAO, B. SREEDHAR, Y. C. RATNAKAR and S. V. J. LAKSHMAN, *ibid.* **92** (1987) 175.
25. R. H. SANDS, *Phys. Rev.* **99** (1955) 1222.
26. B. BLEANEY, K. D. BOWERS and M. H. L. PRYCE, *Proc. Roy. Soc.* **A228** (1955) 140.
27. MANFRED BERRETZ and SMITH. L. HOLT, *J. Amer. Ceram. Soc.* **61** (1978) 136.
28. K. J. RAO, *Bull. Mater. Sci.* **2** (1980) 357.
29. A. KLONKOWSKI, *Phys. Chem. Glasses* **22** (1981) 163.
30. A. DURAN and J. M. FERNANDEZ NAVARRO, *ibid.* **26** (1985) 126.
31. H. IMAGAWA, *Phys. Status Solidi (b)* **30** (1968) 469.
32. D. KIVELSON and R. NEIMAN, *J. Chem. Phys.* **35** (1961) 149.
33. A. KLONKOWSKI, *Phys. Chem. Glasses* **24** (1983) 166.
34. F. E. MABBS and D. J. MACHIN, "Magnetism and Transition Metal Complexes" (Chapman and Hall, London, 1973) p. 154.

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