© 2016 IJSRST | Volume 2 | Issue 4 | Print ISSN: 2395-6011 | Online ISSN: 2395-602X
Themed Section: Science and Technology

EPR and Optical Absorption studies of Cu^{2+} doped $MgO-Li_2O-B_2O_3$-TeO2 Glasses

Kalsani Venkateshwarlu[a], Bachchewal Sreenivas[b]
[a]Department of Physical Sciences, Kakatiya Institute of Technology & Science, Warangal, India
[b]Department of Physics, Osmania University, Hyderabad, India

ABSTRACT

Electron paramagnetic resonance (EPR) and optical absorption studies of xMgO- (25-x) Li_2O-$55B_2O_3$-20TeO2 glasses were made by introducing Cu^{2+} as a spin probe. The EPR spectra of all the glass samples recorded at X-band frequencies have similar spectral features. The Cu^{2+} ions are in well-defined axial sites, but subjected to small distortion leading to the broadening of the spectra. The spin-Hamiltonian parameter values indicate that the ground state of Cu^{2+} is d_{x2-y2} and the site symmetry around Cu^{2+} ions is tetragonal distorted octahedral. The optical absorption spectra exhibited a broadband corresponding to the d-d transition bands of Cu^{2+} ion. By correlating EPR and optical data, the bond parameters were evaluated and the values show purely ionic nature for the in-plane σ bonding and in-plane π bonding. The out-of-plane π bonding is moderately covalent.

Keywords: Electron Spin Resonance, spin-Hamiltonian, Glass, Optical Absorption.

I. INTRODUCTION

Electron paramagnetic resonance (EPR) spectroscopy is an experimental technique sometimes capable of determining the co-ordination and environment of paramagnetic ions in glasses [1,2]. EPR behaviors of oxide glasses doped with transition metal (TM) ions have been extensively studied to obtain information on the glassy network and to identify the site symmetry around the TM ions [3-6]. Glasses containing TM ions exhibit memory and photo conducting properties [7]. Recently, the local structure around Cu^{2+} ion in oxide glasses by EPR spectra. Copper (II) is the most amenable ion for EPR studies[xxx]. The main advantage of using Cu^{2+} as the spin probe is that it EPR spectra can easily be recorded at room temperature, the spectrum is simple and the spread of the spectrum is large enough to detect minute changes in the coordination sphere [8].

By correlating the EPR and optical spectra, one can obtain information regarding the bond parameters which determine the metal-ligand bond in the glasses. The properties of a glass can often be altered by the addition of a network modifier to the basic constituents. The commonly used network modifiers are the alkali and alkaline earth oxides [9]. It was observed that the properties of an alkali oxide glass show a non-linear behavior when one kind of alkali is gradually replaced by another. This departure from linearity is called the mixed alkali effect [10]. Similar observations were made in the case of mixed alkali-alkaline earth oxide glasses [11]. This phenomenon is called mixed oxide effect. In this paper, we report EPR and optical absorption studies of Cu^{2+} spin probe in the quaternary glass system xMgO- (25-x) Li_2O-$55B_2O_3$-20TeO2. The influence of varying the concentrations of Li_2O and MgO, which acts as network modifiers on the spin-Hamiltonian parameters, is discussed.

II. Experimental

Copper (1 mole %) doped glass, samples of composition xMgO- (25-x) Li_2O-$55B_2O_3$-20TeO2 ($0 \leq x \leq 25$) were prepared using the conventional melt-quench technique. Glasses were prepared by mixing the required proportions of the reagent grade Li_2CO_3, H_3BO_3, TeO_2 (May and Baker), MgO (Fluka) and CuO in an electrical furnace using silica crucibles. The furnace temperature is varied from 900- 1000 ^oC depending on the glass composition. For samples taken from different regions of the bulk specimen, the absence of any Bragg peaks in the X-ray diffraction pattern confirmed that the glasses are amorphous and homogeneous.

The room temperature EPR spectra of powdered glass samples were recorded using a JOEL PE-3X EPR spectrometer operating in the X-band and employing a field modulation of 100 kHz. DPPH was used as the standard *g* marker for the determination of magnetic field. The optical absorption spectra of the present glasses in 200 – 800 nm region was recorded by using a Shimadzu spectrometer (model UV-3100) at room temperature.

III. Results and Discussion

The room temperature Cu^{2+} ion doped EPR spectra of the present glasses were shown in Figure 1. The spin–Hamiltonian can be employed in the analysis of the EPR spectra which is given below:

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

where the symbols have their usual meanings [12]. The nuclear quadrupole contribution is neglected. The calculated spin-Hamiltonian parameters are given in Table 1. The general nature of the ligand coordination can be obtained [13] from the fact that $g_{\|}, g_{\perp}, A_{\|}$ and $A_{\perp}$ $g\| > g_{\perp} > 2.0023$. From the *g* values and shape of the EPR spectra, it can be concluded that the ground state of the Cu^{2+} is $d_{x^2-y^2}$ orbital, the Cu^{2+} ions being located in tetragonally distorted octahedral sites [12,14,15].

The $g_{\|}$ and $A_{\|}$ values are found to be dependent on the glass composition while $g_{\perp}$ and $A_{\perp}$ values are essentially constant. The variation of $g_{\|}$ and $A_{\|}$ with MgO content is illustrated in Figure 2. $g_{\|}$ and $A_{\|}$ varies non-linearly as the MgO content increases: $g_{\|}$ decreases and then increases, whereas $A_{\|}$ increases and then decreases indicating the change in the tetragonal distortion of Cu^{2+} ions [16]. The variation in $g_{\|}$ and $A_{\|}$ values may be associated with the change in the environment of Cu^{2+}. With the B_2O_3 glasses, the addition of network modifiers (MgO and Li_2O) leads to an increase in the coordination number of a certain portion of the boron atoms from 3 to 4. It is assumed that the resulting glass is composed of both triangular and tetrahedral units which form a relatively open network with holes between the oxygen atoms of sufficient size to accommodate the Li and Mg ions [17].

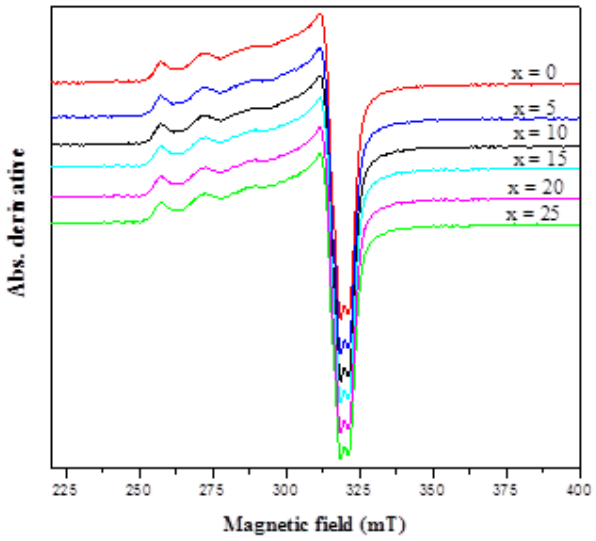

Figure 1. EPR spectra of Cu^{2+} in the present glass system.

Table 1. Spin-Hamiltonian and optical absorption and bonding coefficients for Cu^{2+} ions in $xMgO-(25-x)Li_2O-55B_2O_3-20TeO_2$ glasses.

Parameters	x=0	x=5	x=10	x=15	x=20	x=25
$g_{\|}$	2.367	2.341	2.354	2.363	2.374	2.358
$g_{\perp}$	2.059	2.064	2.069	2.062	2.072	2.078
$A_{\|}$	152	132	149	147	153	139
$A_{\perp}$	32	46	44	41	39	36
λ	747	744	718	732	729	748
ΔE_{xy}	13404	13440	13869	13966	13513	13157
$\Delta E_{xz,yz}$	15,659	15,659	13,887	17,949	17,009	13,143
α^2	0.812	0.801	0.792	0.807	0.815	0.805
β_1^2	0.943	0.949	0.910	0.898	0.864	0.892
β^2	0.747	0.762	0.914	0.991	0.771	0.730
Γ_σ (%)	52	48	46	44	47	46
Γ_π (%)	31	38	57	42	51	35

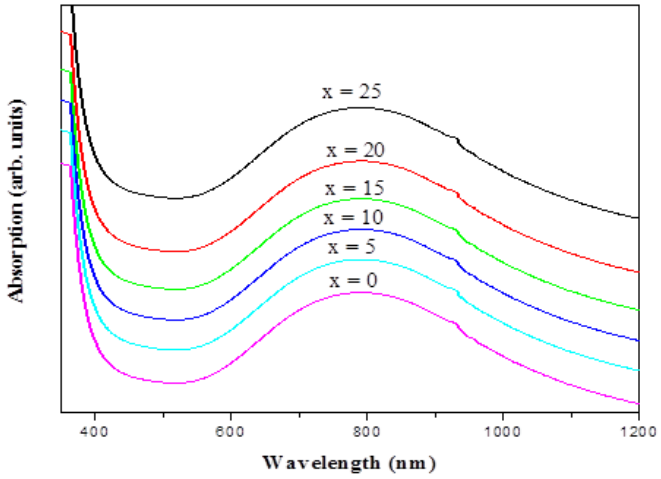

Figure 3. Optical absorption spectra of present glass system

The optical absorption spectra of all glasses studied reveal only a broad absorption band. The optical absorption peak position values are determined by peak pick facility of the spectrometer and are presented in Table 1. In a regular octahedral field, the $3d^9$ configuration would result in a degenerate ground state (^2E_g) and the Jahn-Teller effect gives a marked tetragonal distortion which leads to splitting of energy levels. This single optical band was interpreted as the overlap of all the three transitions. Hence, in the present investigation the observed asymmetric band around 13,192 cm^{-1} is due to the overlap of $^2B_{1g} \rightarrow {}^2A_{1g}$ and $^2B_{1g} \rightarrow {}^2B_{2g}$ transitions. Most of the authors [18,19] assigned the observed optical peak to the $^2B_{1g} \rightarrow {}^2B_{2g}$ transition (ΔE_{xy}) and have used this value in the evaluation of the bond parameters.

The EPR and optical absorption data can be related to evaluate the bonding coefficients of Cu^{2+}. The bonding between the Cu^{2+} ion and its ligands can be described in terms of the covalency parameters α^2, β^2 and β_1^2 where α^2 describes the in-plane σ bonding with the copper $d_{x^2-y^2}$ orbital, β^2 describes the out-of-plane π bonding with the d_{xz} and d_{yz} orbital and the β_1^2 parameter is a measure of the in-plane π bonding with the d_{xy} orbital. The normalized covalencies of Cu (II)-O in-plane bonds of σ and π symmetry are expressed [20] in terms of bonding coefficients α^2 and β_1^2 as follows. The calculated values of α^2, β_1^2, β^2, are presented in Table 1.

IV. CONCLUSION

The quaternary glass system of $xMgO\text{-}(25\text{-}x)Li_2O\text{-}55B_2O_3\text{-}20TeO_2$ ($0 \leq x \leq 25$) were prepared, and their optical and EPR measurements have been studied. The following conclusions were made: From EPR and optical measurements it is clear that Cu^{2+} ions are present in all the glasses investigated and they exist on tetragonally distorted octahedral sites with $d_{x^2-y^2}$. The spin-Hamiltonian parameters are influenced by the composition of glass which may be attributed to the change of ligand field strength around Cu^{2+}. With increasing MgO content. The bond parameter values show purely ionic nature of the in-plane σ bonding and in-plane π bonding.

V. REFERENCES

[1]. A. Edukondalu, V. Sathe, Syed Rahman and K. Siva Kumar, Physica B, 438 120-126 (2014).
[2]. N. Srinivasa Rao, Shashidhar Bale, M. Purnima, K. Siva Kumar and Syed Rahman, Bull. Mater. Sci., 28 6589-592 (2005).
[3]. A. Edukondalu, B. Kavitha, M. A. Samee, Sh. K. ahmmad, Syed Rahman and K. Siva Kumar, J. Alloys Compd., 322 324 -335 (2013).
[4]. M. Purnima Avula Edukondalu, K. Siva Kumar, Syed Rahman, , J. Mater. Res. 20(1) (2017) 46-52
[5]. A. Edukondalu, M. Purnima, CH. Srinivasu, T. Sripathi, A. M. Awasthi, Syed Rahman and K. Siva Kumar, J. Non-Cryst. Solids, 358 2581-2588 (2012).
[6]. H. Kawazoe, H. Hosono and T. Kanazawa, J. Non-Cryst Solids 29 173-186 (1978).
[7]. Abdul Hameed, B.Srinivas, A. Edukondalu, Md. Shareefuddin, M. Narasimha Chary, Phys. Chem. Glasses: Eur. J. Glass Sci. Technol. B, 56 (6) (2015) 263-266
[8]. Avula Edukondalu, T. Sripathi, Shaik Kareem Ahmmad, Syed Rahman, K. Sivakumar, J. Elect. Mater. 46(2) (2017) 808-816.
[9]. A. Edukondalu, CH.Srinivasu, Syed Rahman, V. Sathe, K. Siva Kumar, AIP conf. Proc. 1591 (2014) 836
[10]. G. Van Veen, J. Magn. Res., 30 91-99 (1978.)
[11]. A. Edukondalu, K. Siva Kumar, D. Sreenivasu, Vib. Spect. 71 (2014) 91-97.

[12]. A. Edukondalu, B. Kavitha, Abdul Hameed, R. Vijaya Kumar, K. Siva Kumar, Mater. Today. Proc. 2 (2015) 913-917.
[13]. M. A. Samee, A. Edukondalu, Shaik Kareem Ahmmad, Sair MD. Taqiullah, Syed Rahman, J. Elect. Mater. 42 (2013) 2516.
[14]. A. Edukondalu, Ch. Srinivasu, Syed Rahman, K. Siva Kumar, Int. J. Sci. Eng. Res. 5(3) (2014) 258-262.
[15]. Ch. Srinivasu, Ch. Mallika, G. Sriram, Abdul Hameed, A. Edukondalu, Int. J. Sci. Eng. Res. 5(3) (2014) 263-266.
[16]. A. Edukondalu, M.A.Samee, S. K. Ahmmad, Sair Md. Taqiullah, Syed Rahman,K. Siva Kumar, Int. J. Mod. Phys. conf. ser. 22 (2013) 278-283.
[17]. Ch. Srinivasu, M.A. Samee, A. Edukondalu, Syed Rahman, Int. J. Mod. Phys. conf. ser. 22 (2013) 284-291.
[18]. A. Edukondalu, B. Kavitha, M. A. Samee, Shaik. Kareem ahmmad, Syed Rahman, K. Siva kumar, J. Alloys Compd. 552 (2013) 157 -165.
[19]. A. Edukondalu, B. Kavitha, Abdul Hameed, K. Siva Kumar, IOP Conf. Ser. Mater. Sci. Eng. 73 (2015) 012127.
[20]. Shaik Kareem Ahmmad, M. A. Samee, A.Edukondalu, Syed Rahman, Results in Physics, 2 (2012) 175-18.