A Study of Electron Paramagnetic Resonance on Copper Ions on Alkali-Alkali Earth Zinc Phosphate Glass

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Abstract: $42\%P_2O_5$- $40\%ZnO$- $2\%CaO$- $(16-x)\%Na_2O$-xCu_2O glass system (x=o, 2, 4, 6, 8, 10%mol) were prepared by conventional melt-quenching technique. It was investigated by means of electron paramagnetic resonance (EPR) to study the structural changes induced by different amount of copper ions. The spin Hamiltonian parameters like $g_{\parallel}$, $g_{\perp}$ and $A_{\parallel}$ show that Cu^{+2}ionare in tetrahedral coordination with d_{xy} as the ground state. Modification of EPR band width by increasing copper content suggests that band consists of two overlapping bands; one of them is related to asymmetric band due to isolated copper ions and the other is symmetric due to cluster ions Cu^{+2}-Cu^{+2}. Calculation of the optical basicity indicates to that polarizability decrease by increasing copper content due to increase electron cloud density at the Cu^{2+} site.

Keywords: Glass, Electron Paramagnetic Resonance, Optical Basicity, Polarizability, Cluster Ions

1. Introduction

It is well known that phosphate glasses containing transition metals (TM) have marvelous properties over than silicate or borate glass. This is because their low glass transition temperature (T_g), high refractive index, low melting temperature and have the ability to accommodate high concentration of transition metal ion and remain amorphous [1-4]. However, it has a low chemical durability; the addition of transition metal such as zinc oxide enhances its chemical durability, optical properties and decreases the melting temperature. Also adding of alkali or alkali-earth plays an important role in enhancing electrical and magnetic properties, decreasing the melting temperature and a bubble free [2,3].There are special attention on copper doped phosphate glass due to their wide range applications like solid state lasers, optical filter and super ionic conductors [5, 6]. In general, copper behaves as modifier, but in some situation acts as a former in glass network. Copper can exist as a metallic copper Cu^0, cuprous Cu^{+1}, and cupric Cu^{+2}[7-15]. The electronic structure of copper is $3d^{10} 4s^1$; cuprous Cu^{+1}ion has a completed d shell. Cuprous Cu^{+1} does not have a magnetic moment and does not produce a color [8-15].

While Cu^{+2} have a free spin which is responsible a color according to ligand field theory. EPR technique is used to investigate the valence states and local symmetry (octahedral or tetrahedral). Addition of copper to phosphate glass exhibit anomalous spin parameters A and g [3, 16-19].

Usually incorporation copper into phosphate glass acts as modifier. However, in special cases it can act as a glass former [17, 18]. The aim of the work is studying the mode of distribution around cupric ionsusing EPR spectra for determination of paramagnetic magnetic susceptibility and some parameters such as Fermi-contact and optical basicity.

2. Experimental Work

Copper-doped glasses of varying basic hosts including zinc sodium calcium phosphate (Table1) were prepared by conventional melt-quenching technique. Starting reagent ingredients Na_2CO_3, ZnO, CaO, $(NH_4) H_2PO_4$ and Cu_2O were used for preparation. Appropriate quantities of ingredients are weighed using electric single pan balance of 10^{-3}g sensitivity. The ingredients were then thoroughly mixed by agate mortar. Each composition was taken in an open porcelain crucible and calcined at 340 °C for 1hour to release undesired gases; the furnace was then raised to 950°C for

2hour. The prepared samples were immediately transferred into preheated stainless steel molds for annealing adjusted at

340°C for 4hour. The compositions of the prepared sample are listed in table (1).

Table (1). Chemical composition of the prepared glass.

Cu_2O addedMol (%)	Na_2O Mol (%)	CaOMol (%)	ZnOMol (%)	$2\{(NH_4)H_2PO_4\}$Mol (%)	Sample name
0	16	2	40	42	S_1
2	14	2	40	42	S_2
4	12	2	40	42	S_3
6	10	2	40	42	S_4
8	8	2	40	42	S_5
10	6	2	40	42	S_6

EPR signals of powder glass sample were recorded in X-band at room temperature by using a Bruker EMX spectrometer (Germany), microwave frequency = 9.775 GHz, time constant = 81.92 ms and sweep time = 20.97 s.

3. Result and Discussion

3.1. Spectrum of EPR

$$H=\beta(g_{//}H_z s_z)+ \beta g_\perp(H_x s_x+H_y s_y)+A_{//}s_z I_z+A_\perp(s_x I_x+s_y I_y) \tag{1}$$
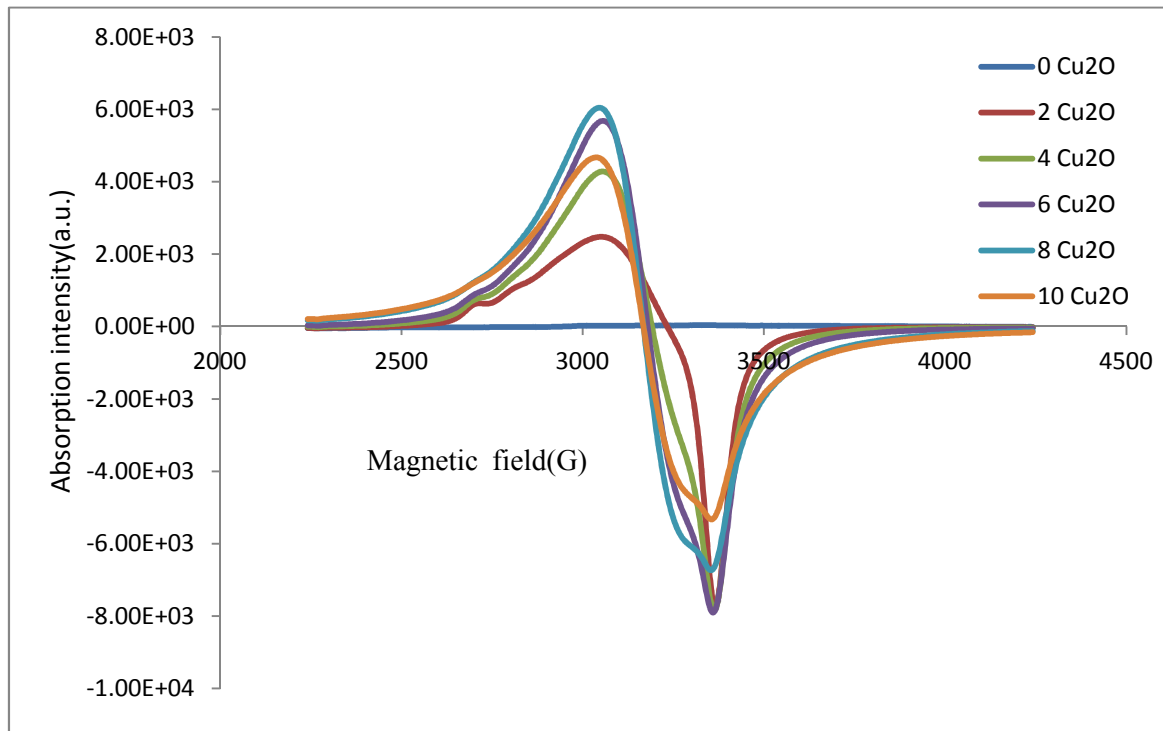

Fig. (1). EPR spectra for obtained system.

Where β is the Bohar magnetrons, $g_{\parallel}$ and $g_\perp$ are parallel and perpendicular principle components of the g tensor (spectroscopic splitting factor). $A_{\parallel}$ and $A_\perp$ are the parallel and perpendicular principle components of the hyperfine coupling tensor respectively, H_x, H_y and H_z are components of the magnetic field, s_x, s_y, s_z and I_x, I_y, I_z are the spin operators component of the electron and nucleus respectively.

Generally, octahedral coordination appears as basic coordination of T.M. ions in alkaline or alkaline-earth phosphate glasses [3, 17, and 18]. In such systems the copper can exhibit three valence states Cu^0, Cu^{+1}, Cu^{+2}. It is assumed

EPR spectra were recorded at R.T for copper doped PZnCaNa glass samples in order to examine the valance state of copper in glass matrix fig.(1). Copper free sample exhibits no EPR signal, i.e., all the obtained EPR spectra are due to Cu^{+2}. Each spectrum was analyzed using the axial spin Hamiltonian [19-22]:

from the literature that Cu^0 are not observed during melting process and Cu^{+1}has no magnetic moment [8-15]. Cu^{2+} ion has the electronic configuration $3d^9$ configuration with^{2}D ground state. $Cu^{2+}$is characterized by g ~2.06, $g_{\parallel}>g_\perp>g_e$ and octahedral tetragonal elongation coordination with$d_{x^2-y^2}$being the ground state. The situation$g_\perp>g_{\parallel}>g_e$, corresponds to a tetragonal compressed tetrahedral configuration with d_{xy} being the ground state. Many authors assume that ^{2}D splits into ^2E_g and $^2T_{2g}$ such states split into different states under effect of tetragonal distortion: $^2E_g \rightarrow ^2B_{1g}+^2A_{1g}$ and $^2T_{2g} \rightarrow ^2B_{2g}+^2E_g$, $^2B_{1g}(d_{x^2-y^2})$ would be the ground state [3].

Such an energetically assumption considers a tetragonal elongated octahedron D_{4h} for the coordination of Cu^{2+} ion. For D_{4h} configuration the values obtained for g_l is <2.4 and for A_l<120 x 10^{-4} cm^{-1}. In the present work the estimated values for $g_\perp > g_l$ and for A_l>120 x 10^{-4} cm^{-1}. To explain the large values obtained for A_l we suggest that Cu^{+2} is acted upon by compressed tetrahedral field T_d and not octahedral tetragonal elongation coordination as it is usually assumed [3, 23-25]. As a result to this structure it is assumed that there is admixing of 3P states with $4d_{xy}$ states [3, 26].

Inspection of fig. (1) reveals that there is no EPR signal was observed for copper free sample, indicating the absence of paramagnetic center in the prepared glasses and the obtained absorption bands are asymmetric. However, no well-defined trend was observed for different copper concentration. This can be accounted for by the fact that the number of Cu^{+2} does not increase by increasing copper content. The hyperfine parameters $g_\parallel$, $g_\perp$, $A_\parallel$ and $A_\perp$ are given in Table 2. Inspection these obtained values reveals that $g_\perp >$ $g_\parallel$ and $A_\parallel > A_\perp$, the values allows to assume that Cu^{+2} is a compressed tetrahedral coordinated configuration since $g_\perp > g$ $_\parallel$[3, 25]. In such a case one should expect admixing of 4P states with $3d_{xy}$ ground states due to compression leading to increase of $g_\perp$ and $A_\parallel$[3, 25].

The change in spin Hamiltonian parameters is related to the changes in the ligand field around the T.M. probe ion. It is assumed that EPR spectra consists of overlapping of two bands symmetric and asymmetric band due to cluster and isolated ions, respectively [27, 28]. A symmetric band has a g $_\perp$~2.27 and $g_\parallel$~2.09,but the asymmetric band has average value of g_0~2.21[27, 28]. Increasing the line width of the parallel spectra ($\Delta\beta_\parallel$) and the perpendicular spectra ($\Delta\beta_\perp$) indicates formation of cluster and vice versa.

As shown in fig. (2) $\Delta\beta_\parallel$ increases with increasing copper content which means formation of clusters, i.e., Cu^{+2}-Cu^{+2} dipole-dipole interaction. While $\Delta\beta_\perp$ decrease with copper content until x=6% due to decrease in isolated ions. After x=6%, there is an increase in clustered ions. The presence of copper as a cluster in the phosphate glass system refers to network modifier of this oxide [27-28].
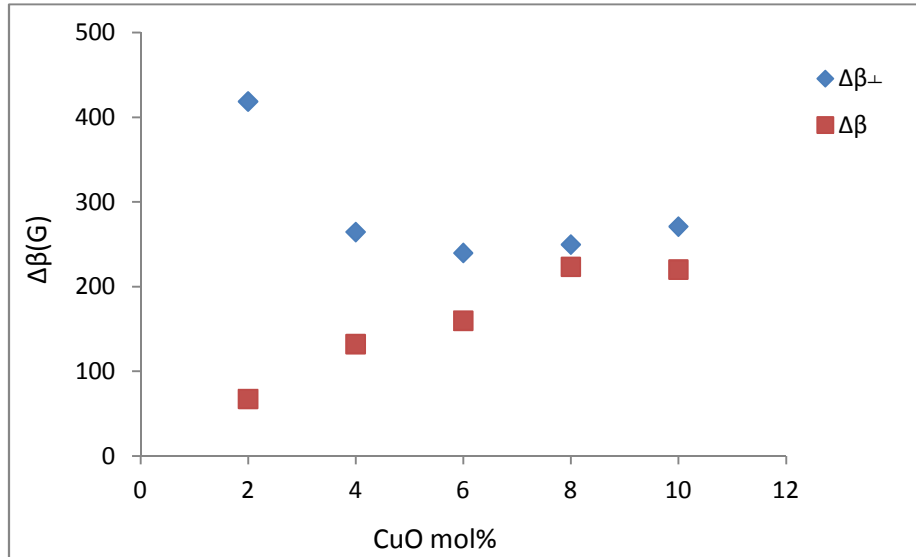

Fig. (2). *Variation of perpendicular ($\Delta\beta_\perp$) and parallel band ($\Delta\beta_\parallel$) width vs copper content.*

Table 2. *Represent the spin Hamiltonian parameters.*

No.	No. of spin	K	$g_{//}$	$g_\perp$	g_0	Δg_0	$A_{//}$x10^{-4} cm^{-1}	$A_\perp$x10^{-4} cm^{-1}	A_0x10^{-4} cm^{-1}
S1	0	0	0	0	0	0	0	0	0
S2	7.66E+21	1.399	2.092	2.2696	2.21	0.21	593.01	346.82	429
S3	9.04E+21	1.345	2.148	2.2698	2.23	0.23	508.74	349.76	403
S4	8.65E+21	1.312	2.171	2.2668	2.23	0.235	472.17	356.12	389
S5	7.85E+21	1.30	2.184	2.275	2.24	0.245	445.16	351.35	383
S6	7.26E+21	1.269	2.188	2.283	2.25	0.25	443.58	329.09	367

From the spin Hamiltonian parameters, the dipolar term (P) and the Fermi-contact term (κ) are calculated using the expressions [29-31]:

$$P=2\varUpsilon_{Cu}\beta_0\beta_N(r^{-3})=0.036cm^{-1} \quad (2)$$

$$\kappa= (A_0/P) +\Delta g_0 \quad (3)$$

Where $\varUpsilon_{Cu}$ is the magnetic moment of copper, β_0 is the

Boharmagneton, β_N is nuclear magnet on and r is the distance from the central nucleus to the electron. The Fermi-contact term κ is a measure of the polarization produced by odd distribution of d-electron density on the inner core s-electron, $A_0 = (A_\parallel+2A_\perp)/3$, $g_0= (g_\parallel+2g_\perp)/3$, $\Delta g_0=g_o-g_e$. The calculated data of κ are listed in table 2. From (table 2), it is found that there is general decrease in these values, i.e., decrease in the polarizabilities[29-32].

3.2. Paramagnetic Susceptibility

The EPR data can be used to calculate the paramagnetic susceptibility of the sample using the formula [33, 34]:

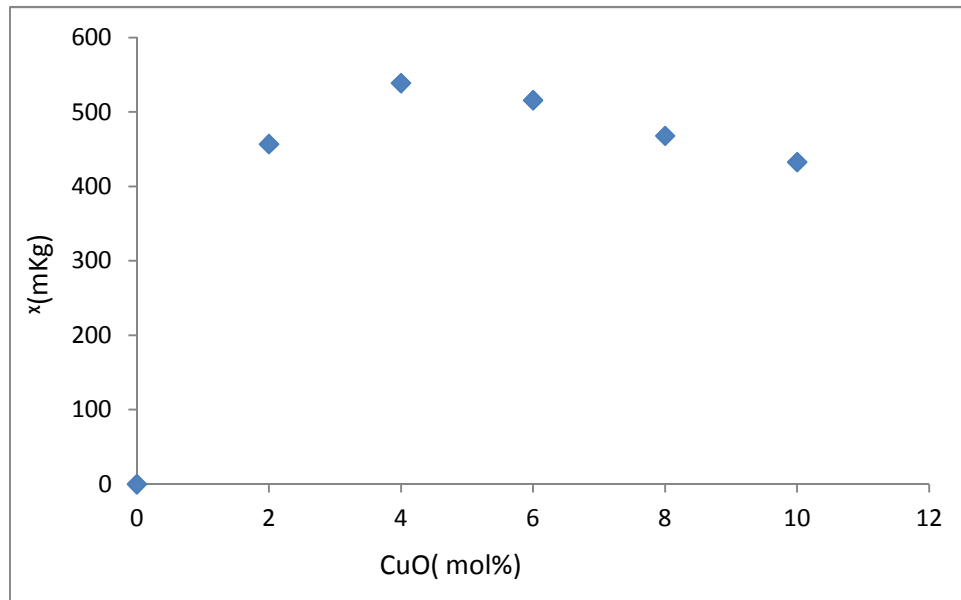$$\chi = \frac{Ng^2\beta^2 j(j+1)}{3k_B T} \qquad (4)$$

Fig. (3). paramagnetic susceptibility (χ) with Cu₂O content.

Where N is the number of spins per cm³, the rest of the symbols have their usual meaning. The paramagnetic susceptibility was calculated at different concentration. Figure (3) shows a plot of paramagnetic susceptibility (χ) of Cu^{2+} ions glass system as a function of concentration.

The figure shows that magnetic susceptibility depends on copper glass-oxide content. So, the change in magnetic susceptibility is due to percentage of Cu^{+2} formation only because the Cu^{+1} ions have zero magnetic moment [16]. So, the increase in the magnetic susceptibility by increasing the copper content up to 4% due to increase in Cu^{+2}. Then, by increasing the copper content over 4%, there is decrease in the magnetic susceptibility due to change Cu^{+1} to Cu^{+2}, i.e., ratio Cu^{+1}/Cu^{+2} increases.

3.3. Optical Basicity (Λ_{th})

On the other hand, the change in the EPR with copper content can be most likely related the change in electron cloud density of oxygen at the Cu^{2+} ions in the glass network. The optical basicity (Λ_{th}) is a measure of electron donor power of oxygen anion around cation (T.M.), i.e., the degree of covalency of bonds between O^{2-} and polarizing ion. The optical basicity (Λ_{th}) for the glass system under study has been calculated using the relation [35]:

$$\Lambda_{th} = x_1(P_2O_5)\Lambda(P_2O_5) + x_2(ZnO)\Lambda(ZnO) + x_3(Na_2O)\Lambda(Na_2O) + x_4(CuO)\Lambda(CuO) + xCaO\Lambda(CaO) \qquad (5)$$

Where x's are the equivalent fractions of the different oxides, i.e., the proportion of the oxide that they contribute to the glass system and $\Lambda(Na_2O)$, $\Lambda(ZnO)$, $\Lambda(P_2O_5)$, $\Lambda(CaO)$

and $\Lambda(CuO)$ are optical basicity values assigned to the constituent oxides. Here the values of $\Lambda(Na_2O) = 1.15$, $\Lambda(ZnO) = 0.82$, $\Lambda(P_2O_5) = 0.4$, $\Lambda(CaO) = 1$ and $\Lambda(Cu_2O) = 0.97$ have been taken from literature. The calculated values of Λ_{th} are presented in Table3. It is found that the optical basicity for the present system lies between 0.696 and 0.681, i.e., decreases with increasing Cu_2O content. According to this calculation, it can be concluded that Cu^{2+} ions are surrounded by mostly bridging oxygen which may increase electron cloud density at the Cu^{2+} site, i.e., decrease in the polarizability and hence the changes in spin-Hamiltonian parameters as observed[36, 37]. Also the change in EPR parameters depends on differences in the field intensities and the cation polarizabilities P^{+5}, Ca^{+2}, Zn^{+2}, Na^{+1} which make fluctuations in the ligand field around Cu^{+2} ions[38]. This is consistent with κ values which indicates the decrease of polarizability[36, 37].

Table 3. represent the magnetic susceptibility and the optical basicity.

No.	χ	Λ_{th}
S2	456.95	0.696
S3	538.87	0.6928
S4	515.85	0.6892
S5	468.032	0.6856
S6	432.73	0.681

4. Conclusion

1- It is found that $g_\perp > g_\parallel$ which mean that Cu^{+2} are present in tetrahedral coordination as well as octahedral distortion and ground state is d_{xy}.

2-Paramagnetic susceptibility (χ) depends on Cu^{+2} concentrations.

3-Calculation optical basicity indicates that there is decrease in the polarizability with increasing copper content which is supported by results of Fermi-contact term (κ).

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