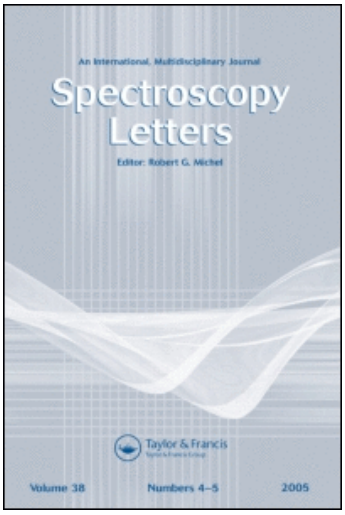

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

EPR and Magnetic Susceptibility of Na_2O-CuO-P_2O_5 Glasses

S. Daoudi[a]; L. Bejjit[a]; M. Haddad[a]; M. E. Archidi[a]; A. Chahine[b]; M. Et-tabirou[b]; P. Molinié[c]
[a] Faculté des Sciences de Meknès, Laboratoire de Spectrométrie, des Matériaux et Archéomatériaux, Zitoune, Meknès, Morocco [b] Faculté des Sciences de Kénitra, Laboratoire de Physico-Chimie du Solide, Kénitra, Morocco [c] Institut des Matériaux Jean Rouxel de Nantes, Nantes, France

To cite this Article Daoudi, S. , Bejjit, L. , Haddad, M. , Archidi, M. E. , Chahine, A. , Et-tabirou, M. and Molinié, P.(2007) 'EPR and Magnetic Susceptibility of Na_2O-CuO-P_2O_5 Glasses', Spectroscopy Letters, 40: 5, 785 — 795
To link to this Article: DOI: 10.1080/00387010701521900
URL: http://dx.doi.org/10.1080/00387010701521900

Spectroscopy Letters, 40: 785–795, 2007

ISSN 0038-7010 print/1532-2289 online
DOI: 10.1080/00387010701521900

EPR and Magnetic Susceptibility of $Na_2O-CuO-P_2O_5$ Glasses

S. Daoudi, L. Bejjit, M. Haddad, and M. E. Archidi
Laboratoire de Spectrométrie, des Matériaux et Archéomatériaux, Faculté des Sciences de Meknès, Zitoune, Meknès, Morocco

A. Chahine, and M. Et-tabirou
Laboratoire de Physico-Chimie du Solide, Faculté des Sciences de Kénitra, Kénitra, Morocco

P. Molinié
Institut des Matériaux Jean Rouxel de Nantes, Nantes, France

Abstract: $(50 - x/2)Na_2O-xCuO-(50 - x/2)P_2O_5$ glasses ($x = 1$, 5, 15, or 30 mol%) have been prepared and characterized by electron paramagnetic resonance (EPR) and magnetic susceptibility measurements. The shape of the Cu^{2+} EPR spectrum depends on the Cu content, and the corresponding computer simulations suggest that the Cu^{2+} ions occupy two different sites in these glasses: one of them is preponderant at low Cu content and the other is preponderant at high content, in which the $Cu^{2+}-Cu^{2+}$ interactions are more important. From EPR parameters, it was found that for the site at low content, the covalency of copper ion bonding with the surrounding ligands is appreciable. The magnetic susceptibility data appear to follow the Curie–Weiss law ($\chi = C/(T - \theta_p)$) with negative paramagnetic Curie temperature θ_p indicating antiferromagnetic interactions between Cu^{2+} ions

Received 6 October 2006, Accepted 17 April 2007

The authors were invited to contribute this paper to a special issue of the journal entitled "Research on Spectroscopy in Morocco." This special issue was organized by Miguel de la Guardia, Proffessor of Analytical Chemistry at Valencia University, Spain.

Address correspondence to M. Haddad, Laboratoire de Spectrométrie, des Matériaux et Archéomatériaux, Faculté des Sciences de Meknès, BP 11201, Zitoune, Meknès, Morocco. E-mail: mhaddad@fs-umi.ac.ma

that are more significant in the samples with high Cu content, in agreement with EPR results.

Keywords: Phosphate glasses, copper ions, electron paramagnetic resonance (EPR), superconducting quantum interface device (SQUID), magnetic susceptibility, covalency

INTRODUCTION

Phosphate glasses exhibit some special properties making them very interesting for many applications. However, their use is limited by their relatively poor chemical durability, and in the past few years, several studies have tried to increase this durability by different methods. It has been found that the addition of various oxides, such as SnO, PbO, ZnO, Al_2O_3, Fe_2O_3, and so forth, to phosphate glasses improves their durability.[1–5] Recently, the phosphate glasses containing copper oxide have received much attention, and their properties have been studied by different techniques.[6–11]

In this context, phosphate glasses containing CuO with chemical composition $(50 - x/2)Na_2O–xCuO–(50 - x/2)P_2O_5$ ($x = 1$, 5, 15, or 30 mol%) have been prepared. Before testing their chemical durability, these glasses have been characterized by X-fluorescence coupled with a scanning electron microscope, which allowed us to determine the different mass concentrations of samples, then by electron paramagnetic resonance (EPR) and by superconducting quantum interface device (SQUID) magnetometer. These last two techniques provided information on the structure and the Cu^{2+}–Cu^{2+} interactions. In this paper, we present and interpret the different results. Another paper containing the results of chemical durability of these glasses will be submitted very soon.

MATERIALS AND METHODS

Batches that produced 8 g of glass were prepared by mixing reagent-grade Na_2CO_3, $(NH_4)H_2PO_4$, and CuO. The platinum crucibles are very sensitive to the attack of the phosphoric acid (H_3PO_4) produced at the time of the operation of pretreatment of glasses. To preserve these crucibles, the pretreatment was carried out at the temperature of 200–250°C in Teflon beakers until disappearance of any gaseous emission. The mixtures thus obtained were calcined in Pt crucibles at 500°C for 2 h to remove water, ammonia, and carbonate. The calcined powders were then melted at 900°C for 15 min. Each liquid was stirred twice with a platinum rod during melting to aid in homogenizing the liquid. After stirring, the liquid was poured onto steel molds to form $1 \times 0.3 \times 0.2$ cm^3 rectangular bars, which were annealed for 1 hr at a temperature of 10°C above T_g and slowly cooled to room temperature. Samples were stored in a desiccator to prevent possible attack by moisture until use.

Table 1. Glass composition, glass transition temperature T_g, density ρ, and molar volume V_m of $(50 - x/2)Na_2O-xCuO-(50 - x/2)P_2O_5$ glasses

x (mol%)	Composition	ρ (g/cm^3)	V_m (cm^3/mol)	T_g (°C)
1	$49{,}5Na_2O-1CuO-49{,}5P_2O_5$	2.51	40.5	279
5	$47{,}5Na_2O-5CuO-47{,}5P_2O_5$	2.57	39.21	279
15	$42{,}5Na_2O-15CuO-42{,}5P_2O_5$	2.74	35.97	296
30	$35Na_2O-30CuO-35P_2O_5$	3.07	31.06	334

Density measurements were carried out at room temperature, using the Archimedes method with diethyl orthophthalate as the immersion fluid. The relative error in these measurements was about ± 0.03 g cm^{-3}. Table 1 reports glass compositions, glass transition temperature, density, and molar volume for all samples.

For CuO additions less than 5 mol%, the glass transition temperature remains constant, showing that CuO has no effect in the glass transition temperature. This absence of effect is attributed to the small bonding energy of copper oxygen bonds (Cu^{+2} acts as a network modifier).

For CuO additions >5 mol%, the glass transition temperature increases. Despite the depolymerization of phosphate chains by CuO, the higher glass transition temperature reflects an increase of the cross-link strength of the glass network as Cu^{+2} ions are introduced (Cu^{+2} acts as a network former).

The mass concentrations of different elements constituting the obtained glasses (Table 2) were determined by using X-fluorescence coupled with a scanning electron microscope.

EPR spectra were recorded at room temperature on a Bruker spectrometer operating at X-band frequencies. Magnetic susceptibility measurements were performed using a commercial SQUID magnetometer (MPMS-5 Quantum Design) in a magnetic field of 5000 G over a temperature range 2–300 K.

Table 2. Mass concentrations in $(50 - x/2)Na_2O-xCuO-(50 - x/2)P_2O_5$ glasses determined by X-fluorescence coupled with SEM

	x (mol%)			
	1	5	15	30
Na (at.%)	20.2 (2)	19.3 (2)	19.2 (2)	19.6 (2)
P (at.%)	19.7 (2)	19.6 (2)	18.5 (2)	16.0 (2)
Cu (at.%)	0.3 (2)	1.1 (2)	3.3 (2)	7.3 (2)
O (at.%)	59.8 (5)	59.9 (5)	59.0 (5)	56.8 (5)

RESULTS AND DISCUSSION

EPR Spectra

Figure 1 shows the X-band spectra recorded at room temperature in $(50 - x/2)Na_2O–xCuO–(50 - x/2)P_2O_5$ glasses with $x = 1$, 5, 15, or 30 mol%. At low concentration of copper, we observe clearly the typical spectrum of Cu^{2+} (Fig. 1a; $x = 1$ mol%) with partially resolved hyperfine structure (HFS),[12,13] and as the Cu content increases, the lines of the hyperfine structure vanish, and at high concentration only an intense and isotropic line is observed (Fig. 1a; $x = 30$ mol%). These spectra are described by the spin Hamiltonian[10]

$$\hat{H} = \beta SgH + \text{SAI},$$

which contains the electronic Zeeman term (β is the Bohr magneton, is the electron spin, g is the g-tensor, and H is the applied magnetic field), perturbed by the hyperfine coupling term between the unpaired electron and the nuclear spin of copper I (A being the hyperfine structure tensor).

The computer simulation of the experimental spectra (Fig. 1a; dashed lines) was made possible only while superimposing two signals that will be called signal 1 and signal 2 (Fig. 1b). The contribution of each one of these signals to the total simulated spectrum depends on the Cu content, and according to their parameters given in Table 3, both of them can be associated with Cu^{2+} ions that seem to occupy two different sites in theses glasses.

Signal 1 (Fig. 1b; dashed line) is characterized by an important peak-to-peak linewidth increasing with Cu content (Table 3), which indicates that in the corresponding site the Cu^{2+} ions are close to each other and thus the Cu^{2+}–Cu^{2+} dipolar interactions can exist, and even the exchange interactions as the lineshape at $x = 30$ mol% is a Lorentzian. The appearance of the HFS on signal 2 (solid line) at $x = 1$ mol% implies that the interactions between the Cu^{2+} ions located in the corresponding site are weak or non-existing, because at low Cu content the Cu^{2+} ions in this site are far from each other. At high concentration ($x = 30$ mol%), signal 2 disappears almost completely.

The parameters that allowed the simulation of signal 2 are listed in Table 3. These values are typical of Cu^{2+} ions in a distorted octahedron.[14,15] The g-factor components are such as $g_{\|=g_z}\rangle\, g_\perp\, (=g_x/2 + g_y/2)\rangle\, g_e\, (=2.0023$ of the free electron), indicating that the distortion is an elongation rather than a compression of the octahedron and that the unpaired spin is localized in the orbital $d_{x^2-y^2}$ (state 2B1g). Using the relationships quoted in Refs. 16 and 17, we have calculated the molecular orbital coefficients α^2, β_1^2, and β^2

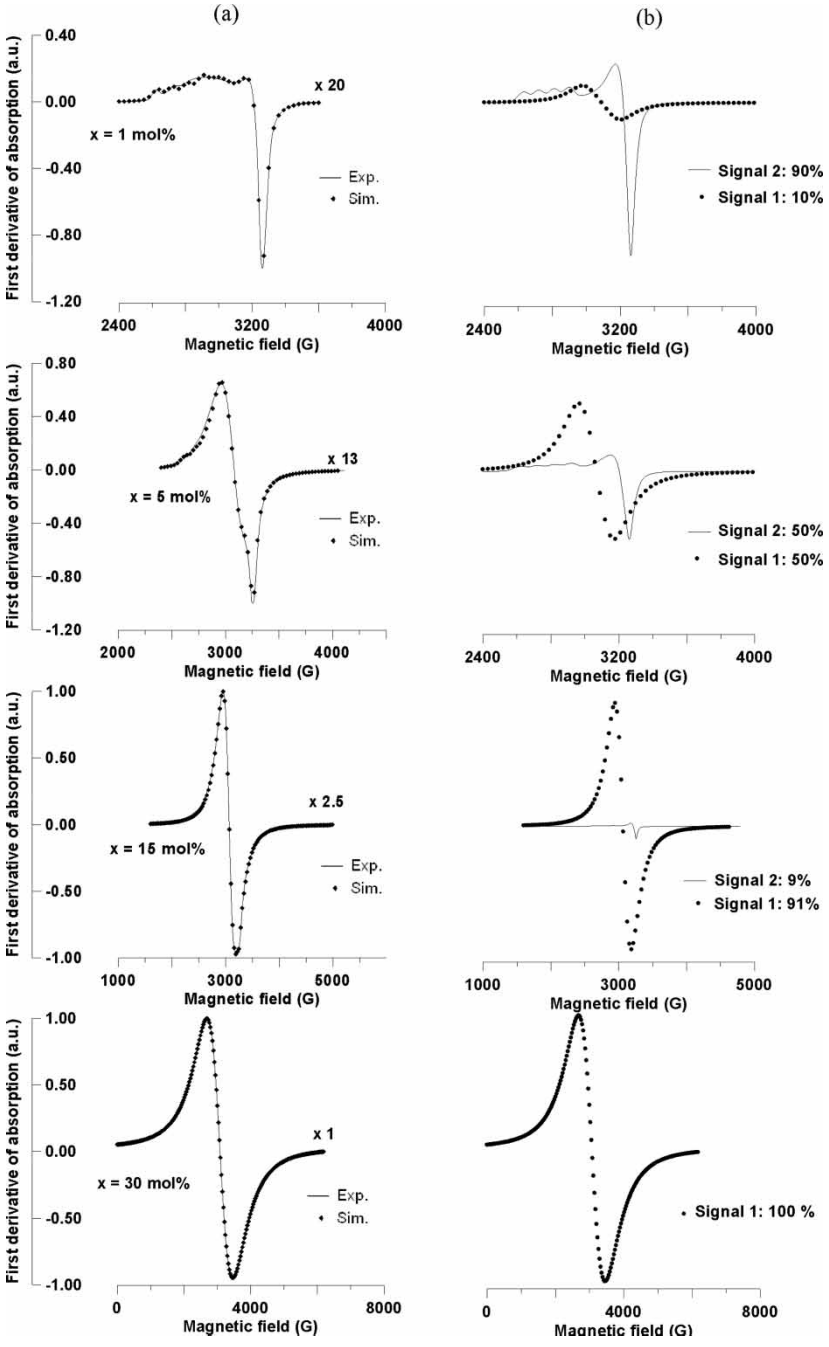

Figure 1. X- band EPR spectra in $(50 - x/2)Na_2O–xCuO–(50 - x/2)P_2O_5$ glasses: (a) experimental and simulated spectra; (b) signals composing the simulated spectrum.

Table 3. EPR parameters of signals 1 and 2 deduced from simulations of spectra

x (mol%)	Signal	%	g_x	g_y	g_z	A_x (G)	A_y (G)	A_z (G)	ΔH (G)
1	Signal 1	10	2.174 ± 0.001			50.74 ± 0.30			120 ± 2
	Signal 2	90	2.074 ± 0.001	2.084 ± 0.0008	2.438 ± 0.002	4.84 ± 0.70	25.29 ± 0.50	102.42 ± 1.60	23 ± 0.2
5	Signal 1	50	2.190 ± 0.001			40.89 ± 1.10			138 ± 2
	Signal 2	50	2.0780 ± 0.0009	2.0920 ± 0.0008	2.435 ± 0.003	9.7 ± 0.3	29.29 ± 0.70	113.66 ± 1.40	25.0 ± 0.2
15	Signal 1	91	2.192 ± 0.001			30.69 ± 0.60			190 ± 2
	Signal 2	9	2.078 ± 0.009	2.090 ± 0.002	2.435 ± 0.003	4.85 ± 0.70	19.51 ± 0.50	113.66 ± 1.40	24.0 ± 0.1
30	Signal 1	100	2.185 ± 0.001			61.19 ± 0.40			655 ± 7
	Signal 2	0							

values, in terms of $g_{\|}$, $g_{\perp}$, $A_{\|}$ and $A_{\perp}$.

$$\alpha^2 = |A_{||}|/P + (g_{||} - g_e) + (3/7)(g_{\perp} - g_e) + 0.04,$$
$$\beta_1^2 = (g_{||}/g_e - 1)\ \Delta E_{xy}/3312\ \alpha^2,$$
$$\beta^2 = (g_{\perp}/g_e - 1)\ \Delta E_{xz,yz}/828\ \alpha^2,$$

where $P = 360\ 10^{-4}\ cm^{-1}$ is the dipolar term.[17]

These coefficients represent respectively the electron densities on $d_{x^2-y^2}$, d_{xy}, and $d_{xz,yz}$ orbitals involved in Cu–O bondings; they describe respectively the covalency of in-plane σ and π bondings and out-of-plane π bondings. The calculations of these coefficients require the use of ΔE_{xy} and $\Delta E_{xz,yz}$ energy values, which correspond with $B_{1g}|d_{x^2-y^2}\rangle \rightarrow B_{2g}\ |d_{xy}\rangle$ and $B_{1g}\ |d_{x^2-y^2}\rangle \rightarrow E_g$-$d_{xz,yz}\rangle$ electronic transitions, respectively; the values 11,919 cm^{-1} and 10,540 cm^{-1}, deduced from the optical spectrum of the studied copper phosphate glasses. These values are very close to those usually found for copper in phosphate glasses.[18] Indeed, the components of the g-factor are expressed by:[19]

$$g_{\perp} = g_e - 2\lambda_{\perp}/\Delta E_{xz,yz} \quad \text{and} \quad g_{||} = g_e - 8\lambda_{||}/\Delta E_{xy}.$$

The constants of spin-orbit coupling λ are altered by the factors of reduction $K_{\|}$ and $K_{\perp}$, according to the relation $\lambda_{\|,\perp} = K_{\|\ \perp}^2\ \lambda_0$, where λ_0 is the value of λ in the case of the free copper ion.

Results of calculations are listed in Table 4. α^2 change little in terms of the composition indicating that the local environment of Cu^{2+} ions is not largely affected. Furthermore, α^2 is close to 1 suggesting that the unpaired electron is almost located in the $d_{x^2-y^2}$ atomic orbital.

The values of $K_{\|}^2$ and $K_{\perp}^2$, calculated from these two relations, are listed in Table 4. They indicate that the Cu–O bond in the (x–y) plane is more

Table 4. Factors of reduction of covalence and coefficients of the orbital molecular of the Cu^{2+} ions occupying site 2

x (mol%)	1	5	15
$g_{\perp}$	2.0790 ± 0.0009	2.0850 ± 0.0058	2.0840 ± 0.0055
$g_{\|}$	2.438 ± 0.002	2.435 ± 0.003	2.435 ± 0.003
$K_{\perp}$	0.698 ± 0.01	0.725 ± 0.0083	0.720 ± 0.0379
$K_{\|}$	0.884 ± 0.0076	0.882 ± 0.0083	0.882 ± 0.0083
$K_{\perp}^2$	0.488 ± 0.0098	0.526 ± 8900.0	0.519 ± 4980.0
$K_{\|}^2$	0.783 ± 21.0	0.778 ± 310.0	0.778 ± 310.0
α^2	0.791 ± 7600.0	0.818 ± 1700.0	0.817 ± 190.0
β_1^2	0.619 ± 10.0	0636 ± 510.0	0.635 ± 710.0
β^2	0.385 ± 10.0	0.43 ± 110.0	0.424 ± 630.0

covalent than the one along the axis of symmetry ($K_\perp < K_\parallel$). The mean values of the coefficients α^2, β_1^2, and β^2 are respectively of values of 0.80, 0.63, and 0.42. The bonds π in the (x–z) and the (y–z) plane have a character therefore more covalent than the bonds σ and the bonds π in the (x–y) plane of the Cu^{2+} ion with its ligands. The Cu^{2+} ions are coordinated therefore essentially by four oxygens in a tetrahedral configuration (Td) but situated in an octahedron of tetragonal elongation (D_{4h}). This model of center is favored by the polymerization of phosphate glasses that induces weak Cu–O bonds along the z axis and a distortion of the four other Cu–O bonds belonging to the plan of the (D_{4h}) structure toward the tetrahedral configuration (Td).

Temperature Dependence of the Magnetic Susceptibility

The temperature dependence of the inverse of magnetic susceptibility χ from the glasses above, whose paramagnetism is due to the Cu^{2+} ions, is shown in Fig. 2. The susceptibility data appear to follow a Curie–Weiss law: $\chi(T) = C/(T - \theta_p)$, where the Curie constant C and the paramagnetic Curie

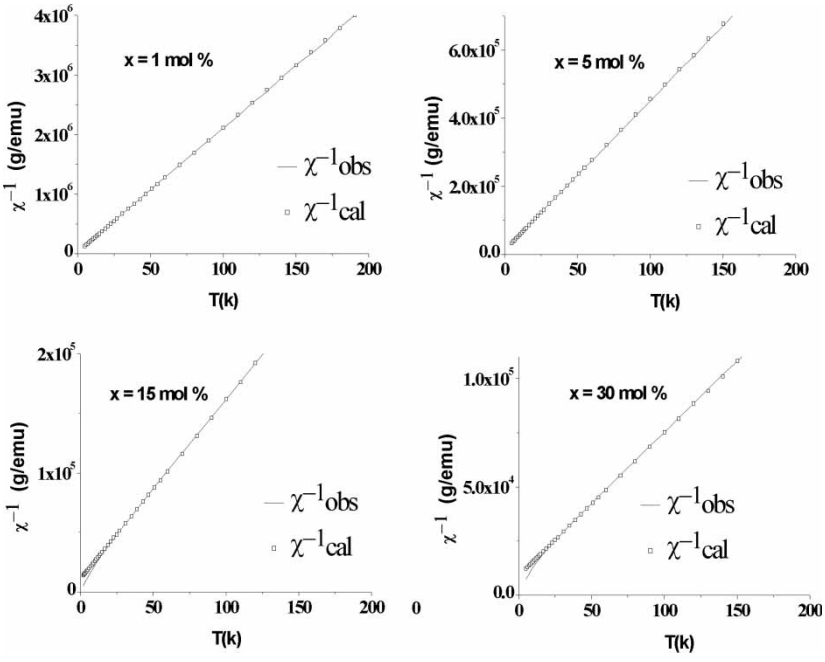

Figure 2. Temperature dependence of the inverse of susceptibility in $(50 - x/2)Na_2O$–$xCuO$–$(50 - x/2)P_2O_5$ glasses. The solid lines are fits of the Curie–Weiss law.

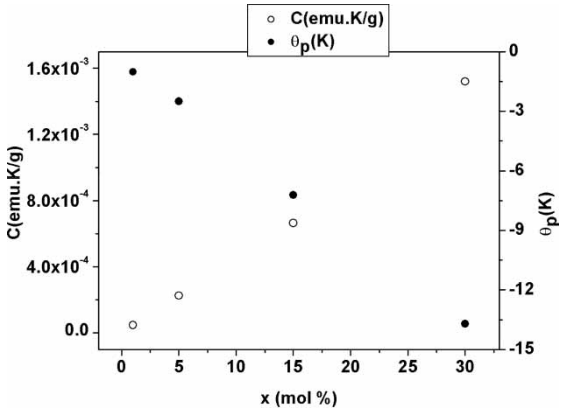

Figure 3. Curie constant C and Curie–Weiss θ_p as a function of Cu concentration.

temperature θ_p depend on the Cu content x as is shown in Fig. 3. We recall that the Curie constant is related to the effective moment p_{eff},

$$C = \frac{N\, p_{eff^2}}{3k_B},$$

where k_B is the Boltzmann constant, and N is the concentration of the magnetic moments contributing to the susceptibility.

A Curie–Weiss behavior with negative temperature θ_p indicates the presence of antiferromagnetic exchange interactions between the Cu^{2+} moments, and θ_p is a rough measure of the strength of these interactions.[20] Thus, a low value of θ_p (-1 K) in the samples with small concentrations of copper ($x = 1$ mol%) means that the Cu^{2+} magnetic moments are weakly coupled, or even isolated from the others. At high concentration, the value of θ_p is significant (-13.66 K at $x = 30$ mol%), indicating stronger Cu^{2+}–Cu^{2+} interactions. These results agree with the conclusions from the EPR study above.

CONCLUSIONS

Phosphate glasses containing CuO have been studied by EPR and magnetic susceptibility measurements. EPR results revealed that the Cu^{2+} ions are situated in two different sites, and important Cu^{2+}–Cu^{2+} interactions exist in the samples with high Cu content. The ground state of the ion in asite corresponding with low content has a predominant $d_{x^2-y^2}$ character and exhibits a large covalent degree of copper ion bonding with surrounding ligands. g and A anisotropies are concluded to be mainly the result of an admixture of $d_{x^2-y^2}$ and d_z^2 orbitals.

The magnetic susceptibility follows a Curie–Weiss behavior with negative paramagnetic Curie temperature indicating antiferromagnetic interactions between Cu^{2+} ions. These results will be very useful for the studies

of durability that we intend to undertake on these materials; the EPR will be used as a probe of possible structural changes.

ACKNOWLEDGMENT

The authors thank Professor M. Kacimi, Laboratoire de Physico-chimie des Matériaux et Catalyse, Faculté des Sciences de Rabat (Morocco), for the optical measurements.

REFERENCES

1. Reidmeyer, M. R.; Rajaram, M.; Day, E. D. Preparation of phosphorus oxynitride glasses. *J. Non-Cryst. Solids* **1986**, *85* (1–2), 186–203.
2. Montagne, L.; Palavit, G.; Delaval, R. Effect of ZnO on the properties of (100–x)($NaPO_3$)-xZnO glasses. *J. Non-Cryst. Solids* **1998**, *223* (1–2), 43–47.
3. Marino, A. E.; Arrasmith, S. R.; Gregg, L. L.; Jacobs, S. D. Durable phosphate glasses with lower transition temperatures. *J. Non-Cryst. Solids* **2001**, *289* (1–3), 37–41.
4. Knowles, J. C.; Franks, K.; Abrahams, I. Investigation of the solubility and ion release in the glass system K_2O–Na_2O–CaO–P_2O_5. *Biomaterials* **2001**, *22* (23), 3091–3096.
5. Brow, R. K. Review: the structure of simple phosphate glasses. *J. Non-Cryst. Solids* **2000**, *263–264*, 1–28.
6. Shih, P. Y.; Chin, T. S. Effect of redox state of copper on the properties of P_2O_5–Na_2O–CuO glasses. *Mater. Chem. Phys.* **1999**, *60* (1), 50–57.
7. Reis, S. T.; Karabulut, M.; Day, D. E. Chemical durability and structure of zinc–iron phosphate glasses. *J. Non-Cryst. Solids* **2001**, *292* (1–3), 150–157.
8. Chahine, A.; Et-tabirou, M.; Elbenaissi, M.; Haddad, M.; Pascal, J. L. Effect of CuO on the structure and properties of $(50 - x/2)Na_2O$–xCuO–$(50 - x/2)P_2O_5$ glasses. *Mater. Chem. Phys.* **2004**, *84* (2–3), 341–347.
9. Khattak, G. D.; Salim, M. A.; Wenger, L. E.; Gilani, A. H. X-ray photoelectron spectroscopy (XPS) and magnetic susceptibility studies of copper–vanadium phosphate glasses. *J. Non-Cryst. Solids* **2002**, *62* (1–3), 66–79.
10. Taoufik, I.; Haddad, M.; Nadiri, A.; Brochu, R.; Berger, R. X and Q band EPR studies of $Cu_{0.5}Zr_2(PO_4)_3$ phosphates. *J. Phys. Chem. Solids* **1999**, *60* (5), 701–707.
11. Shih, P. Y. Effect of CuO on the properties of stannous chlorophosphate glasses. *J. Non-Cryst. Solids* **2003**, *315*, 211–218.
12. Kumar, V. R.; Rao, J. L.; Gopal, N. O. EPR and optical absorption studies of Cu^{2+} ions in alkaline earth alumino borate glasses. *Mater. Res. Bull.* **2005**, *40* (8), 1256–1269.
13. Karthikeyan, B.; Mohan, S. Optical and EPR studies on Cu^{2+}-doped sodium borobismuthate glasses. *Mater. Lett.* **2003**, *57* (24–25), 3789–3792.
14. Debnath, R.; Chaudhuri, J. Optical absorption and EPR of Cu(II) in an alumina rich phosphate glass. *Phys. Chem. Glasses* **1995**, *36* (4), 160–164.
15. Bagratashvili, V. N.; Bogomolova, L. D.; Jachkin, V. A.; Krasilnikova, N. A.; Rybaltovskii, A. O.; Tsypina, S. I.; Chutko, E. A. Electron paramagnetic resonance of color centers in nanoporous glasses impregnated with copper

β-diketonatewith the use of supercritical carbon dioxide. *Glass Phys. Chem.* **2004**, *30* (6), 500–505.
16. Siegel, I.; Jones, E. P. Electronic bonding of Cu^{2+} in amorphous and crystalline TeO_2: EPR and optical spectra. *J. Chem. Phys.* **1972**, *57* (6), 2364–2371.
17. Kivelson, D.; Neiman, R. ESR studies on the bonding in copper complexes. *J. Chem. Phys.* **1961**, *35*, 149–155.
18. Bae, B. S.; Weinberg, C. Optical absorption of copper phosphate glasses in the visible spectrum. *J. Non-Cryst. Solids* **1994**, *168*, 223–231.
19. Abragam, A. L.; Pryce, H. M. The theory of the nuclear hyperfine structure of paramagnetic resonance spectra in the copper tutton salts. *Proc. R. Soc. London Ser. A* **1951**, *206*, 164–1772.
20. Khattak, G. D.; Salim, M. A.; Wenger, L. E.; Gilani, A. H. X-ray photoelectron spectroscopy (XPS) and magnetic susceptibility studies of copper-vanadium phosphate glasses. *J. Non-Cryst. Solids* **2000**, *262*, 66–79.