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XAFS investigation of Cu(I) local environment in two types of glasses of base composition $LaMgB_5O_{10}$ and $LiLaP_4O_{12}$

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Abstract

X-ray absorption spectroscopy (XAFS) has been used to characterise the local environment around Cu^+ ions in two types of glasses of base composition $LaMgB_5O_{10}$ and $LiLaP_4O_{12}$. In both glasses, Cu^+ is surrounded by two oxygens respectively at 1.87 and 1.86 Å. For the first time in glasses, the formation of Cu^+-Cu^+ pairs ($d_{Cu\text{-}Cu} = 2.35$ Å) is clearly evidenced in the phosphate. These results will be discussed with respect to the crystal chemistry of Cu(I) in copper oxides and the specific luminescent properties of an isolated Cu^+ centre or Cu^+-Cu^+ pairs.

Keywords: Cu(I)-containing glasses; Cu(I)-Cu(I) pairs; Borate; Phosphate; EXAFS; XANES; Luminescence

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1. Introduction

The photoluminescence of monovalent copper in insulators has been extensively investigated in oxides: crystals or glasses [1]. Usually it gives rise to broad band luminescence in the visible range under UV excitation. In the model crystal $CuZr_2(PO_4)_3$ two different bands occurring in the violet and in the green region were assigned respectively to isolated Cu^+ and to Cu^+-Cu^+ pairs [1]. These conclusions were supported by the examination of the copper local structure by X-ray absorption spectroscopy (XAFS) [2]. The copper pair was characterised by a small copper copper distance ($d_{Cu\text{-}Cu} = 2.40$ Å). A similar luminescence band can also be observed in glasses but, up to now, the copper(I) coordination has never been studied in such materials. The present paper reports a detailed EXAFS investigation of the copper environment in glasses of base compositions: $LiLaP_4O_{12}$ and $LaMgB_5O_{10}$ for which a blue emission is observed with an additional orange emission for the phosphate [3]. The results will be discussed in the context of the crystal chemistry and of the luminescent properties of the cuprous oxides.

2. XAFS data collection

Material synthesis and preparation have been described elsewhere [4]. Exact glass compositions are respectively: 17.14 La_2O_3, 10.71 Li_2O, 0.99 Cu_2O, 71.16 P_2O_5 and 11.78 La_2O_3, 24.65 MgO, 0.2 Cu_2O, 1 As_2O_3, 62.37 B_2O_3. EXAFS spectra were recorded at LURE (french synchrotron radiation facility) using the EXAFS III spectrometer in fluorescence mode at room temperature. This station is equipped with a two crystal Si (111) monochromator for optimisation of the flux collection in preference to the resolution. During the experiment, the storage ring used 1.85 GeV positrons with an average intensity of 200 mA. Each material sample was a glass plate of about 1 cm^2 area and 2 mm thickness. An air-filled ionisation

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chamber is used to measure the flux intensity before the sample. The fluorescence detector is a Ge solid state multichannel detector. The resolution of this detector allowed us to select only Cu $K\alpha$ and $K\beta$ fluorescences, after calibration with a Cu foil. Five EXAFS spectra have been registered for each material between 8900 and 10000 eV, with 1 eV steps and an accumulation time of 10 s per point. The XANES spectra were registered between 8900 and 9100 eV for 0.5 eV steps and accumulation times of 30 s per point.

2.1. Data analysis

XANES spectra have been calibrated, background subtracted and normalised. EXAFS analysis is performed following a previously described procedure by the use of the EXAFS chain of programs written by Michalowicz [5,6]. Tabulated amplitude and phase functions of Teo and Lee are used [7]. XANES spectra are presented in Fig. 1 while fourier transformed EXAFS signals are given in Fig. 2.

3. Results

3.1. XANES

The spectra contain a feature in the pre-edge region at 8982 eV. For very low copper concentrations in the solid material, this peak is related to an absorption process which can be described in terms of single-ion transitions from a core-state essentially copper atomic orbital 1s to appropriate unoccupied molecular orbitals of the unperturbed oxygen site. The relatively high intensity of this peak is consistent with the electric dipolar transition essentially 1s to 4p and slightly 1s to ligand group orbitals of p character. Polarised single-crystal studies on Cu(I) linear complexes show that the transition corresponding to this peak is (x,y)-polarised [8]. Its fine shape and its intensity (larger than 1) indicate a pure transition 1s to $4p_x$,$4p_y$ non-bonding copper orbitals in linear coordination. When the presence of a more distant third ligand induces the formation of an angle different from 180° between the copper atom and its two nearest neighbours, this peak is broadened consequently to different mixing of $4p_x$ and $4p_y$ copper orbitals with ligand p orbitals (Fig. 3). It can be deduced that XANES spectra for both glasses are consistent with a linear coordination of copper atoms, but the next coordination shells of oxygen atoms probably remove the degeneracy of $4p_x$, $4p_y$ copper orbitals in the borate glass.

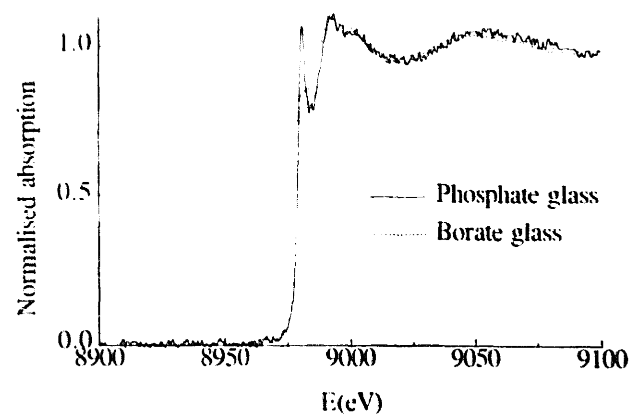

Fig. 1. Normalised XANES spectra.

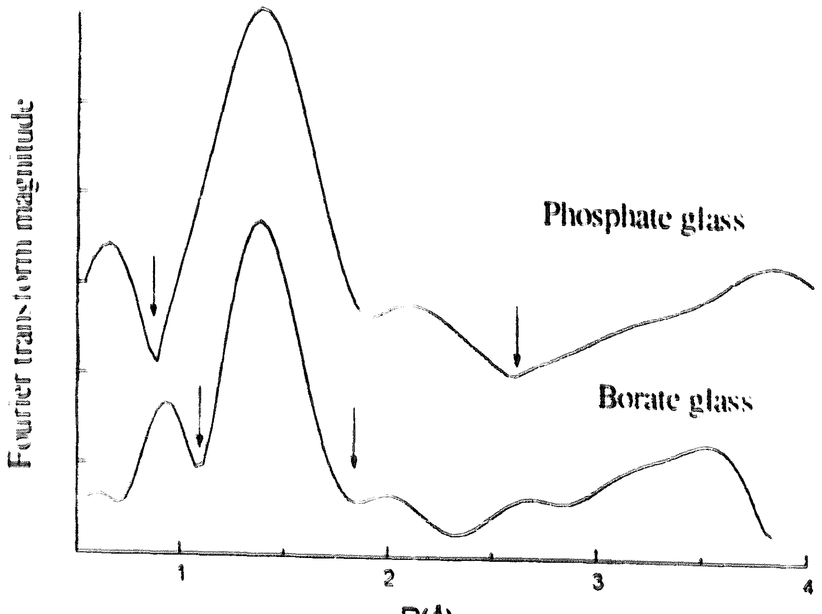

Fig. 2. Radial structure functions, uncorrected for phase shift. The domain limited by arrows match the fitting of the EXAFS signals.

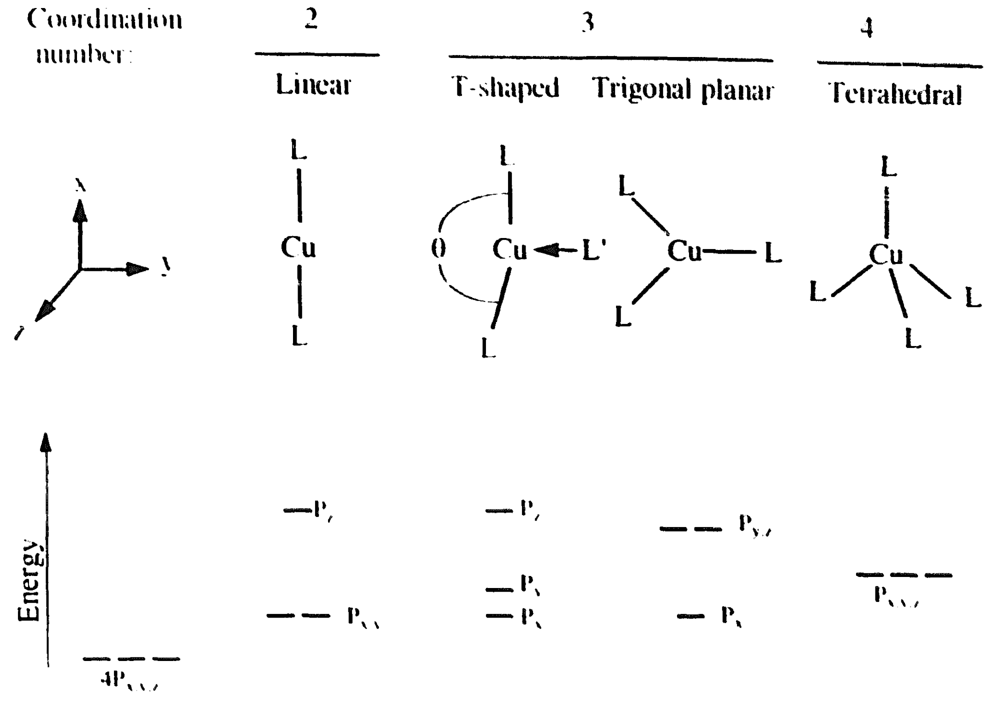

Fig. 3. Ligand field splitting of copper 4p orbitals as a function of the environment [9].

3.2. EXAFS results

Fourier transforms of the EXAFS signals yield radial structure functions (uncorrected for phase shift) consisting of peaks representing the different coordination shells at different distances from the Cu absorber atom. The fourier transforms which are obtained for both glasses present a structure similar to the previously published radial structure functions around copper in crystallised $CuZr_2(PO_4)_3$ and $CuTi_2(PO_4)_3$ [2]. The first shell can be attributed to oxygen atoms nearest neighbours. For the phosphate glass the second shell can be assigned to Cu^+-Cu^+ pairs as was done for $CuZr_2(PO_4)_3$. The second little peak which is observed for the borate glass is probably an artefact of apodized window fourier transforming as was concluded for a similar feature observed for $CuTi_2(PO_4)_3$.

An EXAFS signal for each shell is obtained by fourier backtransforming each filtered corresponding peak. The simulations for the first shell evidence two oxygen neighbours for Cu-O distances equal to 1.87 Å in the borate glass and 1.86 Å in the phosphate glass (Table 1). These distances are comparable to that of the short Cu-O bond observed in Cu(I) oxide, where copper atoms form two collinear bonds to oxygen. A d_{z^2}, 4s hybridization of copper atomic orbitals has been invoked to explain such a short Cu-O distance when compared to the sum of the ionic radii [9]. These results confirm that copper atoms have the same linear coordination in both glasses. Simulations of the second coordination shell EXAFS signal of the phosphate glass have been attempted for each atom which might have been present at this distance. The adjustment in periodicity of the signal is only obtained by using the copper atom phase shift. A simulation of the whole EXAFS signal for the first and second shell together was then attempted showing that a non-negligible number of copper atoms are paired with a very short Cu-Cu distance of 2.35 Å. The best EXAFS signal simulations are given in Fig. 4.

4. Discussion

The crystal chemistry of monovalent copper in insulators is characterised by two trends: a linear coordination by the oxygen and the formation of aggregates mainly as copper pairs. Typical examples of linear coordination of Cu^+ are found in Cu_2O, in Delafossite cuprous oxides, in $CuNbO_3$ etc. [10]. In such

Table 1

EXAFS structural parameters obtained for the best simulations. For both glasses the number of oxygen neighbours was fixed equal to 2, and the number of copper neighbours N, interatomic distances R, Debye-Waller factors $\Delta\sigma^2$ and refinement of the E_0 (the origin of kinetic energy) which was included as a fitting parameter were adjusted by simulations

Glass sample	Shell	R (Å)	N	$\Delta\sigma^2$ (Å^2)	E_0 (eV)
$LiLaP_4O_{12}$:Cu^+	Cu-O	1.86	2	0.008	8992.0
	Cu-Cu	2.35	0.5	0.008	8992.1
$LaMgB_5O_{10}$:Cu^+	Cu-O	1.87	2	0.006	8993.1

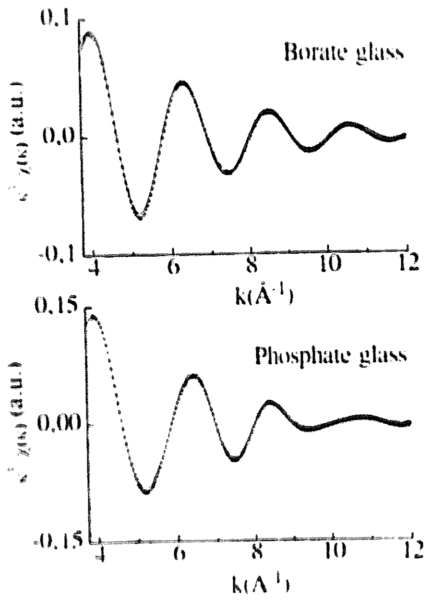

Fig. 4. EXAFS signals obtained by Fourier back-transforming of the first peak (resp. first and second peak) of the radial structure function for the Cu-doped borate glass (resp. Cu-doped phosphate glass) (solid lines) compared to the best least-square fits (crosses).

dumbbell-like configuration the copper oxygen distances are almost identical between 1.798 Å in the case of $CuScO_2$ [11] to 1.861 Å in $CuAlO_2$ [12]. In other words the counter-cation facing the Cu-O bond has no influence on the distance. Decreasing the O-Cu-O angle leads to an increase of the Cu-O distance; e.g. in the distorted tetrahedral sites of $CuNb_3O_8$ or $Cu_4Mo_5O_{17}$ the shortest copper oxygen distances range from 1.93 to 2.25 Å [13,14].

If the copper site becomes larger, the linking of copper by oxygen appears to be a compromise between the classical linear coordination and the geometry of the site. This situation is observed in the elongated antiprismatic site of the Nasicon type structure: the two shorter copper oxygen distances are close to 2.05 Å in the phosphate $CuM_2(PO_4)_3$ (M = Ti, Zr). In addition, copper(I) tends to aggregate and first of all to be paired. Such pairs are encountered in $CuZr_2(PO_4)_3$ ($d_{Cu\text{-}Cu}$ = 2.40 Å) [2] and in $Cu_2CrZr(PO_4)_3$ [15] ($d_{Cu\text{-}Cu}$ = 2.47 Å). Usually short intermetallic distances are found particularly in organo-Cu(I) compounds. The most simple is the cuprous acetate, in which is observed a Cu-Cu distance of 2.56 Å [16]. Other examples of Cu aggregates observed in solid state chemistry have been reviewed by Jansen [17]. Rath et al. [18] have reported several crystal structures of Cu(I) iodide complexes with Cu iodide entities of various structural format and short Cu-Cu distances.

Cu pairs were assumed to be the origin of the green fluorescence in zeolites [19] or copper-doped β″alumina [20]. The correlation between the luminescent properties and the occurrence of copper pairs was studied in detail for $CuZr_2(PO_4)_3$ [1]. The emission in the violet region is associated to isolated copper ions whereas the green emission is due to the pairs. In the glasses investigated a broad band blue emission ($\lambda_{exc.}$ = 250 nm RT) is observed and an additional orange-red fluorescence peaking about 570 nm ($\lambda_{exc.}$ = 310 nm RT) appears only in the copper richest phosphate. The first band can be attributed to isolated copper and the order of magnitude of the Cu-O distance is consistent with a linear coordination of copper by oxygen atoms.

The additional band is due to the copper pairs. By

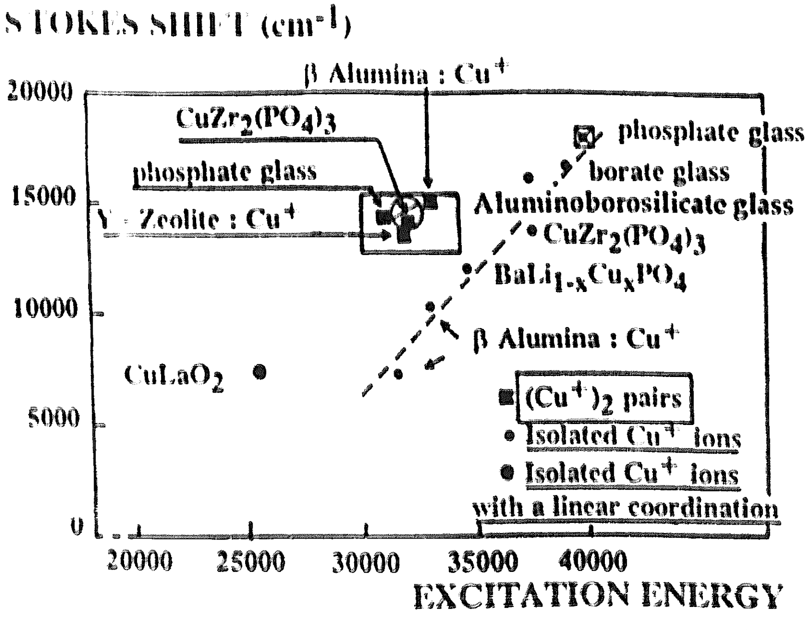

Fig. 5. Stokes shift as a function of excitation energy for various copper activated oxygenated insulators in a crystallised or glassy state: ⊠ $LiLaP_4O_{12}:Cu^+$ and $LaMgB_5O_{10}:Cu^+$ blue luminescence; ⊗ $LiLaP_4O_{12}:Cu^+$ red luminescence.

representing (Fig. 5) the stokes shift in an energy diagram [21] as a function of the excitation energy for materials involving copper pairs, a close localisation of the data including that related to the phosphate studied is observed in spite of the large diversity of the matrices. This figure reveals a quasi-invariance of the copper-copper distance in these entities around 2.40 Å which is lower than the intermetallic distance in copper metal.

5. Conclusion

In conclusion, the local environment of copper in the glasses investigated is in good agreement with previous crystallographic and fluorescence data. The occurrence of a copper(I) pair in phosphate glasses but not in the borate one can be tentatively explained by the more flexible structure of the phosphate chain compared to the three dimensional nature of the boron oxygen former.

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