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Fluorescence Properties of Cu^+ Ion in Phosphate Glasses of the $BaLiPO_4$–P_2O_5 System

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The spectroscopy and the excited state dynamics of Cu^+ ion in phosphate glasses are investigated as a function of the copper concentration and temperature. The blue fluorescence is assigned to single Cu^+ impurity ions occupying various sites. An additional red fluorescence, not detected in weakly Cu-doped samples but which grows with copper concentration, is well interpreted in terms of $(Cu^+)_2$ pair centers.

I. Introduction

Monovalent copper ions, when embedded in glasses, usually give rise to a strong luminescence which depends on the host material (*1–4*). In most cases, the systems exhibit a very broad emission band in the visible, and therefore, are particularly interesting for obtaining tunable laser emission (*5–7*). Light amplification has been reported by Kruglik *et al.* in copper-doped aluminoborosilicate glass (*7, 8*).

The luminescent properties of monovalent copper in solids have been investigated extensively in the past, especially in the case of Cu^+-doped alkali halides (*9–13*). In these simple systems, where the impurity ions occupy well-defined high symmetry sites, the fluorescence mechanisms are now well understood; they involve $3d^94s \rightarrow 3d^{10}$ transitions with parity forbidden in the free ion but partially allowed in the crystal by coupling with lattice vibrations of odd parity. A detailed interpretation of the fluorescence dynamics is obtained by considering the spin-orbit interaction which mixes singlet and triplet states (*14*). On the other hand, in glass hosts Cu^+ ions may occupy a large variety of sites, making the analysis of the fluorescence processes more difficult.

Here are reported the results of an investigation of the luminescence of Cu^+ in phosphate glasses. Two different blue and red fluorescence emission bands, assigned to single Cu^+ ions and $(Cu^+)_2$ dimers, respectively, were observed.

II. Materials

The introduction of monovalent copper impurity ions is difficult and sometimes requires special methods of preparation.

Five samples were prepared with the following molar compositions: 44.5 P_2O_5, 37.0 BaO, $(18.5\text{-}x)Li_2O$, xCu_2O($x = 0, = 0.01$, 0.05, 0.1, 0.2). In the first step of the prepa-

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ration process included the mixing of $BaCO_3$, $\left(\frac{1-x}{2}\right)Li_2CO_3$, $(NH_4)_2$ HPO_4 (without copper), and heating for 15 hr under a controlled nitrogen flow successively at 200, 400, and then 600°C, in order to remove CO_2, H_2O, and NH_3 gas. Copper was then introduced as Cu_2O, and the mixed powder was heated for 1 hr in a vitreous carbon crucible under a nitrogen flow at a temperature between 1000 and 1100°C, depending on the composition. The molten glasses were poured on a carbon plate preheated at 300°C and then annealed at 350°C for 5 hr and cooled down at room temperature at 0.5°C min^{-1}.

No divalent copper could be detected by EPR measurements.

The measurement of the density of the materials (3.42) allows one to estimate the nominal Cu concentration (from 2.95×10^{18} to 5.90×10^{19} ions · cm^{-3}).

DTA investigation of the undoped samples gives the glass transition temperature as $T_g = 362$°C with two recrystallization peaks at 452 and 528°C and two melting points at 640 and 672°C.

The X-ray patterns of the recrystallized products are complex. The main identified phase is the $BaLi_2P_2O_7$ pyrophosphate.

All the samples were carefully polished for optical analysis.

III. Experimental Optical Techniques

The absorption spectra were recorded using a Model 2300 Varian UV–visible–NIR spectrophotometer equipped with a liquid–helium cryostat for low temperature measurements.

The emission spectra were recorded using as the exciting source a Q-switched Nd^{3+} : YAG pumped-dye laser beam (TDL IV model from Quantel) which could be doubled or frequency-doubled and mixed with the fundamental (1.06 μm), for a laser excitation around 320 or 250 nm, respectively. The emissions were dispersed by a Hilger computer scannable 1-m monochromator and detected with a Hamamatsu R 1477 PMT followed by an amplifier/discriminator and a photon counter.

Excitation spectra were obtained a LURE (University of Orsay) using SUPER ACO Synchrotron radiation as a light source and a 3-m homemade vacuum–UV monochromator, spanning the wavelength range from 30 to 800 nm.

Both emission and excitation setups were carefully calibrated and the spectra corrected accordingly.

Decay time measurements were recorded with a multichannel analyzer (35 Plus model from Camberra) with a minimum dwell-time per channel of 200 ns.

IV. Experimental Results

Absorption spectra of various samples were recorded at 10 and 300 K. The more interesting results were obtained from a pure phosphate glass and a sample containing only a trace of copper, both having very good optical quality. For the undoped glass sample, the fundamental absorption edge is near 40,000 cm^{-1} and the spectrum shows a curve which continuously increases. The absorption of the very weakly copper-doped glass starts at lower energy around 27,000 cm^{-1} and the spectrum exhibits a structure below the absorption edge energy of the pure glass. Figure 1 shows the absorption obtained by subtraction of both curves at room temperature. The resulting curve shows a tail (a), followed by a broad unresolved band (b) and a steep rise (c). The resolution of the bands was not improved at 10 K.

The fluorescence emission spectra were recorded under two different excitations at 320 and 250 nm. The choice of these excitations will be justified later after the examination of the fluorescence excitation spectra.

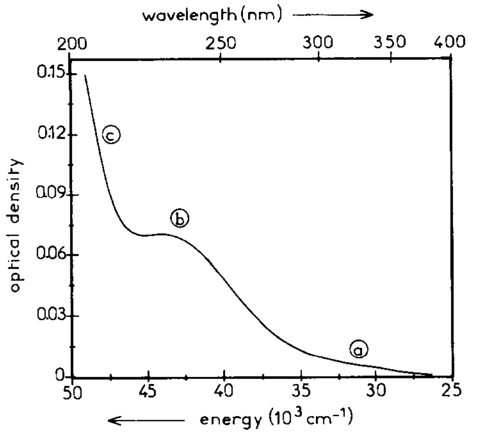

FIG. 1. Absorption spectrum at room temperature resulting from a subtraction of undoped and very weakly Cu-doped glass curves.

Under 320-nm excitation, all the samples exhibit a broad blue and strong emission band centered around 455 nm (22,000 cm^{-1}). When the Cu$^+$ concentration increases, another red fluorescence band peaking near 590 nm (17,000 cm^{-1}) increases (Fig. 2). The latter, not observed in the most weakly doped sample, appears at 0.05 mole% Cu$_2$O concentration and is dominant at higher concentration (0.2 mole% Cu$_2$O). The characteristics of both bands are indicated in Table I. When the temperature increases, the bands broaden, and the blue band shifts toward lower energy. There is also observed a peculiar Cu$^+$ concentration dependence of the blue emission band which first broadens and then strongly narrows (from 0.1 mole% to 0.2 mole% Cu$_2$O as the copper concentration increases). The excitation at 250 nm gives rise only to a broader blue fluorescence band shifted toward higher energy. The copper concentration and temperature dependences are quite similar to the ones previously observed (Table II); the trends are still more evident, probably because the blue band is isolated in this case and therefore the measurement of its moments is more accurate.

The fluorescence excitation spectra were recorded between 100 and 400 nm using the synchrotron radiation of SUPER ACO (Fig. 3). The blue fluorescence exhibits essentially two peaks around 200 and 250 nm, roughly corresponding to the (c) and (b) regions of absorption. The red fluorescence shows a strong peak near 320 nm which could correspond to the (a) absorption tail, and a weaker one around 220 nm which does not coincide with the maxima of the blue fluorescence. The excitation peaks of both fluorescences shift toward higher energies upon cooling.

The decays of both fluorescences were recorded for the four variously Cu$^+$-doped samples under laser excitation at 320 nm and in the 1.5–300 K temperature range. In order to separate well the contributions of the blue and red fluorescences, narrow wavelength ranges ($\Delta\lambda \simeq 1.2$ nm) have been considered

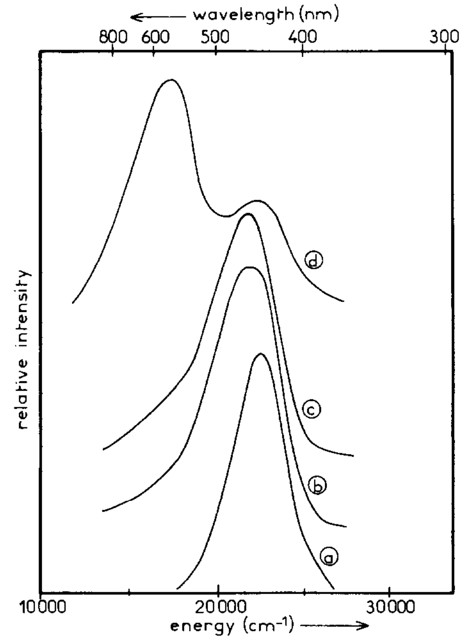

FIG. 2. Emission spectra at T = 20 K under laser excitation at 320 nm of variously Cu$_2$O-doped samples: (a) 0.01 mole%; (b) 0.05 mole%; (c) 0.1 mole%; (d) 0.2 mole%.

TABLE I

FIRST AND SECOND MOMENTS OF THE EMISSION BANDS UNDER 320-nm LASER EXCITATION

	Mole % Cu_2O	T(K): 20	80	300
Maximum (cm^{-1})	0.01	22,366	21,603	21,145
	0.05	21,679	21,450	21,145
	0.10	21,527	21,527	20,916
		22,213	21,908	21,908
	0.20	16,870 r	16,870 r	17,328 r
Half-band width cm^{-1}	0.01	3,664	4,580	4,810
	0.05	4,274	4,504	4,580
		4,732 r	4,636 r	4,886 r
	0.010	4,274	4,274	5,038
		4,580 r	4,580 r	5,190 r
	0.20	3,512	3,664	4,580
		3,970 r	3,816 r	4,274 r

Note. r, red emission band.

around 400 and 600 nm. The decays are exponential. The temperature dependence of the decay-time constant τ of the blue fluorescence is shown in Fig. 4. τ increases slightly upon cooling from 300 to 60 K (inset) then increases strongly between 30 and 4 K. Below the liquid helium temperature, the onset of a plateau is clearly observed. It is also observed that τ increases as the Cu^+ concentration decreases. For the red fluorescence, τ is nearly twice as large. Above 100 K, τ varies similarly (insert in Fig. 5) whereas at lower temperature, τ rises more rapidly but no plateau is detected at very low temperatures (Fig. 5). Furthermore, contrary to the previous case, τ increases with the Cu^+ concentration.

V. Discussion and Interpretation

No luminescence was detected in the undoped glass, indicating that both emissions

TABLE II

FIRST AND SECOND MOMENTS OF THE BLUE EMISSION BAND UNDER 250-nm LASER EXCITATION

	Mole % Cu_2O	T(K): 20	80	300
Maximum cm^{-1}	0.01	22,900	22,366	21,908
	0.05	22,672	22,595	22,214
	0.10	22,672	22,366	22,061
	0.20	22,743	22,366	22,137
Half-band width cm^{-1}	0.01	4,334	4,428	5,114
	0.05	4,428	4,810	4,886
	0.10	4,656	4,962	5,114
	0.20	4,962	5,038	5,268

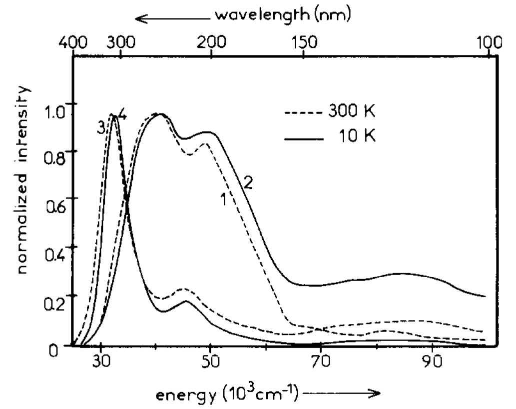

FIG. 3. Excitation spectra of phosphate glass containing 0.2 mole% Cu_2O. Curves 1,2, blue filter (441 nm, $\Delta\hbar\omega \simeq 669\ \mathrm{cm}^{-1}$); curves 3,4, red filter (>570 nm).

are associated with Cu^+ impurity ions in doped phosphate glasses. Moreover, they probably originate from two separate centers since their characteristics are rather strongly different.

It is well-known that crystals doped with increasing amounts of Cu^+ or Ag^+ ions often exhibit, besides the fluorescence due to single impurity ion centers, a new fluorescence with a much larger Stokes shift assigned to $(Cu^+)_2$ or $(Ag^+)_2$ pairs (*15–18*). In the case of the phosphate $CuZr_2(PO_4)_3$, the presence of $(Cu^+)_2$ dimers was clearly established by a detailed EXAFS investigation (*19*). In copper-doped glasses, a very broad emission band is usually observed (*1–4*), which is shown to be characteristic of Cu^+ single ions occupying a large variety of sites. However, Postelnikov pointed out the existence of both blue and yellow fluorescences in aluminophosphate glasses doped with monovalent copper, and assigned them to Cu^+ single ion centers and Cu^+–oxygen vacancy pairs, respectively (*20*). In the present case, the formation of oxygen vacancies must be ruled out owing to the strong covalency of the phosphorus oxygen bond. We assume that the blue and red fluorescences exhibited by our samples are due to Cu^+ single ion and $(Cu^+)_2$ pair centers, respectively. These attributions are supported by comparison with other systems and by consideration of the spectroscopic data.

Let us consider first the blue fluorescence assigned to Cu^+ isolated impurity centers. The small Stokes shift and the temperature dependence of the emission band are typical of localized transitions. Furthermore the variations of the blue emission band as a function of the excitation and of the Cu^+ concentration are well interpreted by considering the presence of a quasicontinuum of impurity sites. As in the case of copper-doped borate glasses, the same schematic representation of the energy levels of Cu^+ occupying various sites (Fig. 3 of Ref. (*4*)) may be used to interpret the data. A high energy photon radiation excites a larger variety of sites than a lower energy excitation. This behavior is consistent with the broad-

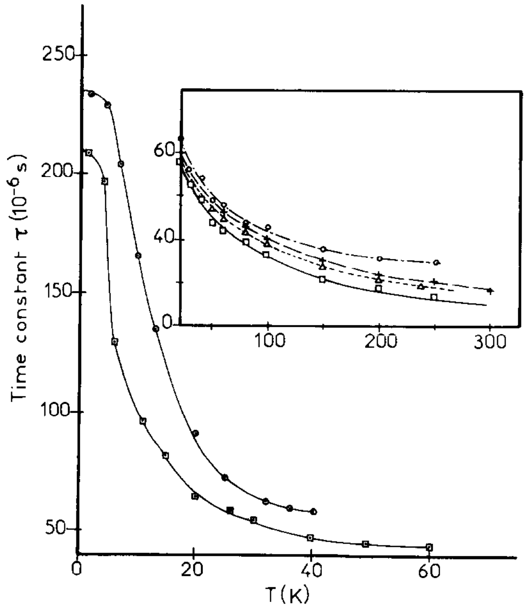

FIG. 4. Temperature dependence of the time constant τ of the blue fluorescence at various Cu_2O concentrations. ○, 0.01 mole%; +, 0.05 mole%; Δ, 0.1 mole%; □, 0.2 mole%. Solid lines represent the best fits to experimental data obtained from expression (1).

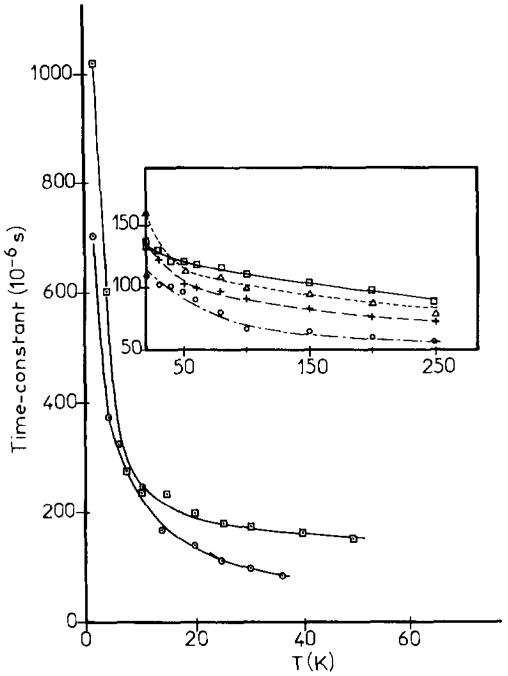

FIG. 5. Temperature dependence of the time constant τ of the red fluorescence at various Cu_2O concentrations. ○, 0.01 mole%; +, 0.05 mole%; Δ, 0.1 mole%; □, 0.2 mole%.

ening of the emission band observed when the energy of the incident photons increases. This simple scheme also explains the red shift of the band when the excitation changes from 250 to 320 nm, and its broadening as the Cu^+ concentration increases since more sites are occupied. However, this latter effect is not observed under 320-nm excitation when the concentration varies from 0.1 mole% to 0.2 mole% Cu_2O (Table I). In contrast, a strong narrowing of the blue band and a shift of its maximum in the opposite direction could reflect a strong decrease in the number of Cu^+ isolated ions situated in minority sites excited at 320 nm, for the benefit of $(Cu^+)_2$ pair concentration. The 250-nm irradiation excites the majority Cu^+ single ions unaffected by this phenomenon and their number would increase continuously with the copper concentration (Table II). These experimental results would mean that some environments are more favorable than others to pair formation. The temperature dependence of the decay time is typical of single Cu^+ impurity ions in crystals. Of course the spectroscopic properties of Cu^+ in glasses and in crystals are not strictly identical; however, some analogy is expected if the next surrounding of the impurity ion is similar. A model, involving two close excited states, the lower being metastable, was successfully used to explain the fluorescence mechanisms of Cu^+ centers in various systems (*4, 10, 12, 14*). The model is still able to describe the present system using the relation (*12, 14*)

$$\tau^{-1} = \frac{A_{31} + A_{21}\exp(-\varepsilon/kT)}{1 + \exp(-\varepsilon/kT)}, \qquad (1)$$

where A_{31} and A_{21} are the radiative transition probabilities between the excited states (upper level 2 and lower level 3) and the ground state (level 1). ε represents the energy mismatch between the two excited states. A_{31} is evaluated as the inverse of the experimental lifetime at very low temperature and the best fit to experimental data obtained from expression (1) (solid lines in Fig. 4). These parameters are listed in Table III along with parameters for other systems which may be useful for comparison.

The spectroscopic characteristics of the red fluorescence are quite different and can be tentatively interpreted in terms of $(Cu^+)_2$ pairs. The two main red fluorescence excitation peaks are shifted toward lower energies compared to the blue ones, as it is usually observed in the case of pairs (*15*). The relative intensity of the red fluorescence increases with the copper concentration and the larger Stokes shift may reflect a stronger delocalization of the excited electron in the pair. This latter observation may also be responsible for the longer fluorescence lifetime. It is clear that the weak metallic character of the excited states, which play a role

TABLE III

SPECTROSCOPIC PARAMETERS OF THE EMITTING LEVELS FOR FEW Cu^+ LUMINESCENT COMPOUNDS

Materials	A_{31}(sec^{-1})	A_{21}(sec^{-1})	ε(cm^{-1})	τ(μs) at 4.2 K
Phosphate glass 0.01 mole% Cu_2O	4270	42,000	15	230
Phosphate glass 0.2 mole% Cu_2O	4807	49,000	12	196
Borate glass 0.14 mole% Cu_2O	2247	28,300	25.7	430
$CuZr_2(PO_4)_3$ (Ref. (*17*))	5920	57,140	31	155

in the dynamics of fluorescence, is a consequence of delocalization of the electron and, therefore, of a substantial decrease of the transition probabilities. Such weak metallic characters were measured in $(Ag^+)_2$ pairs in NaCl (*21*). The larger fluorescence lifetimes of pairs were observed in many cases (*16–18, 22, 23*). The dynamics of the red fluorescence is different from that of the blue emission and cannot be described as previously by a three-level model. In fact, in the case of a $(Cu^+)_2$ pair, it is expected that a splitting of the excited states and therefore a more complex emission mechanism involving four excited levels occurs. It is an important fact that the characteristics of the red fluorescence of the copper-doped phosphate glass and that of the green fluorescence of $CuZr_2(PO_4)_3$ are quite similar (*18, 23*). This comparison is particularly significant since the assignment of the latter to $(Cu^+)_2$ pairs is well supported by EXAFS measurements.

VI. Conclusions

The spectroscopic analysis of Cu^+ imbedded in phosphate glasses showed the occurrence of a blue fluorescence in all the doped samples. In addition a red fluorescence of increasing intensity appeared as the copper concentration increased. The dependence of the fluorescence bands and of the fluorescence decays with temperature, exciting light, and Cu^+ content confirms the multisite structure of glasses and leads to the attribution of the blue and red fluorescences to Cu^+ isolated ions and $(Cu^+)_2$ pairs, respectively. These assignments are also supported by comparison with other similar systems. This is the first time that Cu^+ ion pairs are clearly identified in a vitreous system.

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