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FLUORESCENCE PROPERTIES OF  $\text{Cu}^+$  ION IN BORATE AND PHOSPHATE GLASSES

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**Abstract:** We report the results of an investigation on the luminescence of  $\text{Cu}^+$  in borate and phosphate glasses prepared in our laboratories. The former system exhibits a single very broad and strong emission band in the visible region giving rise to a nearly white fluorescence. The latter compound shows a blue fluorescence and in addition a red one appears as the copper concentration increases. The latter is assigned to  $(\text{Cu}^+)_2$  pairs.

## 1. Introduction

Monovalent copper ions, when embedded in glasses, usually give rise to a rather strong fluorescence. In most cases, the systems exhibit very broad emission bands in the visible, and therefore are particularly interesting for obtaining tunable laser emission. Light amplification has been already reported in copper-doped aluminoborosilicate glass /1/.

Here are reported fluorescence studies of  $\text{Cu}^+$  impurity ion in borate glasses with the composition  $67\text{B}_2\text{O}_3$ , 10 BaO,  $(15-x)\text{Li}_2\text{O}$ ,  $5\text{La}_2\text{O}_3$ ,  $2\text{Al}_2\text{O}_3$ ,  $1\text{As}_2\text{O}_3$ ,  $x\text{Cu}_2\text{O}$ , and in phosphate glasses with the composition  $44.5\text{P}_2\text{O}_5$ , 37.0 BaO,  $(18.5 - x)\text{Li}_2\text{O}$ ,  $x\text{Cu}_2\text{O}$ . The copper concentration was varied from 0.01 to 0.2 mole %  $\text{Cu}_2\text{O}$  and no divalent copper could be detected by EPR measurements.

The experimental procedures were the same as described in previous papers /2,3/.

## 2. Results and discussion

The absorption edge of the glasses investigated was found to be around  $45\,000\text{ cm}^{-1}$ . Consequently accurate measurements of the  $d \rightarrow s$  forbidden transitions of  $\text{Cu}^+$  which occur in the uv range above  $40\,000\text{ cm}^{-1}$  are difficult. Some  $\text{Cu}^+$  shoulders were detected in the region  $40\,000\text{--}45\,000\text{ cm}^{-1}$  and can be assigned to  $3d^{10} \rightarrow 3d^9 4s$  transitions.

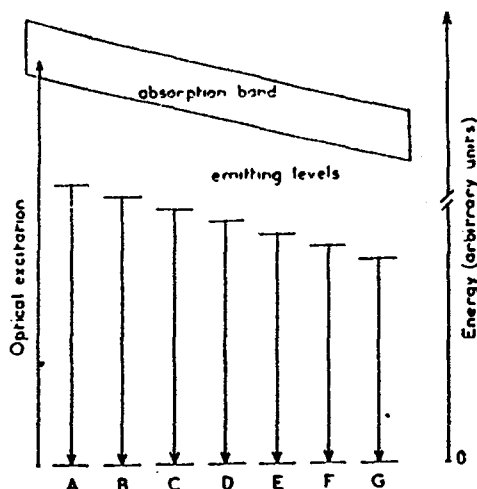


Figure 1: Schematic representation of the energy levels of  $\text{Cu}^+$  occupying various sites from A to G in borate glasses.

Under UV excitation, both systems exhibit a strong luminescence. Copper doped borate glasses emit a nearly white fluorescence while copper doped phosphate glasses give rise to a blue fluorescence and a red emission the intensity of which increases with the  $\text{Cu}$  concentration. Fluorescence excitation spectra related to each emission consists of several peaks in the uv in the  $30\,000\text{--}90\,000\text{ cm}^{-1}$  range. The fluorescence lifetimes are strongly temperature-dependent as it is usually observed in the case of  $\text{Cu}^+$  fluorescent centers /4/. The decay time varies typically from few tens to few hundreds microseconds upon cooling from room to liquid helium temperature. The fluorescence properties of the  $\text{Cu}^+$  doped glassy systems here investigated led us to point out two important aspects.

### 2.1 $\text{Cu}^+$ multisite structure

It is reasonable to suppose that the  $\text{Cu}^+$  fluorescent ions introduced in amorphous media reside in a large variety of sites. The energies of the various ionic levels may therefore differ substantially. This situation is sketched in Fig. 1 where the lowest emitting levels and a hypothetical absorption band are schematically represented for different sites. This crude representation of the impurity ion distribution is very helpful to simply interpret most of the experimental results. The red shift and the narrowing of the emission bands as the excitation wavelength increases, the red shift and the broadening behaviour of the excitation bands when the emission domain considered moves to the red, the non-exponentiality of the decays, the fact that the decay time gradually increases for the longer excitation wavelengths, the results of the time-resolved spectroscopy, all these trends are in good agreement with the multi-site structure of the  $\text{Cu}^+$ -doped glasses.

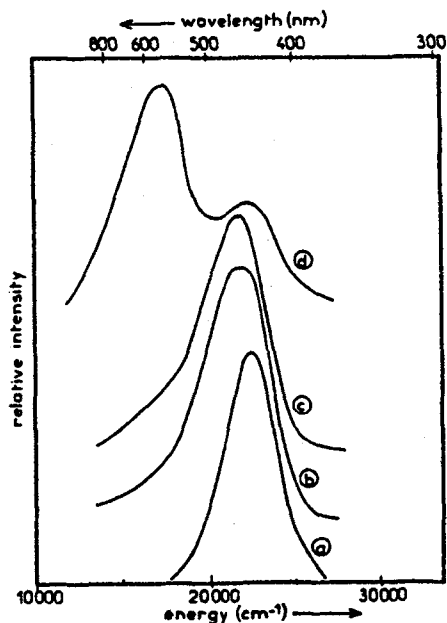


Figure 2: Emission spectra at  $T=20\text{K}$  under laser excitation at  $320\text{ nm}$  of variously  $\text{Cu}_2\text{O}$ -doped phosphate glasses: (a)  $0.01$  mole %; (b)  $0.05$  mole %; (c)  $0.1$  mole %; (d)  $0.2$  mole %.

## 2.2 $(\text{Cu}^+)_2$ pair luminescent centers

It is well-known that crystals doped with increasing amounts of  $\text{Cu}^+$  or  $\text{Ag}^+$  ions often exhibit, besides the fluorescence due to single impurity ion centers, a new fluorescence with a much larger Stokes shift assigned to  $(\text{Cu}^+)_2$  or  $(\text{Ag}^+)_2$  pairs /5/. In the case of the phosphate  $\text{CuZr}_2(\text{PO}_4)_3$ , the presence of  $(\text{Cu}^+)_2$  dimers was clearly established by a detailed EXAFS investigation /6/ and the green fluorescence was assigned to  $(\text{Cu}^+)_2$  centers /7/. The fluorescence properties of this crystal are very similar to that observed in our copper doped phosphate glasses. By comparison with  $\text{CuZr}_2(\text{PO}_4)_3$  and with other systems and by consideration of the spectroscopic data, we assume that the blue and red fluorescences exhibited by our copper doped phosphate glasses (Fig. 2 and 3) are due to  $\text{Cu}^+$  single ion and  $(\text{Cu}^+)_2$  pair centers, respectively.

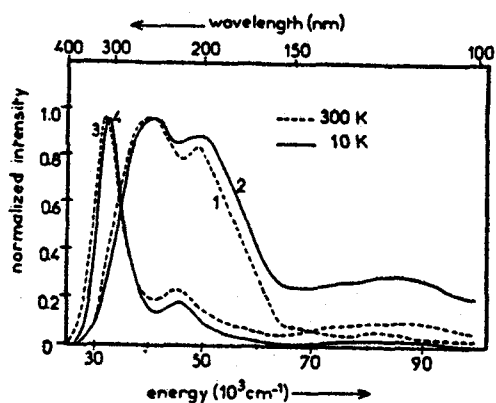


Figure 3: Excitation spectra of phosphate glass containing  $0.2$  mole %  $\text{Cu}_2\text{O}$ . Curves 1,2, blue filter ( $441\text{ nm}$ ,  $\Delta h\nu = 669\text{ cm}^{-1}$ ); curves 3,4, red filter ( $> 570\text{ nm}$ )

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. 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 in the dynamics of fluorescence, is a consequence of delocalization of the electron and, therefore, of a substantial decrease of the transition probabilities.

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#### References

- /1/ KRUGLIK G.S., SKRIPKO G.A., SHKADAREVICH A.P., ERMOLENKO N.N., GORODETSKAYA O.G., BELOKON M.V., SHAGOV A.A. and ZOLOTAREVA L.E., Opt. Spectrosc. (USSR) 59 (1985) 439; J. Luminesc. 34 (1986) 343.
- /2/ ZHANG J.C., MOINE B., PEDRINI C., PARENT C. and LE FLEM G., J. Phys. Chem. Solids 51 (1990) 933.
- /3/ BOUTINAUD P., DULOISY E., PEDRINI C., MOINE B., PARENT C. and LE FLEM G., J. Sol. St. Chem. 94 (1991).
- /4/ PEDRINI C., Phys. Status Solidi (b) 87 (1978) 273.
- /5/ see for example: ATOUSSI B., PEDRINI C., MOINE B. and MADEJ C., Phys. Status Solidi (b) 128 (1985) 683.
- /6/ CARTIER C., DEXPERT H., OLAZCUAGA R., BUSSEREAU I., FARGIN E. and LE FLEM G., submitted to Nature.
- /7/ BOUTINAUD P., PARENT C., LE FLEM G., PEDRINI C. and MOINE B., submitted to J. Phys. Condensed Matter.