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The Luminescence of Cu(I) in Strontium Tetraborate

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The luminescence of Cu(I) in crystalline and glassy SrB_4O_7 is reported and discussed. In the former there is a narrow band emission around 380 nm, in the latter a broad band emission around 450 nm. In the crystal the Stokes shift is small, but in the glass it is larger. For the glass as well as for the crystalline material the luminescence efficiency is high at room temperature and below. These properties are discussed and the differences between the crystalline and the glass modification of SrB_4O_7 : Cu(I) are considered. © 1991 Academic Press, Inc.

1. Introduction

The luminescence of the Cu(I) ion has been studied over a long period of time. Wanmaker *et al.* (*1, 2*) reported on Cu(I)-doped phosphates with high luminescence efficiency. Later, McClure and Pedrini (*3–9*) performed fundamental investigations on the luminescence of Cu(I) in the rocksalt lattice. The emission has been ascribed to a parity- and spin-forbidden $d^9s \rightarrow d^{10}$ transition with a considerable Stokes shift.

In this laboratory the luminescence of Eu(II), Yb(II), and Pb(II) in SrB_4O_7 have recently been investigated. The Stokes shift of these emissions is relatively small, which points to a restricted amount of relaxation in the relaxed excited state. This has been related to the stiffness of the borate host lattice. It seemed interesting to investigate how the Cu(I) ion would behave in this lattice.

We have also investigated luminescent compositions which exist in the crystalline and in the glassy state (*10, 11*). The relaxation of the excited state is always larger in the glass modification. This can have dramatic consequences for the efficiency upon broad band excitation. Since SrB_4O_7 is a composition which exists in the crystalline and in the glassy modification, we extended our studies to Cu(I)-doped SrB_4O_7 tetraborate glass.

The key result of this study is that the Stokes shift of the Cu(I) emission in crystalline SrB_4O_7 is small indeed, whereas that of the emission in glassy SrB_4O_7 is large.

2. Experimental

Crystalline samples of SrB_4O_7 : Cu(I) were prepared and checked by X-ray powder diffraction as described in Ref. (*12*). The La(III) ion was introduced as a charge compensator, since it is about as large as the

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Sr(II) ion. The Cu and La concentrations were 0.5–1.0 mol%.

The investigated glasses are prepared from crystalline SrB_4O_7 doped with 0.5% Cu(I). This material is intimately mixed with 0.5 mol% As_2O_3 before melting the mixture at 1200°C in a vitreous carbon crucible under a N_2 atmosphere. The As_2O_3 was added in order to prevent the oxidation of the Cu(I) ions. The glasses were slowly cooled in the crucible to prevent oxidation of Cu(I) on air. The weight difference before and after the melting was less than 0.1%.

The optical measurements were performed as described in Ref. (*12*). The temperature dependence of the efficiency of the luminescence between 300 and 600 K was determined by using the setup described in Ref. (*13*).

3. Results

3.1 SrB_4O_7 : Cu(I) Crystals

Figure 1A shows the diffuse reflection spectrum of crystalline SrB_4O_7 : Cu(I) powder (curve 1) and crystalline SrB_4O_7 powder (curve 0). The former spectrum shows clearly that, in spite of the presence of a suitable charge compensator, part of the copper is still divalent. We were not able to change this situation by varying the preparation conditions. The crystal-field transition within the 3*d* shell of Cu(II) is observed below 500 nm, and the Cu(II)–O(−II) charge transfer at about 250 nm (*14*).

Nevertheless these samples contain a considerable amount of Cu(I), since they show an intense violet emission. Figure 2A shows the relevant spectra. The emission maximum is at 380 nm, the emission band is rather narrow (~2000 cm^{-1}). The excitation band around 300 nm consists of three components with maxima at 293, 309, and 329 nm. This results in a Stokes shift of ~4000 cm^{-1}. This is a small value for Cu(I) in a crystalline material (*1, 2, 15*). In contrast to other Cu(I)-doped materials, the excitation spectrum shows a rather sharp cutoff on the shorter wavelength side. This may be due to competitive Cu(II) absorption or to photoionization, the monovalent valency obviously being not very stable in this host lattice.

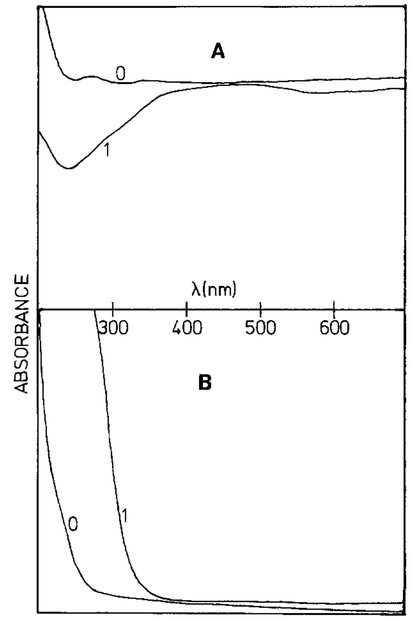

FIG. 1. (a) Diffuse reflection spectra of crystalline SrB_4O_7 : Cu(I) (1) and undoped SrB_4O_7 (0). (1B) Transmission spectra of SrB_4O_7 glass containing 0.5% Cu(I) (1) and undoped SrB_4O_7 glass (0). All spectra were recorded at room temperature.

Since the relevant Cu(I) transitions are of the $d \rightarrow s$ type (see below), they are parity forbidden and, therefore, weak relative to the Cu(II)–O(−II) charge-transfer absorption transition, so that the reflection spectrum seems to overestimate the amount of Cu(II). The emission and excitation spectra do not depend on the excitation wavelength or emission wavelength monitored. This, together with their narrowness, points to one type of Cu(I) ion and suggests association with La(III) ions. The solubility of these pairs in SrB_4O_7 is probably low.

The relative luminescence quantum yield is high and, within the accuracy of the measurements, temperature independent up to the highest temperature of measurement (600 K). However, the absorption strength shows an increase of up to 70% in the temperature region 5–65 K followed by a decrease of the same amount in the region 65–110 K. This is strongly reminiscent of results reported for NaBr : Cu(I) by Holland and Lüty (*16*). It indicates that the Cu(I) ion in SrB_4O_7 is in a shallow off-center position. Actually the Cu(I) ion has a radius 0.4 Å smaller than that of Sr(II) (*17*).

Figure 3A shows the decay times of the luminescence of the crystals. All decay curves are exponential. The temperature dependence of the decay times can be fitted to the well-known expression for a three-level system (*9*)

$$1/\tau = \frac{1/\tau_0 + (1/\tau_1)\exp(-\Delta E/kT)}{1 + \exp(-\Delta E/kT)}, \quad (1)$$

where τ_0 and τ_1 indicate the radiative decay time of the emitting levels in sequence of increasing energy, whereas the energy difference between the levels is indicated by ΔE. The three-level system fit yields ΔE = 28 cm^{-1}, τ_0 = 2024 μs, and τ_1 = 27 μs. These values agree with the results of other workers (*6, 7, 18*).

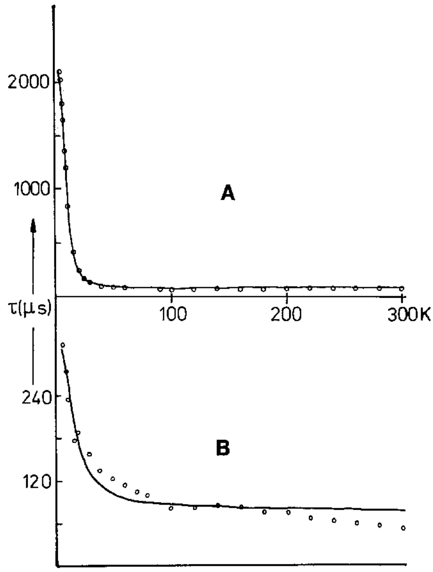

Fig. 3. (a) Temperature dependence of the decay time of the Cu(I) emission in crystalline SrB_4O_7. (b) Temperature dependence of the decay time of the Cu(I) emission in SrB_4O_7 glass. The solid lines are a fit to a three-level scheme (see text).

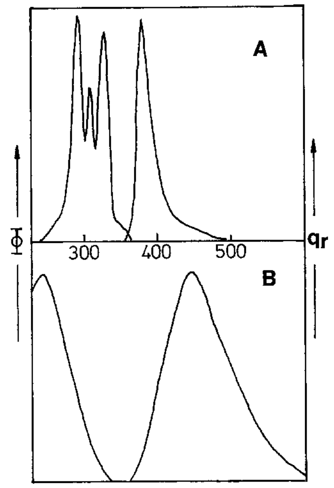

Fig. 2. (a) Emission and excitation spectra of the luminescence of crystalline SrB_4O_7 : Cu(I). Excitation wavelength is 329 nm; monitored emission wavelength, 440 nm. (b) Emission and excitation spectra of the luminescence of Cu(I) in strontium tetraborate glass. Excitation wavelength, 270 nm; monitored emission wavelength is 440 nm. Φ denotes the radiant power per constant wavelength interval and q_r the relative quantum output (both in arbitrary units).

3.2. SrB_4O_7 : Cu(I) Glass

Figure 1B shows the absorption spectra of a SrB_4O_7 glass doped with 0.5% Cu(I) (curve 1) and an undoped glass (curve 0). The copper-doped composition does not contain Cu(II). At room temperature and below, SrB_4O_7 glass doped with Cu(I) shows an efficient luminescence after ultraviolet excitation. The emission consists of a band ranging from 370 to 600 nm. The maximum is at ~450 nm. The excitation band has a maximum at ~250 nm, with a long tail which extends down to ~370 nm. These luminescence spectra show much broader bands than those of the crystalline modification. This is ascribed to inhomogeneous broadening. This is confirmed by the fact that different excitation wavelengths within the excitation band result in emission spectra which are shifted relative to each other (these shifts are about 30 nm). Since the absorption transition to the emitting state is somewhere in the tail on the long-wavelength side of the excitation band, it is impossible to estimate the value of the Stokes shift for the glass. Comparison of Figs. 2A and 2B inform us, nevertheless, that the Stokes shift for the glass is much larger than for the crystal.

The temperature dependence of the relative quantum yield of the emission of the glass is constant up to room temperature. At 600 K it has decreased to about 50% of the room temperature value. Figure 3B shows the decay times from LHeT up to 300 K for the SrB_4O_7 glass. All decay times are exponential. The decay measurements were made for the emission at 450 nm, i.e., the maximum of the emission band. For longer wavelengths the decay times become up to 25% longer; for a small emission area the decays are exponential. For the glass the three-level system fit yields $\Delta E = 13\ \mathrm{cm}^{-1}$, $\tau_0 = 437\ \mu s$, and $\tau_1 = 34\ \mu s$. The values of ΔE are similar to those usually obtained for glasses (*19*) and crystals (*6, 7*).

4. Discussion

4.1. *Crystalline $SrB_4O_7 : Cu(I)$*

The crystal structure of SrB_4O_7 contains only one crystallographic site for Sr. Its site symmetry is C_s (*20*). This site shows nine-coordination by oxygen which can be described in first approximation by a cube with one face capped. The symmetry of the Cu(I) ion in SrB_4O_7 may be even lower than C_s. The small bandwidth in the spectra suggests the presence of one type of Cu(I) ion only, so that the charge-compensating La(III) ions are probably close, which might lower the site symmetry.

The $3d^94s$ excited configuration is expected to split in a cubic eight-coordination in higher E and lower T_2 states. In view of the fact that the site symmetry is lower than cubic, these states will be split by the noncubic components of the crystal field on Cu(I) in SrB_4O_7. Each level consists of an upper spin singlet and a lower spin triplet. The emission is, therefore, ascribed to a spin-forbidden transition from the lowest triplet; the parity selection rule has been relaxed by the low site symmetry. This assignment agrees with the long decay times observed and with assignments given by other authors for Cu(I) in different coordination (*7, 8, 18*).

From the temperature dependence of the decay time (Fig. 3A) it follows that the emitting state consists of two close-lying emitting levels ($\Delta E = 28\ \mathrm{cm}^{-1}$). These are ascribed to the components of the spin-triplet level, following earlier proposals (*8, 21, 22, 23*).

The small width of the emission band shows that the relaxation in the excite state is restricted. If a simple configuration coordinate model would be valid, it seems even improbable that the lowest excitation transition is the reverse of the emission transition. It seems more probable that the excitation transitions are the singlet–singlet transitions in the $d^{10} \rightarrow d^9s$ promotion. Five of such transitions are to be expected in view of the low site symmetry. Only three are observed with a total splitting of $\sim 3900\ \mathrm{cm}^{-1}$. Since the cubic crystal-field splitting has been observed to be larger than this (*6, 16*), we assume that the two missing transitions are at higher energies. The reason why they are not observed has been discussed above.

One might argue that the low-energy tail in the excitation spectrum of crystalline $SrB_4O_7 : Cu(I)$ (see Fig. 2A) corresponds to the lowest singlet–triplet transition. However, the tail in the emission spectrum suggests that the sample contains a small amount of the glassy modification, so that such an assignment cannot be firmly based at all.

From the lowest excitation maximum and

TABLE I

STOKES SHIFTS OF THE Cu(I) LUMINESCENCE IN DIFFERENT HOST LATTICES

Host	Stokes shift (cm^{-1})	Ref.
SrB_4O_7	4,000	This work
NaF	5,500	*(5)*
NaCl	6,700	*(8)*
$CuLaO_2$	~7,000	*(27)*
$Sr_3(PO_4)_2$	11,000	*(1)*
NaI	12,000	*(26)*
KF	13,000	*(18)*
$LiSrPO_4$	~14,000	*(2)*

the emission maximum the Stokes shift is derived to be ~4000 cm^{-1}. The real Stokes shift is even less if the excitation transitions correspond to singlet-singlet transitions. Nevertheless this value is already remarkably small. Table I gives some values for crystalline Cu(I)-doped hosts, those for glasses are always much larger (>15,000 cm^{-1}); this might be due to the fact that the corresponding excitation transition is overlooked in the broad spectra (see also above).

In fact SrB_4O_7 is a host lattice which is well known for very small Stokes shifts: $Eu^{2+} < 1000\ cm^{-1}$ *(12)*, $Yb^{2+} < 1000\ cm^{-1}$ *(24)*, and $Pb^{2+} \sim 4000\ cm^{-1}$ *(25)*. This can be ascribed to the stiff nature of the borate-based crystal structure. No doubt the high quantum efficiency and the quenching temperature of the luminescence of crystalline SrB_4O_7 : Cu(I) and the narrow width of the bands in the spectra are related to this effect. Unfortunately the Cu(I) ion does not seem to be very stable in the SrB_4O_7 lattice.

4.2. *Glassy SrB_4O_7 : Cu(I)*

The assignment of the spectra follows those given in the literature *(19)* and that given for the crystalline modification (Section 4.1). The emission is due to the lowest triplet–singlet transition as is clear from the temperature dependence of the decay times. The small splitting of the excited state shows up in the temperature dependence of the decay times (Fig. 3B). The excitation band is probably a conglomerate of several singlet–singlet transitions. Due to the inhomogeneous broadening all crystal-field components overlap and cannot be separated like in the crystals. The most interesting fact is undoubtedly the considerably larger Stokes shift of the luminescence of Cu(I) in the glass modification. This follows general observations made by us before *(10, 11)*, and has to be ascribed to the looser structure of the glass. Consequently the luminescence shows temperature quenching in the glass at a lower temperature than in the crystals, although this temperature is still high. This can, at least partly, be ascribed to the high energy position of the emitting state *(10, 11)*.

Recently Zhang *et al.* *(19)* have reported the efficient Cu(I) emission in borate glass of a complicated composition viz. 67 B_2O_3, 10 BaO,(15-w)Li_2O, 5 La_2O_3, 2 Al_2O_3 1 As_2O_3, wCu_2O. The largest difference between their result and ours is the fact that their spectra are broader. This can be considered as evidence for a larger inhomogeneous broadening than in the SrB_4O_7 glass. In view of the chemical composition of the glasses involved, this difference is not surprising.

5. Conclusions

We have shown that the stiffness of the crystalline SrB_4O_7 host lattice has a strong influence on the luminescence characteristics of the Cu(I) ion. The restricted amount of relaxation of the relaxed excited state causes a small Stokes shift and a high quenching temperature.

Due to the looser structure of the glass, the Stokes shift of the Cu(I) luminescence in the glass is larger than for the crystalline Cu(I)-doped SrB_4O_7. The larger Stokes shift of the Cu(I) ion in the glass affects the temperature dependence of the luminescence. At room temperature, however, both modifications of SrB_4O_7 : Cu(I) still show efficient luminescence.

References

1. W. L. Wanmaker and C. Bakker, *J. Electrochem. Soc.* **106,** 1027 (1959).
2. W. L. Wanmaker and H. L. Spier, *J. Electrochem. Soc.* **109,** 109 (1962).
3. S. A. Payne, A. B. Goldberg, and D. S. McClure, *J. Chem. Phys.* **78,** 3688 (1983).
4. J. Simonetti and D. S. McClure, *Phys. Rev. B* **16,** 3887 (1977).
5. A. B. Goldberg, D. S. McClure, and C. Pedrini, *Chem. Phys. Lett.* **87,** 508 (1982).
6. C. Pedrini and B. Jacquier, *J. Phys. C* **13,** 4791 (1980).
7. C. Pedrini, *Phys. Status Solidi B* **87,** 273 (1987).
8. H. Chermette and C. Pedrini, *J. Chem. Phys.* **75,** 1869 (1981).
9. G. Boulon, C. Pedrini, M. Guidoni and Ch. Pannel, *J. Phys. (Paris)* **36,** 267 (1975).
10. J. W. M. Verwey and G. Blasse, *Mater. Chem. Phys.* **25,** 91 (1990).
11. J. W. M. Verwey and G. Blasse, *Chem. Mater.* **2,** 458 (1990).
12. A. Meijerink, J. Nuyten, and G. Blasse, *J. Lumin.* **44,** 19 (1989).
13. A. Meijerink and G. Blasse, *J. Phys. C: Condens. Matter* **2,** 3619 (1990).
14. J. Texter, D. H. Strome, R. G. Herman, and K. Klier, *J. Phys. Chem.* **81,** 333 (1977).
15. B. Moine and C. Pedrini, *Phys. Rev. B* **30,** 992 (1984).
16. U. Holland and F. Lüty, *Phys. Rev. B* **19,** 4298 (1979).
17. R. D. Shannon, *Acta Crystallogr. Sect. A* **32,** 751 (1976).
18. S. K. Ramasesha and S. A. Payne, *Physica B* **167,** 56 (1990).
19. J. C. Zhang, B. Moine, C. Pedrini, C. Parent, and G. Flem, *J. Phys. Chem. Solids* **51,** 933 (1990).
20. A. Perloff and S. Block, *Acta Crystallogr.* **20,** 274 (1966).
21. J. M. Berg, R-L Chien, and D. S. McClure, *J. Chem. Phys.* **87,** 7 (1987).
22. J. M. Berg and D. S. McClure, *J. Chem. Phys.* **90,** 3915 (1989).
23. S. A. Payne, R. H. Austin, and D. S. McClure, *Phys. Rev. B* **29,** 32 (1984).
24. G. Blasse, G. J. Dirksen, and A. Meijerink, *Chem. Phys. Lett.* **167,** 41 (1990).
25. A. Meijerink, H. Jetten, and G. Blasse, *J. Solid State Chem.* **76,** 115 (1988).
26. R. L. Bateman and W. J. Van Sciver, *Phys. Status Solidi B* **46,** 779 (1971).
27. J. Doumerc, C. Parent, Z. J. Chao, G. LeFlem, and A. Ammar, *C.R. Acad. Sci. Paris Ser 2* **306,** 1431 (1988).