

Luminescence and Energy Transfer in Lead-Activated Strontium Haloborate (Sr, Pb)₂B₅O₉X (X = Cl, Br)

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Received January 5, 1988

The luminescence properties of Pb²⁺ in Sr₂B₅O₉X (X = Cl, Br) are reported. The emission is situated at very short wavelength (~280 nm). In these compounds the position of the energy levels of the Pb²⁺ ion is determined by the oxygen ions of the borate groups surrounding the Pb²⁺ ion. The influence of the two surrounding halide ions appears in the Stokes shift, which is the smaller for the Pb²⁺ luminescence in the bromoborate. In samples with Pb²⁺ concentrations above 1 at.%, two other types of luminescent centers are observed. They are ascribed to Pb²⁺ pairs and Pb²⁺ ions next to a defect. Energy transfer from the Pb²⁺ ions to these other Pb²⁺ centers and its temperature dependence are discussed. © 1988 Academic Press, Inc.

1. Introduction

The luminescence properties of ions with 6s² configuration in inorganic compounds have been the subject of investigation for many years (1-3). It is well known that the luminescence properties of s² ions depend strongly on the nature of the host lattice. The emission of Pb²⁺ can, for example, range from ultraviolet to red. In this paper we report on the luminescence properties of Pb²⁺ in Sr₂B₅O₉X (X = Cl, Br), a lattice in which Pb²⁺ is known to emit in the ultraviolet (4). It was interesting to study these haloborates in more detail, since the Pb²⁺ emission is at the highest energy reported for oxides until now. Furthermore we investigated the role of the halide ion. This paper reports on the concentration and temperature dependence of the luminescence spectra and on the energy transfer

processes in these lead-activated haloborates.

The compounds Sr₂B₅O₉X and Pb₂B₅O₉X are isostructural with Ca₂B₅O₉X (5). In the orthorhombic crystal structure two slightly different sites are available for the divalent cation. On both sites the cation is coordinated by six oxygen ions at an average distance of about 2.7 Å and by two halide ions and one oxygen ion at about 3.0 Å. The oxygen ions belong to borate groups.

2. Experimental

All measurements were performed on powder samples of composition Sr_{2-x}Pb_xB₅O₉X (X = Cl, Br; 0.002 ≤ x ≤ 2). These compounds were obtained by dissolving Sr(NO₃)₂ (Merck, p.a.) and Pb(NO₃)₂ (Merck, p.a.) in water. Precipitation was carried out by adding a large excess of

$(\text{NH}_4)_2\text{CO}_3$ (Merck, pure) in aqueous solution. After washing and drying, the precipitate was mixed with $\text{SrX}_2 \cdot 6\text{H}_2\text{O}$ ("Baker analyzed"), or PbX_2 (99.999%) for the concentrated systems, and boric acid (Merck, pure) (20% excess) in a ball mill. The mixture was fired for 3 hr at 750°C (700°C for the concentrated compounds) in a nitrogen atmosphere. The samples were checked by X-ray powder diffraction using a Philips diffractometer ($\text{CuK}\alpha$ radiation).

Luminescence spectra were measured using a Perkin-Elmer MPF 44 B spectrofluorometer equipped with an Oxford LF 204 liquid-helium flow cryostat. The excitation spectra were corrected for the xenon lamp intensity using lumogen T-rot GG as a standard. The emission spectra were corrected for the photomultiplier sensitivity. The measurement of excitation spectra at wavelengths shorter than 240 nm was performed on a setup described in Ref. (6).

3. Results

The investigated strontium haloborates activated with Pb^{2+} are efficient luminescent materials. The emission, situated at very short wavelengths, shows no thermal

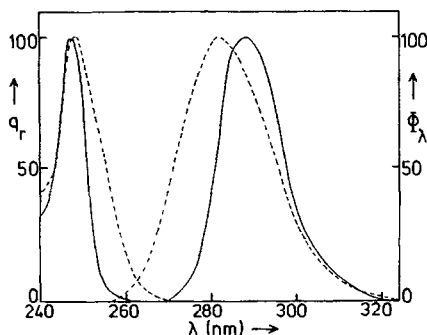


FIG. 1. Excitation and emission spectra ($\lambda_{em} = 287$ nm, $\lambda_{exc} = 250$ nm) of the luminescence of $\text{Sr}_{1.998}\text{Pb}_{0.002}\text{B}_5\text{O}_9\text{Cl}$ at 4.2 K (—) and 298 K (---). q_r gives the relative quantum output and Φ_λ the spectral radiant power per constant wavelength interval in arbitrary units.

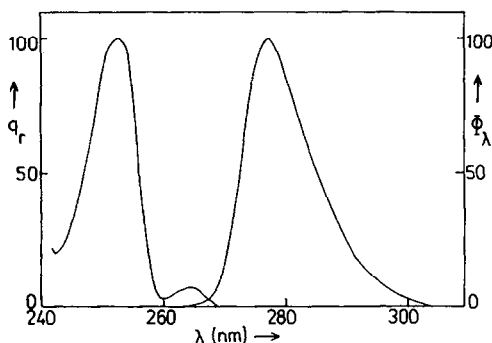


FIG. 2. Excitation and emission spectra ($\lambda_{em} = 278$ nm, $\lambda_{exc} = 250$ nm) of the luminescence of $\text{Sr}_{1.98}\text{Pb}_{0.02}\text{B}_5\text{O}_9\text{Br}$ at 4.2 K.

quenching up to room temperature. The emission and excitation spectra of the most diluted sample, $\text{Sr}_{1.998}\text{Pb}_{0.002}\text{B}_5\text{O}_9\text{Cl}$, are shown in Fig. 1. At 4.2 K the maximum of the emission band is located at 288 nm. With increasing temperature this maximum shifts to shorter wavelengths. Above 100 K and up to room temperature the maximum is located at 282 nm. In the excitation spectrum of this emission, one band is observed with a maximum about 248 nm; it shows a small shift to longer wavelengths at higher temperatures.

In the most diluted sample of $(\text{Sr}, \text{Pb})_2\text{B}_5\text{O}_9\text{Br}$, viz. $\text{Sr}_{1.98}\text{Pb}_{0.02}\text{B}_5\text{O}_9\text{Br}$, more than one excitation band can be observed at 4.2 K (Fig. 2). There is a stronger band around 254 nm and a weaker band with a maximum at 264 nm. The emission band has its maximum at 278 nm. A second emission band seems to be hidden on the longer wavelength side of this emission band.

Increasing the Pb^{2+} concentration has a marked influence on the excitation and emission spectra, as can be seen in Figs. 3 and 4, which show the spectra of the samples with $x = 0.1$. In the emission spectra of $\text{Sr}_{1.9}\text{Pb}_{0.1}\text{B}_5\text{O}_9\text{Cl}$ a broad emission band with a maximum at 410 nm is present. The emission band around 288 nm

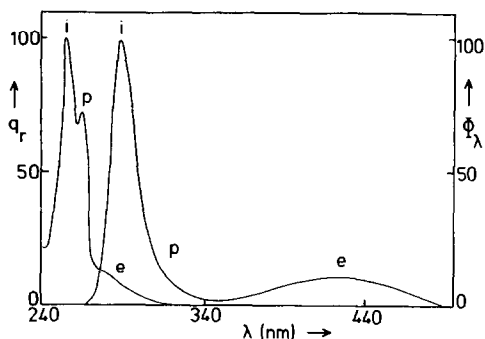


FIG. 3. Excitation spectrum of the long wavelength emission ($\lambda_{em} = 410$ nm) and emission spectrum after short-wave excitation ($\lambda_{exc} = 250$ nm) of Sr_{1.9}Pb_{0.1}B₅O₉Cl at 4.2 K.

has become asymmetrical. Fitting this band to two Gaussian functions indicates the presence of a second emission band with a maximum at about 296 nm. In the excitation spectrum of the 410-nm emission two extra bands can be observed, one band around 259 nm and one broadband starting at 315 nm with a maximum at about 270 nm. This broad excitation band is only observed in the excitation spectra of the broad emission band around 410 nm.

In Fig. 4 the excitation spectra and the shorter wavelength part of the emission spectra of Sr_{1.9}Pb_{0.1}B₅O₉Br are depicted for three different temperatures. The weak excitation band around 264 nm is much stronger for this sample than for the sample with $x = 0.02$. Moreover, a second emission band with a maximum at 284 nm can be observed after excitation in the main excitation band. The relative intensity of this second emission band increases with increasing temperature. Excitation in the band around 264 nm gives rise to the longer wavelength emission with a maximum at 286 nm. Next to the emission bands shown, this sample shows, just as in the chloroborate, a broad emission band at much longer wavelengths with a maximum at 370 nm. The excitation spectrum of this band

TABLE I

POSITION OF THE MAXIMUM OF THE EXCITATION AND EMISSION BANDS OF THE DIFFERENT LUMINESCENT Pb²⁺ CENTERS IN Sr₂B₅O₉X, MEASURED AT 4.2 K

Center	X = Cl		X = Br	
	λ_{exc} (nm)	λ_{em} (nm)	λ_{exc} (nm)	λ_{em} (nm)
Pb _i	248	288	254	278
Pb _p	259	296	264	284
Pb _e	270	410	270	370
Pb ₂ B ₅ O ₉ X (Pb _e)	270	410	280	370

shows, apart from the 254- and 264-nm bands, a broadband starting at 300 nm with a maximum at 270 nm. The positions of the different excitation and emission bands observed in the chloroborate and the bromoborate are tabulated in Table I. In this table we have also introduced a notation for the luminescent centers which will be used from now on.

Because the light output of the xenon lamp vanishes below 240 nm, excitation spectra between 200 and 300 nm were measured using a setup equipped with a deuterium lamp. These spectra show the presence of a dominant excitation band

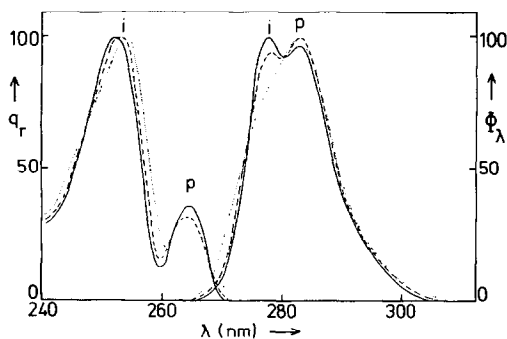


FIG. 4. Temperature dependence of the short wavelength part of the emission ($\lambda_{exc} = 250$ nm) and of the excitation bands ($\lambda_{em} = 278$ nm) of Sr_{1.9}Pb_{0.1}B₅O₉Br: 4.2 K (—), 39 K (---), and 75 K (···).

around 222 nm for $\text{Sr}_{1.9}\text{Pb}_{0.1}\text{B}_5\text{O}_9\text{Cl}$ and around 218 nm for $\text{Sr}_{1.9}\text{Pb}_{0.1}\text{B}_5\text{O}_9\text{Br}$. The intensity of these two bands is about 10 to 15 times stronger than the intensity of the bands around 248 and 254 nm.

The relative intensity of the Pb_e emission band increases with increasing Pb^{2+} concentration. For the samples with $x = 2$ only the Pb_e emission bands are observed (Fig. 5). The intensity of these bands decreases slightly when the temperature is increased from 4.2 to 298 K. The excitation spectra show a sharp edge at 270 nm for the chloroborate and at 280 nm for the bromoborate.

The temperature dependence of the relative intensity of the Pb_e emission bands was measured for the samples with $x = 0.1$. In Fig. 6 it can be seen that the relative intensity of this band increases between 20 and ~ 100 K for $\text{Sr}_{1.9}\text{Pb}_{0.1}\text{B}_5\text{O}_9\text{Cl}$ and between 4.2 and ~ 100 K for $\text{Sr}_{1.9}\text{Pb}_{0.1}\text{B}_5\text{O}_9\text{Br}$. This behavior is representative for the Pb_e emission, also at higher Pb concentrations.

4. Discussion

4.1. Luminescence of Pb^{2+} in $\text{Sr}_2\text{B}_5\text{O}_9\text{X}$

For $(\text{Sr}, \text{Pb})_2\text{B}_5\text{O}_9\text{Cl}$ the luminescence properties of the isolated Pb^{2+} ions can be derived from the diluted system with $x =$

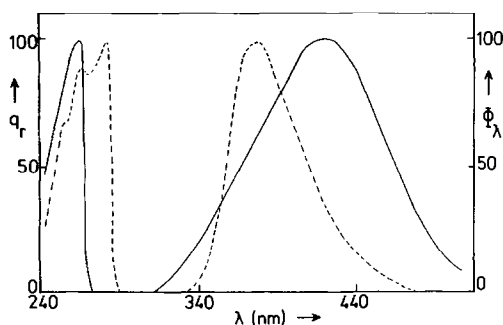


FIG. 5. Excitation and emission spectra of the luminescence of the lead haloborates $\text{Pb}_2\text{B}_5\text{O}_9\text{Cl}$ ($\lambda_{\text{em}} = 410$ nm and $\lambda_{\text{exc}} = 250$ nm) (—) and $\text{Pb}_2\text{B}_5\text{O}_9\text{Br}$ ($\lambda_{\text{em}} = 370$ nm and $\lambda_{\text{exc}} = 250$ nm) (---) recorded at 4.2 K.

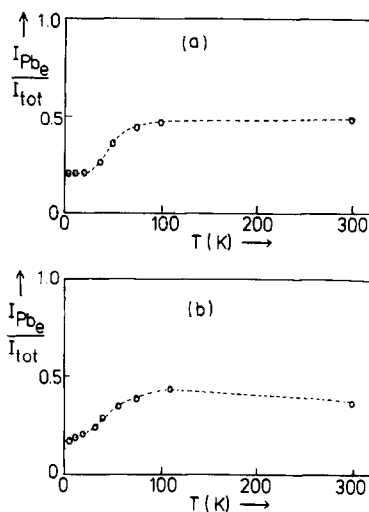


FIG. 6. Temperature dependence of the relative intensity of the Pb_e emission in $\text{Sr}_{1.9}\text{Pb}_{0.1}\text{B}_5\text{O}_9\text{Cl}$ (a) and $\text{Sr}_{1.9}\text{Pb}_{0.1}\text{B}_5\text{O}_9\text{Br}$ (b).

0.002. The emission band at 288 nm, measured at 4.2 K, corresponds to the ${}^3P_0 \rightarrow {}^1S_0$ transition on the Pb^{2+} ions. The shift of this band to higher energies at higher temperatures is due to thermal populations of the 3P_1 level and emission from this level to the 1S_0 ground state. From the shift of the emission band, the energy difference (ΔE) between the 3P_0 and 3P_1 levels is estimated, after correction for the red shift of the excitation band, to be some 600 cm^{-1} . The excitation band with a maximum at 249 nm corresponds to the transition between the 1S_0 ground state and the 3P_1 excited state on Pb^{2+} .

The small Stokes shift of the emission from the 3P_1 level, viz. 5000 cm^{-1} , and the large value of ΔE indicate that the coordination of the Pb^{2+} ion in this lattice is not very asymmetrical (1). Large Stokes shifts and small ΔE values are observed for Pb^{2+} ions occupying an off-center position in the ground state due to the lone pair. An example of small ΔE is PbAl_2O_4 with $\Delta E = 60 \text{ cm}^{-1}$ and a Stokes shift of $19,200 \text{ cm}^{-1}$. A

very high ΔE value has been reported for CaO–Pb with $\Delta E = 950 \text{ cm}^{-1}$ and a Stokes shift of 2000 cm^{-1} (7). The present values are in between these extremes and rather near those for CaO–Pb. In the latter compound the 4.2 K emission consists of 3P_1 and 3P_0 emission, nonradiative decay over a large ΔE not being very effective. In Sr₂B₅O₉Cl–Pb the emission is only from 3P_0 . The high vibrational frequencies available in this host lattice (borate) facilitate the $^3P_1 \rightarrow ^3P_0$ nonradiative decay.

In the case of Sr₂B₅O₉Br–Pb²⁺ the $^1S_0 \rightarrow ^3P_1$ excitation band peaks at 254 nm. The $^3P_0 \rightarrow ^1S_0$ emission band has its maximum at 278 nm. Due to the Pb_p emission band on the lower energy side of this band, and the increase of the Pb_p emission band with temperature, the shift of the $^3P \rightarrow ^1S_0$ emission band with temperature could not be determined. From the measurements at 4.2 K it is clear, however, that the Stokes shift of the 3P_1 emission is about 2000 cm^{-1} smaller for the bromoborate than for the chloroborate. This smaller Stokes shift, together with a smaller bandwidth of the excitation and emission bands for Pb²⁺ in the bromoborate indicates that the relaxation in the excited state of the Pb²⁺ ion is more restricted in the bromoborate than in the chloroborate.

The strong excitation bands in the near vacuum–UV region around 222 nm for the chloroborate and 218 nm for the bromoborate, correspond to the allowed $^1S_0 \rightarrow ^1P_1$ transition on the Pb²⁺ ion. The intensity ratio between the $^1S_0 \rightarrow ^3P_1$ and 1P_1 excitation bands is about 0.07, which is less than reported in the literature (8). It cannot be excluded that the $^1S_0 \rightarrow ^1P_1$ transition is partly overlapped by a charge-transfer transition (9).

Comparison of the results on the Pb²⁺ luminescence in the chloroborate and the bromoborate shows that the halide ion has little influence on the position of the 3P excited states. Normally a shift of the 3P

excited states to lower energies is observed for s^2 ions, because the covalency increases. Jørgensen (8) gives a shift of about 3500 cm^{-1} to lower energy if the Pb²⁺ coordination changes from chlorine to bromine. The absence of this effect in the haloborates indicates that the position of the energy levels is mainly determined by the presence of the six surrounding oxygen ions belonging to the borate groups which are at 2.5–2.9 Å, and not by the two halide ions at $\sim 3.0 \text{ Å}$.

This assumption is confirmed by measurements on the luminescence of SrB₄O₇–Pb²⁺. Here the Pb²⁺ ion is coordinated by nine oxygen ions belonging to borate groups, at distances of 2.5–2.9 Å. The results for the Pb²⁺ luminescence are similar to those obtained for Pb²⁺ in the haloborate. The $^3P_0 \rightarrow ^1S_0$ emission band is located at 310 nm, the $^3P_1 \rightarrow ^1S_0$ band at 300 nm, whereas the $^1S_0 \rightarrow ^1P_1$ and $^1S_0 \rightarrow ^3P_1$ excitation bands have their maxima at 225 and 268 nm, respectively (10).

The main influence of the halogen ion is on the Stokes shift. The smaller Stokes shift in the bromoborate indicates a smaller difference in relaxation after excitation. If we compare the reported Eu²⁺ coordination in Eu²⁺ chloro- and bromoborate (11, 12), it is seen that the oxygen coordination in the chloroborate is more regular than in the bromoborate. In the latter case the Eu(1)–O(6) distance is even larger than the Eu(1)–Br(2) distance, suggesting that the coordination number for oxygen in the bromoborate is not seven, but six. This places Pb²⁺ in the bromoborate in an effectively lower O coordination than in the chloroborate, which results in shorter distances, and therefore weaker relaxation. Unfortunately, the crystallographic data are not accurate enough to prove such a hypothesis.

The Pb_p excitation and emission bands can be ascribed to Pb²⁺ pairs. The interaction between two adjacent s^2 ions is known

to give rise to lower energy levels (2, 13). The concentration dependence of the relative intensity of the pair excitation bands at 264 nm for the bromoborate and 259 nm for the chloroborate follows the relation,

$$I_{\text{rel}} = 1 - (1 - \frac{1}{2}x)^n, \quad (1)$$

where x is the Pb^{2+} fraction in $\text{Sr}_{2-x}\text{Pb}_x\text{B}_5\text{O}_9\text{X}$ and $n = 5 \pm 1$. This observation suggests an interaction between a given Pb^{2+} ion and Pb^{2+} ions on approximately five nearest cation sites. From the structural data on the haloborates (5, 12) it is known that a cation is coordinated by six other cations via a halide ion. Interaction between two Pb^{2+} ions separated by borate groups is not likely to give rise to a Pb^{2+} pair with lower energy levels. If we assume that only interaction between two Pb^{2+} ions linked via a halide ions gives rise to a Pb^{2+} pair, the value of n should be 6. This is in good agreement with the experimental value of 5 ± 1 .

For $\text{Sr}_{1.9}\text{Pb}_{0.1}\text{B}_5\text{O}_9\text{Br}$ the $^1\text{S}_0 \rightarrow ^3\text{P}_1$ pair excitation band at 264 nm and the $^3\text{P}_0 \rightarrow ^1\text{S}_0$ pair emission band at 284 nm can both be observed next to the Pb_i bands. For $\text{Sr}_{1.9}\text{Pb}_{0.1}\text{B}_5\text{O}_9\text{Cl}$, however, only the pair excitation band at 259 nm is observed. The pair emission band is hidden under the Pb_i emission band. This is due to the greater bandwidth of the Pb_i emission and the lower relative intensity of the pair emission band in the chloroborate. The latter fact will be discussed below.

A third emission band, which is detectable for the samples with $x > 0.02$, around 410 nm in the chloroborate and 370 nm in the bromoborate, corresponds probably to a transition on a Pb^{2+} ion next to a defect. A possibility for the latter is an O^{2-} ion on an X^- site. Due to the effective charge of a divalent oxygen ion on a monovalent halide ion lattice site, the energy levels of the Pb^{2+} ion may be lowered due to increasing covalency. The broad excitation band for these ions, with a maximum at about 270

nm, is due to the $^1\text{S}_0 \rightarrow ^3\text{P}_1$ transition on this ion. The large Stokes shift for the Pb_e center is not surprising. The introduction of a defect usually facilitates relaxation of the excited state which results in a larger Stokes shift.

4.2. Energy Transfer Processes in $\text{Sr}_2\text{B}_5\text{O}_9\text{X}-\text{Pb}^{2+}$

From the luminescence spectra it is clear that three types of luminescent Pb^{2+} centers have to be considered, viz. Pb_i ions, Pb_e ions, and Pb_p centers. After excitation a Pb_i ion can lose its energy not only by radiative and nonradiative decay, but also by energy transfer to a Pb_i ion, to a Pb_p center, or to a Pb_e ion.

With the experimental spectral overlap and an oscillator strength of 0.1 (8), the critical distance for the different energy transfer processes has been calculated, using a formula (14) based on work by Dexter (15). The calculated critical distances are tabulated in Table II. In view of the strongly allowed character of the transitions involved, we consider only transfer by dipole-dipole interaction.

The energy transfer to Pb_e ions is very efficient. The broad excitation band of these ions has an efficient spectral overlap with the Pb_i emission band, so that the spectral overlap is nearly independent of temperature. The critical distance for energy transfer is large, due to the great spectral overlap and amounts to 26.7 Å in the chloroborate and 33.3 Å in the bromoborate. Within these distances a Pb^{2+} ion has 770 and 1480 cation neighbor sites, respectively. With these values and the relative intensity of the Pb_e emission band at 4.2 K, the Pb_e concentration can be estimated, when only direct energy transfer to Pb_e ions is taken into account,

$$I_{\text{Pb}_e}^{\text{rel}} = 1 - (1 - x_{\text{Pb}_e})^n, \quad (2)$$

where x_{Pb_e} is the Pb_e concentration and n is the number of cation neighbor sites within

TABLE II
DATA FOR ENERGY TRANSFER PROCESSES IN
Sr₂B₅O₉X-Pb

Energy transfer process	X	T (K)	S.O. ^a (eV ⁻¹)	R _c ^b (Å)	n ^c
Pb _i → Pb _i	Cl	4.2	6.7 × 10 ⁻⁷	2.7	0
		20	1.5 × 10 ⁻⁶	3.1	0
		39	4.3 × 10 ⁻⁶	3.7	0
		60	1.2 × 10 ⁻⁵	4.4	3
		75	3.0 × 10 ⁻⁵	5.1	4
		100	1.4 × 10 ⁻⁴	6.6	14
Pb _i → Pb _p	Cl	298	1.4 × 10 ⁻²	14.2	115
		4.2	1.7 × 10 ⁻⁴	6.8	15
		20	3.3 × 10 ⁻⁴	7.6	16
		39	6.9 × 10 ⁻⁴	8.6	22
		75	3.6 × 10 ⁻³	11.4	58
		100	8.9 × 10 ⁻³	13.2	100
Pb _i → Pb _e	Cl	4.2	0.6	26.7	770
Pb _i → Pb _i	Br	4.2	2.2 × 10 ⁻⁶	3.3	0
		19	5.2 × 10 ⁻⁶	3.8	0
		39	2.5 × 10 ⁻⁵	5.0	4
		75	1.1 × 10 ⁻³	9.3	30
		110	5.8 × 10 ⁻³	12.3	73
		150	2.6 × 10 ⁻²	15.8	150
Pb _i → Pb _p	Br	19	3.0 × 10 ⁻²	16.2	167
		39	4.3 × 10 ⁻²	17.2	193
		75	0.2	22.2	415
		110	0.3	23.7	505
Pb _i → Pb _e	Br	4.2	2.3	33.3	1480

^a Spectral overlap.

^b Critical distance.

^c Number of cation neighbor sites within the critical distance for energy transfer.

the critical distance. For the chloroborate the calculated Pb_e concentration is 0.015% and for the bromoborate it is 0.013%. These are reasonable values for defect concentrations.

When the temperature is increased, the intensity of the Pb_e emission increases at the expense of the Pb_i emission (Fig. 6). Since the spectral overlap is nearly independent of temperature, this increase cannot be explained by the increase of the transfer rate for direct energy transfer. It must be due to another way of energy transfer from Pb_i ions to Pb_e ions. A possi-

ble way is energy transfer via one or more Pb_i ions. When the probability for energy transfer between Pb_i ions increases with temperature, this explains the observed increase of the relative intensity of the Pb_e emission. From the data in Table II it is clear that the critical distances for energy transfer between Pb_i ions calculated from the observed spectral overlap are too small to explain the increase of the relative intensity of the Pb_e emission. It should be realized, however, that at low temperatures the observed spectral overlap is between the ³P₀ → ¹S₀ emission band and the ¹S₀ → ³P₁ excitation band. Kellendonk *et al.* (16) have pointed out that in YAl₃B₄O₁₂-Bi³⁺ energy migration via the ³P₁ level does not vanish at low temperatures. This is possible when the probability for energy transfer to a neighboring ion is large compared to the probability for radiationless decay from the ³P₁ to the ³P₀ level.

The efficiency of this energy transfer process depends on the spectral overlap between the ¹S₀ → ³P₁ excitation band and the ³P₁ → ¹S₀ emission band, which is not observed at low temperatures. In order to check this model, the efficiency of the energy transfer process via the ³P₁ level has been calculated using a hypothetical ³P₁ → ¹S₀ emission band. For the hypothetical ³P₁ → ¹S₀ emission band, the experimental ³P₀ → ¹S₀ band was taken, but the maximum was shifted to a position 600 cm⁻¹ higher in energy than the ³P₀ → ¹S₀ emission band at 4.2 K. The results are tabulated in Table III. They show that the observed increase of the relative intensity of the Pb_e emission, above 20 K in the chloroborate and above 4.2 K in the bromoborate, can be explained by energy transfer via the ³P₁ levels of Pb_i ions to Pb_e ions.

Above ~100 K no further increase of the relative intensity of the Pb_e emission is observed. This indicates that the migration process has become very efficient. The emission above 100 K originates from Pb_e

TABLE III
DATA FOR ENERGY TRANSFER VIA THE 3P_1 LEVEL
OF Pb_i IONS (SEE TEXT)

Energy transfer process	X	T (K)	S.O. (eV ⁻¹)	R _c (Å)	n
Pb _i → Pb _i	Cl	4.2	1.5 × 10 ⁻⁵	4.6	3
		20	2.8 × 10 ⁻⁵	5.1	4
		39	5.8 × 10 ⁻⁵	5.7	6
		60	1.2 × 10 ⁻⁴	6.4	8
		75	1.5 × 10 ⁻⁴	6.7	15
		100	3.8 × 10 ⁻⁴	7.8	20
Pb _i → Pb _i	Br	RT	1.4 × 10 ⁻²	14.2	116
		4	2.1 × 10 ⁻⁴	7.1	16
		19	2.9 × 10 ⁻⁴	7.4	16
		39	7.0 × 10 ⁻⁴	8.6	26
		75	1.3 × 10 ⁻²	14.0	112
		110	3.9 × 10 ⁻²	16.9	182

and Pb_p centers, which act as trapping centers for the excitation energy migrating over the Pb_i sublattice. When the migration process has become very efficient, the intensity ratio R of the Pb_e and Pb_p emission is determined by the ratios of the trapping rates of the excitation energy and the concentrations of these centers. Since the trapping rate is proportional to the spectral overlap, R can be calculated:

$$R = \frac{I_{Pb_e}}{I_{Pb_p}} = \frac{X_{Pb_e} \cdot P_{Pb_i}^{tr} \rightarrow Pb_e}{X_{Pb_p} \cdot P_{Pb_i}^{tr} \rightarrow Pb_p} = \frac{X_{Pb_e} \cdot SO(Pb_i^{em} - Pb_e^{exc})}{X_{Pb_p} \cdot SO(Pb_i^{em} - Pb_p^{exc})} \quad (3)$$

The experimental value of R for Sr_{1.9}Pb_{0.1}B₅O₉Cl at 100 K is 0.87. From Table II SO(Pb_i^{em} - Pb_e^{exc}) and SO(Pb_i^{em} - Pb_p^{exc}) can be found to be 0.6 and 8.9 × 10⁻³, respectively. With a value of 1.5 × 10⁻⁴ for X_{Pb_e} and of 0.013 for X_{Pb_p} the calculated value of R is 0.77, which is in good agreement with the experimental value for R .

For Sr_{1.9}Pb_{0.1}B₅O₉Br the experimental value at 110 K, viz. 0.78, is 10 times larger than the calculated value of 0.08. This indicates that at this temperature back

transfer from Pb_p to Pb_i has already become effective. This is a consequence of the small Stokes shifts in the bromoborate. Back transfer to Pb_i results in population of Pb_e.

In the concentrated systems, Pb₂B₅O₉Cl and Pb₂B₅O₉Br, the efficiency of the energy transfer to Pb_e ions is very high. Energy transfer via migration over the Pb²⁺ sublattice has become efficient, because all cation sites are occupied by Pb²⁺ ions. Moreover, the Pb_e concentration is probably higher because the Pb concentration is higher than in the sample with $x = 0.1$. This makes the energy transfer to the Pb_e centers, even at 4.2 K, complete.

Apart from the energy transfer to Pb²⁺ pairs via migration over the Pb_i sublattice, direct energy transfer to these centers has also been observed. This transfer is more efficient in the bromoborate than in the chloroborate. This is due to a larger spectral overlap, which in turn results from the smaller Stokes shift in the bromoborate. This is the reason why the pair emission band in the bromoborate with $x = 0.1$ can be observed as a separate band, while it is hidden under the Pb_i emission band in the chloroborate with $x = 0.1$.

When the temperature is increased, the relative intensity of the Pb_p emission band increases, as can be seen in Fig. 4. Two processes are responsible for this increase. First, the probability for direct energy transfer to Pb_p centers increases with temperature, because the spectral overlap increases (see Table II). Second, the probability for energy transfer via migration over the Pb_i sublattice increases with temperature. At ~100 K the total transfer has become so efficient that the Pb_i emission is no longer observed.

In conclusion, a considerable number of energy transfer steps take place in the systems Sr_{2-x}Pb_xB₅O₉X ($X = Cl, Br$). For the greater part these have been quantitatively characterized.

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