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Luminescence in the chloroborates $Ba_2Ln(BO_3)_2Cl$

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Abstract

The luminescences of Ce^{3+}, Eu^{2+}, Eu^{3+} and Gd^{3+} in the compound $Ba_2Ln(BO_3)_2Cl$ (Ln ≡ Gd, Y, Lu) are reported and discussed. In $Ba_2Gd(BO_3)_2Cl$ there is energy migration over the Gd^{3+} sublattice. The $^7F_1$ level of Eu^{3+} shows a very large crystal-field splitting. The Ce^{3+} and Eu^{2+} emissions have large Stokes shifts. These are discussed in terms of existing models.

1. Introduction

Recently Khamaganova *et al.* [1] reported the crystal structure of compounds $Ba_2Ln(BO_3)_2Cl$ (Ln ≡ Ho, Yb). The compounds seem to exist for the smaller lanthanide ions only. The crystal structure is rather complicated. There are two Ba positions, one with 9 coordination (5O, 4Cl) and one with 10 coordination (8O, 2Cl). The former forms double sheets, the latter double columns. The Ln positions are 7 coordinated by O with site symmetry C_s. These polyhedra form zig-zag chains by edge sharing. Further, the structure contains triangular BO_3 groups and Cl positions coordinated octahedrally by six Ba positions.

Haloborates and -silicates are suitable host lattices for luminescent materials as shown by the examples of $Ba_2B_5O_9Br:Eu^{2+}$ [2] and $Ba_5SiO_4Br_6:Eu^{2+}$ [3]. For this reason we were interested to know whether the present compounds offer potential as host lattices for luminescent materials. This is probably not the case, but the results show some interesting aspects.

2. Experimental details

Samples were prepared using standard procedures as described before [2, 3]. The firing temperatures were 600–800 °C. Dopant concentrations were about 1 mol.%. In the case of Ce^{3+} and Eu^{2+} a reducing firing atmosphere (N_2/H_2) was used; in the case of Eu^{3+} a neutral one. Sample were checked by X-ray powder diffraction and turned out to be single phase. We were able to prepare $Ba_2Ln(BO_3)_2Cl$ (with Ln ≡ Gd, Y, Lu) with the crystal structure described in the literature [1]. Chlorine could be replaced by bromine, without influencing the luminescence drastically; barium could not be replaced by strontium. The measurements of the optical properties have already been described [2, 3].

3. Results

The Eu^{3+} emission in the three host lattices $Ba_2Ln(BO_3)_2Cl$ (Ln = Gd, Y, Lu) is practically the same. It consists of a strong orange–red emission, the spectral energy distribution of which has been given in Fig. 1. Its excitation spectrum consists of the well-known sharp Eu^{3+} absorption lines, a broad charge-transfer transition

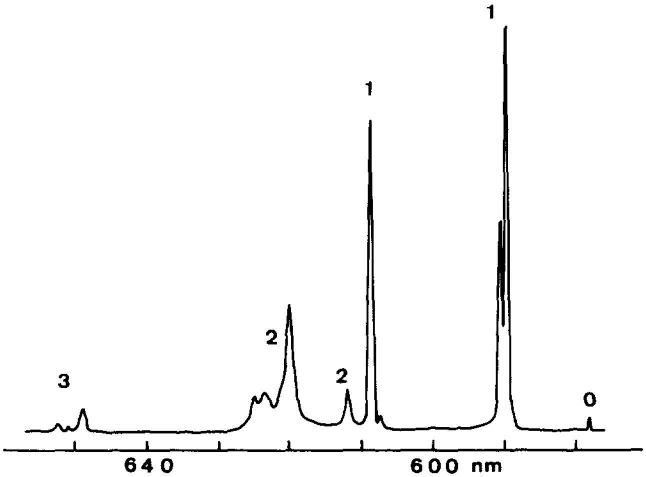

Fig. 1. The emission spectrum of the Eu^{3+} emission of $Ba_2Y(BO_3)_2Cl:Eu^{3+}$ at 4.2 K under 250 nm excitation. The figures denote the values of J in the transitions $^5D_0$–^7F_J.

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with a maximum at about 240 nm, and, in the case of Ln = Gd, sharp Gd^{3+} absorption lines pointing to energy migration over the Gd^{3+} ions to Eu^{3+} [4].

Excitation into the Gd^{3+} lines at 4.2 K yields mainly Gd^{3+} emission and about 5% Eu^{3+} emission, but at 30 K the Gd^{3+} and Eu^{3+} emission intensities are about equal. The low-temperature Gd^{3+} emission can be interpreted as trap emission [4]. The traps are emptied above 20 K feeding the Eu^{3+} ion levels.

The Ce^{3+} emission is quenched at room temperature. At lower temperatures a pale-green emission occurs. Table 1 shows some optical properties, and Fig. 2 gives a characteristic example of the spectra.

The Eu^{2+} ion shows a strong luminescence which consists of two emission bands, one peaking at about 570, the other at 465 nm. The former dominates; the latter is for the greater part quenched at room temperature. Figure 3 gives an illustrative emission spectrum. The excitation spectra of these two emissions consist of broad spectral regions deep into the ultraviolet with an onset at 440 nm for the 570 nm emission band and 410 nm for the 465 nm emission band. Due to the spectral overlap of these broad regions, selective excitation is not possible.

TABLE 1. Some properties of the Ce^{3+} luminescence in $Ba_2Ln(BO_3)_2Cl$ (Ln = Gd, Y, Lu). Band maxima in nanometres and at 4.2 K, Stokes shift in 10^3 cm^{-1}

Ln	Gd	Y	Lu
Emission maximum	415/450	480	480
Excitation maxima	365/340	370/345	370/345
Stokes shift[a]	~5	6.5	6.5
$T_{1/2}$ (K)[b]	180	140	125

[a] In the case of Gd^{3+} the average band maximum is taken to make a comparison possible.

[b] Temperature at which the luminescence intensity has dropped to 50% of the 4.2 K value.

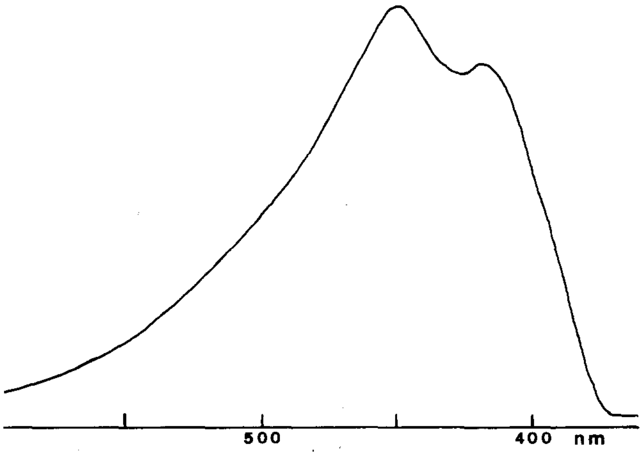

Fig. 2. The emission spectrum of the Ce^{3+} emission of $Ba_2Gd(BO_3)_2Cl:Ce^{3+}$ at 4.2 K under 320 nm excitation.

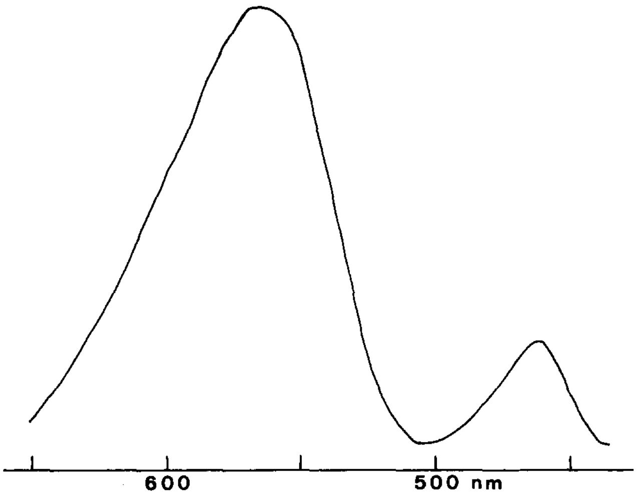

Fig. 3. The emission spectrum of the Eu^{2+} emission of $Ba_2Y(BO_3)_2Cl:Eu^{2+}$ at 4.2 K under 340 nm excitation.

4. Discussion

4.1. The Eu^{3+} luminescence

The emission spectrum of the Eu^{3+} ion in $Ba_2Ln(BO_3)_2Cl$ is somewhat misleading. At first sight the $^5D_0$–$^7F_1$ emission transition seems to consist of two lines which are so close together, viz., 589 and 590 nm, that they suggest a close-to-cubic coordination for Eu^{3+}. In view of the crystal structure this seems improbable. The Ln^{3+} ions are coordinated by a trigonal prism of oxygens, capped by a seventh oxygen; one of the edges of the prism, *i.e.* the one opposite to the capped face, is shared with a borate triangle. Since this coordination is far from cubic, we assign the three sharp lines at 589, 590 and 608 nm to the three components of the $^5D_0$–$^7F_1$ transition. This yields a large splitting of the $^7D_1$ level, viz., some 530 cm^{-1} in total. This, however, is not unusual for Eu^{3+} in borates [5, 6]. The barycentre of this transition is then calculated to be at about 16 800 cm^{-1}, which agrees also with results for borates [5, 6].

There is one $^5D_0$–$^7F_0$ transition. This shows that the sample contains one type of Eu^{3+} ions only, *i.e.* Eu^{3+} on Ln^{3+} sites. There are five $^5D_0$–$^7F_2$ components. The splittings are therefore in line with the C_s site symmetry. The relatively strong intensity of the magnetic–dipole $^5D_0$–$^7F_1$ transition is ascribed to the high-energetic position of the charge-transfer band which reduces the amount of opposite-parity mixing [7]. This emission spectrum is, therefore, qualitatively in line with the results of crystal structure determination.

4.2. The Gd^{3+} emission

The experimental results point clearly to energy migration over the Gd^{3+} sublattice which is hampered below 20 K because of the presence of Gd^{3+} traps.

This type of phenomenon has been observed for many Gd^{3+} compounds and is well understood [4]. A condition for energy transfer between Gd^{3+} ions is that the shortest Gd–Gd distance is less than 6 Å. In the present compounds, the Ln^{3+} ion polyhedra form zig-zig chains with a shortest Ln–Ln distance of about 5.3 Å, so that the condition for migration is satisfied. An obvious choice for the Gd^{3+} traps is a small amount of Gd^{3+} ions on the Ba^{2+} sites.

4.3. The Ce^{3+} emission

The Ce^{3+} ion is known to luminesce efficiently in borates [8, 9]. However, this is certainly not the case in the present chloroborates. The optical transitions involved are of the 4f–5d type. Only for $Ba_2Gd(BO_3)_2Cl:Ce^{3+}$ is the characteristic splitting of the emission band due to the split ground state observed. We assume that in the other two host lattices it is not observed due to broadening of the emission band in agreement with the larger Stokes shift. Table 1 shows that from Gd to Lu the optical transitions move to lower energy, the Stokes shift increases and the quenching temperature decreases.

In order to explain the low quenching temperature of Ce^{3+} luminescence, it might be thought that this is related to the relatively large Stokes shift [4]. It should be realised that the real Stokes shift is some 1000 cm^{-1} less than the values given in Table 1, since the spin-orbit coupling of the ground state has to be taken into account.

However, it is doubtful whether the value of the Stokes shift is large enough to explain the low quenching temperature of the Ce^{3+} emission. Actually the well-known efficient phosphor $Y_3Al_5O_{12}:Ce^{3+}$ has a Stokes shift of about 4000 cm^{-1}, whereas optical transitions are at an even lower energy than in the present case [8]. Most probably thermally activated photoionization will also play a role in the luminescence quenching [10]. This becomes the more acceptable after consideration of the results for Eu^{2+} luminescence.

4.4. The Eu^{2+} emission

The Eu^{2+} emission clearly shows two emission bands. Since the excitation regions overlap, it is hard to estimate a Stokes shift. It is clear, however, that this has a large value, especially for the longer-wavelength emission band. The shorter-wavelength onset of this emission (~500 nm) is at a much longer wavelength than the longer-wavelength onset of the excitation (~440 nm).

Since there are two different Ba^{2+} ion sites in the crystal structure, we assume that the two emissions are due to Eu^{2+} ions on both of these sites. The quenching of the shorter-wavelength emission band upon increasing temperature may be ascribed to thermally-activated energy transfer to the Eu^{2+} centre with the longer-wavelength emission band. The larger Stokes shift of the latter recalls the similar situation for Eu^{2+} in BaF_2 [11] and in some other host lattices ($LiBa_2B_5O_{10}$ [12] and $Sr_2SiO_3Cl_2$ [13]). Especially, the case of $BaF_2:Eu^{2+}$ has been thoroughly investigated. It has been shown that the Eu^{2+} ion shows photoionization in this host lattice and that the emission is due to impurity-bound exciton recombination. The hole of the exciton is bound to europium, the electron to barium. Such a situation can also easily be imagined for the present host lattice.

Simultaneously our results show that this phenomenon is of more importance for one of the two crystallographic sites than for the other. Unfortunately, it is not possible to decide which of the two Eu^{2+} ions shows exciton recombination. To answer this question it is necessary to know the position of the Eu^{2+} energy levels relative to the bottom of the conduction band of $Ba_2Ln(BO_3)_2Cl$. In view of the complicated crystal structure, even a qualitative answer is not easy to give.

In conclusion, the luminescence of some rare earth ions in the host lattice of $Ba_2Ln(BO_3)_2Cl$ shows some peculiar properties. For Eu^{3+} these relate to the splitting of the strong $^5D_0$–$^7F_1$ transition; for Ce^{3+} and Eu^{2+} to the large Stokes shift. One of the two Eu^{2+} sites shows impurity-band exciton recombination. For practical applications, the investigated compounds do not show advantages over known phosphors.

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