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Low-Temperature Ce^{3+} Luminescence in $CsCdBr_3$ Crystals

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Ce^{3+}-doped $CsCdBr_3$ shows several Ce^{3+} emissions due to a diversity of luminescent centers. The nature of these centers is discussed.

Introduction

One of us has reported on a red Ce^{3+} luminescence with large Stokes shift in $CsCdBr_3$ (*1*). Trivalent rare-earth ions in $CsCdBr_3$ form linear RE^{3+}–vacancy–RE^{3+} centers in the $[CdBr_3^-]$ chains of $CsCdBr_3$ (*1–3*). The red Ce^{3+} emission was ascribed to a Ce^{3+}–vacancy–Ce^{3+} center. This assignment could be substantiated by the introduction of Tm^{3+}, so that Ce^{3+}–vacancy–Tm^{3+} centers are formed. In these centers effective energy transfer from Ce^{3+} to Tm^{3+} takes place, so that Tm^{3+} quenches the red emission.

The other authors reported on the luminescence of undoped $CsCdBr_3$ and of Pb^{2+} and Bi^{3+} in $CsCdBr_3$ (*4*). In this letter we report some measurements at liquid helium temperature on Ce^{3+}-doped and Ce^{3+}, Li^+-codoped $CsCdBr_3$ crystals, independently grown in both laboratories. The results indicate that Ce^{3+}-doped $CsCdBr_3$ contains several Ce^{3+} centers with different luminescent properties.

Experimental

Crystals were grown as described previously (*1, 4*). The performance of the luminescence measurements has been described in Ref. (*4*).

Results and Discussion

The results are rather complicated. Under ultraviolet excitation a deep blue as well as a red emission was observed. Their quantum efficiencies at LHeT could not be determined exactly, but are estimated to be high, i.e., near 100%. Decay curves were exponential with decay times of about 100 nsec. This shows the emission to be an al-

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TABLE I

EMISSION AND EXCITATION MAXIMA OF THE RED LUMINESCENCE OF $CsCdBr_3$–Ce^{3+},Li^+ AS A FUNCTION OF TEMPERATURE

T (K)	Excitation (nm)	Emission (nm)
9	360	650
	320	[a]
100	360	640
	320	630
150	360	640
	320	620
210	360	630
	320	605
300	360	620[b]
	320	580

[a] Only bound exciton emission at 380 nm.

[b] For $CsCdBr_3$–Ce^{3+} the results are similar, but no emission was observed for 360 nm excitation at 300 K. In $CsCdBr_3$–Ce^{3+},Li^+ this emission is very weak at 300 K.

lowed transition, as is to be expected for the Ce^{3+} ion (*f–d* transition).

In view of the results reported before (*1*), the red emission is ascribed to a Ce^{3+} ion in a Ce^{3+}–vacancy–Ce^{3+} center. The situation is more complicated, however, than reported before. At LHeT the emission peaks at 650 nm with an excitation band at 360 nm. Above 80 K a new excitation band appears at 320 nm. It turns out that the emissions for both excitations are slightly different (see Table I). At LHeT 320 nm excitation results in a 380 nm emission which was ascribed to bound excitons at stacking faults (*4*). The excitons become mobile at 80 K. This suggests that there are two red centers: one with the 360 nm excitation band which can be excited directly and another one with the 320 nm excitation band which can only be excited via the stacking faults, because its concentration is low. A similar situation was observed for Pb^{2+} and Sn^{2+} in $CsCdBr_3$, and has been discussed at length in Ref. (*4*). The latter center is slightly distorted due to the presence of the stacking fault, so that its emission is at a somewhat different position. These observations were made for crystals $CsCdBr_3$–Ce^{3+} and $CsCdBr_3$–Ce^{3+}, Li^+. This shows that the Ce^{3+}–vacancy–Ce^{3+} center is very stable, since the charge compensator Li^+ is not (completely) used. This assignment needs further confirmation. For this reason crystals codoped with cerium and other rare earth ions are being investigated by one of us (G.L.M.).

The red emission band does not show the well-known ${}^2F_{5/2}$–${}^2F_{7/2}$ ground state splitting. This may be due to the fact that both transitions are very broad due to the large Stokes shift.

The Stokes shift indicates a strong reorganization in the Ce^{3+}–vacancy–Ce^{3+} center upon excitation. We have to assume that the Ce^{3+} ions in the ground state are off-center into the direction of the effectively negative vacancy. Excitation of the Ce^{3+} ion makes the ion more effectively positive (*5*), which may be the origin of the reorganization. The temperature dependence of the emission can also be related to a temperature dependence of the Ce^{3+} position in the Ce^{3+}–vacancy–Ce^{3+} center. This is similar to recent observations for Pb^{2+} (*6*) and Sb^{3+} (*7*).

Although the quenching temperature of the red emission is below room temperature (about 250 K), its value is high in view of the large Stokes shift. In oxides the Ce^{3+} emission is quenched at very low temperatures for such a shift (*8*, *9*). We ascribe this to the fact that the $CsCdBr_3$ lattice has only low phonon frequencies available. This circumstance decreases the nonradiative rates considerably and increases the value of the quenching temperature (*10*).

The red emission excited by 360 nm shows also an excitation band at 345 nm (see also Ref. (*1*)). Their energy difference, ~1200 cm^{-1}, presents the trigonal splitting of the t_{2g} component which results from the excited 5*d* level by the cubic crystal-field

TABLE II

EMISSION AN EXCITATION MAXIMA OF THE BLUE LUMINESCENCE OF $CsCdBr_3$–Ce^{3+} AND $CsCdBr_3$–Ce^{3+},Li^+ AT LHeT[a]

	Excitation (nm)	Emission (nm)
$CsCdBr_3$–Ce^{3+}	330, 350	380, 410
$CsCdBr_3$–Ce^{3+},Li^+	330, 350	380, 410
	350, 370	395, 435

[a] Data on one and the same line relate to one center.

splitting. The value of this noncubic splitting agrees with values reported for other host lattices (*8*).

Let us now turn to the blue emission. The spectra are complicated. In Table II the main emission and excitation bands are tabulated. Weaker bands were omitted. The Ce^{3+}-doped $CsCdBr_3$ shows one dominating blue-emitting center. It is obvious to assume that this center consists of a Ce^{3+} ion on a Cd^{2+} site without a nearby charge compensator. Association with a vacancy is unlikely in view of the arguments given above. The splitting of the emission band is due to the ground state splitting of the Ce^{3+} ion ($4f^1$: $^2F_{5/2}$, $^2F_{7/2}$). The Stokes shift has a normal value. The trigonal splitting of the $t_{2g}(5d)$ level is larger than in the Ce^{3+}–vacancy–Ce^{3+} center (1700 and 1200 cm^{-1}, respectively), which shows that the Cd^{2+} ions are mainly responsible for the strength of the trigonal field.

The Ce^{3+},Li^+-codoped $CsCdBr_3$ crystals show also the unassociated Ce^{3+} center. However, there is also another center with an emission at slightly lower energy. We assign this emission to an associate of Ce^{3+} and Li^+, i.e., $(Ce^{\cdot}_{Cd} \cdot Li'_{Cd})^x$. The other, much weaker Ce^{3+} emissions are ascribed to isolated Ce^{3+} ions which have a compensating defect nearby, but not on the nearest and next-nearest lattice sites.

The results show that the incorporation of trivalent ions in $CsCdBr_3$ can take place in a complicated way. For $CsCdBr_3$–Bi^{3+}, on the other hand, only one center was observed, viz., the Bi^{3+}–vacancy–Bi^{3+} center (*4*).

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