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Band structure and excitons in $CsCdBr_3$

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Abstract

$CsCdBr_3$ has a very unique electronic band structure [J. Kübler, private communication]. The conduction band is split up into two parts: a lower isolated and very narrow band ($\Delta E \sim 4000$ cm^{-1}) and higher lying ones. Just below the lowest conduction band we observe an absorption band of excitons localized at lattice defects. Both of them, the low-lying conduction band as well as the localized excitons, play an important role in the fast and very efficient energy transfer within the crystal. This can be shown by analyzing the decay dynamics of the fluorescence of the dopant RE-ions and of the localized and lattice excitons (excitons of the perfect lattice). Also, excitation into either the excitons or the RE-ion clearly shows an energy transfer back and forth between both of them. We deem this mechanism to be the most important one for the observed upconversion processes in $CsCdBr_3$. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Recombination and trapping; Optical properties; Electronic band structure

1. Introduction

$CsCdBr_3$ is an interesting host material for studying pairs of rare-earth (RE) ions. Predominantly, two RE^{3+} ions substitute for three Cd^{2+} ions thus building pair centres [1]. The single-ion centres are not important with respect to energy transfer processes, because no upconversion effects have been observed from these centres until now [2].

Pr^{3+} shows strong upconversion fluorescence by exciting the $^1D_2 \times {}^1D_2$ state of the symmetric Pr^{3+} pair in $CsCdBr_3$. A detailed energy level structure of the Pr^{3+} ion can be found in [3,4]. The anti-Stokes fluorescence from the levels $^3P_0$ and $^3P_1$ was studied in [4]. The aim of this work was to study the relevant energy transfer processes and to compare the results found with single crystals and with powder samples.

2. Experimental data

The crystals were grown by the Bridgeman technique as described in [4]. The samples were of good optical quality. The concentration of Pr^{3+} ions was 1% in the starting material. The excitation of the single crystals was performed with a SOLAR Nd:YAG-laser pumped tunable dye laser (ELTO). The samples were mounted in a LHe-cryostat. Detection of the signal was carried out in the photon counting regime with a Hamamatsu R3310 photomultiplier tube.

Synchrotron radiation in the UV region was used for excitation of the powder samples.

3. Results: $CsCdBr_3$ single crystal

Excitation into the conduction band (244 nm) at 4 K shows no RE-fluorescence but only broad emission bands at 420 nm and 730 nm (Fig. 1). Fluorescence decay measurements at the maximum positions of these bands show decay times of about 300 ns and 1.5 μs for the 420 nm band and about 140 μs for the 730 nm one. Since these fluorescence bands are not correlated with RE doping their origin has to be in the host lattice. We assign the 730 nm band to the existence of lattice excitons, whereas the 420 nm one seems to be correlated with excitons localized at defects or impurities. The lowest f–d configuration level for Pr^{3+} in $CsCdBr_3$ can be estimated to be in the region of ~250 nm [5]. This estimate is based on measurements on other bromide crystals with the RE-ion in sixfold coordination.

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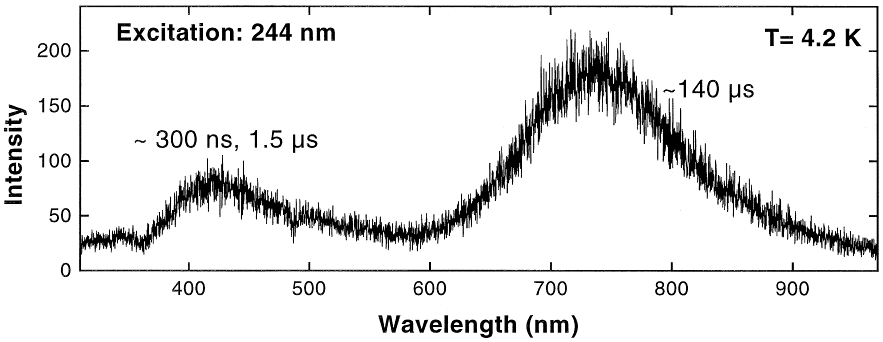

Fig. 1. Fluorescence spectrum of a Pr^{3+}:$CsCdBr_3$ single crystal for excitation into the conduction band (244 nm) at 4 K.

Strong and efficient RE-fluorescence in the wavelength region from 470 nm to 860 nm can be observed (Fig. 2, lower curve) exciting into the states of the localized excitons (260 nm). The corresponding fluorescent levels are labelled and shown in Fig. 3. Fluorescence decay measurements of the $^3P_0$, $^3P_1$ and $^1D_2$ levels (Fig. 3) at 4.2 K show a very fast feeding ($\leq$300 ns) of all levels, even though the energy mismatch between excitation and emission is large (about 18 000 cm^{-1}). The fit of the fluorescence decays to superpositions of exponentials allows the following explanations:

The $^3P_1$ is fed very fast ($\leq$300 ns) by the localized exciton. The decay time of 14 μs is the intrinsic lifetime of $^3P_1$. The fast initial decay of $^3P_1$ with about 1.6 μs points at another deexcitation channel which can not be explained satisfactorily yet.

The $^3P_0$ level is fed very fast ($\leq$300 ns) by the exciton as well. Further, the second feeding time of $^3P_0$ (~11 μs) is in the same range as the intrinsic life time of $^3P_1$ of about 14 μs. This points at a partial population of $^3P_0$ from $^3P_1$. The time constant of 21 μs is close to the intrinsic life time of $^3P_0$ (~20 μs). Finally, the long-term decay shows a time constant of about 140 μs. This corresponds to the lifetime of the lattice exciton indicating an energy transfer from it to the ion.

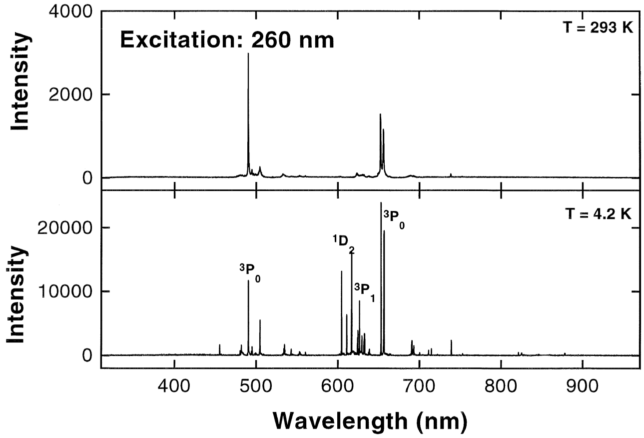

Fig. 2. Fluorescence spectra of a Pr^{3+}:$CsCdBr_3$ single crystal for excitation into the localized exciton states (260 nm) at 4 K and 293 K.

The $^1D_2$ level is also occupied in $\leq$300 ns through the localized exciton. Its decay can not be distinguished from the decay of the lattice exciton independent of excitation. We suppose that the decay time of 140 μs may not be the intrinsic lifetime of the level because of the strong exciton–ion coupling indicated by the fast upconversion from the $^1D_2$ level [2].

The long-term decay of 140 μs was observed for the two latter levels, although they have other intrinsic lifetimes. From this we conclude that these levels are fed from a common reservoir with a lifetime of 140 μs, i.e. from the lattice excitons.

Generally, for different RE-dopings we observe the 140 μs decay always for levels with energies lower than 20 800 cm^{-1} (480 nm); in Pr:$CsCdBr_3$ these levels are $^3P_0$ and $^1D_2$. For states higher than 20 800 cm^{-1}, the 140 μs decay has never been observed. Direct coupling through

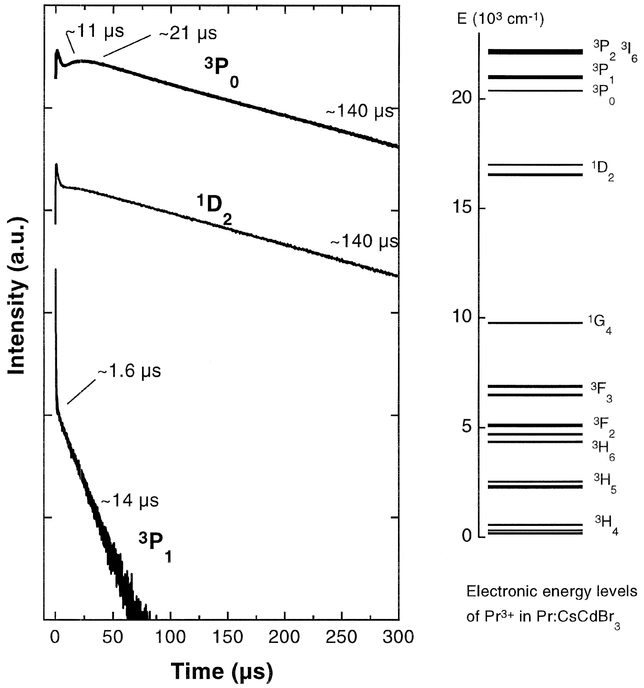

Fig. 3. Fluorescence decay of different energy levels of Pr^{3+} after pulsed excitation into the localized exciton states (260 nm) at 4 K.

energy resonance with the exciton band (see Fig. 1) seems to be unlikely. A forthcoming paper on this finding is in preparation.

Comparing the RE fluorescence at 4 K and at 293 K shows a significant decrease of intensity with rising temperature except for the $^3P_0$ level. In addition the fluorescence lines broaden thermally (Fig. 2, upper curve). In fact, the properties of the localized as well as of the lattice excitons depend strongly on temperature.

4. Results: $CsCdBr_3$ powder

In powders we expected effects related to defect-localized excitons to be stronger than in single crystals. Indeed all defect-related fluorescence lines show larger intensities.

Excitation into the conduction band (244 nm) at 4 K yields a strong host lattice emission for wavelength larger than 700 nm (Fig. 4, upper curve) and weak Pr^{3+} fluorescence lines in the wavelength region from 480 nm to 760 nm. This corresponds well with the results from the single crystal. The absolute intensities in Fig. 4 are much higher than those in Fig. 1 due to the quasi cw excitation and the much higher excitation intensities of the synchrotron. This is the experimental reason why some Pr^{3+} lines, missing in the single-crystal spectrum, show up here.

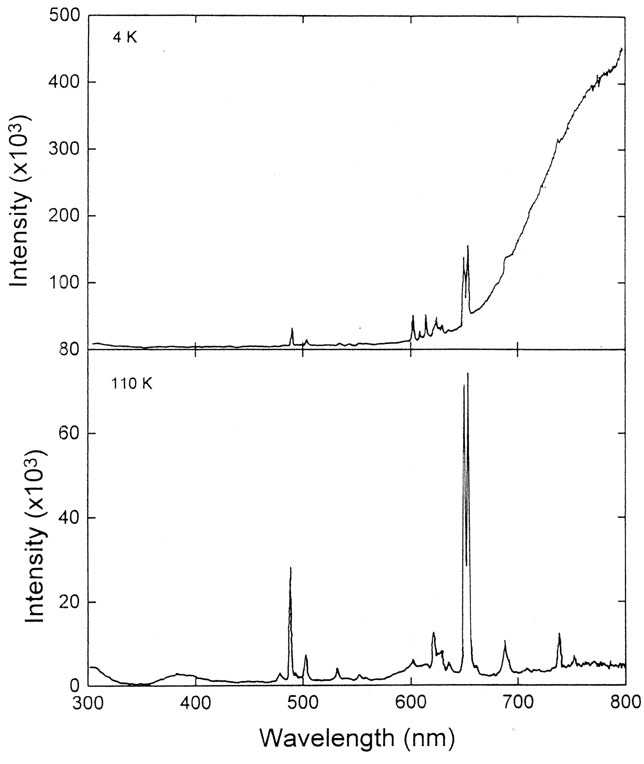

Fig. 4. Fluorescence spectra of Pr^{3+}:$CsCdBr_3$ powder at 4 K and 110 K (excitation wavelength 244 nm).

4 K	490 nm $^3P_0 \rightarrow {}^3H_4$	604 nm $^1D_2 \rightarrow {}^3H_4$	626 nm $^3P_0 \rightarrow {}^3H_6$	657 nm $^3P_0 \rightarrow {}^3F_2$
10 K	490 nm $^3P_0 \rightarrow {}^3H_4$	533 nm $^3P_0 \rightarrow {}^3H_5$	624 nm $^3P_0 \rightarrow {}^3H_6$	656 nm $^3P_0 \rightarrow {}^3F_2$

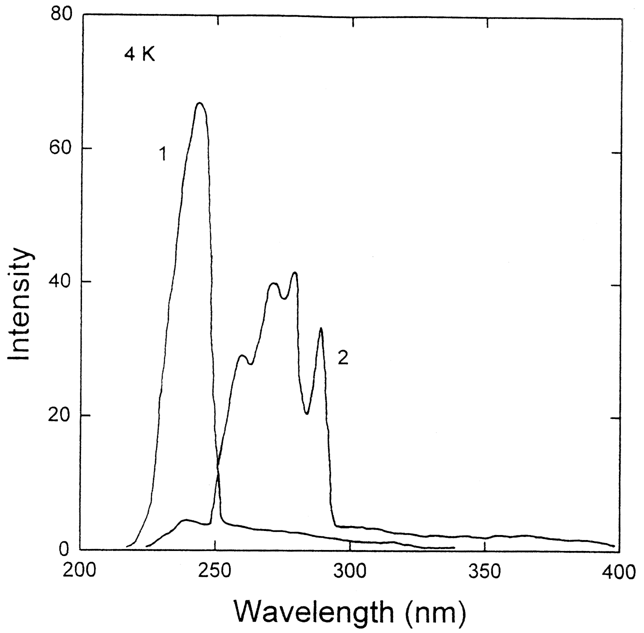

Fig. 5. Excitation spectra of undoped $CsCdBr_3$ powder at 4 K (detection wavelengths 1: 730 nm, 2: 430 nm).

With rising temperature the intensity of the Pr^{3+} lines first increases up to about 100 K. The excitons become more mobile and therefore can transfer their energy more efficient over longer distances. At still higher temperatures the intensity of the Pr^{3+} lines decreases whereas the host lattice emission vanishes completely by thermal quenching (Fig. 4, lower curve). This is also in agreement with the single-crystal results.

The excitation spectrum for an undoped powder sample at 4 K with detection at 430 nm shows a strong structured absorption band between 250 nm and 300 nm which we attribute to localized excitons (Fig. 5, curve 2). The absorption of the lattice excitons for the same sample is shown in an excitation spectrum with detection at 730 nm (Fig. 5, curve 1). The excitation spectrum is identical with the absorption into the narrow isolated conduction band (Fig. 6). Both of these spectra confirm well not only the existence of localized and lattice excitons but also the intensity distribution in Fig. 1: at an excitation wavelength of about 244 nm (excitation wavelength in Fig. 1) the lattice exciton (curve 1, Fig. 5) has a higher intensity than the localized one (curve 2, Fig. 5).

5. Conclusion

The excitation measurements of undoped powder samples yield clear absorption spectra of both kinds of excitons. The existence of localized and lattice excitons is

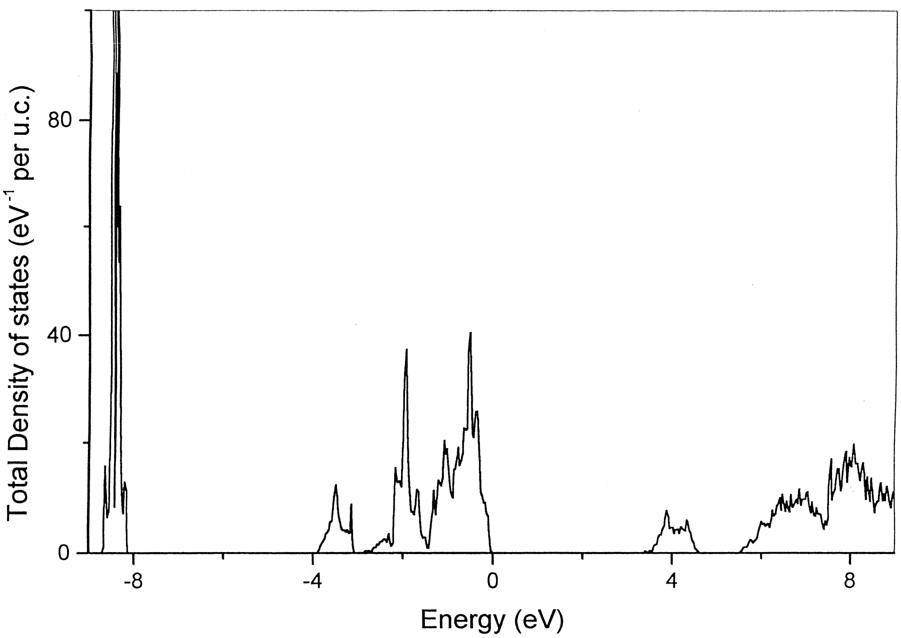

Fig. 6. Total density of states of $CsCdBr_3$ calculated by the density functional method.

also confirmed by fluorescence decay measurements with excitation at 244 nm.

Time resolved measurements exciting at 260 nm show that the localized excitons are responsible for the energy transfer to the RE ions. The results of the fluorescence measurements as function of excitation wavelength and temperature for the powder samples of Pr^{3+}:$CsCdBr_3$ agree well with the ones for the single crystal.

Acknowledgements

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