Exciton emission in BaFBr and BaFCl crystals

E A Radzhabov and A V Egranov
Vinogradov Institute of Geochemistry, Academy of Sciences, Siberian Branch, Favorinskii
Street 1a, PO Box 4019, 664033 Irkutsk, Russia

Received 10 November 1993, in final form 21 February 1994

Abstract. The emission of self-trapped excitons produced by vacuum ultraviolet excitation as well as x-ray excitation or photostimulation in BaFCl and BaFBr crystals was studied. The exciton emission bands at 4.2 and 5.15 eV in BaFBr and at 3.3 eV in BaFCl were observed upon irradiation into the Cl or Br exciton absorption bands. The 5.15 eV emission band in BaFBr thermally transforms to the 4.2 eV band with increasing temperature within the range 50–80 K. The 3.3 eV emission in BaFCl increases in the range 20–50 K in BaFCl, while the lifetime of the emission decreases. These facts indicate rather clearly the potential barrier between two different exciton configurations. The low-temperature exciton configuration was tentatively assigned to the $V_k + e$ type and the other to F+H type.

1. Introduction

The emission of self-trapped excitons (hereafter called briefly excitons) has been intensively studied in various crystals (Williams and Song 1990, Itoh and Tanimura 1990). In many crystals the triplet exciton emission was thermally quenched above liquid-nitrogen temperature. In alkali halide crystals which exhibit correlation of triplet exciton emission quenching and F-centre formation yield, the activation energy must describe the barrier between the exciton luminescent state and the F−H pair. In other alkali halide crystals the activation barrier still governs the crossing to the ground states (Williams and Song 1990). In the alkaline-earth fluoride crystals the triplet $V_k + e$ state is unstable and relaxed to various F+H configurations of the excitons without activation energy (Kabler and Williams 1978).

The $V_k + e$ emission band at 3.25 eV was observed in an x-irradiated BaFCl crystal by F-light excitation at 77 K (Yuste et al 1975). Recently, the 3.3 eV emission band in BaFCl was observed upon excitation into the Cl-exciton absorption band (Radzhabov and Oroshok 1993). The 4.2 eV emission band was produced in the BaFBr crystal by vacuum ultraviolet (VUV) irradiation into Br-exciton bands (Ruter et al 1990). The band near 5.0 eV in the BaFBr crystal also belongs to the exciton emission (Radzhabov and Oroshok 1993).

In this paper we report results on the temperature dependence of the intrinsic exciton emission of BaFBr and BaFCl crystals upon VUV excitation, x-irradiation or visible-light photostimulation. The results show that at least two different radiative exciton configurations separated by a potential barrier are observed in both crystals.

2. Experimental details

The preparation of barium fluorohalide crystals was described elsewhere (Radzhabov and Oroshok 1993). The emission and absorption spectra in the VUV region are obtained from
home-made spectrophotometers. Absorption spectra in the UV and visible region were obtained on a Specord M40 spectrophotometer. Samples were coloured by x-rays through the Al (0.6 mm) window of the cryostat with a 30 kV, 50 mA, Pd tube. The emission spectra were not corrected with respect to the spectral response of the spectrometer, but the spectrometer sensitivity was not significantly changed in the range of measured emission.

Photostimulated emission spectra were measured upon irradiation into the F(Br⁻) or F(Cl⁻) absorption bands of the crystal, which had been x-irradiated at 78 K previously. Upon excitation the electron from the F centre recombines with the V_k centre and a self-trapped exciton is created. This method of exciton production was used earlier in BaFCI (Yuste et al 1975). At 17 K the photostimulated V_k + e emission is much lower than at 78 K. It is known that the photostimulated emission of Eu²⁺ in BaFBr below 60 K is due to the tunnelling of an F-centre electron to the neighbouring Eu after optical excitation (Thoms 1991). Evidently at low temperatures the exciton is created by tunnelling recombination of the F-centre electron with the neighbouring V_k centre. The decay of photostimulated emission was measured by the single-photon technique using the CAMAC time-to-digital converter or by the usual technique using the CAMAC analogue-to-digital converter.

The 5.15 eV band was better observed in crystals with a low oxygen concentration, because the oxygen centres have an absorption band at 5.0 eV (Radzhabov and Otroshok 1993) and reabsorb the high-energy exciton emission. Because of this the 5.15 eV emission was observed from a crystal surface that had been irradiated by VUV light or x-rays.

3. Experimental results

The first absorption bands of Cl and Br excitons were observed at 7.64 and 8.60 eV in BaFBr and BaFCI, respectively (Nicklaus 1979). The fluorine-exciton absorption was not observed in these crystals, but it was assumed that the reflectivity bands within the spectral range between 10 and 15 eV in BaFBr are probably due to fluorine 2p excitations (Ruter et al 1990). We observe the exciton emission bands at 4.2 and 5.15 eV in BaFBr and at 3.3 eV in BaFCI upon excitation, starting at the red wings of the lowest exciton peaks. The excitation peaks of the 4.2 and 5.15 eV bands in BaFBr and the 3.3 eV emission band in BaFCI are within the Br- or Cl-exciton absorption bands, respectively. No bands, associated with fluorine excitons were observed up to 11 eV excitation. Moreover, upon x-irradiation no emission bands, other than those mentioned above, in the range up to 10 eV were observed in BaFBr and BaFCI crystals. The absence of fluorine-related exciton emission is probably due to an efficient Auger-type decay in which the hole transfers from the fluorine to Br or Cl rather than evolves into the F-exciton creation (see also Ruter et al 1990). It is rather unexpected that the emission energy of BaFCI excitons is lower than the energy of BaFBr excitons. The reason for this is not clear.

3.1. BaFBr

The emission bands at 5.15, 4.2, 3.7 and 2.5 eV are produced by irradiation into the Br exciton bands (figure 1). The band at 2.5 eV in figure 1 is due to oxygen-vacancy centres (Radzhabov and Otroshok 1993); the 3.7 eV band is related to an unknown defect. Both these bands were also observed upon 7.0 eV excitation, when excitons are not produced and 4.2 and 5.15 eV bands are not observed. This clearly identifies the 4.2 and 5.15 eV emission bands as the Br-exciton bands. The relation between exciton emissions depends on the temperature. There is anticorrelation between the temperature dependence of the 5.15 eV emission and that of the 4.2 eV emission (figure 2). The temperature dependence shows
clearly that one exciton emission transforms into the other. The temperature dependences of exciton bands were similar in crystals with different oxygen concentrations and even in crystals with different types of oxygen centres. This demonstrates that emission bands are not related to impurities but to unperturbed excitons of different types. The decrease in intensity of the 5.15 eV emission band is explained by introducing a thermally activated transformation one-exciton configuration into the other, which competes with the 5.15 eV radiative transition. The intensity is described by the following equation (Williams and Song 1990):

\[
I = \frac{I_0}{1 + A \exp(-E/kT)}
\]  

(1)

where \(E\) is the potential barrier for transformation, and the constant \(A = \tau_r/\tau_{nr}\) — i.e. the ratio of radiative lifetime to radiationless lifetime. The experimental data can be followed by equation (1) with the numerical values of \(E = 0.064\) eV and \(A = 10^3\) as shown by the solid curve in figure 1. The sum of normalized intensities of the two exciton bands remains constant. Then we can write

\[
I(4.2 \text{ eV}) = 1 - I(5.15 \text{ eV})
\]  

(2)

where \(I(4.2 \text{ eV})\) and \(I(5.15 \text{ eV})\) are the normalized intensities of the 4.2 eV and 5.15 eV emission bands, respectively. The calculated curve correlates well with experimental data (figure 2). The deviation in the intensity from the 4.2 eV band from the calculated curve at temperatures below 50 K is obviously due to overlap of the 3.7 eV band (see figure 1).

![Figure 1](image_url)

Figure 1. Emission spectra of a BaFBr crystal upon 7.7 eV excitation at different temperatures: curve 1, 78.5 K; curve 2, 62 K; curve 3, 17.3 K.

† The two types of oxygen-vacancy centres were assumed to occupy the F–Br and Br–Br pair sites (Radzhabov and Otroshok 1993).
Figure 2. Change in intensities of exciton luminescence bands in BaFBr crystal upon 7.7 eV excitation. The intensities of band were normalized by their sum. The solid curves were calculated using equations (1) and (2) (see text).

Both exciton emissions appear also upon x-irradiation or photostimulation and show similar temperature dependences.

The decay of photostimulated 5.15 eV exciton emission is rather complicated. The decay curve can be divided into three exponential components with lifetimes of 4, 12.0 and 230 μs at 18 K.

3.2. BaFCl

In contrast with the BaFBr crystal, we observe only one emission band at 3.30 eV (with half-width 0.6 eV) related to excitons. This band was observed upon VUV (above 8 eV), x-ray excitation or V_k + e recombination. The energies of the maximum and the half-width of this band are close to those of previously measured V_k + e emission (Yuste et al 1975). With increasing temperature the intensity of the 3.3 eV band increases within the range 20–50 K. At the same time the lifetime of the photostimulated V_k + e emission decreases and takes a constant value above 30 K (figure 3). This lifetime behaviour is rather unusual and can be explained by thermal activated transformation of excitons with one lifetime to excitons with another lifetime. One can, therefore, conclude that in BaFCl also there are two different types of exciton with similar emission bands and with different lifetimes of emission. The emission intensity I_1 of the first type of exciton can be described by relation (1). The intensity I_2 of the second type of exciton can be described by a modified relation (2):

$$I_2 = I_{2\text{max}}(1 - I_1/I_{1\text{max}})$$

where I_{1\text{max}} and I_{2\text{max}} are the maximal intensities of I_1 and I_2 respectively. The temperature dependence of the exciton emission can be satisfactorily explained using equations (1) and (3) for the intensity of the components, assuming that the total intensity is the sum of the intensities of both spectrally indistinguishable components (see figure 3). The experimental data can be followed from the equations with E = 0.017 eV.
Exciton emission in BaFBr and BaFCl

4. Discussion

The results obtained indicate that in the barium fluorohalides BaFCl, and BaFBr the excitons have two configurations separated by an energy barrier. Recombination from both configurations yields emissions which are spectrally indistinguishable in BaFCl having a rather small potential barrier (about 0.017 eV) and which are spectrally well separated in BaFBr with a higher activation energy (about 0.064 eV).

Let us compare the alkaline-earth fluoride and barium fluorohalide results in more detail. The excitons in alkaline-earth fluoride crystals emit one luminescence band near 4 eV. Time-resolved spectroscopy studies indicate that the luminescence decay curve consists of several exponential components (Williams et al 1976). Each of the multiple components has been ascribed to the F–H pair in different configurations (Itoh and Tanimura 1990). The large vibrational energy freed from the $V_k + e$ configuration may allow the formation of several types of self-trapped exciton (Itoh and Tanimura 1990). In contrast with this, at low temperatures, excitons of only one type were created in both alkaline-earth fluorohalide crystals. The other type (or configuration) of exciton can be thermally produced over a potential barrier. The observation of only one type of exciton at low temperatures indicates no large relaxation of triplet excitons occurs after creation, especially when the photostimulated electron is trapped by the $V_k$ centre. We therefore conclude that the low-temperature exciton configuration is of the $V_k + e$ type.

Generally, there are two possibilities of producing another exciton type, namely the formation of $V_k + e$ of another spatial configuration, or an F+H configuration. Experimentally only out-of-plane configurations of the $V_k$ centres were observed in BaFCl (Yuste et al 1975) and BaFBr (Hangleiter et al 1990). The computed defect formation energies of $V_k$ centres in BaFCl and BaFBr show that the in-plane configuration has an energy 0.4–0.8 eV larger than the out-of-plane energy (Baetzold 1989a). This energy can be considered as the energy needed for the transformation of one $V_k$ configuration into the other. Therefore, one may expect that the energy of the exciton with an in-plane $V_k$
centre exceeds the energy of the exciton with an out-of-plane $V_k$ centre by 0.4–0.8 eV. We observed that the potential barrier is rather smaller (0.017 eV for BaFCl and 0.063 eV for BaFBr) and strongly depends on the host material. These facts disagree with the assumption of $V_k + e$ multiple configurations and we consider this to be improbable.

Recently the energy change involved in relaxation of the $\text{Br}_2^-$ exciton by (100) or out-of-plane motions was calculated (Baetzold 1989b). During this relaxation the on-centre exciton (or $V_k + e$) is transformed to the off-centre exciton (or nearest F–H pair). In both cases a stabilization of 0.5–1.2 eV was observed. For (100) motion an activation barrier of a few tenths of an electronvolt was calculated (Baetzold 1989b). Although for out-of-plane motion no potential barrier was calculated, it is not improbable. Our experimental results seem to be consistent with these calculations. The difference between the energies of two exciton emission bands in BaFBr (about 1 eV) can be considered as the energy of exciton stabilization. The measured potential barrier for transformation into another configuration (lower than 0.1 eV) is also in qualitative agreement with the calculated value. These results lead us to conclusion that the most probable alternative exciton configuration in barium fluorohalides is $\text{F(Br}\text{)}^–+\text{H}$.

In many alkali halides the $\pi$ emission of triplet excitons competes with the creation of separated F, H centres (Itoh and Tanimura 1990). It was established that the creation of $\text{F(Br}^++\text{)}$ centres by x-irradiation decreases dramatically as the oxide impurity is removed from BaFBr (Koschnick et al 1992). It was assumed that no $\text{F(Br}^–)$ centres would be formed by $\pi$-irradiation of the ultra-pure material (Koschnick et al 1992). The absence of the creation of $\text{F(Br}^–)$ centres by x-rays in BaFBr means that the radiative decay of close $\text{F(Br}^–)+\text{H}$ pairs, if they are indeed created, is rather probable.

It has been suggested that the self-trapped exciton in many alkali halides is the nearest F–H pair (Williams et al 1986). The low-energy $\pi$ bands of triplet excitons in alkali iodides were suggested to originate from the off-centre configuration (or F+H type), while the other bands of triplet and singlet excitons originate from the on-centre configuration (Kan’no et al 1990). In contrast with this in alkaline-earth fluoride crystals the emission of only the F+H exciton configuration is observed (Williams and Song 1990, Itoh and Tanimura 1990). Perhaps, the barium fluorohalide crystals can be characterized as intermediate materials between alkali halides and alkaline-earth fluorides because emissions from $V_k + e$ as well as F+H exciton configurations are observed.

Now it is difficult to distinguish between possible explanations of the nature of the two radiative exciton configurations observed in barium fluorohalides. More investigations to clarify this question (such as ODESR and transient absorption) are needed.

5. Conclusion

Two types of exciton emission with a potential barrier between them were experimentally observed in BaFCl and BaFBr crystals. We assign the low-temperature exciton configuration to $V_k + e$ and the other to $\text{F(Br}^–)+\text{H}$ or $\text{F(e}^–)+\text{H}$.

Acknowledgment

The authors are grateful to V Otroshok for supplying the crystals and to V Zelskii for experimental assistance.
Exciton emission in BaFBr and BaFCl

Note added in proof. Recently Ohnishi et al (1993) have presented evidence that the BaFBr crystal has at least two intrinsic emission bands of triplet nature, originating probably from different configurations of self-trapped excitons with the Br₂⁺ (V₃) core. Also, a luminescence band peaking at 5.2 eV in BaFBr was attributed to the V₁⁺ + e recombination band (Kondo and Konno 1993).

References