



## EXCITON LUMINESCENCE IN BaFCl CRYSTAL\*

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**Abstract**—The luminescence spectra and decay characteristics of both 5.45 and 3.4 eV bands in BaFCl oxygen-free crystals were investigated at 5–300 K temperature range using vacuum ultraviolet excitation as well as X-ray excitation. The similarities with excitons in alkali halides allow us to consider both excitons in BaFCl as on-center excitons and strong off-center excitons. © 1998 Elsevier Science Ltd. All rights reserved

### 1. INTRODUCTION

Barium fluorohalides crystals with layered structure doped with europium show an outstanding characteristics as image phosphors. However, the defect creation mechanisms by ionizing radiation are not yet well understood. The emission from self-trapped excitons consists of two bands in BaFBr (Radzhabov and Egranov, 1994, Ohnishi *et al.*, 1996), BaFI (Kaňno, 1997) and BaFCl (Ohnishi *et al.*, 1996). The low-energy exciton emission band in BaFBr and BaFI was fully converted into high-energy emission band with decreasing temperature in the range 90–50 K (Radzhabov and Egranov, 1994; Ohnishi *et al.*, 1996; Kaňno, 1997). The two-minima model involved the thermal transition over potential barrier was developed in order to explain the temperature dependence of exciton emission as well as decay behavior in BaFBr (Radzhabov, 1995).

The excitation spectra proved that the emission from Cl, Br, I exciton were observed in BaFCl, BaFBr (Radzhabov and Egranov, 1994; Ohnishi, 1996) and BaFI (Kaňno, 1997). Other possible types of exciton were not observed experimentally.

The situation for BaFCl is more complicated. Formerly only 3.3 eV emission band was assigned to radiative recombination of excitons (Radzhabov *et al.*, 1994; Yuste *et al.*, 1975). Later, another band at 5.36 eV, which appeared below 30 K, was assigned to the luminescence of excitons (Ohnishi *et al.*, 1996). Apart from BaFBr and BaFI, both exciton bands were observed at liquid helium temperature in BaFCl (Ohnishi *et al.*, 1996).

To clarify this situation we study the luminescence spectra and luminescence decay of BaFCl crystals using vacuum ultraviolet excitation and X-ray excitation. Oxygen impurity leads to increased decay time below 30 K. The decay time measure-

ments in Radzhabov and Egranov (1994) below 30 K was influenced by presence of oxygen in crystal.

### 2. EXPERIMENTAL DETAILS

Preparation of barium fluorohalide crystals is described elsewhere (Radzhabov and Otroshok, 1995). Decay of photoluminescence was measured by single-photon technique using CAMAC time-to-digital converters or by the usual technique using CAMAC analog-to-digital converter. The 100 keV X-ray pulses with duration near 0.02  $\mu$ s were obtained from pulsed X-ray tube MIRA2D. The luminescence decay excited by X-ray was registered by oscilloscope. The emission spectra were measured with vacuum monochromator VM4, which have a flat spectral sensitivity in ultraviolet region 3–9 eV. The luminescence spectra were corrected for spectral response of spectrometer. The unfiltered light of a xenon discharge lamp with main emission band at 8.4 eV was used for measurement of exciton emission spectra.

The presence of oxygen was controlled by checking absorption and emission bands (Radzhabov and Otroshok, 1995). The oxygen impurity in BaFCl has the absorption bands above 4 eV (Radzhabov and Otroshok, 1995) and may change the exciton emission.

### 3. RESULTS

The emission bands at 3.4, 5.45 eV and near 4.2 eV were observed in BaFCl under X-irradiation [Fig. 1(a)]. The 4.2 eV band was observed under photo excitation with photo energy lower than that of exciton absorption. This band belongs to an unknown impurity. Two other bands belong to

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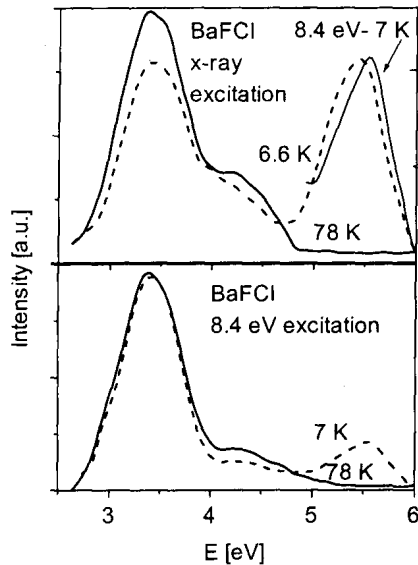


Fig. 1. Emission spectra of BaFCl under vacuum ultra-violet and X-ray excitation. They were measured at 78 K (solid lines) and at 7 K (dashed lines). The emission band near 4.2 eV belongs to unknown impurity. This band is varied from sample to sample and it is excited also by photons with energy lower than the exciton absorption energy.

excitons (Radzhabov and Egranov, 1994; Ohnishi *et al.*, 1996).

The emission spectra of BaFCl under X-ray and photo-excitation (Fig. 1) show two main features. The intensity of a high-energy band relative to 3.3 eV band is much larger under X-ray excitation than that under 8.4 eV photo-excitation. The second feature is that the position of a high-energy band is at a slightly different energy under X-ray excitation and photo-excitation. The X-ray excitation results in a 5.45 eV emission band while photo-excitation results in a 5.55 eV emission band (see Fig. 1).

The position of a 5.55 eV emission band with photo-excitation is slightly higher than 5.36 eV observed by Ohnishi *et al.* (1996).

Under continuous excitation with X-ray intensity of the 3.4 eV emission band decreases in 50–20 K region down to 0.8 of initial value. In the same temperature range the 5.45 eV band appeared and its intensity increased to an intensity of the 3.4 eV band (Fig. 2).

Using X-ray pulses both the 1 and 65  $\mu$ s decay times of the high-energy and the low-energy emission bands at 6.5 K were measured. With increasing temperature the decay time and intensity of the 5.45 eV emission band decreased above 20 K (Fig. 2). The 5.45 eV intensity and decay time are well described by the simple quenching model (Williams and Song, 1990):

$$I(T) \sim \tau(T) \sim \tau_r / [1 - \tau_r / \tau_{nr} \exp(-E/kT)]$$

where  $\tau_r$ ,  $\tau_{nr}$  are radiative and non-radiative decay times,  $E$  can be considered as energy barrier for

thermal quenching. The energy barrier  $15 \pm 3$  meV is close to 17 meV derived earlier from growth of intensity 3.4 eV emission band (Radzhabov and Egranov, 1994). The 3.4 eV band begins to decrease above 120–150 K while decay time decreased above 70 K (see Fig. 2).

In contrast with X-ray excitation, the decay curve of 3.4 eV band under photo-excitation consists of two stages: a build-up stage with rise time near 16  $\mu$ s and decay stage with time 100  $\mu$ s. The rise time does not change within 6–200 K temperature range. The decay time is constant in 6–80 K. The decay time and emission intensity decrease above 80–100 K. The build-up stage is observed at least up to 200 K. The contribution of build-up is maximal at low-energy side of exciton absorption band (8.3 eV), several times lower at high-energy side (at 9.3 and 10 eV). The slow build-up is not observed under X-ray excitation. The absence of temperature dependence indicates a tunnel process.

#### 4. DISCUSSION

It was shown that the two-level scheme is able to describe the transformation between two exciton luminescence bands in BaFBr (Radzhabov and Egranov, 1994; Radzhabov, 1995). The activation energy for transformation of on-center excitons to off-center excitons is slightly higher for intensity measurements than those for decay time measurements.

Let us discuss the possibility of the two-level scheme for BaFCl excitons. Generally the build-up stage of the off-center emission band and absence of full transformation off-center configuration to on-center one can be explained by a tunnel transition. The tunnel transition between states will lead to existence of two bands at low temperatures and to observation of build-up stage on decay of off-center band at low temperature. These features were observed. Nevertheless, there are at least two facts that contradict this model. First, the sum of intensities of the emission bands has to be constant,

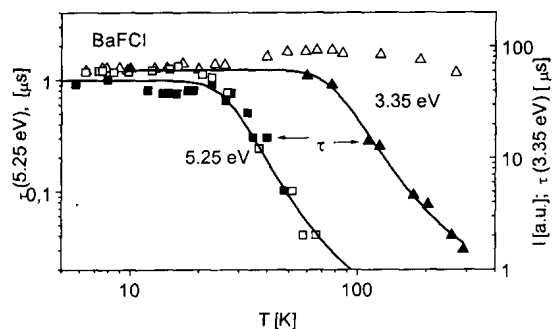


Fig. 2. Decay times (solid squares and triangles) and intensities (open squares and triangles) of both exciton luminescence bands in BaFCl under X-ray excitation.

because there is no thermal quenching below 130 K. From Fig. 1 one can see that the sum of intensities is sufficiently larger at 6 K than at 78 K. Second, according to this model the build-up stage of luminescence of a low-energy band depends on lifetime of high-energy excitons. The rise time has to diminish above 50 K together with decreasing of intensity and decay time of the 5.45 eV band. This is not observed. Therefore, the simple two-level model cannot explain the observed results.

Two exciton emission bands in BaFBr crystals were assigned to on-center and off-center triplet excitons (Radzhabov and Egranov, 1994). The optical properties of many defects in ionic solids vary systematically with host crystal lattice parameter for series of hosts with similar crystal structure (see for example Malghani and Smith, 1997). To see the trend we may use the ionic radii of Cl-Br-I instead of lattice parameter, bearing in mind that the halide radius is responsible for increase of lattice parameter in a row of chlorides-bromides-iodides. On the basis of observed exciton emission bands in BaFI (3.5, 4.5 eV) and BaFBr (4.3, 5.2 eV) one expects to observe exciton emission bands in BaFCl at near 4.5 and 5.5 eV (Fig. 3). The observed exciton band at 5.55 eV in BaFCl is close to this estimated value, while the low-energy exciton band in BaFCl is observed at about 1 eV lower energy. Obviously, the 3.4 eV exciton in BaFCl is more off-center than in BaFBr, BaFI. The 3.4 eV band has a normalized Stokes shift near 0.62,  $(E_{\text{absorption}} - E_{\text{emission}})/E_{\text{absorption}}$ . The observed shift is rather large and corresponds to the strong off-center excitons in alkali halide crystals. One can conclude that 3.4 eV self-trapped excitons in BaFCl obey a large relaxation from on-center positions.

Usually the luminescence of on-center exciton in alkali halides contains the predominant fast singlet-singlet component and slow triplet-singlet component (Song and Williams, 1993). The absence of a fast component in on-center exciton luminescence in BaFCl and BaFBr needs to be more carefully investigated.

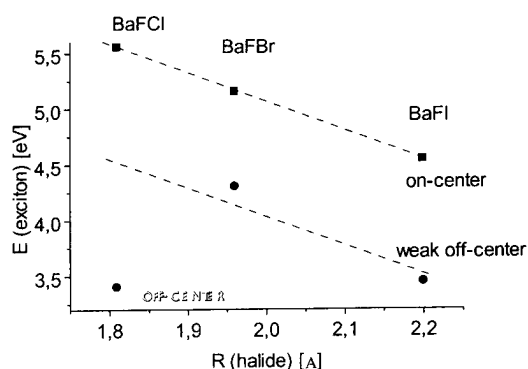


Fig. 3. Position of both exciton luminescence bands in all barium fluorohalides. The lines show the principal trend of exciton energies in different fluorohalides.

## 5. CONCLUSION

The 5.45(5.55) eV and 3.4 eV bands in BaFCl can be assigned to on-center and off-center exciton configurations. However, the relationship between both configurations is not so simple as in other barium fluorohalides.

*Acknowledgements*—I am grateful to K. Kan'no for providing the BaFI spectra before publication.

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