

Decay of exciton emission in BaFBr crystals

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Received 15 July 1994, in final form 21 October 1994

Abstract. The decay of 4.2 and 5.15 eV exciton emission bands of BaFBr crystals was studied. The 5.15 eV decay curve is exponential at all temperatures in the range 50–100 K. Above 50 K the 5.15 eV decay time decreases in parallel to the integral intensity of this band.

The 4.2 eV decay curve consists of a rise stage and decay stage. The rise lifetime decreases drastically from 200 to about 0.1 μ s in the range 60–100 K. The decay time is constant and equal to about 7 μ s.

The results obtained are satisfactorily explained by a simple model with two potential minima in the triplet excited state. The potential barrier between two states derived from the temperature behaviour of the rise time is 47 meV.

1. Introduction

The studies of temperature dependence of the intrinsic exciton emission of BaFBr and BaFCl crystals upon VUV excitation, x-irradiation or visible-light photostimulation show that at least two different radiative exciton configurations separated by a potential barrier have been observed in both crystals [1]. Two exciton emission bands at 4.2 and 5.15 eV were observed in the BaFBr crystal. Upon increasing the temperature above 50 K the 4.2 eV emission increased at the expense of the 5.15 eV band [1]. Recently Kan'no and co-workers [2] 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 $\text{Br}_2^-(V_k)$ core.

In this paper we report results on exciton luminescence decay under direct excitation into exciton absorption bands.

2. Experimental details

The preparation of barium fluorohalide crystals has been described elsewhere [3]. Decay of emission was measured by the single-photon technique using CAMAC time-to-digital converters or by the usual technique using a CAMAC analogue-to-digital converter. The home-made stainless steel flashlamp was filled with argon or hydrogen gas under a pressure of 1–3 atm. The duration of flash was about 0.02 μ s. The sample is excited through a VMR2 vacuum monochromator and emission is observed through an MDR2 grating monochromator. The decay time was independent of the photon energy of excited (or emission) light within the exciton absorption (or emission) band.

The emission from BaFBr was different from that created by $V_k + e$ recombination [1]. The difference probably related to a modification of the decay curve by thermal excitation of electrons from shallow traps during $V_k + e$ creation. Earlier decay curve modification was observed in the exciton emission from alkali iodide crystals [4].

3. Experimental results

The decay of 5.15 eV emission is exponential at all temperatures. At 50 K the lifetime has a value of about 10 μ s. Above 50 K the 5.15 eV band lifetime decreases in proportion to its integral intensity (figure 1). The decrease in intensity of the 5.15 eV emission band was explained by introducing a thermally activated transformation from one exciton configuration into the other, which competes with the 5.15 eV radiative transition [1]. The parallel decrease in decay time with integral intensity is fully in line with this conclusion. They should be parallel in a simple model, when an electron transfers over the potential barrier into another state or into the ground state.

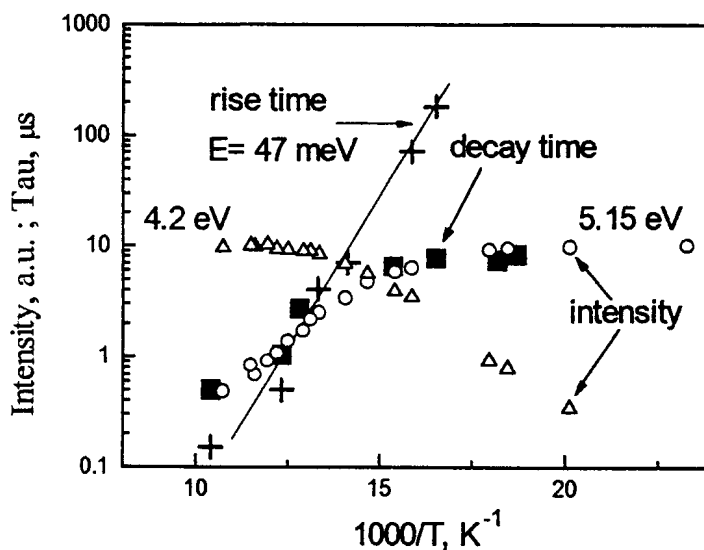


Figure 1. Decay and rise times as well as integral intensities of exciton emissions of BaFBr (a.u., arbitrary units); ○, integral intensity of 5.15 eV emission; Δ, integral intensity of 4.2 eV emission; ■, decay time of 5.15 eV emission; +, rise time of 4.2 eV emission. The decay time of 4.2 eV emission (not shown) is constant and equal to 7 μ s.

The pulse shape of the 4.2 eV exciton emission band is more complicated. It consists of two stages: a rise and a decay (figure 2). The rise is rather short at 80 K but increases drastically with decreasing temperature. The decay time is constant above 80 K and equal to about 7 μ s. At lower temperatures it visually slightly decreases (see figure 1). It also may be connected with the influence of a slow rise on the decay curve.

4. Discussion

The results obtained in the previous paper [1] indicate that in barium fluorohalides (BaFCl and BaFBr) the excitons have two configurations separated by an energy barrier. Recombination from both configurations yields emissions that are spectrally indistinguishable in BaFCl, have 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). The

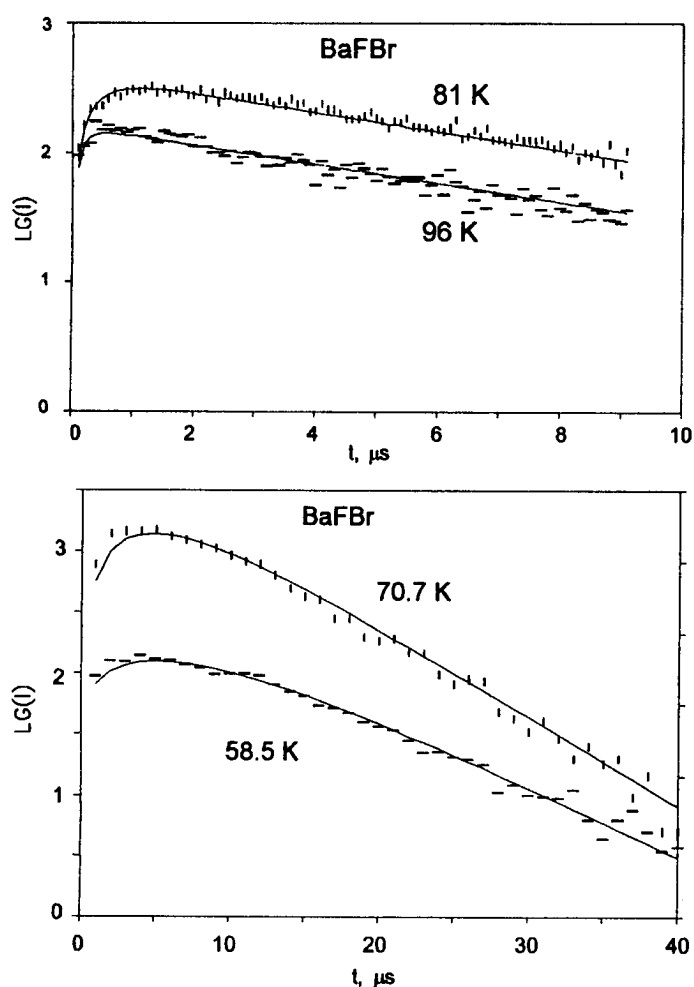


Figure 2. Decay curves of the 4.2 eV emission band in BaFBr crystals. The curves are a least-squares fit of equation (6) to the data points shown.

new results on the decay of exciton luminescence are in reasonably good agreement with this conclusion. The observation of the 4.2 eV emission rise stage, which decreases upon increasing the temperature, indicates that this state is populated from another long-lived state.

The total scheme of the radiative process for BaFBr can be pictured as in figure 3. The system quickly relaxes into the adiabatic potential minimum 1 after excitation. Then, if the temperature is rather low, the electron has only a radiative transition to the ground state with the emission of the 5.15 eV photon. At high temperatures the electrons also transfer over the potential barrier to the adiabatic potential minimum 2. From this minimum the electron has only a radiative transition to the ground state with the emission of a 4.2 eV photon. This scheme of process also follows from the thermal behaviour of integral intensities of the exciton bands of BaFBr [1].

Let us consider the emission process in more detail using this model (figure 3). The

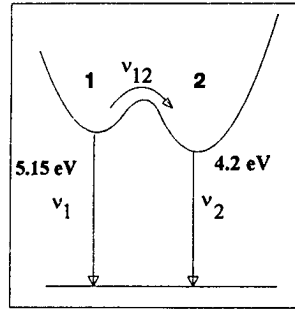


Figure 3. A schematic diagram of the transitions involved in exciton emission of BaFBr crystals. Here ν_1 and ν_2 are the radiative probabilities, and ν_{12} is the probability of radiationless transitions from excited states 1 to 2.

rate equations are

$$dn_1/dt = -(\nu_1 + \nu_{12})n_1 \quad (1)$$

$$dn_2/dt = -\nu_2 n_2 + \nu_{12} n_1 \quad (2)$$

where n_i are the populations of minimum i , ν_i are the radiative transition probabilities from minimum i and ν_{12} is the radiationless transition probability from minimum 1 to minimum 2. The thermal transitions are described as

$$\nu_{12} = \nu_0 \exp(-E/kT) \quad (3)$$

where E is the potential barrier from minimum 1 to minimum 2, k is the Boltzmann constant and $\nu_0 = \tau_0^{-1}$ is the frequency factor. The intensity of emission from minimum i is $n_i \nu_i$. Solving the rate equations, we have the following solutions.

For the first equation,

$$I_1 = I_0 \exp[-(\nu_1 + \nu_{12})t] \quad (4)$$

where I_0 is the initial intensity ($\nu_1 n_{10}$). It describes an exponential decay curve. The normalized integral intensity S decreases in proportion to its lifetime upon increasing the temperature as follows [5]:

$$S_1 = \tau(T)/\tau_0 = 1/[1 + (\tau_1/\tau_0) \exp(-E/kT)]. \quad (5)$$

The emission intensity of the second equation is

$$I_2 = (\nu_2 n_{10}/B) \exp(-\nu_2 t) [1 - \exp(-B \nu_{12} t)] \quad (6)$$

where $B = 1 + (\nu_1 - \nu_2)/\nu_{12}$. On the right-hand side of the equation the first term is the initial intensity, and the second and third terms describe a decay and a rise, respectively, in the intensity. At rather high temperatures the emission rapidly reaches a maximum and then decays with the radiation lifetime $\tau_2 = 1/\nu_2$, which does not depend on the temperature. At these temperatures the decay lifetime may be well determined. At low temperatures when the radiationless probability of transition is lower than the radiative probability of transition, the emission decay curve visually became a little slower. The calculated curves

fit the experimental data reasonable well (see figure 2). There is some deviation between the fit and experimental points at low temperatures (see figure 2) in the first 2 μ s. Possibly this deviation is due to another rise which is somewhat faster.

The normalized integral intensity of emission from second minimum is

$$S_2 = 1 - S_1 = 1/[1 + (\tau_0/\tau_1) \exp(E/kT)]. \quad (7)$$

The determination of the rise time at different temperatures gives us the possibility of establishing ν_0 and E . Earlier these two values were evaluated using the temperature variation in the integral intensities of the 4.2 and 5.15 eV emissions of BaFBr by equations (5) and (7) [1]. The earlier and the new parameters are given in table 1. The disagreement between the potential barriers is rather small, but disagreement between the values of ν_0 is about three decades. If we use the new parameters to calculate the integral intensities, the result is poor.

Table 1. The old [1] and new parameters related to the thermally activated transformation of one exciton configuration into the other in BaFBr crystals.

BaFBr	ν_0 (s^{-1})	E (meV)
Old [1]	1×10^{10}	64 ± 5
New	1.6×10^{13}	47 ± 4

The thermally activated radiationless processes in crystals can be fitted well to an Arrhenius equation over a limited temperature range, although the fitting parameters have an uncertain physical significance [6]. Thus the thermal trap depth should not be identified too literally with specific features of the energy level diagram [6]. Obviously the simple three-states model cannot explain all the features of the exciton emissions of the BaFBr crystal. The integral intensities of both bands and the 5.15 eV band decay time can be better described using the old E and ν_0 parameters [1]. The temperature dependence of the rise time of the 4.2 eV band leads to an energy which is a little lower but to a τ_0 -value which is three decades smaller. The discrepancy between the new and old parameters is much greater than experimental error. Therefore this model is only a rough approximation.

The calculations, based on both extended-ion and *ab initio* Hartree-Fock methods, show that the potential barrier separating the adjacent local minima on the adiabatic potential energy surface of excitons in alkali halides becomes smaller as the lattice is dilated [7]. In NaBr and NaI crystals, extra types of exciton emission band have been observed under dilational strain [8]. Obviously the potential barrier may also be lowered owing to thermal expansion of the lattice. This may be the reason for the discrepancy between the old and the new parameters E and ν_0 .

A similar decay curve with a rise stage was observed for other crystals. In BaF₂ after high-energy pulse excitation the emission of self-trapped excitons increased gradually to a maximum and then decayed. The time to reach the maximum can be decreased from 80 to 30 ns by increasing the temperature from 300 to 330 K. The most likely reason for the intensity increase is that the rate of energy transfer from free excitons to self-trapped excitons is faster than the luminescence decay from self-trapped excitons [9].

The excitons in alkali halide crystals have a symmetry-breaking off-centre instability in the $V_k + e$ configuration. There are multiple local minima in the adiabatic potential energy surface of the lowest exciton energy. Depending on the crystals, each of the three types, which correspond to the on-centre or two different off-centre exciton configurations,

may appear alone or together in the exciton luminescence [10]. Self-trapped excitons in RbI and RbBr:I are stable both in type-II and type-III configurations, which are regarded as accompanied by two different lattice relaxation modes of off-centre type [11]. The population conversion of type III \rightarrow type II occurs via a thermal activation process with a very low frequency factor of $6 \times 10^4 \text{ s}^{-1}$ and a small activation energy of 7 meV [11]. These results are similar to ours, but no long rise stage in the luminescence pulse profile of the type-II exciton was observed.

In the previous paper we tentatively concluded that the low-temperature configuration 1 belongs to the on-centre exciton and the high-temperature configuration 2 belongs to the off-centre exciton [1]. The new results provide more details about the conversion process, but they cannot add more about the nature of these exciton configurations.

5. Conclusion

The decay of the exciton 5.5 eV band of BaFBr is exponential at all temperatures. With increasing temperature above 50 K the decay time decreases in parallel to the integral intensity of this band. The decay curve of the exciton 4.2 eV band shows a rise and a decay. The rise time drastically decreases with increasing temperature. The observed results are satisfactorily explained by a simple model with two potential minima in the excited state. The values of the barrier energy E calculated using the temperature dependence of the rise time are not too different from those calculated using integral intensities.

Acknowledgments

This work was partially supported by the program Radiation Physics of Solid States under the State Committee of Education of Russian grant N 31222/L-4.

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