Configurations of excitons in BaF_2–LaF_3 crystals

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Abstract
Exciton luminescence was investigated in La-doped BaF_2 crystals. Two
luminescence bands at 4.26 and 3.82 eV related to excitons have been observed.
The excitation spectrum of the 4.26 eV band of BaF_2–LaF_3 was similar to that of
the exciton emission band of pure BaF_2 crystals. The excitation spectrum of the
3.82 eV band shows a new band within the 8–9 eV region. The band becomes
most prominent for BaF_2–3 wt% LaF_3 and has a maximum at 8.7 eV at 290 K.

The decay time for the 4.26 eV emission band of BaF_2–3% LaF_3 consider-
ably increased with decreasing temperature like the exciton decay time for pure
BaF_2, where the decay time of unperturbed excitons grows to 121 μs at 17 K. In
contrast to this, the decay time of the 3.82 eV band increases from 4.1 μs at 290 K
to 6.2 μs at 15 K. The significant reduction of the triplet–singlet decay time can
be associated with strong interaction of excited electrons with lanthanum ions.

It was concluded that the 4.26 eV emission band is associated with weakly
perturbed excitons, while the 3.82 eV band is associated with strongly perturbed
excitons. The possible spatial configurations of excitons are discussed.

1. Introduction

Pure BaF_2 crystals are known as the most effective fast scintillators with decay times <1 ns [1].
The fast decay is due to radiative transitions from the valence band to the core Ba band; this
is described as cross-luminescence. The intense slow component of exciton emission can be
considerably suppressed by introducing trivalent rare-earth ions: La [2–4], Ce [5], Nd [5] or
others [6]. Exciton luminescence is also suppressed by introducing the divalent ions Mg, Sr [7]
and Cd [8]. However, the mechanism of suppression is still unclear. In spite of some growth
problems, the BaF_2–LaF_3 system remains very promising. Investigation of impurity-related
excitons may help to clarify the suppression mechanism.

During previous investigations we found interstitial fluorine F_{int}^- levels appearing above
the fluorine valence band for BaF_2–LaF_3 crystals. When the La concentration is increased to a
few per cent, the F_{int}^- levels create a subband. Creation of an interstitial fluorine subband leads

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to decrease of the band gap and to the appearance of a new high-energy cross-luminescence band [9]. It seems that the interstitial fluorine states play a key role in the creation of impurity-related excitons.

We investigate the luminescence of BaF_2 crystals doped with LaF_3 to different concentrations, 0.1–5%, excited by vacuum ultraviolet photons in the exciton and sub-exciton region 8–10 eV. We observe a new emission band which is enhanced by increasing La doping, while the intrinsic exciton luminescence is reduced. We suggest that the two configurations of excitons can be considered as excitons weakly and strongly perturbed by lanthanum ions.

2. Experimental details

The spectra in the 4–10 eV region were measured with a grating vacuum monochromator, VMR2. Emission spectra were recorded using a grating monochromator, MDR2. All emission spectra were corrected for monochromator dispersion and photomultiplier response.

The decay of the photoluminescence was measured by a single-photon technique using CAMAC time-to-digital converters. A free-running high-voltage spark between W electrodes in 2–4 atm of argon gas was used as the pulsed light source. The duration of the excitation pulse at half-maximum was about 10 ns.

The crystals were grown in vacuum with the addition of 0.1–30 wt% of LaF_3. A few per cent of CdF_2 or PbF_2 were added as oxygen scavengers. The crystals were grown in our laboratory by Ivashechkin. Polished samples of BaF_2–LaF_3 and cleaved samples of undoped BaF_2 measuring approximately $8 \times 8 \times 2$ mm were used.

The excitation spectra for individual emission bands were derived from measured excitation spectra. In our case two emission bands are observed. The intensity of light emitted at fixed wavelength λ_{ems} can be written as

$$I_i(\lambda_{ems}) = k_1 I_i(\text{band 1}) + k_2 I_i(\text{band 2}), \tag{1}$$

where I_i are the excitation spectrum intensities for the respective emission bands, k_i are the relative intensities of individual emission bands at the measurement wavelength. The weight coefficients k_i were taken from normalized emission spectra of individual emission bands (figure 2). From excitation spectra at two emission wavelengths, we obtain two sets of equations for two variables. Solving the equations we obtain I_i, the excitation spectra for the individual emission bands.

3. Results

3.1. Excitation

The x-ray-excited emission of undoped BaF_2 crystals consists of a broad band centred near 4.0 eV, which is associated with the luminescence of excitons [10]. This band can be fitted by three Gaussian bands, which have slightly different decay times at room temperature. Three bands have been associated with different spatial configurations of the excitons in BaF_2 [11]. The broad exciton emission band is excited above 8.8 eV for undoped BaF_2 (figure 1).

With La doping, the intensity of the excitation spectra decreases in the region above 9 eV, while it increases at lower energies. The luminescence intensity at 4.0 eV for BaF_2–5% LaF_3 becomes nearly ten times lower than that of undoped BaF_2 under 9.5 eV excitation (see figure 1). This value is similar to that observed under x-ray excitation [9]. A new excitation band appears for BaF_2–LaF_3 in the 8–9 eV region. The band becomes clear for BaF_2 crystals doped with 3% LaF_3 and is centred at 8.7 eV at room temperature (see figure 1).
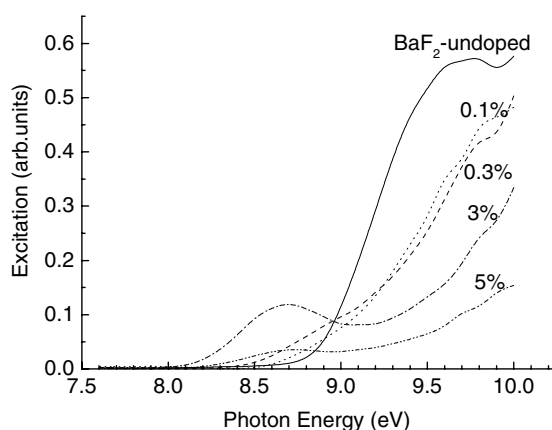
Figure 1. Excitation spectra of the luminescence measured at 4.0 eV for BaF$_2$ and BaF$_2$–LaF$_3$ crystals at room temperature.

3.2. Emission

An exciton emission band with a maximum near 4 eV has been observed for undoped BaF$_2$ crystals excited by light with photons of energies above 9 eV at 78 K. The band is well fitted by a single Gaussian with a maximum at 4.20 eV and halfwidth 0.93 eV (figure 2(b)).

Another emission band was observed for BaF$_2$–LaF$_3$ under excitation in the range 8–9 eV. This band is well fitted by a Gaussian peak with a maximum at 3.82 eV and halfwidth 0.81 eV (figure 2). Usually the impurity-perturbed exciton emission bands of ionic crystals have excitation bands lying in the low-energy tail of the exciton absorption [19]. This tendency was also observed for CaF$_2$ doped with Li$^+$, Na$^+$, Mg^{2+} and Mn^{2+} impurities [20]. It is reasonable to assume that the 3.82 eV emission band relates to the perturbed exciton.

A broad emission spectrum centred near 4.2 eV was observed for BaF$_2$–LaF$_3$ crystal upon excitation above 9 eV at 78 K (see figure 2(b)). The emission spectrum is well fitted by a Gaussian band with a peak at 4.26 eV and halfwidth 1.08 eV. The peak of the emission band is close to that of the exciton emission observed for undoped BaF$_2$, while the halfwidth is 16% wider. The excitation spectrum of the 4.26 eV emission band of BaF$_2$–LaF$_3$ is similar to that of the exciton band of undoped BaF$_2$ (compare figures 1 and 2), while the excitation spectrum for the 3.82 eV band shows an apparent peak at 8.8 eV (see figure 2). One may assume that the 4.26 eV emission band of BaF$_2$–LaF$_3$ arises from emission of weakly perturbed excitons.

At room temperature the short-wavelength side of the 3.82 eV band shifts to higher energies (see figure 2). Increase of the emission monitored at 4.5 eV was observed above 170 K for 8.7 eV excitation of BaF$_2$–LaF$_3$. The emission spectra for 8.7 and 9.5 eV excitations are similar at 324 K, while they are different at lower temperatures (see figure 2). Therefore, above 170 K an exciton perturbed by a lanthanum ion can leave the impurity and become weakly perturbed and vice versa. At 324 K the two excitons are in thermal equilibrium. Taking into account that emission band shapes depend very slightly on temperature, we fit the emission spectrum at 324 K using known parameters for 3.82 and 4.26 eV bands (see figure 2(c)).

3.3. Decay of luminescence

The 3.82 eV emission band overlaps considerably with the 4.26 eV band. However, for excitation above 9.6 eV one obtains 'pure' 4.26 eV emission (see figure 2, excitation
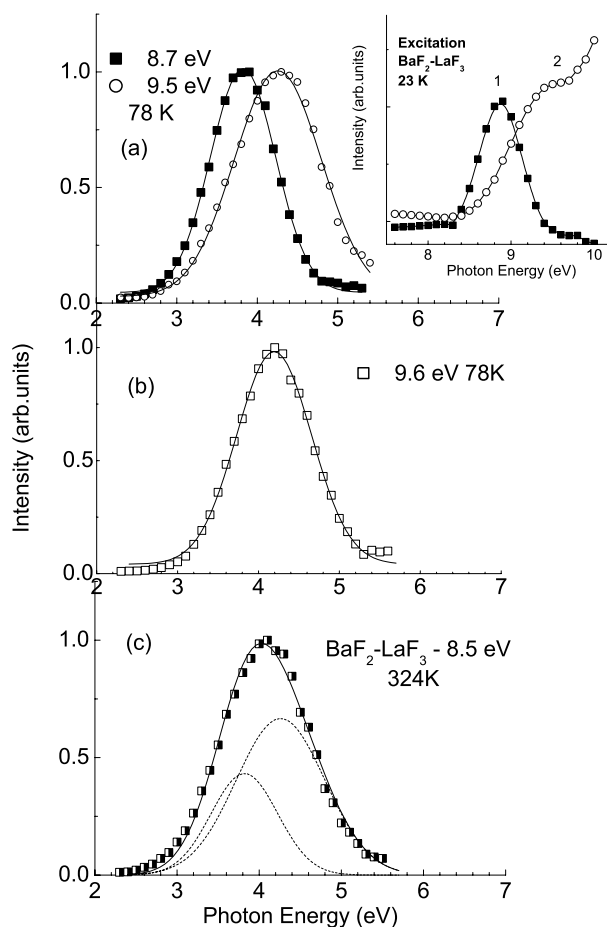
Figure 2. Normalized emission and excitation spectra of undoped BaF_2 and BaF_2–3% LaF_3 crystals. Emission spectra (a)–(c) were measured at the excitation energies and temperatures indicated. The excitation spectra in plot (a) for emission bands at 3.82 eV (1) and 4.26 eV (2) were derived as explained in section 2. Emission spectrum (c) was measured with either 8.5 or 9.6 eV excitation at 324 K. The choice as regards fitting Gaussian bands is described in the text.

spectra (a)). On the other hand, the emission of weakly perturbed excitons cannot be excited below 8.7 eV. Therefore with 8.6 eV excitation one obtain 'pure' 3.82 eV emission (see figure 2, emission spectra (a)).

We observe exponential decay curves for both luminescence bands of BaF_2–3% LaF_3 at room temperature with similar decay times, around 4.1 μs, under excitation throughout the 8–10 eV region. No fast component of decay was observed. The decay time of the 3.82 eV band slightly increased to 6.2 μs at 15 K (figure 3). In contrast to this, the decay times of the 4.26 eV band of BaF_2–3% LaF_3 and the 4.0 eV band of BaF_2 considerably increase with decreasing temperature (see figure 3). The decay curve for the 4.26 eV emission band remained similar throughout the whole region from 3.3 to 4.5 eV at 78 K.

With increasing temperature above 78 K the decay time of the 4.26 eV band is decreased and near 250 K becomes equal to that for the 3.6 eV band (see figure 3). This behaviour accords with the above-mentioned assumption of thermal equilibrium of the two exciton configurations.
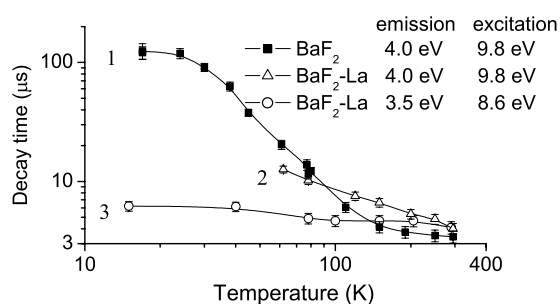
Figure 3. Decay times of emission bands observed for undoped BaF$_2$ (1) and in BaF$_2$–3% LaF$_3$ (2, 3) crystal. The unperturbed exciton emission for undoped BaF$_2$ was monitored at 4.0 eV under excitation at 9.8 eV. Perturbed (3) and weakly perturbed (2) exciton emissions for BaF$_2$–3% LaF$_3$ were monitored at 3.6 and 4.0 eV under excitation at 8.6 and 9.8 eV, respectively. The excitation energies as well as the energies at which the emissions are measured are also indicated in the plot.

Indeed, for a two-level system in thermal equilibrium the decay times of the two levels are equal and can be calculated using

$$\tau = (1/\tau_1 + 1/\tau_2)^{-1}. \tag{2}$$

Here τ_1, τ_2 are radiative decay times. The radiative decay times at 17 K are equal to 121 μs for BaF$_2$ and 6.2 μs for BaF$_2$–LaF$_3$. Therefore, the decay time in equilibrium must be 5.9 μs, which is close to the experimental value, 5 ± 0.4 μs (see figure 3).

The difference in decay time between the unperturbed exciton band of BaF$_2$ and the 4.26 eV band of BaF$_2$–LaF$_3$ is not very large (see figure 3). This clearly indicates that the 4.26 eV excitons in BaF$_2$–LaF$_3$ can be considered as weakly perturbed excitons.

4. Discussion

The structures of the relaxed self-trapped excitons in fluorite crystal and the possible configurations have been revealed in the papers [12, 13]. The self-trapped exciton is composed of a F$_2^-$ molecular ion oriented in a [111] direction, commonly referred to as the H-centre part, and in the F-centre part there is an electron occupying a vacant F$^-$ site. The possible configurations differ in relative positioning of the F- and H-centre parts. The most plausible structure is configuration II which is formed by a dynamic process of self-trapped exciton formation without any additional ionic rearrangement [14]. Recently, exciton luminescence in fluorite crystals has been investigated using femtosecond laser excitation [11, 18].

In fact the excitation band, emission band and decay times of the 4.26 eV band of BaF$_2$–LaF$_3$ and those of the unperturbed exciton band of undoped BaF$_2$ are very similar. However, the decay time for BaF$_2$–3% LaF$_3$ is slightly different from that for unperturbed excitons. Therefore, we assume that the 4.26 eV emission band of BaF$_2$–3% LaF$_3$ arises from weakly perturbed excitons.

There is experimental evidence that interstitial fluorine states in BaF$_2$:LaF$_3$ lie above the top of the valence band [9]. According to quantum chemical calculations for BaF$_2$:LaF$_3$ crystals, interstitial fluorine states appear above the top of the valence band [16, 17] and La states appear below the bottom of the conduction band [16]. Therefore, during illumination into the impurity excitation band of La-doped BaF$_2$ crystal, electrons transfer from interstitial fluorine states to La states. The hole remains on the fluorine interstitial. We suppose that this hole very quickly becomes self-trapped, creating the H-centre part of the exciton. Therefore

the structure of the 3.82 eV exciton in La-doped BaF_2 can be considered as a F_2^- interstitial (H centre) near a La^{3+} ion plus a trapped electron. Considerable reduction of the decay time of triplet–singlet transitions compared against that of 'normal' excitons is evidently associated with the spin–orbital interaction of the trapped electron with the heavy-metal ion. Triplet–singlet transitions in many molecular systems become more allowable in the presence of heavy atoms [21]. One may conclude that, apart from in weakly perturbed excitons, where the excited electron is localized on an anion vacancy, the electron of a perturbed 3.82 eV exciton has to be localized on a La ion. Results show that above 170 K, some of the perturbed 3.82 eV excitons convert to weakly perturbed 4.26 eV excitons (see section 3.2). Above room temperature, the two excitons are in thermal equilibrium. One may conclude that exciton configurations are separated by a potential barrier. The height of the barrier can be roughly estimated as 0.5–1 eV.

On the basis of quantum chemistry calculations as well as previous experimental results, Catlow concluded that an electron loosely trapped by a La ion in CaF_2 is able to create a pair composed of an F centre and a fluorine interstitial [22]. As a result, the so-called photochromic PC^+ centre is created. This process needs some thermal energy, possibly to effect the displacement of the interstitial to a site more remote from the F centre [22]. No stable photochromic PC centres are created in BaF_2 crystals [23]. We conclude that this process can be effective in some way in BaF_2. Indeed, at low temperatures the illumination into the 8.6 eV band creates an exciton in the form of an H centre and an electron trapped at La^{3+}. At high enough temperature the trapped electron creates an F centre and an interstitial. The F centre and neighbouring H centre combine into an exciton weakly perturbed by a La^{3+}–F_i^- pair.

At large enough temperature, the weakly perturbed exciton may transform back to a perturbed exciton. However, the exact spatial structure can be obtained by magnetic resonance investigations.

We assume that the conversion of a weakly perturbed configuration to a perturbed one which we observed in BaF_2–3% LaF_3 plays a role in the suppression of the exciton emission. Indeed, the perturbed excitons have considerably lower quantum yield than unperturbed ones (compare the excitation regions below and above 9 eV in figure 1). This is the reason for the decrease in intensity of the exciton emission at room temperature with increasing La concentration observed earlier for BaF_2 [2]. In general, the process of transformation of weakly perturbed excitons to perturbed ones does not depend on the type of impurity. In accordance with this, exciton luminescence suppression was observed in BaF_2 crystals doped with different Re^{3+} ions [6] or divalent ions [7, 8]. The suppression process may begin with direct trapping of a hole by fluorine interstitials as proposed in the paper [16]. After trapping of a free electron by a positively charged neighbouring La^{3+} ion, the perturbed exciton is created. Now we will go on to perform experiments to clarify the role of interstitials in suppression of exciton luminescence in BaF_2–LaF_3.

5. Conclusions

Two exciton emission bands at 4.26 and 3.82 eV were observed for BaF_2–LaF_3 crystals using vacuum ultraviolet excitation. The 4.26 eV band has a similar excitation spectrum and similar decay times to the intrinsic excitons in undoped BaF_2. The 3.82 eV emission band is excited at lower energies, showing a well shaped excitation band at 8.9 eV. The decay of the 3.82 eV luminescence at low temperatures is considerably quicker than that of the 4.26 eV band, which can be associated with the heavy-atom effect on triplet–singlet transitions. The 4.26 and 3.82 eV bands can be assigned to weakly perturbed and strongly perturbed excitons, respectively.

Acknowledgment

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