

Suppression of self-trapped exciton luminescence in La^{3+} - and Nd^{3+} -doped BaF_2

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1992 J. Phys.: Condens. Matter 4 5281

(<http://iopscience.iop.org/0953-8984/4/23/005>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.96

The article was downloaded on 11/05/2010 at 00:16

Please note that [terms and conditions apply](#).

Suppression of self-trapped exciton luminescence in La^{3+} - and Nd^{3+} -doped BaF_2

P Dorenbos, R Visser, R Dool, J Andriessen and C W E van Eijk

Delft University of Technology, Department of Applied Physics, Radiation Technology Group, Mekelweg 15, 2629 JB Delft, The Netherlands

Received 16 December 1991, in final form 2 March 1992

Abstract. The self-trapped exciton (STE) luminescence at 300 nm with a decay time of 620 ns in pure BaF_2 can be suppressed by La^{3+} or Nd^{3+} doping. Crystals were studied with La concentrations ranging from 0.2 mol% to 22 mol% and Nd^{3+} concentrations between 0.15 and 11 mol%. X-ray induced emission spectra at temperatures from 90 K to 430 K and decay-time spectra are presented. Information about trapping of electrons by La^{3+} ions and the activation energy for thermal quenching of STE luminescence is obtained from a fit of the experimental data to a model calculation. The conclusions obtained for La^{3+} -doped crystals can also be employed for explaining similar aspects of the STE luminescence observed for the Nd^{3+} -doped BaF_2 crystals.

1. Introduction

BaF_2 single crystals are applied as scintillation materials for gamma ray detection in many high-energy physics experiments. Fast timing is possible with these crystals because of luminescence at 195 and 220 nm with the very short decay time of about 0.8 ns. BaF_2 also has an intense, slow emission component at 300 nm with a decay time of about 620 ns at room temperature [1]. This component can cause serious pile-up problems in experiments where high count rates are expected. Future particle accelerators like the superconducting super collider (SSC) and the large hadron collider (LHC) are anticipated to operate at interaction rates of about 10^8 s^{-1} . The suppression of slow emission components will then be a key issue in the design of a fully active electromagnetic calorimeter; see e.g. Lorenz [2].

The slow component is caused by luminescence of self-trapped excitons (STE). This emission component can be suppressed considerably by La^{3+} doping [3,4] without affecting the intensity of the fast component. We suggested two possible mechanisms to obtain a qualitative explanation for this suppression [3]: (i) electrons are efficiently trapped from the conduction band in a La^{3+} ion thus preventing the formation of STEs, (ii) La^{3+} increases the thermally induced non-radiative decay rate of STEs.

In this work we present x-ray induced emission spectra of the La^{3+} -doped crystals recorded as a function of the temperature ($90 \text{ K} < T < 430 \text{ K}$). The STE luminescence photon yield per MeV of absorbed energy was estimated from the emission spectra. A model, based on the two mechanisms mentioned above, was used to interpret the results.

2. Experimental methods

The single crystals used in this work were grown in He atmosphere by means of the Bridgman technique by den Hartog and co-workers at the University of Groningen, the Netherlands. PbF_2 was added to the starting materials as a scavenger for O^{2-} impurities and water vapour. Cylindrically shaped crystals 3 or 5 mm high and with a diameter of 7.5 mm were cut from the original single-crystal boules. The top and bottom faces of the crystals were optically polished. The La or Nd concentrations reported in this work are nominally concentrations as determined from the 'weighted-in' molar ratio of LaF_3 or NdF_3 to BaF_2 . The optical transmission uncorrected for Fresnel reflections, of the La-doped crystals was about 90% at wavelengths between 350 and 600 nm and 60% to 75% at wavelengths near 200 nm. The Nd^{3+} -doped crystals showed characteristic optical absorption lines caused by 4f-4f transitions in Nd^{3+} ions, which were also observed by Woody *et al* [4].

An ARC (Acton Research Corporation) vacuum monochromator (model VM-502) with a 1200 grooves mm^{-1} concave holographic grating blazed in first order at 250 nm was employed to measure the luminescence spectra of the crystals under x-ray irradiation with a wavelength resolution of 4 nm. For studying the scintillation properties as a function of temperature, a cryostat can be mounted on the monochromator. The temperature of a crystal placed in the sample holder of the cryostat can be varied from 95 K to 450 K. X-rays from an x-ray tube with a copper anode operating at 35 kV can enter the cryostat through a 0.3 mm thick Be window. An XP2020Q photomultiplier tube (PMT) operating in current mode is mounted behind the exit slit of the monochromator and measures the transmitted light. The emission spectra presented in this work were not corrected for the quantum efficiency of the PM-tube or for the transmission of the monochromator. This does not affect the conclusions drawn in this paper.

Decay-time spectra of the scintillation emission from the crystals were determined by means of the single-photon counting technique described by Bollinger and Thomas [5]. XP2020Q PMTs were used as start and stop photomultipliers. The crystals studied were mounted with an optical-coupling compound to the window of the start PMT and irradiated by a ^{137}Cs gamma source. The stop photomultiplier detects single photons. The time resolution of the set-up is about 0.5 ns. We first recorded the decay-time spectrum in the time interval 0-800 ns, then in the time interval 0.5-8 μs , and finally in the time interval 5.0-80.0 μs . Detection of single photons was inhibited in the time intervals 0-0.5 μs and 0-5 μs in the latter two recordings; this was necessary in order to improve the signal to noise ratio. The three decay-time spectra together yield one decay-time spectra for the entire interval 0-80 μs . A correction was made for false counts due to random coincidences and Cherenkov light created in the PM window.

3. Experimental results

Figure 1 shows the x-ray induced emission spectra of a pure BaF_2 crystal and five La^{3+} -doped BaF_2 crystals at room temperature. The emission peaks at 195 and 220 nm are caused by cross luminescence (CL) in the BaF_2 host crystal. A third CL maximum which is present at 175 nm [6] is not observed because of optical absorption in a layer of air between the PMT and the exit window of the monochromator. The broad emission band with maximum intensity at 300 nm is the STE luminescence.

Its intensity decreases with increasing La concentration and almost disappears at a La concentration of about 6 mol%. The intensity of the fast component is much less dependent on the La concentration. Similar properties were observed for Nd^{3+} -doped BaF_2 crystals, see figure 2. There are some additional features in these latter spectra: (i) an optical absorption band near 180 nm, caused by 4f-5d transitions in Nd^{3+} ions [7], absorbs part of the CL of the BaF_2 host crystal, (ii) the overall CL intensity decreases with increasing Nd concentration, and (iii) 4f-4f optical absorption bands can be observed near 330 nm and 350 nm and faint 4f-4f emission bands are observed near 360, 380 and 415 nm. Note that the BaF_2 emission spectrum in figure 2 deviates a little from that shown in figure 1 because it pertains to another crystal. The crystal contains about 10 ppm Ce^{3+} which causes a faint optical absorption at 290 nm and faint emissions at 305 and 320 nm.

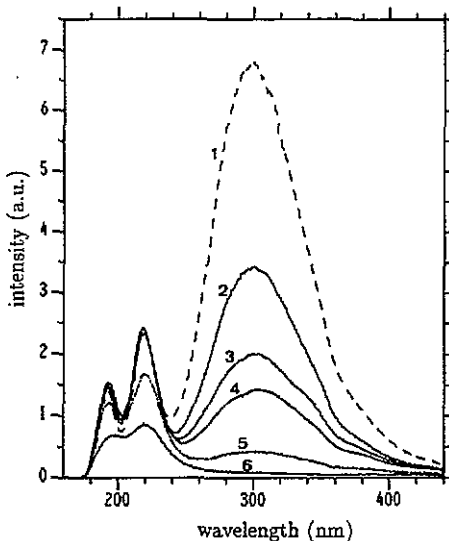


Figure 1. X-ray induced emission spectra of crystals of thickness about 5 mm at room temperature. (1) pure BaF_2 , (2) BaF_2 : 0.2 mol% LaF_3 , (3) BaF_2 : 0.5 mol% LaF_3 , (4) BaF_2 : 1.3 mol% LaF_3 , (5) BaF_2 : 6.0 mol% LaF_3 , (6) BaF_2 : 22 mol% LaF_3 .

Figure 3 shows emission spectra of BaF_2 doped with 0.5 mol% La^{3+} as a function of temperature. We first recorded the emission spectrum at room temperature. After heating the crystal by about 20 K, the next spectrum was recorded. This was repeated until a temperature of 420 K was reached. Then the crystal was cooled to 95 K and the emission spectra from 95 K to room temperature were recorded. The STE luminescence intensity at 300 nm in figure 3 decreases with increasing temperature. Similar thermal quenching behaviour was observed for pure BaF_2 [8] and has been reported for many other inorganic scintillators [9, 10]. The intensity of the CL peaks at 195 and 220 nm remains constant when the temperature increases from room temperature to 420 K, see spectra 1, 2 and 3 in figure 3. However, CL intensity is significantly less at 95 K (spectrum 4) and decreases even more for the subsequently recorded spectra in the temperature range from 95 to 220 K. We attribute this to self-absorption caused by accumulation of radiation damage. An emission band is observed near 350 nm which reaches a maximum intensity at temperatures of about 160 K, see spectrum 5. This emission and the self-absorption below 250 nm

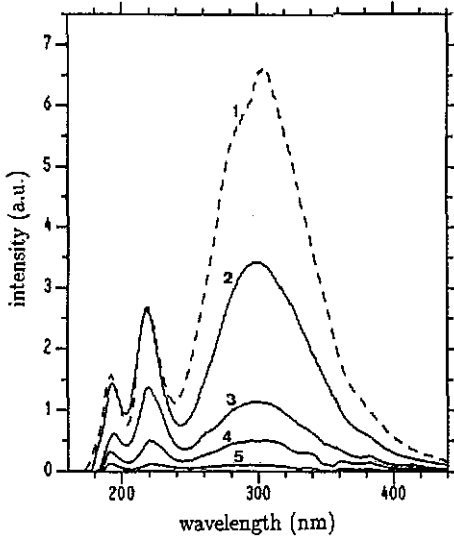


Figure 2. X-ray induced emission spectra of crystals of thickness about 3 mm at room temperature. (1) BaF_2 , (2) BaF_2 : 0.15 mol% NdF_3 , (3) BaF_2 : 2.0 mol% NdF_3 , (4) BaF_2 : 4.8 mol% NdF_3 , (5) BaF_2 : 11.0 mol% NdF_3 .

disappeared at temperatures near 240 K, see spectrum 6. Quite similar features were observed for pure BaF_2 and the other La-doped BaF_2 crystals. The 350 nm emission, was however, not observed for the former.

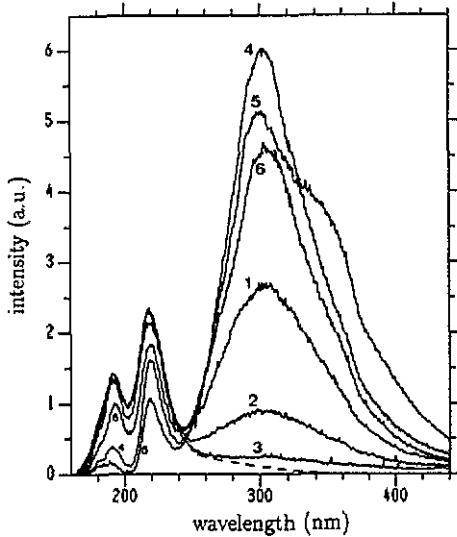


Figure 3. X-ray induced emission spectra of BaF_2 : 0.5 mol% LaF_3 as a function of the temperature. (1) 291 K, (2) 340 K, (3) 400 K, (4) 95 K, (5) 160 K and (6) 260 K. The dashed curve shows the contribution of CL to the emission spectrum.

Integrating the emission spectra of the La-doped crystals from 240 nm to 440 nm provides a measure for the STE light yield. Pure BaF_2 , if excited with gamma rays, has a STE light yield of about 8000 photons MeV^{-1} at room temperature; this number together with the measured emission spectrum of pure BaF_2 at room temperature provides the relation between the photon yield per MeV and the integral of the

emission spectrum. The STE photon yield was corrected for two contributions to the integral value that are not caused by STE luminescence.

(i) A 'tail' in the CL spectrum extends to about 340 nm [6]. The dashed curve in figure 3 shows this tail; it was determined from emission spectra of crystals with a large La concentration recorded at high temperatures. The STE emission is almost completely quenched under these conditions.

(ii) The CL emitted between 175 and 220 nm appears in the spectra with an intensity reduced 50 times between 350 and 440 nm because of second-order transmission by the monochromator.

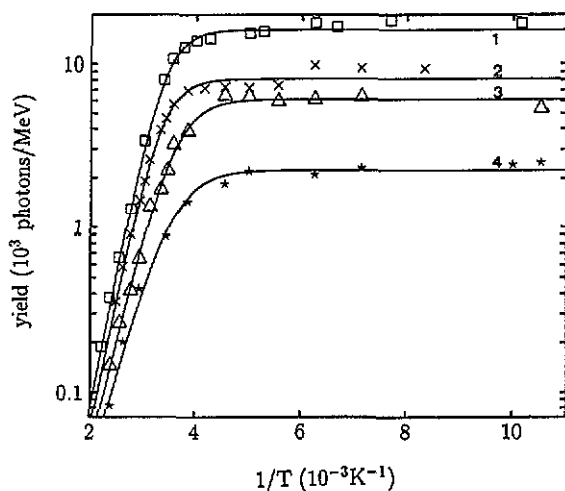


Figure 4. STE luminescence photon yield per MeV of La-doped BaF_2 crystals as a function of the temperature. Curve 1: pure BaF_2 ; curve 2: 0.2 mol% La^{3+} ; curve 3: 0.5 mol% La^{3+} ; curve 4: 6.0 mol% La^{3+} .

Figure 4 shows the resulting photon yields per MeV of the pure BaF_2 crystal and three La^{3+} -doped BaF_2 crystals as a function of the temperature. The STE luminescence for all crystals studied is constant at low temperature, and above 250 K it decreases with increasing temperature. The errors in the data points of figure 4 at temperatures above 250 K are about 6%; they are caused partly by drift in the x-ray intensity and in the photomultiplier tube gain. The errors at temperatures below 250 K are about 13% and are caused partly by accumulation of radiation damage in the crystals. This radiation damage, and consequently the amount of self-absorption, appeared to depend on the thermal and irradiation history of the crystal. The influence of radiation damage was kept minimal by employing low x-ray intensities. In addition there is an absolute error of about 30 photons MeV^{-1} in each data point because of the inaccuracy in the correction for the CL and the second-order transmission.

Figure 5 shows the decay-time spectra of pure BaF_2 and BaF_2 crystals doped with 0.2, 0.5, 1.3 and 6 mol% La^{3+} on a log-log scale. The photoelectron yields per MeV absorbed gamma-ray energy of these crystals if optically coupled to an XP2020Q photomultiplier tube and with 4 μ s spectroscopy-amplifier shaping time are 1790, 990, 750, 520 and 220 photoelectrons MeV^{-1} , respectively [3]. Using these values and the spectroscopy-amplifiers shaping function, the spectra in figure 5 were normalized.

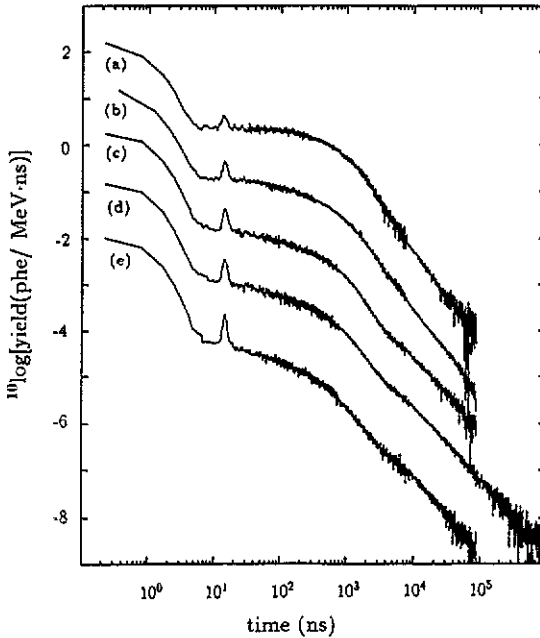


Figure 5. Luminescence decay time spectra of $\text{BaF}_2:\text{La}$ crystals plotted on a $^{10}\log\text{-}^{10}\log$ scale. (a) pure BaF_2 , (b) 0.2 mol% La, (c) 0.5 mol% La, (d) 1.3 mol% La and (e) 6 mol% La. For illustration purposes, spectra (b), (c), (d) and (e) are shifted downwards by 1, 2, 3 and 4 decades respectively.

The curve for pure BaF_2 is described reasonably well by a sum of two exponential decay functions; the fastest one with a decay time of 0.9 ± 0.1 ns is caused by cross luminescence and the slowest one with a decay time of 630 ± 50 ns is caused by STE luminescence. The luminescence decay deviates from a pure exponential STE decay in the time region beyond $3 \mu\text{s}$, where a 'tail' is observed. The small peak near 15 ns is an artifact caused by unwanted pulses in the XP2020Q photomultiplier tube. The STE luminescence curves of the La doped crystals are described less well by exponentially decaying curves than the STE luminescence curve of the pure BaF_2 crystal.

4. Theoretical model

It is well established that the 300 nm luminescence in pure BaF_2 originates from long-lived triplet states of the STE [10]. The STE can decay radiatively with a transition rate Γ_ν and non-radiatively with a thermal quenching rate Γ_q given by

$$\Gamma_q(T) = \Gamma_0 \exp(-\Delta E/k_B T). \quad (1)$$

ΔE is the potential energy barrier for thermal quenching of the STE luminescence, k_B is Boltzmann's constant, T is the absolute temperature, and Γ_0 is a characteristic vibrational frequency for lattice vibrations with typical values of 10^{12} Hz. In this work, we assume that Γ_ν is temperature independent. The probability, $p(T)$, for radiative decay of the STE is then given by

$$p(T) = \Gamma_\nu / (\Gamma_\nu + \Gamma_q(T)). \quad (2)$$

The effective STE decay time, τ_{sc} , is given by [9, 10]:

$$\tau_{sc}(T) = (\Gamma_\nu + \Gamma_q(T))^{-1}. \quad (3)$$

In order to explain the suppression of STE luminescence upon La^{3+} doping we envisage two possible mechanisms [3].

(i) Upon excitation of the crystal with ionizing radiation, electrons are excited to the conduction band and holes are created in the valence band of BaF_2 . The electrons can be trapped by the holes which eventually yields the STE luminescence. The doping with La^{3+} ions introduces extra electron traps, e.g. $La^{3+} + e^- \rightarrow La^{2+}$ which competes with the trapping of electrons by holes. Less STEs are then formed and suppression of STE luminescence will result.

(ii) An increase of the non-radiative decay rates of STEs, e.g. La^{3+} doping, introduces lattice distortions in the BaF_2 host lattice which are likely to influence the potential energy barrier for thermal quenching of nearby STEs. Furthermore, interstitial fluorine ions present in the crystals for charge compensation of the La^{3+} ions may also effect the thermally induced quenching rate.

Let $N(x)$ be the STE photon yield per MeV of absorbed gamma or x-ray energy in a crystal of BaF_2 doped with x mol% La^{3+} and at low temperatures, for which $\Gamma_q = 0$. In the above model, the thermally induced quenching is accounted for by a concentration-dependent quenching rate; i.e. ΔE and Γ_0 in (1) and hence $p(T)$ in (2) are concentration dependent. The STE photon yield per MeV as a function of the temperature and the La concentration, $Y(x, T)$, is then given by

$$Y(x, T) = N(x)\Gamma_\nu / (\Gamma_\nu + \Gamma_q(x, T)). \quad (4)$$

The shape and the position of the STE luminescence peak do not depend on the La concentration, see figure 1. This suggests that STEs responsible for the luminescence in pure BaF_2 are almost identical to STEs responsible for the luminescence in La doped BaF_2 . We have therefore assumed in (4) that the radiative transition rate of STEs is independent of the La concentration.

5. Results and discussion

Table 1 compiles the results of least square fits of (4) to the measured STE luminescence intensities of pure BaF_2 and the La-doped BaF_2 crystals; $N(x)$, $\Gamma_0(x)/\Gamma_\nu$ and $\Delta E(x)$ were the fitting parameters. The resulting fitting curves have been drawn through the experimental data points shown in figure 4. From the measured STE scintillation decay time, $\tau_{sc} = 630 \pm 50$ ns, of pure BaF_2 at room temperature and the fitting results for pure BaF_2 in table 1, a value of 1.3 ± 0.2 μ s for the radiative transition time Γ_ν^{-1} is obtained. Using this value for Γ_ν and the results in table 1, the non-radiative decay time $\tau_q = 1/\Gamma_q$ at room temperature was calculated for all studied crystals.

The potential energy barrier obtained from the fits is 0.32 ± 0.02 eV for pure BaF_2 . The activation energy tends to decrease with increasing La concentration. An activation energy of 0.23 ± 0.02 eV is found for the crystal doped with 6 mol% La. For all crystals, no dramatic decrease of the non-radiative decay time τ_q at

Table 1. Results from fitting the temperature-dependent STE luminescence intensities of $\text{Ba}_{1-x}\text{La}_x\text{F}_{2+x}$ single crystals.

x (mol%)	$N(x)$ (10^3 photons MeV^{-1})	$\ln(\Gamma_0/\Gamma_\nu)$	ΔE (eV)	$\tau_q(293 \text{ K})$ (μs)
0	16.0 ± 0.7	12.6 ± 0.3	0.32 ± 0.02	1.3 ± 0.2
0.2	9.0 ± 0.5	12.1 ± 0.3	0.31 ± 0.02	1.6 ± 0.2
0.5	6.7 ± 0.3	11.8 ± 0.4	0.30 ± 0.02	1.5 ± 0.2
1.3	6.0 ± 0.3	11.1 ± 0.4	0.27 ± 0.02	0.7 ± 0.3
6.0	2.2 ± 0.2	9.4 ± 0.4	0.23 ± 0.02	0.9 ± 0.2

room temperature is observed. The suppression of STE luminescence is therefore not explained by an increase of Γ_q with the La concentration. Instead one should look for mechanisms which cause a decrease of $N(x)$ from 1.6×10^4 photons MeV^{-1} for pure BaF_2 to 2.2×10^3 photons MeV^{-1} for the crystal doped with 6 mol% La^{3+} .

Ershov *et al* [11] studied the STE decay time of pure BaF_2 as a function of temperature. They reported a value of 0.38 ± 0.02 eV for the activation energy of thermal quenching which is somewhat larger than the value found by us. It is not possible to compare the low-temperature STE decay time reported by Ershov *et al* directly with our value of $1.3 \mu\text{s}$ for Γ_ν^{-1} . The STE decay time at low temperature, where $\Gamma_q = 0$, is largely determined by the population rate of the radiative exciton state and appears temperature dependent [11]. The results of our experiments where the time-integrated STE luminescence intensity is obtained are independent on the population rate of the radiative exciton state.

Based on the results presented above and the work by Williams and Song [10] and Beaumont *et al* [12] we propose the following model for the suppression of STE luminescence in La-doped BaF_2 . Upon absorption of ionizing radiation, free electrons and free holes are created in the conduction and valence band of the BaF_2 crystal, respectively. The holes are trapped in the lattice and form so-called V_K centres. The electrons are either trapped by the V_K centres to form STEs or by La^{3+} -related centres. The trapping by the La-related centres causes a decrease of $N(x)$, see table 1, and consequently a suppression of the STE luminescence. The trapped holes will also eventually recombine with the trapped electrons. Their recombination rate depends on the de-trapping rate and the diffusion rate of either the trapped electron or the trapped hole. Both rates are assumed to be thermally activated and decrease exponentially with decreasing temperature. This would imply that the trapped electron and hole become stable at sufficiently low temperature. Apparently this occurs at temperatures below 240 K; the self-absorption in the irradiated crystals observed at wavelengths smaller than 250 nm is then probably related to optical absorption by trapped-hole or trapped-electron centres.

The model described above is supported by work performed by Beaumont *et al* [12] on Tm^{3+} -doped BaF_2 crystals. These authors showed experimentally that upon x-ray irradiation of the crystals at 80 K several types of self-trapped hole centres together with Tm^{2+} are created. During subsequent heating of their crystals other types of hole centres were created. These hole centres start to decay at about 220 K with the electron trapped in Tm^{2+} , yielding Tm^{3+} luminescence. This temperature is close to the temperature below which we observe radiation damage effects in pure and La-doped BaF_2 crystals. La^{3+} and Tm^{3+} are rare earth ions with similar chemical properties. We conclude, therefore, that stable hole centres are formed in

the La-doped BaF_2 crystals at temperatures below about 240 K, causing radiation damage.

An important shortcoming of the model described above is its inadequacy to explain non-exponential decay time spectra. According to (3), we expect an exponentially decaying STE luminescence. A clear exponential decay is, however, not observed for the La-doped crystals, see figure 5. This can be explained partly by assuming a non-instantaneous creation rate of STEs. For example, trapped holes and trapped electrons may recombine to form a STE on a time scale determined by their detrapping and diffusion rates. The observed STE decay is then a function of both the creation rate and the actual STE decay rate, which is exponential. Although this influences the observed luminescence decay it does not affect the total STE light yield per MeV which is a time-integrated quantity. Another effect, not considered in this work, is the quenching of STE luminescence due to energy transfer from the STE to nearby quenching centres. Energy transfer by, e.g. exchange or multipole-multipole interactions [13], might introduce an extra transition rate in (2). Its value depends on the energy transfer mechanism and the configuration of quenching centres surrounding a particular STE. We hope to present a study of this effect and its implications for the interpretation of the results presented in this work in a subsequent paper.

The influence of Nd^{3+} -doping on the STE luminescence is quite similar to that of La^{3+} doping. One might expect to observe Nd^{3+} luminescence when a trapped hole recombines with an electron trapped at a Nd ion. We have observed such luminescence in Nd^{3+} -doped LaF_3 crystals [14]. In BaF_2 , this recombination is apparently radiationless since intense Nd luminescences were not observed.

Summarizing, the results of this work indicate that the suppression of self-trapped exciton luminescence in BaF_2 at room temperature by doping with La^{3+} is not caused by an increase of the thermal quenching rate of STEs. Instead, efficient trapping of electrons from the conduction band by La^{3+} - or La^{3+} -related centres is a likely mechanism. However, suppression of STE luminescence by non-thermally activated energy transfer from STEs to La^{3+} -related quenching centres cannot be excluded. In the case of La^{3+} doping, self-trapped hole centres recombine non-radiatively with the trapped electrons. Nd^{3+} behaves much like La^{3+} , only very weak Nd^{3+} luminescences were observed and non-radiative decay of the trapped holes dominates.

Acknowledgment

These investigations in the program of the Foundation for Fundamental Research on Matter FOM were supported by the Netherlands Technology Foundation (STW).

References

- [1] Laval M, Moszynski M, Allemand R, Cormoreche E, Guinet P, Odru R and Vacher J 1983 *Nucl. Instrum. Methods* 206 169
- [2] Lorenz E 1989 *Proc. ECFA Study Week, CERN report 89-10* pp 621
- [3] Schotanus P, Dorenbos P, van Eijk C W E and Lamfers H J 1989 *Nucl. Instrum. Methods A* 281 162
- [4] Woody C L, Levy P W and Kierstead J A 1989 *IEEE Trans. Nucl. Sci.* NS-36 536
- [5] Bollinger L M and Thomas G E 1962 *Rev. Sci. Instrum.* 32 1044
- [6] Jansons J L, Krumins V, Rachko Z A and Valbis J A 1987 *Phys. Status Solidi b* 144 835
- [7] Loh E 1968 *Phys. Rev.* 175 533

- [8] Schotanus P, van Eijk C W E, Hollander R W and Pijpelink J 1985 *Nucl. Instrum. Methods A* **238** 564
- [9] Birks J B 1964 *The Theory and Practice of Scintillation Counting* (London: Pergamon)
- [10] Williams R T and Song K 1990 *J. Phys. Chem.* **51** 679
- [11] Ershov N N, Zakharov N G and Rodnyi P A 1982 *Opt. Spektrosk.* **53** 89
- [12] Beaumont J H, Hayes W, Kirk D L and Summers G P 1970 *Proc. R. Soc. A* **315** 68
- [13] McClure D S and Kiss Z 1963 *J. Chem. Phys.* **39** 3251
- [14] Dorenbos P, van Eijk C W E, Hollander R W and Schotanus P 1990 *IEEE Trans. Nucl. Sci.* **NS-37** 119