EXCITON LUMINESCENCE SUPPRESSION IN BaF$_2$–LaF$_3$ SOLID SOLUTIONS*

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Abstract—Optical absorption and ESR spectra of X-irradiated BaF$_2$, BaF$_2$–LaF$_3$, LaF$_3$ crystals as well as their luminescence spectra were measured in the temperature range 77–300 K. The spectrum of self-trapped holes was observed in all crystals. The partial restoration of exciton luminescence near 4 eV at low temperatures in BaF$_2$–LaF$_3$ solid solution was concluded to be from "frozen" immobile excitons. © 1998 Elsevier Science Ltd. All rights reserved

1. INTRODUCTION

The BaF$_2$ crystals are known as fast scintillators. The fast ultraviolet emission under X- or electron irradiation is due to cross-luminescence transitions (Aleksandrov et al., 1984). The disadvantage is the much more effective slow exciton luminescence, which has less photon energy than cross-luminescence. It was shown that the suppression of exciton luminescence in BaF$_2$ can be realized using all rare earth impurity ions (Sobolev et al., 1994). For La and Gd doped BaF$_2$ the exciton emission decreased sharply with impurity concentrations up to 1%. Apart from this, the intensity of the fast component decreased slightly. Above 1% concentration the intensities of the fast and slow components are equal and decreased slowly with increasing impurity concentration (Sobolev et al., 1994). Therefore, the intensity ratio between the fast and the slow component of BaF$_2$ emission largely grows up to 1% of rare earth doping concentration and not changed at higher concentrations. Combining the intensity ratio requirement and fast scintillation yield requirement one has to choose the doping level of BaF$_2$ to near 1%. On the other hand, a high doping level of 30% of LaF$_3$ will lead to impurity uniformity and the absence of cleavage planes. Additional to rare earth ions, the alkaline–earth ions Mg, Sr (Hamada et al., 1994) and Cd (Springis et al., 1995) were also found to suppress the exciton luminescence in BaF$_2$.

As an explanation it was tentatively proposed that the excitons migrate to impurity sites followed by nonradiative quenching of exciton energy (Schotanus et al., 1989). The quenching of exciton luminescence introduced by the lanthanum doping is mainly due to non-radiative decay of the excitons due to some kind of quenching centres present in

crystal. However, the decrease of number of excitons formed also play a role, especially at the higher doping level. The precise nature of exciton luminescence quenching was not established. The La^{3+} ion as such cannot cause any multipole transitions, since the energy needed to excite is much larger than energy stored in self-trapped exciton. However, such process cannot be excluded for centres like La^{3+}–O^{2-} (Visser et al., 1992, Dorenbos et al., 1992). Another model suggests that the exciton luminescence is suppressed by capture of self-trapped holes by interstitial fluorine ions, which are charge compensators to lanthanum ions (Gu Mu et al., 1994). Obviously, this explanation is not valid for Mg or Sr doping.

Nevertheless, the processes of the creation of radiation defects and defect interactions in doped barium fluorides are of considerable interest.

2. EXPERIMENTAL

We studied the optical absorption, emission and ESR spectra of solid solutions of BaF$_2$–LaF$_3$. We investigated samples with 1, 10, 20 and 30% of LaF$_3$, as well as pure BaF$_2$ and pure LaF$_3$ crystals. The absorption spectra were taken with a "Specord" spectrophotometer in the 1.5–6 eV region and with a home-made vacuum ultraviolet spectrophotometer in the 6–12 eV region. The crystals were grown by Stockbarger method in either a vacuum or a He atmosphere.

Luminescence in the ultraviolet region was monitored with a vacuum UV monochromator (VM4) and appropriate photomultipliers (FEU39A or solar blind FEU142). The luminescence spectra were corrected for the spectral response of the spectrometer.

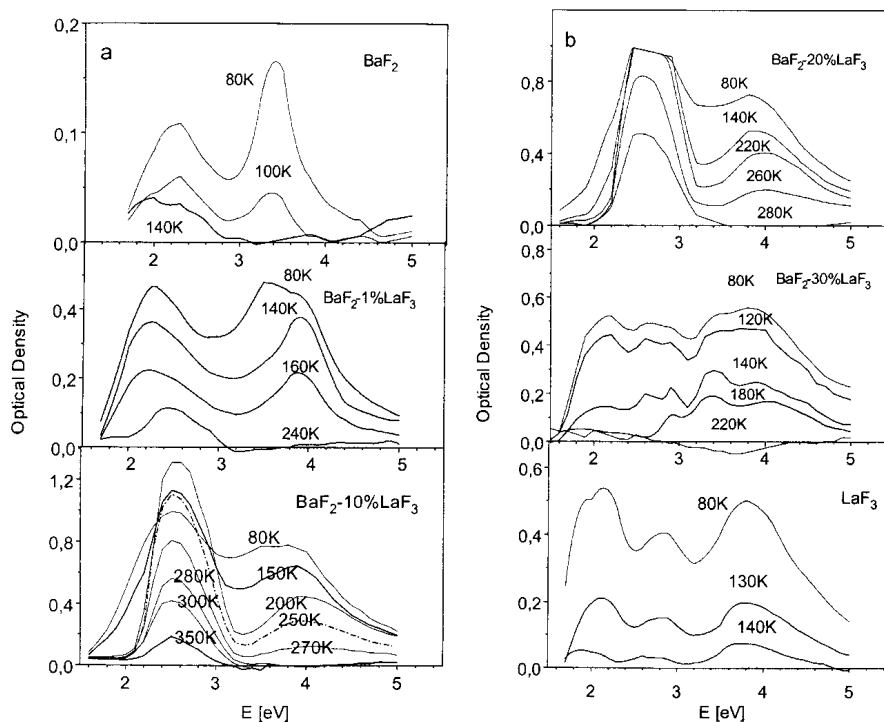*Due to circumstances beyond the Publisher's control, this article appears in print without author corrections

Fig. 1. Absorption spectra of BaF_2, BaF_2–LaF_3, LaF_3 crystals X-irradiated at 80 K and heated to indicated temperatures. The spectra were measured at 80 K.

An X-ray tube with a W anode (25 kV, few mA) was used to excite the luminescence.

For measurement of absorption spectra due to radiation defects the crystals, sized $10 \times 10 \times 2$ mm were X-irradiated at 80 K (40 kV, 40 mA, W) for 0.5–1 h. The ESR measurements were conducted with $3 \times 3 \times 6$ mm^3 samples. The sample was irradiated 3–4 h from two sides.

3. RESULTS AND DISCUSSION

3.1. Optical absorption spectra

The coloration of undoped BaF_2 crystals by X-rays observed to be rather weak (Fig. 1). Two absorption bands at 3.4 and 2.2 eV belong to V_k and Fcentres. They are created when free electrons are captured by some impurities and free holes are self-trapped. The V_k band in BaF_2 is claimed to be at 3.7 eV by other workers (Beumont et al., 1970).

The colouration efficiency increased with the La impurity concentration up to 20% (Fig. 1). Certainly, the absorption band at 3.4 eV, which disappears below 140–150 K, has to belong to V_k centres. The absorption band at 3.9 eV, which remains after heating to 140 K, has to be assigned (to V_{kA} or) to V_H centres. These centres disappear below room temperature. Similar V_k centre transformation was observed earlier in BaF_2 doped with 0.1% Tm (Beumont et al., 1970). The annealing of 3.4 and 2.1 eV bands after heating to 200 K is accompanied by increasing of a 2.6 eV band in the crystals with 10 and 20% of LaF_3 (see Fig. 1).

The absorption spectra of BaF_2–30% LaF_3 are similar to the pure LaF_3 spectra (see Fig. 1).

3.2. ESR spectra

ESR of self-trapped holes was observed at 77 K. No ESR absorption was observed in unirradiated samples. In pure and 1% LaF_3 doped crystals the parameters were very close to those observed in BaF_2 (0.1% Tm) (by Beumont et al., 1970). The linewidth is rather small (a few gauss).

At higher concentrations, the lines become broader (Fig. 2). We have not yet investigated the angular dependence of the ESR spectra. Nevertheless the observed spectra can be described in terms of V_k centres in several orientations to the
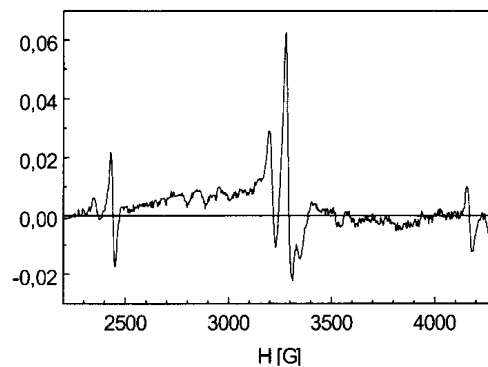

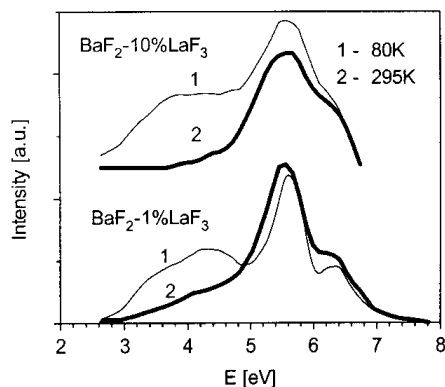Fig. 2. EPR spectrum of BaF_2–5% LaF_3 irradiated for 4 h by X-rays (40 kV, 40 mA W) at 77 K.

Fig. 3. Emission spectra of BaF_2–LaF_3 crystals under X-irradiation (20 kV, 20 mA, W). The spectra were corrected for the spectral response of the spectrometer.

magnetic field. Since the fluorine nuclear spin is 1/2, the hyperfine interaction gives a triplet ESR spectrum near $g = 2.00$ with an intensity ratio of 1:2:1. The largest splitting between the lowest and highest lines was observed near 1800 G (see Fig. 2), which gives the parallel isotropic constant near 900 G. This value is close to that of 897 G observed in BaF_2 (Beumont et al., 1970). The line width in BaF_2 is rather small 5.6 G. (Beumont et al., 1970) and the width is rather large in LaF_3 near 40 G. (Thoma et al., 1997). The line width we observed in BaF_2–LaF_3 was 20 G. This value lies between those of BaF_2 and LaF_3.

No principal changes were observed after heating the sample to 200 K, while the spectrum intensity becomes slightly less. The spectrum is diminished below room temperature.

3.3. Luminescence spectra

Three luminescence bands were observed in BaF_2 crystals in the ultraviolet region: 6.2, 5.6 and 4.0 eV. The first two bands belong to fast core-valence luminescence, the last band belongs to slow exciton luminescence. At room temperature the 4.0 eV exciton luminescence was reduced by factor of 2 in BaF_2 (1% LaF_3) crystals and was not observed in higher doping concentrations. At 80 K in all doped crystals the exciton emission was partially recovered (up to half of the emission in pure BaF_2) (Fig. 3). The maximum of this emission was slightly shifted to lower energy side compared to those in pure crystals.

We propose at least two possible reasons for this appearance of exciton emission at low temperatures. At first, the exciton migration to the lanthanum impurity can be frozen. Secondly, the impurity can lower the potential barrier for thermal quenching of excitons. Than it has to be assumed that excitons are created near the impurity. This is improbable. In the weakly doped BaF_2–LaF_3 crystals, where the some part of exciton luminescence was remaining,

the restoration of exciton luminescence at low temperature was observed as well (see Fig. 3). At liquid nitrogen temperature the created self-trapped excitons are frozen and are able to luminesce. The self-trapped excitons in alkali halide crystals are able to diffuse at temperatures, which are slightly above the temperature of migration of V_k centres. The V_k centres in BaF_2 can migrate above 100 K. In our barium-lanthanum fluoride solid solution the hole absorption band annealed below 150 K. We conclude that between 100 and 150 K the self-trapped excitons move to lanthanum ions and decay nonradiatively.

The precise mechanism of exciton luminescence quenching in BaF_2 by many different impurities is not yet understood. It is clear that mutipole interaction is play no role, because the La^{3+}, Mg^{2+}, Sr^{2+} have no absorption transitions with the energy stored in self-trapped exciton (see also Visser et al., 1992; Dorenbos et al., 1992).

4. CONCLUSION

The results show that even at large concentrations of LaF_3 the creation of V_k centres in BaF_2 is not depressed. Additionally the exciton luminescence in BaF_2–LaF_3 solid solutions is partially restored at liquid nitrogen temperature. Therefore, we conclude that the self-trapped holes (as well as self-trapped excitons) are effectively created in barium-lanthanum solid solutions and exciton luminescence quenching is caused by the migration of excitons to La ions.

REFERENCES

Aleksandrov, YuM, Makhov, V. M. and Rodnyi, P. A. (1994) Sov. Phys. Solid State 26, 89–92.

Beaumont, J. H., Hayes, W., Kirk, D. L. and Summers, G. P. (1970) Proc. Roy. Soc. Lond. A 315, 69–97.

Dorenbos, P., Visser, R., Dool, R., Andriessen, J. and van Eijk, C. W. E. (1992) J. Phys. Cond. Matter 4, 5281–5290.

Gu, Mu, Chen, Lingyan, Li, Qing, Wang, Liming and Xiang, Kaihua (1994) Nucl. Instr. Meth. 00, 393–398.

Hamada, M. M., Nunoya, Y., Sakuragui, S. and Kubota, S. (1994) Nucl. Instr. and Meth. 33(36), 1–3.

Schotanus, P., Dorenbos, P., van Eijk, C. W. E. and Lamfers, H. J. (1989) Nucl. Instr. and Meth. A281, 162–166.

Sobolev, B. P., Krivandina, E. A., Derenzo, S. E., Moses, W. W. and West, A. C. (1994) Scintillator and phosphor materials. Materials Research Society Symposium Proceedings V. 348, Pittsburgh, Pennsylvania, pp. 277–282.

Springis, M., Veispals, A., Kulis, P., Rogulis, U., Tale, I. and Trokss, J. (1995) In: Proc. Int. Conf. Inorg. Scintillators and their Applications, The Netherlands, pp. 403–406.

Thorma, E. D., Shields, H., Zhang, Y., McCollum, B. C. and Williams, R. T. (1996) J. Luminescence 71, N2, 93–104.

Visser, R., Dorenbos, P., van Eijk, C. W. E. and den Hartog, H. W. (1992) J. Phys. Cond. Matter 4, 8801–8812.