



Dependence of the efficiency of various emissions on excitation density in BaF₂ crystals

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Received 20 August 2000; received in revised form 11 January 2001; accepted 14 January 2001

Abstract

The dependence of the intensity of the emission of self-trapped excitons, crossluminescence (CL) and intraband luminescence on the excitation density in BaF₂ by electron pulses (300 keV, 3 ns) has been studied. The energy input above 2×10^{19} eV cm⁻³ causes quenching of 5.5 eV CL due to the recombination of conduction electrons with the outermost-core holes resulting in the formation of cation excitons and the subsequent energy transfer from a cation exciton to a valence electron of a neighbouring anion. The excitation spectra for various fast ($\tau < 5$ ns) and inertial emissions have been measured using synchrotron radiation at 9 K. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Cation excitons; Fast luminescence; Synchrotron radiation; BaF₂

1. Introduction

For a long time the development of dosimeters and detectors of protons, tritons and some heavier particles on a background of γ -rays has been based on the use of the complicated dependencies of the efficiency of impurity and intrinsic emissions on the density of electronic excitations formed by particles in luminescent inorganic materials (Kuzmin et al., 1967; van Eijk, 1997). Super-linear dependence of the electron-hole processes involved in energy transfer to luminescent centres on the excitation density (ED) is used for dosimetry of fast neutrons in the case of impurity recombination emissions of the crystals, where the saturation of non-radiative recombination centres takes place at high values of ED (Jack et al., 1974). In the case of intrinsic emissions from crystals with self-trapping holes the dependence of the intensity of the recombination emission on ED is usually linear. However, in an α -Al₂O₃

crystal and similar systems conduction electrons (e) and holes from the valence band (h) do not undergo transformation into a self-trapped state, and the intensity of the emission of self-trapped excitons (STEs), originating due to the recombination of e-h pairs, depends quadratically on ED (Kirm et al., 1999).

The use of crystals with crossluminescence (CL) is promising for dosimetry as well. The irradiation of such crystals by α particles causes the quenching of CL, while γ -ray irradiation does not decrease the CL intensity (van Eijk, 1997). Although several possible explanations have been proposed (Belsky et al., 1996), the particular mechanism of CL quenching at high values of ED has been identified only for CsCl crystals (Lushchik et al., 2000). It is suggested that at high values of ED the process of cation exciton formation due to the recombination of conduction electrons with the outermost-core holes (h_c) competes with the radiative recombination of valence electrons with h_c .

The aim of the present study was to investigate various intrinsic and impurity emissions as well as the dependence of the intensity of these emissions on the density of excitation in BaF₂ crystals. The ED was varied by changing the

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current density of nanosecond electron pulses or by selective photocreation of only one or several electronic excitations in a small volume using tunable synchrotron radiation. The latter effect of high local ED under the conditions of multiplication of electronic excitations is especially strong in alkali halide crystals.

2. Experimental

The BaF₂ single crystals used in this work were grown in a fluorine atmosphere from a specially purified salt leading to a reduced concentration of oxygen impurity ions. Freshly cleaved crystal plates of dimensions 12 × 12 × 1 mm³ were placed into a helium cryostat ($T = 4\text{--}300\text{ K}$, vacuum about 6×10^{-10} mbar). The photoluminescence experiments were carried out at the SUPERLUMI station of HASYLAB at DESY, Hamburg (Zimmerer, 1991). The reflection spectra and the excitation spectra of various emissions were normalized to equal quantum intensities of synchrotron radiation of 7–36 eV falling onto the (100) plane of a crystal at an angle of incidence 17.5°. The excitation spectra were measured for time-integrated luminescence as well as for the emission detected within one–three time windows (length Δt) correlated with the excitation pulses of synchrotron radiation (delayed by δt).

The experiments with irradiation by an electron beam were carried out at the Institute of Physics, University of Tartu. The duration of a single electron pulse from a GIN-600 generator was $\tau = 3\text{ ns}$, the current density 10–150 A cm⁻², and its average electron energy 300 keV. Fast luminescence was recorded through a double prism (1.2–5.8 eV) or a single grating monochromator (4–8 eV) by a system consisting of photomultipliers, a fast oscilloscope and a telecamera (for details see Ibragimov and Savikhin, 1993).

3. Results

Fig. 1 presents the emission spectra of a BaF₂ crystal at 80 and 300 K in the case of excitation by 300 keV electron pulses. In the region of 4.3–7.3 eV there are several bands with maxima at 5.6, 6.4 and 6.8 eV. The excitation spectrum of the fast emission of BaF₂ was measured by Aleksandrov et al. (1984) and this emission was interpreted as the $2pF^- \rightarrow 5pBa^{2+}$ electron transitions, i.e. the recombination of electrons from a valence band with the outermost-core holes h_c . Later a similar CL of nanosecond duration was detected in CsBr (Aleksandrov et al., 1987) and some other crystals with heavy anions. According to Fig. 1 a fast emission from BaF₂ is also observed in the spectral region of 1.2–2.5 eV. (The decay curve for this emission is depicted in left inset.) This emission corresponds to the so-called intra-band luminescence, when electron transitions occur in-

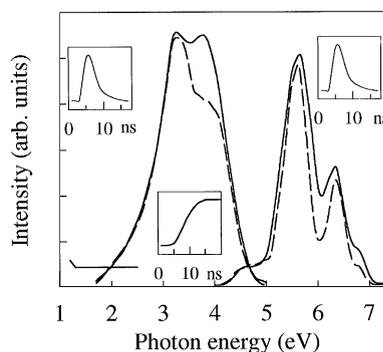


Fig. 1. The emission spectra of a BaF₂ crystal excited by 300 keV electron pulses (80 A cm^{-2}) at 80 K (dashed line) and 300 K (solid line). Insets show the decay curves for emissions in the corresponding spectral regions.

side the conduction band and/or inside the valence band (Vaisburd and Semin, 1992). In CsCl, intraband luminescence in the region of 2–7.5 eV is about 70 times as weak as CL in the region of its maximum at 5.2 eV (Lushchik et al., 1995). The intensity of 1.2–2.5 eV emission in BaF₂ is about 60 times as low as the peak intensity of CL at 5.6 eV. Two bands of inertial emission have been detected in the region of 2.1–4.9 eV in BaF₂ at 80 and 300 K as well. These bands, measured at $t > 10\text{ ns}$, are also presented in Fig. 1. Broadband inertial emission consists of two overlapping bands: STE emission with the maximum at 4 eV and an impurity luminescence band (2.5–3.6 eV). We have detected a new luminescence band with a maximum at 7.55 eV and a half-width of 0.5 eV in the steady luminescence spectrum of BaF₂ at 8 K for excitation by 6 keV electrons. The peak intensity of this band is 30 times as weak as that for CL at 5.6 eV.

Fig. 2 presents the reflection spectrum and the excitation spectra of 5.5, 4.0 and 3.3 eV emissions measured in BaF₂ for time-integrated and fast signals in the region of 8–21 eV at 9 K. The intense reflection peak at 10 eV and a weak band at 10.65 eV correspond to the creation of anion excitons with $n = 1$ and 2, respectively, while the step in the region of 11 eV indicates to the beginning of band-to-band transitions. There is an excitation maximum for 3.3 eV impurity emission at 8.55 eV, i.e. outside the region of fundamental absorption of BaF₂. The emission of 4 eV can be effectively excited by the direct formation of anion excitons by 9.5–11 eV photons, by the creation of e–h pairs by photons of 11–16.8 eV, as well as in the region of formation of cation excitations by 17–21 eV photons. The efficiency of the time-integrated (TI) 5.5 eV emission sharply increases at an exciting photon energy of $h\nu > E_{gc} = 18.2\text{ eV}$, where E_{gc} is the minimum energy of cation photoionization. A weak TI 5.5 eV emission can be detected at the excitation in the regions of impurity absorption and formation of anion electronic excitations. However, a fast 5.5 eV emission of nanosecond duration is excited only in the energy region of

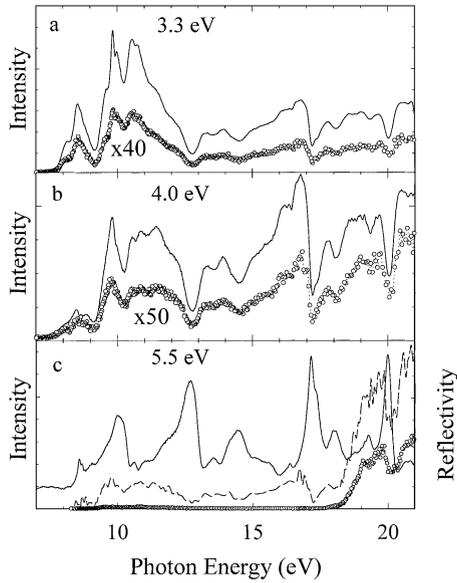


Fig. 2. The excitation spectra of 3.3 eV (a) and 4.0 eV (b) emissions measured for time-integrated (solid line) and fast ($\Delta t = 4.7$ ns, $\delta t = 0.9$ ns) signal (O) at 9 K. The reflection spectrum (solid line) and the excitation spectra of 5.5 eV (c) emission measured for TI (dashed line) and fast ($\Delta t = 4.7$ ns, $\delta t = 0.9$ ns) (O) signals at 9 K in BaF₂ crystal.

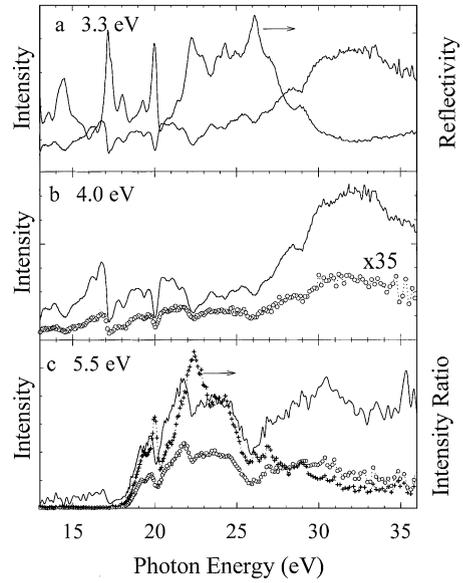


Fig. 3. The excitation spectra of 3.3 eV (a) and 4.0 eV (b) 5.5 eV (c) emissions measured for time-integrated (solid line) and fast ($\Delta t = 4.7$ ns, $\delta t = 0.9$ ns) signal (O) at 9 K. The reflection spectrum (a) and the intensity ratio spectrum (c, +) for the fast emission of 5.5 and 4.0 eV TI signal at 9 K in a BaF₂ crystal.

$h\nu > E_{gc}$ and it is this fast component of emission that forms the CL of BaF₂.

Fig. 3 shows the excitation spectra for TI and fast ($\Delta t = 4.7$ ns, $\delta t = 0.9$ ns) components of 5.5 and 4.0 eV emissions of BaF₂ at 9 K. The efficiency of the fast component of 5.5 eV emission sharply increases in the region of photon energy $h\nu > E_{gc}$. Fig. 3 also shows the intensity ratio spectrum for a fast emission of 5.5 and 4.0 eV TI ($I_{5.5}/I_{4.0}$). The value of $I_{5.5}/I_{4.0}$ is close to zero at the direct formation of CEs (17–18 eV), reaches its maximum value at 22.4 eV and is by an order of magnitude lower at 32–36 eV.

The formation of secondary anion excitons and secondary e–h pairs has been earlier detected in a number of alkali halide crystals (Lushchik et al., 1996). Such multiplication of electronic excitations takes place at $h\nu \geq E_{ga} + E_{ea}$, $h\nu > 2E_{ga}$ and $h\nu > E_{gc} + E_{ea}$ (E_{ea} is the formation energy of anion excitons, E_{ga} is the ionization energy of anions). In BaF₂, the processes of multiplication can be expected in the region of 29–33 eV ($h\nu > E_{gc} + E_{ea}$), 35–36 eV ($h\nu > E_{gc} + E_{ec}$, E_{ec} is the formation energy of CEs), and 37–42 eV ($h\nu > 2E_{gc}$).

Fig. 4 shows the dependencies of the intensity of several fast emissions of BaF₂ on the ED by single nanosecond electron pulses (300 keV, $\tau = 3$ ns, current density varied from 10–150 A cm⁻²). Similar to the case of STE σ emission (4.2 eV) in KI (Kirm et al., 1999), the intensity of STE emission in BaF₂ (4 eV) increases linearly with the increasing

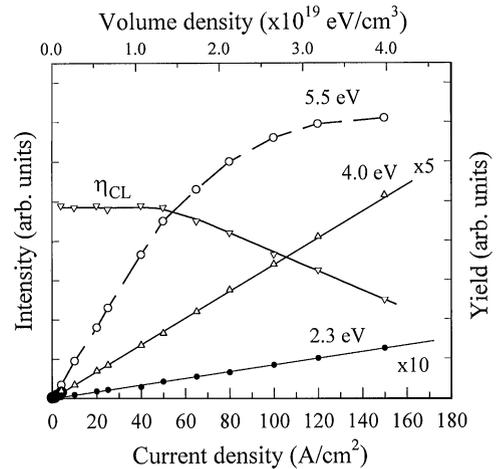


Fig. 4. Dependencies of the intensity of several fast emissions of BaF₂ on the current density of nanosecond 300 keV electron pulses at 295 K. The intensity ratio (∇) for the fast emissions of 5.5 and 2.3 eV (η_{CL}).

electron current density. The intensity of intraband luminescence (measured at 2.3 eV) in BaF₂ depends linearly on ED as well. The intensity of 5.5 eV CL increases linearly with the rise of the electron current density only up to the value of $I_e = 60$ A cm⁻², while at higher values of ED the dependence is sublinear. The intensity ratio for fast emissions

at 5.5 and 2.3 eV can be considered as a relative quantum yield of CL (η_{CL}). The value of η_{CL} decreases three times at $I_e > 60 \text{ A cm}^{-2}$. Taking the penetration depth of 300 keV electrons into BaF_2 to be $l = 186 \mu\text{m}$, we can estimate the volume density of energy input (in eV cm^{-3}) at several values of I_e (see Fig. 4, upper scale). The quenching of CL starts at the energy input of about $2 \times 10^{19} \text{ eV cm}^{-3}$. Considering that the minimum energy of direct photoionization of 5pBa^{2+} in BaF_2 equals $E_{\text{gc}} = 18 \text{ eV}$, we can estimate that the quenching of CL occurs if the density of e-hc pairs exceeds the value of 10^{18} cm^{-3} . According to Lushchik et al. (2000), the same concentration of e-hc pairs causes quenching of CL in a CsCl crystal ($E_{\text{gc}} = 14 \text{ eV}$, $l = 226 \mu\text{m}$ for 300 keV electrons).

4. Discussion

The decay time of the 5.5 eV emission during excitation of BaF_2 by 20 eV photons is $\tau = 0.88 \text{ ns}$ and it decreases down to $\tau = 0.33 \text{ ns}$ in the case of excitation by α -particles (Belsky et al., 1996). So, a high value of ED causes the quenching of a slower component of the emission. In case of excitation by 300 keV electrons the quenching process starts if a single electron pulse forms about 10^{18} e-hc pairs in 1 cm^3 of an excited crystal, i.e. the average distance between h_c is about 12 nm. We can estimate that for the value of ED more than 10^{18} e-hc in 1 cm^3 the recombination time of conduction electrons with h_c should be less than 1 ns. Thus, there is a competition between the creation of CEs and the radiation recombination of electrons from the valence band with the outermost-core holes h_c .

According to our experimental data, the efficiency of CL on the excitation of BaF_2 in the region of the direct formation of CEs by 17–18 eV photons is less than 0.5% of that at the excitation by photons of 22 eV, which form e-hc pairs. Creation of CEs by recombination causes the quenching of CL at high values of ED ($\geq 10^{18}$ e-hc pairs). Photons of 17–18 eV create CEs and excite the emission of STEs (4 eV) as well as the 3.3 eV impurity emission (see Figs. 2–3). According to photoelectric data (Ejiri et al., 1995), 17.2 eV photons cause the formation of electrons inside the conduction band with the kinetic energy by several eV higher than an electron affinity in BaF_2 , $\chi = 0.3 \text{ eV}$. Such photoelectrons can be easily emitted from a thin film of BaF_2 . The above-mentioned luminescent and photoelectric effects occur due to the energy transfer from CEs to the electrons of the valence band (i.e. to neighbouring anions), rapid relaxation of conduction electrons to the bottom of the band and their subsequent recombination with self-trapped anion holes or with holes localized near impurity ions. This results in the appearance of STE emission or 3.3 eV impurity emission, respectively. However, the recombination formation of CEs in BaF_2 at high values of ED (more than 10^{18} e-hc pairs in 1 cm^3) is not accompanied by such a significant enhancement of the fast 4 eV luminescence, that might

cause the superlinear rise of fast STE emission with the increase of I_e from 60 to 150 A cm^{-2} (see Fig. 4). The absence of superlinear dependence for STE emission is partly connected with incomplete recording of this emission of microsecond duration. Some other processes resulting in radiative or non-radiative annihilation of CEs can be important as well. In case of direct or recombination creation of CEs by 300 keV electrons, it is not necessary to consider the possibility that mobile CEs can reach a ‘dead’ near-surface layer of a crystal. The reason of the quenching of these emissions should probably be looked for in high local ED under the conditions of multiplication of electronic excitations.

Acknowledgements

We would like to thank Prof. G. Zimmerer for helpful discussions. This work was supported in part by the Estonian Science Foundation (Grant 3868) and the University Exchange Program between Hamburg and Tartu.

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