

Short-wave UV luminescence of BaF₂ crystals caused by crossover transitions

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The spectrum of the intrinsic luminescence of BaF₂ crystals has been measured over the range 3.5–10 eV. Four short-wave emission bands that are observed are linked to crossover transitions from the 2pF⁻ upper valence band to the 5pBa²⁺ cation band.

A component peaking at 5.7 eV, with a decay time shorter than 1 ns and without thermal quenching at room temperature, was recently discovered in the intrinsic luminescence spectrum of BaF₂ crystals.^{1,2} This emission differs from the known types of intrinsic luminescence of ionic crystals in that it is not excited in a part of the spectrum where low-energy anionic excitons and electron-hole pairs are produced. The threshold for its excitation lies beyond the first peak of cationic excitons and corresponds to the ionization energy of the cations, i.e., to the formation of holes in the 5pBa²⁺ band. The observed luminescence can therefore be linked to transitions of electrons from the 2pF⁻ band to the 5pBa²⁺ band.³ In x-ray spectroscopy, such transitions are called "crossover transitions." They have been observed in several ionic crystals in the ultra-soft-x-ray part of the spectrum, where reabsorption effects are intense.^{4,5} In BaF₂ crystals, on the other hand, the energy spacing between the 2pF⁻ and 5pBa²⁺ bands is less than the gap width,⁶ so that the corresponding emission is seen as an intense component of the intrinsic luminescence.

In view of the large width and complex structure of the valence bands^{6,7} of BaF₂, we decided to study its intrinsic emission over a broader spectral region. For this purpose we measured the spectral-kinetics characteristics of the cathodoluminescence of undoped BaF₂ crystals over the interval 3.5–10 eV with the apparatus and by the procedure of Ref. 8.

In the cathodoluminescence spectra we find, in addition to the known emission bands² at 4.15 and 5.7 eV, two additional bands in the vacuum-UV region, peaking at 6.4 and ~7 eV (Fig. 1). The cathodoluminescence intensity of the short-wave band increases with increasing temperature; the intensity ratio of the bands at 5.7 and 6.4 eV remains essentially constant, while the intensity of the band at 7.0 eV increases slightly more rapidly than the intensities of these other bands. The emission in the region 7.3–10 eV is no more intense than the noise level of the apparatus; i.e., it is at least three orders of magnitude weaker than that at 6.4 eV. The decay time of the luminescence in the bands at 6.4 and 7.0 eV is shorter than 3 ns (the instrumental limit).

The short decay time of the emission and the absence of thermal quenching of the emission suggest that the nature of the emission in the bands at 6.4 and 7.0 eV is the same as that in the band at 5.7 eV; i.e., it is due to crossover transitions of electrons from the 2pF⁻ band to the 5pBa²⁺ band. In view of these results and the results of

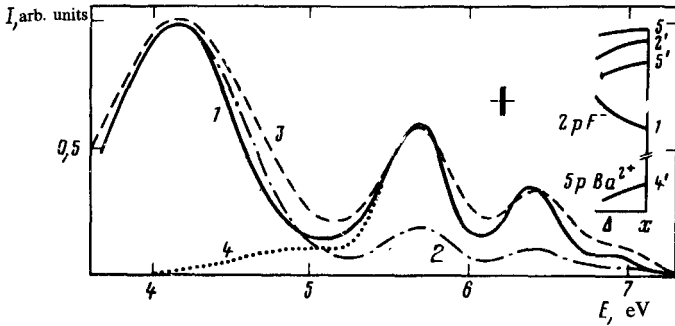


FIG. 1. Normalized spectra of the steady-state cathodoluminescence ($j \cong 1 \mu\text{A}/\text{cm}^2$, $U = 5 \text{ kV}$) of undoped BaF_2 crystals at various temperatures: 1—80 K; 2—220 K; 3—300 K. Spectrum of the long-wave component of the emission with subnanosecond decay (2–4). The insert shows part of the BaF_2 band structure.⁷

Ref. 2, we might suggest that the spectrum of the emission caused by crossover transitions extends from 4.0 to 7.3 eV, in good agreement with the width of the $2pF^-$ band (3.4 eV; Ref. 6). This circumstance, combined with the well-defined bands in the spectrum of the crossover transitions, indicates that a comparatively narrow energy range is occupied by holes in the $5p\text{Ba}^{2+}$ band at the time of the phototransition.

The holes apparently have time to relax to the peak of this band at the X_4 point in the Brillouin zone before the transition occurs. The presence of four bands of crossover transitions may be due to $X_1, X'_5, X'_2,$ and X_5 peaks in the state density caused by four subbands of the $2pF^-$ band.⁷ The minimum energy of the crossover transitions ($\sim 4 \text{ eV}$; Ref. 2) agrees reasonably well with the spacing between the edges of the bands.⁶ The maximum energy of the emission (7.3 eV) apparently gives us an estimate of the difference between the energies of the upper parts of the bands (polarization is taken into account⁵).

It might be hypothesized that the emission at 3.2 eV with a decay time of 5 ns in CsF crystals⁹ and the emission at 4.6 eV in CsCl crystals, which is predominant above room temperature, are also consequences of crossover transitions (from the $2pF^-$ and $3p\text{Cl}^-$ bands, respectively, to the $5p\text{Cs}^+$ band). The observed position of the emission bands agrees with the band structure of cesium halides.¹⁰ Analysis shows that crossover transitions should also be observed in the transparency region of other crystals: CsBr , BaCl_2 , BaBr_2 , and certain halides of rubidium, characterized by a minimal excitation energy (or ionization energy) of the cations and a maximal gap width.

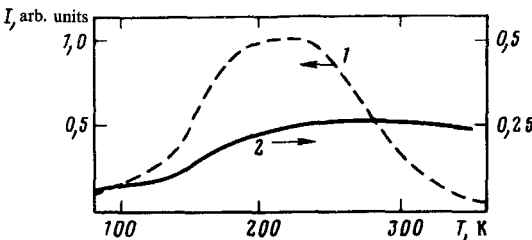


FIG. 2. Temperature dependence of the intensity of the cathodoluminescence in the bands at 4.15 eV (1) and 5.7 eV (2).

We must emphasize the distinctive features of the elementary excitations which are responsible for the crossover transitions: They are fermions (holes) that emit photons in a transition into another band. The holes which go into the upper valence band can of course subsequently participate in "ordinary" recombination processes with electrons from higher-energy states.

A distinctive feature of the crossover transitions in insulators is that there are no absorption transitions which are reciprocals of the emission transitions, since both of the participating bands are completely filled with electrons in the ground state. Holes in the lower band can be produced only if electrons go into the conduction band. The presence of a filled band above the band in which the holes are produced leads to the formation of a population inversion of the levels at essentially any excitation density. However, it would be quite difficult to achieve optical amplification and lasing because of the accompanying formation of short-lived and stable centers that absorb the pump light.¹¹

We note in conclusion that crossover transitions between an upper anionic valence band and an upper cationic valence band are not a weak "satellite" effect, as in the case of transitions to deep-lying cationic bands, which are filled primarily by electrons from high-lying cationic bands. Crossover transitions, the primary channel for the filling of hole states in the upper cationic band, can make a significant contribution to the overall dissipation of the energy of the high-energy particles and photons in these crystals. This circumstance underlies the use of BaF₂ and CsF as fast scintillators.⁹ On the other hand, crossover transitions, particularly in materials in which they correspond to the optical (UV or vacuum-UV) part of the spectrum, may provide detailed information about the structure of the upper valence band.

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