

THE MECHANISM OF ORIGINATION OF ANOMALOUS FEATURES IN THE STRUCTURE OF SHORT-WAVELENGTH SPECTRA OF FLUORIDE MATRICES DOPED WITH RARE-EARTH IONS

K. M. Devyatkova, O. N. Ivanova, V. V. Mikhailin, and S. P. Chernov

A comparative study of the optical and structural parameters was performed for BaY_2F_8 and KY_3F_{10} single crystals doped with Er^{3+} , Ho^{3+} , $\text{Yb}^{2+,3+}$, and $\text{Tm}^{2+,3+}$ ions. An interrelation was established between the occurrence of regular structure imperfections in single crystals and the anomalies in their VUV spectra, which may be utilized to improve the luminescence parameters of the materials studied.

In the spectral studies of fluoride single crystals doped with rare-earth ions [1, 2], certain repeated anomalies were discovered, the explanation of which required a detailed study on the crystal structure of these materials.

In the present communication we report data obtained in a comparative study of the optical and structural parameters of BaY_2F_8 and KY_3F_{10} single crystals doped with Er^{3+} , Ho^{3+} , $\text{Yb}^{2+,3+}$, and $\text{Tm}^{2+,3+}$ ions. The single crystals were grown by the Bridgman-Stockbarger method. The samples used in the experiments represented plates 10 mm in diameter and 1 mm thick, polished normally to the *c* axis. The transmission spectra were studied in the wavelength range from 120 to 300 nm with a VMR-2 vacuum monochromator. The luminescence spectra were studied with an installation comprising two crossed monochromators VMR-2 and DFS-29. As a light source, use was made of a special hydrogen lamp whose emission was cut off with a VMR-2 monochromator. The luminescence emission was analyzed with a DFS-29 vacuum monochromator. In the transmission measurements, the transmitted emission was detected with a FEU-88 phototube equipped with a sodium salicylate transformer of the spectrum; in the luminescence measurements, use was made of a FEU-142 phototube. The transmission and luminescence spectra were registered with a KSP-4 self-recording unit. The single crystals structure was studied by scanning electron microscopy (SEM) which allows structure imperfections 100 to 200 Å in size to be identified. The method is characterized by large information content due to the utilization of secondary electrons, which reveal fine features of the structure, and also reflected electrons, Auger electrons, photons of varied energy, and polarons providing information about the composition, topography, and internal electric and magnetic fields.

Our studies revealed that there exist definite relationships between the presence of regular structure imperfections in fluoride crystals doped with rare-earth ions (REI) and the anomalies observed in their VUV spectra.

Thus, the absorption spectrum of a BaY_2F_8 single crystal doped with Er^{3+} and Ho^{3+} rare-earth ions shows, besides the principal spectrum corresponding to the allowed transitions from the 4*f* shell of a dopant ion to the 5*d* level split in the crystal field of the matrix, an additional absorption band (Fig. 1 a). This band has the following properties: first, the absorption in this band is two orders of magnitude weaker than that in the principal spectrum bands; secondly, for both the Er^{3+} and Ho^{3+} ions, this additional band is separated from the nearest principal absorption band by a distance of about 2400 cm^{-1} .

In the absorption spectrum of a KY_3F_{10} single crystal doped with an Er^{3+} ion, there is a relatively broad band with a maximum at 60 850 cm^{-1} . The half-width and the energy of the respective transition enables one to assign this band to the 4*f*-5*d* transition in the Er^{3+} ion. At the same time, this absorption is two orders of magnitude weaker than that in the principal absorption bands of Er^{3+} in other fluoride matrices [2] and is commensurable with the absorption in the additional band for the absorption spectrum of the Er^{3+} ion in the BaY_2F_8 matrix. Moreover, in the $\text{KY}_3\text{F}_{10}:\text{Er}^{3+}$ single crystal there is observed the most short-wavelength luminescence (among the reported VUV luminescence bands of doped crystals) at

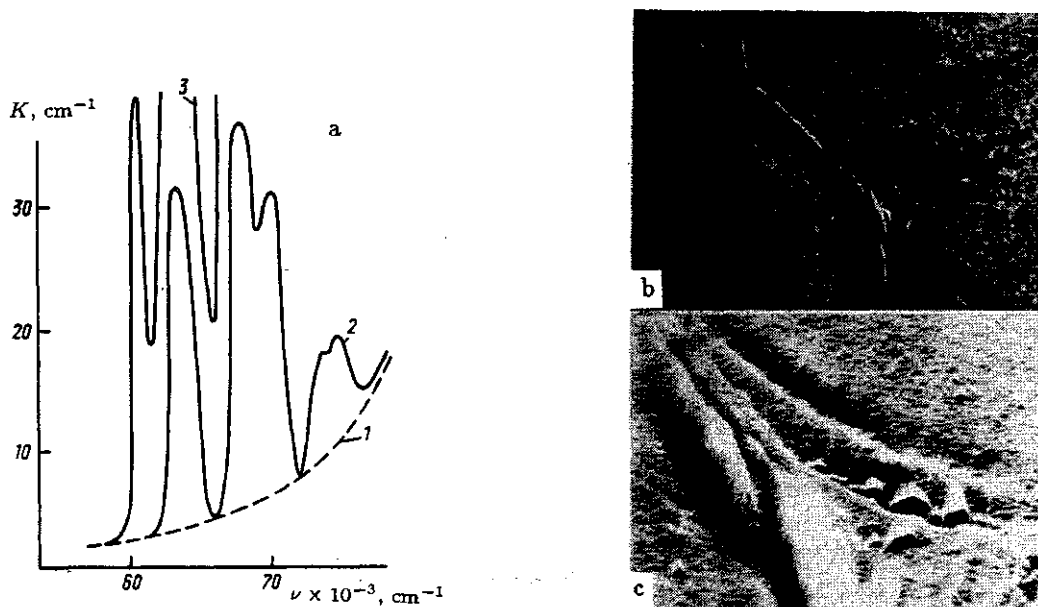


Fig. 1

(a) Spectrum of the $4f-5d$ transitions in the Er^{3+} ion embedded in the BaY_2F_8 single crystal: undoped matrix (1); the BaY_2F_8 single crystal doped with the Er^{3+} ion at a concentration of 0.1 at.% (2) and 9.8 at.% (3). (b) Crystallization picture for the $\text{BaY}_2\text{F}_8:\text{Er}^{3+}$ single crystals (type II structure). Photograph in black-and-white, magnification $\times 150$. (c) Area of encounter of crystallization fronts, which forms with large shear deformations and microtwinning dislocations. Photograph taken in the Y modulation mode, magnification $\times 1000$. The photographs here and in Figs. 2 and 3 were reduced.

1690 Å having a quantum yield no less than 20% [7] (Fig. 2 a and b).

In the absorption spectrum of a BaY_2F_8 single crystal doped with $\text{Yb}^{2+,3+}$ and $\text{Tm}^{2+,3+}$ ions, besides the absorption band corresponding to a transition from the $4f$ shell to the lower sublevel of the $5d$ level split in the crystal field, there is a wide absorption band having the shape of a pedestal tilted toward lower frequencies (Fig. 3 a).

The SEM studies [3, 4] of BaY_2F_8 and KY_3F_{10} single crystals doped with rare-earth ions revealed the presence of two characteristic types of structures. Unexpectedly it was found during the structure analysis that all the samples doped with rare-earth ions differed not by the signs of isomorphism of the dopant ion embedded in these crystals (this sign turns out to be secondary during the formation of the crystal structure), but by the following principle.

When the rare-earth ions show a mixed valence ($\text{Yb}^{2+,3+}$, $\text{Tm}^{2+,3+}$) the structure of the matrices containing these ions is characterized by the production of polysynthetic microtwins with small shear deformations in the (010) split planes; the assumed direction of twinning is [010] (Fig. 3 b and c) (type I structure). The BaY_2F_8 single crystals doped with $\text{Yb}^{2+,3+}$ and $\text{Tm}^{2+,3+}$ belong to this type of structure.

When the rare-earth ions show a valence equal to 3 only, there appears a structure having the following three features (Fig. 1 b and c and Fig. 2 c): sites of continuity breakdown in the form of negatively charged outlets of screw dislocations of the LiF type; concentric crystallization waves originating from these sites; regular closed triangle formations produced when several crystallization fronts run into one another and there are large shear stresses (type II structure). The $\text{BaY}_2\text{F}_8:\text{Er}^{3+}$, Ho^{3+} , and $\text{KY}_3\text{F}_{10}:\text{Er}^{3+}$ single crystals belong to this type of structure.

Our conclusions concerning the occurrence of two types of structure in fluoride matrices doped with rare-earth ions are consistent with the data of X-ray analysis for BaY_2F_8 single crystals doped with rare-earth ions [5]. It has been established in [5] that there exist two types of the $\alpha \leftrightarrow \beta$ polymorphic transition. For

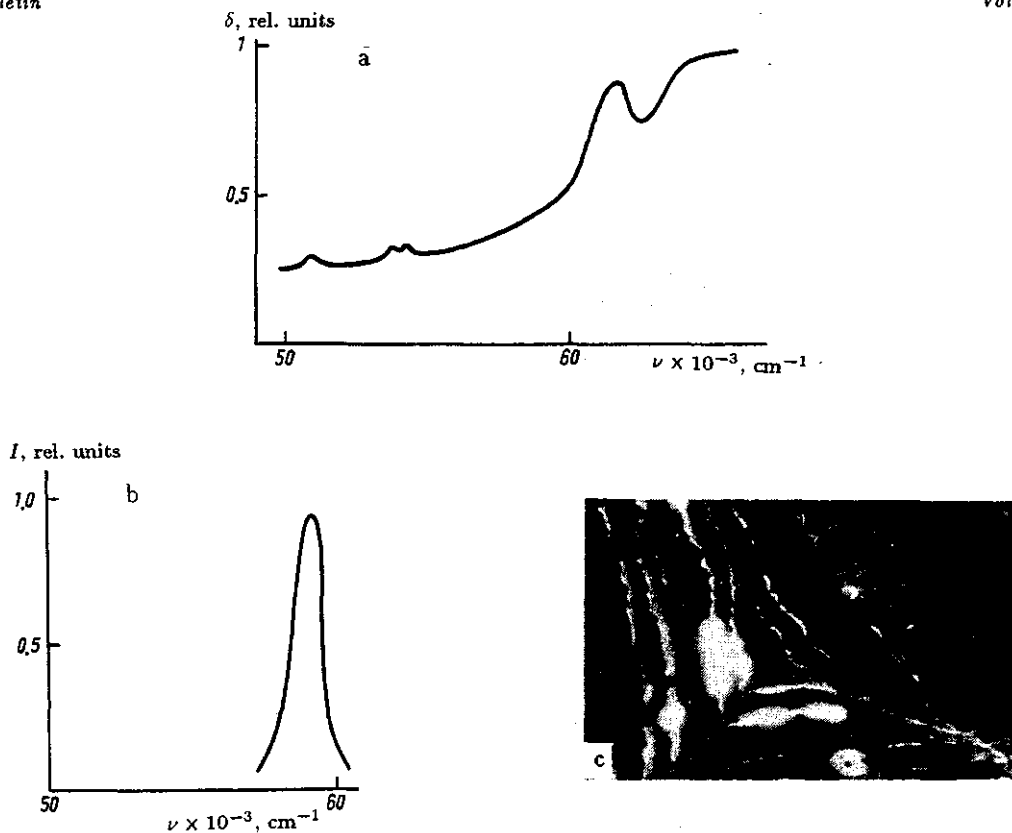


Fig. 2

- (a) Spectrum of the $4f-5d$ transitions in the Er^{3+} ion embedded in the KY_3F_{10} single crystal. (b) Luminescence spectrum of the Er^{3+} ion in the KY_3F_{10} single crystal. (c) Fragment of a regular structure in $\text{KY}_3\text{F}_{10}:\text{Er}^{3+}$. Photograph in X-rays, magnification $\times 1000$.

the first of them, the structure of the high-temperature α -phase is formed due to small relative displacements of Ln-polyhedra with a redistribution of the vertex-edge links, which corresponds to a structure of type I suggested by us. The second type of transition occurs with a change in the coordination number of Ln^{3+} and is accompanied by considerable heat release and large shear deformations. It proceeds with a change in the crystal lattice symmetry from a low-temperature monoclinic (β -phase) to a high-temperature one (α -phase), which corresponds to a type II structure.

The structural studies carried out for the BaY_2F_8 and KY_3F_{10} single crystals doped with rare-earth ions and their identification suggest the following conclusions about the mechanisms of origination of anomalous features in the VUV spectra of the dopant ions under consideration.

The BaY_2F_8 single crystals doped with $\text{Yb}^{2+,3+}$ and $\text{Tm}^{2+,3+}$ ions of mixed valence show a type I crystal structure. In their absorption spectra, a "pedestal" is observed at the principal absorption band (Fig. 3 a and b). A type I structure is characterized by the presence of a translational microtwin with insignificant shear deformations (the displacements of the elementary cell edges are small compared to the cell dimensions). Therefore, the change in the field of a crystal cell located at the boundary between two planes displaced relative to each other turns out to be substantially smaller than the average crystal field of an undeformed cell. So, this change of the crystal field may be considered as a small perturbation. Since the $4f$ sublevels of the rare-earth ions are known not to be much affected by the crystal field, the change of the energy of the $4f-5d$ transition is determined exclusively by the shift of the $5d$ sublevel, which is given by:

$$\Delta E_n = \langle n | e \Delta \varphi | n \rangle,$$

where $\Delta \varphi$ is the perturbation of the crystal field potential arising due to a small deformation of the crystal cell; $|n\rangle$ is the eigenfunction of the $5d$ sublevel; e is the electron charge. The value of ΔE_n is substantially

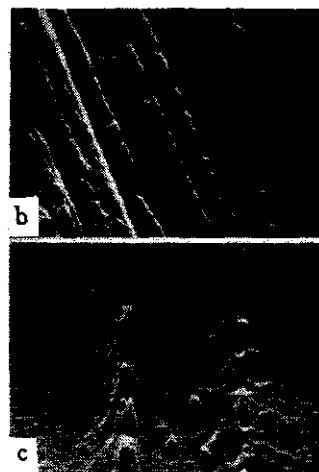
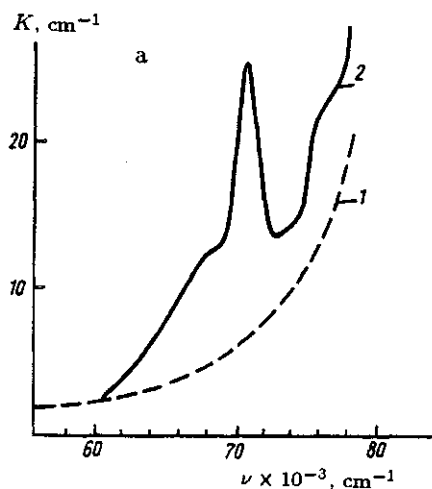


Fig. 3

(a) Spectrum of the $4f-5d$ transitions in the $\text{Yb}^{2+,3+}$ ion embedded in the BaY_2F_8 single crystal: undoped matrix (1); BaY_2F_8 matrix doped with the $\text{Yb}^{2+,3+}$ ion at a concentration of 0.05 at.%. (b) Typical fragment of the $\text{BaY}_2\text{F}_8:\text{Yb}^{2+,3+}$ single crystal structure showing a twinning dislocation array formed at the (010) split planes (type I structure). Magnification $\times 1000$. (c) Separate microtwin, magnification $\times 20\,000$.

smaller than the characteristic splitting of the $5d$ sublevel in the crystal field of an undeformed cell. The small change in the energy of the $4f-5d$ transition in rare-earth ions leads to the appearance of a low-intensity band in the absorption spectrum that is separated from the principal band by the distance ΔE_n . Displacements, differing in magnitude, between different neighboring crystal planes in a twin result in the appearance of a set of low-intensity overlapping absorption bands, which merge into a "pedestal" for the band of the principal spectrum.

The BaY_2F_8 single crystal doped with trivalent Er^{3+} and Ho^{3+} ions has a type II crystal structure (Fig. 1 b), which is characterized by the formation of α -phase islands at the places where the crystallization waves meet. Naturally, the splitting of the $5d$ level of the dopant ion placed in a crystal field of rhombic symmetry occurs in a different way than it does in a crystal field of monoclinic symmetry of the β -phase, and this gives rise to the appearance of additional bands in the absorption spectrum. Since the α -phase occupies a small fraction of the volume (a few percent of the crystal volume), the absorption of the dopant ions embedded in this phase turns out to be about two orders of magnitude smaller than that in the principal part of the spectrum belonging to β -phase. Therefore, no additional absorption bands that would overlap with the principal part of the spectrum are observed (Fig. 1 a).

The only additional absorption band observed belongs to the transition from the ground state to the lower sublevel of the $5d$ level of the dopant ion split in the crystal field of rhombic symmetry. This band is shifted by 2400 cm^{-1} from the last band of the principal absorption spectrum of the dopant ion (Er^{3+} or Ho^{3+}), located in the monoclinic field, toward longer wavelengths.

No luminescence from Er^{3+} and Ho^{3+} ions in the BaY_2F_8 matrix was detected. This is because the lower $5d$ sublevel in these ions, located in the α -phase, is not metastable.

The SEM studies show that the structure of the $\text{KY}_3\text{F}_{10}:\text{Er}^{3+}$ single crystals belongs to type II. The mechanism of appearance of additional bands in its absorption spectrum is therefore similar to that considered above for the $\text{BaY}_2\text{F}_8:\text{Er}^{3+}$ and $\text{BaY}_2\text{F}_8:\text{Ho}^{3+}$ single crystals.

In the $\text{KY}_3\text{F}_{10}:\text{Er}^{3+}$ single crystal, upon emission excitation at 1580 \AA wavelength, there appears an intense luminescence band at 1690 \AA wavelength, which with an accuracy up to the magnitude of the Stokes shift corresponds to the absorption band observed (Fig. 2 a and b) [7]. Luminescence occurs upon transition from the lower $5d$ sublevel of Er^{3+} in the α -phase to its ground $4f$ state. The large quantum yield of luminescence (more than 20%), which is not proportional to the content of the α -phase in the crystal, in our opinion is related to the process of resonant energy transfer taking place in the crystal.

The rate of resonant energy transfer between the dopant ions embedded in the neighboring crystal cells [6], with allowance for the oscillator strength of $4f-5d$ transitions (10^{-2}) and the band half-width (2000 cm^{-1}), is given by:

$$W = kW_0, \quad 0 \leq k \leq 1, \quad (1)$$

where $W_0 \sim 10^{12}\text{ s}^{-1}$ and k is a dimensionless parameter characterizing the extent of overlapping between the emission spectrum of the donor and the absorption spectrum of the acceptor. The shift between the absorption and luminescence spectra of Er^{3+} in the KY_3F_{10} matrix and also the half-width of the spectral bands are equal to 2000 cm^{-1} . So for a Lorentzian shape of the spectrum, the parameter k in (1) has a value between 0.1 and 0.2. Therefore, the rate of resonant energy transfer between the Er^{3+} ions turns out to be three orders of magnitude greater than the rate of radiative decay of the $5d$ sublevel (10^8 s^{-1}), so that transfer of excitation may be expected to occur to a distance up to several hundred nanometers.

The process of resonant migration of excitations acquires essentially new features at the β - α interphase boundary. The shift of the lower $5d$ sublevel of Er^{3+} in the α -phase by 2450 cm^{-1} toward longer wavelengths relative to the lower $5d$ sublevel of Er^{3+} in the β -phase, together with the aforementioned shift by 2000 cm^{-1} in the same direction of the luminescence spectrum relative to the absorption spectrum, results in increased overlapping between the luminescence spectrum of the donor embedded in the β -phase and the absorption spectrum of the acceptor embedded in the α -phase. Since the mismatch between the band maxima in these spectra (450 cm^{-1}) is much smaller than the half-width of these bands, the parameter k in (1) grows, and the rate of excitation transfer from the β -phase to α -phase turns out to be still greater than the rate of their migration within the β -phase. On the other side, the mismatch between the absorption band of the acceptor in the β -phase and the emission band of the excited ion in the α -phase turns out to be 4450 cm^{-1} . These bands do not overlap, and a reverse transfer of excitation to the β -phase becomes impossible.

Therefore, a random energy migration in the $\text{KY}_3\text{F}_{10}:\text{Er}^{3+}$ crystal gives rise to a one-way flow of excitation to the α -phase. This leads to a substantial increase in the population of the metastable $5d$ sublevel and, accordingly, in the intensity of luminescence from this sublevel. Thereby, the Er^{3+} ions embedded in the β -phase play the role of luminescence sensitizers.

The large quantum yield of luminescence and the absence of absorption at this wavelength by Er^{3+} ions embedded in the β -phase make the two-phase $\text{KY}_3\text{F}_{10}:\text{Er}^{3+}$ crystal rather promising for lasing at shortest wavelengths of the VUV spectral range.

Therefore, the investigation of the interrelation between the regular structure imperfections in fluoride single crystals doped with rare-earth ions, revealed by SEM, and the specific features of their spectra may be utilized to improve the luminescence parameters of the materials studied.

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