

Optical and Depolarization Spectroscopy of Doubly Doped Alkaline-Earth Fluorides

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The process of recharging heterogeneous lanthanides in SrF₂ and BaF₂ crystals is studied by parallel measurements of optical absorption spectra and thermodepolarization curves. Electron transfer between lanthanides Yb²⁺–Nd³⁺, Eu²⁺–Yb³⁺ in SrF₂, and between Yb²⁺–Nd³⁺, Eu²⁺–Yb³⁺, and Yb²⁺–Dy³⁺ in BaF₂ is studied. Electron phototransfer between lanthanides, registered by a change in the absorption bands of divalent lanthanides, is accompanied by a backward migration of charge-compensating interstitial fluorine, which is detected by a change in the corresponding thermodepolarization peaks of Ln³⁺–F_i[–].

1. Introduction

Electron phototransfer from divalent to trivalent lanthanide has been studied in a number of works.^[1–3] For the first time, the phototransfer of an electron from the Eu²⁺ ion to the Sm³⁺ ion in crystals CaF₂, SrF₂ and BaF₂ was discovered by Feofilov.^[1] Reversible phototransfer of electrons between rare-earth ions Sm, Tm, and Eu in CaF₂ was found also in previous studies.^[4,5] Thermal bleaching of induced absorption bands in pairs of Eu²⁺–Ln³⁺ ions (where Ln is Nd, Sm, Dy, Er, Ho) during heating with a constant rate was investigated by Arkhangelskaya in CaF₂ and SrF₂ crystals. The processes of photoionization and electron capture in Eu–Sm pairs in SrF₂ and BaF₂ were studied in detail by McClure and coworkers.^[3,6–8] The change in valence was studied by optical methods (absorption, emission, and excitation). During photoexcitation of a divalent ion (this is usually Eu, Sm, Yb), the electron is transferred to a trivalent ion (to Nd, Sm, Dy, Ho, Tm, Yb).^[9] After the capture of an electron, the charge-compensating interstitial fluorine migrates to the initial lanthanide.^[3,6–8]

In several papers the electron transfers between lanthanides in alkaline-earth fluorides and other crystals were considered as intervalence charge transfer (IVCT) or metal-to-metal charge transfer (MMCT).^[10,11] Therefore the total mechanism of electron transfer should be refined.

Crystals with double activation of different lanthanides are used in many applications: as long-afterglow phosphors, up-conversion phosphors, thermoluminescent phosphors, and

others. The lack of full understanding in the mechanisms of electron transfer between different lanthanides in alkaline-earth fluorides requires additional research.

In this article, we investigated the electron phototransfer and transfer of an interstitial fluorine ion in doubly doped alkaline-earth fluorides by means of optical absorption and thermodepolarization (ionic thermocurrent) methods. In this case, the measurements of the optical spectra made it possible to monitor the electron transfer Ln₁²⁺ → Ln₂³⁺, and the measurement of the thermodepolarization curves made it

possible to follow the transfer of charge-compensating fluorine.

2. Experimental Results

The reorientation of dipoles of trivalent lanthanide-interstitial fluorine occurs in the temperature range of 120–150 K for dipoles in which the interstitial fluorine is in the nearest position (NN, C_{4v} symmetry) (in CaF₂^[12] and SrF₂^[13]) and in the interval of 170–210 K for dipoles with fluorine in the next-nearest interstitial position (NNN, symmetry C_{3v}) (in SrF₂^[13] and BaF₂^[14]). A necessary condition is that the temperatures of the depolarization peaks of heterogeneous lanthanides are different. The most convenient is SrF₂ crystal, in which light lanthanides are compensated by fluorine in NN positions, and heavy lanthanides are compensated by fluorine in NNN positions. The ion transfer during lanthanide recharging is registered by decreasing the peak of thermodepolarization of one lanthanide and increasing the peak of another lanthanide. After heating to high temperatures, the initial thermodepolarization curve and the initial optical absorption spectrum are restored.

2.1. SrF₂

Electron and fluorine transfer was found in pairs of lanthanides with initial charges of Yb²⁺–Nd³⁺ and Eu²⁺–Yb³⁺ in SrF₂ crystals.

2.1.1. Yb²⁺–Nd³⁺

SrF₂ crystals with an admixture of trivalent Nd³⁺ or Yb³⁺ ions are characterized by strong absorption bands in the region of the vacuum ultraviolet.^[15] Thermodepolarization curves of SrF₂–Nd³⁺ and SrF₂–Yb³⁺ crystals show peaks at around 140 K and 220 K (**Figure 1**) (see also a previous study^[13]). In crystals with an admixture of the same concentration of both trivalent lanthanides, both thermodepolarization peaks at 220 and

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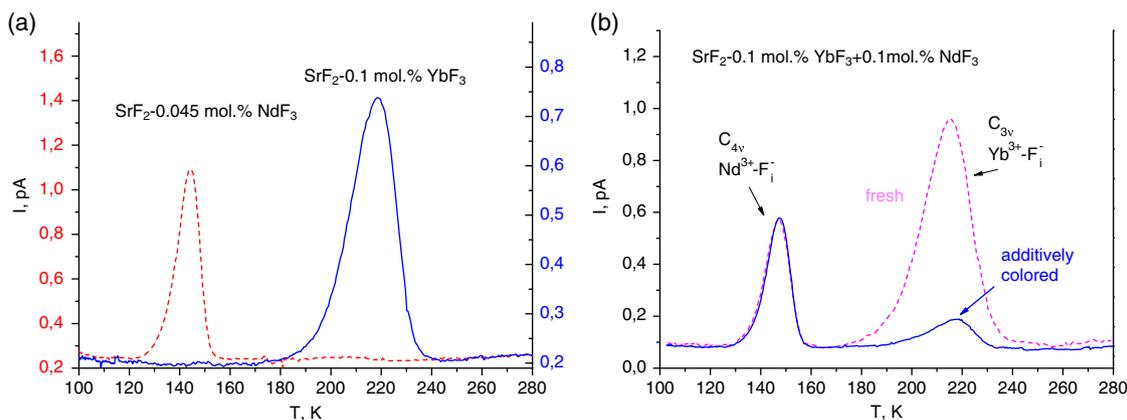


Figure 1. Thermodepolarization spectra of $\text{SrF}_2\text{-YbF}_3$, $\text{SrF}_2\text{-NdF}_3$, and $\text{SrF}_2\text{-YbF}_3\text{-NdF}_3$. a) Thermodepolarization spectra of $\text{SrF}_2\text{-0.1\% YbF}_3$ and $\text{SrF}_2\text{-0.045\% NdF}_3$. b) Thermodepolarization spectra of fresh and additively colored $\text{SrF}_2\text{-0.1\% YbF}_3\text{-0.1\% NdF}_3$.

140 K are observed with an area ratio 2.8:1 (see Figure 1). A larger peak near 220 K is associated with a larger C_{3v} ($\text{Yb}^{3+}\text{-F}_i^-$) dipole moment relative to C_{4v} ($\text{Nd}^{3+}\text{-F}_i^-$). The peak area is proportional to the square of the dipole moment.^[16] From the geometric model, the square of the dipole moment C_{3v} should be three times larger than the dipole moment of the C_{4v} dipole.

In crystals $\text{SrF}_2\text{-Gd}^{3+}$, the ratio of dipole moments was estimated as 2.4, which is 40% more than the value calculated from the simple geometric unrelaxed point ion (UPI) model.^[17] A significant decrease in the dipole moment due to Coulomb attraction for the nearest C_{4v} pair and a slight variation for the C_{3v} pair are assumed.^[17]

After additive coloration, the peak value at 240 K decreases by about eight times whereas the peak at 140 K does not change (Figure 1b), which indicates that about 90% of trivalent Yb ions becomes divalent, and trivalent Nd ions do not change the valence.

$\text{SrF}_2\text{-Yb-Nd}$ crystals after photobleaching with an ozone lamp take on a brown color. The induced absorption bands near 300 and above 400 nm (Figure 2a) belong to the Nd^{2+} ions.^[18] The electron transfer from Yb^{2+} to Nd^{3+} leads to a decrease in the thermodepolarization peak at 140 K ($\text{Nd}^{3+}\text{-F}_i^-$) and an increase

in the peak at 215 K ($\text{Yb}^{3+}\text{-F}_i^-$). The relative values of the decrease in the absorption bands of Yb^{2+} and the decrease in the peak of the depolarization of trivalent $\text{Nd}^{3+}\text{-F}_i^-$ are the same (see Figure 2). This indicates that electron transfer from Yb to Nd is the only ongoing process.

2.1.2. $\text{Eu}^{2+}\text{-Yb}^{3+}$

The study of electron transfer in $\text{SrF}_2\text{-Eu-Yb}$ crystals turned out to be more difficult, due to the fact that the absorption bands of divalent lanthanides Eu and Yb overlap strongly. The initial (or annealed at 700 °C) absorption spectrum of $\text{SrF}_2\text{-Eu-Yb}$ (Figure 3) contains only Eu^{2+} bands. After photobleaching with light of 254 nm, the Eu^{2+} bands are partially reduced and the Yb^{2+} bands appear (see Figure 3).

The absorption spectra belonging to divalent Eu and Yb were previously studied in single-doped $\text{SrF}_2\text{-Yb}^{2+}$ and ^[19] $\text{SrF}_2\text{-Eu}^{2+}$.^[20] When illuminating a double-doped $\text{SrF}_2\text{-Eu}^{2+}\text{-Yb}^{3+}$ crystal into the Eu^{2+} band, a decrease in the Eu^{2+} absorption bands and the appearance of Yb^{2+} bands (bands around

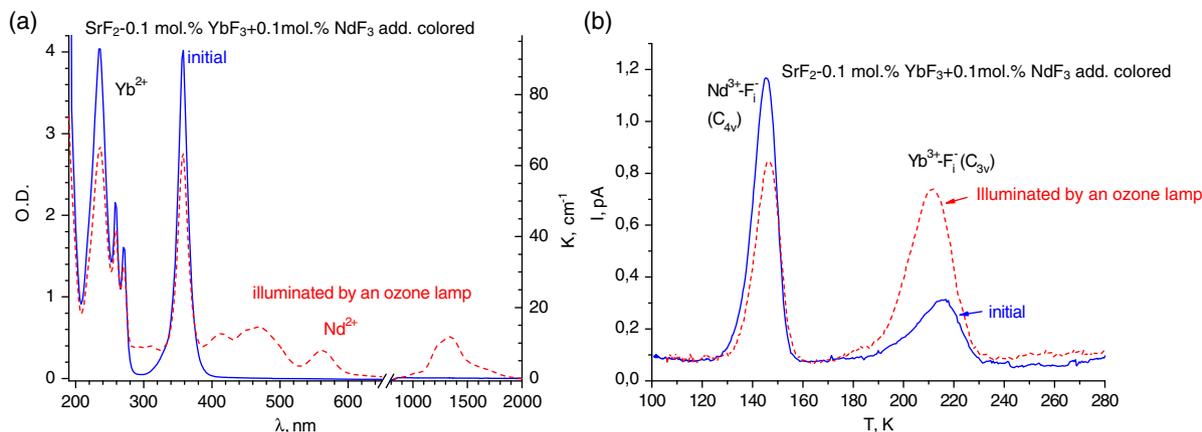


Figure 2. Absorption and thermodepolarization spectra of additively coloured $\text{SrF}_2\text{-Yb-Nd}$. a) Absorption spectra of $\text{SrF}_2\text{-0.1\% YbF}_3\text{-0.1\% NdF}_3$. b) Thermodepolarization spectra of $\text{SrF}_2\text{-0.1\% YbF}_3\text{-0.1\% NdF}_3$.

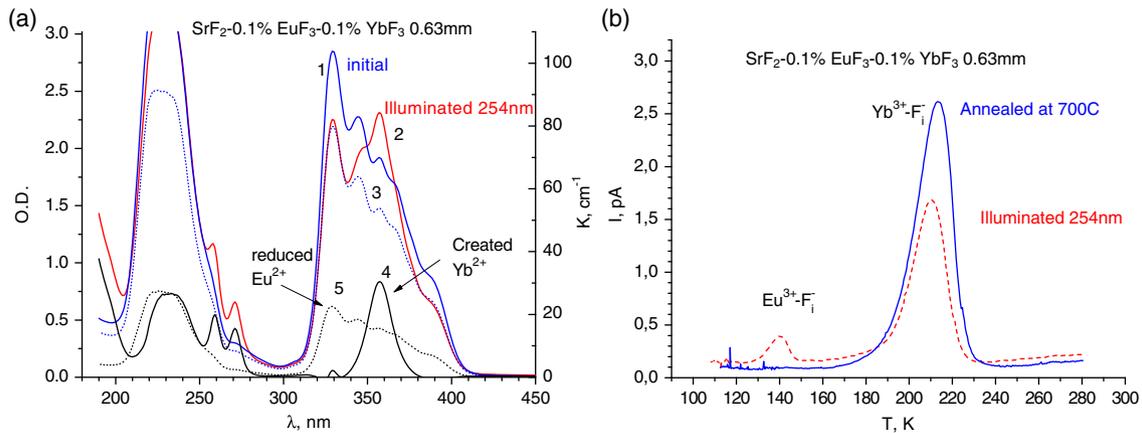


Figure 3. Absorption and thermodepolarization spectra of SrF₂-Eu-Yb. a) Absorption spectra of SrF₂-0.1% EuF₃-0.1% YbF₃. 1—initial spectrum, 2—after illumination 254 nm, 3—reduced spectrum 1, showing the destruction of part of Eu²⁺ ions, 4—difference spectrum 2–3, showing the creation of Yb²⁺ ions, 5—difference spectrum 1–3, spectrum of the destroyed Eu²⁺ ions. b) Thermodepolarization spectra of SrF₂-0.1% Eu-0.1% YbF₃.

360–230 nm and the edge of the band at 180 nm) were observed. In difference spectra, this is clearly shown in Figure 3a.

The depolarization spectrum of the bleached sample shows a decrease in the peak at 215 K (Yb³⁺-F_i⁻) and the appearance of a weak peak at 140 K (Eu³⁺-F_i⁻). The initial (or annealed at 700 °C) sample shows only an enlarged peak at 215 K (Yb³⁺-F_i⁻).

2.2. BaF₂

In BaF₂ crystals, predominantly C_{3v} dipoles were observed with NNN position of interstitial fluorine in relation to trivalent lanthanide.^[14] The temperature of the depolarization peak decreases with a decrease the radius of the lanthanide from light to heavy ions.^[14] The temperature difference reaches 20–30 K. By choosing a pair of lanthanides with different radii, two peaks of thermodepolarization can be distinctly recorded.

In doubly doped BaF₂ crystals, electron and interstitial fluorine transfer is found in the pairs Yb²⁺-Nd³⁺, Eu²⁺-Yb³⁺, and Yb²⁺-Dy³⁺.

2.2.1. Yb²⁺-Nd³⁺

In BaF₂-YbF₃ and BaF₂-NdF₃ crystals, thermal depolarization peaks at 180 and 215 K are observed due to the reorientation of dipoles Yb³⁺-F_i⁻ and Nd³⁺-F_i⁻, respectively. In the BaF₂-YbF₃-NdF₃ crystals, both peaks of depolarization were observed as well as a small peak at 145 K (**Figure 4b** curve 1). Both lanthanides were trivalent as we did not observe divalent absorption bands. The height of 145 K peak is proportional to the height of 180 K peak (Yb³⁺) and is possibly due to C_{4v} Yb³⁺-F_i⁻ dipoles. After the additive coloration, Yb depolarization peaks at 140 and 180 K disappear (**Figure 4b**), and bands at 360 and 220 nm of Yb²⁺ appear in the absorption spectrum (**Figure 4a**). After ozone lamp

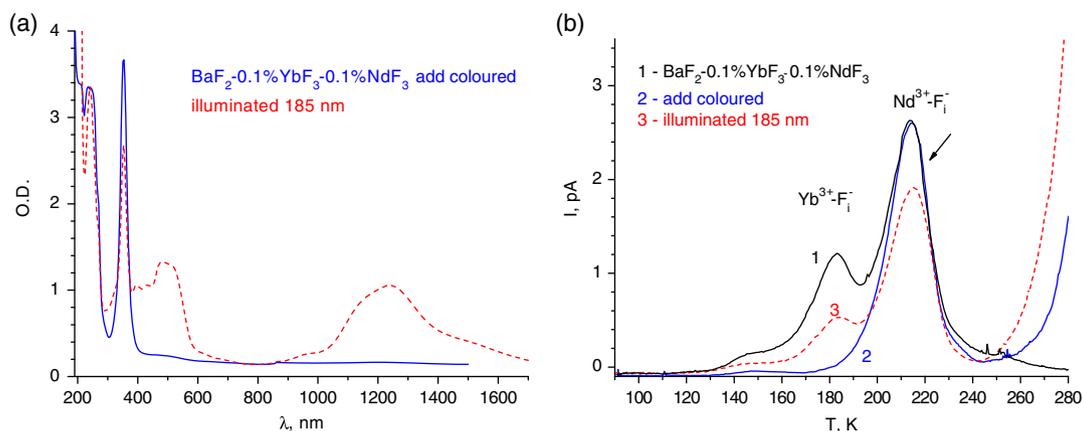


Figure 4. Absorption and thermodepolarization spectra of BaF₂-Yb-Nd. a) Absorption spectra of additively colored BaF₂-0.1% YbF₃-0.1% NdF₃. b) Thermodepolarization spectra of fresh (1) and additively colored (2,3) BaF₂-0.1% YbF₃-0.1% NdF₃.

illumination (185 nm active line), the Yb^{2+} absorption bands decrease by about one-third and the Nd^{2+} bands appear (see Figure 4a). At the same time, a decrease in $\text{Nd}^{3+}-\text{F}_i^-$ peak at 215 K and the appearance of $\text{Yb}^{3+}-\text{F}_i^-$ peaks were observed (see Figure 4b).

2.2.2. $\text{Eu}^{2+}-\text{Yb}^{3+}$

In the $\text{BaF}_2-0.1\%\text{EuF}_3-0.1\%\text{YbF}_3$ crystal, both the absorption bands of Eu^{2+} and the peaks of thermal depolarization of Eu^{3+} and Yb^{3+} are observed. By the magnitude of the absorption coefficient of the Eu^{2+} wavelength band at 325 nm and by the magnitude of the thermal depolarization peak, it can be estimated that about half of europium has turned into a divalent state. The presence of trivalent europium in this crystal is further confirmed by observing the linear spectrum of Eu^{3+} under excitation by the 405 nm laser.

When the crystal is illuminated with a line of 254 nm mercury lamp, the absorption bands of Eu^{2+} decrease and the bands of Yb^{2+} appear (Figure 5a). In parallel with this, the Yb^{3+}

depolarization peaks at 145 and 185 K decrease and the Eu^{3+} peak at 220 K increases (see Figure 5b).

2.2.3. $\text{Yb}^{2+}-\text{Dy}^{3+}$

In the $\text{BaF}_2-\text{Yb}-\text{Dy}$ crystals, the lanthanides were in the trivalent state, as no absorption bands were observed in the wavelength range of more than 200 nm. Such crystals showed thermodepolarization peaks at about 180 K (Yb^{3+}) and at about 205 K (Dy^{3+}). After additive coloration in calcium vapor, absorption bands of divalent ytterbium at 220 and 360 nm appeared (Figure 6a). At the same time, the peak of thermodepolarization at 180 K disappeared, which indicated a complete transformation of the Yb^{3+} ions to the divalent state (see Figure 6b). After the illumination by 185 nm light of the ozone mercury lamp, the absorption bands of Yb^{2+} decreased by one-third and divalent dysprosium bands at 450, 560, 680, and 840 nm^[18] appeared. At the same time, the peak of depolarization of Dy^{3+} at 205 K decreased and peak of Yb^{3+} at 180 K appeared.

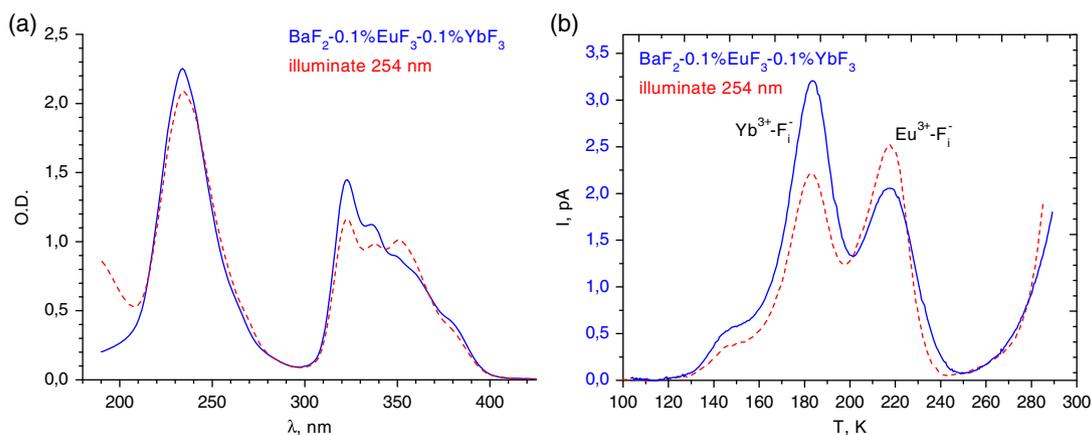


Figure 5. Absorption and thermodepolarization spectra of $\text{BaF}_2-\text{Eu}-\text{Yb}$. a) Absorption spectra of $\text{BaF}_2-0.1\% \text{EuF}_3-0.1\% \text{YbF}_3$. b) Thermodepolarization spectra of $\text{BaF}_2-0.1\% \text{EuF}_3-0.1\% \text{YbF}_3$.

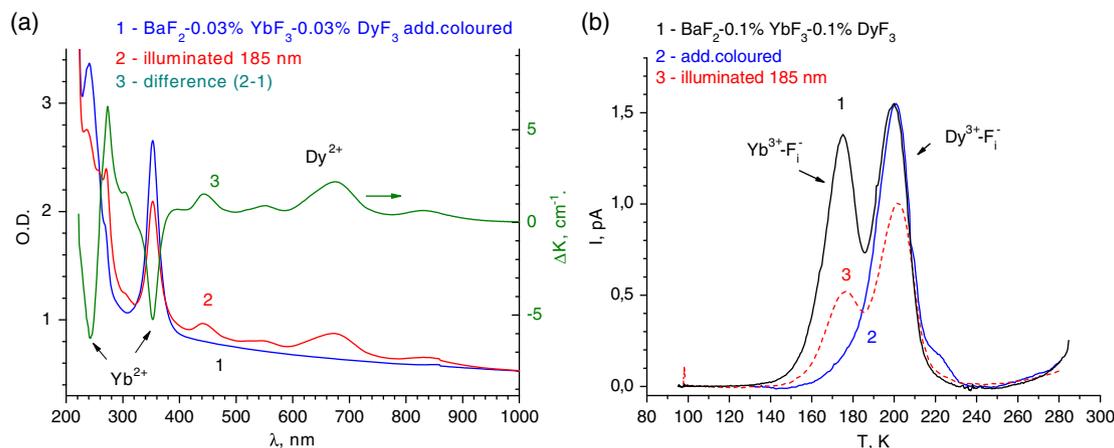


Figure 6. Absorption and thermodepolarization spectra of $\text{BaF}_2-\text{Yb}-\text{Dy}$. a) Absorption spectra of additively colored $\text{BaF}_2-0.1\% \text{YbF}_3-0.1\% \text{DyF}_3$. b) Thermodepolarization spectra of fresh (1) and additively colored (2,3) $\text{BaF}_2-0.1\% \text{YbF}_3-0.1\% \text{DyF}_3$.

3. Discussion

Thermodepolarization (ionic thermocurrents), together with optical spectroscopy, was used to study the behavior of dipoles in alkaline-earth fluorides earlier.^[21–23] Nevertheless, thermodepolarization spectroscopy, together with optical spectroscopy, was used for the first time to apply electron and ion processes during recharging between heterogeneous lanthanides in alkaline-earth fluoride crystals SrF₂ and BaF₂.

When growing crystal MeF₂ under reducing conditions or during additive coloration in host metal vapors, initially trivalent lanthanide with greater electron affinity (defined as the distance from the ground level of divalent lanthanide to the bottom of the conduction band) became divalent, whereas the other lanthanide remained trivalent (see also previous studies^[1–3]). The coincidence of the thermodepolarization peaks for identical lanthanides in BaF₂ or SrF₂ crystals with single and double doping in most cases indicates the absence of strong interaction between heterogeneous dipoles.

Using the molar coefficients for CaF₂ (Table 1), changes in the Eu–Yb concentrations in SrF₂ during photorecharging are estimated at about $2 \times 10^{18} \text{ cm}^{-3}$ (see Figure 3a), whereas the change in the dipole concentration is $0.5 \times 10^{18} \text{ cm}^{-3}$ (Table 2). For BaF₂–Yb–Dy, changes in the concentrations of dipoles during recharging are $0.3 \times 10^{18} \text{ cm}^{-3}$ (Table 3), changes in absorption coefficients (Figure 6a) give an estimate of about $0.6 \times 10^{18} \text{ cm}^{-3}$. Apparently, the molar absorption coefficients of Ln²⁺ in SrF₂ and BaF₂ crystals are lower than that in CaF₂.

Table 1. Wavelength and absorption coefficient for 0.01 mol.% of several Ln²⁺ in CaF₂ crystals.

Impurity	λ [nm]	α [cm ⁻¹]	Reference
Nd	1475	8.1	[18]
Eu	338	17.9	[18]
Dy	715	6.2	[18]
Yb	365	18.1	[24]

Table 2. Released charge Q (in 10^{11} C) and concentration of dipoles N_d in (10^{18} cm^{-3}) in fresh and illuminated 254 nm SrF₂–0.1EuF₃–0.1YbF₃ crystals. In grown crystals all europium was Eu²⁺.

Crystal	Q (Yb, 215 K)	Q (Eu, 140 K)	N_d (Yb)	N_d (Eu)
Fresh	0	1.05	0	1.27
Illum.	0.76	0.64	0.52	0.78

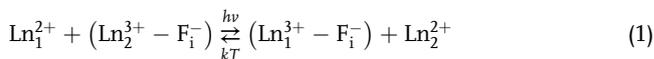
Table 3. Released charge Q (in 10^{11} C) and concentration of dipoles N_d in (10^{18} cm^{-3}) in fresh, additively colored, and illuminated 185 nm BaF₂–0.1YbF₃–0.1DyF₃ crystals. In grown crystals all lanthanides were trivalent.

Crystal	Q (Yb, 175 K)	Q (Dy, 205 K)	N_d (Yb)	N_d (Dy)
Fresh	4.46	6.56	0.73	1.08
Add. col.	0.24	4.87	0.06	1.23
Illum.	1.40	3.54	0.35	0.89

In BaF₂–Yb–Ln, we observed the appearance of a weak Yb³⁺–F_i⁻ peak at 140 K along with the main peak at 180 K for the second lanthanides Nd, Sm, Eu, and Tm. In the remaining cases of BaF₂–Yb–Ln (Ce, Pr, Gd, Tb, Dy, Ho, Er), the appearance of a low-temperature Yb³⁺–F_i⁻ peak of depolarization was not observed. The reason for this is still unclear.

In double-doped BaF₂ and SrF₂ crystals, we observed that about one-third of the divalent lanthanides changes the valence during photobleaching at an impurity concentration of 0.01, 0.03, and 0.1 mol%. This suggests that electron transfer occurs between single ions and not between ions in aggregate complexes. As the average distance between the impurity lanthanides in crystals with a concentration of 0.01 mol% is greater than ten lattice constants, it should be concluded that the transfer occurs through the conduction band. This is also indicated by the fact that the energy required for phototransfer of an electron with Yb²⁺ and Eu²⁺ corresponds to the excitation energy of electrons to the conduction band^[25] and that in BaF₂–Eu²⁺ and BaF₂–Yb²⁺ crystals; with such excitation, photoconductivity was observed.^[19,26,27]

Using optical spectroscopy for MeF₂–Ln₁–Ln₂, we can follow the electron transfer between divalent and trivalent heterogeneous lanthanides. Using a parallel thermodepolarization method, we can follow the movement of interstitial fluorine during the charge exchange process. A set of measurements allows us to record the complete recharge reaction in the form



The reaction proceeds in three almost independent stages.^[3,8,9] At the first stage, the photoexcitation of electrons from Ln₁²⁺ ions to the conduction band occurs. Then, at the second stage, an electron is captured by a trivalent lanthanide of another sort Ln₂³⁺. At the third stage, the migration of interstitial fluorine is made to the trivalent Ln₁³⁺ ion for its charge compensation. At temperatures below thermodepolarisation peak Ln₂³⁺–F_i⁻, the movement of interstitial fluorine is frozen, which leads to a significant decrease in the electron exchange and to the shift of the bands of the formed Ln₂³⁺–F_i⁻ to the red side.^[9]

4. Conclusion

Thermodepolarization spectroscopy makes it possible to monitor changes in the concentrations of Ln³⁺–F_i⁻ dipoles in doubly doped alkaline-earth fluoride crystals during photorecharging and is an important tool for studying ionic processes accompanying electron transfer.

5. Experimental Section

Crystals were grown in vacuum in a graphite crucible by the Stockbarger method.^[13] The graphite crucible contained six cylindrical cavities with a diameter of 10 mm and a length of 80 mm, which made it possible simultaneously to grow six samples with sizes $\varnothing 10 \times 50$ mm with different amounts of impurities. A few percentages of CdF₂ was added into raw materials for purification from oxygen during growth.

MeF₂ crystals were grown with the double activation of lanthanides of one group (Eu, Yb, Sm) and lanthanides of the other group (Nd, Sm, Dy, Ho, Er, Tm, Yb). Both lanthanide impurities were introduced in equal concentrations with levels of 0.01, 0.03, and 0.1 mol%. When alkaline-earth

fluorides were grown, doubly doped with different lanthanides under reducing conditions, only one of the lanthanides became divalent and the other remained trivalent.^[1,9] Often crystals contained both lanthanides in the trivalent state. In this case, the conversion of the trivalent rare-earth ions to the divalent state was achieved by heating the trivalent-containing crystal in vacuum in an atmosphere of the appropriate alkaline-earth metal (additive coloration).^[28–30] The vacuum container with crystals and metallic calcium was heated at 750–850 °C for 1–2 h. After additive coloration, a significant part of the most thermally stable lanthanide became divalent.^[9,31]

The same samples were used for optical and depolarization measurements. Absorption spectra in the range 190–3000 nm were taken with a spectrophotometer Perkin-Elmer Lambda-950. Ionic thermocurrent was measured using a picoammeter A2-4 (MNIPI Minsk). Measurements were done in vacuum with Pt electrode and heating rate as 20 K min⁻¹. At first the sample (diameter near 10 mm and thickness near 1 mm) was polarised usually at room temperature with 2 kV for 2–3 min and then it was cooled down to 80 K. Then electrodes were connected to a picoammeter, sample was heated, and current registered.

When photobleaching Yb²⁺, the 185 nm line of the ozone Hg lamp turned out to be the most effective. The 254 nm Hg discharge line, which was located in the region of the Eu²⁺ absorption band at 230 nm, turned out to be effective for bleaching divalent europium.^[9]

The concentration of divalent ions in alkaline-earth fluoride crystals was estimated from the absorption coefficient of the long-wavelength bands using data for CaF₂.^[18] For CaF₂–Yb²⁺ the cross section of the absorption band 365 nm was found to be $\sigma = 7.4 \times 10^{-18} \text{ cm}^2$.^[24] Then for $N = 0.01 \text{ mol\%}$ one can calculate $\alpha = N \cdot \sigma = 2.45 \times 10^{18} \text{ cm}^{-3} \times 7.4 \times 10^{-18} \text{ cm}^2 = 18.1 \text{ cm}^{-1}$.

The molar absorption coefficients of divalent lanthanides in SrF₂ and BaF₂ crystals are still unknown. Therefore, the data for CaF₂ crystals can be used as approximates for other alkaline-earth fluorides.

The concentration of the Ln³⁺–F_i⁻ dipoles was estimated by the area under the thermodepolarization curve using the equation^[16]

$$P = N_{\text{dip}} \frac{ap^2 E_p}{kT_p} = \int \sigma(t) dt \quad (2)$$

where a is a geometrical factor depending on the possible dipolar orientation (for free rotating dipoles, $a = 1/3$), N_{dip} is dipole concentration, p is dipole moment, E_p is strength of polarization electric field, k is Boltzmann constant, and T_p is polarization temperature.

For the correct calculation of the concentration of dipoles, it is important to know the exact value of the dipole moment. In the first works, it was assumed that the dipole moment was determined by the distance between the lanthanide and the compensating interstitial fluorine in the undistorted-point-ion model. It was subsequently proved that the dipole moment of C_{4v} dipoles in SrF₂–Gd was 2.0 eÅ (instead of 2.9 eÅ), whereas for C_{3v} dipoles it remained 5.0 eÅ.^[32]

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Conflict of Interest

The author declares no conflict of interest.

Keywords

electron transfer, lanthanide impurities, optical absorption, thermodepolarization

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