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IMPURITY CENTERS

Electron Transfer between Different Lanthanide Centers in BaF_2 Crystals—Part II: Transfer Mechanisms

E. A. Radzhabov[a], * and V. A. Kozlovskii[a]

[a] *Vinogradov Institute of Geochemistry, Siberian Branch, Russian Academy of Sciences, Irkutsk, Russia*

**e-mail: eradzh@igc.irk.ru*

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Abstract—Processes of photo-induced electron transfer from a bivalent acceptor lanthanide (Eu, Sm, and Yb) onto a trivalent donor lanthanide (Nd, Sm, Dy, Tm, and Yb) and the inverse thermally activated transfer are studied in barium fluoride crystals. At room temperature, photoinduced electron transfer is accompanied by oncoming displacement of the interstitial charge-compensating fluoride ion. On photoquenching at low temperatures, a bivalent donor lanthanide remains next to the interstitial fluoride ion, which causes a redshift of its 4*f*–5*d* absorption bands. The shift increases as the lanthanide size decreases (as in the series Nd, Sm, Dy, Tm, and Yb). A detailed analysis of the mechanisms of photo and thermal electron transfers between the different lanthanide centers in BaF_2 crystals is provided.

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1. INTRODUCTION

Phosphor crystals doubly activated by different lanthanides have found use as long-persistent, up-conversion, and thermoluminescence phosphors, to name a few, which requires detailed studies of processes of electron (or hole) transfer between different lanthanide centers.

Photoinduced electron transfer from the Eu^{2+} ion onto the Sm^{3+} ion incorporated in host crystals of such earth-alkaline fluorides as CaF_2, SrF_2, and BaF_2, was first reported by Feofilov [1]. Photoinduced electron transfer was studied in great detail in BaF_2–Eu–Sm crystals. The intensity of absorption band due to Eu^{2+} (at 235 nm) reduced by 2/3 and the intensities of Sm^{2+} bands increased accordingly using UV radiation. The reverse thermal transition occurred after heating to 400–600°C and was accompanied by restoration of the initial absorption spectrum [1]. Thermal quenching of induced adsorption bands for Eu–R ion pairs (R = Nd, Sm, Dy, Er, and Ho) that occurred during linear heating was studied by Arkhangelskaya et al. in CaF_2 and SrF_2 crystals. In this study, thermal ionization energies for a series of bivalent lanthanides were determined from thermal quenching curves [2]. Later, the processes of photoionization and electron capture for Eu–Sm pairs incorporated into SrF_2 and BaF_2 were thoroughly investigated by McClure et al. [3–5].

In the first part of this article [6], we addressed in detail the inverse thermal quenching effect and were able to deduce experimental values for ionization energy of bivalent lanthanides. In this part of the paper, we investigate the electron transfer mechanisms in great detail. For clarity, thermally more and less stable bivalent lanthanides are referred to as acceptors and donors, respectively, a definition based on the fact that, on heating, after photoinduced transfer between doping centers took place, a thermal electron transfer from a donor to an acceptor center occurs.

2. SAMPLE PREPARATION AND EXPERIMENTAL TECHNIQUE

Crystals of the fluorides were grown in vacuum by the Bridgman–Stockbarger technique using a three-barrel graphite crucible [7]. A few percent of CdF_2 were added to starting materials to purify them of oxygen. The concentrations of lanthanide fluorides Ln_1F_3 and Ln_2F_3 in the load were 0.01, 0.1, and 0.3 mol %. The growth of doubly activated phosphors in a reducing environment was accompanied by conversion of a fraction of initially trivalent acceptors into a bivalent state, while the donors retained their trivalent states. The two lanthanides remained in a trivalent state when growth was conducted under regular conditions. In this case, we ensured the transition of acceptors into a bivalent form by subjecting them to additive coloring by heating the samples in calcium vapors in vacuum in a steel autoclave [7, 8].

Absorption spectra were measured in the wavelength range of 190–3000 nm on a Lambda-950 spectrophotometer (PerkinElmer).

The most effective light sources for photoinduced transfer between doping centers were specific to the types of emitting centers: an ozone-producing low-pressure mercury lamp with a quartz bulb for Yb^{2+} (operating wavelengths, 185 and 254 nm); a DDS30 deuterium arc lamp or model DKB9 low-pressure mercury lamp for Eu^{2+} (operating wavelength, 254 nm); and a DRSh250 high-pressure mercury lamp for Sm^{2+}. Photoinduced electron transfer between doping centers was much less efficient at reduced temperatures than at room temperature.

To study the effect of neighboring interstitial fluoride atoms on absorption spectra, photoinduced electron transfer was conducted at 7.5 K, and the crystal was then heated to room temperature (295 K), kept at this temperature for 5 min, and then cooled to 7.5 K again. This caused all absorption bands to blueshift, clearly due to withdrawal of the interstitial fluoride from the bivalent lanthanide. This phenomenon was discovered for Eu–Sm pairs in barium fluoride crystals [4].

3. ABSORPTION SPECTRA

Photoinduced electron transfer between centers was determined from changes in absorption bands of crystals doped with such acceptors as Eu, Yb, and Sm, and such donors as Nd, Sm, Dy, Ho, Er, Tm, and Yb. Absorption bands of Yb^{2+}-doped crystals undergone the most substantial alterations. A room-temperature absorption spectrum of $\text{BaF}_2\text{–Yb}^{2+}$ consists of three absorption bands due to Yb^{2+} peaking at 354, 240, and 189 nm. Photoinduced electron transfer was registered at two short-wavelength bands, and the greatest effect was reached by irradiating sample by the ozone-producing mercury lamp (lines, 185 and 254 nm).

Changes in absorption spectra caused by withdrawal of the interstitial fluoride were studied for BaF_2 crystals doped with such lanthanides as Nd, Sm, Dy, Tm, and Yb. Electrons transferred from the Yb^{2+} ions onto the lanthanide ions Nd^{3+}, Sm^{3+}, Dy^{3+}, and Tm^{3+}, and the trivalent ytterbium ion received electrons from Eu^{2+}. All the absorption bands of 4*f*–5*d* transitions blueshifted after crystals were briefly heated to room temperature (Fig. 1).

The absorption bands of Yb^{2+} were most difficult to differentiate against a strong background absorption due to Eu^{2+}. However, in this case, difference spectra suggest the appearance of a $\text{Yb}^{2+}\text{–F}_i^-$ absorption and a shift of the absorption band after heating the crystals to room temperature as well (Fig. 2).

4. BAND SHIFT

We can see that the shift in absorption bands correlates with the atomic number of the lanthanides (Fig. 3): it increases from 200 cm^{-1} for Nd to 320–350 cm^{-1} for Tm and Yb.

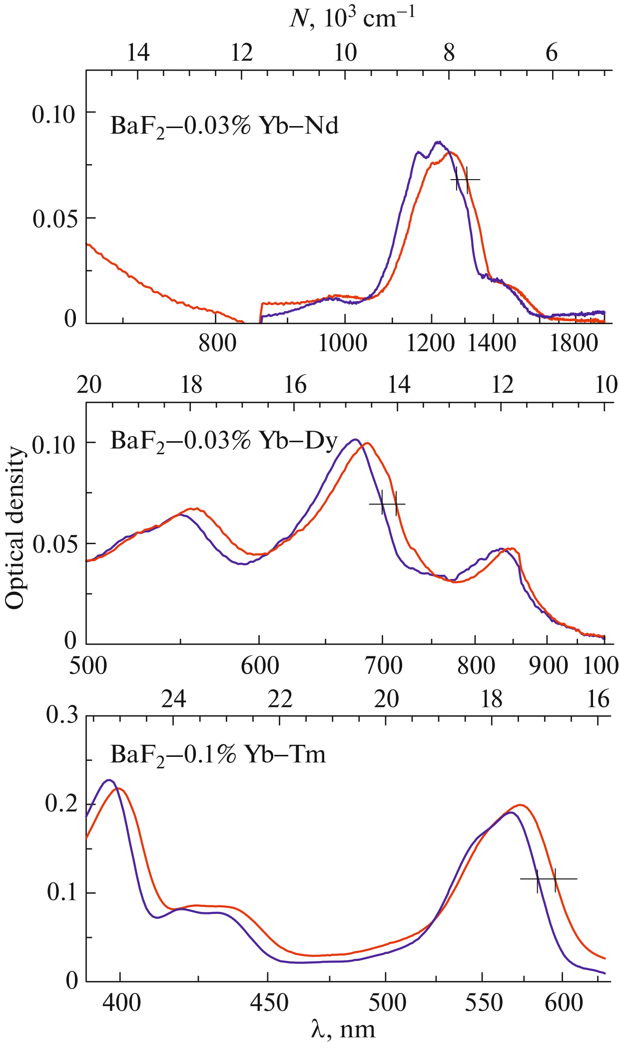

Fig. 1. Absorption spectra of $\text{BaF}_2\text{–YbF}_3\text{–LnF}_3$ crystals recorded at 7.5 K after (right curve) irradiation using an ozone-producing lamp at 7.5 K and (left curve) warming to room temperature.

Considering that the size of lanthanides (including 3+ and 2+ states) steadily decreases with the atomic number [9], we can notice that the band shift diminishes linearly with the growing lanthanide radius (Fig. 3).

The obvious dependence of excitation of optical transitions in the lanthanide centers on their size clearly indicates that perturbation of the *f* and *d* levels in lanthanides by the charge of interstitial fluoride ion grows as the lanthanide radius decreases. This cannot be due to coulombic interaction between them, because the charge on lanthanide equals that of the lattice cation. In barium fluoride crystals, charge-compensating fluoride ion sit in the second coordination shell with respect to a trivalent lanthanide cation, which creates a C_3 symmetry around the defect [4, 10].

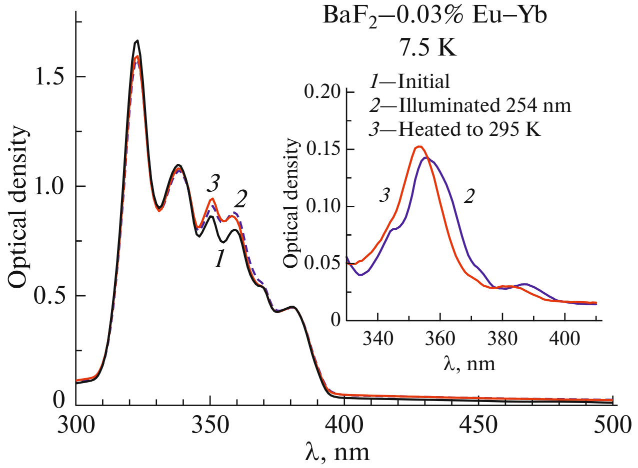

Fig. 2. Absorption spectra of a BaF_2–0.03% Eu–Yb crystal at 7.5 K: (*1*) initial spectrum, (*2*) after irradiation at 254 nm at 7.5 K, (*3*) after warming to 295 K. Inset: difference spectra for the Yb^{2+} absorption band in the long-wavelength region.

We can hypothesize that the distance between lanthanide center and the interstitial fluoride falls as the size of lanthanide decreases, which leads to enhanced perturbation of the orbitals in bivalent lanthanide. We can also anticipate that the observed red shift in SrF_2 and CaF_2 crystals (see Figs. 2 and 3) must be considerably greater than in BaF_2, since the interstitial fluoride in these crystals sits in the first coordination sphere centered around the lanthanide ion [11].

5. THE MECHANISM OF PHOTO- AND THERMALLY INDUCED ELECTRON TRANSFER

The process of photoinduced transfer of the electron from europium onto samarium in BaF_2 crystals was proposed to consist of four stages [4]. Initially, the electron is photoexcited from the bivalent europium ion into the conduction band, which was registered as emergence of photoconductivity in the material [12, 13]. This electron, now residing in the conduction band, is captured by a trivalent samarium ion adjacent to an interstitial charge-compensating fluoride ion. At the third stage, the interstitial fluoride ion moves away from the bivalent samarium by thermally activated migration. At the last stage, the interstitial fluoride ion becomes a charge compensating ion for the trivalent europium. Evidence of thermally activated withdrawal of the fluoride ion from the samarium ion is supported by observation of simultaneous enhancement of intensities of *f–f* emission lines associated with Sm^{2+} ions in a cubic environment and reduction in intensity of emission line associated with Sm^{2+} centers in a trigonal environment in the temperature range of 160–250 K [5]. A thermal depolarization peak due to migration of interstitial fluoride ion around a trivalent lanthanide ion in BaF_2 crystals occurs throughout the temperature range of 160–220 K [10, 14], which coincides with a temperature range in which the symmetry of samarium centers in BaF_2–Sm–Eu crystals changes [5].

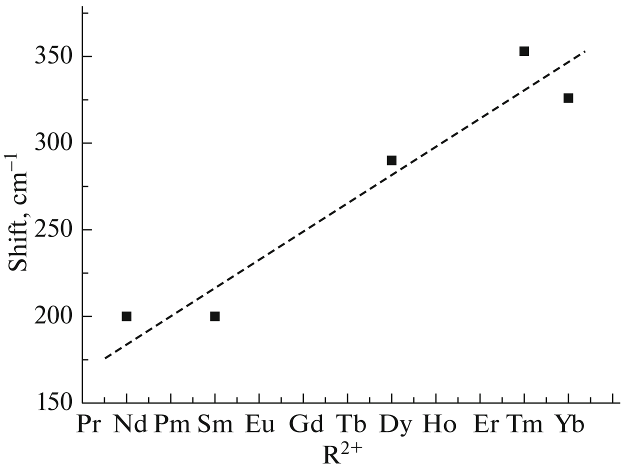

Fig. 3. Shift in absorption bands associated with 4*f*–5*d* transitions for bivalent lanthanides caused by withdrawal of charge-compensating interstitial fluoride ion.

Withdrawal of the interstitial fluoride ion from Sm^{2+} is accompanied not only by shifts in *f–f* emission bands but also in *f–d* absorption bands [4, 5]. On heating our BaF_2–Yb–Sm crystals at a rate of 16 deg/min, enhancement of an absorption band at 565 nm due to a band shift (Fig. 1) started at a temperature of 190 K. The dependence of perturbation intensity for *f–d* transitions on the size of bivalent lanthanide, revealed in this work, can be qualitatively

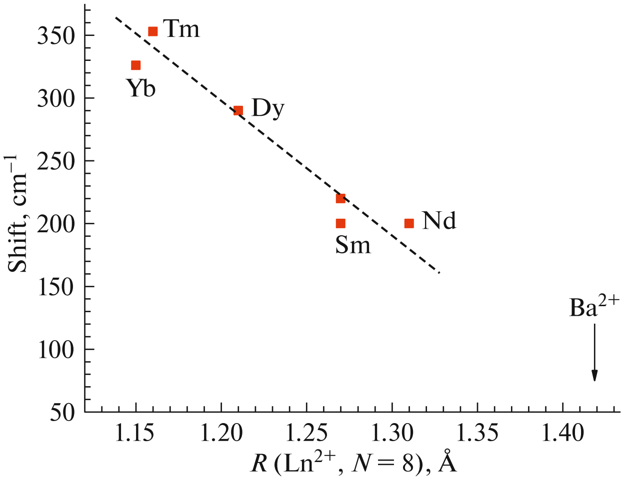

Fig. 4. Shift in absorption bands associated with 4*f*–5*d* transitions for bivalent lanthanides (see Figs. 1 and 2) as a function of their radius.

Table 1. Ionization energies for bivalent lanthanides incorporated into BaF_2 crystals (Ionization energies calculated using the Dorenbos model [15, 16] are provided for comparison)

Ln^{2+}	Ho	Nd	Dy	Tm	Sm	Yb
E, eV	0.725	0.83	0.89	1.18	1.87	2.14
Model E, eV	0.70	0.58	0.83	1.38	1.85	2.67

explained by occurrence of lattice contraction around a lanthanide with a small radius.

The reverse thermal transition from such bivalent donor ions as Ho, Nd, Dy, Tm, Sm, and Yb, onto trivalent acceptor ions enabled us to determine thermal ionization energies for bivalent ions (Table 1) [6]. The experimental values for ionization energies were close to corresponding model-based estimations [15, 16].

Thermal ionization of all donor ions studied herein occurs at temperatures above room temperature and can be described by the equation

$$(Ln_1^{3+} - F_i^-) + Ln_2^{2+} \xrightarrow{kT_1} (Ln_1^{3+} - F_i^-) + Ln_2^{3+} + e^- \xrightarrow{kT_2} Ln_1^{2+} + (Ln_2^{3+} - F_i^-).$$

The electrons initially are thermally excited from the donor ions Ln_2 into the conduction band, followed by capture of electron by the acceptor ion Ln_1 and migration of the interstitial fluoride ion toward the trivalent ion Ln_2. The temperature at which the reaction starts, $T_1 > 300$ K, is crucial to the whole reaction, since T_1 is much higher than the migration temperature T_2 for interstitial fluoride ions.

6. CONCLUSIONS

On illuminating BaF_2 crystals activated with two different lanthanides—Ln_1 (Yb^{2+} and Eu^{2+}) and Ln_2 (Nd^{3+}, Sm^{3+}, Dy^{3+}, Tm^{3+}, and Yb^{3+}) in the UV bands of bivalent lanthanide Ln1—electron transfer occurs at room temperature to form Ln_2^{2+} in a cubic environment. The redshifted absorption bands of Ln_2^{2+} are induced at low temperatures by photoquenching. As the radius of bivalent lanthanide decreases, the redshift grows from 200 cm^{-1} for Nd and Sm to 330–350 cm^{-1} for Tm and Yb.

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