

# Electron transfer between heterogeneous lanthanides in BaF<sub>2</sub> crystals

E.A. Radzhabov\*, V.A. Kozlovsky

Vinogradov Institute of Geochemistry, Russian Academy of Sciences, Favorskii Street 1a, P.O.Box 4019, 664033, Irkutsk, Russia



## ARTICLE INFO

### Keywords:

BaF<sub>2</sub>  
Lanthanide  
Absorption  
Spectroscopy  
Level positions  
Urbach constant  
Electron phototransfer

## ABSTRACT

Forward electron photo-transfer and reverse thermal transfer between divalent and trivalent heterogeneous lanthanides in barium fluoride crystals has been studied using optical absorption. In crystals activated by two heterogeneous lanthanides and grown in reducing conditions, one of the lanthanides becomes divalent whereas the other lanthanide remains trivalent. Illumination of the crystal in the ultraviolet bands led to the transfer of electrons from divalent lanthanides (Eu, Yb, Sm) to trivalent ions (Ho, Nd, Dy, Tm, Sm, Yb). The thermal ionization energies to the conduction band of created lanthanides are determined from the thermal bleaching curves of absorption bands. The experimental energies are compared with the estimated energies of the Dorenbos model.

## 1. Introduction

Crystals with double activation of heterogeneous lanthanides are used as long-afterglow phosphors, up-conversion phosphors, thermoluminescent phosphors and others, which require advanced studies of electron transfer between lanthanides.

For the first time, the phototransfer of an electron from the Eu<sup>2+</sup> ion to the Sm<sup>3+</sup> ion in crystals CaF<sub>2</sub>, SrF<sub>2</sub>, BaF<sub>2</sub> was discovered by P. Feofilov (1961). Electron phototransfer has been studied in most detail in BaF<sub>2</sub>-Eu-Sm crystals. About 2/3 of the initial value of the Eu<sup>2+</sup> absorption bands were photo-bleached with proportional increase of the Sm<sup>2+</sup> bands. The reverse thermal recovery occurred after heating to 400–600°C with the restoration of the initial absorption spectrum (Feofilov, 1961). Reversible photo-transfer of electrons between rare-earth ions Sm, Tm and Eu in CaF<sub>2</sub> was found also in papers (Welber, 1965a, b). Thermal bleaching of induced absorption bands in pairs of Eu<sup>2+</sup>-Ln<sup>3+</sup> ions (where Ln is Nd, Sm, Dy, Er, Ho) during heating with constant rate was investigated by Arkhangel'skaya in CaF<sub>2</sub> and SrF<sub>2</sub> crystals. The thermal ionization potentials of a number of divalent lanthanides were determined from the thermal bleaching curves (Arkhangel'skaya et al., 1969).

Later, the processes of photo-ionization and electron capture in Eu-Sm pairs in SrF<sub>2</sub> and BaF<sub>2</sub> were studied in detail by McClure et al. (Mou and McClure, 1993; Fuller and McClure, 1990, 1987; McClure, 1996).

In the study of electron transfer between lanthanides  $Ln_1^{3+} + Ln_2^{3+} \rightleftharpoons Ln_1^{4+} + Ln_2^{2+}$ , it is proposed to call the lanthanides  $Ln_2$  (Eu, Yb) trapping electrons from the conduction band as acceptors, and the lanthanides  $Ln_1$  (Ce, Pr, Tb) donating electrons to the conduction

band as donors (You et al., 2012; Dorenbos et al., 2013). We study the electron transfer  $Ln_1^{2+} + Ln_2^{3+} \rightleftharpoons Ln_1^{3+} + Ln_2^{2+}$ . Electron phototransfer occurs from one divalent lanthanide  $Ln_1^{2+}$  through the conduction band to another lanthanide  $Ln_2^{3+}$ , which, after electron capture, becomes divalent. Divalent lanthanides with a lower ionization energy will be called donors, and divalent lanthanides with greater ionization energy will be called acceptors. Therefore, we call the less thermally stable lanthanides  $Ln_2^{2+}$  (Er, Ho, Nd, Dy, Sm, Yb) as donors and the stable ones  $Ln_1^{2+}$  (Eu, Yb, Sm) as acceptors.

The main topic of the present paper is to establish the processes of electron transfer between different lanthanides and to determine the positions of ground levels of several divalent lanthanides against conduction band of BaF<sub>2</sub> crystals.

## 2. Experimental

Crystals were grown in vacuum in a graphite crucible by the Stockbarger method (Radzhabov et al., 2012). The graphite crucible contained three cylindrical cavities with a diameter of 10 mm and a length of 80 mm, which made it possible simultaneously to grow three samples with sizes Ø10 × 50 mm with different amounts of impurity. A few percent of CdF<sub>2</sub> were added into raw materials for purification from oxygen during growth.

Absorption spectra in the range of 190–3000 nm were measured using a Perkin-Elmer Lambda-950 spectrophotometer. The absorption spectra in the vacuum ultraviolet region were measured on a home-made set-up with a VMR2 monochromator (LOMO). The light source was a discharge deuterium lamp L7293-50 with a MgF<sub>2</sub> window

\* Corresponding author.

E-mail address: [eradzh@igc.irk.ru](mailto:eradzh@igc.irk.ru) (E.A. Radzhabov).

(Hamamatsu), the radiation detector was a solar-blind FEU-142.

BaF<sub>2</sub> crystals were grown with double activation of lanthanides of one group (Eu, Yb, Sm) and lanthanides of the other group (Nd, Sm, Dy, Ho, Er, Tm, Yb). Europium is an absolute acceptor, while Yb, Sm can be both donors (with respect to Eu<sup>2+</sup>) and acceptors (for the remaining lanthanides). Donor and acceptor lanthanide impurities LnF<sub>3</sub> were introduced in equal concentrations with levels of 0.01, 0.03, 0.1 mol. %.

In few cases, the crystals contained both lanthanides in the trivalent form. With the help of additive coloration, a significant part of acceptors became divalent (Radzhabov, 2018; Radzhabov et al., 2017), while donor lanthanides remained trivalent. The only exception is the Eu-Sm pair, which is characterized by the coexistence of Eu<sup>2+</sup> and Sm<sup>2+</sup> even after heating to 500–600 °C (see also (Feofilov, 1961; Mou and McClure, 1993)). At the same time, in the BaF<sub>2</sub>-Yb-Sm, with a smaller difference in the ionisation energies, only Yb<sup>2+</sup> were observed.

The study of thermal bleaching of divalent lanthanide bands was carried out as follows: the crystals were heated to a certain temperature, kept for 3 min and cooled to room temperature, at which the absorption spectrum was measured. The temperature of the subsequent heating increased by 20°. Compared to measurements at a constant heating rate (Arkhangelskaya et al., 1969), the measurement procedure used by us eliminated errors due to temperature broadening of the absorption bands. Consequently, in our studies of thermal bleaching, the effective heating rate was 0.11 K/s.

The relative efficiency of electron phototransfer and the temperature dependence of the back thermal transfer between lanthanides depended weakly on the impurity concentration.

### 3. Results

#### 3.1. Electron phototransfer

We observed the photo transfer of an electron by the transformation of absorption bands in crystals with acceptors Eu, Yb, Sm and donors Nd, Sm, Dy, Ho, Er, Tm, Yb. The largest transformation of the bands is obtained in crystals with the acceptor Yb<sup>2+</sup>. Electrons Yb<sup>2+</sup> were effectively photoionized by the light of a mercury ozone lamp having main working lines at 185 and 254 nm. Fig. 1 shows the photo bleaching of the bands of Yb<sup>2+</sup> ions at 354, 240, 189 nm and the formation of bands of Sm<sup>2+</sup> ions. The absorption spectrum Sm<sup>2+</sup> is shown by curve 3. During heating the Sm<sup>2+</sup> bands are completely destroyed, restoring the initial absorption of Yb<sup>2+</sup>. In contrast, in BaF<sub>2</sub>-Eu-Sm crystals, even after high-temperature annealing, an equilibrium ratio of concentrations of Eu<sup>2+</sup> - Yb<sup>2+</sup> is remained (see also (Feofilov, 1961)).

BaF<sub>2</sub>-Yb-Nd crystals after photobleaching with an ozone lamp take

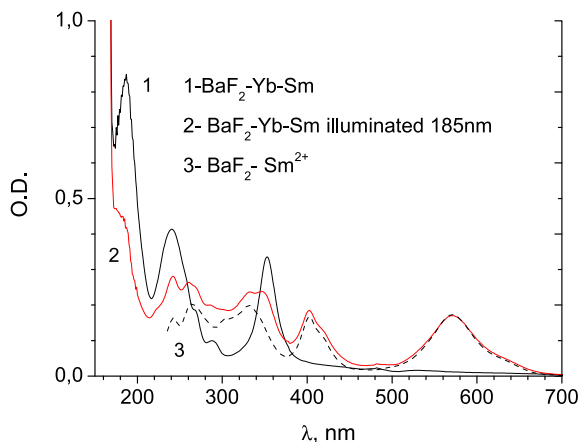


Fig. 1. Absorption spectra of BaF<sub>2</sub>-0.1 mol%YbF<sub>3</sub>-0.1 mol%SmF<sub>3</sub> crystals before (1) and after ultraviolet illumination (2). For comparison, the normalized absorption spectrum of BaF<sub>2</sub>-Sm<sup>2+</sup> is given (3).

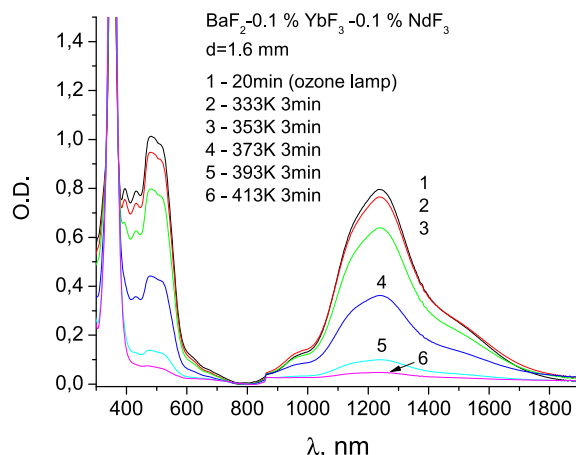


Fig. 2. Absorption spectra of BaF<sub>2</sub>-0.1 mol%YbF<sub>3</sub>-0.1 mol%NdF<sub>3</sub> after ultra-violet illumination and subsequent heating to specified temperatures.

on a brown color. The induced absorption bands in the range of 400–1800 nm (Fig. 2) belong to the Nd<sup>2+</sup> ions (Arkhangelskaya et al., 1967). In BaF<sub>2</sub>-Yb-Nd crystals, the thermal stability of Nd<sup>2+</sup> ions (see Fig. 2) coincides with the stability of Nd<sup>2+</sup> in radiation-coloured BaF<sub>2</sub>-Nd crystals (Basiev et al., 1992), which is obviously due to the thermal ionisation of the electron in both cases.

The study of photo- and thermal electron transfer in BaF<sub>2</sub>-Eu-Yb crystals turned out to be the most difficult, due to the fact that the absorption bands of divalent lanthanides Eu and Yb overlap strongly. The initial absorption spectrum of BaF<sub>2</sub>-Eu-Yb (Fig. 3) contains only Eu<sup>2+</sup> bands. After photobleaching with light of 254 nm, the Eu<sup>2+</sup> bands are partially reduced and the Yb<sup>2+</sup> bands appear (see Fig. 3). In this case, the thermal destruction of Yb<sup>2+</sup> was controlled over a band of 189 nm (see Fig. 3).

#### 3.2. Thermal bleaching of absorption of divalent lanthanides

When the photo-bleached crystals were heated, the bands of divalent donors decreased (Fig. 4) and the bands of divalent acceptors re-covered.

It can be assumed that after the thermal release of the electron from the donor, it returns to the acceptor without re-capture by other donor ions, since the concentrations of acceptors and donors are the same. Consequently, the curve of thermal bleaching of donor absorption bands can be described by the kinetics of the first order (Randall and Wilkins, 1945):

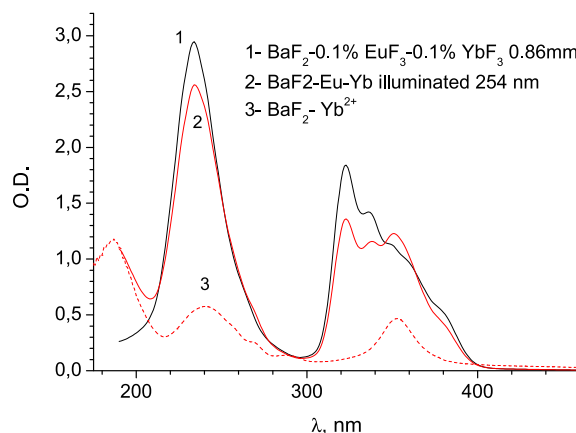
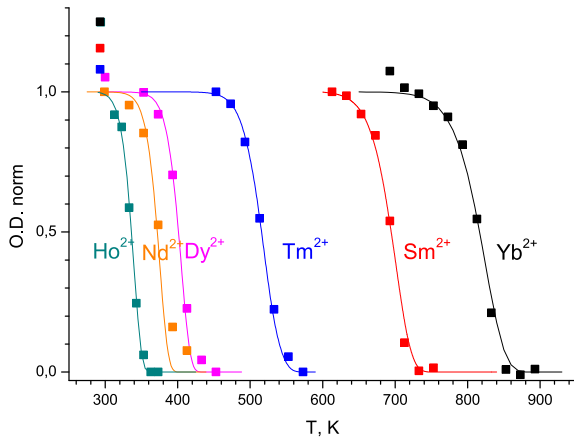


Fig. 3. Absorption spectra of BaF<sub>2</sub>-0.1 mol%EuF<sub>3</sub>-0.1 mol%YbF<sub>3</sub> (1, 2). For comparison, the normalized absorption spectrum of BaF<sub>2</sub>-Yb<sup>2+</sup> is given (3).



**Fig. 4.** Thermal bleaching curves for long-wavelength absorption bands of BaF<sub>2</sub>-Yb-Re crystals and absorption at 189 nm for BaF<sub>2</sub>-Eu-Yb. The measurements were performed at room temperature after warming up for 3 min at the indicated temperatures. Thermal bleaching curves are calculated for the 1st order process (see text).

$$N = N_0 \exp\left(-\frac{s}{\beta} \int \exp\left(-\frac{E}{kT}\right) dT\right) \quad (1)$$

where  $s/\beta$  is the ratio of the frequency factor to the heating rate,  $E$  is the energy of thermal ionisation of an electron,  $k$  is the Boltzmann constant,  $T$  is the absolute temperature.

In order to avoid the uncertainty of the choice of two parameters in the description of the thermal bleaching curves, we additionally measured the ionization energy using isothermal annealing. In this case  $\tau = \tau_0 \exp\left(\frac{E}{kT}\right)$ , where the  $\tau$  is lifetime of the donor lanthanide at constant temperature,  $E$  in our case is the ionization energy. Measuring isothermal bleaching at several temperatures, we obtain ionization energy from Arrhenius plot in coordinates  $\ln(\tau)$  vs  $1/T$  (Fig. 5).

For Nd<sup>2+</sup>, Tm<sup>2+</sup> and Yb<sup>2+</sup>, we determined ionization energies of 0.83, 1.18 and 2.14 eV. The error in determining the ionization energy in all cases is less than 0.08 eV. With consideration of the thermal bleaching results (see Fig. 4), the values of  $s/\beta$  are  $7 \cdot 10^9$  for Nd<sup>2+</sup>, Tm<sup>2+</sup> and  $10^{12}$  for Yb<sup>2+</sup>. Assuming that the frequency factor for Ho<sup>2+</sup>, Dy<sup>2+</sup> is the same as for Nd<sup>2+</sup>, Tm<sup>2+</sup> and frequency factor for Sm<sup>2+</sup> is the same as for Yb<sup>2+</sup>, we obtained from the fitting of thermal bleaching (see Fig. 4) the ionisation energies for the remaining lanthanides (Table 1). One would expect a gradual change in the frequency factor with increasing ionization energy from Ho to Yb. However, taking into account the experimental ionization energies, the calculated curves of thermal bleaching are better described by a jump in the frequency

**Table 1**

Comparison experimental and modelling ionisation energies of divalent lanthanides in BaF<sub>2</sub>. Model energies are taken from the article (Dorenbos, 2003) and refined according to the paper (Dorenbos, 2013).

Ln <sup>2+</sup>	T <sub>1/2</sub>	E(eV)	Model(eV)
Er	≤ 295		0.52
Ho	336	0.725	0.70
Nd	373	0.83	0.58
Dy	400	0.89	0.83
Tm	515	1.18	1.38
Sm	695	1.87	1.85
Yb	823	2.14	2.67

factor from Tm to Sm (see Fig. 4). The reason for this is unclear.

### 3.3. Urbach constant

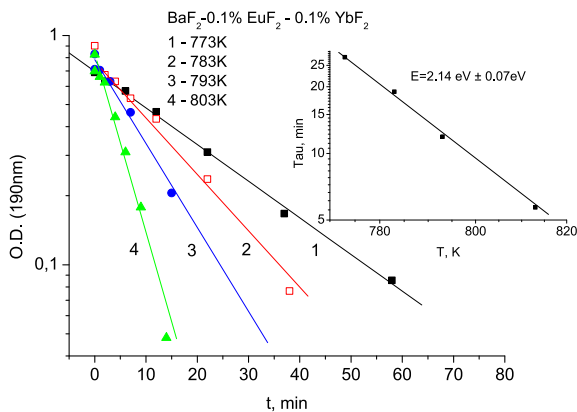
The proportionality of the depth of the trap (in eV) and the temperature of the maximum of the associated peak of thermoluminescence was noted by Urbach (1948) in the form:  $E = \frac{T_m}{A}$  where the value of  $A = 500$  (K/eV).

This Urbach formula can be rewritten as (Bos, 2017):  $E = C_u \cdot k T_m$  where  $k$  is the Boltzmann constant, and  $C_u$  is another form of Urbach constant. The Urbach constant in this form is dimensionless. Since the temperature  $T_{1/2}$  is only few degrees lower than  $T_m$ , the Urbach formula can also be used for thermal bleaching.

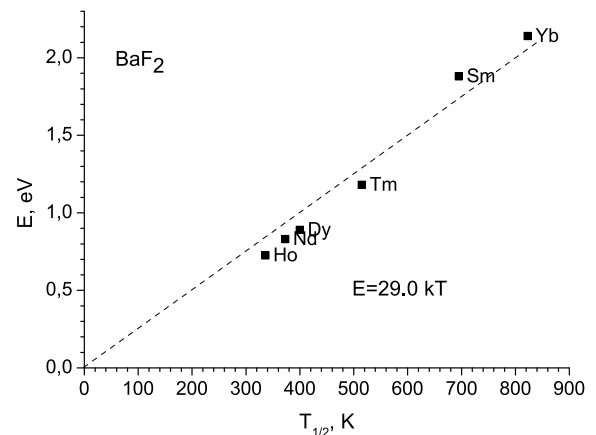
In our case, the Urbach constant  $A$  is equal to 400 (K/eV) (or in the dimensionless format  $C_u = 29.0$ ). The experimental values deviate from the linear dependence by 0.1–0.15 eV (Fig. 6), which indicates the applicability of the Urbach formula for estimating the ionization energies of divalent lanthanides in BaF<sub>2</sub> from the temperature  $T_{1/2}$  (and possibly from the thermoluminescence peak).

## 4. Discussion

Knowledge of the position of lanthanide levels in the band diagram of crystals is extremely helpful in understanding many phenomena (Dorenbos, 2017). The positions of the levels can be estimated with an accuracy of 0.1–0.2 eV, knowing the position of one or several lanthanides relative to the crystal zones (Dorenbos, 2004; Rodnyi et al., 2008). The positions of the levels of divalent lanthanides in crystals have been investigated by the thermoluminescent method in a number of papers (You et al., 2012; Bos et al., 2011; Bos, 2017). Our studies of electron transfer between lanthanides by absorption spectra have a certain advantage over thermoluminescence studies, where there is no direct identification of the nature of traps.



**Fig. 5.** Isothermal bleaching for Yb<sup>2+</sup> absorption at 190 nm of BaF<sub>2</sub>-Eu-Yb crystal. The insert shows the Arrhenius plot to determine the ionization energy Yb<sup>2+</sup>.



**Fig. 6.** Experimental trap depth  $E$  as a function half-thermal bleaching temperature for divalent lanthanides in BaF<sub>2</sub>.

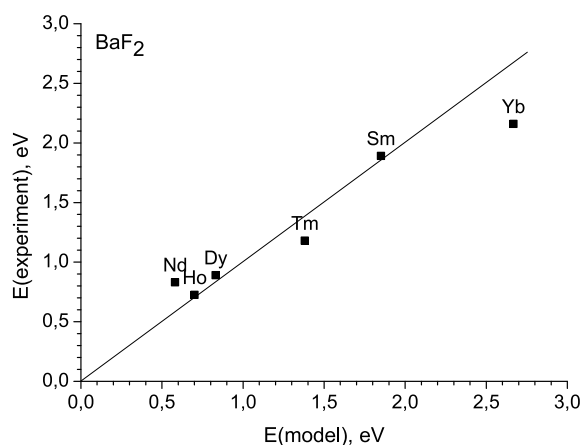


Fig. 7. Experimental thermal ionisation energies against model energies. Model energies are taken from the papers (Dorenbos, 2003, 2013). Line indicates directly proportional dependence of experimental and model energies.

In accordance with our results, the temperature of the half thermal bleaching of  $T_{1/2}$  and the depth of the ground level  $E$  increase in the series Er, Ho, Nd, Dy, Tm, Sm, Yb. The same order of growth of  $T_{1/2}$  temperature is defined earlier for Er, Ho, Nd, Dy in crystals  $\text{CaF}_2$  and  $\text{SrF}_2$  (Arkhangelskaya et al., 1969). However, in the Dorenbos model, the order of the levels of divalent lanthanides is slightly different - Er, Nd, Ho, Dy, Tm, Sm, Yb (Dorenbos, 2013).

There is a linear relationship between the experimental and model values of the ionisation energies (Fig. 7). Experimental energies correlate well with model energies. The largest discrepancy is observed for Yb and to a lesser extent for Nd (see Fig. 7).

## 5. Conclusion

Electron phototransfer from divalent  $\text{Eu}^{2+}$ ,  $\text{Sm}^{2+}$ ,  $\text{Yb}^{2+}$  ions to trivalent ions  $\text{Er}^{3+}$ ,  $\text{Ho}^{3+}$ ,  $\text{Dy}^{3+}$ ,  $\text{Nd}^{3+}$ ,  $\text{Sm}^{3+}$ ,  $\text{Yb}^{3+}$  ions was studied in  $\text{BaF}_2$  crystals. Thermal bleaching of bands of divalent donors is well described by the first-order kinetic. The experimental energies of reverse thermal recharge are correlates well with energies estimated by the Dorenbos model (Dorenbos, 2003, 2013).

## Acknowledgments

The authors are grateful to A.J.J. Bos for a discussion of lanthanide levels and for the idea of Fig.7. The authors are grateful to A.E. Angervaks for providing a copy of the dissertation of V.A. Arkhangelskaya. The authors are grateful to P. Dorenbos for providing a package for evaluating the positions of lanthanide levels in band gap (VRBE generator for Origin). The work was partially supported by the project of Russian Academy of Sciences, Russia 0350-2016-0024. In this work author used the equipment of the Isotopic and Geochemistry

Research Centre for Collective Use, Institute of Geochemistry, Russian Academy of Sciences.

## References

- Arkhangelskaya, V.A., Kiseleva, M.N., Schreiber, V., 1967. Molar absorption coefficients and oscillator strengths of some transitions to mixed (f-d) configurations of  $\text{RE}^{2+}$  ions in fluorite-type crystals. *Optic Spectrosc.* 23, 509–511 (in russian).
- Arkhangelskaya, V.A., Kiseleva, M.N., Schreiber, V.M., 1969. Potentials of thermal ionization of divalent rare earths in crystals of fluorite type. *Solid State Phys.* 11 (4), 869–876 (in russian).
- Basiev, T.T., Mirov, S.B., Sychev, S., 1992. Passive laser q-switches based on  $\text{MeF}_2:\text{Nd}^{2+}$  (Me-Ca, Sr, Ba) crystals. In: *Solid State Lasers and New Laser Materials*, vol 1839. International Society for Optics and Photonics, pp. 182–198.
- Bos, A.J., 2017. Thermoluminescence as a research tool to investigate luminescence mechanisms. *Materials* 10 (12), 1357.
- Bos, A.J., Van Duijvenvoorde, R.M., Van der Kolk, E., Drozdowski, W., Dorenbos, P., 2011. Thermoluminescence excitation spectroscopy: a versatile technique to study persistent luminescence phosphors. *J. Lumin.* 131 (7), 1465–1471.
- Dorenbos, P., 2003. Anomalous luminescence of  $\text{Eu}^{2+}$  and  $\text{Yb}^{2+}$  in inorganic compounds. *J. Phys. Condens. Matter* 15 (17), 2645.
- Dorenbos, P., 2004. Locating lanthanide impurity levels in the forbidden band of host crystals. *J. Lumin.* 108 (1–4), 301–305.
- Dorenbos, P., 2013. A review on how lanthanide impurity levels change with chemistry and structure of inorganic compounds. *ECS J. Solid State Sci. Technol.* 2 (2), R3001–R3011.
- Dorenbos, P., 2017. Charge transfer bands in optical materials and related defect level location. *Opt. Mater.* 69, 8–22.
- Dorenbos, P., Bos, A., Poolton, N., You, F., 2013. Photon controlled electron juggling between lanthanides in compounds. *J. Lumin.* 133, 45–50.
- Feofilov, P.P., 1961. Photoelectron Transfer in Single Crystals of  $\text{MeF}_2:\text{Eu}, \text{Sm}$ . *Optics and Spectroscopy*, pp. 531–533 (in russian).
- Fuller, R., McClure, D.S., 1987. Measurement of ionization rate of photoexcited divalent rare earth ions in fluorite-type crystals. *J. Lumin.* 38 (16), 193–194.
- Fuller, R.L., McClure, D.S., 1990. Determination of photoionization rates of divalent samarium doped in alkaline earth fluorides. *J. Lumin.* 45 (16), 354–356.
- McClure, D.S., 1996. Internal photo-oxidation reduction of impurity ions in crystals: extension of an early feofilov experiment. In: *Tenth Feofilov Symposium on Spectroscopy of Crystals Activated by Rare-Earth and Transitional-Metal Ions*, vol 2706. International Society for Optics and Photonics, pp. 315–327.
- Mou, W., McClure, D.S., 1993. Photoionization and trapping of electrons in the system  $\text{BaF}_2:\text{Eu}:\text{Sm}$ . *Phys. Rev. B* 47 (17), 11031.
- Radzhabov, E., 2018. Spectroscopy of divalent samarium in alkaline-earth fluorides. *Opt. Mater.* 85, 127–132.
- Radzhabov, E., Nagirnyi, V., Kirm, M., Prosekina, E., 2012. 5d-4f emission of  $\text{Nd}^{3+}$ ,  $\text{Sm}^{3+}$ ,  $\text{Ho}^{3+}$ ,  $\text{Er}^{3+}$ ,  $\text{Tm}^{3+}$  ions in alkaline earth fluorides. *Nucl. Sci., IEEE Trans.* 59, 2074–2078.
- Radzhabov, E.A., Egranov, A.V., Shendrik, R.Y., 2017. Formation of  $\text{H}^-$  a hydrogen centers upon additive coloration of alkaline-earth fluoride crystals. *Optic Spectrosc.* 122 (6), 901–905.
- Randall, J.T., Wilkins, M.H.F., 1945. Phosphorescence and electron traps-i. the study of trap distributions. *Proc. R. Soc. Lond. A* 184 (999), 365–389.
- Rodnyi, P., Khodyuk, I., Stryganyuk, G., 2008. Location of the energy levels of the rare-earth ions in  $\text{BaF}_2$  and  $\text{CdF}_2$ . *Phys. Solid State* 50, 1639–1643.
- Urbach, F., 1948. Storage and release of light by phosphors. In: *Preparation and Characteristics of Solid Luminescent Materials: Symposium Held at Cornell University*, October 24–26, 1946. J. Wiley, pp. 115.
- Welber, B., 1965a. Direct charge transfer by x irradiation in the system  $\text{CaF}_2:\text{Eu}, \text{Tm}$ . *J. Appl. Phys.* 36 (9), 2744–2745.
- Welber, B., 1965b. Reversible phototransfer of electrons between rare-earth ions in  $\text{CaF}_2$ . *J. Chem. Phys.* 42 (12), 4262–4264.
- You, F., Bos, A.J., Shi, Q., Huang, S., Dorenbos, P., 2012. Thermoluminescence investigation of donor ( $\text{Ce}^{3+}$ ,  $\text{Pr}^{3+}$ ,  $\text{Tb}^{3+}$ ) acceptor ( $\text{Eu}^{3+}$ ,  $\text{Yb}^{3+}$ ) pairs in  $\text{Y}_3\text{Al}_5\text{O}_{12}$ . *Phys. Rev. B* 85 (11), 115101.