



Anomalous europium luminescence in LaF₃



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HIGHLIGHTS

- Optical spectra and dielectric relaxation were measured for Eu²⁺ in LaF₃.
- Bulk conductivity is directly proportional to absorption coefficient of Eu²⁺ bands.
- Dielectric relaxation peak of LaF₃–EuF₃ is attributed to ipoles Eu²⁺-anion vacancy.
- Broadband Eu emission at 600 is attributed to so-called anomalous luminescence.

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ABSTRACT

Optical spectra (absorption, emission, excitation, decay) and dielectric relaxation were measured for divalent europium and partially for ytterbium in lanthanum fluoride crystals. Optical absorption of LaF₃–Eu²⁺ contains not only asymmetric weakly structured band at 245 nm but also less intense bands at 330, 380 nm. Broadband Eu²⁺ emission at 600 nm appeared below 80 K with decay time 2.2 μs at 7.5 K. Emission at 600 nm is attributed to so-called anomalous luminescence. Bulk conductivity is directly proportional to absorption coefficient of Eu²⁺ bands. Dielectric relaxation peak of LaF₃–EuF₃ is attributed to rotation of dipoles Eu²⁺-anion vacancy. The long-wavelength absorption at 300–400 nm region are assigned to transitions from 4f⁷Eu²⁺ ground state to states of neighbouring fluorine vacancy.

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1. Introduction

Europium Eu²⁺ ions are known as very efficient luminescence centres in dense scintillating hosts. Europium is introduced into halide crystal in divalent or trivalent states. A number of investigations are devoted to trivalent lanthanides in LaF₃ crystals (Carnall et al., 1989; Heaps et al., 1976). At the same time authors noted the tendency of EuF₃ to reduce to EuF₂ at the temperatures required for LaF₃ crystal growth and the strong broadband, associated with Eu²⁺ in the visible and ultraviolet range, is due to 4f–4f5d transitions (Carnall et al., 1978).

Absorption bands of Eu²⁺ were observed at 280 nm in LaCl₃ (Gruen et al., 1956) and at 245 nm in LaF₃ (Heaps et al., 1976). Eu²⁺

luminescence was found in LaCl₃ crystal at 420 nm (Kim and Moos, 1967; Lehmann, 1975). Both absorption and emission are obviously due to transitions between ground 4f⁷ and excited 4f⁶5d¹Eu²⁺ states. No data on luminescence of Eu²⁺ in LaF₃ were found in literature.

Besides the normal 5d–4f luminescence in most materials, the Eu²⁺, Yb²⁺ in certain crystals show “anomalous” broadband luminescence with large Stokes shift (see review (Dorenbos, 2003; Grinberg and Mahlik, 2008)). For such crystals the excited 5d level falls into conduction band. Luminescence occurred after transitions from conduction band states, which have less energy than the 5d level, to 4f level of lanthanide impurity ion (Moine et al., 1989; Dorenbos, 2003).

Divalent europium ion has charge less than the charge of host lanthanum ion, therefore, the additional positive charge is needed for each divalent ion for the electrical neutrality of the LaF₃ crystal. In the absence of oxygen the charge compensation of divalent ion

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Ca^{2+} , Sr^{2+} or Ba^{2+} in LaF_3 is accomplished by fluorine vacancy (Roos et al., 1985a; Igel et al., 1982). Parallel growth of ac (alternating current) conductivity and absorption in the visible region was observed in $\text{LaF}_3\text{--Sm}^{2+}$. Conductivity was attributed to Sm^{2+} -fluorine vacancy reorientation (Radzhabov and Kozlovsky, 2015). The dipoles in solids were thoroughly investigated by dielectric relaxation (Jonscher, 1999; Schönhals and Kremer, 2003).

Conductivity of LaF_3 could be measured at mono-frequency. However, the bulk conductivity determined in this way appears to be mostly too small (Roos et al., 1985b). In previous paper we investigated the conductivity of $\text{LaF}_3\text{--Sm}^{2+}$ at frequency 1 kHz (Radzhabov and Kozlovsky, 2015). While the relation between conductivity of samples with different Sm^{2+} concentrations remains the same, the values of measured conductivity were several times less. Therefore, in this paper we measure true bulk LaF_3 conductivity from frequency dispersion (Schoonman et al., 1980).

The main topic of the present paper is to study the optical and dielectric properties of divalent Eu and Yb in LaF_3 .

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 10 mm in diameter and 80 mm long, which allowed growing three crystals of $\varnothing 10 \times 50$ mm dimensions with different impurity concentrations at the same time. A few percent of CdF_2 were added into raw materials for purification from oxygen impurity during growth. Impurity LnF_3 (Ln – lanthanide) was added into LaF_3 powder in concentration of 0.01, 0.1 and 0.3 mol.%. In $\text{LaF}_3\text{--YbF}_3$ crystals the Ces absorption band at 245 nm and bands at lesser wavelengths were found, which not influenced on Yb^{2+} bands identification. The samples for measurements with sizes of $\varnothing 10 \text{ mm} \times 2 \text{ mm}$ were sawed from the grown rods and were polished.

Absorption spectra in the range 190–3000 nm were taken with spectrophotometer Perkin–Elmer Lambda-950, emission spectra were measured using grating monochromator MDR2 (LOMO). Emission, excitation spectra were measured with photomodule Hamamatsu H6780-04 (185–850 nm). No emission spectrum correction needs to be performed as the sensitivity only weakly changed in the region of Eu emission (400–700 nm). X-irradiation was performed using Pd-tube, operated at 40 kV and 20 mA.

A silver paint (kontaktol "Kettler") was employed as electrode contact material. Diameter of paint electrodes was around 5 mm and sample thickness was around 2 mm. Conductivity measurements were done at room temperature using the imittance (RLC) meter E7-20 (MNIP) in frequency range of 25 Hz–1 MHz. The unit for conductance is S (siemens) which is equal to ohm^{-1} .

3. Results

3.1. Optical spectra

Eu^{3+} ions are easily recognized in LaF_3 (Carnall et al., 1989) and in many other materials by sharp red emission lines due to f–f transitions. No red luminescence due to Eu^{3+} was found in all our $\text{LaF}_3\text{--Eu}$ crystals at 7.5–300 K while intensive ultraviolet absorption was observed. Therefore europium is introduced in divalent form into our LaF_3 crystals. High melting temperature of LaF_3 and reducing conditions due to graphite crucible result in introducing the divalent samarium (Radzhabov and Kozlovsky, 2015) and europium into LaF_3 during crystal growth. In the case of $\text{LaF}_3\text{--SmF}_3$ we obtained the crystal with trivalent Sm and several crystals with different proportions of divalent and trivalent Sm (Radzhabov and Kozlovsky, 2015). Other rare-earth elements are observed in LaF_3 in

trivalent form.

Absorption spectrum of $\text{LaF}_3\text{--}0.01 \text{ mol.}\% \text{ EuF}_3$ contains intensive asymmetric band at 245 nm with unresolved structure and weaker long wavelength bands at 330, 380 nm (Fig. 1). With increasing of EuF_3 doping the ultraviolet absorption becomes larger and at concentration near one percent of EuF_3 the crystal LaF_3 becomes yellow, due to absorption tail above 400 nm (see Fig. 1). The shape of absorption spectra does not depend on concentration of europium up to 0.3 mol.%. At higher concentration the absorption near 245 nm becomes too large. Therefore the long-wavelength bands at 300–400 nm region belong to Eu^{2+} also. Absorption band at 245 nm was ascribed to Eu^{2+} ions (Heaps et al., 1976). The authors have measured absorption spectrum up to 300 nm, which prevents observation of the Eu^{2+} bands at 330, 380 nm.

Red luminescence band at 600 nm was observed in $\text{LaF}_3\text{--Eu}$ at low temperature. Excitation spectrum (see Fig. 1) generally correlates with 245 nm absorption band. However, the red luminescence not observed with excitation into the Eu^{2+} long wavelength bands (see Fig. 1).

With increasing temperature the intensity of luminescence sharply decreases above 40 K (Fig. 2). The decay time of red luminescence was 2.2 μs at 7.5 K. The decay time was sharply decreased above 50 K together with the luminescence intensity (see Fig. 2).

Next most probable divalent lanthanide in LaF_3 is ytterbium. The Yb^{2+} long-wavelength bands were observed around 360, 310 nm in alkaline-earth fluoride crystals (Moine et al., 1989). The Yb^{3+} in LaF_3 shows infrared absorption near 970 nm (Rast et al., 1967). The Yb^{3+} infrared bands grown with increasing of YbF_3 concentration in $\text{LaF}_3\text{--YbF}_3$. No Yb^{2+} ultraviolet bands observed in $\text{LaF}_3\text{--YbF}_3$. After x-ray irradiation of $\text{LaF}_3\text{--YbF}_3$ at room temperature the absorption bands at 270, 300 and 376 nm appear (Fig. 3). Additionally, a very intensive absorption band at 200 nm, belonging to stable at room temperature F_3^- hole defects (Radzhabov, 2016), appear. Evidently the bands at 270, 300 and 376 nm belong to the Yb^{2+} in LaF_3 .

No luminescence in the range 400–1200 nm, excited in the region of Yb^{2+} bands, found in x-irradiated $\text{LaF}_3\text{--}0.3\% \text{ YbF}_3$ at temperatures down to 7.5 K.

3.2. Dielectric relaxation

Fig. 4 presents examples of admittance plots in the complex-

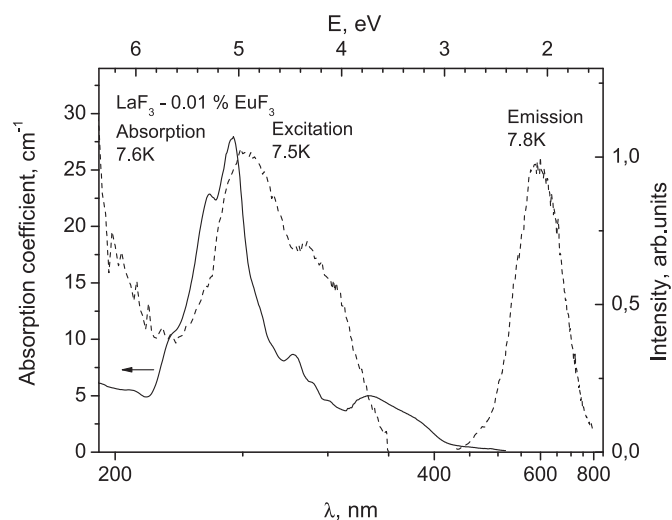


Fig. 1. Absorption spectrum (full curve), excitation and emission (dashed curves) of $\text{LaF}_3\text{--}0.01 \text{ mol.}\% \text{ EuF}_3$ at shown temperatures. Excitation was measured for emission at 580 nm, the emission was measured for excitation at 270 nm.

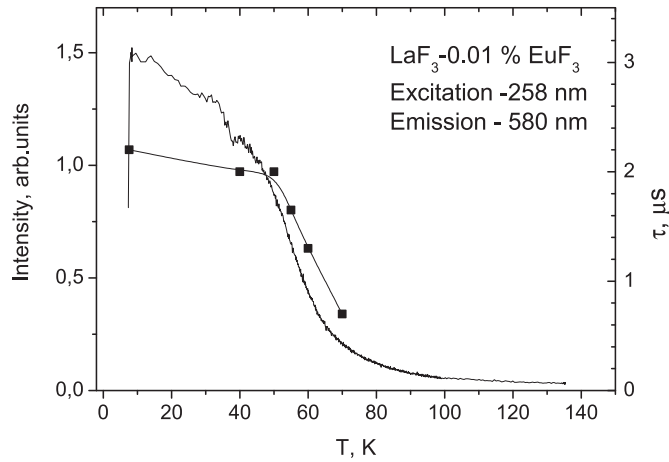


Fig. 2. Temperature dependence of intensity of Eu luminescence (full curve) and decay time (dots) of $\text{LaF}_3\text{-}0.01\% \text{EuF}_3$ crystal.

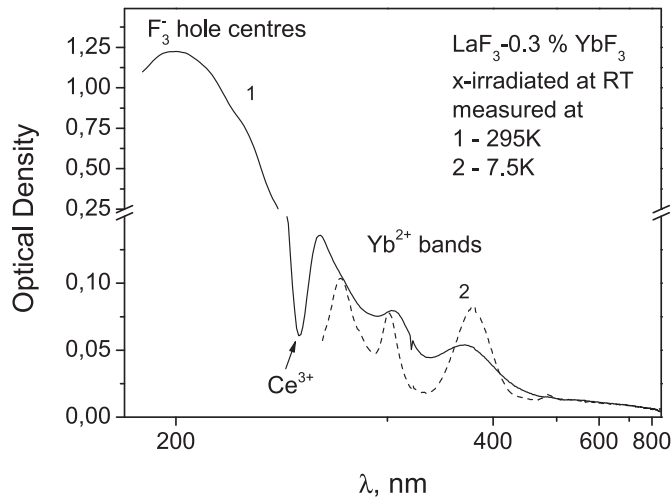


Fig. 3. Absorption spectrum of $\text{LaF}_3\text{-}0.3 \text{ wt.}\% \text{YbF}_3$ at shown temperatures created by x-irradiation at 295 K. LaF_3 crystal also contains unwanted Ce^{3+} , which absorbed at 245 nm and partially transformed under x-irradiation.

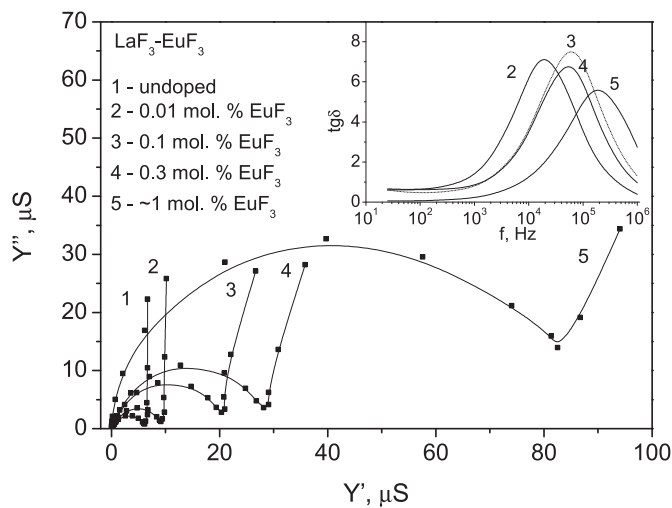


Fig. 4. Complex admittance plot ($Y^* = G_p + i\omega C_p$) for $\text{LaF}_3\text{-EuF}_3$ crystals at 295 K. Frequency range 25 Hz–1 MHz. Inset shows frequency dependence of $\text{tg}\delta$ for the same samples.

plane representation for cells with LaF_3 crystals at 295 K. The admittance plots for $\text{LaF}_3\text{-EuF}_3$ crystals show that the high-frequency data require an equivalent circuit composed of a frequency-independent (bulk) capacitance, C_p , in parallel with a frequency-independent (bulk) resistance, R_p . At zero point frequency is equal 25 Hz and increases till 1 MHz for last point of each curve (see Fig. 4). The high-frequency interception with the real axis represents the true bulk conductance.

The increasing of EuF_3 impurity concentration from 0.01 to 1 mol.% is accompanied by the growth of resistive bulk conductances from 10 to 90 μS (see Fig. 4) and the Eu^{2+} absorption. It should be noted that undoped LaF_3 sample has the bulk conductance around 6 μS . In the case of undoped LaF_3 we may associate this conductance with presence of divalent impurity ions like Ba^{2+} , which have no optical absorption. Specific conductivity of our undoped LaF_3 crystals was near $6 \mu\text{S cm}^{-1}$ and varied few times for different raw materials. The ac conductivity of similar level for undoped LaF_3 was observed by other authors (Roos et al., 1985a; Schoonman et al., 1980).

Absence of low frequency wing of $\text{tg}\delta$ (see Fig. 4) points on absence of steady electrical conduction of $\text{LaF}_3\text{-Eu}$. It means that all of fluorine vacancies are attached to divalent europium at room temperature. Based on temperature dependence of NMR relaxation, it was concluded that free vacancy diffusion in LaF_3 begins at $T \geq 600 \text{ K}$ (Privalov et al., 1989; Hull, 2004).

We compare the absorption and bulk conductances of LaF_3 and $\text{LaF}_3\text{-EuF}_3$ (Fig. 5). The absorption and conductances measured on the same samples to diminish possible errors. The linear dependence observed up to 0.3 mol.% of EuF_3 dopant. Recently, we got a similar relationship between optical absorption and conductivity of $\text{LaF}_3\text{-Sm}^{2+}$ (Radzhabov and Kozlovsky, 2015). Undoubtedly, the conductance of $\text{LaF}_3\text{-EuF}_3$ (as well as $\text{LaF}_3\text{-BaF}_2$ (Roos et al., 1985a; Schoonman et al., 1980)) are due to fluorine vacancies introduced by divalent impurity.

4. Discussion

The investigations of LaF_3 doped with divalent alkaline-earth ions Ca^{2+} , Sr^{2+} and Ba^{2+} were proved that the charge compensators are fluorine vacancies (Igel et al., 1982; Roos et al., 1985a; Privalov et al., 1994). Introduction of divalent ions into LaF_3 led to

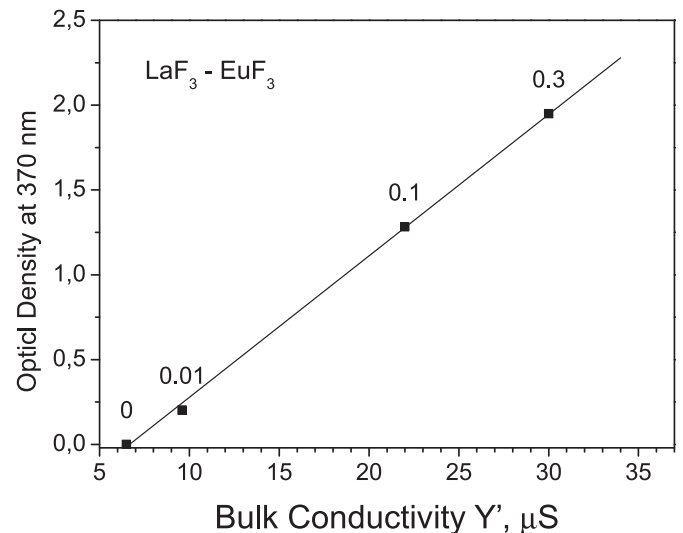


Fig. 5. Bulk conductance against Eu^{2+} absorption at 370 nm of LaF_3 and $\text{LaF}_3\text{-EuF}_3$ crystals.

increasing of ionic conductivity (Roos et al., 1985a), appearing the peaks of thermostimulated depolarisation (Roos et al., 1985a) and peaks of nuclear magnetic resonance of ^{19}F (Privalov et al., 1994). With increasing the Ba^{2+} concentration up to 8% the conductivity monotonically increased (Roos et al., 1984b). All of these phenomena caused by migration of fluorine vacancies. Based on these results one could assume that charge compensator of divalent Eu is fluorine vacancy, concentration of which can be evaluated by conductivity measurements.

We obtained linear increase of LaF_3 conductivity with increasing Eu^{2+} absorption (see Fig. 5). The linear dependence on Fig. 5 are plotted using absorption at 370 nm, straight lines can be obtained for any absorptions within 200–400 nm range, also. These results are proved that anion vacancy accompanied each divalent europium ion. Based on ionic thermodepolarisation (Roos et al., 1985a) and dielectric relaxation investigations of Me^{2+} doped LaF_3 (Roos et al., 1985a, 1984a) one could infer that anion vacancy should be in close vicinity of divalent europium.

Optical spectra of $\text{LaF}_3\text{--Eu}^{2+}$ have similarities with spectra of $\text{LaF}_3\text{--Sm}^{2+}$, investigated in our previous paper (Radzhabov and Kozlovsky, 2015). Indeed, the most intensive absorption bands in both cases belong to $4f^n\text{--}4f^{n-1}5d^1$ transitions in divalent Sm or Eu. The weaker long-wave absorption bands, in which the emission not excited, are present in both cases. In the case of Sm^{2+} we attribute this absorption bands at 600 nm to transitions from 4f ground state of samarium to level of nearest anion vacancy. Preliminary unempirical calculations support this conclusion (Radzhabov and Kozlovsky, 2015). Following to this the Eu^{2+} bands at 330, 380 nm can be attributed to transitions from europium $4f^7$ to vacancy level. Unempirical calculations, which in progress now, will explain the detail of optical spectra. The absence of emissions after excitation into long-wave bands obviously related to larger lattice relaxation around vacancy.

Apart from Eu luminescence no Yb emission was found in LaF_3 crystals. According to this no Yb^{2+} anomalous luminescence was found in BaF_2 , while Yb^{2+} luminescence in CaF_2 , SrF_2 was observed (Moine et al., 1989; Pedrini et al., 2007). It seems the absence of Yb^{2+} luminescence in hosts with large cations related with larger lattice relaxation in excited state due to smaller ionic radius of Yb against that of Eu.

According to Dorenbos empirical model the 4f–5d transitions of Eu^{2+} in LaF_3 should begin at 330 nm and 5d levels fall into the conduction band (Dorenbos, 2013). The absence of $4f^{n-1}5d^1\text{--}4f^n$ emission of divalent europium ions and absence of fine structure of 245 nm absorption $4f^7\text{--}4f^65d^1$ band correlate with the fact that Eu^{2+} 5d level falls into conduction band.

5. Conclusion

The Eu^{2+} broadband luminescence in LaF_3 at 600 nm is an emission from relaxed conduction band states to ground Eu 4f level (anomalous emission). The Eu^{2+} ion is accompanied by fluorine vacancy at room temperature, this leads to appearance of long-wave absorption bands 330, 380 nm and dielectric relaxation peak.

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References

- Carnall, W., Crosswhite, H., Crosswhite, H.M., 1978. Energy Level Structure and Transition Probabilities in the Spectra of the Trivalent Lanthanides in LaF_3 . [tables, diagrams]. Tech. Rep. ANL-78-XX-95. Argonne National Lab., IL (USA).
- Carnall, W., Goodman, G., Rajnak, K., Rana, R., 1989. A systematic analysis of the spectra of the lanthanides doped into single crystal LaF_3 . *J. Chem. Phys.* 90 (7), 3443–3457.
- Dorenbos, P., 2003. Anomalous luminescence of Eu^{2+} and Yb^{2+} in inorganic compounds. *J. Phys. Condens. Matter* 15 (17), 2645.
- 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.
- Grinberg, M., Mahlik, S., 2008. Impurity-trapped excitons: experimental evidence and theoretical concept. *J. Non-Cryst. Solids* 354 (35), 4163–4169.
- Gruen, D.M., Conway, J.G., McLaughlin, R.D., 1956. Color centers and luminescence in single crystals of lanthanum trichloride containing dispositive europium. *J. Chem. Phys.* 25 (6), 1102–1111.
- Heaps, W.S., Elias, L., Yen, W., 1976. Vacuum-ultraviolet absorption bands of trivalent lanthanides in LaF_3 . *Phys. Rev. B* 13 (1), 94–104.
- Hull, S., 2004. Superionics: crystal structures and conduction processes. *Rep. Prog. Phys.* 67 (7), 1233.
- Igel, J., Wintersgill, M.C., Fontanella, J., Chadwick, A., Andeen, C., Bean, V.E., 1982. Electrical properties of the fast-ion conductor lanthanum fluoride. *J. Phys. C Solid State Phys.* 15 (35), 7215.
- Jonscher, A.K., 1999. Dielectric relaxation in solids. *J. Phys. D Appl. Phys.* 32 (14), R57.
- Kim, B.F., Moos, H., 1967. Electron paramagnetic resonance and spectroscopic study of $\text{LaCl}_3\text{:Eu}^{2+}$ and associated color centers. *Phys. Rev.* 161 (3), 869–876.
- Lehmann, W., 1975. Heterogeneous halide-silica phosphors. *J. Electrochem. Soc.* 122 (6), 748–752.
- Moine, B., Courtois, B., Pedrini, C., 1989. Luminescence and photoionization processes of Yb^{2+} in CaF_2 , SrF_2 and BaF_2 . *J. Phys.* 50 (15), 2105–2119.
- Pedrini, C., Joubert, M.-F., McClure, D., 2007. Photoionization processes of rare-earth dopant ions in ionic crystals. *J. Lumin.* 125 (1), 230–237.
- Privalov, A., Vieth, H.-M., Murin, I., 1989. Ionic motion in the LaF_3 superionic conductor studied by 19f nmr with homonuclear decoupling. *J. Phys. Chem. Solids* 50 (4), 395–398.
- Privalov, A., Vieth, H.-M., Murin, I., 1994. Nuclear magnetic resonance study of superionic conductors with tysonite structure. *J. Phys. Condens. Matter* 6 (40), 8237–8343.
- Radzhabov, E., Kozlovsky, V., 2015. Sm^{2+} spectra in lanthanum fluoride. *Phys. Procedia* 76, 47–52.
- Radzhabov, E., Nagirnyi, V., Kirm, M., Prosekina, E., 2012. 5d-4f emission of Nd^{3+} , Sm^{3+} , Ho^{3+} , Er^{3+} , Tm^{3+} ions in alkaline earth fluorides. *Nucl. Sci. IEEE Trans.* 59, 2074–2078.
- Radzhabov, E.A., 2016. F_3^- centres in fluoride crystals. *Opt. Spectrosc.* 120 (2), 307–312.
- Rast, H., Caspers, H., Miller, S., 1967. Fluorescence and energy transfer between Nd^{3+} and Yb^{3+} in LaF_3 . *J. Chem. Phys.* 47 (10), 3874–3878.
- Roos, A., Buijs, M., Wapenaar, K., Schoonman, J., 1985a. Dielectric relaxation properties of tysonite-type solid solutions $\text{La}_{1-x}\text{Ba}_x\text{F}_{3-x}$. *J. Phys. Chem. Solids* 46 (6), 655–664.
- Roos, A., Franceschetti, D., Schoonman, J., 1984a. The small-signal ac response of $\text{La}_{1-x}\text{Ba}_x\text{F}_{3-x}$ solid solutions. *Solid State Ionics* 12, 485–491.
- Roos, A., Franceschetti, D., Schoonman, J., 1985b. Bulk and interfacial polarization phenomena of $\text{La}_{1-x}\text{Ba}_x\text{F}_{3-x}$ crystals. *J. Phys. Chem. Solids* 46 (6), 645–653.
- Roos, A., Van de Pol, F., Keim, R., Schoonman, J., 1984b. Ionic conductivity in tysonite-type solid solutions $\text{La}_{1-x}\text{Ba}_x\text{F}_{3-x}$. *Solid State Ionics* 13 (3), 191–203.
- Schönhals, A., Kremer, F., 2003. Analysis of dielectric spectra. In: *Broadband Dielectric Spectroscopy*. Springer, pp. 59–98.
- Schoonman, J., Oversluizen, G., Wapenaar, K., 1980. Solid electrolyte properties of LaF_3 . *Solid State Ionics* 1 (3), 211–221.