

Energy Dissipation in Impurity Doped Alkaline-Earth Fluorides

Evgeny A. Radzhabov, Marco Kirm, Alexandr Egranov, and Alexandr Nepomnyaschikh

Abstract—Excitation spectra of CaF_2 , SrF_2 and BaF_2 crystals doped by CdF_2 , LaF_3 , YF_3 in vacuum ultraviolet region were investigated at liquid-helium temperature and at room temperature. Spectra of doped BaF_2 at low temperature and CaF_2 , SrF_2 at room temperature show significant decrease of excitation intensity against those in undoped crystals while the intensities in exciton regions remain nearly the same.

The common reason of the suppression of exciton emission by impurity in alkaline-earth fluorides is unradiative electron-hole recombination on impurity sites.

Index Terms—Excitons, impurity, suppression, vacuum ultraviolet.

I. INTRODUCTION

THERE is a practical need to diminish slow excitation luminescence of BaF_2 retaining only fast cross luminescence. Therefore, several trivalent [1] divalent [2], [3], and monovalent [4] impurities have been found as effective exciton suppressors. The concentration of impurity needed for effective suppression is ranging from a few tenths of molar percent for CdF_2 to a few molar percent for LaF_3 or YF_3 [5]. Most prospective impurities should have no optical transitions within the host bandgap. Despite the numerous experimental studies, the mechanism of exciton suppression is not known.

Impurities La^{3+} , Y^{3+} , Cd^{2+} have filled outer shells and have no own absorption bands with energies below 12 eV. However, new strong absorption bands appear very near to the exciton absorption edge in vacuum ultraviolet region [6]. Cadmium introduced impurity states lower the bottom of conduction band states and the transitions from surrounding fluorines to cadmium lead to the appearance of strong absorption just below the exciton edge. The La and Y ions accompanied charge compensated interstitial fluorines, which have atomic p-states higher than top of valence band states. The La, Y impurity bands transitions arise from these states to conduction band states.

In all CaF_2 , SrF_2 , or BaF_2 crystals these impurities considerably suppress the exciton emission [1]–[5], while fast cross-luminescence of BaF_2 remains unaffected. The dependence of intensity and decay times of the exciton luminescence on concentration of La in BaF_2 could not be explained by

interaction of excitons with impurity only [7]. Another possible process is trapping of free charge carriers (electrons or holes), so the number of excitons created through electron-hole interaction is decreased with the increasing numbers of traps. The trapping of holes by charge compensating fluorine interstitials was proposed to lead exciton suppression in BaF_2 doped with LaF_3 impurity [8], [9]. However, comparison of doubly doped BaF_2 – LaF_3 –KF in equal molar concentration (in this case there are no fluorine interstitials in the crystal) with BaF_2 – LaF_3 are proof that fluorine interstitials have weak influence on exciton suppression [10].

Excitons in alkaline-earth fluorides are effectively created from separated free electrons and holes as it follows from excitation spectra of pure crystals. Therefore, one could infer that there are two common ways to suppress excitons. At first, impurity may decrease the number of free electrons and holes by sequential trapping at impurity. Then, excitons may be suppressed due to the interaction of created excitons with impurity. Therefore, one needs to separate the process of interaction of excitons with impurities from those of electron-hole interaction with impurities before creation of exciton. One of possible ways is the comparison of suppression of excitons directly created by photons with suppression of excitons created over free electrons and holes by vacuum ultraviolet (VUV) photons or X-ray.

In this paper, we investigate excitation spectra in exciton and band-to-band regions of BaF_2 , SrF_2 , CaF_2 crystals doped with different closed shell ions— La^{3+} , Y^{3+} , Cd^{2+} . Some preliminary results were published in an earlier paper [5].

II. EXPERIMENTAL

Crystals were grown in vacuum in graphite crucible by the Stockbarger method. In the first step, an oxygen-free crystal was grown with the addition of CdF_2 or PbF_2 as oxygen scavenger in a simple large volume crucible. Then parts of this crystal were used for the growth of impurity doped crystals of smaller size. Concentration of impurities varied from 0.01 to 30 mol. %. Concentration of impurities was measured by the atomic absorption method.

The excitation, absorption spectra in the energy range of 4–12 eV and emission spectra in the range 2–6 eV were measured with grating vacuum monochromator VMR2 and grating monochromator MDR2. In addition, emission and excitation measurements were carried out using a low-temperature luminescence setup SUPERLUMI designed for VUV spectral region, located in HASYLAB at DESY (Hamburg, Germany) [11]. Photons generated by a bending magnet of the storage ring DORIS (5-MHz repetition rate) are tunable in the energy

Manuscript received June 26, 2007; revised September 28, 2007. This work was supported in part under Grant 07-02-01057 from the Russian Foundation for Basic Research (RFBR).

E. Radzhabov, A. Egranov, and A. Nepomnyaschikh are with the Vinogradov Institute of Geochemistry, Russian Academy of Sciences, P.O. Box 4019, 664033 Irkutsk, Russia (e-mail: eradh@igc.irk.ru; alegra@igc.irk.ru; ainep@igc.irk.ru).

M. Kirm is with the Institute of Physics, University of Tartu, Riia 142, 51014 Tartu, Estonia.

Digital Object Identifier 10.1109/TNS.2008.922823

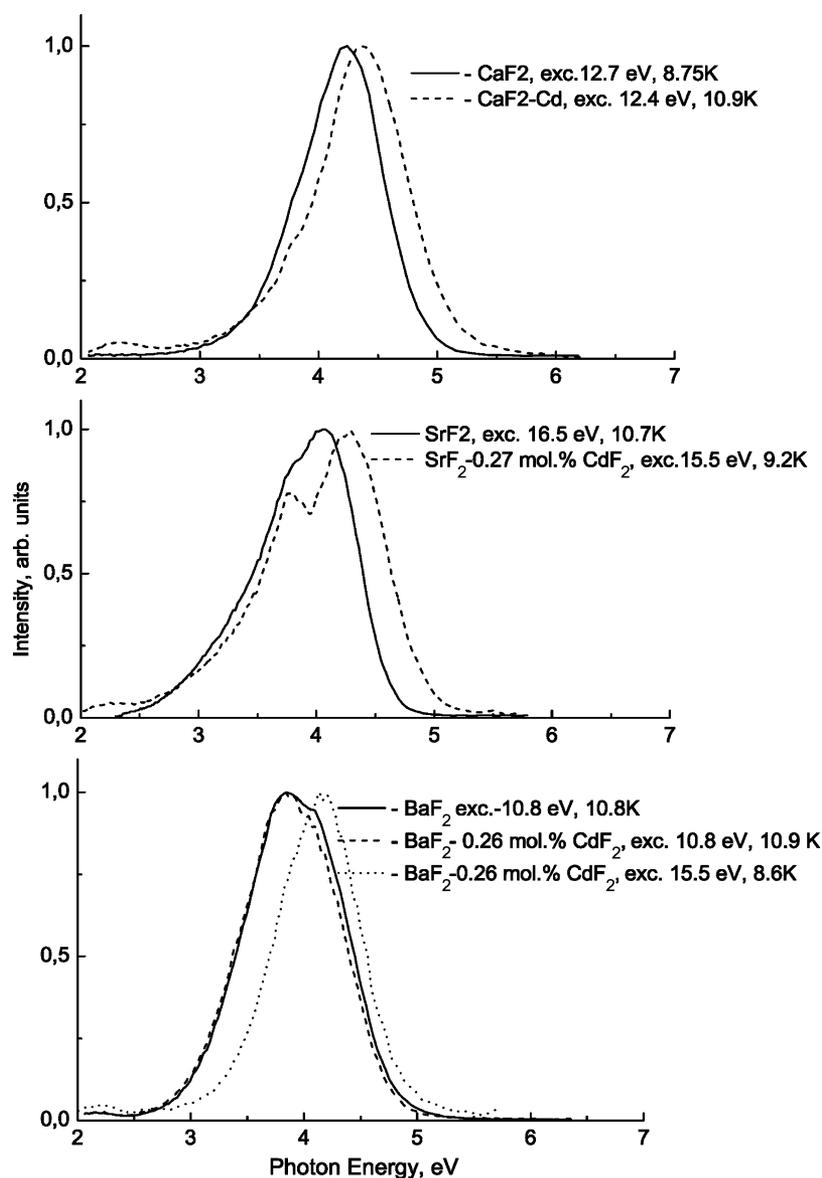


Fig. 1. Normalized emission spectra of pure and doped CaF_2 , SrF_2 , and BaF_2 at low temperatures. All spectra were measured using long time window mode.

range of 4–40 eV using a 2-m normal incidence monochromator with an optical slit width of 0.32 nm. Luminescence was analyzed with a 0.3-m imaging spectrograph SpectraPro308i (Acton Research Inc.). The optical slit width of the secondary monochromator was typically 2 nm. Discrimination between the fast and slow emissions was achieved by recording signals within the time window Δt after the arrival of excitation pulse delayed by δt . All emission spectra presented here were measured in the long time window mode ($\delta t = 30\text{--}50$ ns and $\Delta t = 100\text{--}150$ ns). Emission spectra were not corrected for spectra sensitivity response of monochromator. Excitation spectra were measured in time integrated mode, acquisition time was typically 2 s per each point. Intensities of excitation spectra of particular crystals were normalized to be equal at exciton region.

For comparison of exciton intensity in samples with different concentration of impurities we prepare samples with same $8 \times 10 \times 2$ -mm dimensions sawed from bulk and one-side polished.

We measure emission spectra of different samples with excitation of Kr resonance discharge lamp, having most intensive line at 10.0 eV (123.6 nm). This lamp is suitable for illumination into first exciton peaks of CaF_2 , SrF_2 , and BaF_2 crystals.

III. RESULTS

We compare the intensity of emission spectra of different samples under excitation by resonance Kr lamp. Additionally, we compare the intensity of excitation spectra in exciton region. Both measurements gave similar results. In all studied (Y, La, or Cd) doped crystals, the intensity of exciton emission decreased by only 10–30% against that in undoped crystals. At the same time, the exciton intensity under X-ray irradiation considerably decreased with the increase of impurity concentration (see also [4]).

The emission spectra of excitons are slightly shifted to high energy side by the Cd impurity (Fig. 1) under vacuum ultraviolet excitation. This shift is also observed using X-ray excita-

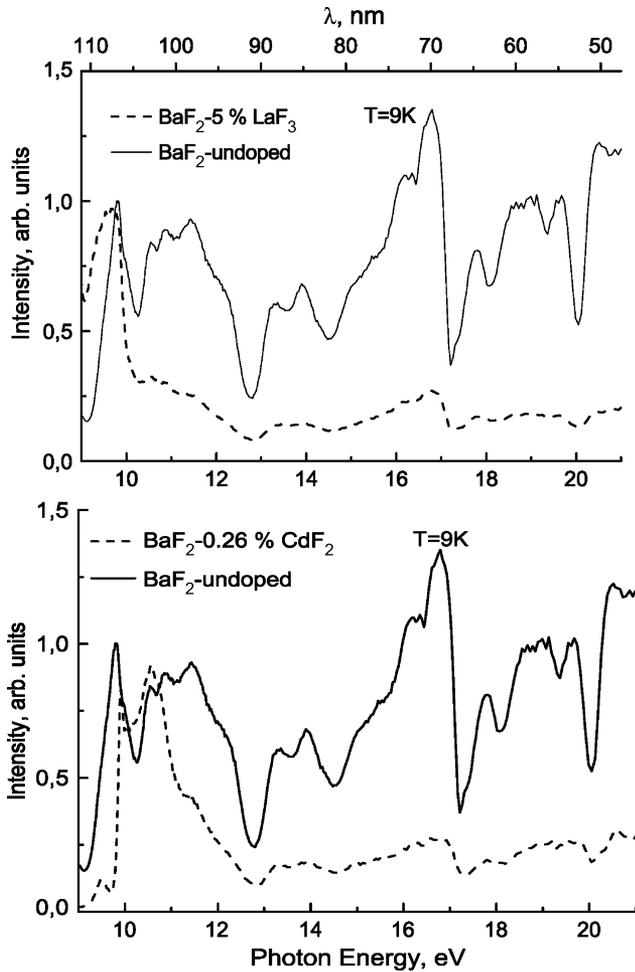


Fig. 2. Excitation spectra of exciton emission at 4.3 eV in pure and doped BaF_2 at 9 K.

tion. This fact points out that exciton luminescence is near to Cd impurity.

The excitation spectra of $\text{BaF}_2\text{-LaF}_3$ (Fig. 2) show two main features. These are the broadening exciton band at 9.8 eV and the appearance of a new excitation band near 9.0 eV. This new excitation band was assigned to transitions from interstitial fluorines [10]. The position of the new band shifts from 9.18 eV in $\text{BaF}_2\text{-0.1\%LaF}_3$ to 8.87 eV in $\text{BaF}_2\text{-5\%LaF}_3$. The shift of position of the excitation band to lower energies with increasing La concentration is probably related to the creation of interstitial fluorine subband.

The excitation spectra of $\text{BaF}_2\text{-Cd}$ crystals are shifted to higher energies (see Fig. 2). The shift was ascribed to be from strong Cd absorption band [6]. In doped BaF_2 crystals we observe a strong relative decrease of excitation intensity above 10 eV against the excitation intensity in undoped crystals (see Fig. 2).

However, no such decrease of exciton luminescence was found in Cd-doped CaF_2 and SrF_2 crystals at 9 K (Fig. 3). The excitation spectra of undoped and CdF_2 -doped CaF_2 and SrF_2 crystals are different, but no significant decrease of intensities of Cd-doped crystals against the undoped ones were observed in the region above 10–11 eV (see Fig. 3).

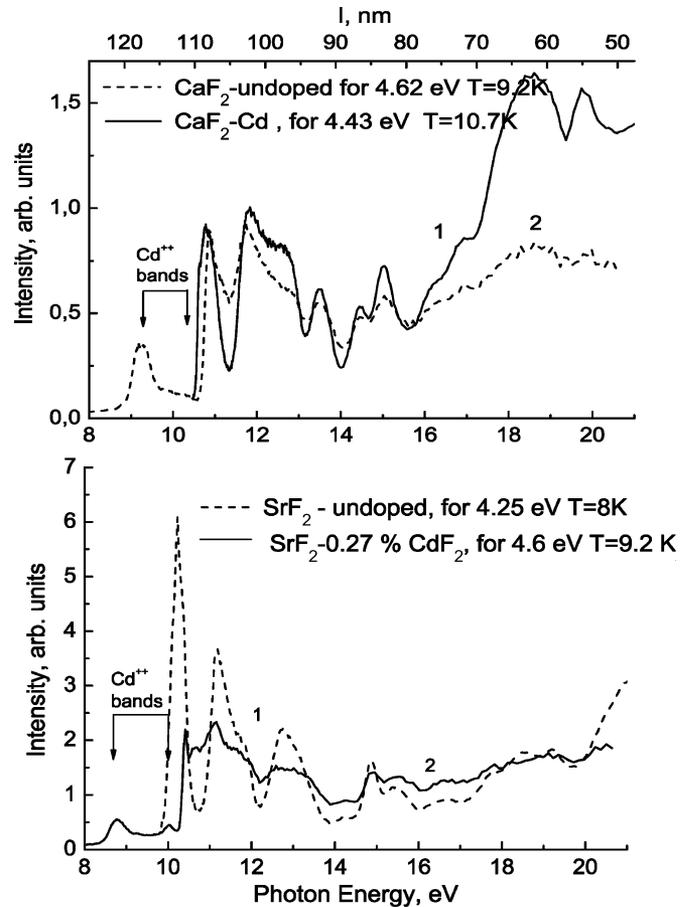


Fig. 3. Excitation spectra of exciton emission of CaF_2 , $\text{CaF}_2\text{-Cd}$, SrF_2 , and $\text{SrF}_2\text{-Cd}$ at liquid helium temperatures.

In separate studies [12], we found a new emission bands in $\text{CaF}_2\text{-Cd}$ and $\text{SrF}_2\text{-Cd}$ crystals, which was excited in Cd impurity region (below the exciton region) (Fig. 3). These new emission bands were found in $\text{CaF}_2\text{-Cd}$ and $\text{SrF}_2\text{-Cd}$ and not found in $\text{BaF}_2\text{-Cd}$ crystals [12]. At temperatures 50–80 K in $\text{CaF}_2\text{-Cd}$ and 40–150 K in $\text{SrF}_2\text{-Cd}$ new emission bands were quenched. Probably Cd-emission altered the excitation spectra in band-to-band region above 11–12 eV. Therefore, to exclude the influence of these bands, we measured the exciton spectra of exciton emission of CaF_2 and SrF_2 crystals at room temperature.

The obvious reduction of excitation intensities in the inter-band region of $\text{CaF}_2\text{-Cd}$ and $\text{SrF}_2\text{-Cd}$ were observed (Fig. 4) as in the case of $\text{BaF}_2\text{-Cd}$, $\text{BaF}_2\text{-La}$ crystals.

IV. DISCUSSION

The ratio of exciton intensity of a doped crystal to that of an undoped crystal should reflect the process of the increase of separation distance between electron and hole with an increase of excitation energy. Indeed, the higher the excitation energy above the exciton peak one, the larger should be the distance between electron and hole. When the distance between the electron-hole pair becomes comparable with the mean distance between impurity ions, the ratio of intensities should reach a constant value. The energy of exciton peak in BaF_2 crystal is 9.8

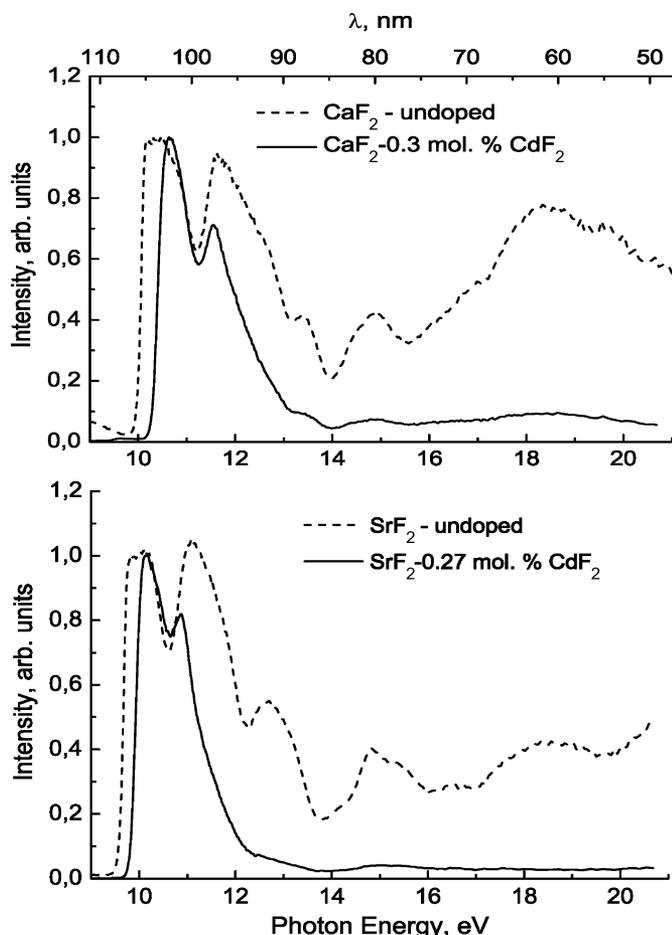


Fig. 4. Excitation spectra of exciton emission of CaF_2 , $\text{CaF}_2\text{-Cd}$, SrF_2 , and $\text{SrF}_2\text{-Cd}$ at room temperatures.

eV, the ratio of exciton intensities decrease twice at energies 10.3 eV in $\text{BaF}_2\text{-5\%LaF}_3$ and 11.3 eV in $\text{BaF}_2\text{-0.26\%CdF}_2$ (see Fig. 2). These energies are close to the exciton reflection peak at 10.0 eV and evaluated, e.g., bandgap energy 10.6 eV [13]. Therefore, we may infer that when photon energy exceeds the exciton energy by $\Delta E = 10.3 - 9.8 = 0.5$ eV the e-h separation becomes equal or less than the mean separation between the La impurity ions. For 5 mol. % of LaF_3 , the mean distance between the La ion is $2.8a_0$ (where a_0 is the lowest cation-cation distance). When photon energy exceed the exciton one by $\Delta E = 1.3$ eV, the e-h separation becomes $6.7a_0$ (in the case of $\text{BaF}_2\text{-0.26 mol.\%CdF}_2$). The ΔE values for $\text{SrF}_2\text{-Cd}$ and $\text{CaF}_2\text{-Cd}$ at room temperatures are equal 1.2 and 1.8 eV, respectively, for the e-h separation near $7a_0$ (see Fig. 4).

Generally, the processes of transfer of absorbed energy to quenching centers and to luminescence centers should be similar. The results of basic experiments such as radioluminescence, VUV spectroscopy, time profiles, and thermoluminescence on rare-earth-activated scintillator materials can be consistently explained assuming that the dominant mechanism of scintillation light production is due to radiative recombination of charge carriers at luminescent rare-earth ions [14]. It was concluded that radiative recombination of unbound electron-hole pairs generated by ionizing radiation provides the only efficient scintillation mechanism in RE-activated fluorides.

The efficiency of the process, however, depends critically on the presence of energy levels in the forbidden energy gap of the host, provided by quasi-stable alternative charge states of the activating ion. An absence of such states is very likely to disqualify a material for useful scintillator applications [15].

In general, one can define three different scintillation mechanisms in Ce-doped crystals corresponding to three different energy transfer mechanisms which occur at different time scales and with different probabilities [16].

- (i) Energy transfer by direct electron-hole capture.
- (ii) Energy transfer by binary electron-hole recombination.
- (iii) Energy transfer by self-trapped exciton diffusion/emission.

For generality we may combine (i) and (ii) processes as energy transfer by electron-hole recombination near to impurity. Another main channel is (iii)—energy transfer via excitons created by electron-hole recombination in unperturbed lattice. Channel (iii) effectiveness can be verified by exciton intensity variation under excitation into exciton absorption band, when only excitons are created and no free electrons and holes are created. The excitation into interband region creates free electrons and holes which have two main channels to release energy—one is creates excitons, another process is transfer energy to impurity.

The dynamics of the relaxation of (e-h) pairs in CaF_2 has been studied by absorption femtosecond technique [17]. Based on the results and their analysis, it has been shown that self-trapped excitons are formed through two distinctive stages. In the first stage, the state responsible for the B band acts as the precursor of self-trapped excitons, and the state is tentatively assumed to be the relaxing hole. As the intermediate state that is responsible for the slow growth of self-trapped excitons, a hypothetical entity of the on-center self-trapped exciton in CaF_2 crystals is proposed [17]. Therefore, we may assume that during thermalization one of the free charge carriers (electron or hole) is captured by impurity or near impurity. Following nonradiative recombination with charge carrier of another sign is a competing process to those of excitons creation in unperturbed lattices. The concentration of Cd needed for effective competition in exciton creation is about ten times less than concentration of La or Y. Obviously, it depends on radii of trapping of the charge carrier by impurity.

Similar results on influence of impurity on excitation spectrum were observed in $\text{BaF}_2\text{-1\%DyF}_3$ crystals [18]. In this crystal, following band-to-band transitions, exciton emission drastically decreases whereas Dy^{3+} emission shows up. The authors concluded that energy transfer arises from the relaxation of free carriers before electron-hole recombination [18].

V. CONCLUSION

Sequential trapping of charge carriers (free electrons and holes) by impurities, followed by nonradiative recombination at impurity sites, is the main reason of suppression of excitonic emission by different impurities in alkaline earth fluorides.

ACKNOWLEDGMENT

The authors wish to thank V. Ivashechkin for the leadership in the growth of studied crystals.

REFERENCES

- [1] B. P. Sobolev, E. A. Krivandina, S. E. Derenzo, W. W. Moses, and A. C. West, "Suppression of BaF low component of x -ray luminescence in non-stoichiometric $Ba_{0.9}R_{0.1}F_{2.1}$ crystals ($R =$ rare earth element)," in *Scintillator and Phosphor Materials, Mat. Res. Soc. Symp. Proc.*, 1994, vol. 348, pp. 277–284.
- [2] M. M. Hamada, Y. Nunoya, S. Sakuragui, and S. Kubota, "Suppression of the slow component of BaF_2 crystal by introduction of SrF_2 and MgF_2 crystals," *Nucl. Instrum. Methods Phys. Res. A*, vol. 353, pp. 33–36, 1994.
- [3] U. Rogulis, J. Trokss, A. Veispals, I. Tale, P. Kulis, and M. Springis, "ODMR of Cd impurity centers in GG irradiated BaF_2 crystals," *Radiat. Eff. Defects Solids*, vol. 135, pp. 859–863, 1995.
- [4] E. Radzhabov, A. Istomin, A. Nepomnyashikh, A. Egranov, and V. Ivashechkin, "Exciton interaction with impurity in barium fluoride crystals," *Nucl. Instrum. Methods Phys. Res. A*, vol. 537, no. 1–2, pp. 71–75, 2005.
- [5] E. Radzhabov, M. Kirm, A. Egranov, A. Nepomnyashikh, and A. Myasnikova, "Mechanism of exciton suppression in alkaline-earth fluorides doped with La, Y, Cd," in *Proc. SCINT 2005*, Alushta, Crimea, Ukraine, Sep. 19–23, 2005, pp. 60–63.
- [6] E. Radzhabov, A. Mysovsky, A. Egranov, A. Nepomnyashikh, and T. Kurobori, "Cadmium centres in alkaline-earth fluoride crystals," *Phys. Stat. Sol. (C)*, vol. 2, pp. 388–391, 2005.
- [7] R. Visser, P. Dorenbos, C. W. E. van Eijk, A. Meijerink, G. Blasse, and H. W. den Hartog, "Energy transfer processes involving different luminescence centres in $BaF_2 : Ce$," *J. Phys.: Condens. Matter*, vol. 5, pp. 1659–1680, 1993.
- [8] M. Gu, L. Y. Chen, Q. Li, and X. Wu, "The influence of lanthanum on slow component in the scintillation light of BaF_2 ," *Commun. Theor. Phys.*, vol. 26, pp. 279–282, 1996.
- [9] A. I. Nepomnyashchikh, E. A. Radzhabov, A. V. Egranov, V. F. Ivashechkin, and A. S. Istomin, "Recombination processes in crystals of solid solutions of $Ba_{1-x}La_xF_2 + x$," *Nucl. Instrum. Methods A*, vol. 486, no. 1–2, pp. 390–394, 2002.
- [10] E. Radzhabov, A. Nepomnyashikh, and A. Egranov, "Configurations of excitons in $BaF_2 - LaF_3$," *J. Phys. Cond. Matter*, vol. 14, pp. 7337–7343, 2002.
- [11] M. Kirm, A. Lushchik, C. Lushchik, A. I. Nepomnyashikh, and F. Savikhin, "Dependence of the efficiency of various emissions on excitation density in BaF_2 crystals," *Rad. Meas.*, vol. 33, no. 5, pp. 515–519, 2001.
- [12] E. Radzhabov and M. Kirm, "Triplet luminescence of cadmium centres in alkaline-earth fluoride crystals," *J. Phys.: Condens. Matter*, vol. 17, pp. 5821–5830, 2005.
- [13] H. W. Hayes, Ed., "Crystals with fluorite structure," in *Crystals With Fluorite Structure*. Oxford, U.K.: Clarendon, 1974.
- [14] A. J. Wojtowicz, "Rare-earth-activated wide bandgap materials for scintillators," *Nucl. Instrum. Methods Phys. Res. A*, vol. 486, pp. 201–207, 2002.
- [15] A. J. Wojtowicz, J. Glodo, D. Wisniewsky, and A. Lempicki, "Scintillation mechanism in RE-activated fluorides," *J. Luminesc.*, vol. 72–74, pp. 731–733, 1997.
- [16] E. V. van Loef, P. Dorenbos, C. W. E. van Eijk, K. W. Kramer, and H. U. Gudel, "Scintillation and spectroscopy of the pure and 3+ Ce-doped elpasolites: $Cs LiYX$ ($X = Cl, Br$)," *J. Phys.: Condens. Matter*, vol. 14, pp. 8481–8496, 2002.
- [17] K. Tanimura, "Femtosecond time-resolved spectroscopy of the formation of self-trapped excitons in CaF_2 ," *Phys. Rev. B Condensed Matter*, vol. 63, p. 184303, 2001.
- [18] J. Becker, G. Zimmerer, and C. Shi, "Anion- and cation-type energy transfer in $BaF_2 : Dy$," *J. Luminesc.*, vol. 72, pp. 906–908, 1997.