

5d-4f Emission of Nd^{3+} , Sm^{3+} , Ho^{3+} , Er^{3+} , Tm^{3+} Ions in Alkaline Earth Fluorides

E. Radzhabov, V. Nagirnyi, M. Kirm, and E. Prosekina

Abstract—Emission and excitation spectra of CaF_2 , SrF_2 , BaF_2 doped with Nd^{3+} , Sm^{3+} , Ho^{3+} , Er^{3+} , Tm^{3+} excited by vacuum ultraviolet photons or by x-rays were studied. Decay times of the Nd^{3+} emission near 180 nm at 7 K were 17.7, 15.3, 12.3 ns in CaF_2 , SrF_2 , BaF_2 respectively. $4f^{n-1}5d^1-4f^n$ luminescence bands were found at 170–200 nm for Sm^{3+} ions and at 140–190 nm for Ho^{3+} .

No excitation of 5d-4f emission of Nd^{3+} and Tm^{3+} was observed in the region of band-to-band transitions below 127 nm (BaF_2), 120 nm (SrF_2) and 115 nm (CaF_2).

Emission spectra of Nd and Er doped alkaline-earth fluoride crystals under x-ray excitation were studied with concentration of impurity from 0.01 to 10 molar %. For the Nd^{3+} and Er^{3+} 5d-4f emissions in SrF_2 the light yields were estimated as 30–40 ph/Mev.

Index Terms—Energy transfer, excitons, scintillator, vacuum ultraviolet.

I. INTRODUCTION

EMISSION from the 5d to 4f shell of rare earth ions doped into ionic crystals was extensively studied in the last decade [1]–[3]. The emission observed in vacuum ultraviolet region has potentiality for exploitation in lasers, scintillators or quantum cutting systems.

From the general point of view the decrease of emission wavelength should lead to the decrease of decay time [4]. Due to this, many attempts were made to find dense and effective scintillation material doped with rare earth ions having emission in vacuum ultraviolet [5]. Among all 14 lanthanide ions only half, the ions with the number of f-electrons up to seven, can be considered as promising for fast scintillating. The heavier lanthanide ions possess slow vacuum ultraviolet emission because the lowest excited $4f^{n-1}5d^1$ state has a larger spin (usually designated as high spin-HS) than the ground $4f^n$ state, so the $4f^{n-1}5d^1-4f^n$ transitions become forbidden by spin rule.

Light lanthanides Ce^{3+} , Pr^{3+} , Nd^{3+} show bright $4f^{n-1}5d^1-4f^n$ luminescence under optical excitation even

Manuscript received November 04, 2011; revised February 08, 2012; accepted February 14, 2012. This work was supported in part by Grant 11-02-00717 from the Russian Foundation for Basic Research (RFBR), by the Estonian Science Foundation (Grants 8893, 8306), and the European Community Research Infrastructure Action under the FP6 Structuring the European Research Area Programme (through the Integrated Infrastructure Initiative Integrating Activity on Synchrotron and Free Electron Laser Science).

E. Radzhabov and E. Prosekina are with the Vinogradov Institute of Geochemistry, Russian Academy of Sciences, 664033 Irkutsk, Russia (e-mail: eradz@igc.irk.ru).

V. Nagirnyi and M. Kirm are with the Institute of Physics, University of Tartu, 51014 Tartu, Estonia.

Color versions of one or more of the figures in this paper are available online at <http://ieeexplore.ieee.org>.

Digital Object Identifier 10.1109/TNS.2012.2188543

at room temperatures, while Gd^{3+} , Lu^{3+} have luminescence at low temperature only [6]. Among the heavy ions only Er^{3+} , Tm^{3+} [7], Ho^{3+} [8], [9] and Tb^{3+} [10] show $4f^{n-1}5d^1-4f^n$ vacuum ultraviolet luminescence. The emission peaks were assigned to the spin-allowed (low spin LS to low spin) and the spin-forbidden (high spin-HS to low spin) transitions between the levels of the $4f^{n-1}5d$ and the levels of the $4f^n$ electronic configuration of the heavy lanthanide ion [2]. Recently we found a weak vacuum ultraviolet luminescence of Ho in CaF_2 [12]. Additionally to this we found now a bright Ho^{3+} luminescence in SrF_2 and BaF_2 and a weak Sm^{3+} vacuum ultraviolet luminescence in all three alkaline-earth fluoride hosts. It should be noted that the Sm^{3+} vacuum ultraviolet luminescence was not yet known in any compound.

It is generally known that the light output of rare-earth doped scintillators decreases in the row of impurities Ce^{3+} , Pr^{3+} , Nd^{3+} [11], however the efficiency and mechanisms of the electron-hole or exciton energy transfer in such scintillators are yet poorly investigated.

The aim of the present paper is to investigate the ultraviolet 5d-4f emission of rare-earth ions and mechanisms of energy transfer in alkaline-earth fluoride crystals CaF_2 , SrF_2 , BaF_2 by vacuum ultraviolet spectroscopy. Some previous results were published in a paper [12].

II. EXPERIMENTAL

Crystals CaF_2 , SrF_2 , BaF_2 doped with REF_3 (RE-Nd, Sm, Eu, Gd, Tb, Ho, Er, Tm, Yb) were grown by the Stockbarger method in a graphite crucible in vacuum. Normally six or more rods with concentration of dopant from 0.005 to 10 molar percent were grown. At concentration less 0.3 mol.% the samples were cutted from grown rod. At higher concentration the sample were sawed from the rod and polished.

Emission spectra in vacuum ultraviolet region were measured with a solar blind photomultiplier FEU142 attached to a VM4 grating vacuum monochromator. Samples were excited either by Xe discharge lamp emitting at 147 or by x-ray tube. The excitation and absorption spectra in the energy range of 4–13 eV were measured with a grating vacuum monochromator VMR2. A discharge deuterium lamp L7293 with a MgF_2 window (Hamamatsu) was used as a vacuum ultraviolet source. Absorption in a vacuum ultraviolet region was measured for all samples at room temperatures to check the absence of unwanted impurities.

Time-resolved spectra were recorded using synchrotron radiation at the SUPERLUMI station of HASYLAB at DESY (Hamburg, Germany) [13].

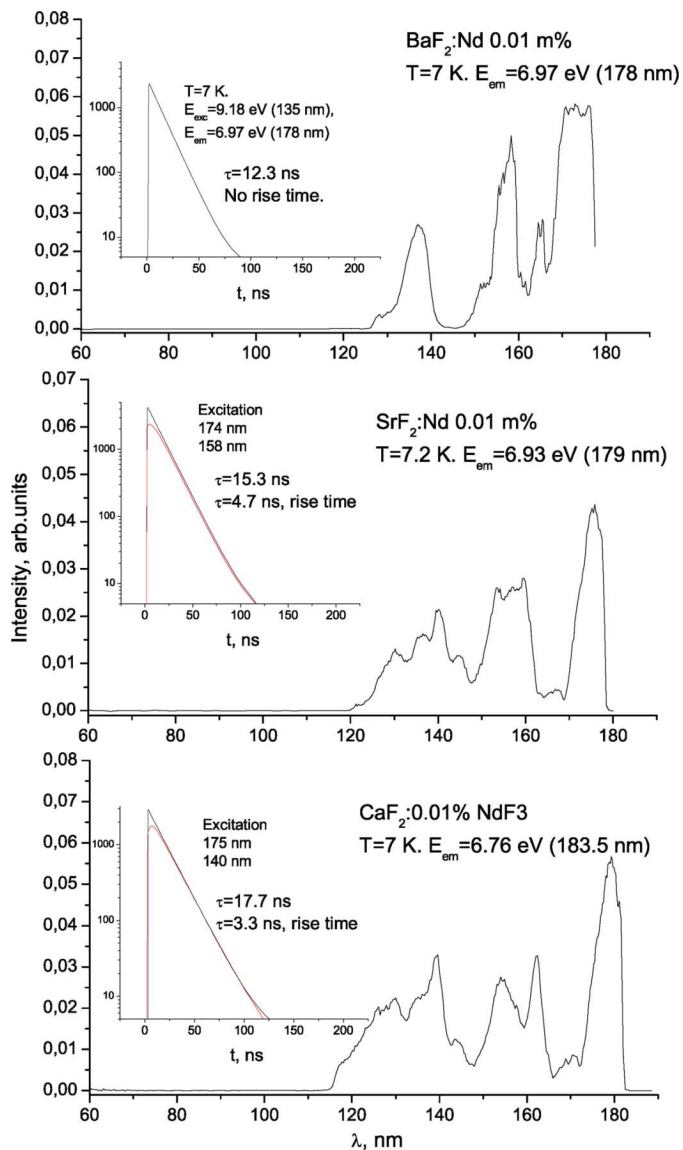


Fig. 1. Excitation spectra of Nd^{3+} emission in CaF_2 , SrF_2 , BaF_2 crystals. Inset shows the decay curves of the Nd^{3+} emission.

For simplicity we used a simpler f-d or 4f-5d notation instead of full notation $4f^n-4f^{n-1}5d^1$.

III. RESULTS

A. Nd^{3+} Emission

The emission spectra of the Nd^{3+} ions in vacuum ultraviolet in all three alkaline-earth fluorides were measured in our previous paper [12]. The details of emission were satisfactorily explained by the transitions from the lowest 5d level to different $4f^n$ terms of the ground state.

The decay times of the Nd emission under optical excitation in the region 180–190 nm at 7 K were 17.7, 15.3, and 12.3 ns in CaF_2 , SrF_2 , and BaF_2 , respectively. The Nd emission decay curves were single exponential when excited in the lowest absorption band 170–180 nm. The rise times of 3–4 ns

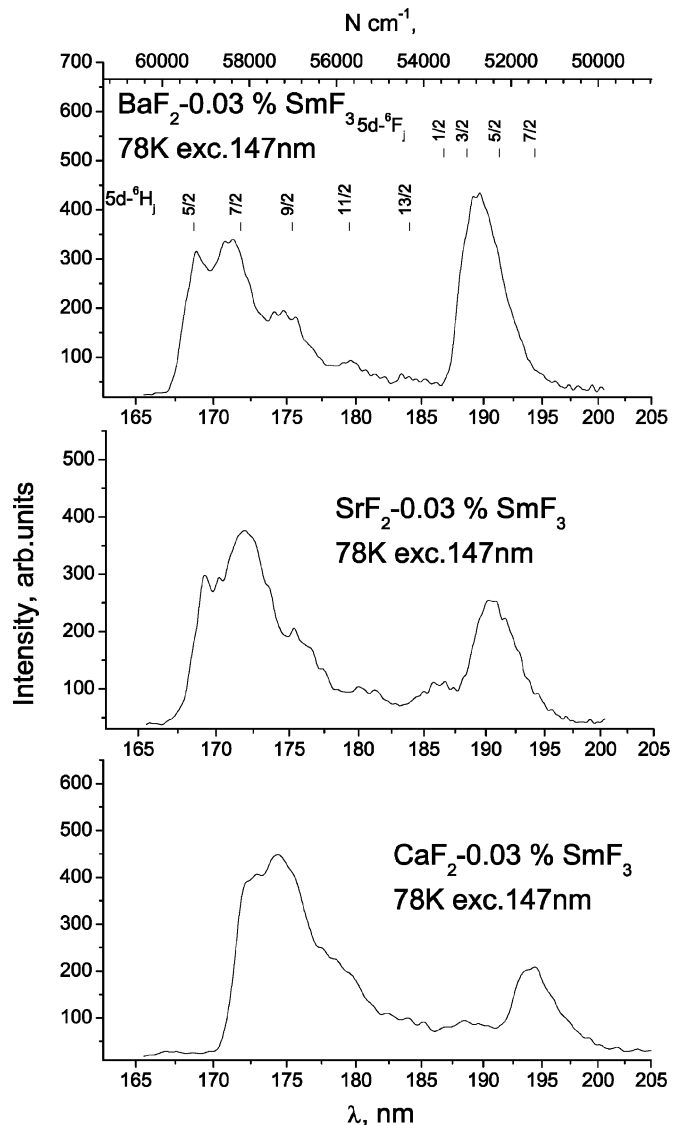


Fig. 2. Emission spectra of Sm^{3+} in CaF_2 , SrF_2 , BaF_2 crystals.

were observed under illumination into the higher lying excitation bands in CaF_2 and SrF_2 . No any rise of emission was observed in BaF_2 -Nd. It seems that a smaller splitting of the 5d levels (e_g-t_{2g}) in BaF_2 increases significantly the probability of non-radiative transitions to the lowest 5d excited level.

The vacuum ultraviolet 5d-4f emission of Nd^{3+} was excited only in the crystal transparency region up to the exciton bands. No vacuum ultraviolet 5d-4f emission of Nd was observed under excitation from 127 nm (10 eV) in BaF_2 , 120 nm (10.5 eV) in SrF_2 and 115 nm (11 eV) in CaF_2 down to 60 nm (20 eV) (see Fig. 1).

B. Sm^{3+} Emission

A weak luminescence of Sm^{3+} ions was found in all the three hosts (Fig. 2) at both low and room temperature also. Two bands at 170–175 and 190–195 nm were observed. The first band shows a weak structure which is most prominent in the BaF_2 -Sm crystal. It can be assigned to the $5d-^6H_j$ transitions, while second band can be assigned to the $5d-^6F_j$ transitions.

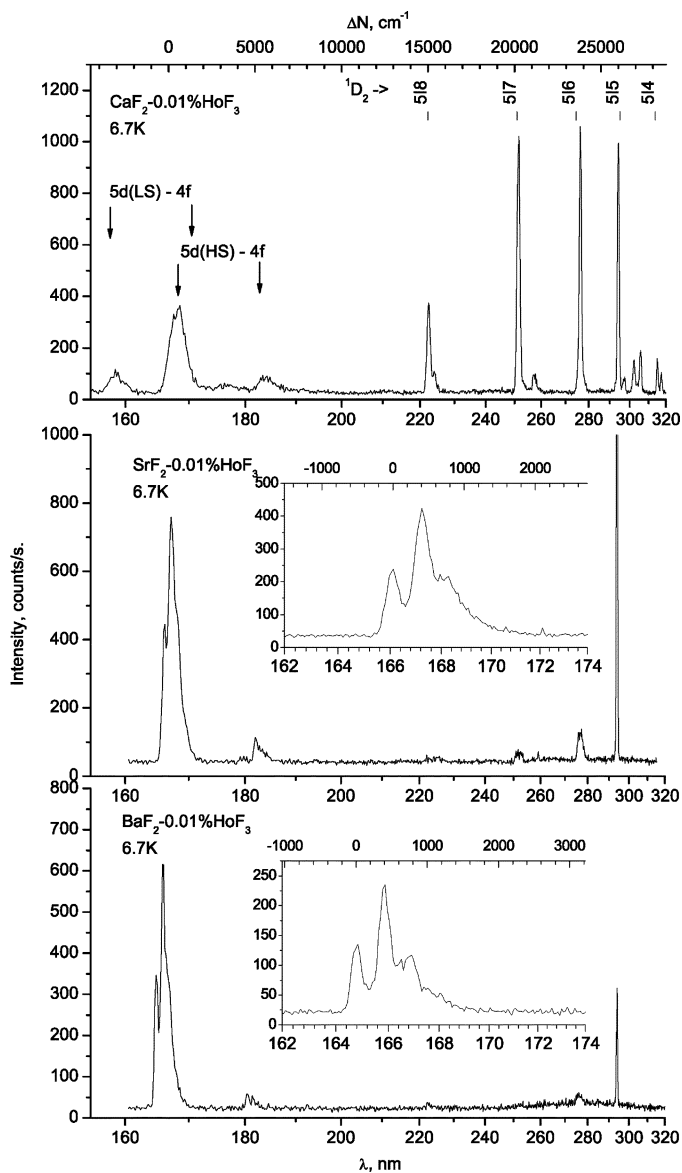


Fig. 3. Emission spectra of CaF_2 , SrF_2 , BaF_2 crystals doped with 0.01 molar % of HoF_3 under 147 nm Xe-lamp excitation at 6.7 K. Sharp lines at 294 nm is due to second order of scattered exciting line at 147 nm.

The splitting of the $5d-{}^6F_j$ transitions are twice less than that of $5d-{}^6H_j$ transitions and correspondingly no structure was observed for it (see Fig. 2).

C. Ho^{3+} Emission

Emission spectra of Ho^{3+} show several bands below 200 nm and many sharp bands above 200 nm (see Fig. 3). The positions of the bands below 200 nm shift to the lower wavelength in a row from CaF_2 to BaF_2 , while the positions of the bands above 200 nm remain the same in all lattices. It is known that the outer 5d levels of rare-earth ions substantially influenced by surrounding lattice ions while the inner 4f levels only slightly depend on surroundings. Therefore one can undoubtedly conclude that the emission bands below 200 nm are due to the 5d-4f transitions while the bands above 200 nm belong to the 4f-4f transitions.

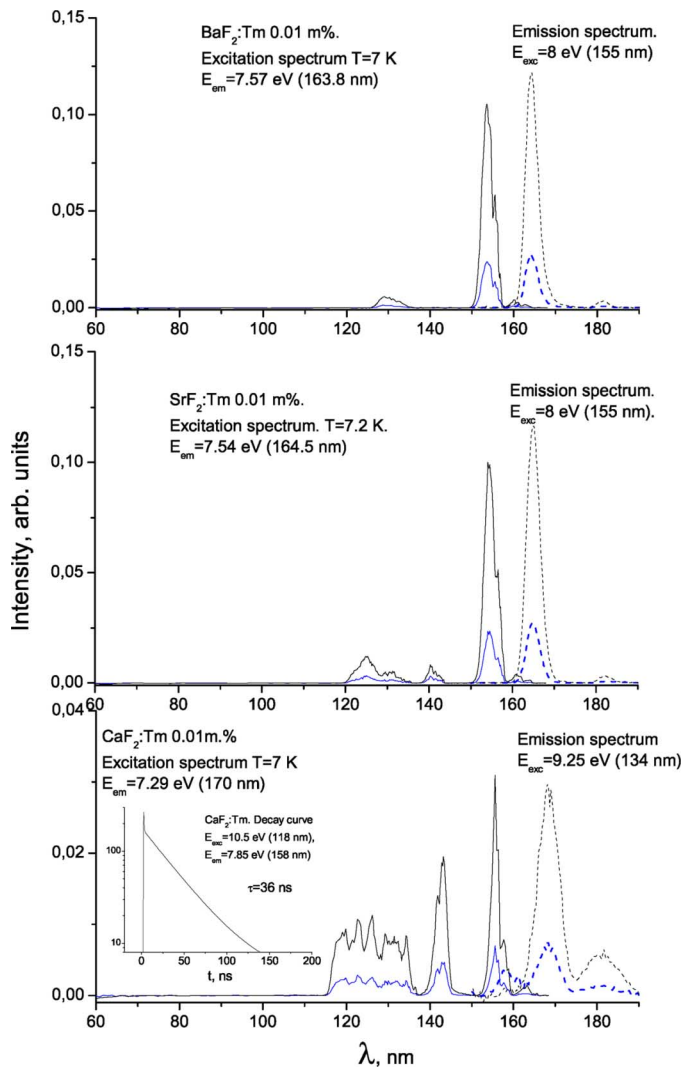


Fig. 4. Excitation and emission spectra of Tm^{3+} emission in CaF_2 , SrF_2 , BaF_2 crystals. Higher intensity curves were measured with long time window (60–100 ns) while lower intensity curves—with short time window (2–10 ns). Inset show decay curves of Tm emission measured at 158 nm.

The 5d-4f emission bands was relatively weak in CaF_2 while they become more intensive in SrF_2 and BaF_2 . Besides the intensity of the 4f-4f emission bands decreases drastically from CaF_2 to SrF_2 , BaF_2 (see Fig. 3). Two Ho^{3+} 5d-4f bands at 165 and 181 nm in BaF_2 , SrF_2 evidently belong to transitions to the 5I_8 ground state and to the 5I_7 first excited state of the $4f^{10}$ configuration. Emission spectrum in CaF_2 is a combination of the 5d(LS)-4f and 5d(HS)-4f bands (see Fig. 3).

D. Tm^{3+} Emission

Time-resolved excitation and emission spectra (Fig. 4) show that a slow emission prevails in all bands. Only the 158 nm emission in CaF_2 -Tm shows a fast decay time (36 ns at 7K). No fast decay bands were observed in BaF_2 and SrF_2 (see Fig. 4). Therefore the 158 nm band belongs to an allowed transition from the 5d low-spin level, while the other intensive bands belong to a spin-forbidden transition from the 5d high-spin level.

The 5d-4f emission of Tm^{3+} was excited only in the photon energy region below the exciton bands. No vacuum ultraviolet

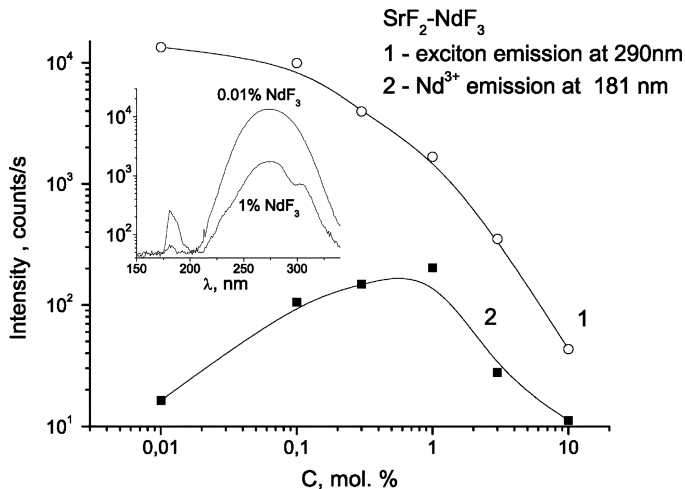


Fig. 5. Emission intensity of $\text{SrF}_2\text{-NdF}_3$ crystals at maxima of exciton band (1) and Nd band (2) with x-ray excitation at room temperature. Inset shows emission spectra of SrF_2 doped with 0.01 mol.% and 1 mol.% of NdF_3 .

5d-4f emission of Tm^{3+} was observed under excitation from 127 nm (10 eV) in BaF_2 , 120 nm (10.5 eV) in SrF_2 and 115 nm (11 eV) in CaF_2 down to 60 nm (20 eV) (see Fig. 4).

E. Scintillation Efficiency

Emission spectra of Nd and Er doped alkaline-earth fluoride crystals under x-ray excitation were studied with concentration of impurity from 0.01 to 10 molar %. The integrated intensity of rare-earth ion emission was compared with that of the exciton emission, which is known to reach 10000 ph/MeV [11]. The most intensive emission of Nd^{3+} and Er^{3+} was observed in the SrF_2 crystals (Fig. 5). The Nd^{3+} emission near 190 nm in BaF_2 is well overlapped with more intensive 196 nm band of crossluminescence and could not be correctly determined. For the Nd^{3+} and Er^{3+} 5d-4f emissions in SrF_2 the light yields were estimated as 30–40 ph/MeV. Light outputs for other rare earth ions was lower. These value are very small for the scintillator applications.

IV. DISCUSSION

The zero-phonon lines of the Ho^{3+} 4f-5d absorption and excitation lines were observed first in CaF_2 at 157.1 nm [18] and 157.5 nm [19], respectively. No spin-forbidden transitions were observed in the excitation spectrum, possibly due to the low Ho^{3+} concentration [19]. To find the spin-forbidden bands we have measured excitation spectra for the integrated emission of all f-f bands within the 220–800 nm wavelength range of all three hosts with concentration of HoF_3 from 0.01 to 0.3 molar %. The spectra were measured at room temperature because the f-f emission under f-d excitation substantially decreases with decreasing temperature. New excitation bands were found on the long wavelength side of the first $4f^{10}\text{-}5d^14f^9$ bands with separation near 9 nm in all the hosts studied. The bands were weak in the samples with 0.01% of HoF_3 , but were evident in the samples containing 0.3% of HoF_3 . Evidently these excitation bands belong to the transitions to the high-spin $5d^14f^9$ states. The energy gaps between the Ho^{3+} $5d^14f^9$ (HS) and $5d^14f^9$ (LS) states

is near 3500 cm^{-1} for all CaF_2 , SrF_2 , BaF_2 hosts, which is close to that observed in $\text{LiYF}_4\text{-Ho}$ (3460 cm^{-1}) [20]. We conclude that the emission band near 158 nm in $\text{CaF}_2\text{-Ho}$ belongs to the spin-allowed transitions from $5d^14f^9$ (LS) and the most intensive emission band near 169 nm belongs to the spin-forbidden transitions from $5d^14f^9$ (HS) to the ground state (see Fig. 3). Energy splittings between the $5d^14f^9$ (HS) and $5d^14f^9$ (LS) emission and excitation bands in $\text{CaF}_2\text{-Ho}$ are the same. No spin-allowed transitions were observed in the $\text{SrF}_2\text{-Ho}$ or $\text{BaF}_2\text{-Ho}$ crystals (see Fig. 3).

In previous paper several emission bands in 150–220 nm region of alkaline-earth fluoride doped with Tm were observed and assigned to transition from $4f^{11}5d^1$ to $4f^{12}$ (3H_j , 3F_j) [12]. Weak emission near 160 nm were observed in $\text{CaF}_2\text{-Tm}$ [12]. In this paper we have measured the fast decay of this 160 nm emission band and slow decay of all other emission bands (see Fig. 4). It follows that the band near 160 nm belongs to allowed 5d-4f transitions from low spin 5d level, and the bands near 168 and 180 nm belong to spin forbidden transition from high spin 5d level.

The intensity of the 5d-4f vacuum ultraviolet emission of Nd^{3+} and Er^{3+} ions under x-ray excitation was maximal at concentration level 0.3–1%. However, this intensity becomes by one or two orders of magnitude smaller than the intensity of the exciton emission in undoped crystals. Therefore one can conclude that the mechanisms of energy transfer to 5d states of Nd^{3+} , Tm^{3+} and Er^{3+} via excitons or electron-hole recombinations at impurity sites is not effective in alkaline-earth fluorides. Excitonic and consecutive electron-hole (or hole-electron) transfer mechanisms are the most efficient ones in scintillating crystals [14], [16]. In alkaline-earth fluorides, only the Ce ions could be excited by the exciton emission. For the Pr ions the electron-hole mechanism proves to be valid in alkaline-earth fluorides [17], [15]. However, the Nd and Tm 5d-4f emission excited by x-ray or band-to-band vacuum ultraviolet light was very weak (see Figs. 1, 4). It follows that the energy of electron-holes recombinations are enough for 4f-5d excitation of Pr^{3+} and not enough for excitation of Nd^{3+} , Tm^{3+} .

V. CONCLUSION

The 5d-4f emission of Ho^{3+} and Sm^{3+} was found in alkaline-earth fluorides. The main features of emission spectra can be satisfactorily explained by the transitions from the lowest energy d level to various terms of the 4f state. The highest-energy emission band at 158 nm in $\text{CaF}_2\text{-Ho}^{3+}$ was assigned to the allowed transitions from the low-spin state. The transitions to the high-spin state was observed as weak excitation bands in all $\text{MeF}_2\text{-Ho}$ crystals.

The emission band near 160 nm with 36 ns decay time, observed in $\text{CaF}_2\text{-Tm}$, belongs to allowed transitions from the 5d low-spin level, while the other bands near 167 nm and 180 nm of alkaline-earth fluorides doped with Tm belong to a spin-forbidden transitions from the 5d high-spin level.

The absence of the excitation of the 5d-4f emission of Nd and Tm in CaF_2 , SrF_2 , BaF_2 crystals as well as the weak light output of the 5d-4f scintillation of rare-earth ions indicate the inefficiency of the electron-hole transfer mechanism.

ACKNOWLEDGMENT

The authors are grateful to V. Ivashchkin and V. Kozlovskii for the growth of studied crystals.

REFERENCES

- [1] V. N. Makhov *et al.*, "VUV spectroscopy of wide band-gap crystals doped with rare earth ions," *Nucl. Instrum. Methods Phys. Res. A*, vol. 470, pp. 290–294, 2001.
- [2] R. T. Wegh and A. Meijerink, "Spin-allowed and spin-forbidden $4f^n-4f^{n-1}5d$ transitions for heavy lanthanides in uoride hosts," *Phys. Rev. B*, vol. 60, pp. 10820–10830, 1999.
- [3] G. Stryganyuk and G. Zimmerer, " RE^{3+} VUV d-f luminescence investigated by synchrotron radiation excitation at HASYLAB," *Phys. Solid State*, vol. 50, pp. 1631–1638, 2008.
- [4] P. Dorenbos, "Absolute location of lanthanide energy levels and the performance of phosphors," *J. Lumin.*, vol. 122–123, pp. 315–317, 2007.
- [5] P. A. Rodnyi, "Progress in fast scintillators," *Radiat. Meas.*, vol. 33, pp. 605–614, 2001.
- [6] M. Kirm, G. Stryganyuk, S. Vielhauer, G. Zimmerer, V. N. Makhov, B. Z. Malkin, O. V. Solovyev, R. Yu. Abdulsabirov, and S. L. Korableva, "Vacuum-ultraviolet 5d-4f luminescence of Gd^{3+} and Lu^{3+} ions in fluoride matrices," *Phys. Rev. B*, vol. 75, pp. 075111-1–075111-13, 2007.
- [7] K. H. Yang and J. A. DeLuca, "Vacuum ultraviolet excitation studies of $5d^14f^{n-1}$ to $4f^n$ and $4f^n$ to $4f^n$ transitions of Nd^{3+} , Er^{3+} and Tm^{3+} -doped trifluorides," *Phys. Rev. B*, vol. 17, pp. 4246–4255, 1978.
- [8] P. S. Peijzel, R. T. Wegh, A. Meijerink, and J. R.-J. Lamminma, "High energy levels and high-energetic emissions of the trivalent holmium ion in LiYF_4 and YF_3 ," *Opt. Commun.*, vol. 204, pp. 195–202, 2002.
- [9] E. Sarantopoulou, Z. Kollia, and A. C. Cefalas, " $4f^{9,5}d-4f^{10}$ spin-allowed and spin-forbidden transitions of Ho^{3+} ions in LiYF_4 single crystals in the vacuum ultraviolet," *Opti. Commun.*, vol. 169, pp. 263–274, 1999.
- [10] E. Sarantopoulou, Z. Kollia, A. C. Cefalas, V. V. Semashko, R. Y. Abdulsabirov, A. K. Naumov, and S. L. Korableva, "On the VUV and UV $4f^{7,5}d-4f^8$ interconfigurational transitions of Tb^{3+} ions in LiLuF_4 single crystal hosts," *Opt. Commun.*, vol. 156, pp. 101–111, 1998.
- [11] S. Derenzo *et al.* [Online]. Available: <http://scintillator.lbl.gov>
- [12] E. A. Radzhabov and E. A. Prosekina, "5d-4f luminescence of Nd^{3+} , Gd^{3+} , Er^{3+} , Tm^{3+} , and Ho^{3+} ions in crystals of alkaline earth fluorides," *Opt. Spectrosc.*, vol. 111, pp. 397–402, 2011, (in russian *Optica i Spektroskopiya* vol. 111, pp. 419–424, 2011).
- [13] M. Kirm, A. Lushchik, Ch. Lushchik, A. I. Nepomnyashikh, and F. Savikhin, "Dependence of the efficiency of various emissions on excitation density in BaF_2 crystals," *Radiat. Meas.*, vol. 33, pp. 515–519, 2001.
- [14] P. Dorenbos, "Systematic behaviour in trivalent lanthanide charge transfer energies," *J. Phys. Condens. Matt.*, vol. 15, pp. 8417–8434, 2003.
- [15] E. Radzhabov and V. Nagirnyi, "Excitation of Pr^{3+} ions in alkaline-earth uorides," in *Proc. IOP Conf. Series, Materials Science and Engineering*, 2010, vol. 15, pp. 012029-1–012029-7.
- [16] P. A. Rodnyi, I. V. Khodyuk, and G. B. Stryganyuk, "Location of the energy levels of the rare-earth ions in BaF_2 and CdF_2 ," *Phys. Solid State*, vol. 50, pp. 1639–1643, 2008.
- [17] R. Shendrik and E. Radzhabov, "Energy transfer mechanism in Pr-doped alkaline-earth fluorides," *IEEE Trans. Nucl. Sci.*, submitted for publication.
- [18] T. Szszyrek and M. Schlesinger, B. Jezowska-Trzebiatowska, J. Legendziewicz, and W. Streck, Eds., "Vacuum ultraviolet absorption spectra of $\text{CaF}_2:\text{Re}^{3+}$ crystals," in *Proc. Int. Symp. Rare Earths Spectroscopy*, Wroclaw, Poland, Sep. 10–15, 1984, World Scientific, Singapore, 1985, pp. 309–330.
- [19] L. van Pieterse, M. F. Reid, R. T. Wegh, G. W. Burdick, and A. Meijerink, " $4f^n-4f^{n-1}5d$ transitions of the heavy lanthanides: Experiment and theory," *Phys. Rev. B*, vol. 65, pp. 045114-1–045114-23, 2002.
- [20] B. Henderson and G. F. Imbush, *Optical Spectroscopy of Inorganic Solids*. Oxford, U.K.: Clarendon, 1989.