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## Radiation Measurements

journal homepage: [www.elsevier.com/locate/radmeas](http://www.elsevier.com/locate/radmeas)Vacuum ultraviolet  $5d^14f^9-4f^{10}$  emission of  $\text{Ho}^{3+}$  ions in alkaline-earth fluoridesE.A. Radzhabov<sup>a,b,\*</sup>, V. Nagirnyi<sup>c</sup>, A.I. Nepomnyashchikh<sup>a,b</sup><sup>a</sup> Vinogradov Institute of Geochemistry, Russian Academy of Sciences, Favorskii Street 1a, P.O. Box 4019, 664033 Irkutsk, Russia<sup>b</sup> Irkutsk State University, Physics Department, Gagarin Boulevard 20, 664003 Irkutsk, Russia<sup>c</sup> Institute of Physics, University of Tartu, Riia 142, 51014 Tartu, Estonia

## HIGHLIGHTS

- ▶ Time-resolved spectra of  $\text{Ho}^{3+}$  in  $\text{CaF}_2$ ,  $\text{SrF}_2$ ,  $\text{BaF}_2$  were studied in vacuum ultraviolet.
- ▶ Emission bands near 168 nm of  $\text{Ho}^{3+}$  ions are caused by the spin-forbidden transitions.
- ▶ Weak spin allowed  $5d^14f^9-4f^{10}$  emission band at 158 nm was observed only in  $\text{CaF}_2\text{-Ho}$ .
- ▶ Fast component of spin-forbidden emissions is due to multiphonon relaxation to  $4f^{10}$  level.

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## ABSTRACT

Time-resolved emission and excitation spectra as well as emission decay kinetics of  $\text{CaF}_2$ ,  $\text{SrF}_2$ ,  $\text{BaF}_2$  doped with  $\text{HoF}_3$  were investigated. Intensive emission bands near 168 nm, having long decay time, are caused by the spin-forbidden transitions from the  $5d^14f^9$  high-spin states to the ground  $^5I_8$  states of  $\text{Ho}^{3+}$  ions. Weak spin allowed  $5d^14f^9(\text{low-spin})-4f^{10}$  emission band at 158 nm was observed only in  $\text{CaF}_2\text{-Ho}$  crystals. Spin allowed and spin-forbidden excitation bands were observed near 166 and 155 nm, respectively, in all studied crystals. Fast component of spin-forbidden emissions due to multiphonon relaxation to low-lying  $4f^{10}$   $\text{Ho}^{3+}$  level also was observed for all crystals.

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## 1. Introduction

The f-d transitions of rare-earth ions doped into wide gap crystals belong to a relatively little explored field of optical spectroscopy (Makhov et al., 2001). The spectroscopic investigation of the  $4f^n-5d^14f^{n-1}$  transitions of rare-earth ions (hereafter simply 4f-5d) in the vacuum ultraviolet region could help in search new scintillators or new ultraviolet laser materials.

Weak emissions were observed for  $\text{Ho}^{3+}$  at 158 nm in  $\text{YF}_3$  and at 167 nm in  $\text{LiYF}_4$  excited at 130 nm (Peijzel et al., 2002). These emissions were attributed to the  $\text{Ho}^{3+}$  spin-forbidden transitions from  $4f^95d$  to the ground state (Peijzel et al., 2002). The emission spectrum of the  $\text{LiYF}_4:\text{Ho}^{3+}$  crystal excited by a  $\text{F}_2$  laser at 157 nm

shows several bands in the region of 157.6–190 nm. The fluorescence peaks were assigned to the spin-allowed and spin-forbidden transitions between the levels of the  $4f^95d$  high-spin (HS),  $4f^95d$  low-spin (LS) and  $4f^{10}$  electronic configurations of the  $\text{Ho}^{3+}$  ion (Sarantopoulou et al., 1999). The vacuum ultraviolet emissions of alkaline-earth fluorides doped by different rare-earth ions including  $\text{Ho}^{3+}$ , excited with a continuous discharge lamp were shortly presented in our previous papers (Radzhabov and Prosekina, 2011; Radzhabov et al., 2012).

The main topic of the present paper is to study the  $\text{Ho}^{3+}$  ultraviolet and vacuum ultraviolet emission using time-resolved spectroscopy in  $\text{CaF}_2$ ,  $\text{SrF}_2$ ,  $\text{BaF}_2$  with concentration of  $\text{HoF}_3$  dopants ranging from 0.01 to 0.3 M%.

## 2. Experimental

Crystals were grown in vacuum in a graphite crucible by the Stockbarger method (Radzhabov et al., 2012). The graphite crucible

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contained three cylindrical cavities 10 mm in diameter and 80 mm long, which allowed growing three crystals of  $\text{O}10 \times 50$  mm dimensions with different impurity concentrations at the same time. The samples  $\text{O}10 \text{ mm} \times 1 \text{ mm}$  cut from the grown rods were typically used for optical measurements.

Time-resolved spectra and decay curves were recorded using synchrotron radiation at the SUPERLUMI station of HASYLAB at DESY (Hamburg, Germany) as described in paper (Kirm et al., 2001). The measurements were performed in a short time window (1–5 ns), in a long time window (55–80 ns), and in a time-integrated regime.

Additionally absorption and excitation spectra were measured using a grating monochromator VM4 (LOMO) under excitation deuterium lamp L7293-50 with a  $\text{MgF}_2$  window and a solar-blind photomultiplier FEU142 as a light detector.

### 3. Results

The absorption spectra of the  $\text{Ho}^{3+}$  ion show several bands below 160 nm in all three crystals (Fig. 1). All bands are shifted by few nm toward shorter wavelengths in the row from  $\text{CaF}_2$  to  $\text{BaF}_2$ . The shift of the absorption 4f-5d and emission 5d-4f bands in the row from  $\text{CaF}_2$  to  $\text{BaF}_2$  is known also for other rare-earth ions. It is due to the decrease of a crystal field splitting of the 5d levels (Radzhabov and Nepomnyashchikh, 2008).

Two 5d-4f emission bands at 167–169 and 180–183 nm were observed with intensity ratio of near 10:1 (Figs. 2–4). The bands were assigned to the transitions from the 5d lowest energy level to the  $^5I_8$  and  $^5I_7$  levels of the 4f shell. The main excitation bands 155, 146, 138 and 130 nm shown in Figs. 2–4 are in good correlation with the observed absorption bands (Fig. 1). In the case of  $\text{BaF}_2$  two high energy  $\text{Ho}^{3+}$  absorption bands is hidden by exciton wing (see Fig. 1). Both emission bands contain slow and fast decay components. The decay time of fast component increased by an order of magnitude in row from  $\text{CaF}_2$  to  $\text{BaF}_2$ . It was equal to 4.2, 15.7 and 50 ns in  $\text{CaF}_2$ ,  $\text{SrF}_2$ , and  $\text{BaF}_2$ , respectively, under excitation into lowest energy band near 155 nm (Fig. 5) and became a few ns longer under excitation into the 146 nm band.

The 5d-4f emission bands are relatively weak in  $\text{CaF}_2$  while they become more intensive in  $\text{SrF}_2$  and  $\text{BaF}_2$ . On the contrary the

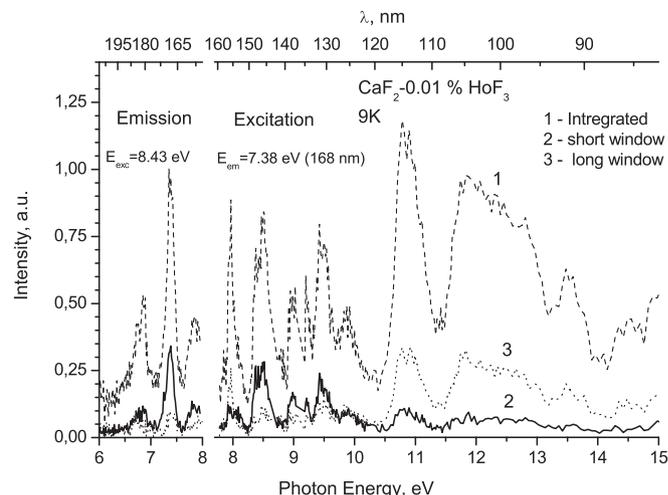


Fig. 2. Emission and excitation spectra of  $\text{Ho}^{3+}$  5d-4f transitions in  $\text{CaF}_2$  crystals doped with 0.01 M% of  $\text{HoF}_3$  at 9 K. The emission spectra were taken with 8.43 eV (147 nm) excitation light, the excitation spectra were taken for 7.38 eV (168 nm) emission.

intensity of the 4f-4f emission bands decreases drastically from  $\text{CaF}_2$  to  $\text{SrF}_2$ ,  $\text{BaF}_2$ . The two main 5d-4f  $\text{Ho}^{3+}$  bands of  $\text{CaF}_2$ ,  $\text{SrF}_2$  and  $\text{BaF}_2$  evidently belong to the transitions to the  $^5I_8$  ground state and to the  $^5I_7$  first excited state of the  $4f^{10}$  configuration. Long decay times of these emissions points that they are spin-forbidden transitions from high-spin 5d state to low-spin ground state. Additional band at 158 nm with fast decay was observed in  $\text{CaF}_2$  (see Fig. 2). This emission band belongs to the spin-allowed transitions from low spin 5d (LS) states (see also (Radzhabov et al., 2012)).

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  $\text{HoF}_3$  from 0.01 to 0.3 M% (Fig. 6). The spectra were measured at room temperature because the efficiency of the f-f emission under f-d excitation substantially decreased with decreasing temperature. New weak excitation bands were found in all hosts at long-

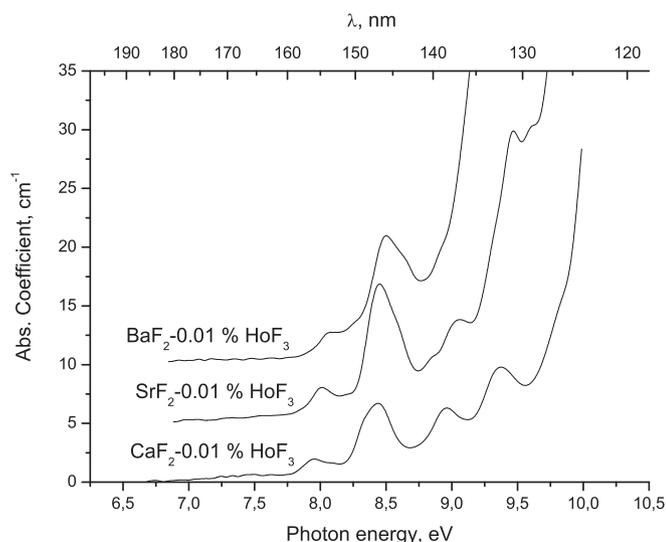


Fig. 1. Absorption spectra of  $\text{Ho}^{3+}$  5d-4f transitions in  $\text{CaF}_2$ ,  $\text{SrF}_2$ ,  $\text{BaF}_2$  crystals doped with 0.01 M% of  $\text{HoF}_3$  at 295 K. Spectra were separated by  $5 \text{ cm}^{-1}$  for better viewing.

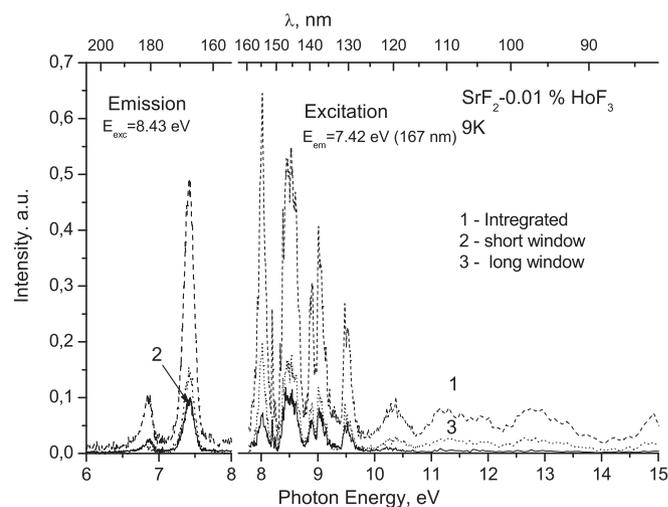
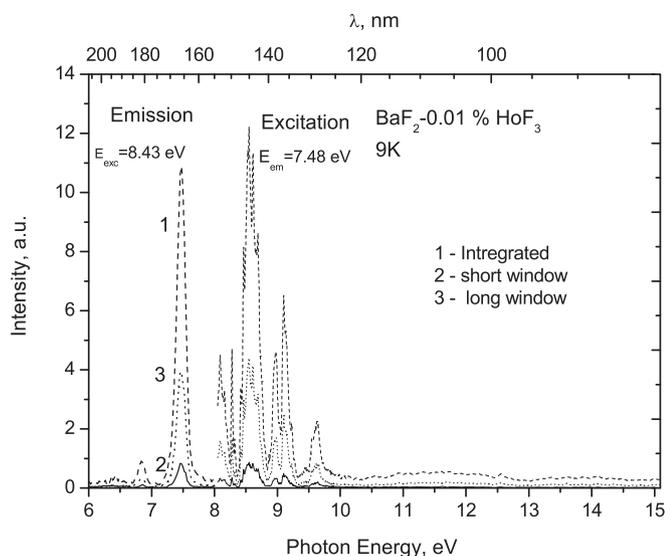
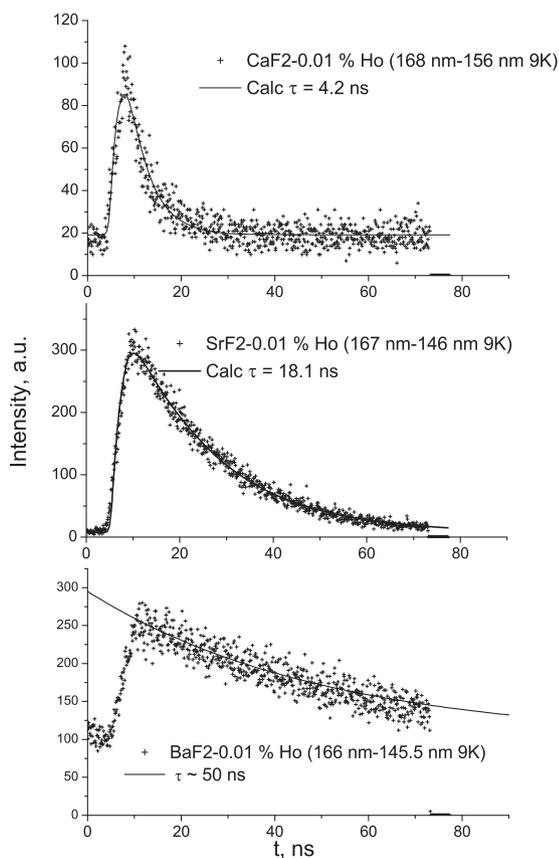


Fig. 3. Emission and excitation spectra of  $\text{Ho}^{3+}$  5d-4f transitions in  $\text{SrF}_2$  crystals doped with 0.01 M% of  $\text{HoF}_3$  at 9 K. The emission spectra were taken with 8.43 eV (147 nm) excitation light, the excitation spectra were taken for 7.42 eV (167 nm) emission.

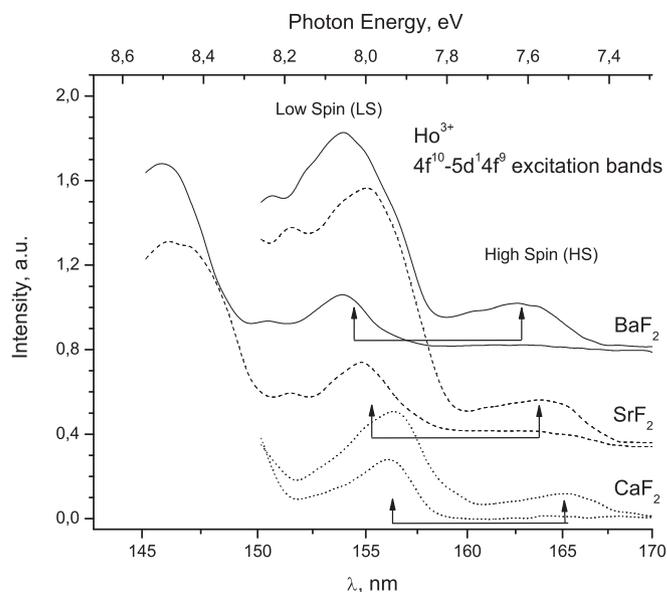


**Fig. 4.** Emission and excitation spectra of  $\text{Ho}^{3+}$  5d-4f transitions in  $\text{BaF}_2$  crystals doped with 0.01 M% of  $\text{HoF}_3$  at 9 K. The emission spectra were taken with 8.43 eV (147 nm) excitation light, the excitation spectra were taken for 7.48 eV (165.8 nm) emission.

wavelength of the first 4f-4f5d bands with separation near 9 nm (see Fig. 6). These weak bands were questionable in the samples with 0.01% of Ho, but were evident in the samples containing 0.3% of  $\text{HoF}_3$  (see Fig. 6).



**Fig. 5.** Decay of  $\text{Ho}^{3+}$  emission bands near 167 nm in  $\text{BaF}_2$ ,  $\text{SrF}_2$ ,  $\text{CaF}_2$  crystals doped with 0.01 M% of  $\text{HoF}_3$  at 9 K. The emission and excitation wavelengths are shown on the plot.



**Fig. 6.** Excitation spectra of  $\text{Ho}^{3+}$  5d-4f transitions in  $\text{CaF}_2$ ,  $\text{SrF}_2$ ,  $\text{BaF}_2$  crystals doped with 0.01 M% of  $\text{HoF}_3$  (lower curves) and by 0.3 M% of  $\text{HoF}_3$  at 295 K. Spectra were separated for best viewing. Splitting of first excitation bands by transitions to low spin and high spin  $5d^4f^9$  states shown by arrows. Excitation spectra were measured for the integrated emission of all f-f bands within the 220–800 nm wavelength range.

#### 4. Discussion

The zero-phonon  $\text{Ho}^{3+}$  4f-5d absorption and excitation lines were observed in  $\text{CaF}_2$  at 157.1 nm (Szszyurek and Schlesinger, 1985) and 157.5 nm (Pieterse et al., 2002), respectively. No spin-forbidden transitions were observed in the excitation spectrum, possibly due to the low  $\text{Ho}^{3+}$  concentration (Pieterse et al., 2002). Weak excitation bands near 164 nm (see Fig. 6) are attributed to transitions to the high-spin 5d4f states. The energy gaps between the  $\text{Ho}^{3+}$  4f5d(HS) and 4f5d(LS) states is near  $3500 \text{ cm}^{-1}$  for all  $\text{CaF}_2$ ,  $\text{SrF}_2$ ,  $\text{BaF}_2$  hosts, which is close to that observed in  $\text{LiYF}_4\text{-Ho}$  ( $3460 \text{ cm}^{-1}$ ) (Pieterse et al., 2001). The energy distances between 4f5d(HS) and 4f5d(LS) emission and excitation bands in  $\text{CaF}_2\text{-Ho}$  are the same (compare Figs. 2 and 6).

It is known that probability of nonradiative transfer between two f levels decreases exponentially with the energy gap between the levels (so called energy gap law) (Henderson and Imbush, 1989; Sole et al., 2005). Reformulation of this law in term of the number of effective phonons allows one to conclude that nonradiative transitions are dominant in processes involving less than 4–6 effective phonons (Henderson and Imbush, 1989). Comparison of the ultraviolet Nd emission in a number of orthoborate and orthophosphate crystals leads to the conclusion that nonradiative transition from the 5d level to the lower lying 4f level is predominant when the energy gap is less than the energy of 5 phonons (Wegh et al., 2001).

The frequencies of longitudinal optic phonons obtained from optical data at 5 K are  $484$ ,  $397$  and  $346 \text{ cm}^{-1}$  for  $\text{CaF}_2$ ,  $\text{SrF}_2$ ,  $\text{BaF}_2$ , respectively (Hayes, 1974). The highest observed  $\text{Ho}^{3+}$   $4f^{10}$  level is  $^3K_7$ , transitions to this level were observed at 170.5 nm in  $\text{LiYF}_4$  (Peijzel et al., 2002). The  $4f^9 5d^1$  (HS) excitation bands were recorded at 162.5, 164, 165 nm in  $\text{CaF}_2$ ,  $\text{SrF}_2$ ,  $\text{BaF}_2$ , respectively (see Fig. 6). Therefore the energy gap between the 5d and lower lying 4f levels are near  $2000$ ,  $2300$ ,  $2900 \text{ cm}^{-1}$  or around 4, 6, 8 phonon frequencies in  $\text{CaF}_2$ ,  $\text{SrF}_2$ ,  $\text{BaF}_2$ , respectively. Consequently, the nonradiative multiphonon energy transfer from the  $5d4f^9$ (HS) to  $4f^{10}$  ( $^3K_7$ ) level should be most efficient in  $\text{CaF}_2$  and much less efficient in  $\text{BaF}_2$ . As a result, the  $5d4f^9\text{-}4f^{10}$  band increases and the  $4f^{10}\text{-}4f^{10}$  bands remarkably decreases in the row from  $\text{CaF}_2$  to  $\text{BaF}_2$ .

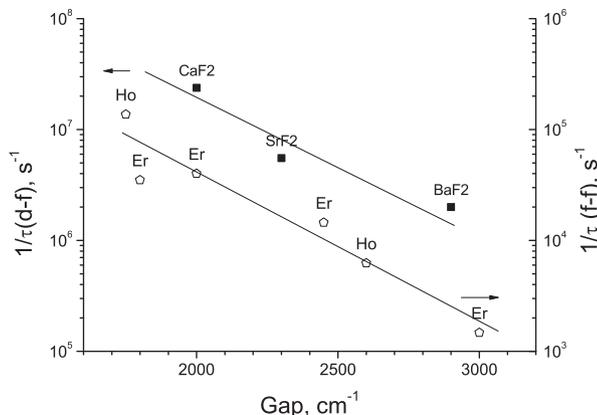


Fig. 7. Energy-gap dependence of the multiphonon transition rate for f-f transition in SrF<sub>2</sub>-RE taken from Riseberg and Moos (1968) and for d-f transition of Ho<sup>3+</sup> in alkaline-earth fluorides.

The fast decay components of the spin-forbidden bands obviously should be assigned to the multiphonon transitions from 5d to 4f<sup>10</sup>. In accordance with the increase in the energy gap the fast decay time becomes drastically longer in the row of CaF<sub>2</sub>, SrF<sub>2</sub>, BaF<sub>2</sub> (see Fig. 5). The nonradiative relaxation rate decreases with decreasing temperature, as the number of phonons reduces (Henderson and Imbush, 1989). Therefore, the intensity of Ho<sup>3+</sup> f-f lines becomes several times smaller from 78 to 6.7 K under f-d excitation (Radzhabov et al., 2012). The variations of 5d-4f and 4f-4f intensity and decay times under 4f-5d excitation could be described in terms of nonradiative multiphonon energy transfer from lowest high spin 5d level to the low-lying 4f<sup>10</sup>(<sup>3</sup>K<sub>7</sub>) level.

The dependence of the multiphonon relaxation probability on the energy gap, disregarding any selection rules, is of the form:

$$k_{NR} = \beta e^{-\alpha \Delta E}$$

where  $\beta$  and  $\alpha$  are constants, which are characteristic of a particular crystal and  $\Delta E$  is the electronic energy “gap” between the 4f levels (van Dijk and Schuurmans, 1983). However,  $\beta$  varies by a factor of 10<sup>5</sup>. This wide variation is due to a considerable dependence of  $\beta$  on the vibrational coupling to the host lattice (van Dijk and Schuurmans, 1983). While there are numbers of papers dealing with the measurements of multiphonon f-f relaxation, no such measurements have been made to our knowledge for the d-f relaxation.

The inverse decay times of the fast components of the spin-forbidden 5d<sup>1</sup>4f<sup>9</sup>-5I<sub>8</sub> bands near 168 nm versus the energy gap between the 5d and nearest 4f levels are plotted in Fig. 7. Three hosts CaF<sub>2</sub>, SrF<sub>2</sub>, BaF<sub>2</sub> have the same crystal structure and slightly differ in anion-cation distances. Therefore, in the first approximation, the data for the d-f multiphonon relaxation in three alkaline earth fluorides could be compared to those for the f-f relaxation in SrF<sub>2</sub>, which we took from the paper (Riseberg and Moos, 1968). Note that the slope  $\alpha$  for both dependencies is nearly the same while the constant  $\beta$  is about three orders of magnitude larger for the d-f multiphonon relaxation (see Fig. 7). The constant  $\beta$  reflects the interaction of orbitals with phonons. Therefore it is not surprising that constant  $\beta$  is much larger for d-f relaxation than for f-f multiphonon relaxation, because the d-orbital has much greater overlap with orbital of surrounding host ions.

## 5. Conclusion

The 5d<sup>1</sup>4f<sup>9</sup>-4f<sup>10</sup> emission of Ho<sup>3+</sup> in ions in vacuum ultraviolet was found in CaF<sub>2</sub>, SrF<sub>2</sub>, BaF<sub>2</sub> crystals. Two bands were observed: the strongest bands at 166–168 nm and weaker ones at 182–184 nm. The bands are associated with the spin forbidden transition from 5d<sup>1</sup>4f<sup>9</sup> to <sup>5</sup>I<sub>8</sub>, <sup>5</sup>I<sub>7</sub> levels of 4f<sup>10</sup> shell, respectively. The weaker spin-allowed 5d<sup>1</sup>4f<sup>9</sup>-<sup>5</sup>I<sub>8</sub> band at 158 nm is observed in CaF<sub>2</sub> only. The decrease of the total intensity of the f-f bands compared to that of the d-f bands as well as the increase of the fast decay times of spin-forbidden emission in the row from CaF<sub>2</sub> to BaF<sub>2</sub> is observed. It is caused by the increasing number of phonons in the process of nonradiative multiphonon energy transfer from the lowest 5d to the nearest 4f<sup>10</sup> excited level.

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