

PROCEEDINGS OF THE XII FEOFILOV WORKSHOP  
“SPECTROSCOPY OF CRYSTALS ACTIVATED  
BY RARE-EARTH AND TRANSITION-METAL IONS”

(Yekaterinburg, Russia, September 22–25, 2004)

## Low-Temperature Time-Resolved VUV Luminescence Spectroscopy of $\text{SrF}_2 : \text{Er}^{3+}$ Crystals

K. V. Ivanovskikh\*, V. A. Pustovarov\*, B. V. Shul'gin\*, and M. Kirm\*\*

\*Ural State Technical University, ul. Mira 19, Yekaterinburg, 620002 Russia

e-mail: ikv@dpt.ustu.ru

\*\*Institute of Physics, Tartu University, Riia 142, Tartu, 51014 Estonia

**Abstract**—Time-resolved excitation and emission spectra of  $\text{SrF}_2 : \text{Er}^{3+}$  upon selective excitation with synchrotron radiation in the VUV and ultrasoft x-ray ranges at  $T = 8$  K were studied. The VUV luminescence of  $\text{SrF}_2 : \text{Er}^{3+}$  derives from high-energy interconfiguration  $4f^{10}5d-4f^{11}$  transitions in the  $\text{Er}^{3+}$  ion. The VUV emission spectrum revealed, in addition to the 164.5-nm band (millisecond-range kinetics), a band at 146.4 nm (with a decay time of less than 600 ps). The formation of excitation spectra for the  $f-f$  and  $f-d$  transitions in the  $\text{Er}^{3+}$  ion is discussed. © 2005 Pleiades Publishing, Inc.

### 1. INTRODUCTION

$\text{SrF}_2$  crystals doped with rare-earth (RE) elements have long been known to be promising scintillators [1]. Present studies of RE-doped crystals pay particular attention to VUV spectroscopy, primarily because of the growing need to develop a new class of fast VUV scintillators and VUV phosphors for plasma display panels and mercury-free fluorescent lamps, as well as solid-state VUV lasers [2–4].

These considerations have motivated our study of low-temperature time-resolved excitation spectra of  $\text{Er}^{3+}$  luminescence in  $\text{SrF}_2 : \text{Er}^{3+}$  in the range 4–25 eV (50–309 nm), as well as of VUV luminescence in the 7–9-eV region (138–175 nm). By properly varying the excitation, we succeeded in detecting a new luminescence band at 146 nm with fast decay kinetics in addition to the previously known 164.5-nm band [5, 6].

### 2. SAMPLES AND EXPERIMENTAL TECHNIQUES

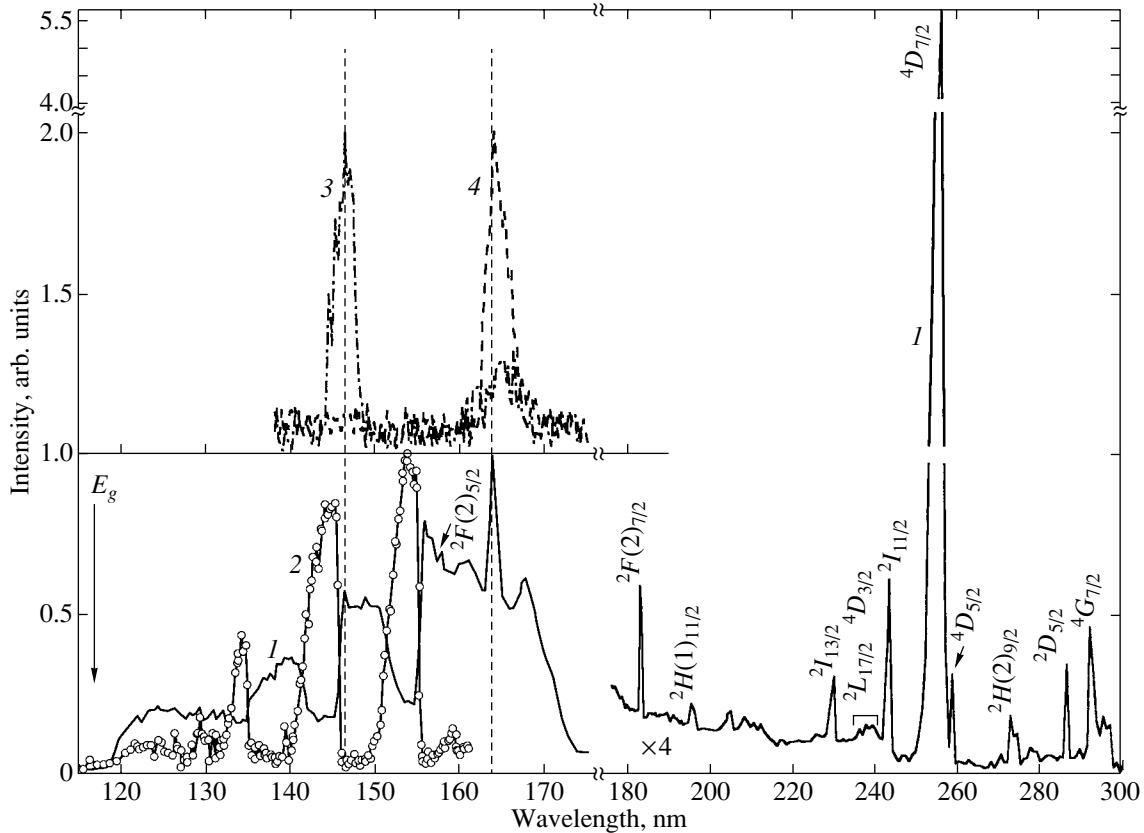
$\text{SrF}_2 : 1\% \text{Er}^{3+}$  single crystals were Stockbarger-grown by K.K. Rivkina and E.G. Morozov at the Pyshma GIREDMET pilot plant.

The excitation and VUV emission spectra were measured under selective excitation by synchrotron radiation (SR) in the VUV and ultrasoft x-ray (USX) regions at the SUPERLUMI station and in the BW3 beamline at HASYLAB (DESY, Hamburg). A 2-m vacuum monochromator with a resolution of 3.2 Å was employed for excitation in the range 4–25 eV. Luminescence in the visible range was detected with a 0.3-m monochromator (ARC Spectra Pro-308i) and an R6358P PM tube (Hamamatsu). Luminescence in the

VUV region was measured with an 0.5-m vacuum monochromator and a sun-blind R6836 PM tube. Undulator radiation and a Zeiss SX700 monochromator in the BW3 beamline provided excitation in the USX region. The VUV luminescence was measured with a 0.4-m monochromator (Seya-Namioka arrangement) and a microchannel detector (MCP 1645 U-09, Hamamatsu). The excitation and emission spectra could be obtained both without time resolution (time-integrated) and in time windows  $\Delta t_1$  (fast component) and  $\Delta t_2$  (slow component) wide delayed with respect to the SR pulse by  $\delta t_1$  and  $\delta t_2$ , respectively. The excitation spectra are normalized against an equal number of photons incident on the sample with the use of sodium salicylate. The VUV emission spectra are presented without correction for spectral sensitivity of the optical channel. Measurements were conducted at  $T = 8$  K in a cryostat providing an oil-free vacuum of  $(2-5) \times 10^{-10}$  Torr.

### 3. EXPERIMENTAL RESULTS AND DISCUSSION

The main features of the excitation spectra of the 551-nm luminescence, which derives from the strongest  $f-f$  transition  $^4S_{3/2} \rightarrow ^4I_{15/2}$  in the  $\text{Er}^{3+}$  ion in a  $\text{SrF}_2 : 1\% \text{Er}^{3+}$  crystal, are seen in the region of crystal transparency and the long-wavelength fundamental absorption edge (curve 1 in figure). In the range 177–309 nm, the excitation spectrum consists of a number of narrow bands of various intensities. The  $f-f$  transition bands in the  $\text{SrF}_2 : \text{Er}^{3+}$  excitation spectrum were assigned by us in accordance with calculations and experimental data on the energy levels of the  $4f^{11}$  configuration of the  $\text{Er}^{3+}$  ion in  $\text{LiYF}_4$  [7, 8]. In the UV



PE spectra (1) of the 551-nm  $f$ - $f$  luminescence ( $4S_{3/2} \rightarrow 4I_{15/2}$ ) and (2) of the 164.5-nm  $d$ - $f$  luminescence ( $4f^{10}5d(\text{HS}) \rightarrow 4I_{15/2}$ ) measured in a slow time window ( $\delta t_2 = 0.68$  ns,  $\Delta t_2 = 103$  ns); VUV emission spectra measured in (3) a fast time window ( $\delta t_1 = 0.6$  ns,  $\Delta t_1 = 1.8$  ns) and (4) a slow time window ( $\delta t_2 = 12$  ns,  $\Delta t_2 = 19.3$  ns). SrF<sub>2</sub> : 1% Er<sup>3+</sup>,  $T = 8$  K.

region, transitions are observed to the multiplet levels  $4G_{7/2}$  (292 nm),  $2D_{5/2}$  (287 nm),  $2H(2)_{9/2}$  (273 nm),  $4D_{5/2}$  (259 nm),  $4D_{7/2}$  (256 nm),  $2I_{11/2}$  (243 nm), nonresolvable  $2L_{17/2}$  and  $4D_{3/2}$  (235–241 nm), and  $2I_{13/2}$  (230 nm). In the VUV region, distinct lines are observed corresponding to transitions to the multiplets  $2H(1)_{11/2}$  (195 nm) and  $2F(2)_{7/2}$  (183 nm). The band deriving from the transition to the  $2F(2)_{5/2}$  level and mentioned in [8] is very weakly seen at 158 nm against the background of a strong, broad, structured band extending from 155 to 173 nm. A strong narrow line at 164 nm stands out in this band. As the incident-light wavelength decreases, broad excitation bands appear in the excitation spectrum at 145–153 and 134–142 nm. At the fundamental absorption edge, the excitation intensity falls off with a sharp drop at 119 nm. At higher excitation energies, the luminescence is suppressed.

In addition to the luminescence in the visible range, Er<sup>3+</sup> ions exhibit luminescence bands in the VUV region, which are due to interconfiguration transitions both from the low-spin (LS) level ( $2S + 1 = 4$ ) (spin-allowed transitions) and from the high-spin (HS) level ( $2S + 1 = 6$ ) (spin-forbidden transitions) to the

$4f^{11}$ -configuration ground-state levels [5, 6, 9–11]. We measured low-temperature time-resolved VUV emission spectra of SrF<sub>2</sub> : Er<sup>3+</sup> in the spectral region 135–175 nm under excitation in the USX region with a photon energy of 140 eV (curves 3, 4 in the figure). In the “slow” time window, the well-known 164.3-nm band is observed; this band is produced by the  $4f^{10}5d(\text{HS}) \rightarrow 4I_{15/2}$  transition [5, 6]. In the fast time window, we succeeded in observing a band at 146.4 nm emitted in the SrF<sub>2</sub> : Er<sup>3+</sup> system. The decay time constant of this luminescence band, as derived from the convolution integral, does not exceed 600 ps.

In the slow time window, the strongest excitation bands of the  $d$ - $f$  luminescence,  $4f^{10}5d(\text{HS}) \rightarrow 4I_{15/2}$ , were observed under excitation near 154, 144, and 134 nm (curve 2 in the figure). One can also see a weak band at 159 nm, which signals the onset of excitation of  $d$ - $f$  luminescence ( $4f^{10}5d(\text{HS}) \rightarrow 4I_{15/2}$ ). Note also the presence of fairly weak bands at 129 and 139 nm in the spectrum.

An analysis of the VUV luminescence and the excitation spectra of  $d$ - $f$  and  $f$ - $f$  luminescence revealed the following features.

(1) The luminescence bands at 164.3 and 146.4 nm coincide in position with the narrow lines in the 551-nm-luminescence excitation spectra ( ${}^4S_{3/2} \rightarrow {}^4I_{15/2}$ ) observed against the background of broad intense bands.

(2) The  $d-f$  and  $f-f$  luminescence yield ( $4f^{10}5d(\text{HS}) \rightarrow {}^4I_{15/2}$  and  ${}^4S_{3/2} \rightarrow {}^4I_{15/2}$  transitions, respectively) falls off near the long-wavelength fundamental absorption edge and subsequently drops sharply when excited by photons with a wavelength of below 119 nm (this region is not shown in the figure).

(3) The difference in energy position between the maxima of the slow (at 164.3 nm;  $4f^{10}5d(\text{HS}) \rightarrow {}^4I_{15/2}$ ) and fast (at 146.4 nm)  $d-f$  luminescence is fairly large (0.91 eV).

(4) The excitation spectra of the  $4f^{10}5d(\text{HS}) \rightarrow {}^4I_{15/2}$  and  ${}^4S_{3/2} \rightarrow {}^4I_{15/2}$  luminescence follow opposite patterns in the range 126–161 nm.

(5) The difference in energy position between the beginning of the strongest broad excitation bands at 155–173 nm in the excitation spectrum of  $f-f$  luminescence and at 154 nm in the excitation spectrum of  $d-f$  luminescence in the nearest VUV region is 0.91–0.95 eV.

The opposite patterns of the excitation spectra of the  $f-f$  and  $d-f$  luminescence reflect the competitive excitation energy transfer to radiating levels of the  $4f^{10}5d$  and  $4f^{11}$  configurations, which is characteristic of the  $\text{Er}^{3+}$  ion in  $\text{SrF}_2$ .

The suppression of impurity luminescence observed to occur under excitation at the onset of interband transitions in  $\text{SrF}_2$  ( $E_g = 11.2$  eV [12]) up to 20 eV should be identified with the low efficiency of energy transfer via the electron–hole mechanism, as well as with the low involvement of excitons in energy transfer to the levels of the  $4f^{10}5d$  configuration of the  $\text{Er}^{3+}$  ion in  $\text{SrF}_2$ .

In terms of its pattern, the 159-nm band in the excitation spectrum of  $4f^{10}5d(\text{HS}) \rightarrow {}^4I_{15/2}$  luminescence can be assigned to the spin-forbidden  $f-d$  transition. According to the Hund rule, this suggests that this spectral region corresponds to the lowest energy state in the  $4f^{10}5d$  configuration of the  $\text{Er}^{3+}$  ion in  $\text{SrF}_2$  and that the strong 154-nm band indicates the onset of spin-allowed  $f-d$  transitions. If this is so, then the nature of the 155- to 173-nm structured band in the  ${}^4S_{3/2} \rightarrow {}^4I_{15/2}$  luminescence excitation spectrum remains unclear.

We estimated the Stokes shift for the low-spin excited state of the  $4f^{10}5d$  configuration of the  $\text{Er}^{3+}$  ion in  $\text{SrF}_2$  as  $1800\text{ cm}^{-1}$ . Assuming the quartet and sextet excited states to have the same Stokes shifts, one could expect the existence of a  $d-f$  band with fast decay kinetics in the range 155–158 nm associated with the spin-allowed transition from the lowest LS excited state. However, this band was not observed either in our

experiments or in the  $\text{SrF}_2 : \text{Er}^{3+}$  studied in [5, 6]. This may be accounted for by the existence of strong nonradiative cross relaxation between the LS and HS  $\text{Er}^{3+}$  levels in  $\text{SrF}_2$ , which are separated by about  $2150\text{ cm}^{-1}$ . This value is substantially smaller than, for instance, that in the  $\text{LiYF}_4$  crystal, where both  $d-f$  luminescence bands are seen and the difference is about  $3300\text{ cm}^{-1}$  [5, 6, 11]. A similar explanation was advanced in [9], where the  $\text{Er}^{3+}$   $d-f$  luminescence in  $\text{KYF}_4$  was found to follow the same pattern. This suggests that the observed fast 146.4-nm luminescence in  $\text{SrF}_2 : \text{Er}^{3+}$  should most probably be assigned to a higher lying radiating low-spin  $4f^{10}5d$  configuration. As far as we are aware, however, information on the observation of these transitions is presently lacking.

#### 4. CONCLUSIONS

The low-temperature VUV emission spectra of  $\text{SrF}_2 : 1\% \text{Er}^{3+}$  have been found to reveal, in addition to the well-known 164.5-nm band associated with the  $4f^{10}5d(\text{HS}) \rightarrow {}^4I_{15/2}$  transition, a new luminescence band at 146.4 nm ( $\tau < 600$  ps), which derives from a transition from one of the high-lying low-spin excited states of the  $4f^{10}5d$  configuration. Competitive excited-state relaxation in the  $4f^{10}5d$  configuration has been found to occur via the radiative  $d-f$  and  $f-f$  transitions. More reliable establishment of the nature of the observed fast 146.4-nm  $d-f$  luminescence and of the mechanisms governing relaxation of the excited states in the  $4f^{10}5d$  configuration of  $\text{Er}^{3+}$  ions in  $\text{SrF}_2$  would require additional studies, in particular, of the excitation spectra of the fast 146.4-nm band, as well as of the emission spectra obtained under selective excitation of the upper excited states of the  $4f^{10}5d$  configuration.

Observation of the fast VUV luminescence band in  $\text{SrF}_2 : \text{Er}^{3+}$  crystals is of interest in connection with the development of fast VUV scintillators for detectors with high time resolution.

#### ACKNOWLEDGMENTS

This study was supported by the Russian Foundation for Basic Research (project no. 02-02-16322); the Ministry of Education, Science, and Technology of the Russian Federation (project no. E02-3.4-362); the program “Universities of Russia” (project no. UR.02.01.023); the Ural Research and Education Center (program “Promising Materials”); and CRDF (project EK-005-XI).

#### REFERENCES

1. B. V. Shul'gin, Yu. A. Fedorovskikh, E. G. Morozov, F. F. Gavrilov, and B. V. Sinitsyn, in *Proceedings of the II All-Union Symposium on Chemistry of Inorganic Fluorides, Moscow, 1970* (Moscow, 1970).

2. C. R. Ronda, T. Justel, and H. Hikol, *J. Alloys Compd.* **275–277**, 669 (1998).
3. C. L. Woody and D. F. Anderson, *Nucl. Instrum. Methods Phys. Res. A* **265**, 291 (1988).
4. V. N. Makhov, J. Y. Gesland, N. M. Khaidukov, N. Yu. Kirikova, M. Kirm, J. C. Krupa, T. V. Ouvarova, and G. Zimmerer, in *Proceedings of the 5th International Conference on Inorganic Scintillators and Their Applications, Russia, Moscow, 1999* (MSU, Moscow, 1999), p. 369.
5. J. Becker, J. Y. Gesland, N. Yu. Kirikova, J. C. Krupa, V. N. Makhov, M. Runne, M. Queffelec, T. V. Uvarova, and G. Zimmerer, *J. Lumin.* **78**, 91 (1998).
6. J. Becker, J. Y. Gesland, N. Yu. Kirikova, J. C. Krupa, V. N. Makhov, M. Runne, M. Queffelec, T. V. Uvarova, and G. Zimmerer, *J. Alloys Compd.* **275–277**, 205 (1998).
7. M. A. Couto dos Santos, E. Antic-Fidancev, J. Y. Gesland, J. C. Krupa, M. Lemaite-Blaise, and P. Porcher, *J. Alloys Compd.* **275–277**, 435 (1998).
8. R. T. Wigh, A. Meijerink, R. -J. Lamminmäki, and J. Hölsä, *J. Lumin.* **87–89**, 1002 (2000).
9. N. M. Khaidukov, M. Kirm, S. K. Lam, D. Lo, V. N. Makhov, and G. Zimmerer, *Opt. Commun.* **184**, 183 (2000).
10. V. N. Makhov, N. M. Khaidukov, M. Kirm, E. Negodin, G. Zimmerer, S. K. Lam, D. Lo, and N. V. Suetin, *Surf. Rev. Lett.* **9** (1), 621 (2002).
11. L. van Pieterse, M. F. Reid, R. T. Wegh, and A. Meijerink, *J. Lumin.* **94–95**, 79 (2001).
12. L. K. Ermakov, P. A. Rodnyĭ, and N. V. Starostin, *Fiz. Tverd. Tela (Leningrad)* **33** (9), 2542 (1991) [*Sov. Phys. Solid State* **33** (9), 1435 (1991)].

*Translated by G. Skrebtsov*