Luminescent VUV spectroscopy of Er^{3+} and Tm^{3+} ions in strontium fluoride crystals

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Abstract

Emission and excitation spectra as well as decay curves of Er^{3+} and Tm^{3+} ions doped into SrF_2 crystals have been studied using time-resolved vacuum-ultraviolet spectroscopy under pulsed synchrotron radiation at 8 K. In emission spectrum for crystals doped with Er^{3+} ions together with well-known emission caused by spin-forbidden $4f^{10}5d \rightarrow 4f^{11}$ transitions (decay constant in the microsecond range), a new fast emission band detected at 146.5 nm (decay constant is less than 0.6 ns) has been revealed. It was shown that excitation spectra of f–f and d–f emission bands for Er^{3+} and Tm^{3+} ions in SrF_2 have opposite behaviors in the spectral range corresponding to energy of their $4f^{n-1}5d$ configurations. These peculiarities and energy transfer mechanisms were analyzed.

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1. Introduction

The study of crystals doped with rare-earth (RE) ions with optical activity in vacuum ultraviolet (VUV) is a promising field of researches [1]. One of the important problem is research on $4f^{n-1}5d$ excited states. In eightfold cubic coordination, the 5d electronic states are split by crystal field, spin–orbit and Coulomb interactions. The crystal-field interaction gives rise to strong splitting of the 5d orbitals into the low-energy 2E and high-energy 2T_2 sets. The Coulomb interaction between 4f and 5d electrons leads to appreciable complication of $4f^n \rightarrow 4f^{n-1}5d$ excitation spectra. Pieterse et al. [2,3] have demonstrated that the bands connected with transitions involving the 2E sub-configuration showed fine structure and it was missing for the bands caused by transitions to the high-energy crystal-field levels. That was explained by the presence of photoionization processes of latter states.

In this work, the time-resolved VUV spectroscopic study for Er^{3+} and Tm^{3+} ions in SrF_2 crystals have been

performed and some interesting luminescence features were observed.

2. Experiment

$\text{SrF}_2:\text{RE}^{3+}$ crystals were grown in fluorine atmosphere by the Stokbarger technique at Pyshminsky plant GIR-ETMET (Russia).

The experiments were performed at the SUPERLUMI station (HASYLAB, DESY). For excitation, a 2 m McPherson monochromator was used. In VUV range, measurements of emission spectra and spectral selection for decay time measurements were performed with a 0.5 m Pouey-type monochromator equipped with a solar-blind photomultiplier R6836 (Hamamatsu) for spectral measurements, and with a microsphere plate detector for decay measurements. For detection in visible range, an ARC Spectra Pro-308i spectrograph-monochromator with a photomultiplier R6358P were used. The time-resolved measurements were performed in time-integrated mode and in two independent time windows, Δt_1 and Δt_2 delayed with respect to the arrival of synchrotron radiation (SR) pulse on δt_1 and δt_2 , respectively. The excitation spectra were corrected for the wavelength-dependent

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intensity variation. The temperature was near liquid He (8–10 K).

3. Results and discussions

The time-resolved emission and excitation spectra in the VUV range of Er^{3+} in $\text{SrF}_2:1\%\text{Er}^{3+}$ crystal are shown in Fig. 1. The “slow” component in the VUV-emission consists of the known spin-forbidden transitions from the lowest high spin HS state of $4f^{10}5d$ configuration to the different $4f^n$ multiplets (the assignments are shown in the figure). In the “fast” time window, an emission band peaked at 146.4 nm is observed. This band was discovered in Ref. [4] under soft X-ray excitation. The decay time for this emission determined by means of the convolution integral is about ~ 0.5 ns (Fig. 1, inset). No emission from a low spin LS state of $4f^{10}5d$ configuration is observed. It is caused by a small energy separation ($\sim 2150\text{ cm}^{-1}$) between the LS and HS states that makes multi-phonon non-radiative relaxation highly probable.

The excitation spectrum of the erbium d–f emission at 164.5 nm demonstrates well-structured bands with maxima at 155, 145, 134 and 129.5 nm, denoted, respectively, by A, B, C and D in the figure. These bands are assigned to the transitions to $4f^{10}5d$ states involving the 2E levels coupled to the lowest states of $4f^{10}$ core, which can be written as

$^2E(^5I_8)$, $^2E(^5I_7)$, $^2E(^5I_6)$ and $^2E(^5I_5)$, respectively. The spin-forbidden $^4I_{15/2} \rightarrow 4f^{10}5d$ (HS) transition is observed as low intensity band at 159 nm.

The excitation spectrum of emission at 146.4 nm has presented as homogeneous band at 133 nm without fine structure (Fig. 1, curve 4). Long wavelength side of this band to some extent correlates with the band at 134 nm in the excitation spectrum for the d–f emission at 164.5 nm. But still they are characterized by differing steepness. A maximum and center of excitation band for 146.4 nm emission is slightly shifted to shorter wavelengths with respect to the excitation band for the emission at 164.5 nm. It indicates that the excitation bands can belong to different excited states of $4f^{10}5d$ configuration. Therefore, we assume that the fast luminescence originates from the $^2T_2(^5I_8)$ excited state of Er^{3+} ions situated at the low symmetry sites, in which energy difference between 2E and 2T_2 can be noticeably smaller. Under such conditions, radiative transition probability of this state is sufficiently high enough and the respective luminescence due to transition into the $4f^{11}$ ground state can be observed.

Excitation spectra monitoring the $4f^{10}5d(\text{HS}) \rightarrow ^4I_{15/2}$ and $^4S_{3/2} \rightarrow ^4I_{15/2}$ emission (550 nm) show their opposite behavior. It reflects partly variation of absorption coefficient in the transparency range and competition in the energy transfer processes to the emitting levels of $4f^{10}5d$

Fig. 1. $\text{SrF}_2:1\%\text{Er}^{3+}$, $T = 8\text{ K}$. Emission spectra upon f–d excitation at 134 nm in “slow” (1) and “fast” (2) time windows; excitation spectra for the $4f^{10}5d(\text{HS}) \rightarrow ^4I_{15/2}$ emission at 164.5 nm in “slow” time window (3), for emission at 146.4 nm in “fast” time window (4) and for $^4S_{3/2} \rightarrow ^4I_{15/2}$ emission at 550 nm in “slow” time window. “Fast” time window had $\Delta t_1 = 1.8\text{ ns}$, $\delta t_1 = 0.8\text{ ns}$, and “slow” time window had $\Delta t_2 = 78\text{ ns}$, $\delta t_2 = 65\text{ ns}$. On inset: decay curve for emission at 146.4 nm (6) and SR pulse (7).

Fig. 2. SrF_2 : 1% Tm^{3+} , $T = 8$ K. Emission spectra upon f–d excitation at 155 nm (1); excitation spectra for the $4f^{11}5d(\text{HS}) \rightarrow {}^3\text{H}_6$ emission at 167 nm (2) and for ${}^1\text{G}_4 \rightarrow {}^3\text{H}_6$ emission at 451 nm (3).

and $4f^{11}$ configurations in Er^{3+} . We can assume that there is increased probability of spin-forbidden f–d transitions. As a result, the f–f emission is effectively excited enough at all possible levels of $4f^{10}5d$ configuration. The opposite behavior of excitation spectra for f–f and d–f emission is observed because intensity of f–f emission is decreased under excitation at spin-allowed states since the most probable way for relaxation of such states is the so-called non-radiative intersystem crossing, which populates the lowest HS state. From this state, $4f^{10}5d(\text{HS}) \rightarrow {}^4\text{I}_{15/2}$ emission is observed.

The VUV-emission of Tm^{3+} upon f–d excitation is presented by slow luminescence decay component only (in microsecond range). The emission bands are connected with the spin-forbidden $4f^{11}5d(\text{HS}) \rightarrow 4f^{12}$ transitions (Fig. 2).

Rich energy level structure of the $4f^{11}5d$ configuration is observed in the excitation spectra for d–f emission at 166 nm (Fig. 2, curve 2). The bands at 155 (A), 141 (B) and 132 nm (C) can be assigned to the transitions of $4f^{11}5d({}^2\text{E})$ state where $4f^{11}$ continuum consists of the ${}^4\text{I}_{15/2}$, ${}^4\text{I}_{13/2}$, ${}^4\text{I}_{11/2}$ states. The spin-forbidden ${}^3\text{H}_6 \rightarrow 4f^{11}5d(\text{HS})$ transition is observed at 162 nm. The transitions to the high-energy ${}^2\text{T}_2$ states are not revealed due to host absorption.

For Tm^{3+} in SrF_2 as well as for Er^{3+} , the excitation spectra of the d–f and f–f emission demonstrate opposite behavior (Fig. 2, curve 2 and 3, respectively). The excitation spectrum for ${}^1\text{G}_4 \rightarrow {}^3\text{H}_6$ emission at 451 nm has most intensity in broad bands at 159, 146, 136 and 128 nm. Such behavior of excitation spectra for f–f emission in comparison with those for d–f emission in the range of $4f^n \rightarrow 4f^{n-1}5d$ absorption is not always observed for RE ions in other matrices (see, e.g., [5,6]).

The f–f emission of Er^{3+} or Tm^{3+} has enough high excitation efficiency in the range of long-wavelength fundamental absorption edge of the host. For d–f emission,

on the contrary, such mechanism is suppressed. This phenomenon can be connected with autoionization state when one electron from ground state is promoted to high-energy 5d-states located in conduction band at absorption. Finally, an exciton-like $\text{Ln}^{4+} + e^-$ formation that relaxes predominantly into the $4f^n$ manifold through dipole–dipole or multipole interactions, is created for example [7]. However, the excitation mechanisms for f–f emissions are more complicated including also such possibilities as charge transfer absorption and energy transfer via intrinsic and/or extrinsic host excitations [8].

4. Conclusion

Time-resolved VUV spectroscopic properties of Er^{3+} and Tm^{3+} ions in SrF_2 crystals have been studied under SR excitation.

In Er^{3+} -doped crystals, besides well-known $4f^{10}5d(\text{HS}) \rightarrow {}^4\text{I}_{15/2}$ emission at 165.4 nm, the fast emission at 146.4 nm with a decay time of about ~ 0.5 ns was revealed. A nature of this band is tentatively assigned to the radiative relaxation from the ${}^2\text{T}_2({}^5\text{I}_8)$ -excited level of the Er^{3+} ions situated at low symmetry sites. For Er^{3+} and Tm^{3+} ions in SrF_2 , no emission from the LS state is observed that was caused by the efficient non-radiative relaxation between LS and HS states.

One of the rather surprising features of Er^{3+} and Tm^{3+} in SrF_2 consists of clearly observed opposite behavior of the excitation spectra for f–f and d–f emissions.

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References

- [1] J. Becker, J.Y. Gesland, N.Yu. Kirikova, J.C. Krupa, V.N. Makhov, M. Runne, M. Queffelec, T.V. Uvarova, G. Zimmerer, *J. Alloy Compounds* 275–277 (1998) 205.
- [2] L. van Pieterse, M.F. Reid, A. Meijerink, *Phys. Rev. Lett.* 88 (2002) 067405.
- [3] L. van Pieterse, M.F. Reid, G.W. Burdick, A. Meijerink, *Phys. Rev. B* 65 (2002) 045114.
- [4] K.V. Ivanovskikh, V.A. Pustovarov, M. Kirm, B.V. Shulgin, *HASYLAB Annual Report, Part I*, 2004, p. 507.
- [5] V.N. Makhov, N.M. Khaidukov, N.Yu. Kirikova, M. Kirm, J.C. Krupa, T.V. Uvarova, G. Zimmerer, *Nucl. Instrum. Methods A* 470 (2001) 290.
- [6] N.M. Khaidukov, N.Yu. Kirikova, M. Kirm, J.C. Krupa, V.N. Makhov, E. Negodin, G. Zimmerer, *Proc. SPIE* 4766 (2002) 154.
- [7] A.N. Belsky, J.C. Krupa, *Displays* 19 (1999) 185.
- [8] M. True, M. Kirm, E. Negodine, S. Vielhauer, G. Zimmerer, *J. Alloy Compounds* 374 (2004) 36.