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Time-resolved luminescent VUV-spectroscopy of pure and doped by rare earth ions crystals of strontium fluoride

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Abstract

The spectroscopic properties SrF_2–Eu(1%), SrF_2–Er(1%) and nominal pure SrF_2 crystals have been studied using time-resolved vacuum ultraviolet (VUV) spectroscopy under pulsed synchrotron radiation excitation. The $4f^k \leftrightarrow 4f^{k-1}5d$ (f–d) and $4f^k \leftrightarrow 4f^k$ (f−f) excitation spectra and emission spectra (with and without of time resolution) have been investigated in the wide energy region at 8 and 295 K. Moreover, the emission and excitation behaviors of intrinsic luminescence SrF_2 have been studied at 8 K, when the fast and slow components given by singlet and triplet relaxation of self-trapped excitons (STE) are observed. Special attention is devoted to VUV emission of Er^{3+}-doped SrF_2 due to spin-allowed and spin-forbidden $4f^{10}5d \rightarrow 4f^{11}$ transitions.

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Keywords: VUV-spectroscopy; Synchrotron radiation; SrF_2; Rare-earth ions

1. Introduction

The crystals with fluorite structure possess a set of unique physical and luminescent properties. They are practically feasible and can be grown to have sufficient size and optical quality to create optical media [1]. From the fundamental point of view, among other ionic crystals, the homologous series of fluoride of II group is a model for studying the most general objective laws of interaction of impure ion with matrix.

In the last few years significant interest has been shown in vacuum ultraviolet (VUV) spectroscopy of rare-earth (RE) ions doped into wide-gap crystals, which is determined by the necessity of creating new class of VUV-phosphors. Such materials are widely applied today. Major applications are in mercury-free fluorescent lamps and plasma display [2,3].

In the present paper, the spectroscopic properties of SrF_2, SrF_2–Eu(1%) and SrF_2–Er(1%) single crystals have been studied. Mechanisms of transfer

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of energy to impurity sites are analyzed. The measurements of luminescence and excitation spectra as well as decay kinetics of luminescence were carried out using of time-resolved luminescent spectroscopy under selective excitation by synchrotron radiation (SR) in VUV and soft X-ray energy regions.

2. Samples and experimental details

Samples for this investigation were single crystals SrF_2–Eu(1%), SrF_2–Er(1%) and nominal pure SrF_2 grown in fluoric atmosphere by means of modified Stokbarger technique at Pyshminsky pilot plant GIREDMED (Russia).

The measurements were carried out at the SUPERLUMI station of HASYLAB (DESY, Hamburg) [4]. Investigations by using soft X-ray have been performed at the BW3 beamline of HASYLAB and "Luminescence with time-resolution" station of storage ring VEPP-3 (Budker INP SR of RAS, Novosibirsk). The time-resolved measurements could be carried out in various time windows Δt delayed with respect to SR pulses on δt. In this work, two independent time windows with Δt_1, δt_1 (fast component) and Δt_2, δt_2 (slow component) were used. For SrF_2 values of windows were $\delta t_1 = 2.4$ ns, $\Delta t_1 = 15.2$ ns, $\delta t_2 = 72$ ns, and $\Delta t_2 = 102$ ns, and for SrF_2–Er(1%) they were $\delta t_1 = 0.6$ ns, $\Delta t_1 = 1.8$ ns, $\delta t_2 = 12$ ns, and $\Delta t_2 = 20$ ns. The excitation spectra were corrected for the wave-length-dependent variation using sodium salicylate. The emission spectra were not corrected for the spectral sensitivity of detection system.

3. Experimental results and discussion

The time-resolved emission spectra of SrF_2 due to annihilation of STE are shown in Fig. 1. These spectra were obtained under excitation by photons with energy of 11.8 eV at 295 and 8 K. At 295 K the wide band of luminescence has a maximum of about 313 nm and is characterized only by a slow component. Luminescence at 8 K is submitted by two components: fast with maximum near 354 nm and slow with maximum near 317 nm whose contribution to the general light yield is dominating. According to Refs. [5,6], the fast component of intrinsic luminescence is due to spin-allowed singlet–singlet transitions of excitons and slow component is due to transitions from triplet level of excitons, which are possible because of presence of spin–orbit interaction.

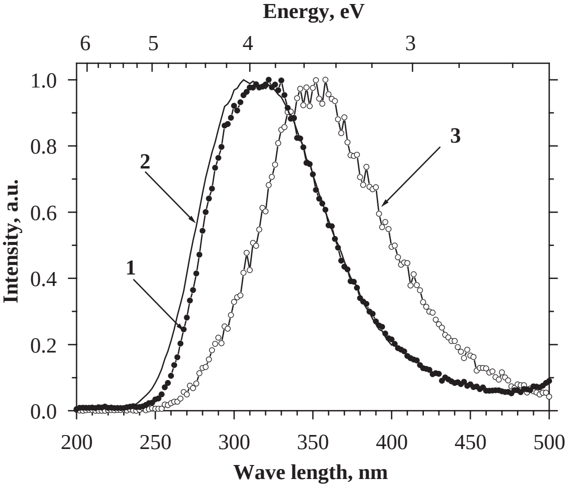

Fig. 1. Emission spectra of SrF_2 at 295 (1) and 8.2 K (2, 3), excited with 11.8 eV photons: (1) time-integrated; (2) slow time window; (3) fast time window.

The excitation spectra of triplet and singlet components of STE luminescence measured at $T = 8$ K are presented in Fig. 2. They show distinctions that confirm similar results received earlier by group [6] at 90 K. The position of threshold of excitation of the slow component of luminescence corresponds to the beginning of fundamental absorption of crystal SrF_2 and creation of excitons with the least energy. It is submitted as a long-time increasing peak of excitation in an interval of 8–10.3 eV. The spectrum of excitation of fast components, on the contrary, is characterized by sharp increase of intensity of a luminescence at excitation near 10.1 eV with a maximum at 10.4 eV. The fast component is most effectively excited at 10.4 and 11.2 eV. At a greater energy of photons, excitation intensity of fast component makes no more than 25% concerning those in the field of fundamental