

Comparison of Ce^{3+} and Pr^{3+} activators in alkaline-earth fluoride crystals

E.Radzhabov and A.Nepomnyaschikh

Abstract—The emission spectra of Ce^{3+} or Pr^{3+} doped CaF_2 , SrF_2 , BaF_2 excited by vacuum ultraviolet photons or by x-ray as well as excitation and absorption spectra in vacuum ultraviolet region (6-13 eV) were studied. The transfer of exciton energy is the main channel for Ce^{3+} excitation in alkaline-earth fluorides. Three different stages of energy transfer were observed. Pr^{3+} excited by two processes, slow f-f luminescence excited by excitons, fast d-f luminescence excited by some fast process.

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

I. INTRODUCTION

ION Ce^{3+} still remains most popular activator for halide and oxide scintillators introducing both high efficiency of registration and fast decay time [1]. Two Ce^{3+} emission bands are due to 5d-4f transitions having energy of transitions in fluorides near 4 eV. Emission decay of Pr^{3+} ions is faster than that of Ce^{3+} ions [2]. Energies of several 5d-4f transitions of Pr^{3+} are in 3.5-5.5 eV region. Other rare-earth ions show even faster decay, however energies of radiative transitions are shifted to vacuum ultraviolet region (above 6 eV), making difficult the detection of emission. Bromide and iodide matrices have the largest light yield, mostly due to smallest band gap. It seems that Ce^{3+} ion only could effectively luminesce in these materials, while the emission of other rare-earth ions is quenched because the ground $4f^n$ levels of these ions are in valence band [3]. In this paper we compare the emission of Ce^{3+} and Pr^{3+} ions in alkaline-earth fluoride crystals.

II. EXPERIMENTAL

Crystals CaF_2 , SrF_2 , BaF_2 doped by CeF_3 or PrF_3 were grown by Stockbarger method in graphite crucible in vacuum. Concentration of dopant varied from 0.005 to 10 molar percent. The excitation, absorption spectra in the energy range of 4-13 eV were measured with grating vacuum monochromator VMR2. The discharge hydrogen lamp VMF25 with MgF_2 window and dyoplasmatron were used as vacuum ultraviolet sources. Emission spectra were measured with grating vacuum monochromator VM2 (160-500 nm) and grating monochromator MDR2(200-900nm). Emission spectra were not corrected for spectral sensitivity response of monochromator and photomultipliers. Decay of emission was measured by digital oscilloscope 'Bordo-411' under excitation by 10ns pulse of

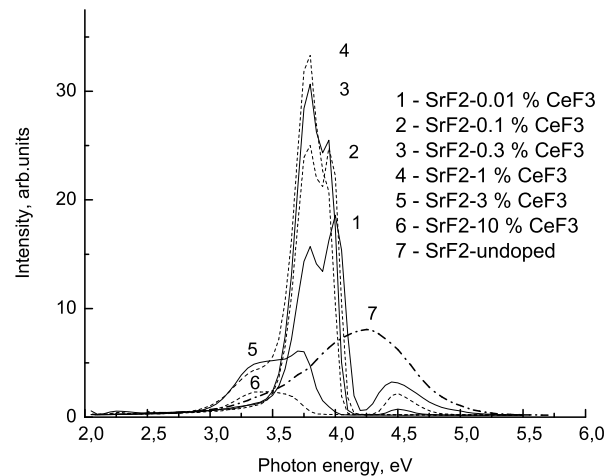


Fig. 1. Emission spectra of SrF_2 crystals with different cerium concentration at 295K under x-ray excitation.

x-ray tube 'Mira 2d'. Stationary emission was excited by Pd x-ray tube with 35 kV and 2-10 mA.

At concentration less 0.3 mol.% the samples were cutted from grown rod. At higher concentration the sample were sawed from the rod and one side polished. For simplicity we used a simple notation f-d or 4f-5d instead of full notation $4f^n-4f^{n-1}5d^1$.

III. RESULTS

Ce^{3+} emission

For all crystals the exciton luminescence continuously decreased with increasing of cerium concentration. Exciton emission becomes negligible near 1 mol.% of CeF_3 (Fig.1). Dependence of integral intensity of emission bands of Ce^{3+} ions against of Ce concentration is shown on Figure. The highest light yield was found for SrF_2 -1 mol. % CeF_3 crystal. The highest light yield of Ce^{3+} emission for all crystals are close to initial light yield of exciton emission of undoped crystals (Fig.2). The concentration of maximal light yield of BaF_2 -Ce is the same as that observed in earlier paper [4]. It seems that the transfer of exciton energy is the main channel for Ce^{3+} excitation.

Emission decay of cerium ion doped into alkaline-earth fluorides under optical excitation into lowest energy absorption bands is equal about 30 ns [4], [5], [6]. Under vacuum ultraviolet excitation into exciton and higher energies region the

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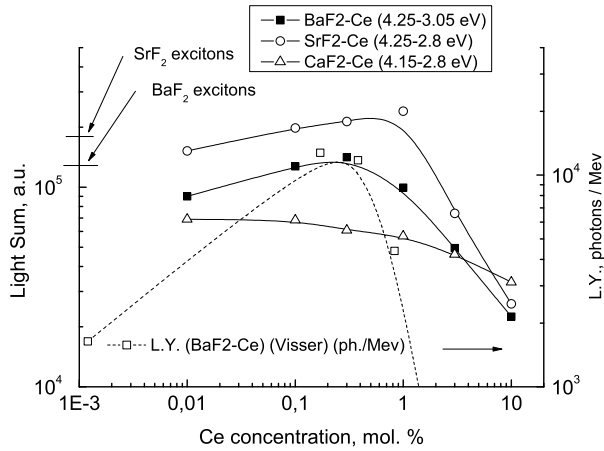


Fig. 2. Integral lightsum of Ce^{3+} emission against of cerium concentration in CaF_2 , SrF_2 , BaF_2 crystals.

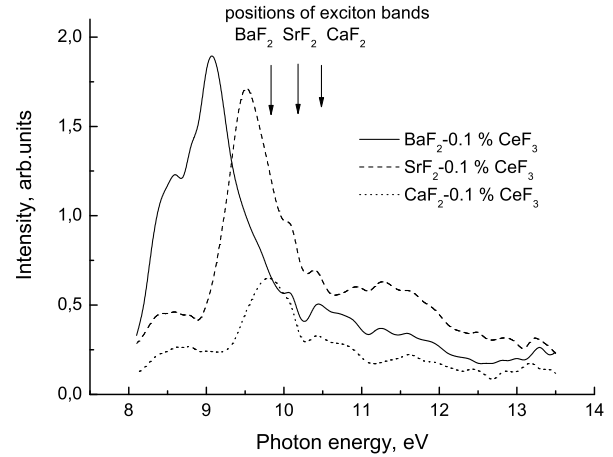


Fig. 4. Excitation spectra of Ce emission of CaF_2 , SrF_2 , BaF_2 crystals doped by 0.1 mol.% of CeF_3 at 295 K.

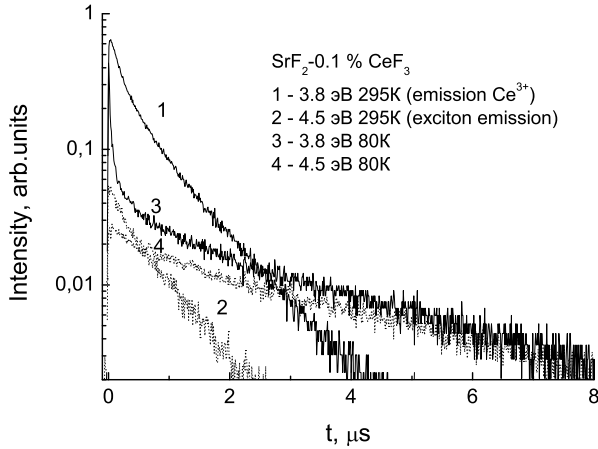


Fig. 3. Emission decay of SrF_2 0.1 mol.% PrF_3 crystals measured at 295K and 80K. Sample was excited by 10 ns x-ray pulses.

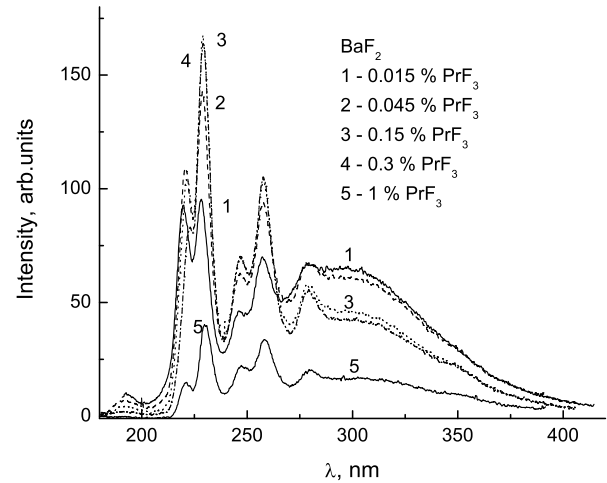


Fig. 5. Emission spectra of BaF_2 crystals with different PrF_3 concentration at 295 K under x-ray excitation.

decay of $\text{BaF}_2\text{-Ce}$ became unexponential [6]. Under x-pulses excitation the decay curves is also unexponential (Fig.3). Decay curve can be fitted by few exponents, similar to exciton decay [7]. With increasing of cerium concentration decay becomes faster. At low temperature the fast decay component becomes more pronounced (see Fig.3). Whole decay curve can be described by at least three processes. Fast stage could be ascribed to resonance energy transition in nearest pairs of exciton and cerium ion. Middle stage up to microsecond range reduced by cooling of crystals (see Fig.3) and could be ascribed to thermoactivated processes such as jumping of self-trapped excitons or holes. Slowest stage obviously connected with reabsorption of exciton emission over large distances.

Excitation spectra of cerium emission show prominent peak at energies which is near 0.7 eV less than the exciton peak energies (Fig.4). Similar peaks were observed for many activators in alkali halides. These bands usually assigned to excitons which were created in vicinity of activators.

Pr^{3+} emission

Pr^{3+} ions have two groups of emission bands. Bands 5d-4f are observed at 220-300 nm region (5.7-4 eV) (Fig.5). Bands 4f-4f are observed at region larger 400 nm (less 3 eV). For characterization of relative intensity of both groups of lines we choose the maximal intensity bands at 230 nm (5d-4f) and 490 nm (4f-4f) (Fig.6). With increasing of Pr concentration the intensity of exciton emission continuously decreased, however, in much slower rate in comparison with Ce doped samples. Maximal intensity of Pr emission was observed at 0.1-0.3 mol. % of PrF_3 concentration (see Fig.6). Concentration dependences of both groups lines are different (especially for CaF_2 and SrF_2), which points on different mechanisms of energy transfer. Relative intensity of 5d-4f emission against of exciton emission significantly decreased in a row of $\text{BaF}_2\text{-SrF}_2\text{-CaF}_2$.

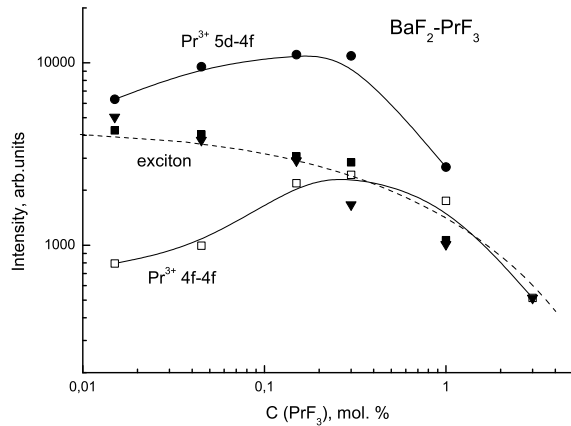


Fig. 6. Intensities of Pr^{3+} 290nm(d-f), 500nm(f-f) bands and 290nm exciton emission band against of PrF_3 concentration in BaF_2 crystals.

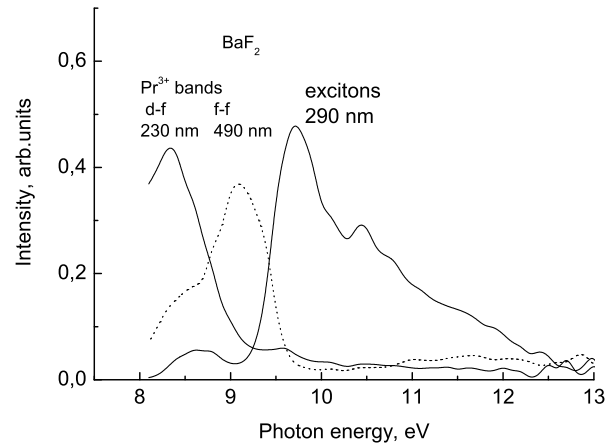


Fig. 8. Excitation spectra of BaF_2 -0.1 mol.% PrF_3 crystals at 295 K.

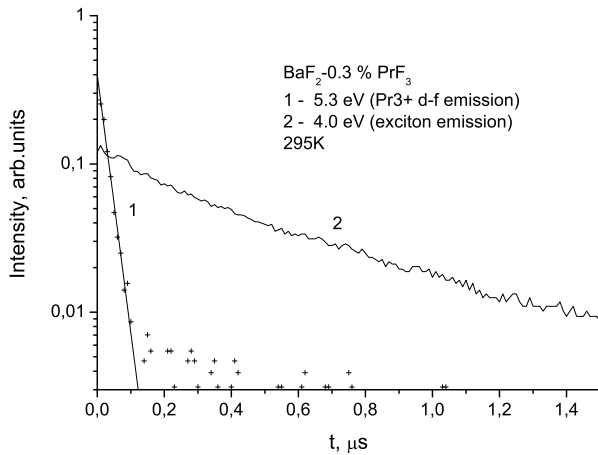


Fig. 7. Emission decay of BaF_2 -0.3 mol.% PrF_3 crystals measured Pr d-f band and exciton band at 295 K under x-ray pulse excitation.

Decay of 5d-4f Pr emission in BaF_2 is equal to near 27 ns (Fig.7), decay do not depends on temperature and praseodymium concentration. The decay time is slightly longer than 22 ns measured under optical excitation in BaF_2 -0.3 % PrF_3 earlier [8]. The fast decay of 5d Pr^{3+} emission in several fluoride compounds was observed in 19-26 ns region [9], [10]. It seems the excitons have no influence on Pr 5d-4f emission.

Excitation spectra for both Pr groups of transitions are different also (Fig.8). Excitation spectra of f-f bands contains apparent peak on low energy side of exciton bands. Contrary to this the excitation spectra of d-f emission do not show any peaks above 4f-5d high energy band up to our limit at 13 eV (see Fig.8). Evidently 5d-4f emissions are excited at higher energies.

IV. DISCUSSION

Excitation spectra of intraconfigurational f-f transitions of trivalent Nd, Er, Tm, Pr ions doped into several trifluorides

were measured in early paper [11]. Excitation bands on low-energy wing of exciton were observed in all cases. Evidently excitonic mechanism of transfer energy to f-shell have common character. One can assume that the energy of self-trapped exciton (4 eV in fluorides) transfer to appropriated excited f-levels of rare-earth ions. Evidently the exciton energy transfer have a low probability for Pr ions in alkaline-earth fluorides, it follows from weak exciton emission quenching by praseodymium ions (see Fig.5). The exciton energy is not enough for excitation of 4f-5d transitions for all rare-earth ions but Ce^{3+} .

The overlapping self-trapped exciton emission and Ce^{3+} absorption, excitation spectra is high enough and above 1% of CeF_3 all exciton energy is transferred to cerium ions (see Fig.2). Because of slow decay of excitons and respectively cerium ions the alkaline-earth fluorides are not suitable for developing of fast scintillators.

The decay of Pr emission under x-ray pulses is fast as decay under optical excitation into f-d band. Intensity and decay time was not varied at temperatures from 80K to 300K (and even to 500K [12]). Fast d-f emission of BaF_2 -0.3% PrF_3 are excited above 18 eV, when excitation of core barium zone begins [8]. In the case of BaF_2 and some other crystal the excitation of core band results in so-called crossluminescence, when electrons transfer from upper valence band to low-lying highest core band. Emission spectrum of crossluminescence in BaF_2 significantly overlap with absorption of Pr^{3+} ions. Possibly it is the origin of highest BaF_2 - Pr^{3+} light yield among the other alkaline-earth fluorides, because in the CaF_2 or SrF_2 the crossluminescence is absent. The crossluminescent transition is absent in CaF_2 , SrF_2 where the 5d-4f Pr luminescence observed also, but with lower intensity.

The results of excitation spectra measurements show clearly that in $\text{LiYF}_4:\text{Er}^{3+}$ the efficiency of the energy conversion from the matrix to Er^{3+} d-f luminescence is extremely low in the region of fundamental absorption of the crystal till the energy of excitation reaches the threshold for processes of electronic excitations multiplication [13]. This threshold lies

in $\text{LiYF}_4 : \text{Er}^{3+}$ crystals at photon energy 22 eV, which is less than $2E_g$ ($E_g=12.5$ eV is the band gap for LiYF_4), and the effect is more pronounced at higher concentration of Er^{3+} . These features indicate that the mechanism of the energy transfer from the matrix to Er^{3+} d-f luminescence in $\text{LiYF}_4:\text{Er}^{3+}$ is the so-called impact mechanism of electronic excitations multiplication when fast photoelectrons excite directly (by impact) emission centers (Er^{3+} ions) in the crystal [13]. This mechanism of excitation was thoroughly studied in thallium doped alkali chlorides [14]. This mechanism could operate in alkaline-earth fluoride doped by praseodymium. In the case of BaF_2 the mechanism of excitation by hot photoelectrons can be reinforced by energy transfer from crossluminescent transitions. Future measurements of excitation spectra of $\text{CaF}_2\text{-Pr}$ and $\text{SrF}_2\text{-Pr}$ could refine the details of energy transfer in Pr-doped alkaline-earth fluorides.

$\text{BaF}_2\text{-PrF}_3$ is prospective media for developing of fast and thermal stable scintillator.

V. CONCLUSION

The transfer of exciton energy is the main channel for Ce^{3+} excitation in alkaline-earth fluorides. Three different stages of energy transfer were observed. Pr^{3+} excited by two processes : slow f-f luminescence excited by excitons, d-f luminescence excited by some other fast process.

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