



ELSEVIER

Contents lists available at ScienceDirect

Journal of Luminescence

journal homepage: www.elsevier.com/locate/jlumin

Peculiarities of cascade photon emission and energy storage in $M_{1-x}Pr_xF_{2+x}$ ($M=Ca, Sr, Ba, x \approx 0.35$) crystals

N. Shiran^{a,*}, A. Gektin^a, V. Nesterkina^a, Y. Boyarintseva^a, V. Baumer^a, G. Stryganyuk^b, A. Voloshinovskii^b, K. Shimamura^c, E. Villora^c

^a Institute for Scintillation Materials NAS of Ukraine, 60 Lenin Avenue, 61001 Kharkov, Ukraine

^b Ivan Franko National University of Lviv, 8 Kyryla i Mefodiya Street, 79005 Lviv, Ukraine

^c National Institute for Materials Science, 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan

ARTICLE INFO

Article history:

Received 26 March 2009

Received in revised form

26 May 2010

Accepted 6 July 2010

Available online 21 July 2010

Keywords:

Luminescence

Cascade photon emission

Energy storage

Solid solution

Color center

ABSTRACT

Peculiarities of cascade photon emission (CPE) and energy storage in $M_{1-x}Pr_xF_{2+x}$ ($M=Ca, Sr, Ba, x \approx 0.35$) crystals were studied. The investigation of lattice parameters revealed that these solid solutions belong to the fluorite structure type with the lattice constant noticeably different from that of MF_2 crystals. Absorption, emission and excitation spectra of $M_{0.65}Pr_{0.35}F_{2.35}$ were measured at LHeT and RT. As it turned out the typical for $4f^2 \rightarrow 4f^2$ transition in Pr^{3+} emission lines are broadened as compared with the PrF_3 crystal. The analysis of the excitation spectra broadening does not allow bringing out the type of the superlattice, which is inherent to the material, but it indicates clearly the simultaneous presence of different types of the Pr centers in mixed crystals. Yet another specific feature is the higher radiation sensitivity of these fluorides relatively PrF_3 , MF_2 and Pr-doped MF_2 crystals. Coloration efficiency enhances in direction $Ca \rightarrow Sr \rightarrow Ba$, and the positions of induced absorption band depend on composition of the solid solution. Colorization, thermo-stimulated luminescence and afterglow of the $M_{1-x}Pr_xF_{2+x}$ crystals denote high radiation sensitivity as compared with $M_{1-x}Ce_xF_{2+x}$.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

Fluorite-structured MF_2 ($M=Ca, Sr, Ba$) crystals are transparent in a wide spectral range and being doped by rare earths (RE) are applied as lasers and radiation detectors. Surplus charge of RE^{3+} ions is compensated by interstitial fluorine ions. Contrary to $MF_2:RE$, in highly concentrated $M_{1-x}RE_xF_{2+x}$ solid solutions RE^{3+} ions are not distributed statistically and form nano-sized inclusions with a certain atomic composition [1]. It is supposed that the clusters and fluoride phases in nonstoichiometric crystals form nanostructures. EPR and neutron diffraction studies of $M_{1-x}RE_xF_{2+x}$ systems have shown the presence of extensive disorder in the form of vacancies in the anion sublattice and a large excess of interstitial atoms over dopant trivalent cations [2,3].

Fluorite-structured solid solutions are promising superionic conductors for medium temperatures [4,5]. Large regions of heterovalent solid solutions (up to $x=0.5$) and a high concentration of mobile charge compensating defects result in a high ionic conductivity already near the room temperature.

Generally, highly RE concentrated fluoride solid solutions represent a new class of materials promising for the design of wide-gap converters of VUV and ionizing radiation to be used for medical, scientific and industrial applications. For the first time these attempts produced a positive result for $Ca_{0.65}Eu_{0.35}F_{2.35}$ crystals [6]. As it was found this compound has good prospects to be applied as a red phosphor and display material due to bright trivalent Eu^{3+} ion luminescence under UV, VUV, X- and γ -excitation.

Recently, Pr-doped crystals have become an object of new scintillation media research. The cascade photon emission (CPE) of Pr-doped fluorides is yet another argument in favour of the research, since this phenomenon enables to produce two photons per one absorbed quantum. CPE is typical of broad gap dielectrics, allowing initiating two low-energy photons from an excited state, in other words, making it possible to increase the light yield of Pr-doped materials [7,8]. The first results concerning the luminescence characteristics of $M_{0.65}Pr_{0.35}F_{2.35}$, as compared with MF_2 and PrF_3 crystals, were presented at SCINT'07 Conference [9].

The goal of this research was to study the effects of concentration and structure state of praseodymium ions on peculiarities of the luminescence, as well as on implementation of the photon cascade emission and energy storage in $M_{1-x}Pr_xF_{2+x}$ crystals.

* Corresponding author. Tel.: +380 573 410 367; fax: +380 573 404 474.
E-mail address: shiran@isc.kharkov.com (N. Shiran).

2. Experimental

Pure and Pr-doped MF_2 crystals as well as PrF_3 and $\text{M}_{1-x}\text{Pr}_x\text{F}_{2+x}$ ($\text{M}=\text{Ca}, \text{Sr}, \text{Ba}, x \approx 0.35$) were grown by Czochralski technique in CF_4 atmosphere. Lattice parameters were determined by the X-ray diffraction method (XRD) at Oxford Diffraction Xcalibur-3 single crystal diffractometer (MoK α radiation, graphite monochromator, Sapphire 3 CCD detector, $7^\circ \leq 2\theta \leq 87^\circ$). The phase structure tests with material powder were performed using the Siemens D500 powder diffractometer (CuK α , graphite monochromator, scan step of 0.01° within $20^\circ \leq 2\theta \leq 155^\circ$, a dwell time 40 s) (see details in Ref. [6]). Luminescence spectra were recorded using time-resolved FLS 920 spectrometer (Edinburgh Instruments) and synchrotron radiation at the SUPERLUMI station, HASYLAB at DESY [10]. Absorption was measured using SPECORD 40 spectrophotometer. Irradiation was performed by an X-ray tube (160 kV, 10 Gy/min).

3. Results

The investigations of lattice parameters by the XRD method have confirmed that $\text{M}_{1-x}\text{Pr}_x\text{F}_{2+x}$ ($\text{M}=\text{Ca}, \text{Sr}, \text{Ba}, x \approx 0.35$) crystals belong to the fluorite structure type (the fcc lattice, space group $\text{Fm}\bar{3}\text{m}$) with the lattice constant (a) noticeably differ from that of MF_2 (Table 1). A partial deficiency in the fluorine positions and excessive interstitial fluorine ions (F_i^-) were revealed. This feature most likely determined the change in the crystal lattice (Δa) of MF_2 and $\text{M}_{1-x}\text{Pr}_x\text{F}_{2+x}$. The similar arrangement was found earlier in $\text{M}_{1-x}\text{RE}_x\text{F}_{2+x}$ structures containing different RE^{3+} ions in the positions of divalent alkali earth ones [1]. It should be noted that any clusters and phases were not revealed in studied compounds.

A priori, the optical properties of mixed crystals would be similar to the crystal-forming compound, i.e. MF_2 or PrF_3 . From this standpoint, all of the absorption and luminescence characteristics are compared with similar data of the base compounds.

Absorption spectra of PrF_3 and $\text{M}_{0.65}\text{Pr}_{0.35}\text{F}_{2.35}$ ($\text{M}=\text{Ca}, \text{Sr}, \text{Ba}$) crystals are shown in Fig. 1. The lines belonging to $^3\text{H}_4 \rightarrow ^3\text{P}_j$ ($j=0,1,2$) transitions in Pr^{3+} ions are distinctly revealed in all solid solutions.

The synchrotron radiation excited emission spectra of $\text{M}_{0.65}\text{Pr}_{0.35}\text{F}_{2.35}$ crystals measured at 8 K are presented in Fig. 2. Intensity of typical Pr^{3+} ion emission in the 220–280 nm range (5d 4f bands and $^1\text{S}_0 \rightarrow ^3\text{H}_6, ^3\text{F}_4, ^1\text{G}^4, ^1\text{D}_2$ lines) decreases in a row $\text{Ca} \rightarrow \text{Sr} \rightarrow \text{Ba}$. It is remarkable that the energy gap (E_g) of CaF_2 , SrF_2 and BaF_2 is close to $\sim 12.1, 11.2$ and 10.57 eV, respectively. Long wave $4f^2 \rightarrow 4f^2$ luminescence at 482 nm ($^3\text{P}_0 \rightarrow ^3\text{H}_4$), 553 nm ($^3\text{P}_0 \rightarrow ^3\text{H}_5$), ~ 609 nm ($^3\text{P}_0 \rightarrow ^3\text{H}_6$), 638 nm ($^3\text{P}_0 \rightarrow ^3\text{F}_2$), 721 nm ($^3\text{P}_0 \rightarrow ^3\text{F}_4$) reveals an opposite tendency. The set of overlapped bands between 5.0 and 9.0 eV in excitation spectra of 5d 4f \rightarrow 4f 2 and 4f $^2 \rightarrow$ 4f 2 emissions are assigned to 4f \rightarrow 4f 5d transitions in Pr^{3+} ion (Fig. 3). At lower energies, $E < 5.0$ eV only narrow 4f $^2 \rightarrow$ 4f 2 lines typical of Pr^{3+} ions are observed (not presented in Fig. 3). The weak excitation line at 5.8 eV, which is well resolved

Table 1

Lattice constant (a) of MF_2 , $\text{M}_{0.65}\text{Pr}_{0.35}\text{F}_{2.35}$ and PrF_3 crystals.

Crystal	a (Å)	Δa (Å)
CaF_2	5.46305	
$\text{Ca}_{0.65}\text{Pr}_{0.35}\text{F}_{2.35}$	5.61359(4)	+0.15055
SrF_2	5.79960	
$\text{Sr}_{0.65}\text{Pr}_{0.35}\text{F}_{2.35}$	5.81578(2)	+0.01618
BaF_2	6.20000	
$\text{Ba}_{0.65}\text{Pr}_{0.35}\text{F}_{2.35}$	6.03744(6)	-0.16255
PrF_3	7.2390	

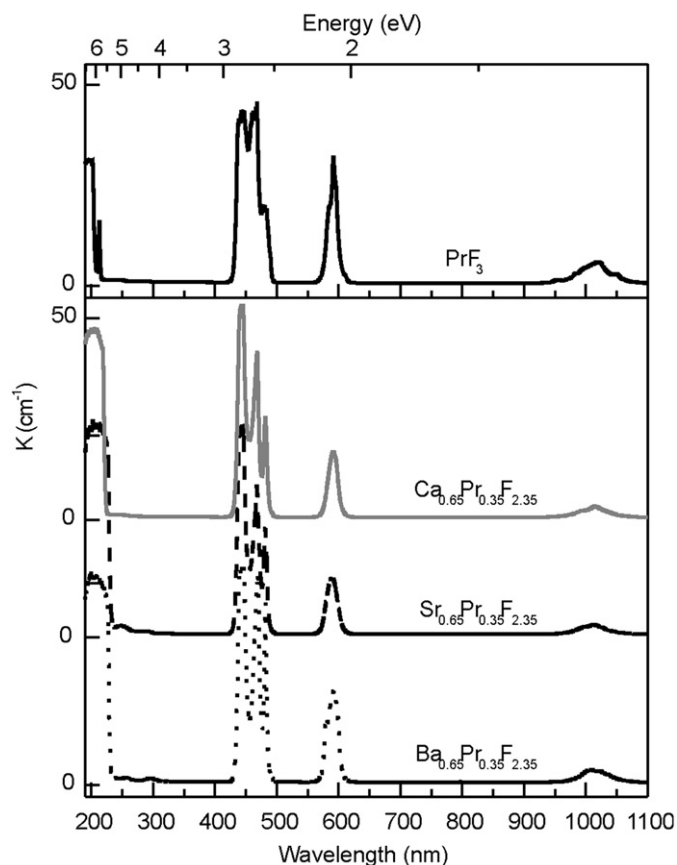


Fig. 1. Absorption spectra of PrF_3 and $\text{M}_{1-x}\text{Pr}_x\text{F}_{2+x}$ crystals.

in $\text{Ca}_{0.65}\text{Pr}_{0.35}\text{F}_{2.35}$ crystals corresponds to $^3\text{H}_4 \rightarrow ^1\text{S}_0$ transition. While excitation of $\text{Ca}_{0.65}\text{Pr}_{0.35}\text{F}_{2.35}$ in the high-energy region (8.0 eV) gives rise to emissions mainly from $4f^2 \rightarrow 4f^2$ transitions, stimulation at low-energy band (5.6 eV) results in strong 5d 4f \rightarrow 4f 2 emission as well as long wave 4f $^2 \rightarrow$ 4f 2 luminescence. This fact points to the presence of several types of emission centers with different 5d 4f levels location. In $\text{Sr}_{0.65}\text{Pr}_{0.35}\text{F}_{2.35}$ crystals the redistribution between 5d 4f \rightarrow 4f 2 and 4f $^2 \rightarrow$ 4f 2 transitions upon selective excitation is less pronounced.

The weak broad excitation bands in the range 9.0–12.0 eV may be connected with CT transitions to Pr^{3+} ion [11,12] and perturbed excitonic states near Pr^{3+} . Light yield is low at high excitation energies ($E > E_g$) due to large energy losses in the process of energy transfer.

X-ray luminescence spectra of $\text{M}_{0.65}\text{Pr}_{0.35}\text{F}_{2.35}$ crystals measured at 77 K are similar to photoluminescence spectra under the excitation within the range 6.0–12.0 eV. This fact points to energy transfer from the host to the emission centers.

Typical decay curves under photo- and X-ray excitation for $\text{Ca}_{0.65}\text{Pr}_{0.35}\text{F}_{2.35}$ crystal is shown in Fig. 4. UV luminescence with the decay component of 14 ns corresponded to 5d 4f transitions in Pr^{3+} whereas for emission originating from $^1\text{S}_0$ level the decay time $\tau_2 \geq 160$ ns is typical. Slow component ($> 2 \mu\text{s}$) was observed for long-wave emission (482–608 nm) connected with ($^3\text{P}_0 \rightarrow ^3\text{H}_{4,5,6}$) transitions. In addition, the ultrafast decay component ($2 < \tau < 5$ ns) was found which may be due to the energy transfer between 5d 4f and $^1\text{S}_0$ levels of different emission centers.

Luminescence of mixed compounds under photo- and X-ray excitation decreases with temperature rise from 8 to 297 K. At RT 5d 4f \rightarrow 4f 2 and $^1\text{S}_0 \rightarrow ^3\text{H}_6, ^3\text{F}_4, ^1\text{G}^4, ^1\text{D}_2$ transitions are dominant while emission originating from $^3\text{P}_0$ level is quenched.

Download English Version:

<https://daneshyari.com/en/article/5402245>

Download Persian Version:

<https://daneshyari.com/article/5402245>

[Daneshyari.com](https://daneshyari.com)