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Study of the photoluminescence kinetics of heterogeneous nanostructured $Pb_{0.30}Cd_{0.70}I_2$ solid solutions

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HIGHLIGHTS

- Photoluminescence kinetics of strongly heterogeneous $PbCdI_2$ alloys was analyzed.
- Nature of various PL bands in PbI_2 NCLs embedded in CdI_2 matrix are discussed.
- Fitting the data via KWW and a sum of simple exponential functions were compared.
- Rate constant and lifetime distributions were obtained using these two methods.
- A way to develop new fast effective scintillation nanomaterials was pointed out.

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ABSTRACT

The study of photoluminescence (PL) kinetics for strongly heterogeneous materials such as nanostructured scintillator $Pb_{0.30}Cd_{0.70}I_2$ solid solutions was carried out. Fitting the obtained results by Kohlrausch-Williams-Watts exponential function allows us to obtain the effective lifetime and the lifetime distribution for the PL decay. At the same time, fitting by a sum (about several hundreds) of single exponential functions enables us to determine the lifetime distribution associated with different radiative recombination processes characteristic of the investigated novel semiconductor materials. It was found that the radiative recombination of free electrons and holes associated with the deep surface acceptor centers is a fast process. The obtained results open a way to optimize defect structure of the investigated semiconductor materials in order to obtain high-sensitive fast non-cooled radiation detector material for X- and γ-rays suitable for biomedical and industrial imaging applications.

1. Introduction

At present, there is a strong need to develop new semiconductor materials for use in modern optoelectronics. In particular, the study of novel scintillation materials relates to very important tasks in solid-state physics, chemistry and materials science. It allows us to elaborate effective scintillator detectors which are suitable for the biomedical and industrial imaging applications [1–5]. One of the important parameters of devices, developed on the basis of the semiconductor materials is a fast response, which greatly determines their performance [6–8]. This parameter, which depends on the presence of the intrinsic and impurity defects in the materials, is determined by their electronic properties. In this case various radiative recombination processes with different lifetimes may occur due to the existence of different defects in such materials.

It is known that time-resolved photoluminescence (PL) spectroscopy of semiconductor materials allows us to study the time evolution of PL spectra and thus to obtain information about their nature [9]. Another spectroscopic method based on the measurements of PL decay gives us the opportunity to measure kinetics of the PL spectra [10,11]. As a result, we can obtain such important information as an average lifetime as well as the lifetime distribution. It should be noted that in the case of studying the PL decay it is very important to establish the nature of radiative recombination processes of the investigated materials since this allows us to obtain information about the type of defects associated with these processes. The control of structural defects opens up the possibility to optimize the performance of semiconductor materials.

In this report we study the PL kinetics of $Pb_{0.30}Cd_{0.70}I_2$ solid

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solutions, which relate to novel nanostructural scintillation materials [9,12–14], using different analysis methods. This allows us to determine the lifetime distribution characteristic of the investigated highly heterogeneous semiconductor materials. It was shown that observed three lifetime distribution bands in the time range from several tens of ns to about one μs are associated with different radiative recombination processes in $Pb_{1-X}Cd_XI_2$ solid solutions. In particular, it was found that the radiative recombination of free electrons and holes associated with the deep surface acceptor centers is a fast process. We also discuss ways to improve the performance of these materials on the basis of the obtained results.

2. Methods

The steady state PL measurements were carried out using a MAYA2000-pro spectrometer (Ocean Optics) with a variable temperature liquid-helium cryostat. The temperature stabilization performed by the UTREKS system was 0.01 K [18–20]. The PL spectra were excited by LED with $\lambda = 385$ nm and the power of 100 mW.

The results of PL decay were obtained at room temperature using an Edinburgh Instruments LifeSpec2 lifetime spectrometer. In this case the crystal samples were excited using LED pulse laser with a wavelength of 405 nm (EPL405). The temporal width of the pulse was about 60 ps with a peak power of 80 mW.

Analysis of experimental results was performed using two methods. The first method is based on fitting the experimental data by Kohlrausch-Williams-Watts function, that is, using the following equation: $I(t) = I_0 e^{\left(-t/\tau\right)^{\beta}}$ [15]. This allows us to get a number of important kinetic parameters for the investigated crystals such as the average lifetime and the common lifetime distribution. The other method allows us to obtain the lifetime distribution using fitting the experimental data by a sum of exponential functions $I(t) = \sum_{i=1}^{N} F_{\tau_i} e^{-\frac{t}{\tau_i}}$ (up to several hundreds) with fixed lifetime intervals. In this case we can determine the lifetime distributions with more than one peak that are associated with different recombination processes.

3. Results and discussion

3.1. Characterization of $Pb_{1-X}Cd_XI_2$ solid solutions

The $Pb_{1-X}Cd_XI_2$ ($X = 0.70$) semiconductor solid solutions show intense photo- and X-ray luminescence both at low and room temperatures [9,12,13]. Thus, these materials have promising prospects for applications in new generations of devices for biomedical diagnostics and industrial imaging applications.

The $Pb_{0.30}Cd_{0.70}I_2$ alloys were grown by the vertical Bridgman technique. The synthesis of the crystals was performed by means of direct alloying of the constituents in sealed quartz ampoules under vacuum of 10^{-5} Torr. The melting point of alloys was 410 C. The crystal growth was performed by dropping the ampoule at a rate of about 3 mm/h. We prepared an ingot of 30 mm length and 8 mm in diameter. Then we cleaved it perpendicular to c-axis. The area of each sample was 4×7 mm^2 and the thickness was about 3 mm. The investigated alloys are single crystals.

It should be pointed out that both PbI_2 and CdI_2 are layered semiconductor crystals with hexagonally close-packed lattice [16,17]. Earlier, we have shown that PbI_2 nanoclusters (NCLs) are naturally formed during $Pb_{1-X}Cd_XI_2$ growth and have different sizes (from several nm to hundreds nm) [9]. Their surface morphology obtained using a JEOL JSM-T220A scanning electron microscope is shown in Fig. 1. Here a back-scattered electron (BSE) regime was used. In this case the high-energy electrons are reflected or backscattered out of the sample volume by elastic scattering interactions with sample atoms. The image of heavy atoms is brighter than that for light atoms since the former backscatter electrons more strongly. Therefore, the brightness contrast of BSE images indicates the areas with different chemical compositions. The atomic number of Pb atoms (82) is considerably larger than that for Cd atoms (48). Thus, the bright spots in the SEM images indicate the formations of NCLs in the alloys with the participation of Pb atoms. This indicates that the bright spots in SEM image of $Pb_{1-X}Cd_XI_2$ alloys correspond to various sizes PbI_2 NCLs. For example, Fig. 1 shows small NCLs (about 10 nm) in the area 1, and large NCLs (a few hundred nm or crystallites of submicron sizes) in the area 2.

As a result of X-ray diffraction measurements performed using STOE STADI P diffraction system, it was shown that only PbI_2- (43.5 mol %) and CdI_2- phases (43.5 mol %) of 4H-polytype as well as PbI_2- and CdI_2- phases of 2H-polytypes (13 mol %) are present. The absence of any metallic inclusions of Pb or Cd atoms was shown. It should be noted that the formation of the cadmium clusters was observed for non-stoichiometric pure CdI_2 crystals as a result of the long-term effects of aging [21–23]. It was shown that the presence of these metallic clusters may affect the optical properties of CdI_2 crystals.

It should be noted that both PbI_2 and CdI_2 crystals of 4H-polytype relate to a space group of $P6_3mc$ symmetry. In this case a unit cell includes two layers (I-Pb-I or I-Cd-I), which are shown in Fig. 2. Here, as for any three-dimensional lattice, there are three vector lengths (a, b, c) and three angles between them (α, β, γ). The lattice parameters and the angles for PbI_2 and CdI_2 crystals of 4H-polytype are presented in Table 1.

As can be seen from Table 1, the angles for both crystals are the same and the lattice parameters for CdI_2 are slightly less than for PbI_2. The unit cell volumes of these crystals are 251.022 Å^3 and 212.829 Å^3 for PbI_2 and CdI_2, respectively. Thus, there are favorable conditions for partial replacement of I-Cd-I layers by I-Pb-I. This means that it may be easy for $Pb_{1-X}Cd_XI_2$ solid solutions to form. However, it should be noted that $Pb_{1-X}Cd_XI_2$ alloy is a non-isoelectronic system because the valence electrons of Pb and Cd atoms belong to the different electronic configurations, namely ($5d^{10}6s^26p^2$) and ($4d^{10}5s^2$), respectively [1,3,4]. PbI_2 energy structure is such that the valence band and the conduction band are composed mainly of electronic states of Pb^{2+} ions (p-state of Pb^{2+} and 90% s-state Pb^{2+}, respectively). In this crystal the appearance of excitons is due to the excitation of Pb^{2+} ions and the transfer of energy between them. For CdI_2 crystal the valence band and the conduction band are formed by the p-state of I and s-state of Cd^{2+} ions, respectively.

In our opinion, the formation of bulk nanostructured $Pb_{0.30}Cd_{0.70}I_2$ alloys is a result of non-isoelectronic substitution of cation sites and may be associated with spinodal decomposition of these alloys. Bulk nanostructured materials are defined as bulk solids with nanoscale or partly nanoscale microstructures. These materials have very complex crystal structures. Their heterogeneous structure on a nanometer scale is crucial for many of their properties and distinguishes them from glasses, which are microstructurally homogeneous.

The spinodal decomposition phenomenon is well-known in various intermetallic [24] and polymer blend systems [25,26], but less is known about it in semiconductors [27–30]. As a result of spinodal decomposition a solution of two or more components can separate into distinct phases with different chemical compositions and material concentrations. Phase separation may also occur outside of the spinodal decomposition region via the nucleation and growth mechanism. It should be noted that the mechanism of the phase segregation depends on the local composition [31].