Journal of Luminescence 185 (2017) 83–91

Contents lists available at ScienceDirect

Journal of Luminescence

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

Full Length Article

Nature of radiative recombination processes in layered semiconductor $PbCdI_2$ nanostructural scintillation material

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ARTICLE INFO

Article history:
Received 14 July 2016
Received in revised form
5 December 2016
Accepted 28 December 2016
Available online 7 January 2017

Keywords:
Semiconductor scintillation nanomaterials
nanoclusters
luminescence
excitons
deep surface states

ABSTRACT

We report on the efficient photoluminescence (PL) and radioluminescence (RL) of the PbI_2 nanoclusters (NCLs), which are naturally formed in the nanostructured $Pb_{1-X}Cd_XI_2$ alloys (X=0.70). Here, we carried out the studies of the nature of radiative recombination processes in the NCLs of various sizes by measuring PL temperature evolution. Our results indicate that at low temperatures the PL is mainly caused by exciton emission and recombination of donor-acceptor pairs, generated in volume of large NCLs. The broad bands, which are associated with the deep intrinsic surface states, including self-trapped excitons (STEs), are dominant in the PL spectra at higher temperature (> 100 K). Our work shows that the nature of emission, associated with RL bands is analogous to that for PL bands. It was shown that the investigated nanostructured material is strongly radiation-resistant. Thus, the $Pb_{1-X}Cd_XI_2$ alloys can be considered as new effective layered semiconductor nanostructured materials which can be suitable for the elaboration of perspective semiconductor scintillators. These nanomaterials have promising prospects for applications in new generations of devices for biomedical diagnostics and industrial imaging applications.

1. Introduction

The quantum confinement effect in semiconductor nanocrystals has attracted considerable attention due to their intriguing physical and chemical properties and potential use in opto-electronic and electronic devices [1–3]. The main consequence of the effect is observed shift of the exciton photoluminescence (PL) bands towards higher energies in relation to the bulk crystals, which increases when the size of the nanocrystals goes up. It makes it possible to tune the PL spectra from ultraviolet to near-infrared wavelengths by means of changing the sizes of the nanocrystals. Small nanoparticles, in particular, nanoclusters (NCLs), have important characteristic: the large ratio of surface to volume atoms, which causes numerous surface defects trapping the carriers. Thus, the optical and electronic properties of NCLs strongly depend on their sizes and the crystal structure of semiconductor materials.

The semiconductors with layered structure are of great interest, because small NLCs with the sizes of several nm contain one or multiple crystal layers [4,5]. Thus, these nanostructured materials are similar to low-dimensional materials that are intensively researched due to their excellent electronic properties and potential applications in the nanoelectronics [6]. Among the semiconductor NCLs with layered structure, PbI_2 is an attractive material because of the wide band-gap (2.53 eV) for the bulk crystals and its large exciton binding energy of 63 meV [7-10]. It was found that these crystals show exciton luminescence at room temperature with nano- and subnanosecond lifetime [11–14]. A number of works are available devoted to the study of the lead iodide optical properties, because this semiconductor crystal is considered as a very perspective high-sensitive non-cooled radiation detector material for X- and γ-rays suitable for biomedical and industrial imaging applications [15–19]. The use of $Pb_{1-X}Cd_XI_2$ alloys may allow to expand the luminescence spectral range of such materials and thus to improve their scintillator characteristics. At the same time, the mechanisms of radiative recombination in any semiconductors used as scintillation materials remain relatively unexplored.

PbI_2 is a direct semiconductor with repeating unit of hexagonally closed-packed I–Pb–I of 0.7 nm-thick layers arranged perpendicularly along the *c* axis [19,20]. Usually, the PbI_2 NCLs are formed as colloidal solutions, in borosilicate glass matrix, in polymeric and porous silica films [12,21–27]. Besides, the room temperature PL of the PbI_2 NCLs embedded in $Pb_{1-X}Cd_XI_2$ alloys was studied [9–11,13, 14,20,28]. It should be noted that these NCLs are naturally formed in $Pb_{1-X}Cd_XI_2$ as a result of non-isoelectronic

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http://dx.doi.org/10.1016/j.jlumin.2016.12.054
0022-2313/

substitution of cation sites and may be associated with spinodal decomposition of these alloys. It was found that PbI_2 NCLs in the alloys show the room-temperature PL and the radioluminescence (RL) of strong intensity [10,29]. It should be noted that at present the moderately dense PbI_2 semiconductor is considered as ideal scintillator, since this material may provide a combination of high light output and short decay time [30,31]. Thus, the nature of the radiative recombination processes in these materials requires detailed study that will allow optimizing scintillation properties of these materials.

It has been shown that the intrinsic defects, including the self-trapped excitons (STEs), largely determine the PL properties of PbI_2 nanoparticles [11,14,28]. It was shown theoretically by using silicon nanocrystals of small sizes as an example, that the STEs are intrinsic localized states, which act as deep luminescent surface states and are characteristic of any semiconductor materials [32–34]. However, a number of issues still remain open. In particular, there are insufficient experimental studies of the formation of these surface states by means of excitation of delocalized excitonic states in NCLs of various sizes for strongly structurally heterogeneous systems.

In the study presented here, we have investigated the nature of radiative recombination processes in the layered PbI_2 NCLs of various crystallite sizes and their temperature evolution. Understanding of these processes is an important issue that is of interest both for physics and materials science, because the deep surface states in the layered NCLs may play an important role in the intense RL at room temperature and thus the output of these scintillating materials. It is expected that radiation detectors based on PbI_2 nanoscintillators have promising prospects for applications in new generations of devices for medical and industrial diagnostics as well as radiation monitoring of nuclear reactors.

2. Experimental

The $Pb_{1-X}Cd_XI_2$ alloys were grown by the Bridgman technique. The synthesis of the crystals was performed by means of direct alloying of the constituents in sealed quartz ampoules under vacuum. We prepared the ingot of 30 mm length and 8 mm diameter. Then we cleaved it perpendicular to c-axis. The area of each sample was 4x7 mm^2 and the thickness was 3 mm. The investigated alloys are single crystals. The resistivity of the investigated crystal samples was estimated to be about 10^{14} Ωcm. The sample composition was determined by the electron probe microanalysis. As a result of X-ray diffraction measurements performed using STOE STADI P diffraction system, it was shown only the presence of 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 %). The absence of any metallic inclusions of Pb or Cd atoms was shown.

The steady state photoluminescence measurements were carried out using an MAYA2000-pro spectrometer (Ocean Optics) with a variable temperature liquid-helium cryostat. The temperature stabilization by the UTREKS system was 0.01K [35,36]. The PL spectra were excited by LED with $\lambda = 385$ nm and the power of 100 mW. In this case uniform illumination of the sample surface was provided using a fiber with the diameter of 600 µm. Photodiffusion current (PDC) spectra were measured using the mesh and continuous In-Ga-Sn paste electrodes deposited on the polished front and rear faces of the plane-parallel crystal samples, respectively. The illumination of the samples produces a PDC perpendicular to the crystal surface, which lead to nonuniform depth-distribution of excess minority carriers in the crystal. Unlike photoconduction (PC) measurements of photoionization transitions, caused by optical transitions between defect (donor or acceptor) levels and energy bands of the crystal, the PDC method makes it possible to determine not only the energy but also the type of photoionization (from a defect level to the conduction band or from the valence band to defect levels). Analysis of the PDC spectra let us obtain more complete data regarding the photoionization transitions. This technique is described in more detail in work [37].

3. Results and discussion

3.1. Photoluminescence of excitons and donor-acceptor pairs in large PbI_2 NCLs

It should be noted that PbI_2 and CdI_2 crystals have the same crystal structure of D_{3d} – symmetry that corresponds mainly to 4H polytype [38,39]. Since the valence electrons of Pb and Cd atoms belong to the different electronic configurations, namely ($6s^26p^2$) and ($5s^2$), respectively, $Pb_{1-X}Cd_XI_2$ alloy is a nonisoelectronic and nonuniform system [10,13]. Thus, such alloys present the three-dimensional nanostructured semiconductor material with randomly distributed PbI_2 NCLs [11].

For PbI_2, the valence band and the conduction band are determined mainly by the electronic states of Pb^{2+} ions. So, the appearance of excitons in these crystals is caused by the excitation of Pb^{2+} ions and the transfer of energy between them. The observed exciton PL line for the alloys is associated with two exciton states of Γ_3^- and Γ_1^- symmetry, which are related to the $^3P_1$ – and $^3P_0$ – states of free Pb^{2+} ions, respectively. Here, the optical transitions from the lowest Γ_1^-– state are dipole-forbidden and from exciton Γ_3^- state are partially dipole-allowed [13,40]. For isolated Pb^{2+} ions, the energy between these state is equal to 75 meV [13]. For PbI_2 crystals, this value corresponds to 2 meV and should increase for small PbI_2 NCLs.

The temperature dependence of steady state PL spectra of the investigated $Pb_{1-X}Cd_XI_2$ (X=0.70) alloys is presented in Fig. 1A. It contains multiple peaks with different intensity, location and width. We used "Peak Analyzer" tool in OriginPro 8 to fit the obtained spectra [41]. It was found that the observed PL spectra at different temperatures can be described by six components as it is shown in Fig. 1B at T=4.5 K.

At low temperatures, the intense emission is observed in short-wavelength spectral region. The narrow PL line at 4947 Å (2.508 eV) corresponds to the emission of excitons bound on the neutral donors, i.e., D^oX-line [39]. The energy position of this line is close to that of the exciton line (2.509 eV) observed for $Pb_{1-X}Cd_XI_2$ alloys of 4H-modification with small Cd atoms concentration (X=0.02) [9]. This means that the observed narrow PL line at 2.508 eV is caused by the exciton emission in the large PbI_2 NCLs with low concentration of Cd atoms.

The temperature dependences of the energy position, full width at half maximum (FWHM) and the integrated intensity of this PL line, which we named E line, are shown in Fig. 3. In particular, the temperature dependence of the energy position of this line (Fig. 2A) indicates that its energy position is unchanged up to 10 K and then it is shifted to 4927 Å (2.516 eV) at T=80 K. It should be noted that the energy position is determined by the emission of both the bound and free excitons. The latter contribution increases with temperature and becomes dominant at T $\geq$ 50 K. This assumption is supported by the measurements of the temperature dependence of the FWHM value of exciton PL line (Fig. 2B) which initially increases with temperature up to about 50 K, and then it decreases at higher temperatures. This indicates that the emission of free excitons is a decisive factor in the temperature range above 50 K. Strong decrease of integrated intensity of exciton line at T $\leq$ 50 K is also caused by the reduction of the bound exciton