Fast Scintillation Processes in CsCl Crystals Comprising Semiconductor Nanocrystals

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Abstract

We analyzed the scintillation mechanism in CsCl single crystals comprising CsPbCl₃-like semiconductor nanocrystals. A decay component with a subnanosecond lifetime was observed and ascribed to the exciton luminescence in the nanocrystals. This is the first observation of scintillation from semiconductor nanocrystals. In addition, slower components were observed and ascribed to the intraionic transition at isolated Pb²⁺ ions and the Auger-free luminescence in the CsCl matrix. Furthermore, it was shown that the nanocrystals absorbed and reemitted the scintillation photons from the isolated Pb²⁺ ions. The results in this report clearly indicates that the semiconductor nanocrystals function as ultrafast “luminescent centers,” and complicated scintillation dynamics are observed due to the luminescence from different components in the crystal and the radiative energy transfer between them.

Introduction

A vast number of luminescent materials based on semiconductor nanostructures have been developed during the past two decades, and excellent luminescent properties have been reported. Luminescence from semiconductor nanostructures arises mainly from excitons, i.e., the hydrogen-atom-like bound state of an electron and a hole. The characteristics of excitons in semiconductor nanostructures are considerably different from those in corresponding bulk semiconductors due to the confinement of semiconductor nanostructures to a nanometer scale, leading to luminescent properties that are characteristic to semiconductor nanostructures. The main characteristics of the exciton luminescence in semiconductor nanostructures are high efficiency and fast decay, and these characteristics are suitable for their use as scintillating materials.

Scintillating materials with high luminescence efficiency and fast scintillation decay have been desired for constructing an advanced scintillation detector having excellent timing properties, high energy resolution, and the ability to operate at a high counting rate. In most conventional scintillating materials, scintillation occurs due to luminescence from luminescent centers such as rare-earth or transition metal ions, and the scintillation lifetime is several tens of nanoseconds or longer. Due to the limited number of dopant elements, it is very difficult to fabricate scintillating materials having a considerably shorter lifetime by a conventional approach. Thus, another approach is necessary for achieving both high efficiency and short lifetime, and semiconductor nanostructures are one of the promising scintillating materials. In fact, the authors have been fabricating scintillating materials based on semiconductor quantum wells and reported their excellent scintillation properties (Shibuya et al., 2002, 2004a, 2004b).

In this paper, we report the scintillation mechanism of scintillating materials doped with semiconductor nanocrystals. We investigated the scintillation properties of CsCl:Pb single crystals comprising CsPbCl₃-like semiconductor nanocrystals. Thus far, luminescent properties of these nanocrystals have been investigated by optical excitation (Nikl et al., 1995, Aceves et al., 2001, Voloshinovskii et al., 2001a, 2001b). In particular, an extremely short radiative lifetime was

reported under optical excitation and was attributed to the large oscillator strength of free excitons (Nikl et al., 1995). Thus, this system is considered to be a promising candidate for a fast scintillating material. However, the scintillation properties of this system have not yet been analyzed. In contrast to the case of optical excitation, the deexcitation process of excited states produced by ionizing radiation is complicated due to the following reason: excited states are mainly produced in an insulating matrix as well as in semiconductor nanocrystals, while under optical excitation, excited states are produced only in the nanocrystals. Thus, the luminescence from the insulating matrix is also important. In this paper, the scintillation dynamics of scintillating materials comprising semiconductor nanocrystals are presented, and a scintillation component due to free excitons in the nanocrystals is observed for the first time.

Experimental

Single crystals of CsCl:Pb were fabricated by the Bridgman-Stockbarger method. The starting materials were high-purity powders of CsCl (99.999%) and PbCl₂ (99.999%) purchased from Aldrich, and these powders were used without further purification. The molar concentrations of PbCl₂ in the melt were 0.1, 2, and 10%, and these samples are hereafter referred to as CsCl:0.1%Pb, CsCl:2%Pb, and CsCl:10%Pb, respectively. After crystal growth, the sample crystals were annealed at 673K and 473K in order to isolate and aggregate the Pb²⁺ ions, respectively. A single crystal of CsPbCl₃ was also grown and used as a sample for comparison. Typical sample size was 5mm × 5mm × 1 mm. Luminescence spectra of the samples were measured under excitation at 325 nm by using a He-Cd laser to analyze the luminescent properties of CsPbCl₃-like aggregates and the CsPbCl₃ single crystal.

The scintillation characteristics of the samples were measured using a pulsed electron beam from a linear accelerator at the Nuclear Professional School, The University of Tokyo. Scintillation from the samples, induced by the pulsed electron beam, was monitored using an multi-channel-plate (MCP)-mounted photomultiplier tube (PMT; Hamamatsu, R3809-50), and the output signal was

recorded using a digital oscilloscope (HP, Infinium 54845A). The time resolution of the measuring system was approximately 300 ps. In order to analyze the decay characteristics in different wavelength regions, optical bandpass filters were placed in front of the PMT window. Details of the measuring system have been reported elsewhere (Shibuya et al., 2007).

Results and Discussion

Figure 1 shows the luminescence spectra of the Pb-aggregated CsCl:10%Pb crystal and the bulk CsPbCl₃ crystal under 325-nm excitation at room temperature. In this case, only the CsPbCl₃-like nanocrystals were excited in the CsCl:10%Pb crystal. For both samples, sharp luminescence bands were observed in the range 400–420 nm, similar to the observation reported in a previous report (Nikl et al., 1995), and these bands possibly resulted from free excitons or shallow-trapped excitons. The luminescence wavelengths of the free excitons in the bulk crystal and nanocrystals were different and ascribed to the following two factors (Nikl et al., 1995). (i) The quantum confinement effect may occur due to the small nanocrystalline size. In this case, the exciton luminescence shifts to a shorter wavelength. (ii) A slight mismatch between the lattice structures of CsCl and CsPbCl₃ crystals causes a slight distortion in the lattice structure of the CsPbCl₃ nanocrystals. In this case, the bandgap energy changes according to the distortion in the crystal structure, leading to the change in the exciton luminescence wavelength.

The temperature dependence of the luminescence intensity under the 325-nm excitation is shown in Fig.2. The luminescence intensity of the bulk crystal was high at low temperature and decreased strongly with increasing temperature. In contrast, the decrease in the luminescence intensity of the CsCl:Pb sample was weaker, and the intensity was higher at room temperature. This result clearly shows that thermal quenching is reduced in the nanocrystals. This can be explained partly by the enhanced binding energy of the free excitons in the nanocrystals due to the quantum confinement effect, leading to higher thermal stability. Another possible reason is the limited motion of the free excitons confined in the nanocrystals, which results in a lower probability of their

encounter with nonradiative centers; this in turn leads to less reduction in the luminescence intensity at elevated temperatures.

Figure 3 shows the scintillation time profiles for the Pb-aggregate samples with different Pb^{2+} concentrations. The spike-like noise after 10 ns is considered to be RF noise from the linear accelerator (Shibuya et al., 2007). An ultrafast decay component was observed as the Pb^{2+} concentration increased, and this component is possibly a result of the exciton luminescence in the nanocrystals. This hypothesis is supported by the result shown in Fig.4, where the scintillation time profiles of Pb-aggregated and Pb-isolated CsCl:10%Pb are compared. The ultrafast decay component can be observed only for the Pb-aggregated sample. Hereafter, we focus on samples with the largest Pb^{2+} concentration, i.e., CsCl:10%Pb, because it is anticipated that the scintillation from the nanocrystals of these samples can be observed at the highest intensity.

The time profiles shown in Fig.4 were fitted with the sums of two or three exponentially decaying functions. The obtained functions are shown in Fig.4 along with the experimental data, and the obtained lifetimes and relative intensities are summarized in Table 1. It should be noted that the scintillation time profile of Pb-aggregated CsCl:10%Pb had a subnanosecond component, and this component was not observed for the Pb-isolated sample. In addition, two components were obtained from the scintillation time profile of the Pb-isolated sample, and these components almost coincide with two longer components of the Pb-aggregated sample.

Next, the decay kinetics in each wavelength region are analyzed by a spectroscopic method using bandpass filters centered at 286, 359, and 413 nm, which correspond to the Auger-free luminescence of CsCl (Kubota et al., 1988), luminescence from isolated Pb^{2+} ions, and the free exciton luminescence in the nanocrystals, respectively. The scintillation time profiles were fitted with the sums of 1–3 exponentially decaying functions, and the obtained lifetimes and relative intensities are presented in Table 2.

We observed a single component with a lifetime of 2.0 ns at around 286 nm. Similar decay characteristics were also observed for a pure CsCl single crystal, and these characteristics are attributed to the Auger-free luminescence (Itoh et al., 1997).

It is clearly observed that a subnanosecond component dominates the scintillation time profile of the Pb-isolated sample at around 413 nm. The lifetime of this component almost coincides with that of the shortest component of the Pb-aggregated sample under the condition of no filtering, and this subnanosecond component is observed only for the Pb-aggregated samples. It was reported that under optical excitation at 10 K, the free excitons in the CsPbCl₃ nanocrystals have a subnanosecond luminescence lifetime (Nikl et al., 1995). As shown in Fig.2, the luminescence intensity of the nanocrystals decreases with temperature, resulting in a shorter luminescence lifetime. Thus, the excitons in the nanocrystals are expected to have a subnanosecond luminescence lifetime at room temperature, and the subnanosecond scintillation component can be ascribed to the luminescence of the excitons in the nanocrystals. To the best of our knowledge, this is the first observation of scintillation from semiconductor nanocrystals. The two longer components observed in this wavelength region are discussed later.

The scintillation time profile of the Pb-isolated sample at around 359 nm consists of two components, and these components can be attributed to the luminescence from the isolated Pb²⁺ ions. It is natural to consider that multiple energy levels are involved in the luminescence from the isolated Pb²⁺ ions (Aceves et al., 1998); however, a detailed study of this luminescence is necessary for further verification. Similar decay components are observed in the case of the Pb-aggregated sample at around 359 nm, and this result indicates that some of the isolated Pb²⁺ ions remain even after annealing at 473K. In addition, a subnanosecond component that can be attributed to the free exciton luminescence at around 413 nm is observed, and this component cannot be excluded due to the wide FWHM (full width at half maximum) of 32 nm of the bandpass filter.

Next, we discuss the origin of the two longer components observed in the case of the Pb-aggregated sample at around 413 nm. The lifetimes of these components are similar to those of the luminescence from the isolated Pb²⁺ ions. However, judging from the narrow FWHM of the bandpass filter (10 nm), the luminescence from the isolated Pb²⁺ ions is substantially eliminated. The abovementioned similarity can be explained by considering the absorption of the luminescence from the isolated Pb²⁺ ions and reemission by the nanocrystals. The nanocrystals can absorb the

luminescent photons from the isolated Pb^{2+} ions because the energy of the luminescent photons lies above the bandgap energy of CsPbCl_3 . In this experiment, the entire sample was excited by the electron beam, and the maximum optical pass length of the emitted photons is as long as 1 mm. Thus, some of the luminescent photons at around 359 nm from the isolated Pb^{2+} ions are absorbed by the nanocrystals, and subsequently, luminescent photons are emitted from the nanocrystals at around 413 nm. Because the luminescence lifetime of the nanocrystals is considerably shorter than that of the isolated Pb^{2+} ions, the scintillation lifetimes due to absorption and reemission almost coincide with those of the isolated Pb^{2+} ions. Similar behavior was observed for similar samples under UV excitation (Voloshinovskii et al., 2001a), and this process of absorption and reemission, or radiative energy transfer process, is often used in organic scintillating materials for shifting the scintillation wavelength. It may be anticipated that the second longest component of the Pb-aggregated sample at around 359 nm is due to the absorption of the Auger-free luminescence and reemission by the isolated Pb^{2+} ions. However, it is considered that the contribution of absorption and reemission is very small due to the following reasons. (i) If the isolated Pb^{2+} ions do not have any luminescence lifetime component that is faster than the Auger-free luminescence, the reemission lifetime should be significantly longer than that of the Auger-free luminescence. Thus, the second longest component at around 359 nm does not correspond to the absorption of the Auger-free luminescence and reemission. (ii) If the isolated Pb^{2+} ions have a luminescence lifetime component faster than the Auger-free luminescence, the second longest component may correspond to the absorption and reemission of the Auger-free luminescence, and the component faster than the Auger-free luminescence should appear. However, such a component cannot be observed. Thus, in this case as well, the absorption and reemission of the Auger-free luminescence are excluded from being the origins of the second longest component.

On the basis of the abovementioned discussions, we discuss the scintillation process in the Pb-aggregated sample. Figure 5 shows the schematics of the Pb-aggregated sample and the corresponding scintillation components. The CsCl matrix emits scintillation photons in a lifetime of 2.0 ns, as confirmed in the scintillation time profile filtered at around 286 nm. There are two

components in the scintillation time profile of the isolated Pb^{2+} ions, and some of the scintillation photons are absorbed by the nanocrystals. In addition, there are three components in the scintillation time profile of the nanocrystals, and the two longer components are ascribed to the absorption and reemission of the luminescent photons from the isolated Pb^{2+} ions. Thus, we can ascribe the three components of the scintillation time profile of the Pb-aggregate $\text{CsCl:10\%Pb}$ to the following factors. (i) The first component is ascribed to the free exciton luminescence in the nanocrystals. (ii) The second component is attributed to the combination of the Auger-free luminescence in the matrix, the fast component of the isolated Pb^{2+} ions, and the absorption of this fast component and reemission by the nanocrystals. (iii) The longest component can be ascribed to the long component of the isolated Pb^{2+} ions and the absorption of this long component and reemission by the nanocrystals.

Conclusion

The scintillation dynamics of CsCl:Pb single crystals were observed. CsPbCl_3 -like semiconductor nanocrystals as aggregated Pb^{2+} ions were formed in this crystal by annealing at appropriate temperature, and luminescence due to both the nanocrystals and the isolated Pb^{2+} ions was observed under optical excitation. For the first time, we observed a subnanosecond decay component due to the semiconductor nanocrystals. In addition, we observed scintillation components due to luminescence from the isolated Pb^{2+} ions and the Auger-free luminescence in the CsCl matrix. Furthermore, it was suggested that the coexistence of isolated and aggregated Pb^{2+} ions leads to the absorption of luminescent photons from the isolated Pb^{2+} ions and their reemission by the nanocrystals. It was clearly observed that semiconductor nanocrystals functioned as ultrafast luminescent centers, although the scintillation process in the multicomponent system was complicated.

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Table 1 Lifetimes and relative intensities of scintillation time profiles of CsCl:10%Pb with aggregated and isolated Pb^{2+} ions.

CsCl:10%Pb	Lifetime	$0.42 \text{ ns} \pm 5\%$	$2.0 \text{ ns} \pm 5\%$	$18.3 \text{ ns} \pm 41\%$
(Pb^{2+} aggregated)	Relative intensity	27%	62%	11%
CsCl:10%Pb	Lifetime		$1.7 \text{ ns} \pm 0.4\%$	$17.0 \text{ ns} \pm 9\%$
(Pb^{2+} isolated)	Relative intensity		86%	14%

Table 2 Lifetimes and relative intensities of scintillation time profiles of CsCl:10%Pb with aggregated and isolated Pb^{2+} ions in different wavelength regions.

sample	filter		1st	2nd	3rd
CsCl:10%Pb (Pb^{2+} aggregated)	286 nm	Lifetime	2.0 ns $\pm$ 5%		
		Relative intensity	100%		
	359 nm	Lifetime	0.33 ns $\pm$ 4%	1.9 ns $\pm$ 8%	21.7 ns $\pm$ 41%
		Relative intensity	28%	50%	22%
	413 nm	Lifetime	0.37 ns $\pm$ 4%	2.1 ns $\pm$ 27%	31.5 ns $\pm$ 77%
		Relative intensity	50%	24%	26%
CsCl:10%Pb (Pb^{2+} isolated)	359 nm	Lifetime		1.5 ns $\pm$ 1%	27.5 ns $\pm$ 4%
		Relative intensity		66%	34%

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Fig.1 Luminescence spectra of CsPbCl₃ single crystal and CsCl:10%Pb with aggregated Pb²⁺ ions under 325-nm excitation.

Fig.2 Temperature dependence of exciton luminescences of CsPbCl_3 single crystal and $\text{CsCl:10\%Pb}$ with aggregated Pb^{2+} ions.

Fig.3 Scintillation decay profiles of CsCl:0.1%Pb, CsCl:2%Pb, and CsCl:10%Pb with aggregated Pb²⁺ ions.

Fig.4 Scintillation time profiles of CsCl:10%Pb single crystals with isolated and aggregated Pb^{2+} ions.

Fig.5 Schematic representation of CsCl:10%Pb with aggregated Pb ions²⁺ and the corresponding scintillation components.

Aggregated Pb²⁺ ions (CsPbCl₃-like nanocrystal)

Free exciton luminescence: first component

Absorption and reemission of the luminescence from an isolated Pb²⁺ ion: second and third components

CsCl matrix

Auger-free luminescence: second component

Isolated Pb²⁺ ion

Luminescence from the Pb²⁺ ion: second and third components