Luminescence of CsPbCl₃ Nanocrystals Dispersed in a CsCl Crystal under High-Energy Excitation

A. VOLOSHINOVSKII (a), S. MYAGKOTA (a), A. GLOSKOVSKI¹⁾ (a),
and S. ZAZUBOVICH (b)

(a) *Ivan Franko National University of Lviv, 8 Kirila I Mefodiya Str., 79005 Lviv, Ukraine*

(b) *Institute of Physics, University of Tartu, Riia Str. 142, 51014 Tartu, Estonia*

(Received August 25, 2000; in revised form January 4, 2001; accepted February 2, 2001)

Subject classification: 71.35.Cc; 78.55.Fv; 78.67.Bf; S9.16

The luminescence spectral and kinetic characteristics of CsPbCl₃ nanocrystals, thermally created in a CsCl:Pb single crystal and dispersed in a CsCl matrix, have been studied under excitation by synchrotron radiation in the VUV spectral region (4 to 20 eV). Various components found in the decay kinetics of the 2.98 eV emission have been connected with the direct excitation of the CsPbCl₃ luminescence and with the reabsorption of luminescence of other emitting centers by the CsPbCl₃ nanocrystals. A high-energy shift of the free exciton emission band maximum of the CsPbCl₃ nanocrystals with respect to that observed for a CsPbCl₃ single crystal as well as the shortening of the luminescence decay time are considered from the point of view of quantum size effects.

1. Introduction

CsPbCl₃ nanocrystals produced in CsCl:Pb single crystals, containing 0.05 up to 1 mol% of lead in the melt, in the course of their prolonged (from 20 up to 100 h) annealing at 180 to 220 °C are a new type of semiconducting nanocrystals dispersed in a dielectric matrix showing a clear quantum size effect [1, 2]. The creation of Pb-based nanocrystals, dispersed in a CsCl matrix is accompanied with a structural redistribution of single Pb²⁺v_c⁻ centers creating a cluster like a CsPbCl₃ molecule. A similar redistribution of the single Pb²⁺v_c⁻ center neighbourhood in a NaCl matrix leads to the creation of activator halide nanocrystals, dispersed in a NaCl matrix [3]. This situation is realized in a KCl:Ag crystal, where the increase of activator concentration leads to the creation of AgCl nanocrystals, dispersed in a KCl matrix [4].

A CsPbCl₃ single crystal is characterized by an intense luminescence of free excitons with a decay time of $\tau_f \leq 0.5$ ns [5]. It has been considered as a perspective material for fast scintillators [6]. Owing to that, CsPbCl₃ nanocrystals are of great interest in view of the search of materials suitable for the registration of high-energy radiation in the nanosecond time interval.

The study of luminescence decay kinetics of CsPbCl₃ nanocrystals dispersed in a CsCl matrix is necessary for the clarification of the mechanism of high-energy radiation transformation into intrinsic electronic excitations of CsCl matrix and CsPbCl₃ nanocrystals. From the practical point of view, such investigations allow to establish the possibility of application of these materials for the registration and visualization of high-energy radiation.

¹⁾ e-mail: glos@bigfoot.com

In the present paper, the results of the study of spectral and decay kinetic characteristics of the luminescence of CsPbCl₃ nanocrystals dispersed in a CsCl single crystal lattice obtained under excitation by synchrotron radiation in the VUV spectral region (4 to 20 eV), have been reported.

2. Experimental

Single crystals of CsCl:Pb were grown by the Stockbarger method from zone-refined CsCl salt containing 0.5 mol% of PbCl₂ in the melt. To produce CsPbCl₃ nanocrystals dispersed in a CsCl matrix, the CsCl:Pb crystal was annealed for 20 h at 200 °C after its fast quenching down from 450 °C. Such thermal treatment results in a partial transformation of Pb²⁺v_c⁻ centers, existing in a quenched CsCl:Pb crystal (v_c⁻ is a cation vacancy), into CsPbCl₃ nanocrystals of a fixed size. As not all Pb²⁺v_c⁻ centers were thermally transformed into CsPbCl₃ nanocrystals, both Pb²⁺v_c⁻ centers and CsPbCl₃ nanocrystals were observed in the annealed CsCl:Pb crystal studied.

The time-resolved spectroscopy method was used for the study of the luminescence characteristics. The experiments were carried out at SUPERLUMI station in HASY-LAB (Hamburg, Germany). The crystal was excited by synchrotron radiation passed through a normal incidence 2 m vacuum monochromator (the spectral width of the entrance slit was about 0.2 nm). The luminescence of the crystal located on a crystal holder of a helium cryostat was detected by a photomultiplier through another monochromator B & M. The luminescence decay kinetics was studied under pulse synchrotron excitation (the pulse duration ≈ 0.1 ns; repetition period 480 ns). Time-correlated single-photon counting method with time-to-amplitude conversion was used. The decay time response of the photomultiplier for the exciting pulse was 0.4 ns. The luminescence decay times were determined with account of the exciting pulse duration by using the well-known deconvolution procedure. This procedure allows to estimate the decay times which are about three times as short as the duration of the photomultiplier response for an exciting pulse. The emission and excitation spectra were studied with time resolution. The spectra recorded within a short time window of $\Delta t = 5$ ns we call as fast component, and the spectra recorded within a long time window of $\Delta t = 50$ ns and with a 150 ns delay with respect to the exciting pulse we call as slow component. The experimental procedure was described in more detail in [7].

3. Experimental Results and Discussion

3.1 Spectral characteristics of luminescence

The luminescence spectrum of the annealed CsCl:Pb crystal excited at 10 K in the transparency region of a CsCl:Pb crystal ($E_{\text{exc}} = 5.12$ eV, i.e., 242 nm) is shown in Fig. 1 (curve 1). The narrow (halfwidth FWHM = 0.03 eV) band peaking at $E_{\text{em}} = 2.98$ eV (416 nm) is similar to the free exciton emission band of a CsPbCl₃ single crystal ($E_{\text{em}} = 2.954$ eV, i.e., 419.6 nm; FWHM = 0.025 eV) observed under the same excitation (curve 2). The similarity of the spectra points to the fact that the thermal treatment results in the production of CsPbCl₃ nanocrystals in the CsCl:Pb crystal dispersed in a CsCl matrix.

As the excitation energy increases up to 7.3 eV (170 nm), besides the above-mentioned narrow 2.98 eV band, a broader complex band peaking at 3.94 eV (315 nm) is

Fig. 1. Luminescence spectra of CsPbCl_3 nanocrystals dispersed in a CsCl matrix (curve 1) and a CsPbCl_3 single crystal (curve 2), both measured under 5.12 eV (242 nm) excitation at 10 K

observed in the emission spectrum of the annealed CsCl:Pb crystal (Fig. 2). According to [8], this band arises from the radiative decay of the triplet relaxed excited state of $\text{Pb}^{2+}\text{v}_c^-$ centers in CsCl:Pb . Thus, under excitation of the annealed CsCl:Pb crystal in the CsCl matrix transparency

region (at $E_{\text{exc}} < 7.85$ eV at 10 K [9]), the emission of both $\text{Pb}^{2+}\text{v}_c^-$ centers and CsPbCl_3 nanocrystals is observed. Unlike the single crystal of CsPbCl_3 where only the fast 2.954 eV luminescence has been observed, the fast and the slow components can be detected in the decay kinetics of the 2.98 eV emission of the annealed CsCl:Pb crystal under excitation in some energy regions (Fig. 2, curves 1 and 2). The reason of the appearance of the additional decay components will be explained later.

The excitation spectra of the fast (curve 1) and slow (curve 2) components of the 2.98 eV emission of CsPbCl_3 nanocrystals in a CsCl crystal, of the 2.954 eV emission of a CsPbCl_3 bulk (curve 3) as well as of the fast (curve 4) and slow (curve 5) components of the $\text{Pb}^{2+}\text{v}_c^-$ emission, all measured in the spectral range $E_{\text{exc}} \leq 8$ eV, are shown in Fig. 3. The maxima of the excitation spectrum measured for the fast component of the CsPbCl_3 nanocrystal emission (indicated by arrows) coincide with the corresponding minima in the excitation spectrum of the free exciton luminescence of the CsPbCl_3 single crystal (compare curves 1 and 3). It means that the excitation spectrum of the emission of CsPbCl_3 nanocrystals coincides with their absorption spectrum and that,

unlike in the case of a CsPbCl_3 single crystal, this excitation spectrum is not distorted by the absorption at the nanocrystalline surface. This effect is caused by the small size of the CsPbCl_3 nanocrystals dispersed in the

Fig. 2. Luminescence spectra of the fast (curve 1) and slow (curve 2) decay components measured at 10 K for CsPbCl_3 nanocrystals dispersed in a CsCl matrix under $E_{\text{exc}} = 7.29$ eV (170 nm)

Fig. 3. Excitation spectra a) of the fast (curve 1) and slow (curve 2) decay components of the 2.98 eV emission of the annealed CsCl:Pb crystal, b) of the free exciton 2.954 eV emission of a CsPbCl₃ single crystal (curve 3), and of the fast (curve 4) and slow (curve 5) decay components of the triplet (3.94 eV) emission of Pb²⁺v_c⁻ centers in CsCl:Pb; *T* = 10 K

CsCl crystal lattice. As result of the small size of the nanocrystals, quantum size effects are probably realized, appearing in the high-energy shift of the free exciton emission band of CsPbCl₃ nanocrystals (on about 26 meV) with respect to that observed in a CsPbCl₃ single crystal. Assuming a spherical shape of the nanocrystals, their size can be determined from the relation

$$\Delta E = \frac{\hbar^2 \pi^2}{2\mu R^2},$$

between the value of the high-energy shift ΔE of their emission band and a nanocrystal radius *R* [10]. (Here $\mu = m_0$ is the reduced exciton mass in the CsPbCl₃ single crystal; m_0 is the free electron mass [11, 12].) The average size of the CsPbCl₃ nanocrystals studied is estimated to be about 4.7 nm, which allows to consider them as nanocrystals.

The quantum size effect may not be the only reason of the high-energy shift of the free exciton emission band maximum. In principle, the compression of a nanocrystal by a matrix may be considered as another possible reason of the high-energy shift of the emission of the nanocrystals, dispersed in a dielectric matrix. However, a CsPbCl₃ single crystal is characterized by an anomalous temperature shift of both the fundamental absorption edge and the free exciton emission band. Indeed, as the temperature decreases from LNT to LHeT (resulting in the compression of a crystal lattice), both the exciton absorption and emission bands are shifted to the low-energy side [11]. Thus, the compression of the nanocrystals by the CsCl matrix does not have influence in this case.

The excitation efficiency of the fast component of the CsPbCl₃ nanocrystal emission decreases noticeably at $E_{\text{exc}} > 6.8$ eV (Fig. 3, curve 1). It may be explained by the more effective excitation of the Pb²⁺v_c⁻ emission in this energy region (see curves 4 and 5).

The appearance of the slow component in the decay kinetics of the 2.98 eV emission of CsPbCl₃ nanocrystals is a result of the reabsorption by CsPbCl₃ nanocrystals of the 3.94 eV emission of the Pb²⁺v_c⁻ centers where the slow component is the dominating one. The presence of reabsorption is evident from the similarity of the excitation spectra measured in the 6.8 to 7.8 eV spectral range for the luminescence of CsPbCl₃ nanocrystals (Fig. 3, curve 2) and Pb²⁺v_c⁻ centers (curves 4, 5).

Fig. 4. Excitation spectra of the fast (curve 1) and slow (curve 2) decay components of the 2.98 eV emission of the annealed CsCl:Pb crystal and of the 2.954 eV emission of a CsPbCl₃ single crystal (curve 3). Curve 4 shows the core-valence luminescence spectrum of a CsCl crystal. The arrows indicate the spectral positions of the low-energy exciton absorption peak and the edge of the band-to-band transitions in a CsCl matrix; $T = 10$ K

In the band-to-band transition region of a CsCl crystal (from 8.3 to 14 eV), the direct optical excitation of CsPbCl₃ nanocrystals as well as their indirect excitation (e.g., due to their interaction with the electronic excitations of a CsCl matrix) does practically not occur (Fig. 4, curves 1 to 3).

Under excitation by photons of energy $E_{\text{exc}} > 14$ eV, a fast core-valence luminescence of CsCl is observed peaking at 4.6 and 5.2 eV (Fig. 4, curve 4) [13]. This luminescence can be effectively reabsorbed by CsPbCl₃ nanocrystals dispersed in a CsCl matrix due to the coincidence of its spectrum (curve 4) with the absorption spectrum of CsPbCl₃ (curve 1). This channel of fast CsPbCl₃ luminescence excitation in the annealed CsCl:Pb crystal explains the presence of fast X-ray luminescence of CsPbCl₃ nanocrystals dispersed in a CsCl matrix [14].

The conclusions on the mechanisms of the CsPbCl₃ nanocrystal luminescence excitation made above are confirmed also by studies of their luminescence decay kinetics.

3.2 Luminescence decay kinetics

The decay curve of CsPbCl₃ nanocrystal luminescence obtained under excitation from 3.5 to 6.0 eV, i.e., in the transparency region of a CsCl:Pb crystal, is shown in Fig. 5

Fig. 5. Decay curves obtained for the luminescence of CsPbCl₃ nanocrystals dispersed in a CsCl matrix (curve 1) and a CsPbCl₃ single crystal (curve 2) under excitation in the 3.5–6.0 eV energy range. Curve 3 shows the apparatus excitation pulse; $T = 10$ K

(curve 1). This curve can be approximated by two exponents with decay times $\tau_{f1} = 0.14$ ns and $\tau_{f2} = 12.1$ ns. For the 2.954 eV emission of CsPbCl₃ single crystal, the corresponding values are $\tau_{f1} = 0.48$ ns and $\tau_{f2} = 7$ ns (curve 2). For comparison, the excitation pulse is shown by curve 3. The smaller value of σ_{fl} obtained for CsPbCl₃ nanocrystals as compared with that characteristic of a CsPbCl₃ single crystal is explained as a manifestation of the quantum size effect (see also [1]).

In our case the radius of free exciton in CsPbCl₃ is less than the nanocrystal size (according to our estimates $r_{ex} \approx 10$ Å). Thus, changes in exciton configuration are probably not the evidence of decay kinetic changes (as it has been observed in the case of AgCl nanocrystals, dispersed in a KCl matrix [4]).

There may be another reason for the shortening of the nanocrystal luminescence decay time: the nonradiative exciton decay caused by the presence of some defects inside the nanocrystals or on their surface. In our opinion, the contribution of this effect should be small. Indeed, according to our studies of CsPbCl₃ nanocrystals and single crystals as well as from the data of other authors [1], the exciton emission intensities are comparable with those of CsPbCl₃ nanocrystals and CsPbCl₃ single crystals, while their free exciton emission decay times differ strongly.

Under excitation in the 6.0 to 7.8 eV energy range, the decay kinetics of the CsPbCl₃ nanocrystal emission coincides with that of the triplet 3.94 eV emission of Pb²⁺v_c⁻ centers (Fig. 6, curves 1 and 2). Indeed, two fast components with $\tau_{f1} = 2.6$ ns, $\tau_{f2} = 25$ ns and $\tau_{f1} = 2.4$ ns, $\tau_{f2} = 27$ ns are observed in the luminescence decay kinetics of CsPbCl₃ nanocrystals and Pb²⁺v_c⁻ centers, respectively. In both cases a slow component is also present. In the case of Pb²⁺v_c⁻ centers, the presence of the slow (≈ 1 ms [6]) component is caused by the location of a metastable minimum under the emitting minima in the triplet relaxed excited state responsible for the 3.94 eV emission. The two fast (ns) components arise from the radiative decay of the emitting minima split into two levels due to the presence of a cation vacancy v_c⁻ near a Pb²⁺ ion. As the luminescence decay curves obtained for CsPbCl₃ nanocrystals and Pb²⁺v_c⁻ centers coincide, one may expect that the decay time of the slow component of the CsPbCl₃ emission is also about 1 ms. The observed decay kinetics of the CsPbCl₃ emission points to the reabsorption of the Pb²⁺v_c⁻ emission by the CsPbCl₃ nanocrystals in the annealed CsCl:Pb crystals studied.

Fig. 6. Decay curves obtained for the luminescence of CsPbCl₃ nanocrystals dispersed in a CsCl matrix under excitation in the 6.0–7.8 eV (curve 1) and >14 eV (curve 3) energy ranges. Curve 2 is the decay curve of the 3.94 eV emission of Pb²⁺v_c⁻ centers in CsCl:Pb obtained under 6.0–7.8 eV excitation; $T = 10$ K

Under excitation by photons of energy $E_{\text{exc}} > 14$ eV, the initial part of the luminescence decay curve of the CsPbCl_3 nanocrystals studied can be described as consisting of two exponents with decay times $\tau_{f1} = 1.3$ ns and $\tau_{f2} = 18.6$ ns (Fig. 6, curve 3). This is a result of the reabsorption by CsPbCl_3 nanocrystals of the CsCl core-valence luminescence which has a decay time of about 1.5 ns and can be excited only at $E_{\text{exc}} > 14$ eV.

Thus, the fast luminescence decay of the CsPbCl_3 nanocrystals with $\tau_f = 0.14$ ns is observed only under the direct optical excitation of CsPbCl_3 nanocrystals in the transparency region of CsCl:Pb . The presence of the fast component with $\tau_f = 1.3$ ns under $E_{\text{exc}} > 14$ eV excitation is the result of the reabsorption of the CsCl core-valence luminescence by CsPbCl_3 nanocrystals. The overlapping of the CsPbCl_3 absorption spectrum and the emission spectrum of $\text{Pb}^{2+}\text{v}_c^-$ centers leads to the appearance of two fast components (2.6 and 25 ns) and one slow component (~ 1 ms) in the luminescence decay kinetics of CsPbCl_3 nanocrystals under excitation in the energy range where the luminescence of $\text{Pb}^{2+}\text{v}_c^-$ centers can be excited. The quantum size effect becomes evident in the smaller value of the luminescence decay time observed in the case of CsPbCl_3 nanocrystals dispersed in a CsCl crystal matrix (0.14 ns) as compared with that obtained for a CsPbCl_3 single crystal (0.48 ns).

4. Summary

1. A prolonged (20 h) annealing of a CsCl:Pb (0.5 mol% of PbCl_2 in the melt) single crystal at 200 °C leads to the formation of CsPbCl_3 nanocrystals with an average radius of about 4.7 nm dispersed in a CsCl crystal matrix. Besides the CsPbCl_3 nanocrystals, $\text{Pb}^{2+}\text{v}_c^-$ centers are also present in the crystal studied.

2. In the transparency region of a CsCl:Pb crystal, the luminescence of CsPbCl_3 nanocrystals is excited directly and it decays with the time characteristic of the free exciton luminescence (0.14 ns). A part of the excitation energy is also absorbed by $\text{Pb}^{2+}\text{v}_c^-$ centers that remained in the CsCl:Pb crystal after annealing.

3. In the absorption region of $\text{Pb}^{2+}\text{v}_c^-$ centers and in the region of the band-to-band transitions, the main mechanism of the CsPbCl_3 nanocrystal luminescence excitation is the reabsorption of $\text{Pb}^{2+}\text{v}_c^-$ emission (3.94 eV) and CsCl core-valence luminescence (4.6 and 5.2 eV) by CsPbCl_3 nanocrystals. In this case their luminescence decay kinetics coincides with that characteristic of the triplet luminescence of $\text{Pb}^{2+}\text{v}_c^-$ centers in a CsCl:Pb crystal and of the core-valence luminescence of a CsCl crystal, respectively.

4. The quantum size effect is considered as the most probable reason for the high-energy shift of the free exciton emission band of CsPbCl_3 nanocrystals (about 26 meV) and of the shortening of its decay time (down to 0.14 ns) as compared with that characteristic of a CsPbCl_3 single crystal (0.48 ns).

5. The presence of the slow decay component in the luminescence of CsPbCl_3 nanocrystals thermally created in the CsCl:Pb crystal as well as the small efficiency of energy transfer from the CsCl matrix to CsPbCl_3 nanocrystals may limit possible applications of this system.

Acknowledgements The authors are thankful to Prof G. Zimmerer for assistance in the measurements on HASYLAB and discussion of experimental results. This work was partially supported by INTAS (Grant 99-01350) and the Estonian Science Foundation grant No. 3875.

References

- [1] M. NIKL, K. NITSCH, K. POLAK, G. P. PAZZI, P. FABENI, D. S. CITRIN, and M. GURIOLI, *Phys. Rev. B* **51**, 5192 (1995).
- [2] S. V. MYAGKOTA, A. S. VOLOSHINOVSKII, and V. B. MIKHAILIK, *Int. Conf. Inorganic Scintillators and Their Application, SCINT 97*, Shanghai, September 22–25, 1997, Shanghai Institute of Ceramics (China) 1997 (p. 40).
- [3] M. NIKL, K. POLAK, K. NITSCH, G. P. PAZZI, P. FABENI, and M. GURIOLI, *Radiat. Eff. Defects Solids* **135**, 289 (1995).
- [4] H. VOGELSANG, O. HUSBERG, U. KOHLER, W. VON DER OSTEN, and A. P. MARCHETTI, *Phys. Rev. B* **61**, 1847 (2000).
- [5] A. S. VOLOSHINOVSKII, V. B. MIKHAILIK, S. V. MYAGKOTA, M. S. PIDZIRAILO, and I. P. PASHUK, *Ukr. Fiz. Zh.* **38**, 1012 (1993).
- [6] A. N. BELSKY, P. CHEVALLIER, P. DHEZ, P. MARTIN, C. PEDRINI, and A. N. VASILEV, *Nucl. Instrum. Methods Phys. Res. A* **361**, 384 (1995).
- [7] G. ZIMMERER, *Nucl. Instrum. Methods Phys. Res. A* **308**, 178 (1991).
- [8] R. ACEVES, V. BABIN, M. BARBOZA FLORES, P. FABENI, E. MIHOKOVA, V. NAGIRHYI, M. NIKL, K. NITSCH, G. P. PAZZI, R. PEREZ SALAS, and S. ZAZUBOVICH, *J. Phys.: Condens. Matter* **10**, 5449 (1998).
- [9] K. I. IBRAGIMOV, A. CH. LUSHCHIK, CH. B. LUSHCHIK, A. G. FRORIP, and N. A. YANSON, *Sov. Phys. – Solid State* **34**, 1690 (1992).
- [10] AL. L. EFROS and A. L. EFROS, *Sov. Phys. – Semicond.* **16**, 772 (1982).
- [11] I. P. PASHUK, N. S. PIDZYRAILO, and M. G. MACKO, *Sov. Phys. – Solid State* **23**, 1263 (1981).
- [12] L. N. AMITIN, A. T. ANISTRATOV, and A. I. KUZNETSOV, *Fiz. Tverd. Tela* **21**, 3535 (1979).
- [13] P. A. PODNYI, *Opt. Spektrosk.* **47**, 1068 (1989).
- [14] S. V. MYAGKOTA, *Opt. Spektrosk.* **87**, 311 (1999).