

Diffusion of 5p-holes in BaF₂ nanoparticles

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ARTICLE INFO

Keywords:

BaF₂ nanoparticles
Core-valence luminescence
Luminescence quenching
Diffusion length
Core holes

ABSTRACT

The kinetic parameters of core-valence luminescence for BaF₂ nanoparticles with different sizes were studied under synchrotron radiation excitation with photon energy of 18.8 eV at room temperature. In contrast to BaF₂ single crystals the decay kinetics of nanoparticles is shown to be non-exponential indicating the luminescence quenching. We assume that the quenching of core-valence luminescence is caused by the diffusion of core holes to nanoparticle surface. The diffusion length of the core holes in BaF₂ has been estimated as 2–3 nm using diffusion model of luminescence quenching in nanoparticles.

1. Introduction

BaF₂ is used as a scintillator for registration of fast processes due to the presence of luminescence with subnanosecond decay time constant. This luminescence reveals the band with maximum at 220 nm [1,2], which is interpreted as the result of radiative recombination between outermost core holes and valence electrons. It arises only under high-energy excitation, when holes are formed in 5pBa²⁺ core band of crystal. Different terms are used for this luminescence: core-valence luminescence (CVL) [3], cross-luminescence [4], Auger-free luminescence [5]. In addition to the short luminescence decay time (~1 ns), among the features of core-valence luminescence are relatively high light output (2000 photons/MeV for BaF₂) and high thermal stability of these parameters [6]. Crystals possessing CVL attract continuous attention as potential fast scintillators [7].

Recently, researches directed their efforts for studying the nanostructural materials, in order to find new luminescence properties or to improve luminescence parameters. The intensity of exciton and impurity luminescence of nanoparticles is known to decrease in comparison with their single crystal analogues under high-energy excitation [8–12]. Such dependence of luminescence intensity of BaF₂ nanoparticles on their size was studied in Refs. [11,12]. At the same time, the rather weak dependence of CVL intensity on the size of nanocrystals, in contrast to the luminescence of self-trapped excitons (STE) was revealed. The weak dependence of CVL intensity on nanoparticle size originates from CVL emission mechanism. By the comparing bulk and

nanoscale crystals, the certain spatial confinements for scintillation process in nanoparticles are observed. The ratio between electron thermalization length and nanoparticle size has major influence on the STE luminescence intensity under high-energy excitation [13,14], whereas in the case of CVL the migration processes of core holes have significant influence. The latter is due to the fact that the behavior of the hole in core 5pBa²⁺ band is determinative for CVL. Then, CVL quenching can occur due to non-radiative relaxation of core holes. In the case of nanoparticles, non-radiative relaxation of the core holes can be associated with their diffusion to the surface. Therefore, the main parameter that determines CVL quenching processes in nanoparticles is the diffusion length of holes in the core band. Thus, the study of CVL decay processes in nanoparticles with different sizes should allow the evaluation of core hole diffusion length. Some estimations of this value are known. The dependence of luminescence decay kinetics on excitation penetration depth using different incidence angles of excitation quanta on BaF₂ crystal were studied in Ref. [15]. It can be concluded from these studies that core hole diffusion length is equal to several nanometers in BaF₂. In Ref. [16], the core hole migration length in BaF₂ is evaluated to be less than 3 nm. The estimation of Rb⁺ core hole diffusion length in Rb_{1-x}Cs_xF system (x = 0.008) by the authors of [17] gives 1.5 nm.

In this paper, we try to estimate the hole diffusion length in 5pBa²⁺ core band studying the influence of nanoparticle size on the shape of CVL decay kinetics curves, since the decrease of luminescence decay time parameters is caused by the luminescence quenching arising from

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<https://doi.org/10.1016/j.optmat.2019.03.011>

Received 21 November 2018; Received in revised form 1 March 2019; Accepted 11 March 2019

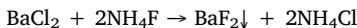
Available online 20 March 2019

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the core hole diffusion to the nanoparticle surface. The estimation of core hole diffusion length was made using model of luminescence quenching for nanoparticles proposed in Ref. [18].

2. Experimental

BaF₂ nanoparticles were synthesized by chemical precipitation method. For nanoparticle synthesis, aqueous solutions of BaCl₂·6H₂O and NH₄F salts were used in stoichiometric ratio. Aqueous solution of BaCl₂·6H₂O was added dropwise to the aqueous solution of NH₄F at continuous stirring with magnetic stirrer. Ethyl alcohol was added to slow down the reaction in order to obtain nanoparticles of the smallest size. The basic equation of reaction is as follows:



After the reaction, white precipitate was obtained. Precipitate was separated by the centrifuge and washed with distilled water several times. Synthesized nanoparticles were placed in vacuum chamber for further drying to constant mass.

The nanoparticles of 20 nm size were obtained by this synthesis method. To get the larger nanoparticles, they were annealed at 400 °C for 2 h. The average size of annealed nanoparticles was 60 nm. The sizes of as-synthesized and annealed nanoparticles were determined from X-ray diffraction peak broadening [19].

Luminescence and kinetic studies of BaF₂ nanoparticles were carried out on the equipment of SUPERLUMI station in HASYLAB (DESY, Hamburg) [20]. The luminescence excitation spectra was measured by time resolved spectroscopy in the time window of $\Delta t = 5$ ns width (fast window) just after the excitation pulse and corrected using sodium salicylate. Luminescence spectra were measured in time integrated modo and were not corrected on spectral sensitivity.

3. Results and discussion

Beside the luminescence of self-trapped excitons ($E_{\text{em}} = 4.0$ eV), the core-valence luminescence ($E_{\text{em}} = 5.45$ eV) reveals in BaF₂ crystals under synchrotron radiation excitation with photon energy of 18.8 eV. The same luminescence spectrum is observed for nanoparticles (Fig. 1a). The only difference is that in nanoparticles the intensity of the CVL can be higher than the luminescence intensity of STE (Fig. 1a). The reasons for this are the different dependences of the CVL and the STE luminescence intensity on the nanoparticle sizes, as shown in Ref. [11]. The excitation spectra of BaF₂ nanoparticles exhibit the same structure

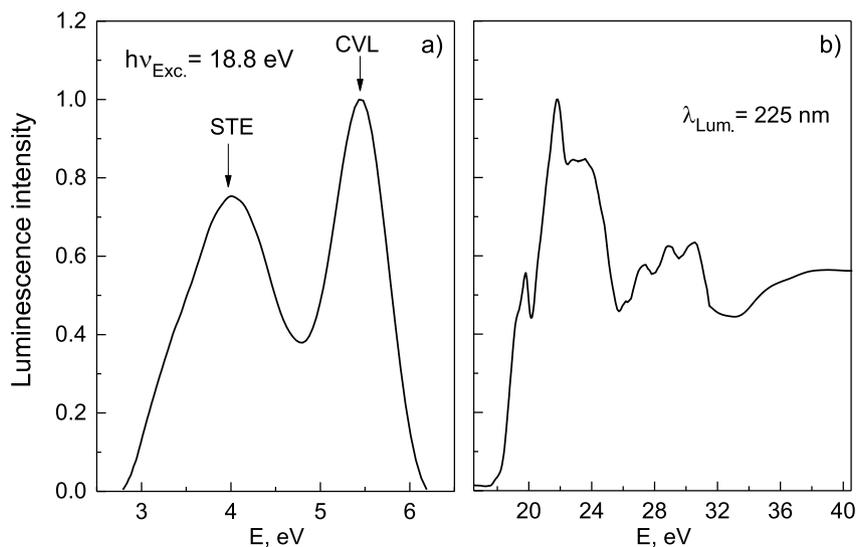


Fig. 1. Luminescence (a) and excitation (b) spectra of BaF₂ nanoparticles ($a_0 = 60$ nm).

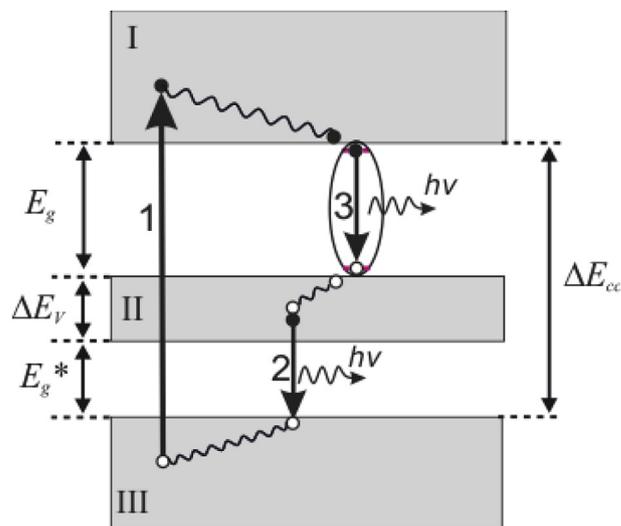


Fig. 2. The schematic draw of energy band structure and electron transitions corresponding to CVL (2) and STE luminescence (3) in BaF₂ crystals. I - conduction band; II - valence band; III - core band; ΔE_{cc} - energy gap between the bottom of conduction band and the top of core band, E_v - width of valence band, E_g - band gap, E_g^* - energy gap between core and valence bands.

as single crystal (Fig. 1b). The excitation threshold of core-valence luminescence in BaF₂ can be estimated approximately at 18 eV, which corresponds to the electronic transition from the 5pBa²⁺ states to the conduction band (Fig. 2).

The hole created due to electronic transition 1 (Fig. 2) relaxes to the top of core 5pBa²⁺ band and then recombines with any electron from the entire continuum of the valence band (transition 2) with the creation of core-valence luminescence quanta. The creation of hole in core band is the sufficient condition for appearance of core-valence luminescence in BaF₂, since the electron component for the recombination process is always present in the valence band. Therefore, the quenching processes of core-valence luminescence are determined by the possibility of non-radiative relaxation of core hole. Such quenching mechanism of core-valence luminescence is characterized by the weak sensitivity of emission intensity to nanoparticle sizes compared to exciton luminescence [11].

Despite the expected weak dependence of CVL parameters on nanoparticle sizes, the quenching of core-valence luminescence in

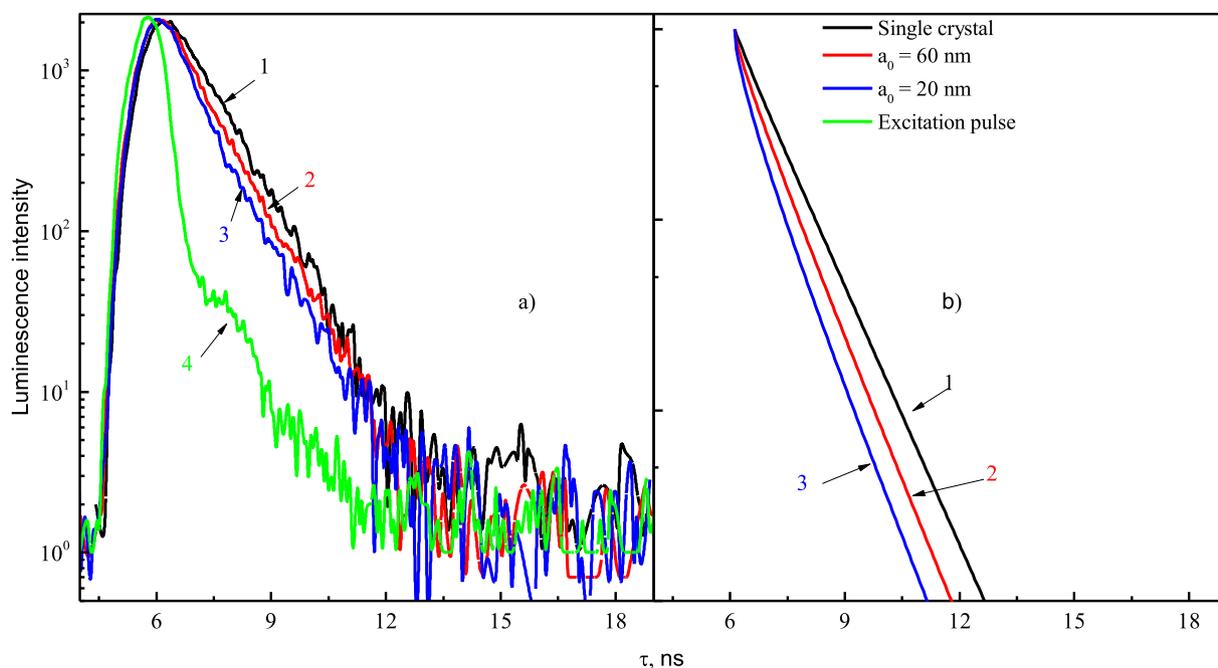


Fig. 3. Decay kinetics curves of BaF₂ single crystal and nanoparticles with different sizes excited by quanta with $h\nu = 18.8$ eV (a), and the decay kinetics curves of CVL obtained by deconvolution (b): 1 - single crystal, 2 - $a_0 = 60$ nm, 3 - $a_0 = 20$ nm, 4 - excitation pulse.

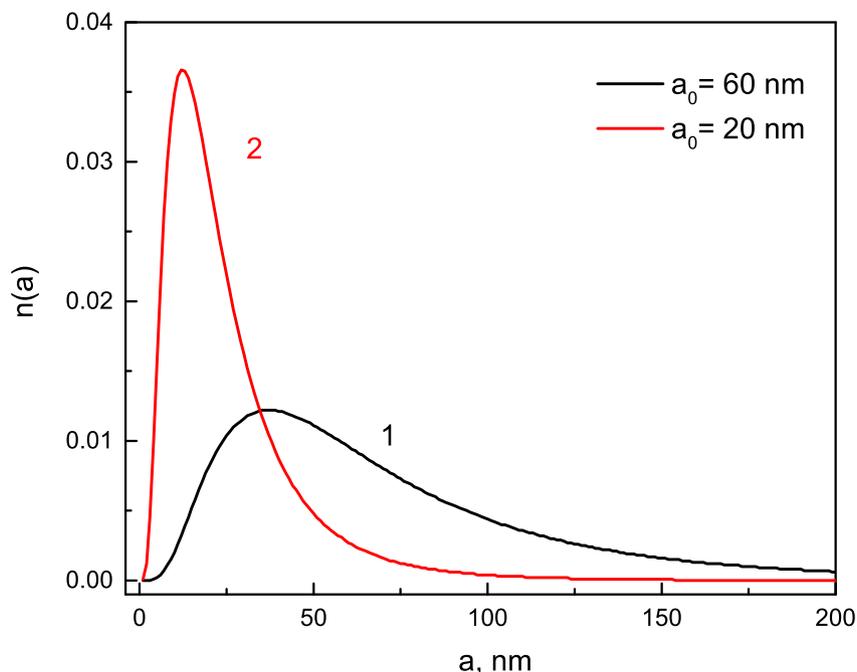


Fig. 4. Normal logarithmic distribution of nanoparticles with different average size: 1–60 nm, 2–20 nm. ($\sigma = 2$).

Table 1

The fitting parameters of equation (1) for BaF₂ decay luminescence curves. a_0 – average nanoparticle size, τ - decay time constant, L – diffusion length of core holes.

a_0 , nm	τ , ns	L , nm
20	0.95	1.9
60	0.95	2.7

nanoparticles is observed, however. This can be clearly seen from the decay kinetics of CVL. Fig. 3 shows the luminescence decay kinetics curves of BaF₂ nanoparticles with different sizes excited by quanta with

$h\nu = 18.8$ eV. As it can be seen from Fig. 3a, the CVL decay kinetics of nanoparticles shortens going from single crystals to nanoparticles and at decreasing the nanoparticle size. We assume that the quenching of CVL is due to the diffusion of core holes to nanoparticle surface.

It should be noted that as possible quenching mechanism of CVL the effects associated with high density of excitations also can be considered. This is observed from the change in the CVL intensity in the case of excitation by cathode rays with a different current density [21]. In our case, the CVL decay kinetics of a single crystal is one-exponential. This implies the absence of excitation density influence on the decay kinetics. Since all samples (single crystal and nanoparticles) were studied under the same conditions, the change in CVL decay kinetics at

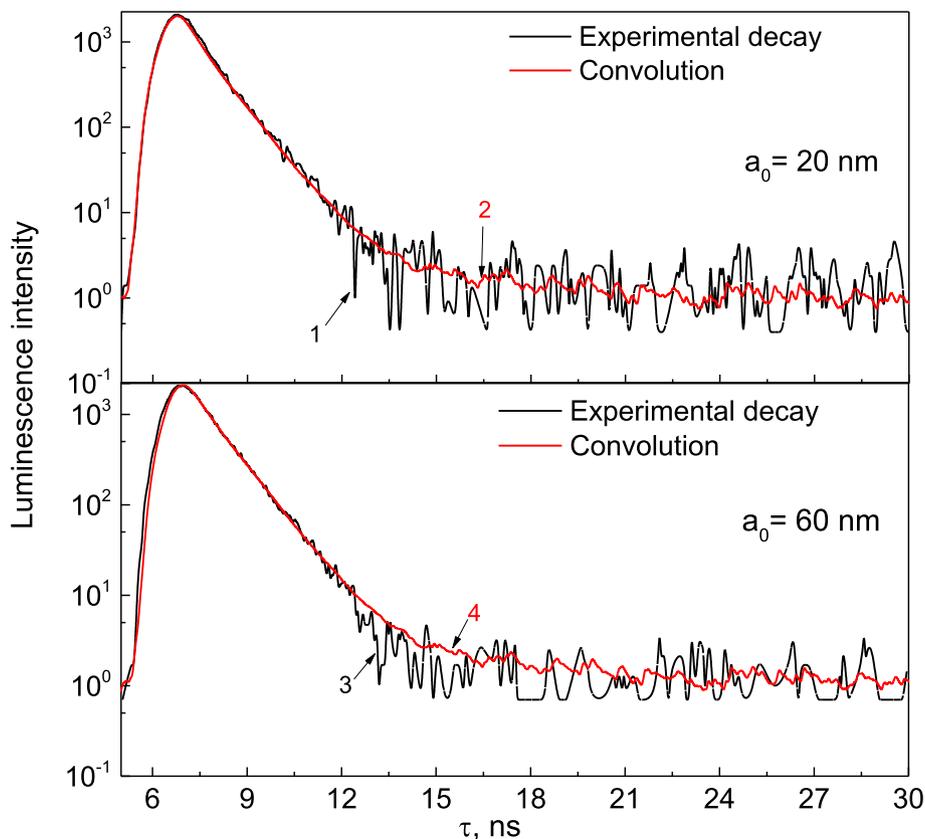


Fig. 5. Experimental curves of CVL decay kinetics for BaF₂ nanoparticles of different sizes (curves 1, 3) and convolution results (curves 2, 4) of both the CVL decay kinetics obtained using equation (1) and the excitation pulse.

transition from single crystal to nanoparticles is mainly due to the diffusion of core holes to the nanoparticle surface, and the excitation density effects can be neglected.

We have used the diffusion model proposed in Ref. [18] to analyze the kinetics of CVL quenching in BaF₂ nanoparticles. This model takes into account the diffusion of electronic excitations to nanoparticle surface with following non-radiative relaxation at infinitely high speed. According to the mentioned diffusion model, the luminescence decay kinetics of nanoparticles is described by the equation:

$$I(t) = \int_0^{a_{\max}} I_{lum}(0) \exp\left(-\frac{t}{\tau}\right) \left(R\left(\frac{L^2 t}{a_0^2 \tau}\right)\right)^3 n(a) da, \quad (1)$$

where $R(x) = \frac{8}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{(2n+1)^2} \exp(-2n+1)^2 \pi^2 x$, $n(a)$ – size distribution of nanoparticles, a_0 – average nanoparticle size, L – diffusion length of core hole, τ – CVL decay time constant of BaF₂ single crystal.

The analysis of the CVL decay kinetics in BaF₂ is complicated by the fact that the value of decay time constant is in nanosecond range and is comparable with the duration of excitation pulse (Fig. 3, curve 4). Therefore, we performed the deconvolution of experimental curves to obtain the actual decay kinetics of CVL (Fig. 3b). The deconvolution was performed using DecayFit 1.4 software package [22]. As it can be seen from decay curves obtained after mathematical deconvolution procedure (Fig. 3b, curves 2 and 3), the decay kinetic of CVL in nanoparticles is non-exponential, in contrast to that for the single crystal (Fig. 3b, curve 1).

The distribution of nanoparticles by size is required for fitting the decay kinetics curves with equation (1). From X-ray diffraction measurements only the average nanoparticle size can be estimated. To obtain the distribution of nanoparticles by sizes, the normal logarithmic distribution was used, as in the work [18]:

$$n(a) = \frac{1}{\sqrt{2\pi} a \ln(\sigma)} \exp\left[-\frac{1}{2} \left(\frac{\ln\left(\frac{a}{a_0}\right)}{\ln(\sigma)}\right)^2\right]$$

where a_0 – average nanoparticle size, σ – parameter defining the dispersion of size distribution. Fig. 4 presents the dispersion curves for nanoparticle sizes with an average size of 20 and 60 nm.

The fitting parameters of equation (1) for the actual CVL decay kinetics curves (Fig. 3b) are given in Table 1. The convolution of approximation curves obtained using formula (1) and the excitation pulse curve (Fig. 3a, curve 4) was performed in order to check the reliability of fitting. The obtained convolution curves and the experimental curves of CVL decay kinetics are compared in Fig. 5. As it can be seen from the figure, the convolution results well match with the experimental curves of CVL decay kinetics of BaF₂ nanoparticles of different sizes.

In conclusion, the decay kinetics study of CVL in BaF₂ nanoparticles indicates the non-exponential character of core-valence luminescence decay curve, unlike the BaF₂ single crystal. Non-exponentiality increases with decrease of nanoparticle sizes. The quenching processes of luminescence due to diffusion of core holes to the surface of nanoparticles is assumed to explain the non-exponential character of CVL decay kinetics. The diffusion length of $L = 2-3$ nm for 5pBa²⁺ core holes was estimated using the diffusion model for quenching of core-valence luminescence in BaF₂ nanoparticles. The proposed approach to use non-exponentiality of CVL decay kinetics of nanoparticles for estimation of diffusion length of core holes can be used for other materials.

Acknowledgment

This research is supported by a European Union's Horizon 2020 research and innovation program under the COST Action TD1401 (FAST) and by Ministry of Education and Science of Ukraine (project

No. 0118U003606). The financial support of this projects is greatly acknowledged.

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