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Modeling of X-ray excited luminescence intensity dependence on the nanoparticle size

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HIGHLIGHTS

- Distribution of secondary electrons thermalization length is calculated for $LaPO_4$ and $LuPO_4$.
- Dependence of X-ray excited luminescence intensity on the nanoparticle size was simulated.
- Correlation of experimental and simulated dependencies was found.
- The search criteria for scintillating nanoparticles is proposed.

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ABSTRACT

The thermalization length distribution of electrons over their kinetic energy in a conduction band is calculated on the basis of the data on the electron effective mass, density of states in conduction band, dielectric permittivity and energy of longitudinal optical phonons. The method of modeling of a recombinational luminescence intensity dependence on the nanoparticle size is proposed on the basis of the assumption that the contribution to a recombinational luminescence gives only those charge carriers which in the result of thermalization did not reach a near-surface layer of nanoparticles. Using such the approach the theoretical dependence of recombinational luminescence intensity on the nanoparticle size for $LaPO_4$ and $LuPO_4$ are calculated. The revealed correlation of experimental and theoretical dependences confirms that the commensurability of electron thermalization length with nanoparticle size is the main reason of the sharp decrease of X-ray excited luminescence intensity when the nanoparticle size decreases.

1. Introduction

Studies of the nanoparticle luminescence parameters dependence on their size are driven by a possibility to use the nanoparticles in particular as luminescent biolabels, nanoscintillators for radiotheraphy or components of the composite nanostructured scintillators. For an impurity luminescence in case of intracenter excitation it is known that the intensity of the emission usually decreases with the reduction of the nanoparticle sizes. It is explained with a nonradiative relaxation of the luminescent centers due to the interaction with surface defects. However the drop in luminescence intensity when the nanoparticle size decreases in case of intracenter excitation is not as notable as in a case of band-to-band or X-ray excitation. If excitation energy is transferred to the luminescence centers by free charge carriers, the new channel of a nonradiative relaxation appears: created free charge carriers can reach a nanoparticle surface, where they have an opportunity to transfer excitation energy to surface defects or to leave a nanoparticle. It results in strong dependence of a recombinational luminescence on the nanoparticle size. The probability to reach a surface by free charge carriers is determined by the ratio of thermalization length (distance passed by an electron or a hole in the

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thermalization process) to the nanoparticle size. The thermalization length of holes is considered to be rather small (for alkali halides it is estimated as a few nanometers (Bizarri et al., 2009)) due to high effective masses and possible self-trapping processes. Therefore, the thermalization length of electrons is considered as a decisive factor for the scintillation process in nanoparticles.

For verification of this assumption the attempt to simulate the dependences of X-ray excited luminescence intensity on the nanoparticle size for $LaPO_4$-Pr and $LuPO_4$-Pr which are considered as possible candidates for use as nanoscintillators for radiotheraphy is made in this work. For such possible practical use the dependence of X-ray excited luminescence intensity on their size is studied (Fig. 1). Nanoparticles were obtained and characterized as described in (Malyy et al., 2013; Vistovskyy et al., 2014). As one can see from the figure the intensity of X-ray excited luminescence sharply decreases in the range of 15–40 nm nanoparticle sizes. According to the assumption these values of the nanoparticle sizes should be commensurate to the average electron thermalization length.

2. Calculations of thermalization lengths distribution for secondary electrons

The thermalization lengths distribution of secondary electrons was calculated for simulation of X-ray excited luminescence intensity dependence on the size of nanoparticles. Nowadays the theory necessary for an assessment of electron thermalization length is quite well developed. For calculation of average thermalization length of electrons with initial kinetic energy E_{e0} for the case of one branch of longitudinal optical phonons the following equation is used:

$$l^2_{e,LO}(E_{e0}) = \frac{8}{9}a_B^2\left(\frac{\widetilde{\varepsilon}}{m_e^*/m_0}\right)^2 \tanh\left(\frac{\hbar\Omega_{LO}}{2k_BT}\right)\cdot\left(\frac{E_{e0}}{\hbar\Omega_{LO}}\right)^3 \Big/ \ln\left(\frac{4E_{e0}}{\hbar\Omega_{LO}}\right),$$

where a_B – Bohr radius, $\widetilde{\varepsilon}$ – effective dielectric permeability ($\widetilde{\varepsilon}^{-1}\equiv\varepsilon_\infty^{-1}-\varepsilon_{st}^{-1}$, ε_∞ – optical dielectric permeability, ε_{st} – static dielectric permeability), m_e^* – effective mass of an electron, m_0 – mass of an electron, $\hbar\Omega_{LO}$ – energy of optical phonons (Vasil'ev and Gektin, 2014).

In our estimations we take into account only one phonon branch possessing the highest energy. The thermalization on phonons with lower energies was not taken into account. In result of such approximation the obtained values of thermalization length will be slightly underestimated (see Fig. 6 in (Vasil'ev and Gektin, 2014)).

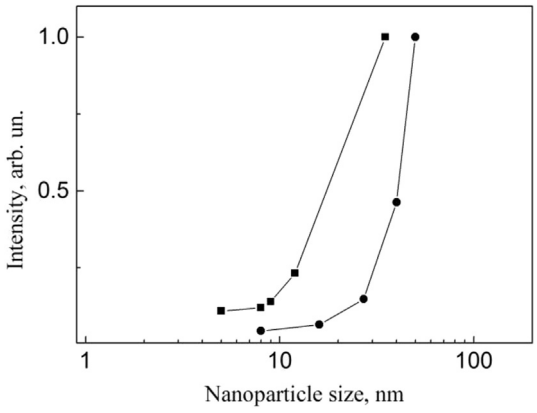

Fig. 1. Dependence of X-ray excited luminescence intensity on the nanoparticle size for $LaPO_4$–Pr (circles) and $LuPO_4$-Pr (squares).

The input data for calculation of electron thermalization length distribution such as density of electronic states in conduction band and the effective mass of an electron are obtained from electronic energy structure of $LnPO_4$ (Ln = La, Lu) crystals. For a $LaPO_4$ crystal the electronic energy structure from (Syrotyuk et al., 2013) was used. The electronic energy spectrum for a $LuPO_4$ crystal (Fig. 2) was calculated, using the PAW formalism (Blochl, 1994) taking into account the strong local correlations in a PBE0 GGA approach. The effective mass of electrons for $LnPO_4$ crystals was estimated from dispersion of the lower branch of conduction band at Γ-point. The effective masses and other parameters of the crystals are specified in Table 1.

Calculations of thermalization length distribution for secondary electrons were carried out by the technique described in (Vasil'ev and Gektin, 2014) with only one difference: the density of electronic states in conduction band was taken into account for distribution of secondary electrons over kinetic energy. Instead of the n(Ee0) function (Vasil'ev and Gektin, 2014) the n(Ee0)·g(E) product, where g(E) - density of electronic states in conduction band (Fig. 3), was taken. Results of calculation of secondary electrons distribution over thermalization lengths are presented in Fig. 4. As one can see from the figure the average thermalization length of electrons for $LaPO_4$ is smaller in comparison with that for $LuPO_4$.

3. Simulation of recombinational luminescence intensity dependence on the nanoparticle sizes

Dependence of recombinational luminescence intensity on the nanoparticle size was simulated assuming that the commensurability of secondary electrons thermalization length and the nanoparticle size is the main reason of their luminescence quenching upon the X-ray excitation. In other words, if in the result of thermalization the electron reaches a nanoparticle surface, then its relaxation will be nonradiative, for example, with the participation of surface defects. Also, it is assumed that the formation of excitons

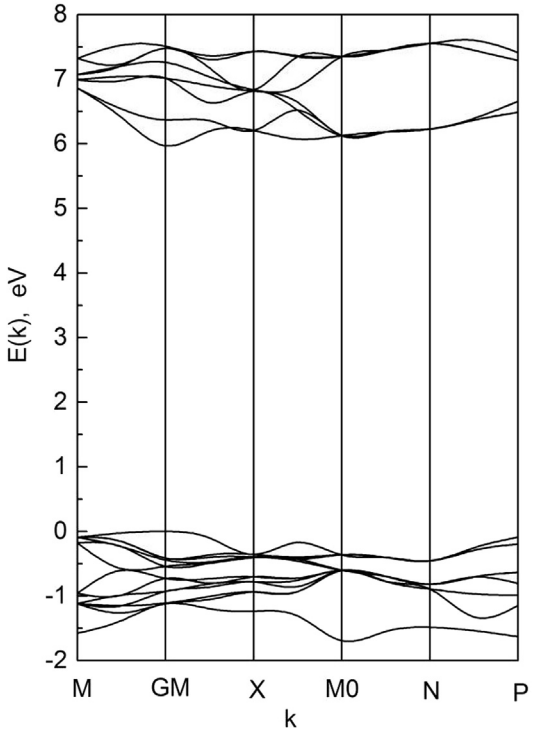

Fig. 2. Energy band structure of a $LuPO_4$ crystal.