Kinetics of the cathodoluminescence flash in crystals with competing trapping centres

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Abstract. The present work aims to bring proof of possibility of the existence of the process to increase the number of luminescence centers in the radiative state. That apparently has the effect of the buildup of luminescence excited by a pulsed electron beam. To demonstrate the possible influence of competing centers on the decay kinetics of luminescence materials were selected on the basis of crystal $YLiF_4$ and $YLiF_4$: Nd^{3+}. Found that the kinetics of flash luminescence when excited $LiYF_4$: Nd crystals pulse electron beam at room temperature in the initial stage of a flare-up of up to 300 ns was observed. The model of the exchange of electronic excitations between the centers of the emission and capture is discussed.

1. Introduction

Exposure of wide-band gap materials to short time pulses radiation initiates a luminescence flash which then decays in time. In the kinetics of some materials under certain experimental conditions the luminescence intensity is found to increase at the initial period after excitation in time exceeding the duration of the excitation pulse. The effect of the luminescence buildup under excitation by a pulsed electron beam was observed in [1-3]. The luminescence buildup at the initial period after exposure may be caused by increase in the amount of luminescence centers in a radiative state due to transfer of energy from the trapping centers excited by radiation pulse. The present research sets out to prove the possibility of this process and to develop the model of the luminescence buildup in the crystal with competing luminescence and trapping centers.

2. Test samples and experimental technique

The shape of the kinetic curves of the pulsed cathodoluminescence flash depends on a number of factors: the type of the material, the temperature of the sample under excitation, the history of the sample, the excitation power, and etc. To demonstrate the possible effect of the competing centers on the luminescence decay kinetics we chose $YLiF_4$-based materials. In these materials, at temperatures close to room temperature the cathodoluminescence buildup is well manifested after exposure to radiation pulse. Undoped "pure" $YLiF_4$ crystals and those doped with Nd^{3+} grown in INCROM Ltd were studied. The test samples were cleaved from a single crystal at an angle of 45° to the crystal optical axis C and then polished.

The samples were excited by pulsed electron beams with the following characteristics: FWHM of 10 ns pulse duration, the average electron energy of 250 keV, and the energy density of the excitation pulse equal to 15 mJ/cm^2. The pulsed cathodoluminescence (PCL) of the crystals was investigated in the spectral range of 2.0–4.0 eV at temperatures ranging from 80–300 K, and the kinetics of the luminescence flash in the time interval of $1 \cdot 10^{-8}$–$1 \cdot 10^{-4}$ s after the end of the pulse action. To record the luminescence and change in optical absorption we used PMT-106, PMT-84-6, a digital oscilloscope Gwinstek GDS-2204, Tektronix TDS-2014 and monochromators MDR-206 and MDR-3.

3. Experimental results

The structure of the PCL spectra of pure YLiF$_4$ crystals, and those doped with impurities is complex [4, 5]. Two groups of bands are distinct in the PCL spectrum: in the ranges of 3.7 ... 5.5 and 2.0 ... 3.7 eV. The characteristics of the two groups of bands differ due to different luminescence centers. The long-wave region of the spectrum is caused by uncontrolled impurities which occur in the crystal in its growing. Intentional doping with impurities suppresses the luminescence of the uncontrollable impurities and changes the spectrum.

Figure 1 shows the PCL spectra in the region of 2.0 ... 3.7 eV measured after 10 and 200 ns after the end of the excitation pulse for YLiF$_4$ crystal doped with 0.7 mol% Nd at 300 K. The spectrum measured instantaneously after the end of the excitation pulse is found to be a superposition of the spectra caused by the uncontrollably entered impurity and intentionally doped neodymium. In time after the excitation, the radiative spectrum caused by the uncontrolled impurity disappears and after 200 ns its contribution is negligible. The luminescence caused by the doped neodymium with the bands characteristic of this chemical element becomes dominant. The shape of the spectrum changes and the intensity of the neodymium luminescence increases in time.
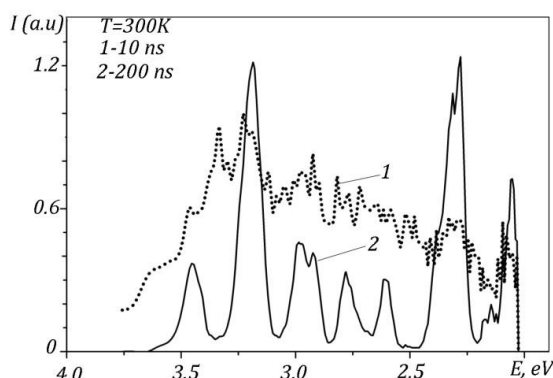

Figure 1. Luminescence spectra for LiYF$_4$-0.7 mol% Nd measured after 1–10 ns and 2–200 ns at T = 300 K

Figure 2 shows the kinetic curves of the change in the luminescence intensity at 2.3 and 2.5 eV. One of the main lines of the neodymium luminescence is found at 2.3 eV, and the greatestspectrum notching accounts for 2.5 eV. In this region, intense luminescence after 10 ns is caused by the luminescence of the uncontrolled impurity. The research results show a substantial difference in the kinetic curves.
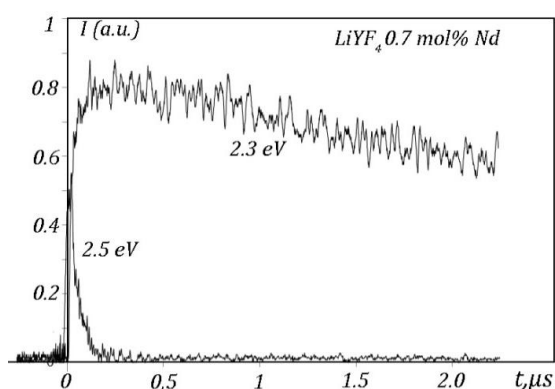

Figure 2. Kinetic curves of PCL initiated by pulsed electron beam in the YLiF$_4$-0.7 mol% Nd crystal at 2.5 eV and 2.3 eV at 300 K

At 2.5 eV, the luminescence decays after 200 ns, whereas at 2.3 eV, the luminescence grows in the range of 200–300 ns, and in the microsecond time range, the luminescence decays. We can conclude that the excitation energy is transferred in time from the luminescence centers responsible for the luminescence at 2.5 eV to the neodymium centers responsible for the luminescence at 2.3 eV.

3.1 Model of the luminescence flash buildup kinetics

Consider the model of the process shown in Figure 3. Assume that the crystal contains two competing centers of excitation energy trapping. In the energy scheme of the process, E_1, E_2, I_1 and I_2 are the energies and intensities of transitions in C_1 and C_2 centers, and ΔE_1 and ΔE_2 are the energy barriers for the exchange of the electron excitation between the centers.

Assume that the characteristics of the luminescence centers (trapping centers) are as follows:

1. The radiation efficiency of the luminescence centers C_1 is high (high light yield). The radiation efficiency of the trapping (luminescence) centers C_2 is low or transition to the ground state is nonradiative.

2. The luminescence centers C_1 appear to be deeper electron excitation traps than C_2 centers. However, the cross section of electron excitation trapping by C_2 centers is larger than that by C_1 centers.
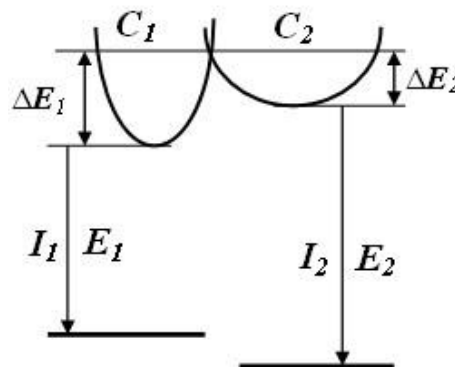

Figure 3. Energy scheme of the model of the competing centers excitation relaxation.

3. Exchange of electron excitations between the luminescence centers is considered to be possible. Since, according to the model ΔE_2, the activation energy of the transition of electron excitation from C_2 to C_1 is less than ΔE_1, the activation energy of the transition of C_1 to C_2, the transfer of the electron excitation energy will occur mainly from C_2 to C_1.

4. The lifetime τ_2 of C_2 luminescence centers in an excited state is much shorter than the lifetime τ_1 of C_1 centers.

Recombination in the radiative center C_1 is followed by generation of radiation with the intensity of I_1. The radiation intensity and the power of radiation from the unit of the crystal volume are determined by the recombination rate:

$$I_1 = k_{11} \frac{dN_1^*}{dt}, \tag{1}$$

where k_{11} is the radiation energy yield, N_1^* is the concentration of the excited centers per time t disappearing within time Δt. The concentration of C_1 centers in an excited state is determined by the concentration of the luminescence centers entered in the crystal and the density of the absorbed excitation flux energy. The concentration of the luminescence centers in phosphor crystals is typically more than 10^{18} cm^3. The density of the absorbed energy of the excitation pulse is typically less than 1 J. At high pulse energies, mechanical fracture of the crystal occurs. In case the probability of the electron excitation energy transfer to the luminescence center is k_{21}, the concentration of the luminescence centers excited by instantaneous energy pulse will be:

$$N_1^* = k_{21} N_1 p \tag{2}$$

where P is the density of the absorbed energy of the excitation pulse, N_1 is the concentration of the entered luminescence centers.

The luminescence centers in an excited state spontaneously transfer to the ground state with the lifetime of τ_1:

$$N_1^* = k_{21} N_1 p \cdot e^{-\frac{t}{\tau_1}}, \qquad (3)$$

In this case the radiation intensity caused by the luminescence centers is:

$$I_1 = k_{11} k_{21} N_1 p \tau_1 \cdot e^{-\frac{t}{\tau_1}}, \qquad (4)$$

According to the model, the electron excitations can be trapped by a different luminescence center (trapping center). The concentration of C_2 centers in an excited state and relaxation of the excitation in C_2center can be written by analogy with (3.4):

$$N_2^*(t) = k_{22} N_2 p \cdot e^{-\frac{t}{\tau_2}}, \qquad (5)$$

$$I_2 = k_{12} k_{22} N_2 p \tau_2 \cdot e^{-\frac{t}{\tau_2}}, \qquad (6)$$

The case with k_{12}=0 means that relaxation is nonradiative.

The model assumes that the electron excitations can be exchanged between the luminescence centers. Since the depth of the trap under condition of C_2 is less, the transition of electron excitations occurs mainly from $C_2$to C_1. In this case the number of the excited states of C_1 centers is to increase in time by the value proportional to the decrease in the concentration $N_2^*(t)$. Assume that one part $N_{21}^*(t)$ of a number of the excited states $N_2^*(t)$ recombines at time t radiatively (or nonradiatively) during transition to the ground state. The other part of the excited states $N_{22}^*(t)$ (electrons, excitons and etc.) jumps barrier ΔE_2 under certain conditions and after that it is found in C_1 center. The change in the balance of the centers in an excited state in time can be written as:

$$N_2^*(t) = N_{21}^*(t) + N_{22}^*(t), \qquad (7)$$

The number of the excited states which can jump the barrier at time t is determined by the expression:

$$N_{22}^*(t) = k_{30} \cdot e^{-\frac{\Delta E_2}{kT}} N_2^*(t), \qquad (8)$$

where is the probability of the electron excitation transfer from C_2 center to C_1 center.

Assume that the law of variation in time $N_{22}^*(t)$ and $N_2^*(t)$ is described by an exponential. This assumption is satisfied if one of the processes of relaxation of the excited C_2 centers (to the ground state or transition to C_1 state) is dominant. Consequently:

$$N_{22}^*(t) = k_{30} e^{-\frac{\Delta E_2}{kT}} \cdot k_{22} \cdot N_2 \cdot p \cdot e^{-\frac{t}{\tau_2}} \qquad (9)$$

Transition of electron excitations from C_2 state to C_1 state C_2 causes increase in the concentration of centers $N_1^*(t)$ at time t by the value:

$$\Delta N_{1add}^*(t) = \int_0^t N_{22}^*(t) dt = k_{30} e^{-\frac{\Delta E_2}{kT}} \cdot k_{22} \cdot N_2 \cdot p \cdot (1 - e^{-\frac{t}{\tau_2}}) \qquad (10)$$

The total concentration of the excited C_1 centers at time t with account of recombination in these centers in time τ_1 (with $\tau_1 > \tau_2$) becomes equal to:

$$N_{1n}^*(t) = N_1^*(t) + N_{1add}^*(t) = k_{21} \cdot N_1 \cdot p \cdot e^{-\frac{t}{\tau_1}} + k_{30} e^{-\frac{\Delta E}{kT}} \cdot k_{22} \cdot N_2 \cdot p \cdot (1 - e^{-\frac{t}{\tau_2}}) \cdot e^{-\frac{t}{\tau_2}} \qquad (11)$$

Hence, the kinetics of the luminescence flash in centers C_1 is to be described by the expression:

$$I_{1II} = k_{11} \cdot k_{21} \cdot N_1 \cdot p \cdot \tau_1 \cdot e^{-\frac{t}{\tau_1}} + k_{11} k_{22} k_{30} \cdot e^{-\frac{\Delta E_2}{kT}} \cdot N_2 \cdot p \cdot (\tau_1 \cdot e^{-\frac{t}{\tau_1}} - \tau_2 \cdot e^{-\frac{t}{\tau_2}}) \qquad (12)$$

Figure 4 shows, as an example, the calculation results for the kinetic curve of the cathodoluminescence flash initiated by instantaneous excitation pulse at different ratios of the characteristic relaxation times of C_1 and C_2 centers.
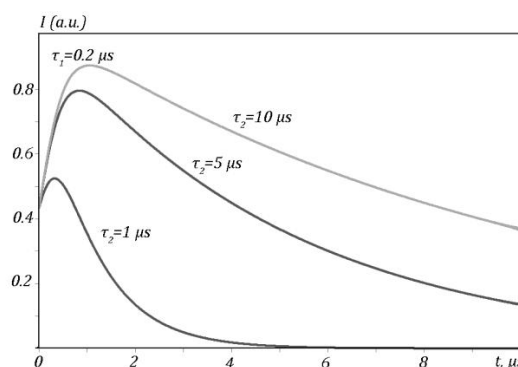
Figure 4. The results of the calculation of the kinetic curve flash cathodoluminescence initiated instantaneous excitation pulse at different ratios of the characteristic relaxation times

4. Conclusion

In the kinetics of the luminescence flash in LiYF$_4$: Nd crystals excited by nanosecond electron beam at room temperature, the buildup is observed at the initial stage up to 300 ns. The buildup of PCL can be attributed to the transfer of the excitation energy stored in the trapping centers to the luminescence centers. A model of the exchange of electron excitations between the luminescence and trapping centers is suggested. According to the model, the buildup stage becomes possible if a number of conditions have been fulfilled. The buildup is possible only for certain ratios of the characteristic times of excitation relaxation in competing centers, concentration of these centers, the sample temperature and excitation power. Typically, the excitation pulse energy is not instantaneous in relation to the time resolution of the measuring system. The temporal resolution of the device is to be adjusted to the chosen pulse duration to obtain the maximum relevant measurement. In case the pulse shape is known and takes the form of *p(t)*, substitution of the function *p(t)* in (12) makes it possible to take into account the impact of the pulse shape on the luminescence flash kinetics. Moreover, it allows us to obtain information with a high temporal resolution by means of mathematical processing.

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