Optical Materials 42 (2015) 325–330

Contents lists available at ScienceDirect

Optical Materials

journal homepage: www.elsevier.com/locate/optmat

Two possible causes of the stage of emission buildup after excitation by a nanosecond electron flux pulse

V.M. Lisitsyn [a], L.A. Lisitsyna [b], Z.T. Karipbayev [c], D.T. Valiev [a], S.A. Stepanov [a,*]

[a] National Research Tomsk Polytechnic University, Lenin Avenue 30, 634050 Tomsk, Russia
[b] Tomsk State University of Architecture and Building, Soljanoj Street, 2 Tomsk, Russia
[c] L.N. Gumilyov Eurasian National University, Astana, Kazakhstan

ARTICLE INFO

Article history:
Received 6 September 2014
Accepted 18 January 2015
Available online 7 February 2015

Keywords:
Luminescence
$LiYF_4:Nd^{3+}$
$LiF–WO_3$
Decay kinetics
Time-resolved luminescence spectroscopy
Electron excitation

ABSTRACT

Impact of short-time radiation pulse on optical materials initiates luminescence flash, formation and transformation of color centers (defects) in them. The present paper is devoted to the study of the mechanisms of the occurrence of the luminescence buildup stage in $LiF–WO_3$ and $YLiF_4:Nd^{3+}$ crystals in which this effect is found to be steady at 300 K after exposure to the high-energy electron flux pulse of nanosecond duration, also proposed a model to describe the kinetics of cathodoluminescence growth under pulsed excitation.

1. Introduction

The action of hard radiation pulses on optical materials leads to the creation of electron excitations in the host, excitation of the existing emission centers, formation of new and transformation of the existing defects. Relaxation of electron excitations in a wide time interval after the end of the radiation pulse action is followed is by emission [1,2], transformation of the radiation defects formed by radiation into stable ones under the conditions of the experiment [3].

Exposure of crystals to radiation pulses of nanosecond duration has revealed the existence of the emission buildup stage of short duration. In [4–6] it is shown that after exposure of the tungsten-doped LiF crystal to a high-energy electron flux pulse at 300 K the emission intensity is found to increase after the end of the pulse action. Increase in the luminescence after exposure to the radiation pulse is found in CsI (Tl) crystal [7]. The occurrence of the buildup stage and the shape of the kinetic curves of cathodoluminescence relaxation depend on many factors: the type of the material, the temperature of the sample under excitation, the history of the sample and excitation power.

For different materials and different experimental conditions at least two factors may lead to rise of the emission stage after exposure of the crystal to the ionizing radiation flux pulse, as a result of the recovery of the crystal transparency due to the destruction of transient color centers created by the radiation pulse or due to the redistribution of the excitation energy between the competing centers.

This paper focuses on the mechanisms of the occurrence of the emission buildup stage in $LiF–WO_3$ and $YLiF_4:Nd^{3+}$ crystals in which this effect is found to be steady at 300 K after exposure to the high-energy electron flux pulse of nanosecond duration.

2. Test samples and experimental technique

LiF crystals doped with tungsten were grown in air at the ISMA NAS of Ukraine (Kharkov). The distribution of the dopant throughout the height of the crystal is nonuniform. The concentration of the dopant toward the bottom of the crystal is much higher than that at the top. The tested samples were cleaved from a monoblock of the grown crystal at different distances from its bottom. A steep transparency cutoff in the region above 4.5 eV testifies to different impurity concentration entered in the crystal. The transparency cutoff from the bottom of the samples is found to be the steepest in the long wavelength region of the spectrum. In pure, not intentionally doped LiF crystals, the transparency cutoff is found at 11.5 eV.

* Corresponding author at: National Research Tomsk Polytechnic University, Institute of High Technology Physics, Department of Lasers and Lighting Engineering, Tomsk, Russia. Tel.: +7 38 22 42 05 67; fax: +7 38 22 41 98 31.
E-mail address: stepanovsa@tpu.ru (S.A. Stepanov).

http://dx.doi.org/10.1016/j.optmat.2015.01.022
0925-3467/

The undoped and doped Nd^{3+} $LiYF_4$ crystals were grown in vacuum in INCROM Ltd.

The parameters of the electron pulses (EP) to excite the samples were as follows: 10 ns duration, the average electron energy of 250 keV, the energy density of the excitation pulse of 15 mJ/cm^2. The energy of a single pulse absorbed in the LiF crystal was 8×10^2 Gy. We studied pulsed cathodoluminescence (PCL), pulsed photoluminescence (PPL) and induced transient absorption in the spectral range of 2.0–3.5 eV in the temperature range of 80–300 K. The kinetics of the emission relaxation and the relaxation of the induced absorption was measured in the time interval of 1×10^{-8}–1×10^{-4} s after the end of the excitation pulse action. The photoluminescence was excited by the 4th harmonic (4.66 eV) of the Nd:YAG laser, model LQ929. The emission and changes in the absorption were recorded with PMT-106, PMT-84-6, a digital oscilloscope Gwinstek GDS-2204 (200 MHz bandwidth/transmission band), Tektronix TDS-2014 (100 MHz), and MDR-206 and MDR-3 monochromators. The emission spectra were reconstructed from a set of measurements of the decay kinetic curves of emission relaxation at specific wavelengths. To obtain one spectrum the crystal was excited by 30–50 electron or laser radiation pulses.

3. Experimental results

The action of EP or laser pulse with the photon energies of 4.66 eV on the LiF:WO_3 crystal excites a characteristic emission in the range of 3.5–2.0 eV with the band maximum at 2.7 eV and FWHM of 0.6 eV. Fig. 1a shows the PCL spectrum of the LiF–WO_3 crystal measured after 30 μs after the end of the excitation pulse action at 300 K before irradiation and after irradiation of the crystal by EP. Repeated exposure of the crystal to EP does not change the shape of the spectrum. The photon energy of 4.66 eV is sufficient to excite the emission centers responsible for the emission at 2.7 eV. At high concentrations of tungsten the crystal transparency decreases sharply in the spectral region above 4.5 eV. As the dopant concentration in the crystal grows, the emission intensity at 2.7 eV decreases. In "pure" crystal the photoluminescence at 2.7 eV is not excited.

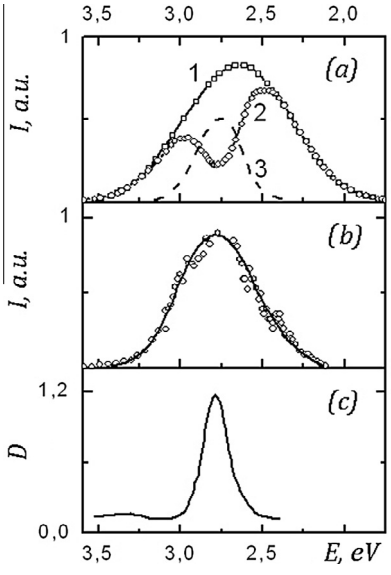

Fig. 1. (a) PCL spectrum measured with 30 μs delay at 300 K in LiF–WO_3 crystals before (1) and after electron irradiation at 300 K ($D = 8 \times 10^4$ Gy) (2), the difference spectrum (3). (b) PCL spectrum of the LiF–WO_3 crystal irradiated ($D = 8 \times 10^4$ Gy) at 200 K measured at 15 K with a time delay of 30 μs. (c) Fragment of the absorption spectrum of the LiF–WO_3 crystal irradiated with an electron dose of $D = 8 \times 10^4$ Gy at 300 K.

Quite similar PCL spectrum is excited in the same crystal at 15 K after pre-irradiation at 200 K (Fig. 1b). Pre-irradiation of the crystal at low temperatures does not change the PCL spectra.

In the same region of the spectrum in the LiF–WO_3 crystal the action of the electron flux (EP train) induces optical absorption (Fig. 1c) caused by complex color centers. In the spectral region of 2.5–3.2 eV, where the absorption bands of the F_2, F_{3+}, F_3 electron color centers are overlapped, the induced absorption changes most profoundly [8–10]. Irradiation of the sample by EP with the photon energy of 4.66 eV does not result in the formation of new radiation-induced defects. Therefore, laser excitation makes it possible to find out the effect of the color centers pre-induced by EP on the radiative characteristics of the crystal.

Pre-irradiation of LiF–WO_3 crystals with a dose of 8×10^4 Gy significantly changes the photoluminescence spectrum (Fig. 1a, spectrum 2). Fig. 1a, spectrum 3, shows the difference between the photoluminescence spectra of the unirradiated LiF:WO_3 crystals and those exposed to the electron flux with a dose of 8×10^4 Gy. The difference spectrum is found to be similar to the absorption spectrum of the LiF crystal with the (F_2, F_3^+) color centers given in Fig. 1c. This suggests that the induced absorption causes emission degradation in the LiF–WO_3 crystal [6].

Alkali halide crystals are known for highly efficient formation of color centers [11–13]. The radiation defects formed predominantly annihilate, and a small part of the defects remains unchanged [3]. Therefore, we can expect that the color centers induced by EP and the additional optical absorption caused these centers can affect the efficiency of the cathodoluminescence excited by the same pulse. Since the color centers annihilate in time, the induced transient optical absorption may affect the emission decay kinetics due to destruction of the centers and decreased absorption since the spectral regions of the emission and absorption are overlapped. Note that in LiF–WO_3 crystals complex the color centers are formed more efficiently at low irradiation doses than those in "pure" LiF crystals since vacancies, interstitial ions and oxygen, hydrogen and OH ions enter the crystal with the dopant to compensate for excess charges and to relieve local stresses [14].

Fig. 2 shows the measurement results for the changes in the cathodoluminescence kinetics in time in the absorption band maximum after excitation at 300 K. The emission kinetics was measured in two time intervals. In a nanosecond range (Fig. 2a), within the time of pulse excitation the emission intensity reaches a specific limit value, and then after a small decline it gradually grows. Increase in the emission intensity is found in the microsecond range of 2–4 μs. After that, as seen from the results (Fig. 2b), the growth is followed by decay with a characteristic decay time equal to 25 μs.

The occurrence of the buildup stage depends on the temperature of the crystal under the EP action. Fig. 3 shows the results obtained for the cathodoluminescence kinetics of LiF–WO_3 crystal at 80 and 300 K. At low temperatures, after exposure to EP the emission is observed only to decline. Pre-irradiation of the LiF–WO_3 crystal by EP does not cause any change in the described patterns: at 300 K, after the end of the excitation pulse action, we can observe the stage of the emission buildup.

As the temperature of the sample falls down to 250 K, the buildup stage disappears.

Fig. 4 shows the results obtained for the relaxation decay kinetics of the absorption induced by EP in the radiation spectral range. As can be seen from the results in Fig. 4, additional absorption in the band maximum (2.75 eV) increases rapidly after exposure to EP, then within a microsecond time interval it falls. The change in the optical density of the induced absorption in time beyond the band, at 3.1 eV as an example, is much smaller.