Pulsed cathodoluminescence of LiF-Fe2O3 crystals

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Abstract. We have conducted an in-depth study of pulsed cathodoluminescence of LiF-Fe$_2$O$_3$ crystal at temperatures $20 - 300$ K and the time interval of 10 ns – 10 µs for the first time. It is shown that two types of luminescence centers can be formed on the basis of O^{2-} ion. The first center is excited by the doped impurity, and the second center is the part of the impurity complex. It is found that the processes of formation and accumulation of primary radiation defects affect the parameters and characteristics of the activator luminescence in LiF-Fe$_2$O$_3$ crystals.

1. Introduction

Lithium fluoride can be used as an efficient scintillator for systems to record astrophysical neutrinos and dark matter [1]. Under ionizing radiation, LiF crystals containing no activator impurity luminesce weakly and at low temperature only [2]. High yield of luminescence of lithium fluoride crystals is characteristic of lithium fluoride doped with metal oxides: LiF-WO$_3$, LiF-TiO$_2$ and others [1,3,4]. Previously, it was found that under electron irradiation the behavior of LiF-WO$_3$, LiF-TiO$_2$, LiF-Fe$_2$O$_3$ crystals is identical, and the patterns of pulsed cathodoluminescence (PCL) are similar [5,6]. For example, in all the crystals under electron irradiation, the reaction of O^{2-} center formation occurs as a result of destruction of the OH$^-$ groups present in the crystal. A long-lasting buildup stage is characteristic of the activator luminescence in these crystals.

The behavior patterns of LiF-WO$_3$, LiF-TiO$_2$, LiF-Fe$_2$O$_3$ crystals under irradiation by electron beam are similar, apparently, due to the same set of defects present in the activator impurity in the crystal during its growth, for example, to compensate the excess charges. The main impurities are oxygen, OH$^-$ groups and other hydrogen-oxygen defects [3]. The presence of OH$^-$ is indicated by the reaction of transformation of OH$^- \rightarrow$ O$_2^-$ and by IR absorption spectra, and atomic oxygen ions can be indicated by the absorption bands in the VUV spectral range. It is evident that these defects affect the scintillation properties and degradation characteristics of scintillators based on lithium fluoride in long-term exposure to radiation.

Previously, we have studied accumulation of O$_2^-$ centers, F-, F- aggregate color centers in LiF-WO$_3$, LiF-TiO$_2$, LiF-Fe$_2$O$_3$ crystals under irradiation by electron beam [7]. However, the mechanism of luminescence excitation and the exact structure of the activator luminescence center have not been clarified so far. This data is of primary importance to improve characteristics of scintillation detectors. The aim of this research is to study the features of the activator luminescence in LiF-Fe$_2$O$_3$ crystals under irradiation by electron beam.

2. Technique

PCL was excited by the electron beam generated by a nanosecond pulsed accelerator. The parameters of the electron beam were as follows: the duration of the electron current pulse was 2–10 ns; the probable current densities of the electron beam varied in the range of 0.1–1000 A/cm^2; the average electron energy was 200 – 250 keV. The spectral characteristics of the luminescence were recorded with the time resolution of 7 ns with MDR 204, PMT 97, 83 and oscilloscope Tektronix. The technique is described in detail in [8]. The stationary luminescence spectra were measured with Cary Eclipse spectrofluorometer at 300 K. The absorption spectra were measured with SF-256UVI spectrophotometer.

3. Research results

In LiF-WO$_3$ and LiF-TiO$_2$ crystals, the bands of activator absorption are found in the spectral range of 190–300 nm, and photoexcitation in this range leads to intense activator luminescence. The absorption in this spectral region in LiF-Fe$_2$O$_3$ crystal is not distinct. Excitation with the wavelength of 200 nm is known to cause photo-luminescence of O^{2-} oxygen centers (absorption band at 6.2 eV in LiF is reported in [9]). Optical absorption by oxygen centers can be observed in LiF- Fe$_2$O$_3$ crystals as well. Therefore, LiF-Fe$_2$O$_3$ can be used to study the photoluminescence of oxygen centers under excitation in the region of 6.0 eV.
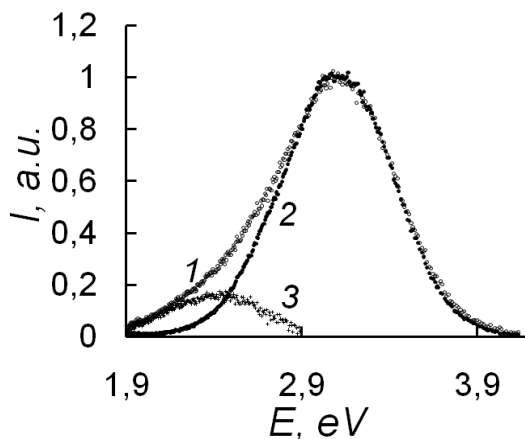

Figure 1. Photoluminescence spectra of LiF-Fe$_2$O$_3$ (1) and LiF-Li$_2$O (2) crystals under excitation with E = 6.05 eV at 300 K. 3 is a difference spectrum
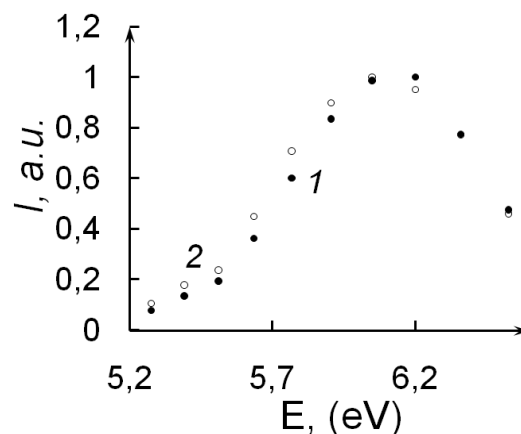
Figure 2. Excitation spectra of LiF-Li$_2$O (1) and LiF-Fe$_2$O$_3$ (2) crystals at 300 K.

Figure 1 shows the luminescence spectra of LiF-Li$_2$O and LiF-Fe$_2$O$_3$ crystals under photoexcitation by photons with the energy E = 6.05 eV. In lithium fluoride containing only oxygen, the luminescence is represented by one Gaussian band with the maximum at 3.1 eV and FWHM at 0,76 eV. This photoluminescence (PL) band is caused by (O^{2-} − V$_a$) centre, where V$_a$ is an anion vacancy [3,4]. The luminescence excitation spectrum of this center measured at E = 3.1 eV is shown in figure 2 (curve 1). It consists of a band with the maximum at E = 6.0 eV.

Under excitation by photons with the energy E = 6.05 eV, the photoluminescence spectrum of LiF-Fe$_2$O$_3$ crystal is found to consist of two bands (figure 1, curve 2). The first band is identical to the luminescence band of O^{2-} oxygen ion, and the maximum of the second band is in the point where E = 3.1 eV. The excitation spectra of both luminescence bands are found to coincide figure 2 (curve 2).

We conducted an in-depth study of the spectral and kinetic characteristics of the activator PCL of LiF-Fe$_2$O$_3$ crystal in the temperature range of 20 – 300 K over the time interval of 10 ns – 10 ms. The kinetics of the activator luminescence decay after excitation by nanosecond electron pulse can be described as the sum of two exponentials.

$$I = I_{01}exp\ (-t/\tau_1) + I_{02}exp\ (-t/\tau_2)$$

At room temperature, at E = 3.0 eV: I_{01} =8 a.u., I_{02} = 1 a.u., τ_1 =1.9 µs, τ_2 = 74µs. Figure 3 (curves 1 and 2) show the normalized spectra of slow (decay within a millisecond time interval) and fast (decay within a microsecond time interval) components of PCL decay for LiF-Fe$_2$O$_3$ crystal at 300 K. The maxima of the luminescence bands in these spectra are at 2.65 eV and 2.9 eV. The bands of each component of PCL decay are asymmetrical and can be formally decomposed into two Gaussian components with the maxima in the regions of 3.05 eV and 2.6 eV, and FWHM equal to 0.47 eV and 0.51 eV. The results of this decomposition of the spectra at 300 K are shown in figure 3 (curves 3, 4, 5, 6). It is seen that the relations of the luminescence bands of the fast and slow decay components are different.

If the temperature of the sample decreases to 20 K, the PCL is shifted to the region of higher energies. At low temperatures, the spectrum can also be represented as the sum of two bands. The relation of these bands differs from that at 300 K, and the luminescence decay kinetics at 20 K is described only by one exponential with τ_1 = 3.4ms.
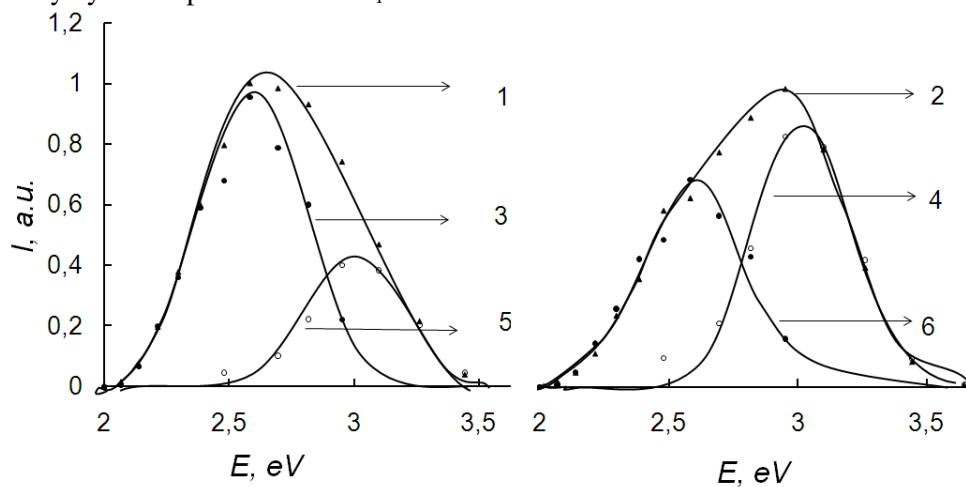

Figure 3. Normalized spectra of PCL for LiF-Fe$_2$O$_3$ crystal at 300 K. 1 is a slow decay component; 2 is a fast decay component; 3, 4, 5, 6 are results of decomposition into Gaussian components.

In case the temperature of the crystals under irradiation by electron beam changes, all the parameters of the kinetics of the activator luminescence decay change: decay time constant τ, intensity I, and the emitted light sum (S = I×τ). The dependences of the parameters of the fast and slow PCL decay components on temperature are different.
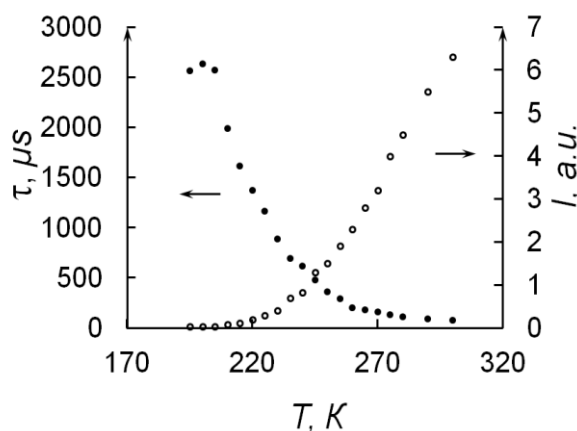

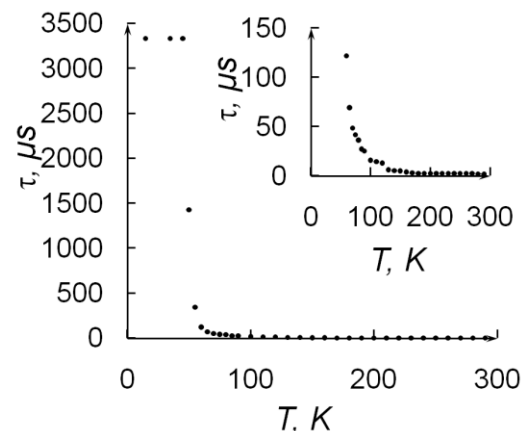**Figure 4.** Temperature dependences of τ and I of the slow component of PCL decay for LiF-Fe$_2$O$_3$ crystal.

Figure 5. Temperature dependence of τ of the fast component of PCL decay for LiF-Fe$_2$O$_3$ crystal

Figure 4 shows the temperature dependence of τ and I for the luminescence of the slow decay component. In the temperature interval of 20 – 300 K τ of the slow decay component varies from 2.7 ms to 74 µs. The luminescence intensity in the range of 200 – 300 K increases. If temperature increases, the emitted light sum S increases starting from 200 K with a tendency to saturation at T > 250 K. From the results obtained it follows that at temperatures below 200 K, the slow decay component in PCL spectra is not observed due to strong decrease in the amplitude intensity. Therefore, at 15 K, both bands are represented by the fast component of the activator PCL decay only.

Figure 5 shows the temperature dependences of the parameters of the fast component of PCL decay for LiF-Fe$_2$O$_3$ crystal. It is seen that τ is constant at low temperatures, whereas at T > 50 K it sharply decreases. As temperature grows, τ keeps decreasing but at a slower rate. The second temperature point of significant change in τ falls within the range of 110 – 140 K (inset in figure 5). The luminescence intensity significantly increases at T > 50 K, and at temperatures above 120 K the intensity rapidly increases if temperature of the sample grows. The dependence of S = I×τ on temperature is shown in figure 6. This dependence reveals a number of characteristic temperature regions in which the emitted light sum S rapidly changes. These regions account for the temperature ranges of 40 – 60 K and 100 – 120 K.
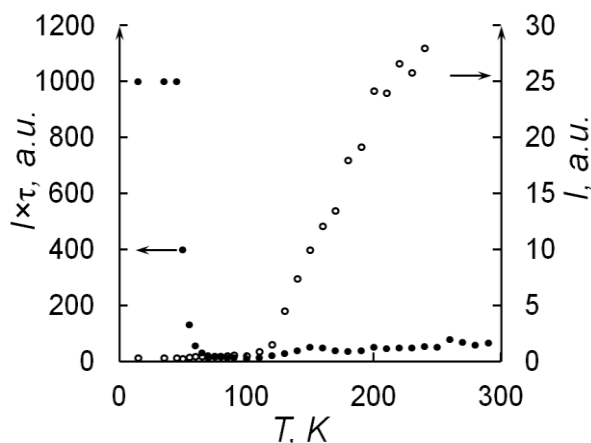

Figure 6. Temperature dependences of S = I×τ and I of the fast component of PCL decay for LiF-Fe$_2$O$_3$ crystal.

4. Discussion

PL spectra differ from PCL spectra in the positions of the maxima of bands and their FWHM. Therefore, different groups of luminescence bands are excited under photostimulated action and under irradiation by electron beam. These groups belong to different types of activator centers. Each group consists of two bands. The nature of each band can be substantiated by the following facts.

Only one luminescence band can be observed in the PL spectra of LiF- Li$_2$O crystal. As it has been shown in previous studies [3.4], this band may be due to the radiative transition in the $(O^{2-}-V_a)$ center where V_a is anion vacancy. The band at 3.1 eV can be attributed to the emission of O^{2-} nearby the impurity. This is confirmed by the coincidence of the excitation spectra of the bands at 3.1 and 2.42 eV. The emission band in the spectral range 2 – 3 eV in crystals containing Mg impurity is described in [4]. Therefore, the two photoluminescence bands may belong to the radiative transitions in two types of $(O^{2-} - V_a)$-centers, weakly excited (3.1 eV) and strongly excited (2.4 eV) by iron impurity. The excited state of the center is always exposed to greater impact of the nearby defect. For this reason, the absorption spectra of the two types of $(O^{2-} - V_a)$-centers can be similar, whereas the emission spectra can be different.

The alternative interpretation is that both photoluminescence bands in LiF-Fe$_2$O$_3$ crystal belong to one type of the impurity $(O^{2-} - V_a)$-center, but to different electronic transitions. In this case, the impact of the activator center causes the second photoluminescence band. That is the iron impurity

allows radiative electron transition at 2.4 eV. In both cases, excitation of the photoluminescence occurs as a result of the absorption of the energy by O^{2-} oxygen ion.

Both the PCL spectra of the activator luminescence and the PL spectra of LiF-Fe$_2$O$_3$ crystal consist of two luminescence bands. Under photoexcitation at 300 K, the parameters of these bands (peak position and FWHM) do not coincide with the parameters of the luminescence bands in ($O^{2-} - V_a$)-oxygen centers. It is evident that this is an activator intracenter luminescence. The electronic structure and nuclear configuration of the radiative state in this center are different from those of ($O^{2-} - V_a$)-center under photoexcitation. Therefore, two types of oxygen centers can be observed in the PL and PCL spectra of LiF-Fe$_2$O$_3$ crystal. The first type is ($O^{2-} - V_a$)-centre excited by impurity, and the second type is the complex which contains O^{2-} oxygen ion and activator impurity. The example of the second type of the luminescence center for LiF-TiO$_2$ crystal is reported in [4]. The cause of the two luminescence bands in PCL spectra may be the same as in the case of PL spectra, i.e. the existence of two types of nuclear configuration or two types of electronic transitions in the complex.

The analysis of the temperature dependences of the PCL decay parameters shows that abrupt changes of the values of these parameters are associated with characteristic temperature intervals of the formation and accumulation of color centers in pure lithium fluoride crystals. This distinguishes LiF-Fe$_2$O$_3$ crystal from LiF-WO$_3$, LiF-TiO$_2$ crystals. It is known that in pure crystals of lithium fluoride in the temperature range of 20 – 60 K, different types of the self-trapped excitons (STE) transform, the luminescence decays, and H-centers are delocalized [2]. In lithium fluoride crystal at temperatures close to 125 K, V_κ - centers accumulated at low temperatures are delocalized. At 100 – 120 K, the efficiency of Frenkel defect formation grows. The characteristic points of the abrupt change of the decay time, the intensity of the emitted PCL light sum are observed in the same temperature range (figures 4−6).

The causes of the stage of luminescence buildup in LiF-WO$_3$, LiF-TiO$_2$, LiF-Fe$_2$O$_3$ crystals are crucial for understanding the mechanisms of PCL excitation. This stage indicates the inertial mechanism of energy transfer from the base of the scintillator (lithium fluoride) to the luminescence center. The results of our research suggest that LiF-Fe$_2$O$_3$ crystal is an appropriate system to study these processes. In contrast to LiF-WO$_3$, LiF-TiO$_2$ crystals, in this crystal we can find temperature regions within which we can observe change in the parameters of PCL and in the parameters of formation and accumulation of radiation defects.

5. Conclusion
1. It has been found that two types of luminescence centers can be formed on the base of O^{2-} ion: the center excited by the doped impurity; the center as a part of the impurity complex. Each of the two types of centers consists of two radiation bands.

2. The processes of formation and accumulation of primary radiation defects are found to affect the parameters and characteristics of the activator luminescence in LiF-Fe$_2$O$_3$ crystals. This allows an in-depth study of the mechanisms of energy transfer from LiF crystal to the activator radiative center.

Acknowledgement

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