Degradation of emission parameters in LiF-MeO crystal scintillators

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Abstract. The paper presents the results of the research in spectral and kinetic parameters of the luminescence in phosphors based on LiF-MeO crystals. The potential of these phosphors used as scintillators in the ionizing radiation field is discussed.

1. Introduction

Scintillating materials based on oxygen compounds may be divided into two types: scintillators of a doped type and natural scintillators. LiF crystal is the scintillator of a doped type. The prospect of widespread using of this material based on the features of doped crystals structure making light output dopant emission comparable to that in natural scintillators [1, 2]. Application of oxygen-containing crystal phosphors as radiation detectors in medical diagnosis, customs control, detectors for fundamental science is being discussed in [3-5, 6, 7]. However, the potential of these materials as scintillators in the ionizing radiation field cannot be assessed since no data of the effect of radiation-induced defects in lattice crystals on scintillation characteristics of the material is available. (It is known that LiF lattice is very sensitive to ionizing radiation). Furthermore, information on radiation modification of the oxygen-containing impurity in the composition of the luminescence centers especially important for the understanding of the aging process in doped crystals placed in radiation field.

2. Object and Method

We used pulse spectroscopy methods to investigate LiF crystals doped with oxides of various metals (Me: W, Ti, Fe, Li). Imperfection of the crystals (initial and induced by ionizing radiation) was estimated through the analysis of the infrared absorption spectra in the range of 4000–1000 cm$^{-1}$ at 300 K, pulsed photoluminescence (PPL) and pulsed cathodoluminescence (PCL) spectra in the spectral region of 6–1 eV and in the time interval of $10^{-8}$–$10^{-1}$ s after the action of exciting pulses. PPL was excited at 300 K by laser pulses with photon energy of 4.66 eV and 10 ns pulse duration. PCL was excited by single electron pulse (EP) with the following parameters: pulse width of 10 ns, the average electron energy of 250 keV. The magnitude of the electron fluence per pulse was varied in the range of $10^{10}$ – $10^{13}$ cm$^{-2}$.

Irradiation of the crystal was carried out by electron pulses with repetition rate of $2 \times 10^{-2}$ Hz in the temperature range of 100–300 K.

The temporal and spectral resolutions of the measurement path were equal to 20 ns and 2 nm, respectively. The transparency cutoff of undoped LiF crystal and all doped crystals LiF was found in the UV region near 12 and 6 eV, respectively. The IR spectra of the LiF crystals doped with oxides of W, Ti or Fe contained a band at 3730 cm$^{-1}$ that belongs to hydroxide, and a number of narrow bands in...
the region of 3500–3600 cm$^{-1}$, which belong to Me-OH complexes. The LiF-Li$_2$O crystals were transparent in the IR region up to 1000 cm$^{-1}$.

Under exposure to laser radiation with photon energy of 4.66 eV, in all the as-grown crystals the PPL at 3.1 eV occurred ‘figure 1’. It was inertialess relative to the excitation pulse.

The kinetics of the dopant PPL decay at 300 K is described as a sum of two exponential functions:

$$ J(E,t) = J_{01} \exp(-\frac{t}{\tau_1}) + J_{02} \exp(-\frac{t}{\tau_2}), $$

(1)

where: $J_{01}, J_{02}$, and $\tau_1$, $\tau_2$ are the peak values of the emission components intensity and the magnitudes of the characteristic decay times, respectively ‘figure 1b’; $j$ is type cation-dopant (Li, Ti, W, Fe); $E$ is the energy of the emitted photon. The inequality observed for all the crystals are $\tau_1 << \tau_2$ and $J_{01} > J_{02}$.

![Figure 1. PPL spectrum at 300 K of the as-grown LiF-WO$_3$ crystal (a), and the kinetics of PPL decay at 2.8 eV (b).](image)

The contribution of the PPL long-living decay component in amplitude value of emission intensity at 3.1 eV does not exceed 20% at 300 K.

The spectra of the PPL decay components are found to be different ‘figure 2’. The peak position of the short-living dopant emission band (3.1 eV) with FWHM equal 0.5 eV ‘figure 2a’ and the emission duration ($\tau_j \leq 20$ ns) do not depend on the type of the cation-dopant. The peak position of the long-living dopant emission band depends on the type of the dopant and occurs at 2.7 (LiF-WO$_3$), 2.8 (LiF-TiO$_2$), 2.9 (LiF-Fe$_2$O$_3$) and 3.1 eV (LiF-Li$_2$O) at 300 K ‘figure 2b’.

![Figure 2. PPL spectra of short-living (a) and long-living components (b) at 300 K measured with 10 ns (a) and 10 µs time delay with respect to the end of the laser pulse action in as-grown LiF crystals doped with Li$_2$O (1), Fe$_2$O$_3$ (2), TiO$_2$ (3) and WO$_3$ (4). The spectra are normalized.](image)

The luminescence spectra of the decay components were measured as $J_0 = f(E)$, where $J_0$ is amplitude value of the intensity of the respective component at the emission energy $E$. 
The duration of the long-living dopant emission component PPL decay depends on the cation dopant type. It is shown that when its mass reduces, the dopant emission decay time increases ‘figure 3’.

3. Results and Discussion

1.1. Luminescence spectra of the preliminary irradiated doped crystals

Exposure to ionizing radiation (flux of 250 keV electrons) of the crystals causes formation of intrinsic primary electron and hole color centers (CCs) F₁ and Fᵢ₀, where F₁ is an electron localized at anion vacancy (Vₐ), Fᵢ₀ is a fluorine atom in interstitial state. At \( T \geq 250 \text{K} \) addition to primary CCs complex CCs are created (F₂, F₂⁺, F₃⁺…) under ionizing radiation of crystal. In PPL spectrum in addition to dopant emission bands new bands at 2.33 and 1.85 eV belonging to radiative transitions in the F₃⁺ and F₂ CCs, respectively, occur. The characteristic decay time of the additional bands coincides with the laser pulse duration. Figure 4 shows the PPL spectrum of the LiF-Li₂O crystal irradiated by electrons beam at 300 K and measured with time delay of 10 ns (curve 1) and 10 µs (curve 2) with respect to the end of the laser pulse action. (In both spectra, the bands at 3.1 eV belong to short-living and long-living components of the dopant center PPL. F₃⁺ and F₂ emission bands positions are marked with arrows).

![Figure 3](image3.png)

**Figure 3.** Dependence of the decay time of the long-living dopant PPL emission at 300 K on the cation-dopant mass.

![Figure 4](image4.png)

**Figure 4.** PPL spectra of the irradiated LiF-Li₂O crystal at 300 K measured with a time delay of 10 ns (curve 1) and 10 µs (curve 2) with respect to the end of the laser pulse action. D=10³Gy. (F₃⁺ and F₂ emission bands are marked with arrows).

It was found that the absorption band of F₂ and F₃⁺ CCs (2.75 eV) and emission long-living band (at 3–2.7 eV in different crystals ‘figure 2b’) occur in the same spectral region. The dopant emission is revealed to be reabsorbed by CCs that causes degradation of the dopant emission band ‘figure 5’. The reabsorption efficiency depends on CCs concentration and the degree of the CCs absorption band and dopant emission band overlapping (minimum overlapping of these bands occurs in LiF-Li₂O crystal).

It is evident from figure 5 that emission intensity due to degradation of the dopant emission band decreases in the region of 2.75 eV, i.e., in the region of maximum sensitivity of phosphor to radiation. The effect increases if concentration of F₂ (F₃⁺) CCs increases with increasing absorbed dose by crystals.

To avoid a decrease in the sensitivity of the scintillator due to the reabsorption of the dopant emission by radiation defects it is necessary to decrease the temperature of operation of the scintillator (at \( T \leq 250 \text{K} \) the efficiency of creating F₂ and F₃⁺ CCs is low), or enter a limited amount absorbed by the scintillator dose \( D₀ \), below which no dose dependence of emission intensity occurs. The following condition will be satisfied: if \( D < D₀, \quad J \neq f(D) \).

In addition to CCs formation, exposure to ionizing radiation of LiF-MeO (Me: W, Ti, Fe) crystals results in the destruction of hydroxide ions followed by creation of molecular \( \text{O}_2^- \) ions in an emission...
state with the absorbed dose-dependent efficiency. In the LiF-Li\textsubscript{2}O crystals transparent in the IR spectral region, ionizing radiation does not induce creation of molecular oxygen ions.

The PCL spectrum of the molecular oxygen ions is excited within the nanosecond EP at $T \geq 100K$ and consists of ten equidistant bands with 0.15 eV band spacing (‘figure 6’). PCL of O\textsuperscript{2−} ions is short-living and the value of the characteristic decay time at 300 K is 40 ns. The O\textsuperscript{2−} ion emission cannot be optically excited with quantum energy of 4.66 eV in LiF-MeO crystals. Figure 6 shows, for example, the PPL and PCL spectra for irradiated LiF crystal doped with iron oxide measured in a nanosecond time interval after the end of the excitation pulse action.

Result presented in figure 6 shows that in one the same irradiated crystal spectra PPL and PCL are different. PPL spectrum consists of dopant band at 3.1 eV and the bands at 2.33 and 1.85 eV belonging to F\textsuperscript{3+} and F\textsubscript{2−}CCs, respectively. PCL spectrum consists of the CCs bands at 2.33 and 1.85 eV and electron-vibronic bands belonging to O\textsuperscript{2−} ions. Weak dopant bands at 3.1 and 2.8 eV are covered with emission of O\textsuperscript{2−} ions.

1.2. Effect of irradiation temperature on PCL kinetic parameters

The temperature dependence of the characteristic time of the short-living dopant emission with the spectrum in the form of the band at 3.1 eV is shown in figure 7a. The character of dependence and the decay constant values recorded at different temperatures do not depend on the cation dopant type, and these are identical for all the investigated crystals. The temperature dependences of the characteristic decay time of the long-living dopant emission in LiF crystals doped with tungsten or titanium oxide are shown in figure 7b.

It is found that the temperature of the crystal under irradiation affects the kinetics of the long-living dopant luminescence buildup. If $T < 250K$, for all crystals the PCL buildup occurs within a nanosecond electron pulse action (‘figure 8a’). In the range 270–300 K, an additional post-radiation buildup stage is observed in all the studied crystals (‘figure 8b’). The common feature of the crystals is their non-transparency in UV energy $\geq 6$ eV, which is largely associated with the presence of oxygen-containing impurities.

So, post-radiation dopant emission buildup is observed only in the PCL spectra and absent under optical excitation of the same irradiated crystals. The PCL kinetics at the long-living dopant band at, $T \geq 270K$, compared with PPL decay kinetics described in equation (1), can be described as follows:

$$J(E, t) = J_{p0} \exp\left(-\frac{t}{\tau}\right) + \left[J_{w0} + J_{v0}(1 - \exp\left(-\frac{t}{\tau_{j1}}\right) \exp\left(-\frac{t}{\tau_{j2}}\right)\right]$$

where $\tau$ is emission decay time (ns) of three types of short-living centers in excited state (F\textsuperscript{3+} CCs, O\textsuperscript{2−} and O\textsuperscript{2−} ions) which emission bands overlap with long-living dopant emission band; $\tau_{j1}, \tau_{j2}$ are the characteristic time of long-living dopant emission buildup and decay, respectively.
Thus, inertialess buildup of dopant emission occurs in the excitation of the crystals as both laser and electron pulses ‘figure 1b’ and ‘figure 8a’ However, stage of post-radiation buildup dopant emission occurs only when crystals are excited by EP at high temperature. It means that post-radiation buildup is not an inherent property of the dopant and it occurs due to energy transfer from lattice to the dopant with participation of radiation defects which are mobile in temperature region of ≥270 K.

A superposition of delay emission process, realizing with delay parameter \( \tau_j \), and process of the post-radiation buildup, realizing with buildup parameter \( \tau_3 \), leads to degradation of the emission pulse form ‘figure 8b’ and the increasing of duration PCL pulse. In one and the same irradiated crystal the duration of PCL dopant emission pulse longer than the duration of PPL dopant emission pulse due to stage of post radiation buildup of the dopant cathodoluminescence ‘figure 8’.

The nature of the doped crystal emission can be interpreted as follows.

1. The band in the region of 3.1 eV belongs to allowed intracenter transition on free \( \text{O}^{2-} \) ions being present in all the studied crystals can be described by equation (3):

\[
O^{2-} + E \rightarrow (O^{2-})^n \quad \rightarrow O^{2-} + h\nu_0,
\]

(In equation (3) \( h\nu_0 = 3.1eV \), \( \tau_1 \) is time decay allowed emission transition in free \( O^{2-} \) ion).

2. The long-living dopant emission with spectral-kinetic parameters, which depend on the type of the cation-dopant, is the result of allowed intracenter transition on \( O^{2-} \) ion being located in the \( \text{Me}^n \text{mO}^{2-} \) complex, where \( n \) is charge state of dopant in crystal lattice, \( m \) is the number of oxygen ions coordinated with \( \text{Me}^n \). The structure of the impurity complex defines both the value of the energy emitted by oxygen ion and the probability of the radiative transition. Long duration of the allowed emission transition on \( O^{2-} \) ions is determined by the duration of the intermediate reversible transfer of the charge from \( (O^{2-})^n \) ion to \( \text{Me}^n \) ion and can be described by equation (4):

\[
\text{Me}_j^{(n-1)mO^{2-}} + E \rightarrow \text{Me}_j^{(n-1)mO^{2-}} \quad \text{O}^{2-} \quad \rightarrow \text{Me}_j^{mO^{2-}} \quad \text{O}^{2-} \quad \rightarrow \text{Me}_j^{(n-1)mO^{2-}} + h\nu_j,
\]

\( \text{Me}_j^{mO^{2-}} + E \rightarrow \text{Me}_j^{mO^{2-}} \quad \text{O}^{2-} \quad \rightarrow \text{Me}_j^{mO^{2-}} \quad \text{O}^{2-} \quad \rightarrow \text{Me}_j^{mO^{2-}} + h\nu_j \).
where: \( \text{Me}_j \) and \( n \) are the type cation-dopant and its charge state in lattice, respectively (\( \text{Me}_j: \) W, Ti, Fe or Li and \( n: 6, 4, 3, 1 \), respectively).

For \( \text{Me}_j: \) W, Fe, Ti the observed inequality is \( h\nu_j < h\nu_0 \). Apparently the value of \( \Delta E_{em} \) equal to \( (h\nu_0 - h\nu_j) \) is the characteristic of an energy loss in the process of lattice relaxation to create the appropriate type impurity complex \( \text{MeO} \) during LiF crystal growing. According to results presented in figure 2b, value \( \Delta E_{em} \) is equal to 0 (in LiF-Li_2O), 0.2 (in LiF-Fe_2O_3), 0.3 (in LiF-TiO_2), 0.4 eV (in LiF-WO_3). The value of \( \Delta E_{em} \) is determined not only by type on cation-dopant but also the number of oxygen ions coordinated with it.

In equation (4) the observed inequality is \( \tau_{2j} \gg \tau_1 \). The value of \( \tau_{2j} \) is determined by original valence of the dopant; the dopant mass; the degree of overlapping of the wave functions of the cation-dopant and the oxygen ion in the excited state; duration of the transfer of hole \( (\text{O}^-) \) between equivalent (or nonequivalent) \( \text{O}^2^- \) ions coordinated with \( \text{Me}^{n+} \); a degree of lattice relaxation during the charge transfer to the cation-dopant. (The fact that the electron of the excited \( \text{O}^2^- \) ion is easily transferred to the neighboring defect having an effective positive charge and that this reaction is reversible are proved in [8]).

4. Conclusions

In the process operation of phosphorus based on crystals LiF-MeO in the field of ionizing radiation a decrease of light output of the scintillators and a change in the parameters of the scintillation pulse occur with increasing absorbed dose.

Reducing the light output due to the decrease in the intensity of the long-living dopant emission is caused by the reabsorption of the dopant emission by intrinsic radiation-induced defects, which concentration increases when the absorbed dose grows. The external parameters such as the value of the absorbed dose or the temperature of the crystal by irradiation may lead to an invariance of the dopant emission. So, if \( T \leq 250K \), ionizing radiation virtually does not lead to creation of complex electron CCs, and hence, it does not cause dopant emission reabsorption. In the operation of the scintillator in the field of ionizing radiation at \( T \geq 250K \) post-radiation dopant emission buildup of the PCL occurs. Overlapping emission decay and emission buildup results in changing the shape of the scintillation pulse in PCL and, as a result, the increase in the duration of the scintillation pulse.

The duration of the scintillation pulse can be maintained stable through the introduction of restrictions on the temperature of crystal operating in field of ionizing radiation. At \( T \leq 250K \) no emission buildup process can be observed. The radiation fields with photon energy less than the band-gap are considered to be most favorable for operation of scintillators based on LiF-MeO. This provides the stability of the emission pulse duration and high light output.

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