

## Structure of oxygen centers in lithium fluoride with metal impurities

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The work presents the results of the study of luminescence of LiF–Fe<sub>2</sub>O<sub>3</sub>, LiF–TiO<sub>2</sub> and LiF–WO<sub>3</sub> crystals during photoexcitation in the region of 4.0...6.2 eV (impurity absorption) at temperatures of 80...300 K. It was established that in LiF with multivalent metal impurities that replace Li<sup>+</sup> ions, two types of luminescence centers are created in the form of pairs of O<sup>2-</sup>–V<sub>a</sub><sup>+</sup> ions located in neighboring nodes and O<sup>2-</sup>–Me, which correspond to two luminescence bands 3.1 eV and 2.6 eV. The center O<sup>2-</sup>–Me (Fe, Ti, W) creates absorption bands in the region 4.0...6.2 eV with parameters similar for the same type of bands in crystals with different metals. The number of these bands is determined by the valence of the metal, that is O<sup>2-</sup> – the number of ions necessary to compensate for the excess charge of the metal, which are located in the nodes closest to it and form a single complex color center.

**Keywords:** photoluminescence, lithium fluoride, metal impurities, oxygen centers.

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### Introduction

The interest in studies of luminescence of LiF crystals with metal impurities is due to the fact that they can be used as effective scintillators for detection of dark matter particles [1–4] and as model systems for studying the processes of directed formation of the defect structure, including the creation of luminescence centers by substituting matrix lattice ions with other ions [5–7]. The possibility of using lithium fluoride as an optical memory for constructing a three-dimensional image of a beam of hard X-ray radiation in the form of a density distribution of color centers was also shown in [8].

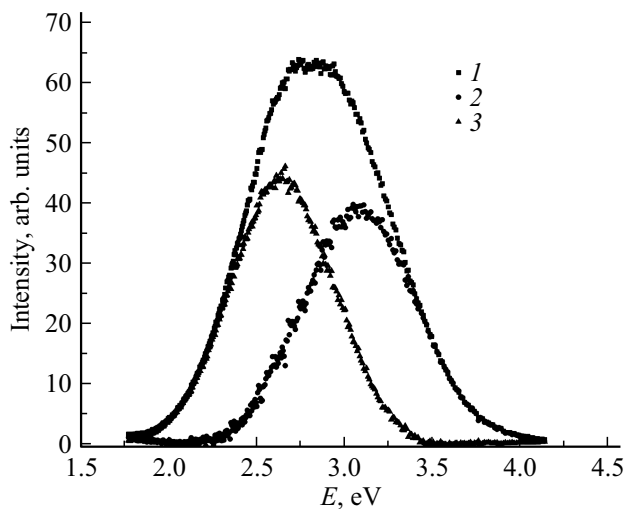
The growth of ionic crystals doped with impurities of a different valence than the base ions must be accompanied by the incorporation of ions compensating for excess (or deficient) charge and/or the creation of intrinsic defects. It is known that impurities of multivalent metals are introduced into LiF crystals in the form of oxides [1,5–7], since oxygen can serve as a compensator ion for the excess charge of metal. Therefore, luminescence centers, including those with scintillation properties, must be complexes containing metal, oxygen impurities, and intrinsic structure defects, such as O<sup>2-</sup>, Me<sup>2+</sup>–O<sup>2-</sup>, O<sup>2-</sup>–V<sub>a</sub><sup>+</sup>, etc. [5,6]. At the same time, impurities and defects should provide electrical neutrality in a local area of the crystal, and this determines the specific structure of a luminescence center.

Such oxygen centers are found in LiF crystals doped with oxygen O<sup>2-</sup>, OH<sup>-</sup> groups, and multivalent metals. The most studied is the (O<sup>2-</sup>–V<sub>a</sub><sup>+</sup>) center, which is easily created in LiF–Li<sub>2</sub>O crystals. This center absorbs upon excitation by quanta with energies  $E > 6.1$  eV and produces a luminescence band with a maximum around 2.95–3.1 eV.

The structure of this center [5] has been established reliably. The absorption is assumed to result from charge transfer from the  $p$  orbital of oxygen O<sup>2-</sup> to the  $s$  orbital of the  $F$ -center (vacancy). The reverse transition results in luminescence.

It was demonstrated that oxygen centers of the O<sup>2-</sup>–Me type may be produced in addition to (O<sup>2-</sup>–V<sub>a</sub><sup>+</sup>) centers. A model of such an impurity oxygen center in LiF–MgO was substantiated in [6]. Magnesium and oxygen are incorporated into the lattice as strongly bound complexes Mg<sup>2+</sup>–O<sup>2-</sup>, where Mg<sup>2+</sup> and O<sup>2-</sup> ions are located at the nearest cation and anion sites. In crystals with metal impurities, oxygen centers in LiF–TiO<sub>2</sub> have been investigated most thoroughly. They suggest the possibility of creating similar complexes in which electronic transitions upon absorption in Ti–O centers proceed from the  $2p$  state of oxygen to  $3d$  levels of Ti [5]. The titanium center variant was described in [7] and consists of an Ti<sup>4+</sup> ion at a cation site, an O<sup>2-</sup> ion at an anion site, and two cation vacancies. However, there is no comprehensive and credible justification for this type of center. There are also no assumptions about the influence of the valence of metal embedded in the crystal lattice on the structure and efficiency of oxygen luminescence centers, including the influence of charge-compensating defects on the properties of such a center.

We have recently shown [1,9,10] that pulsed cathodoluminescence spectra of LiF–Fe<sub>2</sub>O<sub>3</sub>, LiF–TiO<sub>2</sub> and LiF–WO crystals are not elementary and consist of two bands with sufficiently close parameters for all types of crystals. The existence of two photoluminescence bands in LiF–TiO<sub>2</sub> crystals has also been reported in earlier studies [5].



**Figure 1.** PL spectrum of LiF–TiO<sub>2</sub> (1) and its components (2, 3); excitation at 230 nm (5.39 eV), 300 K.

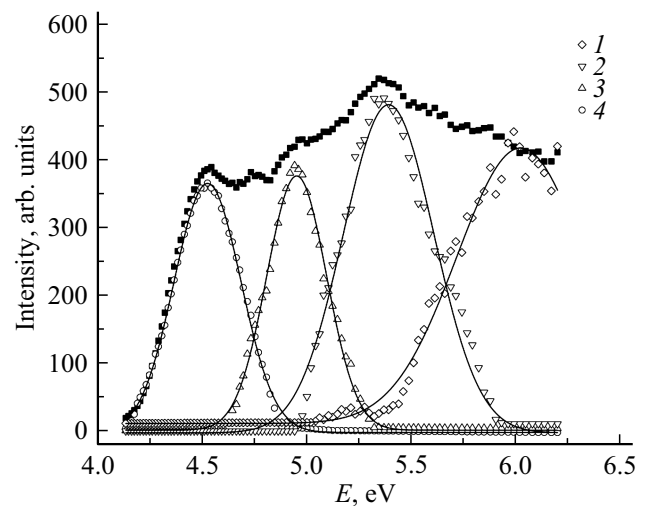
The present work is focused on the study of luminescence properties of LiF–Fe<sub>2</sub>O<sub>3</sub>, LiF–TiO<sub>2</sub>, and LiF–WO<sub>3</sub> crystals under selective photoexcitation in the 4.0...6.2 eV region (impurity absorption) at temperatures of 80...300 K. The set of crystals studied is interesting in that metals introduced during growth differ in valence, i.e., have a different number of combinations (and possibly differ in type) of defects created to compensate for the excess charge of metal compared to the charge of a lithium fluoride cation they replace. Thus, the radii of ions Fe<sup>3+</sup>, Ti<sup>4+</sup>, Ti<sup>3+</sup>, W<sup>6+</sup>, and W<sup>4+</sup> are close to the radius of the Li<sup>+</sup> ion, and the radii of ions O<sup>2-</sup> and F<sup>-</sup> are the same. Consequently, metal and oxygen ions can be easily incorporated into the lattice sites of lithium fluoride.

Crystals were grown at the Institute of Scintillation Materials (Kharkiv). The concentration of W, Ti, and Fe impurities in the charge in crystals was within the range of 0.01–0.02 mass%.

A Cary Eclipse spectrofluorimeter (Agilent, USA) was used for the studies. The decomposition of photoluminescence (PL) and luminescence excitation (LE) spectra into elementary components was performed by the Alentsev–Fock [11] method.

### Photoluminescence spectra

It was found that in all investigated lithium fluoride crystals with metal impurities, photoexcitation in the 4.0...6.0 eV region leads to the emergence of two PL bands. The spectral parameters of same-type bands (their maxima and half-widths) are close, but differ in crystals with different metals. The ratio of band intensities depends on the wavelength of excitation light, temperature, and type of embedded metal. The PL spectrum and the results of its decomposition into components at 300 K in LiF–TiO<sub>2</sub> are shown as an example in Fig. 1. The band maxima are



**Figure 2.** LE spectrum of LiF–WO<sub>3</sub> and results of its decomposition into Gaussian components 1–4; monitoring at 2.88 eV, 300 K.

positioned at 2.6 and 3.1 eV, and the half-widths are 0.58 and 0.62 eV, respectively.

The strongest differences in parameters of the PL bands in different crystals are observed when the crystal temperature decreases. Table 1 presents these parameters in the studied crystals at 80 K. It can be seen that the maxima of the high-energy band (1) in different crystals are close to those for the (O<sup>2-</sup>–V<sub>a</sub><sup>+</sup>) center emission band. However, the half-widths of this PL band in LiF–TiO<sub>2</sub> and LiF–WO<sub>3</sub> crystals are very different from the half-width of the (O<sup>2-</sup>–V<sub>a</sub><sup>+</sup>) center PL band.

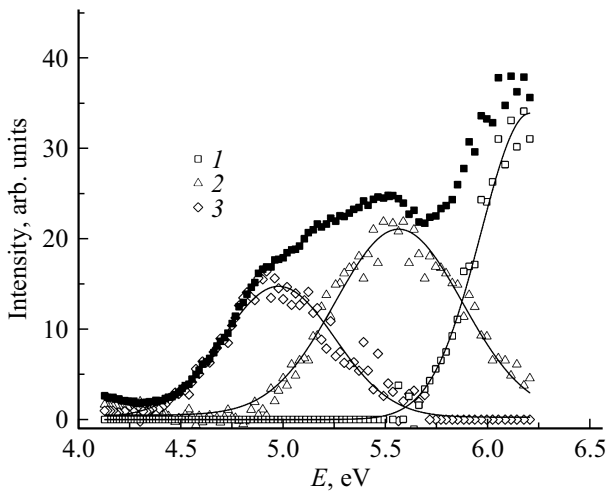
Under the same excitation and luminescence monitoring conditions, the ratio of intensities of PL bands 1 and 2 reaches its maximum in LiF–Fe<sub>2</sub>O<sub>3</sub> and is close to unity in LiF–TiO<sub>2</sub>; in LiF–WO<sub>3</sub>, the low-energy PL band (band 2) dominates.

### Photoluminescence excitation spectra

Luminescence excitation spectra were studied in detail when monitored in both PL bands. Several LE bands were found in the explored spectral region of 4.0...6.2 eV. Their number depends on the type of impurity in the crystal: two in LiF–Fe<sub>2</sub>O<sub>3</sub>, three in LiF–TiO<sub>2</sub>, and four in LiF–WO<sub>3</sub>. The high-energy LE band (band 1) is present in all crystals. Three LE bands (1, 2, 3) in LiF–TiO<sub>2</sub> have half-widths and maxima similar to those of the first three bands (1, 2, 3) in LiF–WO<sub>3</sub>. Examples of LE spectra and the results of their decomposition into elementary components in LiF–WO<sub>3</sub> and LiF–TiO<sub>2</sub> at 300 K are shown in Figs. 2 and 3. It can be seen that the LE spectra consist of four bands with maxima at 4.5, 4.95, 5.4, and 6.1 eV in LiF–WO<sub>3</sub> at 300 K and of three bands with maxima at 4.96, 5.5, and 6.1 eV in LiF–TiO<sub>2</sub>. The LE band parameters for all metals at 80 K are given in Table 2.

**Table 1.** Parameters of PL bands in different crystals at 80 K

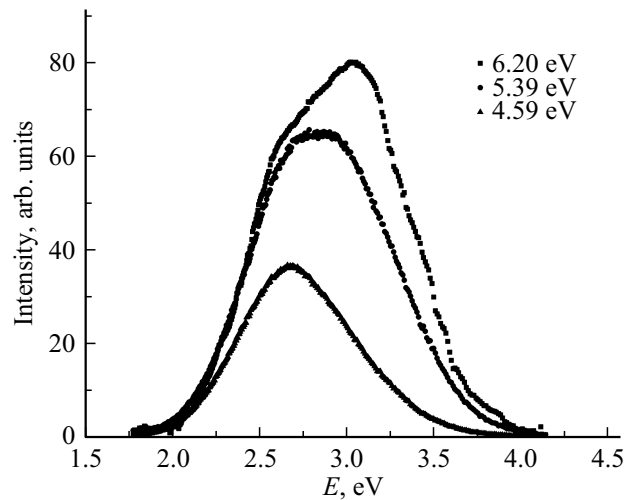
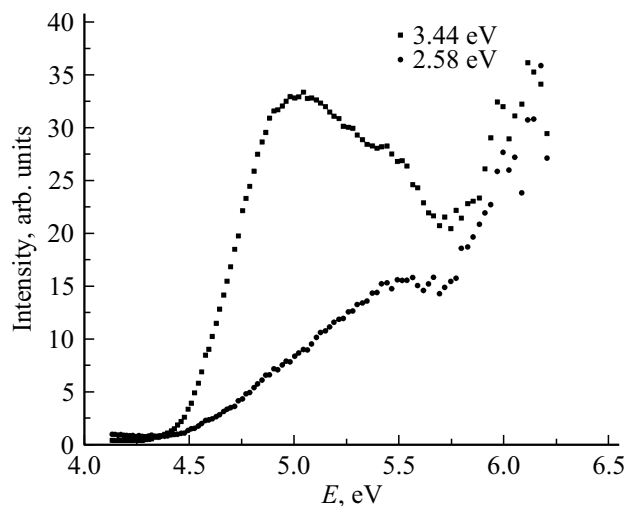
Crystal	Band maximum 1, eV	Band maximum 2, eV	Band half-width 1, eV	Band half-width 2, eV
LiF–Fe <sub>2</sub> O <sub>3</sub>	3.10 ± 0.04	2.60 ± 0.04	0.70 ± 0.05	0.68 ± 0.05
LiF–TiO <sub>2</sub>	3.0 ± 0.1	2.63 ± 0.05	0.58 ± 0.05	0.58 ± 0.05
LiF–WO <sub>3</sub>	2.9 ± 0.1	2.55 ± 0.05	0.5 ± 0.1	0.5 ± 0.1

**Figure 3.** LE spectrum of LiF–TiO<sub>2</sub> and results of its decomposition into elementary bands (1–3), 300 K; monitoring at 3.1 eV.

It follows from the LE spectra that in each crystal with metal impurities of different valence there are the same (close in energy) electronic transitions, and an increase in the valence of metal introduced into the lithium fluoride matrix leads, in addition to the formation of the same centers as in crystals with metal impurities of lower valence, to the emergence of new LE bands in the low-energy region of the spectrum.

At 300 K in LiF–Fe<sub>2</sub>O<sub>3</sub>, the ratio of intensities of LE bands 1 and 2 is in favor of band 1 (band 2 is weak); in LiF–TiO<sub>2</sub>, the intensity ratio changes in favor of bands 2 and 3; and in LiF–WO<sub>3</sub>, low-energy LE bands (2, 3, 4) dominate. The ratio of LE bands also depends on the PL band in which the emission is monitored and on the crystal temperature. However, as in the PL spectra, the position of the band maxima in the LE spectra in LiF–WO<sub>3</sub> does not change too much when monitoring luminescence in the 2.2... 3.6 eV region.

A characteristic feature of all crystal types is that exposure to light from the spectral region of LE bands (4.0... 6.2 eV) leads to the emergence of both photoluminescence bands. The ratio of their intensities depends on the type of metal in the crystal, the wavelength of the excitation radiation (LE band), the crystal temperature, and other factors. For example, at 300 K in LiF–TiO<sub>2</sub>, excitation in all bands at quanta energies equal to 6.2 eV (band 1), 5.64 eV (band 2),

**Figure 4.** PL spectra of LiF–TiO<sub>2</sub>, excitation: 6.2, 5.39, and 4.59 eV; 300 K.**Figure 5.** LE spectra in LiF–TiO<sub>2</sub> monitored at 3.44 and 2.58 eV, 300 K.

and 4.59 eV (band 3) leads to the emergence of both PL bands (Fig. 4). However, the 3.1 eV PL band is predominantly excited in the short-wavelength LE band, and the 2.6 eV PL band is predominantly excited in band 3 in the LE spectrum (4.59 eV). This can be seen clearly from the photoluminescence excitation spectra in Fig. 5 monitored in different PL bands.

**Table 2.** Parameters of LE bands in crystals LiF–Li<sub>2</sub>O, LiF–Fe<sub>2</sub>O<sub>3</sub>, LiF–TiO<sub>2</sub> and LiF–WO<sub>3</sub> at 80 K

Crystal	LiF–Li <sub>2</sub> O	LiF–Fe <sub>2</sub> O <sub>3</sub>	LiF–TiO <sub>2</sub>	LiF–WO <sub>3</sub>
Position of LE bands (absorption) maxima at 80 K, eV	6.1	5.35, 6.1	4.96, 5.45, 6.1	4.5, 4.96, 5.35, 6.1

A reduction in the sample temperature also leads to a change in the ratio of intensities of high-energy and low-energy LE bands in favor of the former. For example, when the temperature of the LiF–WO<sub>3</sub> sample is lowered from 300 to 80 K and luminescence is monitored at 3.1 eV, the ratio of luminescence intensities under excitation in the region of 6.1 eV increases by a factor of 3 compared to excitation at 5.25 eV.

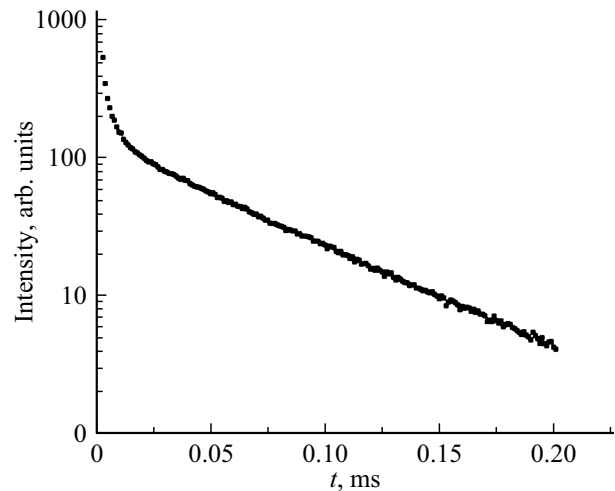
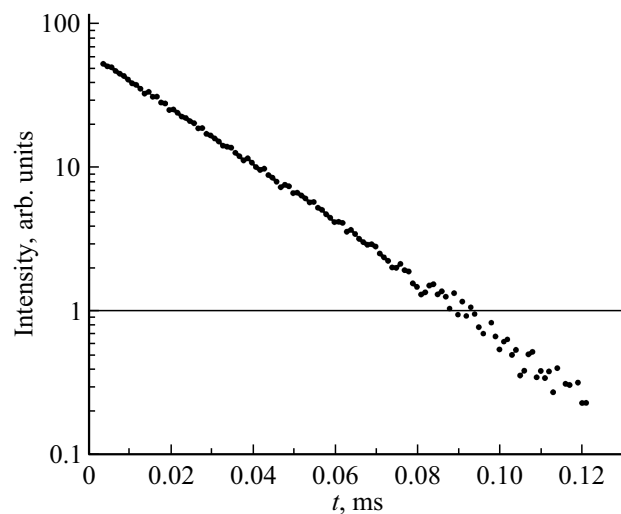
## PL decay

We have measured the kinetics of luminescence decay upon excitation in the LE bands defined above while monitoring the intensity in both PL bands. Measurements were made only in the microsecond time range and in the 80...300 K temperature range. The parameters of luminescence decay kinetics are found to depend on the LE band, the PL monitoring band, and the crystal temperature.

It was found that in LiF–WO<sub>3</sub> at 300 K, after excitation in the region of the high-energy LE band (6.1 eV), the decay of luminescence in both PL bands (3.1 and 2.6 eV) occurs in the  $t < 2 \mu\text{s}$  („fast“ component) and  $t > 15 \mu\text{s}$  (slow component) time ranges. Two components of PL decay are clearly visible already at 80 K in the microsecond range. Apparently, this is due to the fact that the characteristic time of decay of all components at low temperatures increases, which is characteristic of transitions forbidden by the selection rules. However, the presence of a „fast“ decay component, which was also present at 300 K, is noticeable. Note that PL decay in all samples follows an exponential law, which is characteristic of intracenter transitions in luminescence centers.

The luminescence decay in LiF–WO<sub>3</sub> after excitation in all low-energy LE bands (4.5, 4.96, and 5.35 eV), when luminescence of the low-energy PL band (2.6 eV) is predominantly excited, occurs in both PL bands only in the microsecond time range. There is no third „fast“ component. Luminescence decay times  $\tau$  of the slow component have close values for both PL bands when excited in different low-energy LE bands. These results suggest that emission transitions originate from two relaxed excited states of the luminescence center that produce the 3.1 and 2.64 eV PL bands and are filled after excitation in the high-energy and low-energy LE bands.

The elementary PL and LE bands were also determined from the kinetic curves. The decomposition method is based on the fact that the decay kinetics have different decay parameters both when excited in the region of different wavelengths from the impurity absorption range and when

**Figure 6.** PL kinetics at 430 nm (2.88 eV) in LiF–TiO<sub>2</sub>; excitation at 200 nm (6.2 eV), 300 K.**Figure 7.** PL kinetics at 470 nm (2.6 eV) in LiF–WO<sub>3</sub>; excitation at 230 nm (5.4 eV), 300 K.

monitored in different PL bands. The LE and PL spectra thus determined were found to be identical to those determined from steady-state photoluminescence measurements. Similar LE and PL patterns were determined in LiF–TiO<sub>2</sub>.

Tables 3 and 4 show characteristic decay times  $\tau$  ( $\mu\text{s}$ ) of the slow luminescence component under excitation in different LE bands in LiF–WO<sub>3</sub> and LiF–TiO<sub>2</sub> at 300 and 80 K in the PL bands of 3.1 and 2.6 eV. Typical kinetic curves of PL decay in LiF–TiO<sub>2</sub> and LiF–WO<sub>3</sub> at 300 K

**Table 3.** PL decay kinetics parameters  $\tau$  ( $\mu\text{s}$  in  $\text{LiF}-\text{WO}_3$ )

$T$ , K	300				80			
	370		500		370		500	
Monitoring band, nm								
Decay stage	1	2	1	2	1	2	1	2
Excitation 200 nm	1.28	21.11	1.18	14.68	1.54	11.69	2.01	11.37
Excitation 250 nm		19.08		21.57	5.09	46.35	5.57	58.15

**Table 4.** PL decay kinetics parameters  $\tau$  ( $\mu\text{s}$ ) in  $\text{LiF}-\text{TiO}_2$ 

$T$ , K	300						80					
	400			500			400			500		
Monitoring band, nm												
Decay stage	1	2	3	1	2	3	1	2	3	1	2	3
Excitation at 200 nm (6.1 eV)	< 1.83		57.17	< 0.95	16.68		< 1.06			< 1.22		
Excitation at 250 nm (4.96 eV)	< 2.70	20.38	85.69	< 0.53	12.89	34.62	< 2.07	13.19	345.78	< 3.4	39.39	478.93

and under excitation in different LE bands are shown in Figs. 6 and 7.

The main regularities of the processes causing photoluminescence of  $\text{LiF}-\text{Fe}_2\text{O}_3$ ,  $\text{LiF}-\text{WO}_3$ , and  $\text{LiF}-\text{TiO}_2$  crystals, which have been revealed in studies, are as follows:

— after the introduction of metal oxide impurities, complexes (centers) are created in  $\text{LiF}$  crystals, which have additional absorption in the form of separate bands in the 4.0... 6.2 eV region;

— the 6.1 eV LE band is present in all crystals, and the number of low-energy bands depends on the valence of metal;

— there are similar LE bands (with close absorption parameters) in crystals with different metals;

— excitation in all bands causes luminescence with a spectrum consisting, at least at 300 K, of two bands;

— LE and PL band parameters are close, but individual for each type of crystal;

— when the sample temperature is lowered to 80 K, the luminescence excitation efficiency in all low-energy bands decreases compared to the 6.1 eV band;

— each LE band (group of bands) corresponds to its preferential PL band (the 6.1 eV LE band corresponds to the 3.1 eV PL band, and the 2.6 eV PL band corresponds to the group of long-wavelength LE bands);

— excitation in each LE band leads to PL in both bands (3.1 and 2.6 eV), but with individual ratios of their intensities;

— parameters of luminescence decay kinetics in the microsecond time range for different types of crystals (with different impurities) are very different;

— parameters of luminescence decay kinetics in the microsecond time range for one type of crystal (one impurity) are close for all LE and PL bands, but are also individual;

— PL excitation in the 6.1 eV band in all crystals creates an additional „fast“ (apparently, nanosecond) decay component when monitored in the 3.1 eV PL band.

## Discussion

It follows from the analysis of the obtained results that two types of excitation (absorption) bands can be distinguished. The first one is the band with a maximum in the region of 6.1 eV, because, for example, only this band is characterized by excitation of the 3.1 eV PL band with a fast component of luminescence decay.

All low-energy LE bands should belong to the second group, since they are characterized by the same behavior at decreasing temperature, close values of the luminescence decay time under excitation in these bands in one type of crystal, and the presence of LE bands with the same parameters in crystals with different metal impurities.

To explain the origin of the LE and PL bands and their interrelation in the studied objects, it can be assumed that the same fragment of the impurity complex is excited upon absorption of light quanta from the 4.0... 6.2 eV region. This can explain, for example, the excitation of both types of PL bands upon excitation in all LE bands. As shown by the analysis of the defect structure (configuration) in the region of introduction of metal impurities, only  $\text{O}^{2-}$  can be such a common fragment.

Based on this, we construct possible configurations of the defect area of lithium fluoride after the introduction of metal oxides of different valence. As noted above, metal ions  $\text{Fe}^{3+}$ ,  $\text{Ti}^{4+}$ ,  $\text{Ti}^{3+}$ ,  $\text{W}^{6+}$ , and  $\text{W}^{4+}$  can easily substitute  $\text{Li}^+$  ions, while oxygen ions  $\text{O}^{2-}$  may substitute  $\text{F}^-$  ions at lattice sites. Anion vacancies may also be created in the process. The impurity complex (or separate complexes) is formed from these fragments.

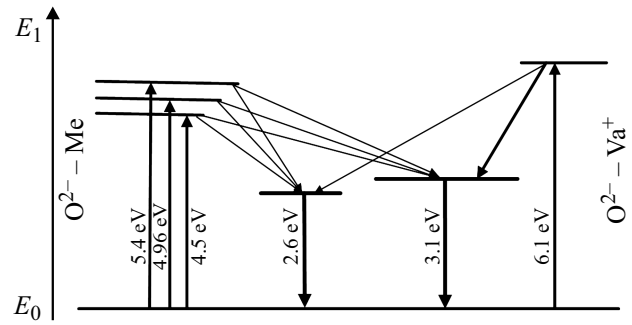
Let us consider high-energy PL and LE bands first. It turned out that the positions of maxima of these bands, the value of  $\tau$  ( $< 2\mu\text{s}$ ), and other features suggest that they can be identified as the absorption and luminescence bands of a  $(\text{O}^{2-}-\text{V}_a^+)$  center studied in  $\text{LiF}-\text{Li}_2\text{O}$ . However, the half-width of bands in  $\text{LiF}-\text{WO}_3$  and  $\text{LiF}-\text{TiO}_2$  crystals is smaller than that of the  $(\text{O}^{2-}-\text{V}_a^+)$  center. This can be explained by the presence of a nearby perturbing defect (metal impurity or other fragment of the impurity complex). The fact that perturbation by impurity can lead to a decrease in the half-width of the center bands was shown, for example, in [12]. Note that the absorption and luminescence of such a center result from charge transfer between  $\text{O}^{2-}$  and  $\text{V}_a^+$ . Apparently, such  $(\text{O}^{2-}-\text{V}_a^+)$  centers, which are weakly perturbed by impurities, are predominantly formed in  $\text{LiF}-\text{Fe}_2\text{O}_3$ ; therefore, the 3.1 eV PL band with a half-width corresponding to the band of this center in  $\text{LiF}-\text{Li}_2\text{O}$  and weak low-energy PL and LE bands is observed in this crystal.

The origin of the low-energy PL and LE bands can be explained in a similar way. Charge transfer from a  $\text{O}^{2-}$  ion to a metal impurity located at a neighboring lattice site leads to the emergence of these absorption bands, and the reverse transition leads to luminescence represented by the 2.6 eV band, as substantiated in [6] for  $\text{LiF}-\text{MgO}$ . The number of low-energy LE bands is determined by the valence of the introduced metal. This is easily explained as follows.

In the case of  $\text{LiF}-\text{TiO}_2$ , two  $\text{O}^{2-}$  ions must be positioned at neighboring anion sites to compensate for the  $\text{Ti}^{4+}$  charge. This leads to the emergence of two low-energy LE bands. In a  $\text{LiF}-\text{WO}_3$  crystal, three oxygen ions  $\text{W}^{6+}$  are required to compensate for the  $\text{O}^{2-}$  charge, and this leads to the appearance of three low-energy LE bands in it.

Less straightforward is the emergence of a similar single band in  $\text{LiF}-\text{Fe}_2\text{O}_3$ . This crystal requires at least one  $\text{O}^{2-}$  at the neighboring site and a cation vacancy or complex in the form of two iron ions and three oxygen ions to compensate for the iron charge. Other charge compensation options are also possible, including those that create anion vacancies and, consequently, more  $(\text{O}^{2-}-\text{V}_a^+)$  centers, which dominate in luminescence of this material. In any case, only one variant of the complex is created in  $\text{LiF}-\text{Fe}_2\text{O}_3$  in the form of  $\text{Fe}_2^{6+}$  and  $\text{O}_2^{6-}$  located at neighboring vacancies; therefore, only one low-energy LE band is present. However, additional data are required to substantiate the luminescence center model for this crystal.

The results of studies show that all absorption and luminescence bands in the studied crystals are created within the absorption and emission of a single complex of two centers or spaced centers  $\text{IO}^{2-}-\text{V}_a^+$  and  $\text{O}^{2-}-\text{Me}$ , wherein luminescence excitation occurs upon absorption of energy by oxygen ion  $\text{O}^{2-}$ . That is, excitation in the whole spectral range of 4.0...6.2 eV leads to charge transfer from an  $\text{O}^{2-}$  ion to other fragments of the complex (metal or anion vacancy). Charge transfer from an  $\text{O}^{2-}$  ion to an anion vacancy creates a high-energy LE band (6.1 eV band).



**Figure 8.** Energy diagram of transitions in luminescence centers for  $\text{LiF}-\text{WO}_3$ .

Reverse transitions from the relaxed excited state induce the 3.1 eV PL band. This PL mechanism is reasonable for defect-free  $(\text{O}^{2-}-\text{V}_a^+)$  centers in  $\text{LiF}-\text{Li}_2\text{O}$  [5]. Perturbation changes the PL band parameters. Charge transfer from an  $\text{O}^{2-}$  ion to metal creates low-energy absorption bands the number of which is determined by the valence of the latter. Reverse transitions from the relaxed excited state lead to luminescence, which is represented by the 2.6 eV band.

Both PL bands can emerge upon excitation of  $\text{O}^{2-}$  in any of the LE bands; i.e., there is a possibility of charge transfer from the excited states of  $\text{O}^{2-}-\text{V}_a^+$  and  $\text{O}^{2-}-\text{Me}$  centers to both radiative states of oxygen ion  $\text{O}^{2-}$  within these centers. This process requires an activation energy, as follows from the results presented in Fig. 5.

The considered processes of luminescence production in the studied crystals can be presented in the form of the energy diagram shown in Fig. 8.

## Conclusions

1. It was found that in LiF crystals with multivalent impurities of metals substituting ions  $\text{Li}^+$ , two kinds of luminescence centers are created. They can be in a single complex or separated in space in the form of bound ions  $\text{O}^{2-}-\text{V}_a^+$  and  $\text{O}^{2-}-\text{Me}$  located at neighboring sites. These two centers produce two luminescence bands with maxima around 3.1 and 2.6 eV.

2. The  $\text{O}^{2-}-\text{Me}$  center creates absorption bands in the 4.0...6.0 eV region with parameters close to those of the same bands in crystals with different metals. The number of these bands is determined by the valence of metal, i.e., the number of  $\text{O}^{2-}$  ions needed to compensate for the excess charge of metal that are located at sites nearest to it and form a single center (apparently, with different orientation of the dipole axes).

3. Energy transfer to other centers can occur under excitation by quanta of light from different absorption bands, leading to the emergence of both PL bands. This process requires activation energy.

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## Conflict of interest

The authors declare that they have no conflict of interest.

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