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Impurity Centers in LiF:Li₂O

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There are some papers on the optical properties of centers with O⁻ oxygen ions in alkali halides /1 to 3/. But data on alkali fluoride are rather incomplete. The present note deals with the optical properties of lithium fluoride doped with Li₂O in the vacuum ultraviolet region up to the LiF absorption edge.

Undoped crystals and crystals doped with Li₂O from 0.01 to 0.1 wt% in the melt were studied. The crystals were grown in our laboratory (by N. Verchinin and S. Mironenko) by the Kyropoulos method in an inert atmosphere. The crystals were heated at 600 °C for 15 min and cooled in air. The basic optical equipment was described elsewhere /4/. The major improvement to the existing system was the addition of an SM1 minicomputer and a duoplasmatron /5/ as light source. The minicomputer can make measurements of absorption, emission, excitation spectra, correct the emission spectra, store the spectra on a magnetic disc, and plot the spectra.

There are some bands with maxima at 6.5, 8.1, 9.5, 10.4, and 11 eV in the absorption spectra of LiF:Li₂O (Fig. 1). The optical density of the 9.5 and 10.4 eV bands is roughly proportional to the Li₂O melt concentration. The optical absorption spectra are not changing due to annealing of crystals from room temperatures up to 200 °C. The main annealing effect at higher temperatures is a decrease of the bands at 6.5 and 11 eV and an increase of the 9.5 eV band (see Fig. 1). The annealing effect on the optical absorption is more pronounced in crystals with a sufficient concentration of 6.5 eV centers. The long-time annealing at 300 °C increased the 9.5 eV absorption band and the 10 to 11 eV absorption in crystals without a 6.5 eV band, too.

Emission spectra of LiF:Li₂O crystals consist of two bands with peaks at 2.9 and 3.7 eV and high energy bands with maxima at 4.15, 4.6, and 5.0 eV.

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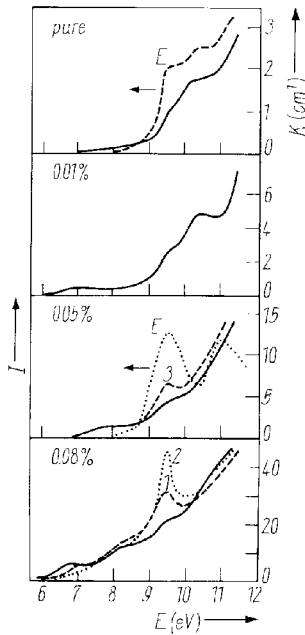


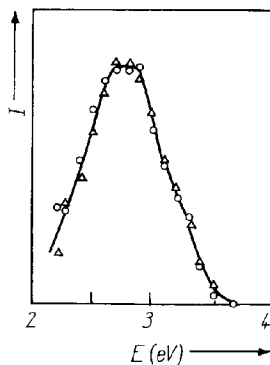
Fig. 1. Absorption and excitation spectra of LiF undoped and LiF:Li₂O crystals at room temperature. Excitation spectra were measured with FS6 filter (pass-band 3.2 to 4 eV) and marked E. The melt concentration of Li₂O is marked on the left upper corner of the plots. The annealing was done at 300 °C for (1) 1, (2) 2, and (3) 15 h

The 2.9 eV emission band has been measured on crystals with absorption bands in the 6 to 7 eV region only. The emission spectrum (in the 2 to 4 eV region) of LiF:Li₂O with 6.4 eV excitation was the same at 80 and 9 K (Fig. 2). The 3.7 eV band has been measured in all crystals. Consequently, the 2.9 and 3.7 eV bands are not related to one type of centers. The bands at 4.15, 4.6, and 5.0 eV are

resolved at liquid nitrogen and lower temperatures. The nature of the bands will be discussed in a future paper.

The 2.9 eV emission is excited in the 6 to 8 eV region /6/ and in the 9.3, 10.2, and 11 eV bands. The low-energy excitation band shows a growth in Li₂O doped crystals. The 3.7 eV emission is commonly excited in the 9.5 and 11 eV bands (see Fig. 1).

The $O^{--}V_a^+$ centers in alkali halides at appropriate temperatures (above room temperature) were diffused and aggregated in dimers or in larger complexes. The aggregation of $O^{--}V_a^+$ dipoles leads to a decrease of the $O^{--}V_a^+$ absorption bands and to an increase of the absorption of $O^{--}V_a^+$ complexes /2/.



The energy of diffusion is determined by the relation between the host anion and the O^{--} ion radii. The energy of $O^{--}V_a^+$ reorientation increases with increasing radius of the impurity O^{--} ion /7/. The ion

Fig. 2. Uncorrected emission spectra of LiF crystals doped by 0.08 wt% Li₂O with 6.4 eV excitation. Spectra were measured at 80 K (○) and 9 K (Δ) and normalized to unit intensity

Table 1

Position of maxima E (eV) of $O^{--}V_a^+$ emission bands at 20 K (KBr, KCl) /2/ and 9 K (LiF)

	E (eV)		
	KBr	KCl	LiF
$O^{--}V_a^+$	2.36	2.64	2.9
$O^{--}V_a^+$ aggregates	2.99	3.05	3.7

radii are: O^{--} 1.4 Å, F^- 1.3 Å, Cl^- 1.81 Å, Br^- 1.96 Å /8/. A comparison of the ion radii shows that the $O^{--}V_a^+$ diffusion in fluorides is more difficult than in chlorides and bromides and can be only expected at higher temperatures. The annealing of LiF:Li₂O at temperatures below 200 °C does not change the optical absorption. The annealing at higher temperatures decreases the 6.5 and 11 eV bands and increases the 9.5 eV band (see Fig. 1). From these results we see that the 11 eV band together with the 6.5 eV band is an $O^{--}V_a^+$ band. The 9.5 eV band is a band of $O^{--}V_a^+$ aggregates. The long-time annealing at 300 °C leads to an increase of the 9.5 and 11 eV bands (see Fig. 1). The same effect of annealing on the $O^{--}V_a^+$ optical absorption was measured earlier in KCl and KBr crystals /2/.

The 3.7 eV emission was excited in the 9.5 and 11 eV bands. This emission increased and its high energy and low energy satellites diminished after a 300 °C, 15 h annealing. Consequently, the 3.7 eV emission is due to a transition into $O^{--}V_a^+$ aggregates.

After excitation in the $O^{--}V_a^+$ second absorption band, there is a radiative transition to the ground state at low temperatures ($T < 60$ K) in sodium chloride and bromide /2/. In a previous paper we concluded that the 2.9 eV emission is related to $O^{--}V_a^+$ centers in lithium fluoride /6/. The new results support this conclusion. Firstly, the 2.9 eV emission is related with the 6.5 eV absorption band ($O^{--}V_a^+$ band). Secondly, there are no additional emission bands in the 2 to 4 eV region in LiF:Li₂O at 9 K to compare with the emission at 80 K (see Fig. 2). The energy of the $O^{--}V_a^+$ emission increases with decreasing radius of

the host anion in the bromide-chloride-fluoride sequence (Table 1). The energy of $O^{--}V_a^+$ aggregate emission is higher than that of $O^{--}V_a^+$ centers and increases from bromides to fluorides, too.

The experimental results lead to the following conclusions:

- The 6.5 and 11 eV absorption bands are the bands of $O^{--}V_a^+$ centers.
- The 2.9 eV emission band is the band of $O^{--}V_a^+$ centers. Unlike the emission in sodium bromides and chlorides the emission of $O^{--}V_a^+$ centers in lithium fluoride can be measured at higher temperatures up to room temperature.

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