Magnesium Color Centers at 3.5 and 5.0 eV in Lithium Fluoride

By

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Centers at 3.5 and 5.0 eV are created by X-irradiation of LiF:Mg or by optical bleaching of Mg\textsuperscript{2\textsuperscript{+}}V\textsubscript{A}V\textsubscript{C} (at 4.0 eV) centers in LiF:Mg at 80 K. Both centers have [100] and [110] absorption dichroism. The thermal bleaching of centers at 3.5 eV is related with a glow peak at 150 K which obeys second-order kinetics. The energy of the absorption band of Mg\textsuperscript{2\textsuperscript{+}}V\textsubscript{C} -centers in LiF is calculated to be about 3.5 eV. The absorption band shape and the oscillator strength of the centers at 5.0 eV and F-centers are almost equal. The color centers at 3.5 eV seem to be Mg\textsuperscript{2\textsuperscript{+}}V\textsubscript{C} -centers and those at 5.0 eV seem to be F-centers near Mg\textsuperscript{2\textsuperscript{+}}V\textsubscript{C} dipoles.

1. Introduction

Magnesium color centers in alkali halides are good electron traps [1 to 3]. This property of magnesium color centers in lithium fluoride is widely used in thermoluminescence dosimetry [4]. Some authors propose that magnesium color centers in LiF with absorption band at 4.0 eV are Z\textsubscript{2} -centers and centers at 5.5 eV are Z\textsubscript{3} -centers [5 to 7]. In a previous paper we have studied the thermal and optical bleaching of color centers at 4.0 eV from 85 to 440 K and found that the conversion of centers at 4.0 and 5.5 eV does not correspond to the Z\textsubscript{2} -Z\textsubscript{3} center conversion in other alkali halides. We propose that centers at 4.0 eV are Mg\textsuperscript{2\textsuperscript{+}}V\textsubscript{A}V\textsubscript{C} -centers and those at 5.5 eV are magnesium atoms at anion site associated with cation vacancies [8]. The optical bleaching of the centers at 4.0 eV at liquid nitrogen temperatures leads to a creation of new centers at 3.5 and 5.0 eV [5, 6, 8], the nature of which is still unknown. The studies of centers at 5.0 eV are difficult due to the neighbourhood of the absorption bands of these centers and those of F-centers (at 5.1 eV at 80 K). We have studied LiF crystals with a large magnesium concentration (700 ppm) and there is no F-band in our crystals after X-irradiation at 85 K and warming up to 400 K. The present work deals with the nature of magnesium centers at 3.5 and 5.0 eV in LiF:Mg crystals.

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2. Results and Discussion

When the temperature is rising, the centers at 3.5 eV are bleaching at about 150 K (Fig. 1). Centers at 5.0 eV have three ranges of thermal bleaching at about 150, 230, and 320 K. Thermal bleaching of centers at 3.5 and 5.0 eV leads to an almost perfect recovery of \( \text{Mg}^+_c \text{V}_a^+ \text{V}_e^- \)-centers. One can conclude the centers at 3.5 and 5.0 eV to be magnesium electron-trapping centers.

A pile of six fused silica plates was used to obtain absorption spectra with polarized light. Exposure of LiF:Mg to [001] polarized light at about 4.0 eV results in the preferential bleaching of \( \text{Mg}^+_c \text{V}_a^+ \text{V}_e^- \)-centers having a definite orientation and in the creation of centers at 3.5 and 5.0 eV with the same orientation (Fig. 2). Curves on Fig. 2b show the [100] anisotropic absorption spectra which were obtained by subtracting the spectra taken with [010] polarized light from that taken with [001] light. By the

![Fig. 1. TSL curve (1) and bleaching curve at 3.5 eV (2) of LiF:Mg crystal after optical bleaching of \( \text{Mg}^+_c \text{V}_a^+ \text{V}_e^- \)-centers at 85 K.](image)

![Fig. 2. Anisotropic absorption spectra of LiF:Mg crystal with \( \text{Mg}^+_c \text{V}_a^+ \text{V}_e^- \)-centers after exposure to polarized light at (1) 4.14 eV, (2) 4.0 eV at 80 K and (3) 4.14 eV at 160 K.](image)
same way we obtained the [110] anisotropic spectra (Fig. 2a). These spectra coupled with [100] anisotropy show that all three centers are [110] polarized. We mark that the exposure of LiF:Mg with the centers at 3.5 and 5.0 eV to polarized light at 3.5 or 5.0 eV leads to a very small dichroism in these bands.

2.1 Color centers at 3.5 eV

The bleaching of these centers is related with thermostimulated luminescence (TSL) (Fig. 1) and with the recovery of MgO\[\_1\]V\[\_3\]V\[\_c\]. One can find the order of TSL kinetics from the relations:

\[
\ln \left( \frac{I}{\sqrt{T}} \right) = \text{const} \cdot -E/kT \quad \text{for first order,}
\]

\[
\ln \left( \frac{I}{(\sqrt{T})^2} \right) = \text{const} \cdot -E/kT \quad \text{for second order.}
\]

The TSL at about 150 K obeys a second-order kinetics (Fig. 3).

Color centers at 3.5 eV are created by X-irradiation of LiF:Mg crystals at 85 K too, but the absorption of these centers lies under the large absorption of V\[\_k\]-centers (at 3.57 eV [9]). The V\[\_k\]-centers in LiF are bleaching when the crystal is warming up to 145 K. After that the glow curve peak at 150 K is separated from the V\[\_k\]-peak and the TSL at about 150 K obeys a second-order kinetics, too (Fig. 3). The two absorption bands in X-irradiated LiF:Mg bleached in the range 145 to 170 K (Fig. 4). One band is the absorption band of the centers at 3.5 eV and the other one lies within the range of V\[\_k\] absorption and is probably a V\[\_F\] band (in literature there are no data about the shape of the V\[\_F\] band in LiF). Consequently, heating releases electrons from centers at 3.5 eV and they may be retrapped or recombine with hole (V\[\_F\], X\[\_3\]) centers.

Two centers with Mg\[\_+\] ions are created in NaCl crystals after X-irradiation and F-bleaching at room temperature: Mg\[\_+\] and Mg\[\_+\]V\[\_3\]V\[\_c\]-centers [1]. The calculation concludes that the absorption band energy of these centers in alkali halides has to be shifted to longer wavelength than the absorption energy of the free Mg\[\_+\] ions [10]. The shift is inversely proportional to the lattice constant [11], i.e.

\[ E = \text{const}/d, \]

where \( E \) energy shift, \( d \) lattice constant. The energy of the 3s\[\_1\]–3p\[\_1\] transition of the free Mg\[\_+\] ion is 4.43 eV [12]. We calculated the absorption band energy of Mg\[\_+\] and

![Fig. 3](image-url)

Fig. 3. Determination of the order of TSL kinetics in the peak at 150 K, after bleaching of Mg\[\_+\]V\[\_3\]V\[\_c\]-centers (1a and 1b) at 85 K and (2) after X-irradiation of LiF:Mg at 85 K

![Fig. 4](image-url)

Fig. 4. Absorption band of the centers which are bleaching in the range 145 to 170 K in X-rayed LiF:Mg crystals. Dashed curves show the resolved bands.
Mg\textsuperscript{2+}V\textsuperscript{a}V\textsuperscript{c} in LiF and KCl crystals on the base of the absorption band energy of these centers in NaCl crystal (Table 1). One can see that the calculated and experimental data for the known centers are in good agreement. The calculated absorption band peak of Mg\textsuperscript{2+}-centers in LiF lies at 3.5 eV. The Sn\textsuperscript{2+} electron transitions in KCl are shifted by cation vacancies in nearest neighbour position by about 0.1 eV [13]. Consequently Mg\textsuperscript{2+}V\textsuperscript{c}-centers in LiF must have the absorption band near 3.5 eV. This center has [110] orientation. We can conclude that centers at 3.5 eV seem to be Mg\textsuperscript{2+} ions, connected with cation vacancies in nearest neighbour positions.

### Table 1

<table>
<thead>
<tr>
<th>centers</th>
<th>NaCl</th>
<th>Mg\textsuperscript{2+}</th>
<th>Mg\textsuperscript{2+}V\textsuperscript{a}V\textsuperscript{c}</th>
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<tr>
<td></td>
<td></td>
<td>absorption band (eV)</td>
<td>absorption band (eV)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(\Delta E) (eV)</td>
<td>const (10\textsuperscript{6} eV m)</td>
</tr>
<tr>
<td></td>
<td></td>
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<td>exp.</td>
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<td>3.76</td>
<td>0.68</td>
<td>1.93</td>
</tr>
<tr>
<td>Mg\textsuperscript{2+}V\textsuperscript{a}V\textsuperscript{c}</td>
<td>4.14</td>
<td>0.30</td>
<td>0.85</td>
</tr>
</tbody>
</table>

2.2 Color centers at 5.0 eV

When the Mg\textsuperscript{2+}V\textsuperscript{a}V\textsuperscript{c}-centers are bleaching at 85 K, electrons do not enter the conduction band, because there is no photoconductivity of X-rayed LiF: Mg crystals with 4.0 eV light at room temperatures [14]. Consequently, electrons of excited levels of Mg\textsuperscript{2+}V\textsuperscript{a}V\textsuperscript{c}-centers are trapped by levels of other centers due to a tunneling process. Electrons may be trapped by anion vacancies from Mg\textsuperscript{2+}V\textsuperscript{a}V\textsuperscript{c}-centers and this creates F-centers near the Mg\textsuperscript{2+}V\textsuperscript{c} dipoles. There are also some other results which support this conclusion:

1. When excited by polarized light Mg\textsuperscript{2+}V\textsuperscript{a}V\textsuperscript{c}-centers are converted into centers at 5.0 eV with the same orientations (see Fig. 2).
2. The absorption band at 5.0 eV is near the F-band. Experiments have shown the band at 5.0 eV to be asymmetric (Fig. 5). The high energy side of this band is about 20% wider than the low energy side. A similar asymmetry is found for the F-band [3, 6].

![Fig. 5. Experimental shape (points) and theoretical shape (line) of the absorption bands at 5.0 eV](image)
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Fig. 6. a) Thermal bleaching of the centers at 5.0 eV at about 320 K and b) determination of the order of bleaching kinetics

3. We determined the relative oscillator strength \( f(4.0 \text{ eV})/f(5.0 \text{ eV}) = 1.1 \pm 0.1 \) in LiF:Mg crystals (where \( f \) is the oscillator strength of the corresponding bands). The relative oscillator strength \( f(3.8 \text{ eV})/f(F) = 1.19 \) in KCl:Mg crystals (where the band at 3.8 eV is the absorption band of Mg\(_{2}^{+}\)-centers) [11]. Because \( f(F) \) in LiF is almost equal to \( f(F) \) in KCl [15] the oscillator strengths of the centers at 5.0 eV and F-centers differ only slightly. It is well known that the oscillator strength of F-centers does only weakly depend on the surroundings (for example Z\(_{2}\)-centers [15]).

4. When the temperature rises the centers at 5.0 eV are bleaching and converting into Mg\(_{2}^{+}\)V\(_{2}^{-}\)centers. The bleaching at about 320 K obeys a first-order of kinetic (Fig. 6). Electrons are probably tunneling from the F-center levels to the levels of neighbouring Mg\(_{2}^{+}\) ions.

Consequently centers at 5.0 eV seem to be F-centers near Mg\(_{2}^{+}\)V\(_{2}^{-}\) dipoles.

References


(Received July 7, 1981)