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A Model of Titanium Luminescence Centers in Lithium and Sodium Fluorides

By

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The absorption, emission, excitation spectra, and polarized luminescence of titanium centers in lithium and sodium fluorides are studied. The 2.42 and 3.1 eV emissions in $\text{LiF}:\text{TiO}_2$ and 2.2 and 2.95 eV emissions in $\text{NaF}:\text{TiO}_2:\text{MgF}_2$ are related to the electronic transitions of titanium centers. The low energy emissions at relatively low temperatures have the same azimuthal dependence of the polarisation degree as the emission of oscillators oriented along the C_2 crystal axis. The high energy emissions are polarized along the C_3 crystal axis. The high temperature stability of the polarization degree shows that the luminescence centers have point defects near the titanium ion. The efficiency of transformation of titanium luminescence centers by X-irradiation grows above 200 K. This points out that the cation vacancies are part of luminescence centers. A model of titanium luminescence centers in lithium and sodium fluorides is suggested. The center consists of a Ti^{4+} ion at cation site, an O^{2-} ion at anion site, and two associated cation vacancies.

Исследованы спектры поглощения, излучения, возбуждения и поляризованная люминесценция титановых центров в кристаллах фтористого лития и натрия. Свечение с максимумами волнес при 2,42 и 3,1 eV во фтористом литии и при 2,2 и 2,95 eV во фтористом натрии обусловлено электронными переходами в титановых центрах. Свечение в низкоэнергетических полосах при относительно низкой температуре имеет такую же азимутальную зависимость степени поляризации как зависимость для ориентации излучателей по C_2 осям кристалла. Свечение в высокоэнергетических полосах поляризовано по C_3 осям кристалла. Высокая температурная устойчивость степени поляризации свечения свидетельствует о том, что около ионов титана находятся точечные дефекты. Эффективность радиационного преобразования титановых центров люминесценции растет при температурах выше 200 K, что указывает на вхождение катионных вакансий в состав центров люминесценции. Предложена модель титанового центра люминесценции в кристаллах фтористого лития и натрия. Центр состоит из Ti^{4+} иона в катионном узле, O^{2-} иона в анионном узле и двух катионных вакансий.

1. Introduction

Titanium color centers in lithium fluoride thermoluminescence dosimeters are used as luminescence centers [1], but the nature of the titanium centers in alkali halides is still unknown. The centers in lithium fluoride have some optical absorption bands in the vacuum ultraviolet [2, 3]. The 6.2 eV absorption band is directly proportional to the titanium concentration [1]. There is also an absorption band at 2.0 eV, usually observed in solids with Ti^{3+} ions. Some authors correlate these and the vacuum ultraviolet bands with the optical transitions in Ti^{3+} ions on cation sites [2, 3]. But on the basis of ENDOR studies Davies concluded that Ti^{3+} ions are formed after X- or γ -irradiation of $\text{LiF}:\text{Ti}$ crystals only [4]. Therefore, before irradiation lithium fluoride

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contains the atomically dispersed titanium impurity as Ti^{4+} ions [4, 5]. Photoluminescence of titanium color centers in lithium fluoride was found by Zimmerman and Jones [6].

The present paper deals with the nature of titanium luminescence centers in lithium and sodium fluorides.

2. Experimental Procedure

The lithium and sodium fluoride crystals were melt-doped by TiO_2 impurity. On the basis of ultraviolet absorption [1, 2] the titanium color center concentration in LiF and NaF was about 15 ppm. To the sodium fluoride crystal was added also 0.2 wt% of MgF_2 in the melt. Before the crystals were heated at 680 K for 5 to 10 min and quenched in air to room temperature. Optical spectra between 5.0 and 8.0 eV were obtained with a vacuum ultraviolet monochromator VMR-2 and deuterium lamp LD(D). Luminescence light was detected with FEU-79 in the photon counting regime through a filter or grating monochromator MDR-2. The azimuthal dependence of the polarization degree of a certain emission was taken by a gold polarizer [7] and suitable filters under the angle 45° to the passing beam. The qualitative azimuthal polarization dependence of the emission of oscillators with axis along the C_2 , C_3 , C_4 crystal axes is not changing due to this method.

3. Experimental Results

3.1 Lithium fluoride

Two bands with maxima at 2.42 and 3.1 eV have been observed in the photoluminescence spectra of a LiF: TiO_2 crystal. The 2.42 eV emission has relatively strong growth at 80 K. The 3.1 eV emission centers are oriented along the C_3 crystal axis and the 2.42 eV centers probably are oriented along the C_2 crystal axis (Fig. 1). Both photoluminescence bands are equally decreased by X-irradiation and equally restored by a following heat treatment. The excitation of both centers lies within the energy range of absorption which is due to a TiO_2 impurity in LiF crystal (Fig. 2). Consequently the 2.42 and 3.1 eV emissions relate with the titanium centers in lithium fluoride.

The polarization degree of the 3.1 eV emission is stable up to 570 K. The behaviour of the polarization degree of the 2.42 eV emission is more complicated (Fig. 3). The temperature dependence of the polarization degree of the 2.42 eV emission can be

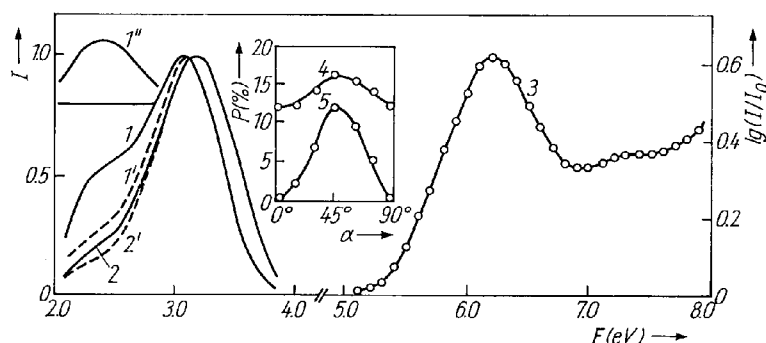


Fig. 1. Corrected emission (1, 2) and absorption (3) spectra and the azimuthal dependence of polarization degree of the 2.42 eV (4), 3.1 eV (5) emissions of LiF: TiO_2 crystals at 80 K (1, 1') and 295 K (2 to 5). The emission spectra are measured with 6.2 eV (1, 2) and 7.2 eV (1', 2') excitation light. The 1'' curve is the difference curve between (1) and (1'). (Intensity is always in rel. units.)

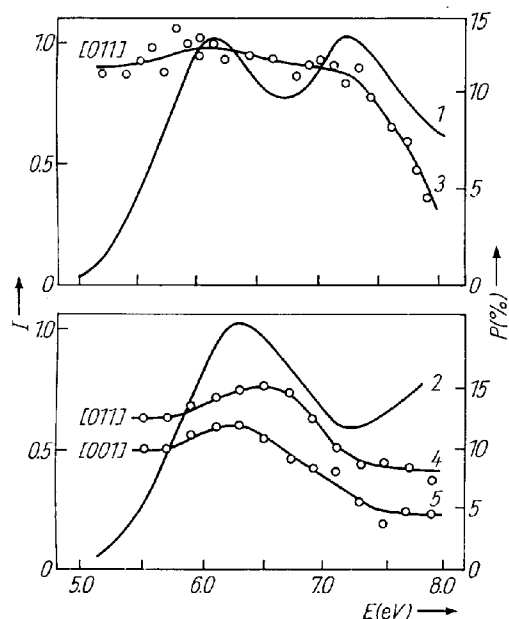


Fig. 2. Excitation (1, 2) and polarization (3 to 5) spectra of the 3.1 eV (1, 3) and 2.42 eV (2, 4, 5) emissions of LiF:TiO₂ crystals at 295 K

explained as follows: a) the total light consists of two components with light intensities I_1 , I_2 and polarization degrees P_1 , P_2 ; b) the ratio of intensities $k = I_2/I_1$ grows when temperature rises; c) the polarization degree P_1 falls when crystals are heated. The total polarization degree is equal to [8]

$$P = \frac{(P_1 + kP_2)}{1 + k}.$$

Taking into account the points a), b) for calculating the temperature dependence of the polarization degree of emission we obtain the curve 1 (see Fig. 3 b), but with points a), b), c) we obtain the curve 2. Curve 2 is a better explanation. The results show that the 3.1 eV emission penetrates into the 2.42 eV emission and $k = I(3.1 \text{ eV})/I(2.42 \text{ eV})$

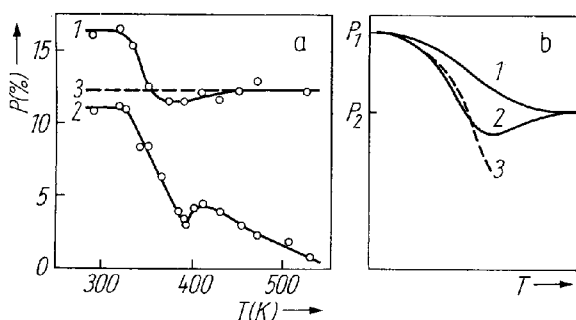


Fig. 3

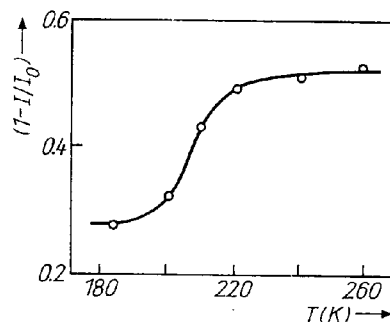


Fig. 4

Fig. 3. a) Temperature dependence of polarization degree of the 2.42 eV (1, 2), 3.1 eV (3) emissions of LiF:TiO₂ crystals. b) The calculated curves. (1, 2) curves calculated on the basis of the points a), b) and a), b), c) (see text). (3) The temperature decrease of polarization degree P_1 , the lower part of curve 3 is unmarked because of indefiniteness

Fig. 4. Temperature dependence of transformation efficiency of titanium center photoluminescence (under 6.2 eV excitation) by X-irradiation of LiF:TiO₂ crystals

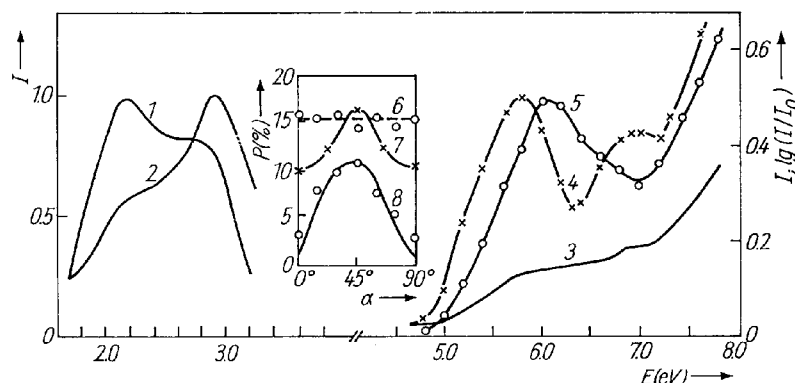
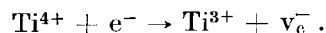


Fig. 5. Corrected emission (1, 2), absorption (3), and excitation (4, 5) spectra and the azimuthal dependence of polarization degree of 2.2 eV (6, 7), 2.95 eV (8) emissions of NaF:TiO₂:MgF₂ crystals at 80 K (1), 200 K (7), and 295 K (2 to 6, 8). Emission spectra measured with 5.8 eV excitation light. Excitation spectra measured for 2.2 eV (4) and 2.95 eV (5) emission light

grows with temperature rise. Therefore, the polarization degree of the 2.42 eV emission decreases above 330 K.

The temperature dependence of the efficiency of titanium center transformation by X-irradiation was studied by means of photoluminescence decrease. Two stages have been observed: at about 140 and 210 K. The stage at 140 K is in accordance with the conclusion that the titanium centers are hole traps [9]. At about 140 K holes in LiF begin to move and can be trapped by the titanium centers. This leads to an increase of the transformation efficiency of titanium centers. The transformation efficiency of the titanium centers grows also above 200 K (Fig. 4). The cation vacancies in lithium fluoride begin to move at temperatures above 220 K [10]. Probably the growth of transformation efficiency of titanium centers above 200 K is due to the loss of associated cation vacancies by the reaction



Earlier, on the basis of ionic conductivity investigations Jain and Sootha concluded that some part of titanium impurity in lithium fluoride is connected with cation vacancies [11]. The present results show that cation vacancies are a part of titanium luminescence centers in lithium fluoride.

3.2 Sodium fluoride

The NaF:TiO₂:MgF₂ crystal has similar optical properties as LiF₂:TiO₂ (Fig. 5). Two bands with maxima at 2.2 and 2.95 eV have been observed in photoluminescence spectra. The 2.95 eV emission centers are oriented along the C₃ crystal axis. The 2.2 eV emission centers are oriented along an axis which is close to the C₂ crystal axis at 200 K. The azimuthal dependence of the polarization degree of the 2.2 eV emission at room temperature is close to a straight line. All emission and excitation bands of titanium luminescence centers in sodium fluoride are shifted by about 0.2 eV to lower energy as compared with the bands of titanium centers in lithium fluoride. Therefore, titanium luminescence centers in lithium and sodium fluorides have the same nature.

4. Discussion

The Ti³⁺ centers have been observed after X- or γ-irradiation of titanium-doped lithium fluoride. The center is identified as Ti³⁺ ion displaced by 0.02 to 0.03 nm in

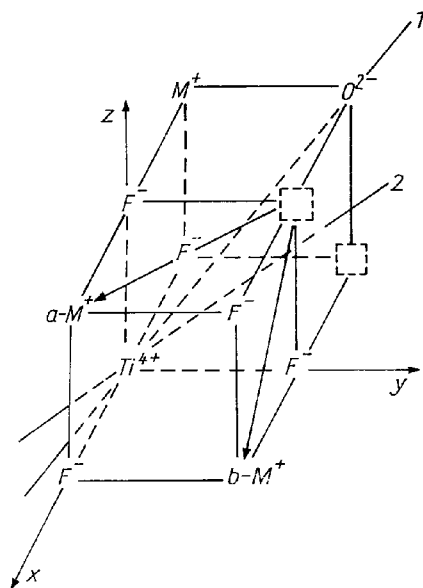


Fig. 6. A model of titanium luminescence centers in lithium and sodium fluorides

[111] direction from a lithium site [4]. The 6.2 eV absorbance in lithium fluoride depends on both titanium impurity and oxygen or hydroxide impurity concentrations [1, 12]. The high-temperature stability of the polarization degree of both emissions shows that the luminescence centers are point defects near the titanium ions.

On the basis of earlier and present results it has been concluded that the titanium luminescence center consists of Ti^{4+} ion, O^{2-} ion on anion site, and two associated cation vacancies (Fig. 6). The high-energy emission of titanium luminescence centers is caused by the titanium-oxygen bond. The oxygen ion is in the next-nearest-neighbor (nnn) anion site, and the emission centers are oriented along the C_3 crystal axis. The polarization of the low-energy emission is caused by two cation vacancies in next-nearest (nn) positions to the Ti^{4+} ion. Since the Ti^{4+} ion can be displaced from lithium and sodium site (as the Ti^{3+} ion in lithium fluoride [4]), the electrostatically most probable locations of cation vacancies are in [011], $[\bar{1}10]$, $[10\bar{1}]$ sites. Therefore the low-energy emission center will be oriented along the axis between the two positions (see Fig. 6).

The azimuthal dependence of emission polarization degree of an oscillator with such an orientation was calculated by the Feofilov method [8, 13]. The calculated "axial" azimuthal dependence is the same as the dependence of emission of oscillators

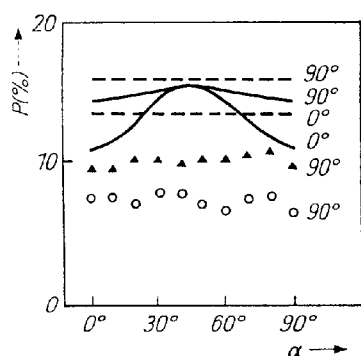


Fig. 7. Calculated (lines) and experimental (points) azimuthal dependence of polarization degree of 2.2 eV emission of $NaF:TiO_2:MgF_2$ (triangles) and 2.42 eV emission of $LiF:TiO_2$ (circles). The angle of measurement with respect to the beam direction is marked in the figure. The dashed lines show the azimuthal dependence of centers in which some part of cation vacancies is shifted to a , b -sites (see Fig. 6)

which are oriented along the C_2 crystal axis, but the "perpendicular" dependence is close to a straight line (Fig. 7). The calculated dependences correlate with the experimental results (see Fig. 1, 5, 7). At a relatively high temperature the cation vacancy begins to move to other sites a , b (with higher energy) (see Fig. 6). For the a -site the oscillator will be oriented along the C_2 crystal axis and for the b -site along the C_4 crystal axis. On a certain condition the calculated "axial" azimuthal dependence of the emission polarization degree is close to a straight line like the dependence of the 2.2 eV emission of sodium fluoride at room temperature (see Fig. 5).

The existence of two emission bands of titanium luminescence centers with different oscillator orientation shows that in a first approximation we can distinguish two subsystems of the emission center. One subsystem is the O^{2-} ion and the other is the $(TiF_6)^{2-}$ molecular complex. Because of the similar emission and excitation spectra related with oxygen in $LiF:TiO_2$ and $LiF:Li_2O$ [14], the 3.1 eV emission is related with the electron transitions "inside" the O^{2-} ions. The polarization of the 3.1 eV emission is due to the attraction of oxygen electrons by the titanium ions. The emission transitions are oriented along the Ti-O (C_3) axis. Probably the electronic transitions of the $(TiF_6)^{2-}$ complex are of the charge-transfer type between the fluoride ions and the central Ti^{4+} ion. The electronic transitions of $(TiF_6)^{2-}$ complexes are modified by the presence of two cation vacancies. The orientation of emission transitions depends on the positions of the cation vacancies.

5. Conclusion

The experimental results lead to the following conclusions: a) 2.42 and 3.1 eV emissions in $LiF:TiO_2$, 2.2 and 2.95 eV emissions in $NaF:TiO_2$ are related to the titanium luminescence centers, b) the center in lithium and sodium fluorides consists of a Ti^{4+} ion on a cation site, a O^{2-} ion on an anion site, and two cation vacancies.

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