

Relaxation properties of defect complexes in SrCl₂-Tl⁺ crystals

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Received January 8, 2004

Two maxima are observed in the thermograms of the thermostimulated depolarization currents of SrCl₂-Tl⁺ crystals have been observed: a low-temperature one ($T_m = 107$ K, $\varepsilon_m = 0.24$ eV), caused by the reorientation of Tl⁺V_a⁺ dipoles, and high-temperature one ($T_m = 215$ K, $\varepsilon_m = 0.46$ eV) related to thermal dissociation thereof. Tl⁺V_a⁺-dipoles possess C_{3v} symmetry, that results in splitting of the absorption A-band ($^1S_0 \rightarrow ^3P_1$ transition) into two components with maxima at 234 and 247 nm. At low-temperature irradiation ($T < 140$ K), Tl⁺V_a⁺-dipole concentration (at the stage of a crystal coloring saturation) is decreased by 15–20 % as a consequence of charge carrier capture by Tl⁺-ions.

На термограммах токов термостимулированной деполяризации кристаллов SrCl₂-Tl⁺ наблюдаются два максимума: низкотемпературный ($T_m = 107$ К, $E_m = 0.24$ эВ), обусловленный реориентацией Tl⁺V_a⁺ — диполей, и высокотемпературный ($T_m = 215$ К, $E_m = 0.46$ эВ), обусловленный их термодиссоциацией. Tl⁺V_a⁺-диполи обладают C_{3v} — симметрией, что обуславливает расщепление А-полосы поглощения (переход $^1S_0 \rightarrow ^3P_1$) на две компоненты с максимумами при 234 и 247 нм. При низкотемпературном облучении ($T < 140$ К) концентрация Tl⁺V_a⁺-диполей (на стадии насыщения окрашиваемости кристалла) уменьшается на 15–20 %, что является следствием захвата носителей заряда Tl⁺-ионами.

Thallium is among the most widely used activators of ionic crystals. Tl activated crystals are perspective material for lasers on color centers [1–3]. Thallium is included in the form of substituting Tl_c⁺(6s²) ions in the lattice of alkali halide crystals. Under ionizing irradiation, the localization of the charge carriers on thallium ions and formation of Tl⁰ and Tl²⁺-activating color centers take place [1]. At $T > 200$ K, when anion vacancies become mobile, Tl⁰(1) and Tl⁰(2) color centers are formed additionally in relatively low concentrations [2]. The Tl⁰(1) and Tl⁰(2) centers include a neutral Tl⁰ atom

perturbed by field of one or two nearest-neighbour anion vacancies, respectively [3].

In SrCl₂-Tl⁺ crystals irradiated with X-rays at 78 K, the Tl_c⁰(1) and Tl_c²⁺(2) color centers are formed [4]. These centers have low thermal stability and at $T > 140$ K, due to ionic processes, are transformed into Tl_c²⁺ and Tl_i⁰(1) ones, respectively [5]. The ionic thermostimulated processes in SrCl₂-Tl⁺ crystals have not been studied yet, although this problem is of both scientific and practical interest. The available literature data on ionic processes in SrCl₂ crystals were obtained on the crys-

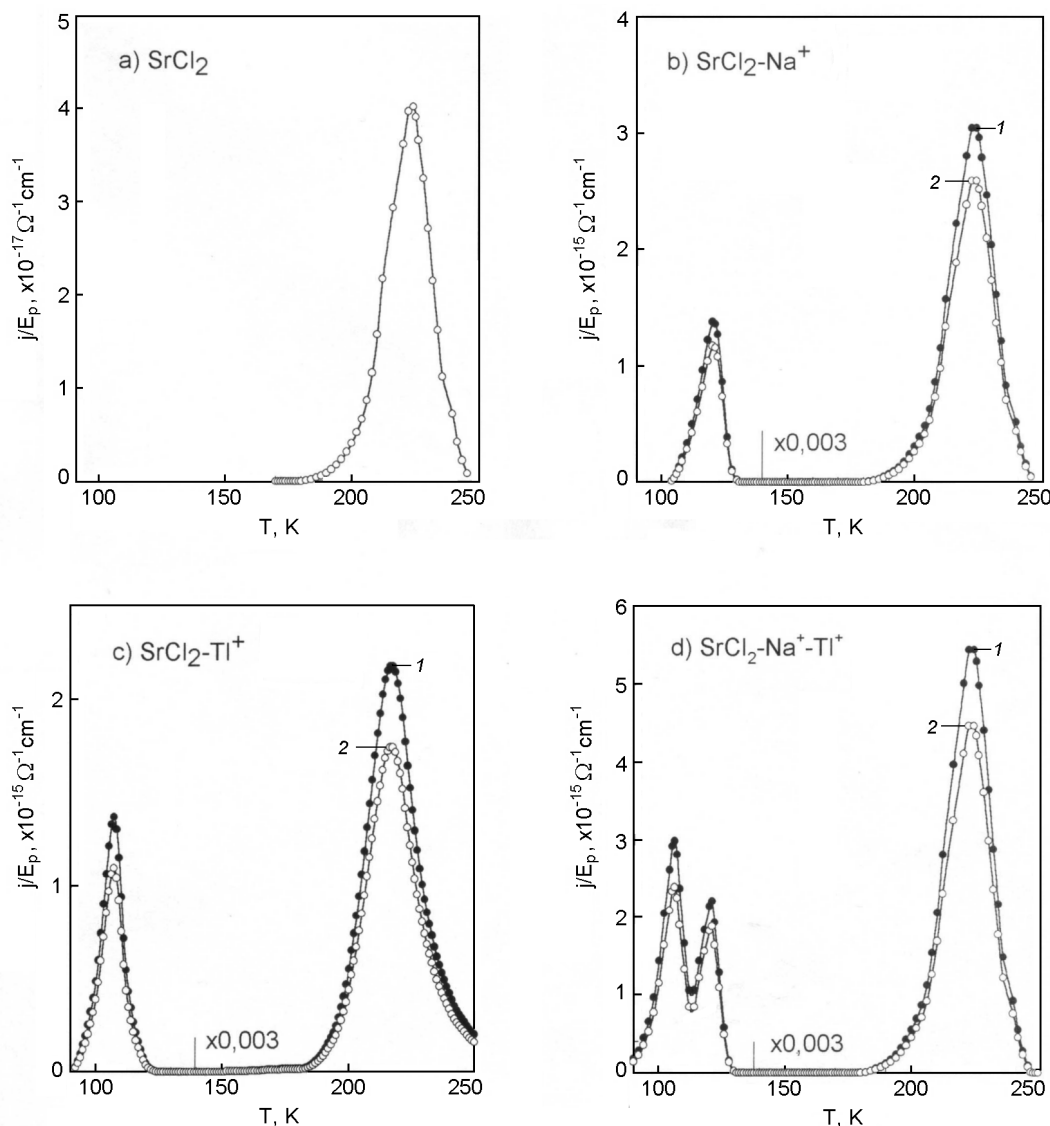


Fig. 1. Thermostimulated depolarization currents in $\text{SrCl}_2\text{-Ti}^+$ crystals ($E_p = 6000 \text{ V/cm}$), prior to (1) and after (2) irradiation.

tals doped with alkali cations only (Na^+ , K^+ , Rb^+ , Cs^+) [6].

The crystals were grown by the Stockbarger technique in quartz ampoules. Four groups of crystals were obtained, namely, "pure" SrCl_2 crystals; $\text{SrCl}_2\text{-Ti}^+$ crystals (0.05–0.2 mol% of TiCl in the melt); $\text{SrCl}_2\text{-Na}^+$ ones (0.05–0.2 mol% of NaCl in the melt); and $\text{SrCl}_2\text{-Na}^+\text{-Ti}^+$ ones (0.05–0.2 mol % of NaCl and TiCl in the melt). The samples used in these experiments were shaped as $10 \times 10 \times 1 \text{ mm}^3$ plates cleaved from single crystals perpendicularly to the crystallographic $\langle 111 \rangle$ -axis.

The standard procedure was used to measure the thermal depolarization. The sample was polarized to saturation in an

electric field $E = 6000 \text{ V/cm}$ at appropriate temperature T_p such that any dipoles present are sufficiently mobile to become oriented in the field. The polarization cell was then cooled down to a low temperature at which the motion of dipoles is frozen and the electric field was removed. On warming up at a constant rate (3 K/min), the thermostimulated depolarization current pulses were recorded in the temperature range where the frozen-in polarization disappears as the dipoles randomize. The optical spectra were measured using a double grating monochromator.

Fig. 1 illustrates the thermostimulated depolarization (TD) in SrCl_2 crystals prior to and after irradiation (curves 1 and 2, respectively). In the thermogram of TD of

"pure" crystals a maximum at 220 K is observed (see Fig. 1a, curve 1). For $\text{SrCl}_2\text{-Na}^+$ crystals (see Fig. 1b, curve 1), two maxima are observed: low-temperature one at $T_1 = 122$ K ($\epsilon_1 = 0.28$ eV) and high-temperature one at $T_2 = 220$ K ($\epsilon_2 = 0.52$ eV). In $\text{SrCl}_2\text{-Tl}^+$ ones (see Fig. 1c, curve 1), two maxima of TD currents also occur: $T_1 = 107$ K ($\epsilon_1 = 0.24$ eV) and $T_2 = 215$ K ($\epsilon_1 = 0.46$ eV). As to $\text{SrCl}_2\text{-Na}^+\text{-Tl}^+$ crystals, two maxima at $T = 107$ K and $T = 122$ K are observed in the low temperature range as well as a maximum at 220 K (see Fig. 1d, curve 1).

It follows from the TD thermograms shown in Figs. 1b,c (see curves 1) that in doped crystals, ($T < 130$ K) one TD maximum is observed in the low temperature range, the peak location and activation energy depending on the type of impurity ion. In the crystals doped with two activators, two low-temperature TD maxima are observed (see Fig. 1d, curve 1). By analogy with $\text{SrCl}_2\text{-Me}^+$ crystals ($\text{Me}^+ = \text{Li}^+, \text{Na}^+, \text{K}^+, \text{Rb}^+$) [6], we conclude that the maximum at 107 K in $\text{SrCl}_2\text{-Tl}^+$ is due to the reorientation of Tl^+V_a^+ dipoles while at 215 K, to thermal dissociation thereof. The thermal dissociation of the dipoles ($\text{Tl}^+\text{V}_a^+ \rightarrow \text{Tl}^+\text{V}_a^+$) is accompanied by spatial migration of anion vacancies. As a result, the intensity of the 215 K TD current peak is two orders higher than that of the dipole relaxation. The existence of this peak in "pure" SrCl_2 crystals (see Fig. 1a) is caused by the presence of non-intentional impurities of monovalent metals in the crystal.

In SrCl_2 crystals, the Tl^+V_a^+ -dipole symmetry is C_{3v} . The presence of vacancies is the reason for the lowered thallium center symmetry and the splitting of its 3P_1 state into two sublevels. A double band ($A_1 + A_2$) is resolved into two subbands (see Fig. 2, curve 1). The absorption peaks are: $\lambda_{A_2} = 234$ nm (5.30 eV) and $\lambda_{A_1} = 247$ nm (5.02 eV) at 80 K. The splitting of the two absorption peaks is 0.28 eV. The A_2 and A_1 band half-widths are 0.18 and 0.21 eV, respectively. The area under A_1 band is larger than that under A_2 one. The photoluminescence excited in A-bands of absorption consists of one band with a maximum peaked at 380 nm (3.27 eV) and half-width 0.39 eV at 80 K (Fig. 2, curve 2). This emission is due to transitions of the thallium ions from the 3P_1 excited state into the 1S_0 ground one. The photoexcitation spectrum of the

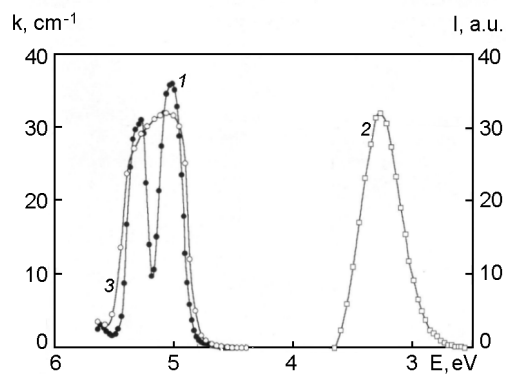


Fig. 2. Absorption spectra of $\text{SrCl}_2\text{-Tl}^+$ crystals irradiated at temperatures (K): 90 (1), 300 (3) and photoluminescence spectrum at 90 K (2).

380 nm emission band reproduces the shape of the absorption A-band.

Pure SrCl_2 crystals are radiation-resistant materials and are not colored under X-ray irradiation. The coloration induced by the radiation is observed in the crystals doped with alkali cations [6] or thallium [3, 4]. Moreover, the coloration in $\text{SrCl}_2\text{-Me}^+$ crystals is accompanied by decreasing the dipole relaxation currents (see Fig. 1b, curves 2) [6]. The same takes place in $\text{SrCl}_2\text{-Tl}^+$ crystals. Fig. 1 (see curves 2) illustrates the thermograms of the dipole relaxation currents in crystals irradiated at low temperatures at the stage of crystal coloring saturation. As follows from the Figure, the dipole relaxation currents in colored crystals are by 15–20 % lower than in non-irradiated ones (see curves 1). This means that dipoles are destroyed in the course of the crystal irradiation. The dipole destruction efficiency at low temperatures ($T < 140$ K) is independent of the impurity type in $\text{SrCl}_2\text{-Tl}^+\text{-Na}^+$ crystals at the stage of crystal coloring saturation, the part of destroyed Tl^+V_a^+ and Na^+V_a^+ dipoles is approximately the same to within experimental error. The efficiency of the radiation dipole destruction at low temperatures in $\text{SrCl}_2\text{-Tl}^+$ crystals does not depend on whether a dipole is in the "frozen" state ($T < 107$ K) or a vacancy is in rotational motion around the impurity ($T > 107$ K). The sharp increase of dipole destruction efficiency takes place at $T > 140$ K and is accompanied by the change of the color center structure.

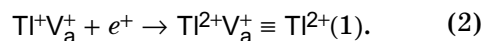
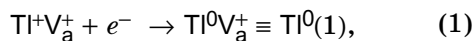
It follows from the results of the TD study that Tl^+ ions, as well as of alkali metal ones, are included into the lattice of a crystal as impurity-vacancy Tl^+V_a^+ dipoles. At $T < 107$ K, the impurity-vacancy

dipoles are "frozen" in the lattice of SrCl₂-Tl⁺ crystal. In the temperature range of 107 to 225 K, the anion vacancy moves rotationally around Tl⁺ ion by jumping along eight equivalent positions (local migration). At $T = 215$ K, the thermal dissociation of dipoles is observed, (Tl⁺V_a⁺ → Tl⁺ + V_a⁺), the spatial migration of anion vacancies and formation of isolated Tl⁺ ions take place. At the same time, the dipole reconstruction occurs according to the following scheme: Tl⁺ + V_a → Tl⁺ + V_a⁺. Thus, at $T > 215$ K, thallium is in the lattice of a crystal both in the form of Tl⁺V_a⁺-dipoles and isolated Tl⁺ ions.

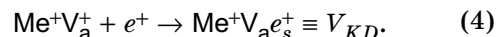
In Tl⁺V_a⁺ dipoles, an anion vacancy replaces one of the eight nearest neighbour anions of the Tl⁺. In this case, the C_{3v} symmetry of the perturbed Tl⁺ center can explain the formation of the double absorption band (A₁ + A₂). The unperturbed Tl⁺ center symmetry is O_h. Let us assume, as it was observed in the case of the F_A center, that the oscillator strengths related to each of the three transitions are equal [5]. The electric transitions of the dipoles responsible for the A₁ and A₂ bands are perpendicular and parallel to the axis of rotation, respectively.

It was observed in the thermal depolarization experiment (see Fig. 1) that at 215 K, the Tl⁺V_a⁺ dipoles are thermally unstable and release the anion vacancy. The anion vacancy moves away restoring the O_h symmetry of the Tl⁺ ions and, as a result, the splitting of the absorption A-band should disappear. However, as is seen in optical absorption spectra, splitting of the A-band still exists at room temperature (see Fig. 2, curve 3). This indicates that at this temperature, the majority of thallium ions still exist in the crystal lattice as Tl⁺V_a⁺-dipoles.

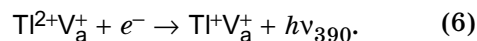
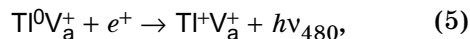
The ratio of intensities of absorption subbands and their maximum positions do not depend on the measurement temperature. That is why we consider that the splitting cannot be preconditioned by the Jahn-Teller effect, as it is observed in the case of KF-Tl⁺ crystals [7]. At low-temperature irradiation ($T < 140$ K) of SrCl₂-Tl⁺ crystals, Tl⁰(1) and Tl²⁺(2) centers are being generated [3] and the concentration of Tl⁺(1) dipoles decreases (see Fig. 1c, curve 2). The radiation-induced destruction of Tl⁺(1) centers and coloration appearance are due to the following reactions [4]:



In SrCl₂-Me⁺ crystals (Me⁺ = K⁺, Na⁺, Rb⁺, Cs⁺), the radiation-induced dipole destruction at low temperatures goes according to the scheme [6]:



The difference between the reactions (1)–(2) and (3)–(4) consists in the localization of charge carriers on dipoles. However, this difference does not influence the efficiency of dipole destruction (generation of color centers), which is practically the same for both Tl⁺V_a⁺ and Na⁺V_a⁺ and amounts to 15–20 %. At the dipoles concentration of 10¹⁹ cm⁻³ order, as is in our case, this pre-determines the concentration of color centers of 10¹⁸ cm⁻³ order. The thallium color centers formed in the crystals under low temperature irradiation, possess an efficient electrical charge with respect to the crystal lattice, and play the part of the recombination centers [5]:



Due to the reactions (1)–(2) (generation of coloring centers) and (5)–(6) (bleaching action of radiation), a dynamic equilibrium between thallium color centers (Tl⁰(1) and Tl²⁺(1)) and Tl⁺V_a⁺ dipoles is realized. At $T > 140$ K, when "free" anion vacancies become mobile [6], the electrically neutral thallium coloring centers are formed [8, 9], the bleaching action of X-rays decreases, and the crystal coloration efficiency increases. These processes are accompanied by the rise of the additional peaks of ionic thermal currents.

Thus, the relaxation processes in SrCl₂-Tl⁺ crystals are of ionic nature. Those are connected with the change of charge state of defect complexes under X-irradiation and thermal influence.

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Релаксаційні властивості дефектних комплексів у кристалах $\text{SrCl}_2\text{-Ti}^+$

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На термограмах струмів термостимульованої деполяризації кристалів $\text{SrCl}_2\text{-Ti}^+$ спостерігаються два максимуми: низькотемпературний ($T_m = 107$ К, $E_m = 0.24$ еВ), зумовлений реорієнтацією Ti^+V_a^+ -диполів, і високотемпературний ($T_m = 215$ К, $E_m = 0.46$ еВ), зумовлений їх термодисоціацією. Ti^+V_a^+ -диполі володіють C_{3v} -симетрією, що зумовлює розщеплення А-смуги поглинання (перехід $^1S_0 \rightarrow ^3P_1$) на дві компоненти з максимумами при 234 і 247 нм. При низькотемпературному опроміненні ($T < 140$ К) концентрація Ti^+V_a^+ -диполів (на стадії насичення забарвлення кристала) зменшується на 15–20 %, що є наслідком захоплення носіїв заряду Ti^+ -іонами.