

# Study on radiation sensitivity of SrCl<sub>2</sub>-K crystals

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Parameters of radiation sensitivity of SrCl<sub>2</sub>-K crystals have been estimated using dimensional model. The maximum concentrations of color centers depending on the concentrations of alkali metal impurities have been determined. Analysis of the obtained results and their comparison with the experimental data has been performed.

В одномерной модели рассчитаны параметры радиационной чувствительности кристаллов SrCl<sub>2</sub>-K. Определены предельные концентрации центров окраски в зависимости от концентрации примеси щелочного металла. Осуществлен анализ результатов исследований и их сопоставление с экспериментом.

## 1. Introduction

According to its radiation characteristics SrCl<sub>2</sub>-K crystals are similar to crystals of fluorides of alkalinity [1, 2]. Pure SrCl<sub>2</sub> crystals are stable for ionize irradiation that allows using them as scintillates [3–5].

On the other hand, the crystals of SrCl<sub>2</sub>, alloyed by alkaline metals are characterized by very high radiation susceptibility [6–10].

In the present study within the framework of the ion chain model [11, 12] radiation parameters of SrCl<sub>2</sub>-K crystals depending on the quantity of alloying additives and irradiation temperature were estimated. The results of calculations were compared with the spectral experimental data.

SrCl<sub>2</sub>-K crystals were grown in a soldered quartz ampoule by the modified method of Stockburger. The additive concentrations were 0.04 and 0.4 mol % KCl. The actual amount of the additive was estimated by the method of thermo-stimulated depolarization and calculated by Bucchi formula [7, 8] and it was 10<sup>18</sup> and 10<sup>19</sup> 1/cm<sup>3</sup>, correspondently.

Samples of SrCl<sub>2</sub>-K sized 10×1×1 mm<sup>3</sup> were irradiated by X-rays within the temperature range of 80÷250 K. As source of

irradiation it was used X-ray unit, working under the following parameters:  $U = 55$  kV,  $I = 1$  mA, the time of irradiation of the samples  $t = 1$  h. An estimation of the spectra of directed absorption and the spectra of thermo-stimulated depolarization were conducted according to the standard methodology.

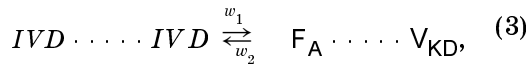
## 2. Research results

At low temperatures alkali metal ions (K<sup>+</sup>) are included in the SrCl<sub>2</sub>-K crystal lattice as impurity-vacancy dipoles (IVD) Me<sup>+</sup>V<sub>a</sub><sup>+</sup>-type, where Me<sup>+</sup> is negatively charged in relation to the lattice of alkali metal ion, and V<sub>a</sub><sup>+</sup> is a positively charged anion vacancy. As it was shown in previous works [11, 12] if crystals are irradiated at low temperatures, then they generated {F<sub>A</sub>-V<sub>KD</sub>} – complementary pairs of color centers produced by the localization of the charge carriers on IVD:



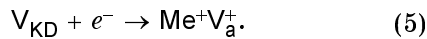
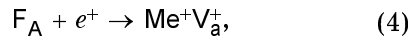
A structure of impurity-vacant dipoles, F<sub>A</sub>- and V<sub>KD</sub>-color centers are presented in

Fig. 1, and the mechanism of their formation can be described by the following scheme:



where  $IVD \cdots \cdots IVD$  – ion chain fragment with the length limited by impurity-vacant dipoles;  $w_1$  – is a probability of charge carriers ( $e^-$ ,  $e^+$ ) capture by IVD and a pair  $\{F_A-V_{KD}\}$ -pair color centers formation;  $w_2$  – is a probability of  $\{F_A-V_{KD}\}$ -pair color centers destruction due to the ( $e^-$ ,  $e^+$ ) charge carriers localization on the color centers and thus the IVD couple reduction.

With accumulation of the color centers an opposite reaction takes effect, which is the consequence of  $F_A$ -centers holes and  $V_{KD}$ -centers electrons capturing [10]:



As a result, the bleaching of each pair of the color centers is accompanied by the arising of an appropriate pair of dipoles. At the stage of color crystal saturation the dynamic balance is reached between the processes of generating the color centers and bleaching induced by radiation exposure. Concentration of the color centers at the color saturation stage is determined by the equation [12]:

$$C_1 = \frac{w_1}{w_1 + w_2} C_0, \quad (6)$$

where  $C_1$  is  $\{F_A-V_{KD}\}$  – complementary pairs concentration in saturated crystal,  $C_0$  – IVD pairs concentration in the crystal before irradiation.

$\{F_A-V_{KD}\}$ -pairs are thermally stable under temperatures values lower than of  $T = 140$  K [6–8]. At higher temperatures, the anion vacancy parts thermo actively from the hole center. Mobile vacancy is localized on  $F_A$ -center and  $M_A^+$  center is formed. As a result of impulsive heating of colored crystal to temperatures of  $T > 140$  K the  $\{F_A-V_{KD}\}$ -pair centers disappear in the crystal and  $(M_A^+-V_{KA})$ -complementary pair of the color centers is formed. The models of  $M_A^+$  and  $V_{KA}$ -centers are shown in Fig. 1, and the mechanism of their formation can be described as following:

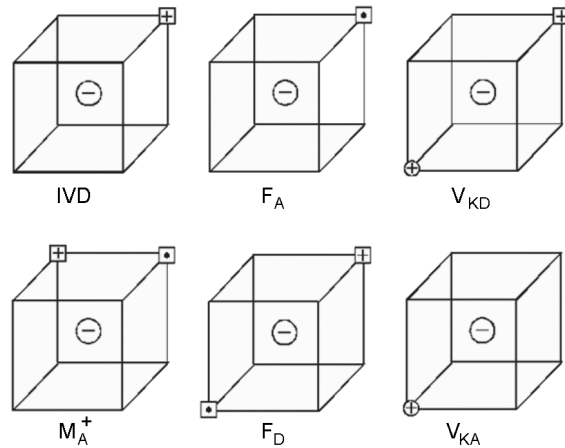
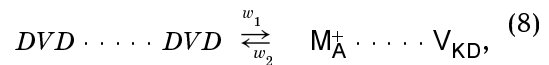


Fig. 1. Models of color centers.



$\{M_A^+-V_{KA}\}$ -pairs are generated not only after the pulse heating the crystal to the temperature of  $T = 140$  K (Eq. (7)), but also directly during the exposure at  $T > 140$  K [8].

The process of the color centers formation and bleaching induced by radiation can be described in the form of the following scheme:



where  $w_1$  and  $w_3$  are the probabilities of formation of  $\{M_A^+-V_{KA}\}$ -complementary pairs of the color centers and their bleaching, respectively.

Since the  $M_A^+$  and  $V_{KA}$  are defects of dipole type, the probabilities of  $w_1$  and  $w_3$  are coincided by the value. Therefore, the critical concentration of  $\{M_A^+-V_{KA}\}$ -pairs formed in crystals irradiated at temperatures  $T > 140$  K is described by the equation:

$$C_2 = \frac{w_1}{w_1 + w_2} C_0 = \frac{C_0}{2}, \quad (9)$$

where  $C_2$  is a concentration of  $\{M_A^+-V_{KA}\}$ -pairs on the color saturation stage of the crystal irradiated at  $T > 140$  K and  $C_0$  is a concentration of IVD pairs before the crystal exposure.

The Table shows the results of calculations of radiation sensitivity of fluorites crystals alloyed by alkali metals depending on the impurity concentration and irradiation temperature.  $C$  is a molar concentration of impurity ions (IVD) in the crystal;  $l$

Table. The parameters of radiation sensitivity of SrCl<sub>2</sub>-K crystals

$C$ , %	$l$	$w_1$	$w_2$	$C_1/C_0$	$C_2/C_0$	$C_2/C_1$
0.4	4b	0.107	0.417	0.204	0.,5	2.449
0.2	5b	0.0888	0.425	0.173	0.5	2.893
0.05	8b	0.0333	0.375	0.082	0.5	6.131
0.025	10b	0.0263	0.361	0.068	0.5	7.363
0.0075	15b	0.021	0.35	0.057	0.5	8.833

– an average distance between impurity ions in the crystal lattice;  $b$  – parameter of ion chain in crystallographic direction ( $b = \sqrt{3}a$ ) [111], where  $a$  – crystal lattice constant;  $w_1$  and  $w_2$  – probabilities of the color centers formation and their bleaching by the electron-hole pairs decay, respectively;  $C_1$  and  $C_2$  – concentrations of the complementary pairs of the color centers formed in the crystal after irradiation at temperatures  $T = 90$  K and  $T > 220$  K respectively,  $C_0 = C/2$  – concentration of pairs of dipoles in the crystal before its exposure,  $E$  – energy of ionizing radiation, which is necessary to form the color centers pair.

### 3. Discussion

Fig. 2 shows an induced absorption spectra of crystal SrCl<sub>2</sub>-K exposed to X-rays (X-ray apparatus parameters:  $U = 55$  kV,  $I = 12$  mA,  $t = 0.5$  h) at  $T_1 = 120$  K (curve 1) and at  $T_2 = 160$  K (curve 2), that is at  $T_1 < T_d < T_2$ , where  $T_2 = 140$  K is a thermal dissociation temperature of  $V_{KD}$ -center (Eq. (7)). As shown in Fig. 2 induced absorption spectra (IAS) of crystals irradiated at 120 K (curve 1) and 160 K (curve 2) differ significantly. IAS at 120 K contains band of  $V_{KD}$  absorption centers (band 390 nm) and a doublet absorption band of  $F_A$ -centers (band 580 and 640 nm). IAS at 160 K consist of the 380 nm band ( $V_{KD}$ -center absorption band), triplet absorption of  $M_A^+$ -centers (bands at 444, 535 and 760 nm) and F-band (580 nm band) (curve 2).

Thus, the study of the induced absorption spectra confirms that the formation of the color centers occurs according to the equations (3) and (8).

From the equations of (3) and (8) it follows that, regardless of the value of crystals irradiation temperature, a formation of the color centers occurs due to localization of charge carriers on impurity-vacancy dipoles, and hence the process is accompanied by radiation destruction of dipoles. Reducing the concentration of the dipoles in the

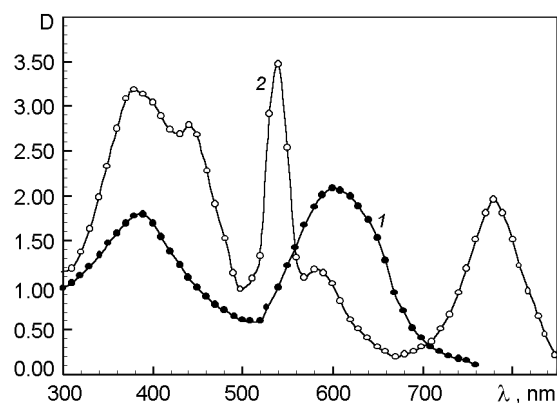


Fig. 2. The spectra of induced absorption in the crystals of SrCl<sub>2</sub>-0.4KCl (1 – after irradiation at  $T = 120$  K, 2 – after irradiation at  $T = 160$  K).

crystal can be registered by measuring the value of thermally stimulated depolarization (TSD) currents before and after exposure of the crystal to X-rays beams.

Figure 3 (curve 1) shows TSD thermogram currents of the SrCl<sub>2</sub>-KCl crystal irradiated by X-rays beams at 78 K. TSD thermogram has three maximums:

- 112 K – caused by the reorientation of dipoles;
- 140 K – caused by thermal  $V_{KD}$ -center decay;
- great maximum at 210 K is associated with the IVD thermal dissociation.

Figure 3 (curves 2 and 3) shows curves which characterize the dependence of currents value at maximum of 112 K of irradiation temperature of different samples. As seen from this figure the maximum destruction of dipoles occurs in the range of 150–160 K and reaches the value of 30–40 % of initial IVD concentration. If the crystal is rayed at  $T < 140$  K the portion of destroyed by radiation dipoles makes up the value of 9–15 % of IVD concentration. And when the structure of the color centers is changed ( $F_A \rightarrow M_A^+$  thermally induced conversion), the effectiveness of the process of radiation destruction of dipoles increases 2–3.5 times more. All these data qualitatively coincide with the results of theoretical calculations for high-allowed crystals (Table 1). The data presented in Fig. 3 imply that the average efficiency of radiation induced destruction is maximal at 160 K, and consequently the maximum of crystal coloration is to be achieved exactly at a given temperature.

Owing to an absence of literature data on oscillator strength as for electronic as for hole color centers, an information on the

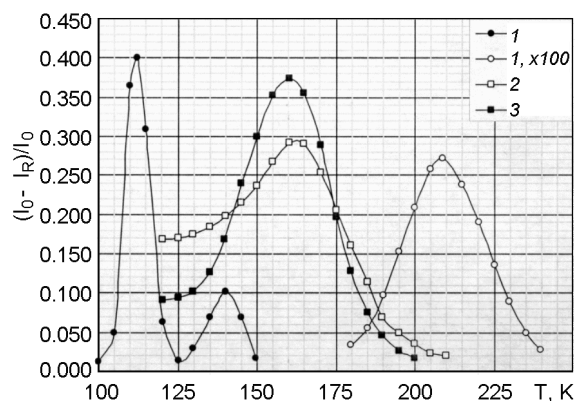


Fig. 3. TSD currents in the crystals of  $\text{SrCl}_2\text{-K}$ : 1 – TSD currents in irradiated crystals of  $\text{SrCl}_2\text{-0.04 \% KCl}$ ; 2 and 3 – relative concentration of radiation-damaged IVD in the crystals of  $\text{SrCl}_2\text{-0.04 \% KCl}$  and  $\text{SrCl}_2\text{-0.3 \% KCl}$ , respectively.  $I_0$  – the value of TSD currents before irradiation;  $I_R$  – the TSD currents value after irradiation of the crystal by X-rays (irradiated time  $t = 30$  min).

color value in  $\text{SrCl}_2\text{-K}$  crystals can be obtained by measuring the area under the absorption spectra (area under the graph of optical density  $D$  as a function of  $h\nu$ ).

In Fig. 4, curves are shown, which reflect the area value under the contour of  $F_A$  and F-absorption bands (curve 1),  $M_A^+$  absorption bands (curve 2) and  $F_A$ , F and  $M_A^+$  bands (curve 3).

From this figure we can see that the crystal coloration occurs under the conditions of irradiation of the crystal in the temperature range of 150–160 K (curve 3) and it is concerned with the  $M_A^+$ -centers formation in the crystal matrix (curve 2). After thermally induced transformations the value of crystal coloration increases about 3.5 times more, that is consistent with the data of theoretical calculations (Table 2).

Thermal bleaching of  $\text{SrCl}_2\text{-K}$  crystals at  $T > 160$  K is caused by  $V_{KA}$ -centers thermal dissociation.

Fig. 4 (curve 4) shows the thermogram of thermally stimulated luminescence (TSL) for  $\text{SrCl}_2\text{-K}$  crystals. It manifests maxima at 103, 135 and 190 K caused by thermal dissociation of  $V_K$ ,  $V_{KD}$  and  $V_{KA}$ -centers respectively. Thermally released holes recombine with electronic centers and cause the crystal discoloration.

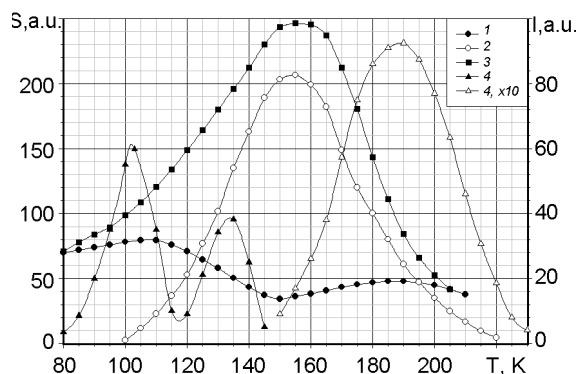


Fig. 4. Dependences of area under the absorption bands of electrical color centers of the crystal  $\text{SrCl}_2\text{-0.04 \% KCl}$  from temperature of the crystal exposure: 1 – for  $F_A$  and F-centers, 2 – for  $M_A^+$ -centers, 3 – total absorption of all color centers, 4 – thermally stimulated

Table 2. Formation energy of complementary pair of the color centers ( $E$ ) and maximum values of concentration of the color centers in the crystals of  $\text{SrCl}_2\text{-K}$ , irradiated at 80 K ( $n_1$ ) and 160 K ( $n_2$ )

$C, \%$	$E, \text{eV}$	$n_1, 1/\text{cm}^3$	$n_2, 1/\text{cm}^3$
0.400	140	$4.08 \cdot 10^{18}$	$1 \cdot 10^{19}$
0.200	169	$1.73 \cdot 10^{18}$	$5 \cdot 10^{18}$
0.050	450	$2.04 \cdot 10^{17}$	$1.25 \cdot 10^{18}$
0.025	570	$8.49 \cdot 10^{16}$	$6.25 \cdot 10^{17}$

#### 4. Conclusions

Good correlation between the experimental data on  $\text{SrCl}_2\text{K}$  crystals radiation sensitivity and theoretical calculations results obtained by the ionic chain model pointed out the advisability to apply this approach. The model was developed for crystals of fluorites and other classes of ionic crystals: alkali halide crystals, halide compounds of alkaline earths, metal oxides and others, and the approach allows to classify the ionic crystals by their radiation sensitivity.

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## Радіаційна чутливість кристалів SrCl<sub>2</sub>-K

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В одновимірній моделі розраховано параметри радіаційної чутливості кристалів SrCl<sub>2</sub>-K. Визначено граничні концентрації центрів забарвлення залежно від концентрації домішки лужного металу. Здійснено аналіз результатів дослідження та їхнє зіставлення з експериментом.