Sub Threshold Mechanisms of Defects Creation in Sulfates of Alkaline and Alkali Earth Metals

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Abstract – A mechanism of creation and storage radiation defects was investigated by methods of thermo activation and VUF spectroscopy, X-ray luminescence, cathodoluminescence and photoluminescence in sulphates of alkali and alkaline haloids metals. Primarily radiation defects created when localization e- h pairs at anionic complexes had shown. In secondary process primarily radiation defects transformed in more stable electronic- and hole- capture centers.Introduction. The sub threshold mechanisms of defects creation in alkali halide crystals (AHC) are the formation of the Frenkel pairs. The Frenkel pairs – the interstitial anions and anionic vacancies- arise at the decay of self trapped anionic excitions or the recombination of the electrons with self trapped holes. These mechanisms of the defect creation in AHC are experimentally and theoretically well-founded.

1. Introduction

The sub threshold mechanisms of defects creation in oxianionic crystals, particularly, in sulfates of alkali and alkaline earth metals (AEM) more varied than in AHC. The specific particularity is the localization of the low-energy electronic excitation -the electrons and the holes on the anionic complexes of lattice [1]. Formation of capture centers for electron and hole by this mechanism in sulfates of alkali and of AEM concerns to the fundamental processes. A similar process in AHC is not fundamental. Formation of the electronic and holes- capture centers in sulfates of alkali and AEM activated by the ions of heavy metals were studying because of its practical applications as of the thermoluminescent dosimeters. For example, in the crystal of $CaSO_4 - Dy$ at capture electrons $(Dy^{3+} + e^- \rightarrow Dy^{2+})$ and holes $(Dy^{3+} + e^+ \rightarrow Dy^{4+})$ forms electronic centers Dy^{2+} and holes centre Dy^{4+}. In opinion of some authors [2], defects creation it is explained this reaction. The creation of defect, concerned with the decay of anionic complexes (anionic excitions in oxianionic crystals) are not discussed scientific literature. Using experimental results it is able to state, that discovered electronic and holes capture centers were formed by the subthreshold mechanisms in irradiated oxianionic crystals. However, the details of these mechanisms are not experimentally and theoretically investigated.

2. Experiment

Single crystals of sulfates for researches were grown from water solutions by method of "slow evaporation". In some cases natural crystals of $CaSO_4 \cdot H_2O$ with an impurity Ce^{3+} were used. Cathodoluminescence of a crystal of $CaSO_4$ is measured in Institute of Physics of Tartu University (Estonia) at excitation by a stationary beam of electrons (0.5–9 keV, 0.5–1 mA/cm^2) at temperature 8 K. Spectrum of excitation and the luminescence of crystals of K_2SO_4, Na_2SO_4 and $CaSO_4$ were measured in the energy range 2–11 eV by use of vacuum monochromator VMR-2; objects is irradiated by X-rays also. The anode current of a tube with the copper anticathode is 10 mA., a voltage is 45 kV. The radiation of flowing hydrogen is a source of excitation.

3. Experimental results and their discussion

Location of the electrons and holes on the anionic complexes are well investigated of mechanisms of the defect creation in oxianionic crystals. For example, in works of authors [3], electronic excess centers SO_4^{3-} were observed in irradiated alkaline sulfates by the EPR method. In sulfates, these centers form by the complementary hole centers SO_4^- at the low temperature. In our previous works [4] experimentally showed, that hole centers SO_4^- form at the wide range of temperature 80–300 K. SO_4^--centers partially delocalizes at the 190–200 K in time of phase transformation in K_2SO_4 and it is completely annealing at the temperature 340–350 K. Thermally stimulated luminescence (TSL) at 190–200 K; 340–350 K (Fig. 1b) appears at the recombination of the delocalizated holes (SO_4^-) with electronic excess centers SO_4^{3-}.

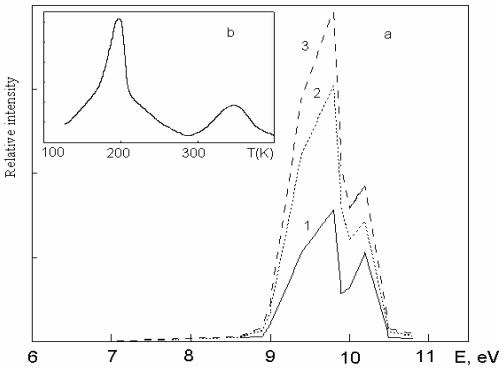

Fig. 1. The creation spectra for peaks TSL of K_2SO_4
1 – at the temperature 220 K
2 – at the temperature 280 K
3 – at the temperature 350 K

Given peaks appear at the irradiation of the crystals by photons with energy over 9.0 eV, where are formed free electron-hole pairs (see Fig.1 a). We have showed [4], the radiation of the self-trapped excitions 3.65–3.8 eV, appears at the recombination of the electrons with self-trapped holes SO_4^-, and effectively excited by photon energy the over range 9–10.5 eV. These and other experimental facts indicates, that SO_4^- hole centers are complementary with the electronic excess centers, and formed at the energy of photons, which has energy more than width of the forbidden bands of the sulfates of alkaline metals. It is necessary to note, that electronic excess centers as $\left[SO_3^{2-} \cdot O^-\right]$ must be stable only at the low temperatures. We guess, that the electronic excess centers $\left[SO_3^{2-} \cdot O^-\right]$ must be transforms into more inconvertible radicals at temperature over 300 K. Similar experimental results are obtained for a crystal of Na_2SO_4. In the next stage, for the purposes of investigation, we have chosen a natural crystal $CaSO_4 - Ce$ which was burning in vacuum. Identical capture centers are formed in a natural crystal of $CaSO_4 - Ce$ after irradiated by photons with an energy 9–11 eV or X- rays. When heating irradiated at 80 K crystal appear peaks of TSL at 120–190 K with a maximum 180 K; 270–280 K; 390–400 K and 470–480 K (Fig. 2 b).

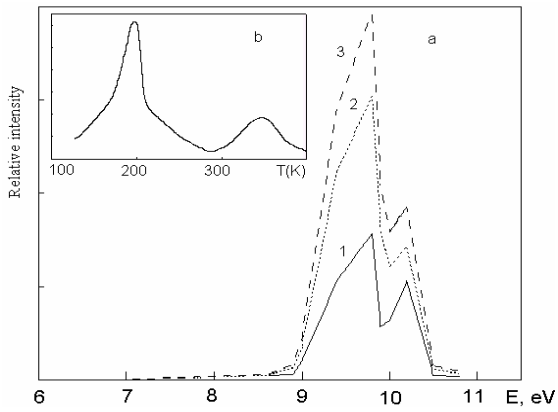

Fig. 2. (a) Temperature dependence of the X-ray luminescence: 1 – for E_m= 4.4 eV, 2 – for E_m= 3.9 eV (b) TSL of $CaSO_4$

Similar peak of TSL appears at the excitation by photons with energy 10–11 eV. The measurement of the spectrum distribution of peaks of TSL in irradiated $CaSO_4 - Ce$ showed that for peak of TSL 120–190 K stand out radiation at 4.4–4.5 eV, 3.9 and 3.65 eV. And for remaining three peaks of TSL is stand out 3.9 and 3.65 eV. It is known that, the 3.9 and 3.65 eV radiation corresponds to intracenteric electronic transitions in the ion Ce^{3+} in matrix ionic crystals $5d \rightarrow {}^2F_{5/2}$ and $5d \rightarrow {}^2F_{7/2}$. All four peaks of TSL appear as from energy of a photon 9.4–9.8 eV. X-ray luminescence (the curve 1), a cathodoluminescence (the curve 2), photoluminescence (the curve 3) and phosphorescence (the curve 4) which arise after a stop irradiation of X-ray at 80K are shown in Fig. 3.

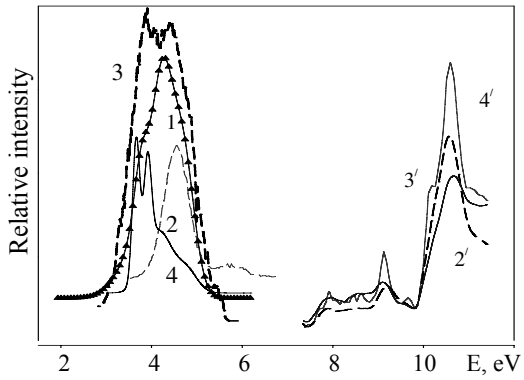

Fig. 3 Spectrum X-ray luminescence (curve 2), cathodoluminescence (curve 1), photoluminescence (curve 4), phosphorescence, after the termination of X-ray radiation (a curve 3), spectrums of excitation for radiation 4.4 eV (curve $4^/$), for 3.9 eV (curve $2^/$) and for 3.65 eV (curve$3^/$) for a crystals $CaSO_4$

The cathodoluminescence with a maximum 4.4–4.5 eV appears in polycrystalline example of $CaSO_4 - Dy$ at 8K after irradiation by electrons. The emission 4.4–4.5 eV is it effectively excited by photons with energy 10.6 eV (Fig 3 curve$4^/$). Besides in this range energy 9.5–11 eV are effectively created free electron-hole pairs. We guess that the emission with a maximum 4.4–4.5 eV arises at recombination electrons with the localized holes SO_4^-. The emission with a maximum 3.9 eV, 3.65 eV efficiently excites in the range of fundamental absorption of a crystal $CaSO_4$ is shown in Fig. 3 curve$2^/$, $3^/$). The experimental results show that the part of an energy of electron-hole pair transfers to impurity Ce^{3+} during to the relaxation.

In the next stage, the nature of capture centers are discussed at irradiation by X-rays or photons with energy 10–11 eV at 80 K. The generated hole during to the relaxation can self-trapped as radical SO_4^- at temperature 80 K. Mobile electrons can be trapped by anionic radicals SO_4^{2-} impurity Ce^{3+} by the reaction: $Ce^{3+} + e^- \rightarrow Ce^{2+}$ .According to authors [5] the ground state of electronic capture center Ce^{2+} is almost imposed by conductivity band of the matrix. We guess, that the complementary capture center are hole SO_4^- and electronic excess complex $\left[SO_3^{2-} \cdot O^-\right]$ appears in irradiated crystal $CaSO_4 - Ce$. Electronic excess complexes can be transformed to more stable electronic centers.

The hole delocalizated and recombines with electronic capture center during polymorphic transition as in sulphates of alkali metals when heating up. The energy of recombination process is transfer to the im-

purity Ce^{3+}; excited impurities transition into the ground state emission photons with energy 3.65 and 3.9 eV. Transfer energy of the recombination process to impurity in $CaSO_4 - Dy$ the range of temperatures 20 ÷ 300 K was observed by other authors also [6].

We expect, low-temperature peaks of TSL 120–190 K; 270–280 K appear at a partial delocalization of the self-trapped hole SO_4^- during the polymorphic transferring. High-temperature peaks of TSL are related with thermal annealing of the nonequivalent localized centers SO_4^-.

Measurement of temperature dependencies of X-ray luminescence for different lengths of the waves are shown in Fig. 2. It has been established, that intensity of emission with a maximum 4.4–4.5 eV exponential falls mainly in four temperature ranges: 120–190 K; 240–300 K; 360–400 K 420–440 K (see fig. 2). Intensity of emissions 3.9 and 3.65 eV inflames up in the same temperature ranges (temperature of inflame coincides with spectrum of TSL of the irradiated crystal). We guess, that the quenching of X-ray luminescence in four range of temperature is related to the delocalization of nonequivalently located holes (SO_4^-). Delocalized holes have recombined with the electronic capture centers. The radiation excited for impurity Ce^{3+} emitted at recombination of the complementary defects. Inflame of the emission 3.65 and 3.9 eV in four temperature areas is related to the delocalization f holes different thermal stability.

Using experimental results it is possible to guess, that the correlated defects are hole centers SO_4^- - and electronic complexes $\left[So_3^{2-}O^-\right]$ of the irradiated crystal. The correlated pair of defects is more effectively formed in crystal, which has distorted lattice, near expressly Ce^{3+} impurity. Authors [5] offer reaction of creation complementary defects for the irradiated crystal of $CaSo_4 - Dy$:

$$\begin{array}{ccc} Dy^{3+} + e^- & & Dy^{2+} \\ | & \longrightarrow & | \\ SO_4^- & & SO_4^- \end{array}$$

To accumulation

$$\begin{array}{ccccc} Dy^{3+} & & \left(Dy^{3+}\right)^* & & Dy^{3+} + hv \\ | & \longrightarrow & | & \longrightarrow & | \\ (SO_4^{2-})^* & & SO_4^{2-} & & SO_4^{2-} \end{array}$$

Recombination emission during of heating or the tunneling

Electronic impurity centers Ce^{2+} appear by similar reaction – are not stable according to authors [5]. The ground state of Ce^{2+} is almost imposed by conductivity band. Therefore, in the crystal $CaSo_4 - Ce$ the formation of the correlated pairs SO_4^- - and Ce^{2+} is not efficient. We suppose more fundamental reaction of the formation of the correlated defects.

The storage of the defects can proceed by following reaction:

$$\begin{array}{ccccccc} (SO_4^{2-})^* & \rightarrow & SO_4^{3-} & & SO_3^{2-}V_a^+e^- - O_i^0 & & SO_3^{2-}V_a e^- - O_i^0 \\ & & | & \longrightarrow & | & \longrightarrow & | \\ & & SO_4^- & & SO_4^- & & SO_4^- \end{array}$$

The mobile radical O_i^0 interact among themselves and form O_2^0 - radicals. In the following stages the mobile radicals O_2^0 interact with a central anionic complex at the reaction: $O_2^0 + SO_4^{2-} \rightarrow \left[\ SO_3^- + O_3^-\ \right]$.

Herewith it appears stable holes center $\left[SO_3^- + O_3^-\right]$. The electronic center $SO_3^{2-}V_a^+e^-$ and hole centers SO_4^- may be stable at the low temperatures, which appears in one act of the capturing. At higher temperatures this complex $SO_3^{2-}V_a^+e^-$ may be transformed into the stable electronic center at the reaction:

$$SO_3^{2-}V_a^+e^- - SO_4^- \rightarrow SO_3^-V_a^+e^- - SO_4^- + e^- \rightarrow SO_3^-V_a^+e^- - (SO_4^{2-})^* \rightarrow$$
$$\rightarrow SO_3^{2-}V_a^+e^- - SO_4^{2-} + hv \rightarrow SO_3^-V_a^+e^-$$

Thus, electron centers $SO_3^-V_a^+e^-$ complementary to him hole complexes $\left[\ SO_3^- + O_3^-\ \right]$ creation in irradiated sulfates. They are stable before high temperature.

4. Conclusion

On the basis of experimental results of investigation of defect creation in sulphates of alkali and AEM, we assume that initial defects are formed by the sub threshold mechanisms. Same defects are formed in crystals at the excitation of by X-rays, by electrons and photons with energyE_g. Localization of electrons and holes on the anionic complexes of the matrix with formation of the electronic capture centers and hole capture centers is main and the most studied mechanism of defect creation. Initial defects are stable only at the low temperatures. Initial defects are transforming in more stable electronic capture centers and hole capture centers at high temperatures.

Energy is effectively transferred to the impurity appears recombination of electrons or holes on the capture centers.

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