The Phase Transitions and Radiation Induced Processes LiKSO₄

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In crystal with complex anions or cations the mechanisms formation of defect possible conditionally to divide into two types: primary and secondary. The primary mechanisms are realized as a result of disinteration and transformations of the electronic excitation. The second are realized on postradiative stage as a result of interactions of the products radiolysis. It is obviously that migration of the products radiolysis is structured-sensitive. Consequently, the polymorphic phase transitions in crystals must influence on formation and accumulation of the radiation defects. Thereby, transformation of the crystalline lattice allows under determined condition to separate the mechanisms of the formation defect. We shall consider this on example of crystals LiKSO₄.

The particularity of the crystals $LiKSO_4$ is presence the two polymorphic phase transition in temperature range 80–300 K: at180 K and 250 K in mode of the heating [1]. The phase transition at 180 K is first kind, at 250 K – second [2].

The crystals $LiKSO_4$ were grown from the saturation water solution in thermostat with temperature 40°C. By the roentgen phase analysis it was shown that under these condition from solution with equal moles of K₂SO₄ and Li₂SO₄ the single-phase system is formed.

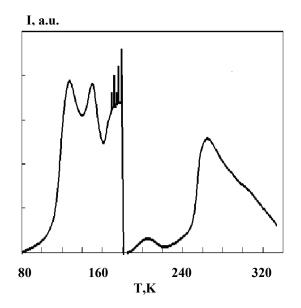


Fig. 1. The TL curve for crystal LiKSO₄ after irradiation with doze 150 kGr by x-rays

They are transparent within the range of the waves lengths 200–800 nm. It is installed that this crystals are not colored by ionizing irradiation. The thermoluminescence (TL) was measured after irradiation by x-rays at the liquid nitrogen temperature (Fig. 1). The enough complex picture was received. The TL curve have maximums of the recombination luminescence about 125 K, 150 K, 205 K and 260K. Besides, there are the growth emission in the range 170 K-180 K accompanied by the stochastic flashes of intensities. The last peak TL emission is complex since there is "shoulder" on the high-temperature wing. This is indicative on presence of the one peak with smaller light sum and powerfully overlaying with luminescent peak at 260 K.

The TL curve have the row an anomalies at 180 K and 250 K. At 180 K intensity of the recombination luminescence sharply drops to zero, on the other hand sharp growth of emission at 250 K. The position of this anomalies well comply with the temperature of polymorphic phase transition in crystal. We link these phenomena with transformation of the crystalline lattice.

It is installed that light sum or appearance of the TL peak at 205 K 205 K depends on velocities of the heating. Under it is enough slow increase of the temperature this peak disappears. It was shown that the emission at 170–180 K and 205 K appease as result of the same recombination process. We consider that their temperature division is connected with the polymorphic phase transition, which occurs in crystal at 180. The transformation crystal lattice increases the energy activation of the recombination processes.

At 250 K the intensity of recombination luminescence anomalous sharply increases. This phenomena we explain the reduction of the energy activation at transformation of the crystalline lattice by phase transition.

By experimentation it was established that number, temperature position and intensity of stochastic flashes recombination luminescence at 170–180 K are changed from measurement to measurement. Unchangeable remains the range of their observation and position of the last flash. We shall note that in unirradiated crystal of this phenomena is absent. Consequently, it has recombination nature. Above it was mentioned that the phase transition at180 K is a first kind. It is accompanied the separation of the heat. The appearance of the stochastic flashes possible to explain by formation of a "germs" new phase. The appearing heat stimulate the recombination processes Formation of "germs" new phase has probability nature. It is reflected on the characteristic these flashes.

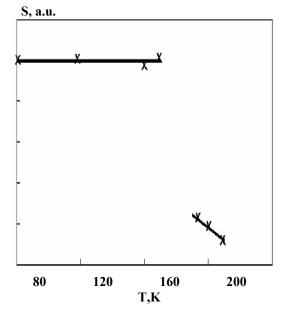


Fig. 2. The dependence of light sum for the TL peak at 260 K from temperature irradiation

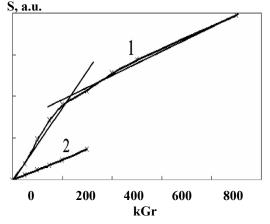


Fig. 3. The curves of light sum accumulation in TL peak at 260 K in $LiKSO_4$ from doze of irradiation at 80 K (1) and 210 K(2)

The TL peak at 260 K in crystal LiKSO₄ does not change the form when increase the dose of the irradiation. This allows to take measurements of the dependence of accumulation light sum from temperature irradiation without division on separate peaks. The dependence of light sum for the TL at 260 K from the temperature of the irradiation are brought in Figure 2. This result was received for unchangeable condition and parameters of the irradiation and geometries of the experiment. It is seen that the value of light sum this TL peak does not depend on the temperature of the irradiation up to 180 K. Above temperature of the phase transition it is decreased greatly. The dependency of light sum TL peak at 260 K from the temperature of the irradiation after the polymorphic phase transition is connected with partial disintegration of defects during irradiation. Such behaviour witnesses that TL peak at 260 K in mixed sulphate lithium and potassium connect with disinteration of the defects appearing at transformation of the primary defects. In alkaline metals sulphate the defects SO_4^- , SO_3^- , SO_3^{2-} and O⁻ are known [3–5]. From all this known radiation defects in sulphate, secondary is single. It is SO_3^- –[5]. This hole centers formation by transformation of other hole centers SO_4^- . This result allow to suggest, that TL peak at 260 K connect with disintegration of defects SO_3^- , which recombinate with O⁻. By methods of the quantum chemistry it is established that ions SO_3^- are formed at interaction of ions SO_4^- with oxygen atom.

For determination of the reasons change in accumulation light sum TL peak at 260 K from temperature of the irradiation it was measured the curves to dependencies of the light sum from doze of the irradiation. After irradiation at 80K the curve of light sum accumulation is well approximated by two linear dependencies: with dose before 300 kGr and from 300 kGr before 900 kGr (Fig. 3, the curve 1). The presence of two stages is connected with presence the different of mechanism formation defects. The similar measurements were organized at the temperature of the irradiation 210 K. In Fig. 3 (the curve 2) presents the dependency of light sum accumulation measured at the temperature irradiation by x-rays at 210 K. It. is seen that as a result of the polymorphic phase transition at 180K one channel of the formation radiation defects becomes unefficient. Consequently, one channel of formation defects is structured-sensitive, the second - no.

Formation defects SO_3^- are connected with transformation radicals SO_4^- . One of the formation cannel of ions SO_3^- is interaction of atom oxygen with SO_4^- . It is obviously that this process is structured-sensitive. The structured-non-sensitive channel of the formation defect can be an ionizing ions SO_3^{-2-} . The free electrons are captured by anions SO_4^{-2-} . Then dissociation occurs with formation of ions O⁻ and SO_3^{-2-} [4] Thereby concentration ion SO_3^{-2-} does not change.

The study of the influence of phase transitions on recombination luminescence allows to separate primary and secondary processes of formation defects. The new mechanism of the formation defect SO_3^- is offered connected with ionizing ion SO_3^{2-} .

References

- Aleksandrov K.S., Besnosikov B.V. Structured Phast transition in crystals, Novosibirsk, Russia, 1993, 287 p.
- Iskornev I.M., Flerov I.N., Gorev M.V., Grankina V.A. Fizika tverdogo tela (Russia) 26, 3199 (1984).
- 3. Kumar V.S.K., Sastry S.B.S., Acharyulu B.S.V.S.R. Phys.Stat.Sol.(b) **155**, 679(1989).
- 4. Byberg J.L., J. Chem. Phys. 84, 6083 (1986).
- 5. Hariharan N., Sobhanandri J. Mag. Res. **1**, 639 (1969).