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RADIATION PROCESSES IN CRYSTALHYDRATES

L. M. Kim, Zh. T. Ismailov

Karaganda State University named after E.A.Buketov, Universitetskaia Str. 28, Karaganda, 100026, Kazakhstan

In given work the results on study of radiation induced processes in monohydrate of lithium sulphate and the glauberite salt are given. Thus crystallohydrates are dehydrated easy, that allows to study and to understand a role of crystal water in radiating processes. It is established by methods of the optical and thermoactivation spectroscopy, that radiolysis or photolysis of crystal water molecules result in disintegration of sulphate anions and to suppression of the exit recombination luminescence. The mechanisms are offered for explaining given phenomena.

Keywords: radiation, crystals, recombination luminescence, monohydrate, X-ray exposure.

The objects of study in this paper are sulphate crystal hydrates of the alkali elements. They have covalent, ionic and hydrogen chemical bonds. The processes of effects of ionizing radiation on the crystals with hydrogen bonds were not thoroughly studied to date. There is a number of works on the effects of hydroxyl groups on the processes of radiation coloration of alkali-halide crystals (see, for example, [1, 2]). It was found that radiolysis of OH-ions leads to significant changes in the accumulation of F-centers; there is formation of defects of type U, U_1 and U_2 [2].

We were able to produce single crystals of the lithium sulphate monohydrate ($Li_2SO_4 \cdot H_2O$) and the glauberite salt ($Na_2SO_4 \cdot 10H_2O$). This choice of study was made due to the fact that these crystal hydrates alkali metal sulphates could be readily transferred to the waterless form. Comparative analysis of crystal hydrates and dry samples allows establishing the role and the influence of the crystal water molecules in the radiation processes. In waterless sulphates of the alkali metals the following radiation defects were established: SO_3-, SO_4-, SO_3^{2-} and O^- [3-5]. Comparison analysis of the crystal hydrates and waterless samples allows identifying the role and the influence of the crystalline water on the radiation processes. In [6] there were measurements of the absorption spectra of crystals of lithium monohydrate. It was found that there are no radiation-induced absorption bands when crystal hydrates of lithium sulphate monohydrate are exposed to irradiation with X-ray quanta of in the range of 200-800 nm. This result was obtained at the room temperature and at the temperature of liquid nitrogen. Absence of radiation-induced absorption bands considerably complicates the study of radiation-stimulated processes in these crystals. In general, the absence of color is characteristic of all non-activated crystals of alkali metal sulphates. At the time, this led to the erroneous conclusion that the sulphate of potassium, for example, is a radiation-resistant [7]. Radiation-induced absorption band related to defects in the matrix, found only in the activation of potassium sulphate by the divalent transition metal ions (see, e.g., [8]). Figure 1 shows the experimental curves of the thermally stimulated luminescence (TL) for the monohydrate and dehydrated lithium sulphate. Curve 1 in Figure 1 is a TL for the monohydrate. It was obtained when the crystals of Li_2SO_4 were exposed to X-ray irradiation at the dose of 200 kHz. In·the lithium sulphate monohydrate in the temperature range 80-300K, there are two main peaks of the recombination luminescence with maxima at 100K and 130K.

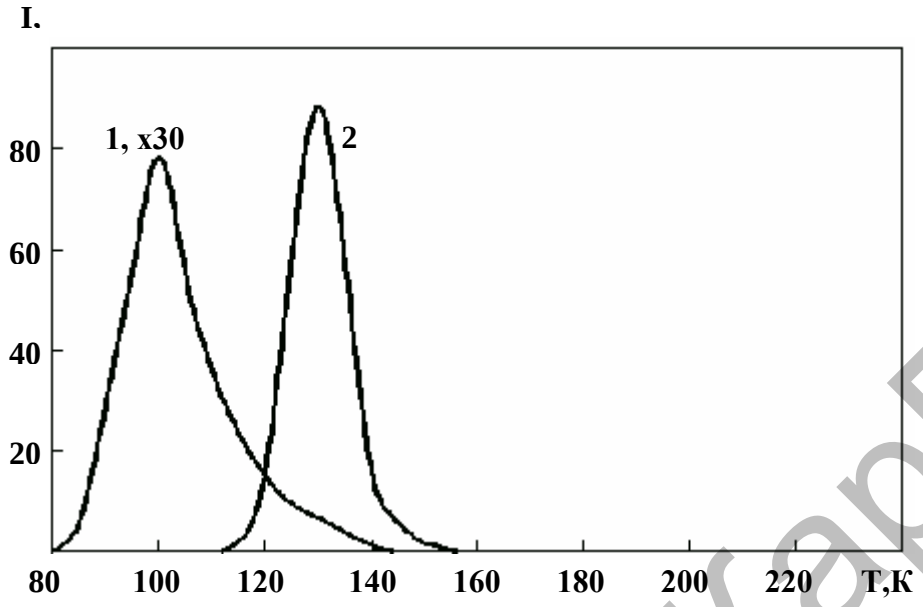

Fig. 1 TL curves for monohydrate (1) and waterless lithium sulfate monohydrate (2)

According to the accumulated light sum, the dominant of these is the low-temperature peak of recombination luminescence. The peak at 130K is manifested in the form of prolonged temperature "shoulder" on high-temperature wing of the main peak with a maximum at 100K. Isothermal annealing of irradiated crystals of lithium sulphate monohydrate at 100-110K will allow the peak at 130K. The observed thermally stimulated luminescence is associated with the emergence of radiation defects, because in this temperature range there is no luminescence in the unirradiated samples.

Dehydrated samples were obtained as a result of the preliminary thermal heating of the monohydrate at 600°C. After dehydration TL curve of the lithium sulphate undergoes significant changes. The TL curve of the dehydrated lithium sulphate is represented by curve 2 of figure 1. It is evident that the peak disappeared completely following the recombination luminescence with the maximum at 100K. The rate of accumulation of light sum at TL peak at 130K has increased significantly. This presented result is obtained at an irradiation dose of 100g. When measuring this TL curve the sensitivity of photoelectric registration of the channel was reduced by 30 times. These parameters of the sample X-ray exposure and the conditions of registration recombination luminescence allow quantifying the change in radiation sensitivity of lithium sulphate as a result of heat treatment. For anhydrous samples it is approximately 10^3-10^4 times higher when compared to crystal hydrate.

Significant qualitative changes of the recombination processes as a result of heat treatment of the monohydrate can not be explained by changes in the crystal lattice. Indirectly, this is supported by the fact that the mono-and dehydrated samples the peak of thermally stimulated recombination luminescence is observed at the same temperature. Therefore, the observed changes of TL curves presented in Figure 1, are naturally associated with a change in the chemical composition of the studied crystals as a result of the heat treatment, i.e., with the presence or absence of molecules of crystalline water in them. Hence it can be argued that the processes that are responsible for the peak of the TL curve are the recombination processes, associated with the products of radiolysis of crystalline water, and the processes responsible for the luminescence peak with maximum at 130K are the processes of recombination of the defects in sulphate subsystem.

Figure 2 shows TL curves for the glauberite salt. Measurement of TL curves shown in Figure 3 (a), were held on the same sample at constant conditions of irradiation and recording the signal. At

the TL curve there are two peaks of the recombination luminescence with the maxima at 100K and in the area around 140K. It is the low temperature one that dominates in the accumulated light sum. The figure shows that with subsequent exposure of the specimen to x-ray irradiation, there are changes in the accumulation of the light sum for luminescence peaks. At the low-temperature peak of the recombination luminescence the light sum decreases, at the second peak of the TL - increases. This suggests that the effects of ionizing radiation occurring in the crystals of glauberite salt are irreversible.

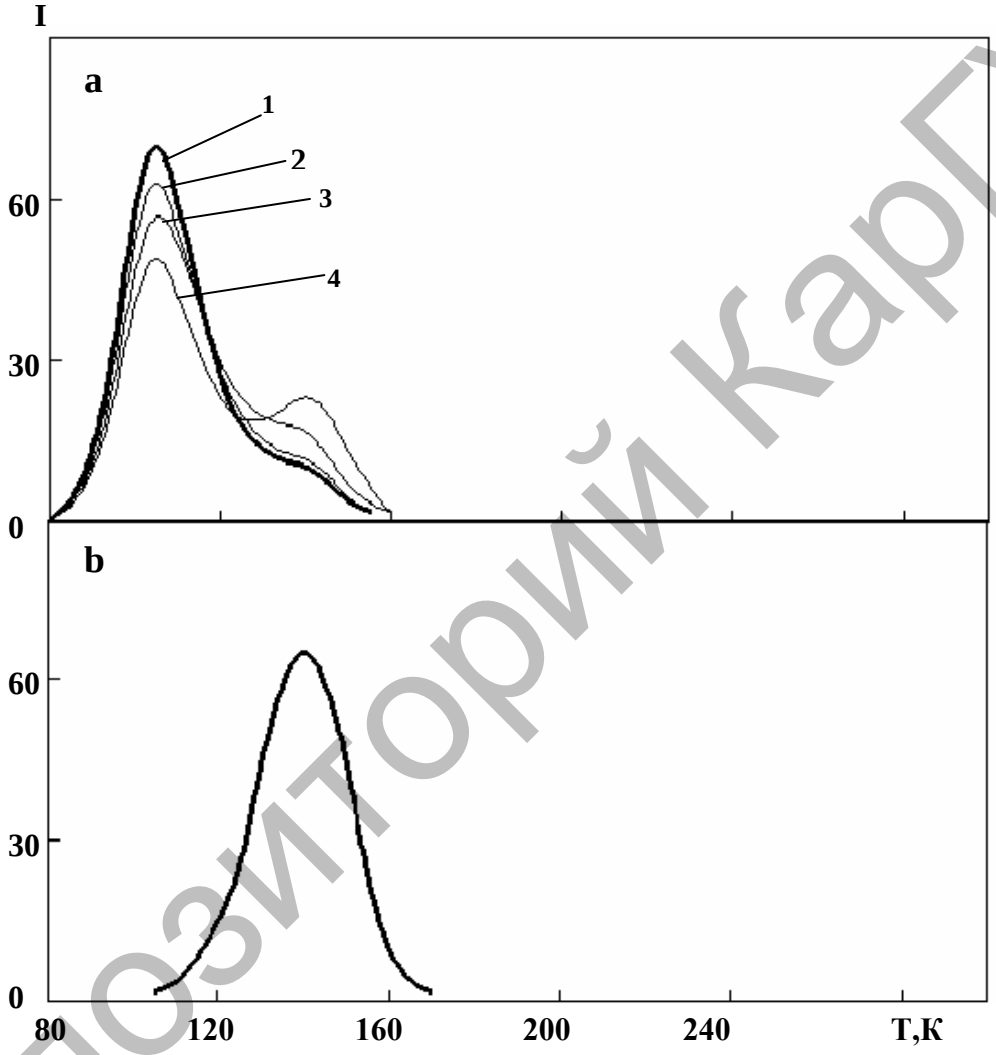

Fig. 2 a – TL Curves $Na_2SO_4 \cdot 10H_2O$ after irradiation by X-ray quanta with the doses of 100 kg (1), 150 kg (2), 200 kg (3), 300 kg (4). b – TL Curve of dehydrated sodium sulphate. Irradiation dose 50 g.

When heated, glauberite salt decomposes. At the temperatures above 27°C 10-hydrated sodium sulphate passes into anhydrous form. Figure 3(b) shows the TL curve for anhydrous sodium sulphate. It is evident that as in the case of lithium sulphate, as a result of dehydration, one recombination luminescence peak disappears, and the rate of accumulation of light sum significantly increases. It was experimentally established that with partial dehydration of the compound the same changes were observed in the accumulation of the light sum at the peak of TL, as in Figure 3 (a). It was suggested that crystal hydrate partially dehydrates as a result of exposure to ionizing radiation. This was tested by direct measurements at a temperature of 23°C. We prepared two powdery samples of $Na_2SO_4 \cdot 10H_2O$, one of which was a control sample. One of the sample was subjected to irradiation dose of X-ray quanta 600g. Its initial weight was 1073.22 mg.

After exposure to X-ray quanta the weight decreased to 1051.16 mg. The weight of the sample was 1193.8 mg. During irradiation the weight of the control sample decreased and amounted to 1190.3 mg. This is because glauberite salt partially decomposes at the temperature of 23°C. Thus, the weight loss of the irradiated sample amounted to 2.06%. A control sample lost 0.3%. Therefore, a sharp increase in weight loss occurs as a result of the irradiation. There is no weight loss of the control sample observed at lower temperatures.

During the full dehydration of sodium sulphate, on the TL curve we observe only one peak of the recombination luminescence with the maximum at 140K. This result is also presented on the Figure 3 (b). Consequently, the luminescence peak at 100K is related with the radiolysis products of water molecules, while the peak with the maximum at 140K is related with the collapse of the radiation defects in sulphate subsystem. It should be noted that the dose of radiation in the measurement of the TL curve of anhydrous sodium sulphate was only 50g, i.e., more than three orders of magnitude smaller than for crystal hydrate.

Thus, the crystalline water participates in the radiation-stimulated processes in at least two ways. First, in the subsystem of crystalline water there are the defects formed, which cause recombination luminescence. Second, the crystalline water either increases the radiation resistance of crystals or significantly suppresses recombination processes in the sulphate subsystem. It was experimentally established that the influence of water molecules on the radiation processes is more complicated [9]. It turned out that the formation of radiation defects in lithium sulphate monohydrate significantly change depending on the energy of the falling quanta. Figure 3 shows the TL curve of lithium sulphate monohydrate, which was irradiated by the light LD(D) -400 through the UV type filter. The time of the exposure of the sample in the irradiation of UV light was 120 minutes. The TL curve has the appearance of a broad peak with a maximum at 140K. At its low temperature wing there is a bend in the 110-120K area. Isothermal annealing at 110K allowed to isolate a single TL peak with a maximum at 130K. Thus, the broad TL curve peak with the maximum at 140K is a superposition of two TL curve peaks with a maximum at 100K and 130K, with approximately the same light sum. In lithium sulphate monohydrate during irradiation with X-ray quanta light sum peak at 100K is times higher than that of the peak with the maximum at 130K (see Figure 3).

X-ray quanta and UV-rays stimulate the electronic subsystem of the crystal. Obviously, the energy of these types of radiation is not sufficient for the direct mechanisms of the shock type for the formation of radiation defects.

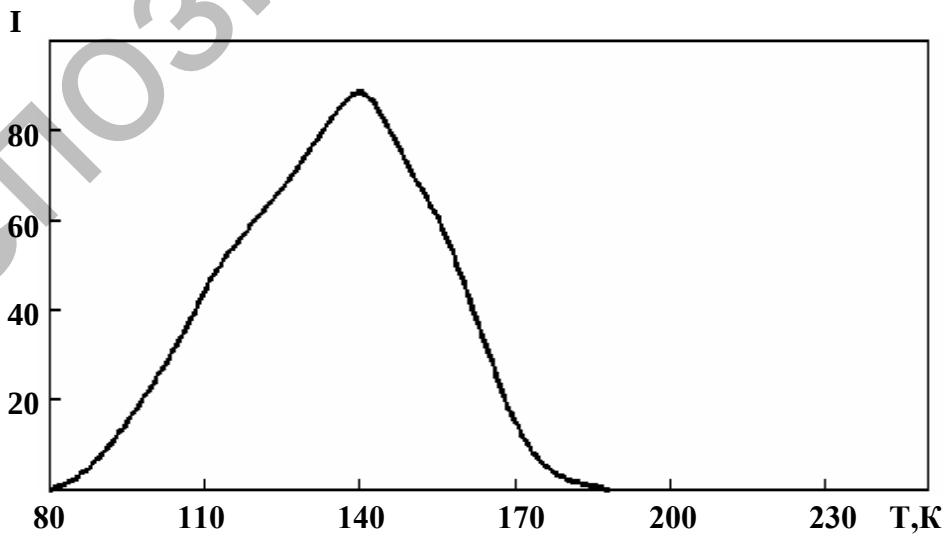

Fig. 3 TL curve of lithium sulphate monohydrate following UV-irradiation

Therefore, the main cause of radiation instability of the studied crystals are subliminal mechanisms for the creation of defects at the expense of conversion of electronic excitations. It is known that irradiation of crystals of potassium sulphate and lithium-potassium sulphate in the near-ultraviolet spectral region (200-300 nm) does not lead to an accumulation of light sum. This is because in the given compounds energy of the falling quanta is not sufficient for the electronic transitions of type zone-zone. The same result is obtained for anhydrous lithium sulphate. Therefore, the observed recombination luminescence in lithium sulphate monohydrate after UV exposure is associated with the formation of the defects as a result of photolysis of the molecules of crystalline water. In addition, the products of the photolysis of water molecules leads to defects in sulphate subsystem of the lithium sulphate monohydrate [10] provides a spectres of absorption of non-activated lithium sulphate monohydrate, measured at room temperature. During the values of the falling energy quanta in the range of 5.6-6.2 eV, we observe an increase of optical density of the crystal. It was experimentally established that during the stimulation of the $Li_2SO_4 \cdot H_2O$ crystal in said the optical range at room temperature photoconductivity is absent. Therefore, the observed absorption is not associated with transitions of the type of zone-zone and does not constitute a band of charge transfer. It is also obvious that this is not the exciton absorption. With the stimulation of the lithium sulphate monohydrate in this spectral range neither at room nor at liquid nitrogen temperature do we not observe photoluminescence, which is different from the recombination luminescence of the matrix. In addition, the exciton absorption bands are usually narrower and occur at the edge of fundamental absorption bands. We are not aware of published data on the size of the width of the forbidden band for the mono-and dehydrated lithium sulphate. But it is known that the potassium sulphate is a wideband dielectric with a width of the forbidden band around 8.5 eV [11]. In crystals $LiKSO_4$ the estimate of the width of the forbidden band obtained from optical measurements, is about 9 eV [12]. In haloids of the alkali metals with a decrease in the sequence number in the periodic table, the width of the forbidden band gap of the increases [13]. On this basis, we can assume that the width of the forbidden band of the crystals of lithium sulphate is more than 9 eV. Therefore, we link the observed absorption with the UV light absorption by the crystalline water. During the irradiation of water vapour in the area of 180 nm there are the processes of their photodissociation. In the crystal matrix absorption bands usually shift to the long-wave side of the spectrum. For dehydrated samples the absorption spectrum could not be measured. This is because the heat formed some powder samples. During the re-crystallisation from the melt monocrystal could not be obtained, because as a result of the structural transition from β-phase in α-phase destruction of crystals occurs. Therefore, in the range of 5.0-6.2 eV, we have measured the spectra of the diffused reflectivity of pressed tablets of dehydrated lithium sulphate relative to the magnesium oxide. Magnesium oxide was depositing on a metallic substrate from the burning of magnesium metal in the atmosphere. After recalculation of the spectrum from the diffused reflectivity into the absorption spectrum using the method of Kubelk-Munch [14] we found that when the energy of the falling quanta in the range of 5.0-6.2 eV from the dehydrated sample does not have absorption. On this basis, we conclude that the absorption of radiation by lithium sulphate monohydrate, which is observed in the UV spectral region, is related to crystalline water. Thus, it was found that after irradiation of lithium sulphate monohydrate by the UV light in the spectral range of 200-230 nm, the occurrence of recombination luminescence is caused by the photolysis of molecules of crystalline water. TL peak at 130K during the x-ray irradiation is observed in both crystal hydrate, and anhydrous lithium sulphate. As mentioned above, the UV-stimulation of dehydrated samples does not cause recombination luminescence. When lithium sulphate monohydrate is irradiated by the UV light, we observe not only the TL peak at 100K, which is related to the photolysis products of crystalline water molecules, but also the TL peak at 130K, the occurrence of which is connected with recombination of the defects of the sulphate subsystem. Since the energy UV light quanta are not sufficient to create defects in sulphate

subsystem, there is the suggestion that the photolysis products of crystalline water molecules may participate in reactions that result in defects in the formation of sulphate subsystem.

Experiments similar to the above, have been conducted on the crystals of the glauberite salt $Na_2SO_4 \cdot 10H_2O$. It was found that, during the UV irradiation, we observe accumulation of the light sum at the TL peaks with maxima at 100K and 140K. Generally, the type of the curves of recombination luminescence of the glauberite salt and those of lithium sulphate monohydrate are similar.

Experimental results demonstrate that during the photolysis of water molecules, there is occurrence of the processes that cause defects in sulphate subsystem. The main issues that arise in this are as follows: first, how the products of photolysis of water molecules lead to the dissolution of sulphate anions, and second, why there are recombination processes in monohydrate.

One of the products of photolysis or radiolysis of water molecules is atomic hydrogen. Products of water molecules dissolution, in particular, atomic hydrogen, interacts with other defects that arise during the dissolution of sulphate anions. The assumption that the water molecules increase the radiation resistance of the crystal contradicts the results of excitation of monohydrate by the UV light. It is therefore natural to assume that the sharp decline in output of the recombination luminescence in the lithium sulphate monohydrate, caused by the decomposition of defects in the sulphate subsystem, is due to the fact that they are "disabled" by the products of radiolysis of water. As mentioned above, the sulphate sublattice in addition to the ions of O^-, there are centres of type SO_3^-, SO_4^- and SO_3^{2-}.

To date, there are no data on the existence of defects of type O^- in the crystals of sodium sulphate. However, within these compounds we have found the hole centers SO_3^-, SO_4^-. Since the alkali metal sulphates are similar to each other, the existence of this electron center in a lithium sulphate is probable.

Obviously, the atomic hydrogen arising from the photolysis or radiolysis of crystalline water molecules interacts with ion O^- forms a defect OH^-. This ion has a sufficiently large binding energy. Consequently, as a result of this interaction part of the ions O^- is "excluded" from the recombination processes. However, in our opinion, the above is not the only channel that could explain such a significant difference in the output of recombination luminescence in the mono-and dehydrated lithium sulphate crystals.

The hole center is SO_3^- has a pyramidal structure with the symmetry of the point group C_{3V}. In [22] it is shown using the methods of quantum chemistry that the atoms of hydrogen are profiting energetically from joining the SO_3^- with the formation of sustainable non-paramagnetic complex. This complex decomposes as follows:

$$(SO_3H)^- \rightarrow SO_3^0 + H^-$$

The energy required for this reaction is 4.7 eV. It is therefore cannot be thermally activated. Thus, in the interaction of ion SO_3^- and atomic hydrogen forms stable complex. The ions of SO_4^- may capture the atoms of hydrogen. This is favourable from the energy point of view . The reverse reaction is as follows:

$$(SO_4H)^- \rightarrow SO_3^- + OH^0$$

This requires energy equal to 3.5 eV. Such a process can not be thermally activated in a temperature range up to the melting temperature of crystals.

The last of the known defects in sulphates, the interaction of which with atomic hydrogen we examined, is the ion is SO_3^{2-}. It was found that it is favourable for the hydrogen atom to accede to the ion along the C_3 axis. This process leads to a decrease in the total energy of the system and

occurs without activity. We have calculated the energy necessary for the separation of the hydrogen atom from this complex. The energy of separation of the hydrogen atom is about 0.5 eV. This process can be thermally activated. Consequently, the SO_3^{2-} may be ion traps for atomic hydrogen. Research of recombination luminescence of crystals and monohydrates of lithium sulphate and glauberite salt caused by UV irradiation shows that the photolysis of molecules of the crystalline water creates the defects in sulphate subsystem. Most probable is the interaction of atomic hydrogen with the anion SO_4^{2-}. It shows [23-25] that complex ($H^0SO_4^{2-}$) disintegrates with the formation of ions SO_3^- and OH^-.

The above data show that atomic hydrogen is energetically favourable to form stable complexes with radiation defects of the sulphate subsystem O^-, SO_3^- и SO_4^-. Therefore, the sulphate matrices cannot form U-type centres. Since the result is the formation of non-paramagnetic centers, this is consistent with the experimental facts. During interaction of the H^0 atom with the anion SO_4^{2-} there is potential defect SO_3^-. This channel of hole centre SO_3^- formation allows the to explain the emergence of a TL peak in lithium sulphate monohydrate at 130K when exposed to UV-light.

Therefore, products of photolysis and radiolysis of crystalline water molecules on the one hand "disable" the defects from the recombination processes in sulphate subsystem, and on the other hand to the atomic hydrogen can lead to the dissolution of sulphate anion. This is explains the features of the radiation-stimulated processes in crystal hydrates of the alkali metals.

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