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The effect of pre-irradiation defects on the recombination luminescence in activated crystals K_2SO_4

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Abstract

The recombinational luminescence of crystals of K_2SO_4-Mn^{2+} and K_2SO_4-Ni^{2+} is studied in the article. It is established that impurity ions form the radiation induced centers. The cause of changes of the distribution of lightsum on TSL peaks of a matrix is established. It is proposed that it is related to pre-radiation defects in crystals. It is established from this effect that ions of Mn^{2+} and Ni^{2+} selectively replace cations in a crystal lattice of potassium sulfate.

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Keywords: Potassium sulphate, recombinational luminescence, defects.

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1. Introduction

Recombination luminescence in alkali metal sulfate has been studied mainly as an example, potassium sulfate. One of the first studies in which a given model of the recombination process in the potassium sulfate is Kumar et al. (1989). The thermally stimulated luminescence (TSL)of K_2SO_4-Eu^{2+} crystals are irradiated at room temperature is studied by Kumar et al. (1989). Crystals doped with divalent europium, have an absorption band in the region of 5.33 eV, the weak band at about 3.85 eV and 4.3 eV. During irradiation the optical density of the absorption band at 5.33 nm increases. After the thermal annealing at 460 K, the optical density is restored to the initial value. Luminescence excitation spectrum has a maximum at 3.88 eV. In the main absorption band of 5.33 eV photoluminescence is not excited. Maximum of the emission spectrum upon photoexcitation in the optical band is 3.88 eV at room temperature at 3.1 eV. This band impurity luminescence elementary.

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When exposed to ionizing radiation, non-activated alkali metal sulfates are not colored, i.e. in the transparency of their spectra do not appear radiation-induced absorption bands. Therefore, they are considered to be radiation-resistant. EPR studies have shown that these compounds as a result of exposure to ionizing radiation having different radicals. Atkins et al. (1970) generalized the earliest results of the studies of radiation defects in sulfates. By EPR spectroscopy revealed that in these compounds when exposed to ionizing radiation having paramagnetic centers and type SO_4^- and SO_3^-. Both of these ions play the role of hole centers.

This paper presents results of the study of the effect of pre-irradiation defects on the recombination luminescence. For this purpose crystal K_2SO_4 was activated by divalent metal ions Mn^{2+} and Ni^{2+}, because according to Meyerson et al. (1993) and Tagayeva (2010), nickel or manganese ions are included in the crystal lattice of potassium sulfate as divalent Me^{2+} and substitute K^+ cation nodes. The peculiar structure of the crystal lattice of potassium sulfate is the presence of two types of cationic nodes. They differ in their oxygen environment. One type of nodes has a coordination number 9, the second type's coordination number is 10 according to Kim et al. (2009). In work by Tagayeva (2010) it is shown that these impurity ions in this matrix in its transparency band there are optical absorption bands. The presence of impurity absorption allows for tracking its impact on the radiative processes.

2. Experimental procedures

The main research methods were the methods of thermoactivation spectroscopy. The samples were irradiated with X-rays at liquid nitrogen temperature at a voltage of 35 kV and I=10 mA. The monocrystals of potassium sulfate were grown from saturated aqueous solutions isothermal evaporation of the solvent at the temperature of 40 ^{0}C with addition to the initial solution of nickel and manganese sulfate salts in an amount of 0.1 mol%. When measuring curves thermoluminescence (TSL) curves the heating rate was 9 K/min. Activated monocrystals obtained by adding to the initial solution of soluble metal salts. Amount of activator is added to the solution, determined by the formula:

$$m_1 = m_2 \frac{M_1 n}{M_2 (100 - n)} \tag{1}$$

where m_1 and m_2 are the masses of the activator and of the basic substance, M_1 and M_2 are correspondingly the molar masses of the activator and a basic substance, n is the desired molar percentage of the activator in the optical spectrum. The absorption spectra of crystals and additional absorption spectra in the region 200-800 nm were measured photoelectrically on an SF-16 to the standard method.

3. Experimental results and discussion

Obtained for these objects TSL curves (Fig. 1) were compared with curves for pure potassium sulfate from work by Baltabekov et al. (2011). It can be assumed that the presence of impurity ions leads to a substantial change in the shapes of the TSL curves. In crystals of potassium sulfate doped with manganese and nickel ions, new peaks appear in the TSL curves at 160 K and 260 K, respectively.

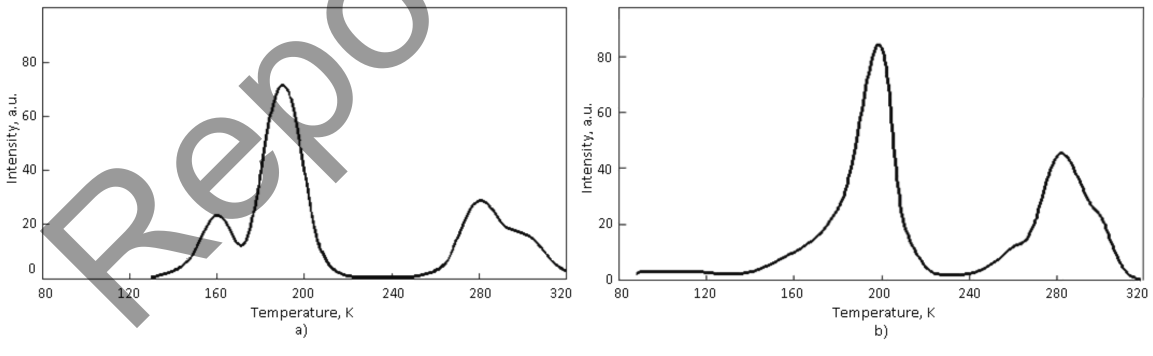

Fig. 1. TSL curves of (a) K_2SO_4-Mn^{2+} and (b) K_2SO_4-Ni^{2+}.

To clarify the nature of the new TSL peaks in the crystal K_2SO_4-Mn^{2+} absorption spectrum was measured before and after irradiation with X-rays. Obtained new absorption band at 5.5 eV is partially annealed at around 190 K and is completely annealed in 260 – 300 K region, i.e. where there TSL peaks of the matrix are observed. Potassium sulfate is not colored. In crystals of K_2SO_4-Ni^{2+} a similar radiation induced absorption band is observed at 5.39 eV. In activated crystals the distribution of lightsums by TSL peaks of the matrix has changed. The impact of impurity ions of manganese and nickel on recombination luminescence is due to the formation of radiation-induced impurity defects and pre-irradiation defects in the crystal lattice. The former lead to the new glow peaks of TSL curve in activated crystals. Formation of additional cationic vacancies leads to a redistribution of lightsums by TSL peaks of the matrix.

In Fig. 2a shows the absorption spectrum of potassium sulfate crystals doped with divalent manganese before and after irradiation with X-rays.

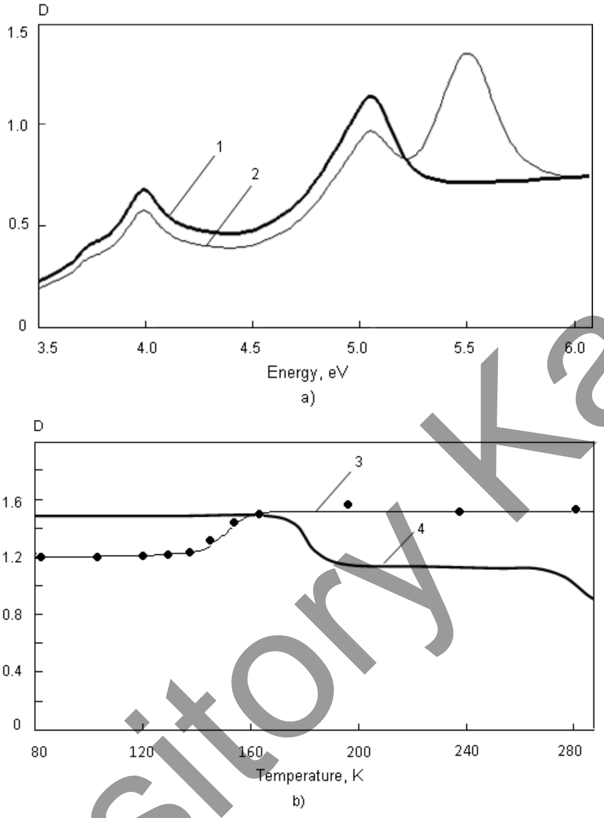

Fig. 2. Spectra crystal absorption K_2SO_4-Mn^{2+} (a) and temperature dependence of the absorption bands after irradiation dose of 350 kGy (b): 1 - before irradiation with X-rays; 2 - X-rays after irradiation; 3 - for the impurity absorption with a maximum 5.0 eV; 4 for the radiation-induced absorption with a maximum of 5.49 eV.

The figure shows that after irradiation of the sample with X-rays there is a new absorption band with a maximum at 5.49 eV, and there is a decrease in the optical density of the impurity absorption band. In Fig. 2b shows the temperature dependence of the optical density of the impurity absorption band with a maximum at 5.0 eV and thermal bleaching curve for radiation-induced absorption bands. Restoring the concentration of divalent manganese ions occurs in 150-170 K. Hence, the emergence of a new peak with a maximum at TSL 160 K due to the thermal decomposition of the impurity radiation-induced centers. Curve thermal bleaching radiation induced absorption band has two stages. The first stage is in the 190 K, the second stage is in the 280-300K. The shape of this curve is similar to the behavior of the radiation-induced absorption bands in K_2SO_4-Cu^{2+} and K_2SO_4-Co^{2+} crystals. This suggests that the occurrence of radiation-induced absorption bands in the samples due to the impurity ions perturbed hole centers matrix SO_3^-.

In Fig. 3a shows the absorption spectrum of the crystal K_2SO_4-Ni^{2+} before and after irradiation with X-rays. The figure shows that as a result of exposure to ionizing radiation is a change in the charge state of impurity nickel ions. On the long-wavelength wing of the shortwave absorption band appears "shoulder", which indicates the appearance of new radiation-induced absorption bands. Measure it thermal bleaching fails because of the strong overlap of the optical bands.

In Fig. 3b shows the temperature dependence of the impurity absorption band for a crystal K_2SO_4-Ni^{2+} with a maximum at 5.17 eV after irradiation with X-rays. Restoration of the optical density of the impurity absorption occurs in the 260 K. Thus, the new TSL peak at 260 K associated with the thermal decomposition of the radiation-induced impurity centers.

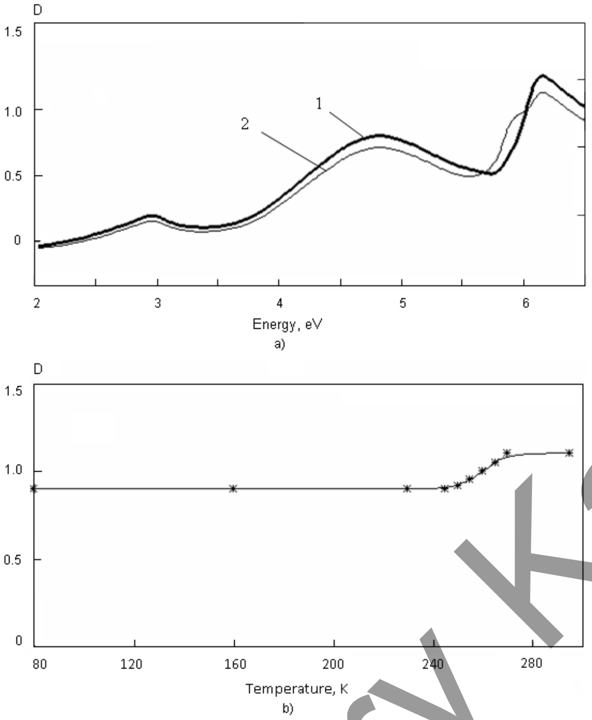

Fig. 3. (a) the absorption spectra of K_2SO_4 – Ni^{2+} crystal at 80 K and
(b) temperature dependence of the impurity absorption band with a maximum at 4.13 eV.

In general, the effect of manganese ions and nickel on radiation-induced processes in crystals of potassium sulfate seems to be. Of the identity of the role of transition metal ions in these processes indicate accumulated light sums at the peak of the recombination luminescence of the matrix with a maximum at 190 K.

4. Conclusion

Impurity ions of manganese and nickel increase the rate of accumulation of the light sum in this TSL peak. Therefore, these impurity ions are also the centers of the electron capture. In addition, it can be argued that the impurity manganese ions in crystals of potassium sulfate are more effective traps for electrons. This is evidenced by a large rate of accumulation of the light sum.

Thus, based on the study of the impact of transition metal ions on the distribution of lightsums by TSL curve peaks of the matrix it is proposed that impurity ions Mn^{2+} and Ni^{2+} occupy in the crystal lattice the cationic nodes with higher coordination by oxygen atoms. In this case, the vacancies will also be distributed selectively.

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