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Luminescence of potassium sulphate crystals doped by Eu^{3+} ions

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Abstract. This paper presents results of the study some spectral-luminescent properties of potassium sulphate crystals activated europium trivalent ions. The observed changes might be connected with the fact of crystals having Eu^{3+} ions and NO_3^- impurity ions. There was a proposition of the possibility of selective creation of impurity centers with the help of using various salts is normal for all the transition metal ions.

1. Introduction

K_2SO_4 crystals are considered as one of the most important construction materials in modern technology. The area of their usage keeps on expanding and the exploitation rules are becoming more and more complicated. The following problems which appear after this require a behavior forecast of construction materials in extreme conditions and modification of physical properties or creation of new materials with specific features. Transition metal trivalent europium ions are one of the traditional activators to study the spectral luminescence properties of crystals. Trivalent europium ions give rise to a narrow-band long-lived red luminescence that is not affected by incorporation of potassium ions. Divalent europium ions emit a UV-blue luminescence, consisting of a large spectral band centered at ca 430 nm. [1]. The photophysical properties of the Eu^{3+} ions oriented in K_2SO_4 crystal matrices were studied. The luminescence data for these doped crystals revealed them to be highly luminescent materials [2]. Rare earth nanomaterials with nanometer to submicrometer crystalline sizes are an important class of materials displaying interesting physical and chemical properties especially in luminescence and catalysis fields. In the last decade, the synthetic chemistry and exploring of novel properties on rare earth nanomaterials have been developed rapidly. This review on the topic of controlled synthesis and properties of rare earth nanomaterials should be useful with these literatures mostly up to 2009 [3]. K_2SO_4 crystal, as well as potassium dihydrophosphate is a crystal with the composite anionic complex. Due to the practical application of these crystals in the last decades specific features of characteristic and impurity electronic exaltations are widely investigated [4]. Potassium sulphate is of interest for the study of luminescence, recombination and radiation processes and associated color centers. It is stable to radiation and the energy of activation is effectively transferred from the sulphate matrix to impurities [5]. The low symmetry of the lattice points of potassium sulphate gives confidence that we can avoid ambiguity in the interpretation of the nature of the electronic states of the color centers. This is the relevance of this study.

2. Experimental

The main investigation objects were K_2SO_4 doped by Eu^{3+} ions. $\text{K}_2\text{SO}_4\text{-Eu}^{2+}$ crystals were grown from aqueous solutions. The impurity concentration was the same and equal to 0.1 mol%. Europium ions

included in the crystal lattice of K_2SO_4 , during crystal growth from an aqueous solution. The thickness of the majority of the objects is approximately 1.5 mm.

The growth of K_2SO_4 crystals was produced of saturated aqueous solutions using isothermal evaporation of the solvent at $40^{\circ}C$. After 10-12 days this process, there were 5 mm to 40 mm sized crystals distracted from a saturated K_2SO_4 solution. Sizes of the ready crystals radically vary depending on the components added into the final impurity solution. Activated single crystals were received after soluble metal salts were added to the final solution. Usually, concentration of the components added to the final solution is around 0.1 mol%.

Our work in particular included measurements of the absorption spectra of the luminescence excitation and emission at different temperatures which were used from the optical research methods. Absorption spectra of crystals and induced absorption spectra in the area of 200 – 800 nm were measured using photoelectron method on spectrophotometer SPh-16. Measuring optical density of the crystals was done relating to the air. Additional absorption spectra were measured towards non radiated crystals. Although, the certain number of situations involved using slightly radiated crystals. The last one took place to learn the influence of ionizing radiation on impurity absorption. Measurement of the absorption spectra was done at 80 – 320 K temperature range. The sources of light varied depending on the spectra range, starting with incandescent lamp ending with DDS-30 hydrogen lamp.

In all the optical measurement procedures, the research object was put into a nitrogen cryostat and then was cooled down to the temperature of liquid nitrogen and radiated with X-ray through beryllium window of URS-55a device. X-ray tube had a molybdenum anode. Measuring crooked thermo luminescence was done by supporting the constant speed of the heat in 9 K/min, which was controlled with the help of differential copper-constantan thermo steam.

To define the absorbed dose of the X-ray radiation we used Frike chemical dosimeter. Dosimeter readings do not depend on power of the absorbed radiation dose up to $10^5 Gy \cdot s^{-1}$. Accuracy of Frike dosimeter measuring is approximately $\pm 5\%$. As a result of the produced measurements it is defined that the power of radioactive dose from URS-55a X-ray device with X-ray tube and copper anode at the voltage of 35 kV and current of 10 mA makes about $150 \pm 10 kGy \cdot s^{-1}$.

3. Results and Discussion

Figure 1 represents the typical thermally stimulated luminescence (TSL) curve for virgin potassium sulphate crystals with the radiated dose of X-ray quanta at the liquid nitrogen temperature 100 kGy (curve 1) and 200 kGy (curve 2). The image shows that there are two TSL peaks with the maximum points at 190 K and 280 - 300 K.

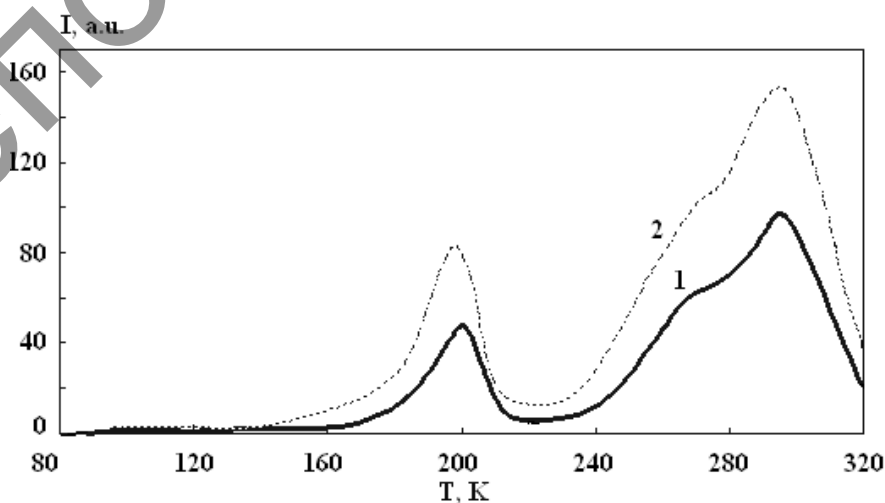


Figure 1. TSL curve for virgin potassium sulphate crystals

Figure 2 shows the accumulated lightsum (S) at the peak of the thermally stimulated luminescence in the 200K on the exposure dose of radiation. Dependence on time lightsum potassium sulphate irradiation with X-rays is linear. When exposure doses up to 90 minutes a tendency to saturation at the peak of the light sum in the recombination radiation were found at 200K. The presence of an energy barrier for light activation, and dependence of the accumulated light sum of the exposure dose of radiation are signs that the observed luminescence is the nature of recombination. The accumulation of defects responsible for the recombination process depends linearly on the radiation dose.

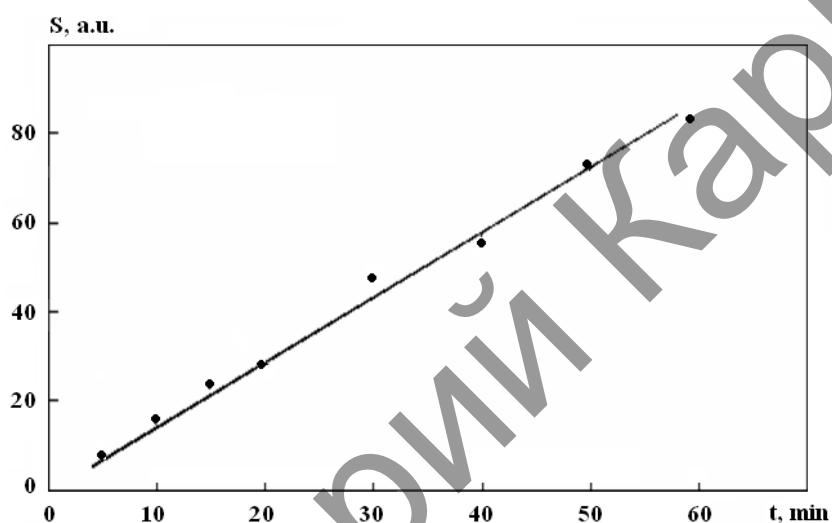


Figure 2. The dependence of the lightsum of the time of exposure dose of radiation TSL peak at 200K the crystal K_2SO_4

Figure 3 shows the TSL curve for K_2SO_4 - $Eu(NO_3)_3$ (0.1 mol%) crystal. The dose of radiation X-rays at the temperature of liquid nitrogen was 4 kGy. Compare TSL curves in Figures 1 and 3 shows the high quality of their coincidence. Observed the same peaks of the recombination luminescence with peaks at 190K and 300K. The difference from the results shown in Figure 1 is a dramatic change in the attitude of the accumulated light sum in the peaks glow in the TSL curve.

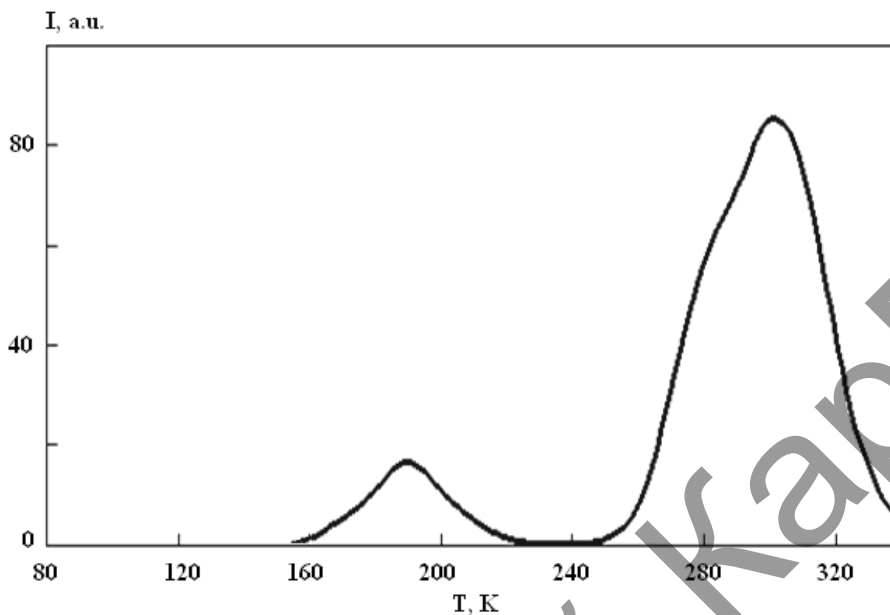


Figure 3. TSL curve of $K_2SO_4-Eu(NO_3)_3$ crystal (0.1 mol%)

The crystals doped with transition metal ions dominant recombination luminescence peak in the TSL curve is a glow with a maximum at 280K. The potassium sulphate activated by trivalent europium nitrate. The luminescence peak of research object does not stand out at 280K. The dominant is a glow with a maximum at 300K. New recombination luminescence peaks were not detected. To determine the effect of europium ions in the processes of formation, accumulation and recombination of radiation defects, TSL curves for crystals of $K_2SO_4-KNO_3$ were measured. TSL type curve for this sample is similar to that shown in Figure 3. The situation is complicated by the fact that the spectral composition of the TSL peaks for crystal $K_2SO_4-Eu(NO_3)_3$ with a maximum radiation were found at 3.5 eV.

The radiation in the optical band with a maximum at 3.1 eV is present in all the peaks of the TSL curve. However, this radiation is characteristic for non-activated potassium sulphate crystals. Therefore, to determine the impact of europium ions change the type of TSL curves and spectral composition of the radiation is not possible. The only thing that could set: at least up to doses of 50 kGy ratio lightsum low peak in the curve of the TSL and the group of high-temperature for $K_2SO_4-Eu(NO_3)_3$ crystals and $K_2SO_4-KNO_3$ does not depend on the dose of radiation and is 0.035 and 0.048, respectively.

It is known that the nitrate ions NO_3^- are acceptors for electrons [6]. Their presence in the matrix leads to a more rapid accumulation of hole centers. Also, europium ions increase the rate of accumulation of hole centers. The irradiation of ionizing radiation at room temperature, the optical density of a decrease in the absorption bands of 3.85 eV and 4.43 eV, and its increase in the band is 5.33 eV, which we associate with trivalent europium.

4. Conclusions

Thus, upon exposure to ionizing radiation divalent europium ions form with respect to the inner circle hole centers. TSL peaks in the region 280 - 300K associated with the electronic nature of the recombination process, i.e., the mobility of electrons or electron-rich center recombines with fixed hole. Reducing the ratio of the light sum in the TSL peaks in the sample doped with europium, it shows that radiation-induced impurity defects is the center of recombination. Thus, recombination processes in crystals of potassium sulphate ions europium activated involved impurity ions in the divalent state source. They are under the influence of ionizing radiation are transformed into venues

hole nature, which occur at the recombination processes of thermal activation. It can be argued that the dissociative electron capture anion is sufficiently effective channel for the flow of free electrons in the crystals of sulfate and formation of radiation defects.

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