Luminescence of potassium sulphate crystals activated by Sn$^{2+}$ ions

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Abstract. The aim of this paper is to study some spectral-luminescent properties of sulphates activated by tin ions. The paper presents the photoluminescence excitation spectra of K$_2$SO$_4$-Sn$^{2+}$ crystal. In this spectrum, peaks are observed at 240 nm and 260 nm. In the long-wavelength wing, the emission band has a "shoulder" indicating the presence of the second emission band. Thus, the presence of two bands of photoluminescence excitation suggests that K$_2$SO$_4$ formed two types of the impurity luminescence center differing in the immediate surroundings.

1. Introduction

Potassium sulphate, as well as potassium dihydrophosphate is a crystal with the composite anionic complex. Due to practical application of these crystals in the last decades, specific features of characteristic and impurity electronic excitations [1] have been widely investigated. Potassium sulphate is of interest for the study of luminescence, recombination and radiation processes and associated color centers [2]. It is stable to radiation and the energy of activation is effectively transferred from the sulphate matrix to impurities. Moreover, a 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 indicates the relevance of this study.

2. Experimental

The main investigation objects were K$_2$SO$_4$ activated by Sn$^{2+}$ ions. K$_2$SO$_4$-Sn$^{2+}$ crystals were grown from aqueous solutions. Due to the fact that the salt has reverse SnSO$_4$ solubility, in the stock solution SnCl$_2$ salts were added. The impurity concentration was the same and equal to 0.1 mol%. The thickness of the majority of the objects was approximately 1.5 mm.

Chloride ions are included in the crystal lattice of K$_2$SO$_4$ during crystal growth from aqueous solution. Meanwhile K$_2$SO$_4$ Cl$^-$ ions do not absorb in the field of transparency of a crystal and do not form luminescence centers excited by X-rays. Sn$^{2+}$ ions belong to the group of mercury-like ions. They, as well as Tl$^+$, have two s-electrons on the external electronic shell.
3. Results and Discussion

Figure 1 shows the radiation spectra of K$_2$SO$_4$-Sn$^{2+}$ crystal measured at 80 K. In all spectra of photoluminescence excitation and emission spectra, the necessary correction for the spectral sensitivity of the photomultiplier and the spectral distribution of the source of UV emission is made.

![Graph showing radiation spectra of K$_2$SO$_4$-Sn$^{2+}$ crystal measured at 80K.](image)

As it is seen in Figure 1, the type of the radiation spectrum is strongly dependent on the position of the excitation band. Curve 1 was obtained in the excitation of the crystal in the region of 230 nm. The maximum of the emission band is observed at 335 nm. In the long-wavelength wing of the emission band there is a "shoulder" indicating the presence of the second emission band. Curve 2 was measured in excitation of the crystal in the region of 270 nm. Upon excitation of the crystal in the field emission maximum is observed at 360 nm. The emission band with a maximum at 335 nm is shown in the short-wave wing spectrum in the form of a "shoulder". Since these emission bands are not observed in the pure crystal of potassium sulfate or potassium sulphate in the crystal activated by chloride ions, therefore, they can be referred to ions Sn$^{2+}$.

The spectra of excitation of photoluminescence of K$_2$SO$_4$-Sn$^{2+}$ crystal measured at 80 K are given in Figure 2. Curve 1 in Figure 1 represents the excitation spectrum measured when observing the emission in the field of 325 nm. Curve 2 is the excitation spectrum measured in observation of the emission in the field of 365 nm. The choice of the observation field is explained by aspiration to reduce overlapping of emission bands. The excitation spectra measured at the temperature of fluid nitrogen have maxima at 240 nm and 260 nm. It is apparent from Figure 1 that the emission band with maximum at 335 nm is mainly excited in the band with maximum at 240 nm, and the emission band with maximum at 360 nm is mainly excited in the band with maximum at 260 nm.

By analogy with the alkaline haloid crystals and the ammonium-haloid crystals activated by mercury-like ions, we connect the excitation bands observed in K$_2$SO$_4$-Sn$^{2+}$ with A, the band with the ion Sn$^{2+}$, replacing the cation in nodal situation [1].
Figure 2. Spectra of excitation of $\text{K}_2\text{SO}_4$-$\text{Sn}^{2+}$ crystal at temperature 80 K. 1 – emission band in the field of 325 nm, 2 – emission band in the field of 365 nm.

Curves of temperature suppression of photoluminescence of $\text{K}_2\text{SO}_4$-$\text{Sn}^{2+}$ crystal are given in Figure 3. In the figure it is seen that for different emission bands the nature of suppression is different. At increased temperature, $\text{K}_2\text{SO}_4$-$\text{Sn}^{2+}$ emission spectrum tends to widening.

Figure 3. Curves of temperature suppression of photoluminescence of tin in potassium sulphate. 1 – for the emission band with $\lambda_{\text{max}}=335$ nm, 2 – for the emission band with $\lambda_{\text{max}}=360$ nm.

From $\text{K}_2\text{SO}_4$-$\text{Sn}^{2+}$ emission spectra it is obtained that half-width of the emission band with $\lambda_{\text{max}}=335$ nm at a temperature of 80 K makes 335 nm 0.11 eV, and at 120 K, it is 0.13 eV. From temperature dependences of half-widths of emissions for the band with $\lambda_{\text{max}}=335$ nm, it is obtained that the efficient oscillation frequency is equal to $2.35 \times 10^{-12}$ s$^{-1}$, and for the band with $\lambda_{\text{max}}=360$ nm, it is $4.6 \times 10^{-12}$ s$^{-1}$. Different values of frequencies demonstrate that these luminescence centers either
differently interact with a crystal lattice, or have various efficient mass of oscillators. As it is the impurity ion of one nature, different values of frequencies are related to various surrounding [2].

Curves of thermally stimulated luminescence (TSL) of crystals $K_2SO_4$-Sn$^{2+}$ and $K_2SO_4$-Pb$^{2+}$ are given in Figure 4. From the figure, it is seen that in addition to own peaks of TSL of the matrix there are luminescence peaks which can be connected with the impurity centers. The curves indicating TSL show that presence of heterovalence impurity ions of tin reduces the light sum of TSL peaks of the matrix in the area of 300 K. This phenomenon is followed by emergence of padding cationic vacancies.

![Figure 4. Curve for TSL of the potassium sulphate activated by 1 – tin, 2 – lead.](image)

In the spectra of TSL of potassium sulphate crystals activated by ions of the transitional metals in addition to the relative decrease of the light sum of high-temperature peaks, its redistribution is observed as well. Similar redistribution of the light sum in crystals of potassium sulphate activated by ions of chlorine or mercury-like ions is not observed. The experimental data show that the influence of the studied ions of the transitional metals: Cu$^{2+}$, Co$^{2+}$, Ni$^{2+}$ on high-temperature peaks of TSL is identical. It is known [1] that Cu$^{2+}$ occupy cationic knot with larger coordination on oxygen in potassium sulphate lattice. It is known that the manganese ions which are transient, also advantageously occupy this cationic knot. Thus, it is possible to claim that Sn$^{2+}$ ions replace base cations in nodal similar to copper ions.

4. Conclusion

According to the type of the emission spectrum, we can conclude that ions of divalent tin in the matrix of potassium sulphate form two types of luminescence centers. We assume that it is related to the fact that the tin ion is heterovalent concerning the replaced cation. Thus, the impurity ions of the transitional Sn$^{2+}$ metals are the centers of electron capture in $K_2SO_4$. These impurity ions influence the emergence of additional cationic vacancies in $K_2SO_4$ crystal.

References

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[2] Myrzakhmet M and Satayeva G, et al 2015 J. of Luminescence 169 B 804