ABOUT LUMINESCENT PROPERTIES OF MONOCRYSTALS OF THE DIFFICULT SULFATES ACTIVATED BY THALLIUM


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Luminescence centres in the ammonium sulphate crystals with an impurity of thallium and in the mixed crystals are explored. It is shown, that these centres are the one-charging thallium ion. Two various positions of replacement feebly affect scintillation performances of these crystals.

Keywords: luminescence centres, mixed crystals, scintillation performances, radio luminescence, spectra of absorption.

Introduction

Crystals of sulfate of ammonium and the mixed crystals of sulfate of potassium and lithium are interesting with some phases caused by various behaviors of cations and anions at various temperatures.

Ammonium sulfate at 223 K to turns from high-temperated the para-electric form I in segne-electrical phase II [1]. Forms are orotorombical, group forms I $P_{nma}$, and forms II - $P_{na21}$ is spatial. Under a condition for orotorombical elementary cells>> with, the axis with in a phase II is a direction spontaneous polarization. The phase I possesses three mirror planes ab, bc both the expert and the inversion center, and the phase II doesn't have center of inversion and a reflection plane ab.

In both forms, para-electric and segneelectric, for ammonium ions in a lattice there is environment of two types. Types of ions corresponding to them are designated as NH$_4$ (I) and NH$_4$ (II [1]. Ion NH$_4$ (I) has five sulfates-ions in the nearest environment, and ion NH$_4$ (II) - six (in both phases). Ions NH$_4$ (I) are less mobile, than ions of the second type. With increase in the maintenance of ions of potassium temperature transition energy of activation of ions NH$_4$ (I) decreases also decreases. Moreover, last type of ions is mainly replaced, and in enough enriched ions potassium the mixed crystals there are only ions NH$_4$ (II). From measurements of time of a relaxation on a phase I of salt (NH$_4$)$_2$SO$_4$ follows that above 300 K ammonium ions begin to diffuse in a lattice with energy of activation 75 kJ/mol [2].

Transition II→I partially smooth as thermal capacity measurements have shown. It is accompanied by the gradual reduction of volume reaching as a result approximately 1,5%, thus compression is concentrated only along an axis and [3]. However, though transition is also stretched on an interval approximately in 50 K, it comes to the end nevertheless isothermally. Thus, in the Curie point sharp change of spontaneous polarization [3] and factors of an elastic pliability [4] is observed. Nevertheless, there is no a sharp change in frequencies of librational (torsional) fluctuations that has been established on long-wave infra-red spectra [5], infra-red spectra and spectra of combinational dispersion [6], in effective section of dispersion of neutrons [7].

For ammonium sulfates, and also the mixed sulfates of potassium and the lithium activated by thallium, remain unsolved questions:

- distinction of optical properties of ions TI$^+$ for two various positions of potassium with which they replace,
- optical properties of pair centers TI$^+$ in these crystals.

Experiment

Crystals of sulfate of ammonium and the mixed sulfates of lithium and potassium pure and in the presence of a thallium impurity are grown up from a water solution by a method of slow
evaporation at room temperature at the Eurasian national university of L.N.Gumilyov. Measurements of optical properties of these crystals are carried on the equipment of department of optical materials of Institute of Physics of Academy of Sciences of the Czech Republic in Prague.

Absorption of crystals was measured at room temperature by means of installation Shimadzu 3101PC, a luminescence in a wide range of temperatures from temperature of liquid nitrogen to 500°C – spectrofluorimeter HJY 5000M.

In fig. 1 - 2 are shown the comparison with standard scintillator BGO spectra X-ray all measured by us it is exemplary. The samples activated by thallium always show more intensive strip of radiation with various intensity (depending on the form of the sample, concentration of thallium, quality of a material).

![Fig. 1. Radio luminescence of crystals LiKSO₄](image1.png)

![Fig. 2. Radio luminescence of crystals NH₄SO₄ in comparison with the data for ammonium chloride](image2.png)
Fig. 3. Spectra of absorption of samples at room temperature.

Fig. 3 spectra of absorption of samples with thallium impurity – A-strip Ti$^+$ with a maximum about 220-230 nanometers are shown.

Fig. 4. Samples LiKSO$_4$

Fig. 5. Spectrum of the photoluminescence of the investigated samples
The excitation spectrum in this strip approximately repeats an absorption A-strip (Fig. 6), there is a high intensity of this strip, most likely, because of high value spectral absorptive abilities and arising thereof geometrical effects.

![Excitation spectrum of LiKSO4-Tl](image1)
![Excitation spectrum of NH4Cl: Tl](image2)

Fig. 6. A spectrum of excitation of the investigated samples

The photoluminescence and excitation spectra in all crystals are measured by us corresponded to X-ray and to absorption, accordingly. Time of attenuation of luminescence is homogeneous everywhere for a strip of radiation and 410 nanoseconds, the disintegration form single-exponent give for crystals LiKSO4-Tl approximately, that is the radiation center is unique and well defined. In radiation spectrum (NH4)2SO4 there are two strips approximately 295 nanometers and weaker of 380 nanometers. The spectrum of excitation dominating corresponds to absorption spectrum. Time of attenuation of a photoluminescence of the basic strip of 300 nanometers approximately 360 nanoseconds, and for weaker strip of 380 nanometers is longer - approximately 600-800 nanoseconds.

Photoluminescence NH4Cl: Tl is well studied earlier [8]. The photoluminescence spectrum reaches a maximum approximately 370-380 nanometers and there correspond to one strip X-rayed and its time of attenuation approximately 360 nanoseconds.

Conclusions

Thus, we have investigated the luminescence centers in the crystals of sulfate of ammonium activated by thallium and in the mixed crystals. It is shown that these centers are one-charging ion of thallium. Two various positions of replacement poorly affect luminescent characteristics of these crystals.

References: