

UDK 53.043; 535.247

LUMINESCENT PROPERTIES OF CRYSTALS OF THALLIUM DOPED LiKSO_4 , IN A TEMPERATURE RANGE OF 77-495 K

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Sulfates, as we know, are good thermoluminescent materials. It was appeared that materials on the basis of crystals of $\text{LiKSO}_4:\text{Tl}$ are luminophores with high thermoluminescent sensitivity which are irreplaceable in thermoluminescent dosimetry of ionizing emission. In the recent years there have made works on studying of luminophores on the basis of sulfates which possess some properties used for dosimetry of thermoluminescent ionizing emission. These researches showed that LiKSO_4 luminophores activated by thallium possess higher sensitivity, than LiF crystals. In this article optical characteristics of such phosphors on the basis of crystals of LiKSO_4 activated by thallium are considered.

Keywords: luminescent properties, activated with thallium, thermoluminescent material, luminophores, thermoluminescent dosimetry

Introduction

In thermoluminescent dosimetry high emission sensitivity and good thermal stability of materials are important for measurement of extent of external impact on materials in the field of physical medicine. Only some luminophores of LiF , $\text{Li}_2\text{B}_4\text{O}_7$, MgB_4O_7 and BeO have such properties. LiF crystals, the activated Mg and Ti are widely used. All these luminophores have shortcomings, for example, LiF has a difficult curve of a luminescence [1], $\text{LiF}:\text{Mg}$, Cu , P are sensitive to thermal processing [2], $\text{MgB}_4\text{O}_7:\text{Dy/Tm}$ shows high sensitivity to change of concentration [3], $\text{Li}_2\text{B}_4\text{O}_7:\text{Mn}$ has low sensitivity to external emission [4], $\text{Li}_2\text{B}_4\text{O}_7:\text{Cu}$ has high optical extinction. At low doses of illumination in BeO the big noisiness of a signal of a thermoluminescence [5] is observed.

Methods of measurement

Research of spectral and kinetic characteristics of a luminescence was made on a spectrometer described in [6]. Technical possibilities of a spectrometer: spectral area of measurements – 200 ...1200 nanometers; time range – 7 ns; a temperature range of measurements – 15 ...700 K; duration of an impulse of a current of electrons – 2 ...10 ns; density of a current of a bunch of electrons – 0,1 ...1000A/cm²; average energy of electrons – 250 keV. As receivers of emission FEU-97, FEU-83 were used. Measurement of ranges and kinetics of extinction of a luminescence was made by means of the monochromator MDR-204 and Tektronix oscilloscope. Temperature range of measurements: 15 ...300 K; time interval: 10⁻⁸ ...10⁻³ sec. All ranges of luminescence are constructed taking into account a spectral characteristic of sensitivity of a measuring way of a spectrometer.

Experiment

Pure monocrystals of LiKSO_4 are transparent in wide spectral area up to 8,0 eV [7] and do not show absorption or fluorescence in wide spectral area of 200-800 nanometers before x-ray illumination of samples [8].

Spectrum of absorption of the thallium doped LiKSO_4 crystals gives bands with maxima 5,7 and 7,3 eV, connected with transitions in Tl^+ ion with a maximum of emission 4,2 eV [9]. With increase in concentration of thallium there are additional bands of absorption 5,65 and 4,4 eV which intensity changes linearly with concentration of the activator; the necessary maximum of emission is on 3,5 eV.

In the heating of the irradiated crystals there is observed the intensive thermoluminescence in a range of 90~200 K in a emission band with a maximum 2,35 eV. At high temperatures ranges of a thermoluminescence give bands with maxima 4,2 and 3,5 eV, coinciding with bands of an intra center luminescence of Tl^+ ions.

As shown in [11] by the EPR method, x-ray emission effectively creates the Tl^{2+} centers. Authors [7] connect emergence of a luminescence of Tl^+ centers in thermoluminescence ranges with a recombination of electrons.

The monocrystals of LiKSO_4 activated by thallium give an absorption band in ultra-violet area with a maximum 5,85 eV. After emission of crystals by X-rays intensity of this band decreases slightly, and the weak baseline grows in area of 5,5-5,6 eV [8].

Spectra of emission consist of two bands: an intensive band 4 eV and a weak band in the field of 2,02-2,05 eV. The spectra of excitation corresponding to these bands of emission are similar – have at most 5,4 eV and a baseline from higher energy in the field of 5,8-5,9 eV. The scale of illumination of crystals does not give any new bands of excitation or emission.

Thermostimulated luminescence show three peaks for low doses of emission with maxima 340, 395 and 445 K. The low-temperature peak with increase in a dose of emission is closed by the second peak. There is a considerable background after usual doses of emission. Spectral structures of background, as well as a thermoluminescence under various peaks, consist of two bands 2,04 eV and 4 eV. The low-energy band is quite weak at room temperature and lower temperatures, but its intensity considerably grows at more high temperatures.

In optical spectra of absorption the band of absorption of Tl^+ -ions is shown. Fluorescence shows Tl^+ emission owing to transitions from $^3\text{P}_1$ and $^3\text{P}_0$ levels on $^1\text{S}_0$ level. Excitation in this band also brings to the same emission translating electrons from singlet to triplet excited levels. The scale of illumination causes change of valency some of Tl^+ ions. Tl^+ behaves during emission as an electronic trap. There is formed Tl^0 turning into Tl^+ at the moment of a recombination with the hole center in the heating, and this recombination causes an observable thermoluminescence. Spectra of emission of a thermoluminescence contain the same bands of Tl^+ as it is observed in fluorescence.

In [10] it is shown that x-ray emission of crystals at temperature of liquid nitrogen leads to formation of the Tl^0 and Tl^{2+} centers. In heating crystals to room temperature the intensive thermoluminescence connected with disintegration of these centers is observed.

Thus, for thallium doped LiKSO_4 crystals remain a number of questions which are not solved up to the end:

- uncertainty of a form and provision A-, B-, C-of bands of absorption of Tl^+ ions,
- distinction of optical properties of Tl^+ ions for two various positions of kalium which they replace,
- optical properties of the pair centers Tl_2^+ in these crystals.

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

Absorption of crystals was measured at room temperature on the Shimadzu 3101PC device, a luminescence in a wide range of temperatures from temperature of liquid nitrogen to 500 °C was measured on spectrofluorometer HJY 5000M.

In figure 5 spectra of all measured radioluminescence are shown in comparison with a standard scintillator of BGO. The samples activated by thallium always show more intensive band of emission with various intensity (depending on a form of a sample, concentration of thallium, quality of a material).

Excitation of a luminescence was carried out on wavelength of 220 nanometers which was defined on the basis of research of spectrum of excitation at room temperature and at temperature 77 K (Figure 3).

The spectrum of excitation is displaced in long-wave area concerning to an absorption band (see Figure 2). There is a high intensity of this band mostly because of high value of spectral absorptive ability and arising thereof geometrical effects.

Optical absorption.

There were studied spectra of optical absorption of not alloyed samples for comparison with the alloyed samples. Samples of LiKSO_4 have no optical absorption (Figure 1).

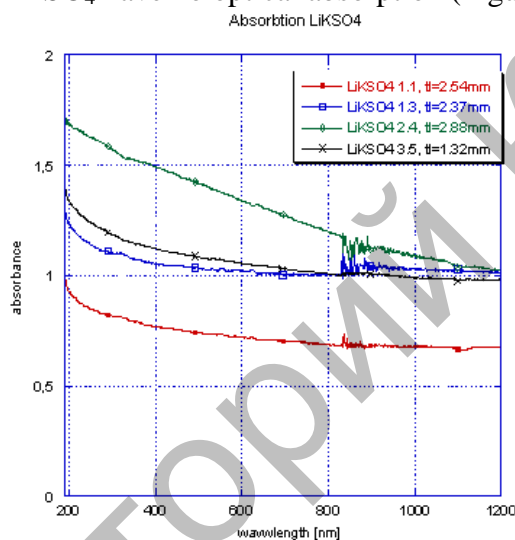


Fig. 1. Spectrum of absorption of undoped LiKSO_4 crystals

Samples of $\text{LiKSO}_4:\text{Tl}$ have bands of optical absorption on wavelength of 225 nanometers (Figure 2).

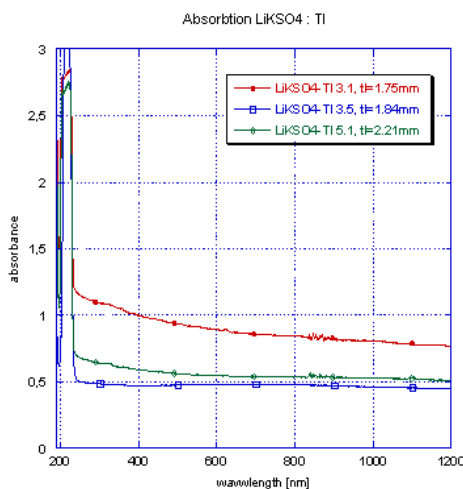


Fig. 2. Spectrum of absorption of thallium doped LiKSO_4 crystals.

Excitation spectrum

Crystals of LiKSO_4 have no absorption bands even after illumination (from 200 to 800 nanometers). Samples alloyed by Thallium have bands of strong absorption on 5,51 eV.

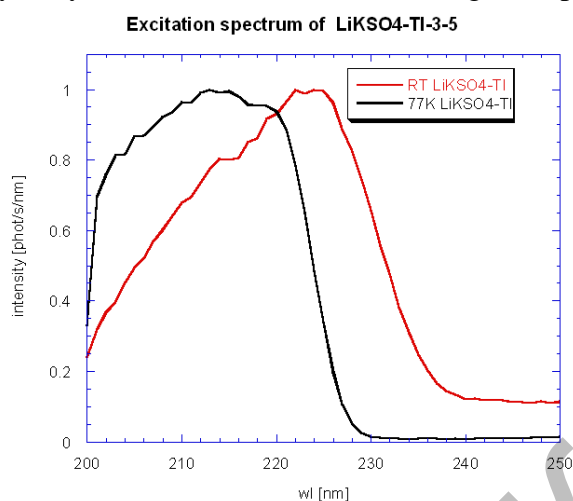


Fig. 3. Spectrum of excitation at room temperature and at temperature of 77 K.

Emission spectrum

At excitation in a band around 220 nanometers there is found the emission band with a maximum of 273 nanometers which can be carried to Tl^+ emission (Figure 4). At stage-by-stage increases in temperature with 77 K to 495 K, intensity of a maximum of a range of emission evenly decreases. In a range of temperatures from 77 K to 250 K a maximum of a band of emission remains on length of a wave of 273 nanometers. And in a range of temperatures from 350 K to 495 K at most it is displaced in more short-wave area from 270 nanometers to 260 nanometers.

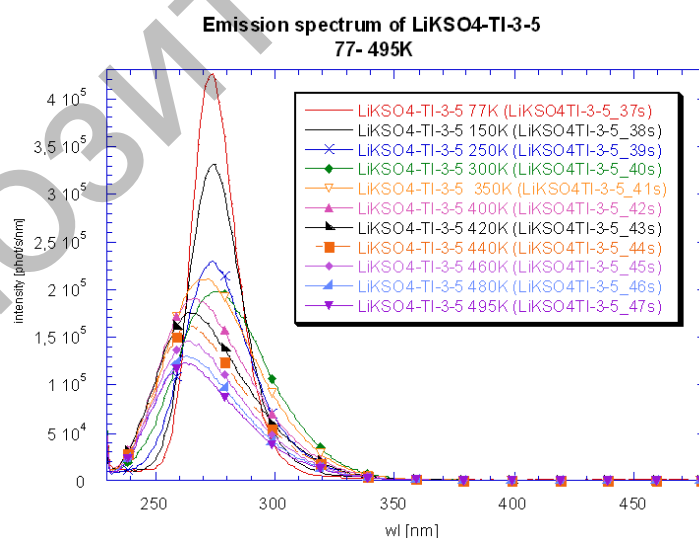


Fig. 4. Emission spectrum of $\text{LiKSO}_4\text{:TI}$ in a range of temperatures 77 K to 495 K.

In a range of temperatures from 77 K to 250 K a band of emission consists of one band, and in a range of temperatures from 300 K to 495 K this band consists of obviously expressed two bands with maxima on lengths of waves of 260 nanometers and 275 nanometers. Also that is characteristic intensity of a band on 260 nanometers decreases with temperature growth, and intensity of a band

on 275 nanometers also decreases with temperature growth, but not with such speed as a band by 260 nanometers

Radioluminescence spectra.

Research of a radioluminescence of these crystals shows that intensity of a luminescence of the activated crystal is higher in 1000 of times than intensity of undoped crystal (Figure 5).

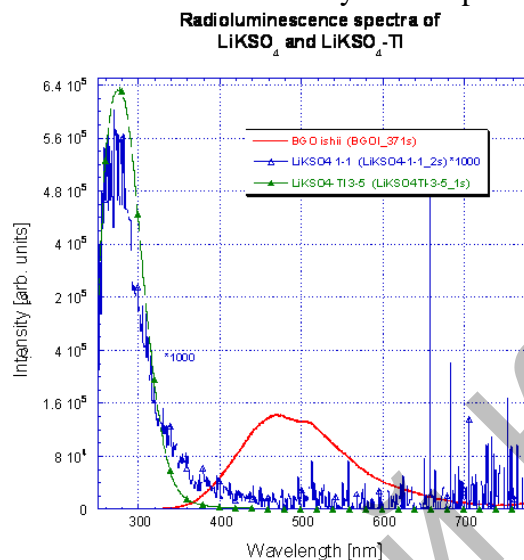


Fig. 5. Radioluminescence spectra of crystals LiKSO₄ and LiKSO₄:Tl.

Conclusion

Thus, we investigated the luminescence centers in the thallium doped LiKSO₄ crystals which show absorption with a maximum 5,5 eV and emission with maxima from 4,76 eV to 4,54 eV in a range of temperatures from 77 K to 495 K. There is shown that in a range of temperatures from 77 K to 250 K a band of emission consists of one band, and in a range of temperatures from 300 K to 495 K a band of emission consists of obviously expressed two bands with maxima on lengths of waves of 260 nanometers and 275 nanometers. Also that is characteristic intensity of a band on 260 nanometers decreases with temperature growth, and intensity of a band on 275 nanometers also decreases with temperature growth, but not with such speed as a band on 260 nanometers. The kinetic measurements which results will be stated in our following work will give more detailed research of the thallic centers.

REFERENCES

- 1 Ben S. B., Horowitz Y. S., Radiat. Prot. Dosim. 22, 87 (1987).
- 2 Barbina V., Content G., Furetta C., Molisan M., Padovani R. Radiat. Eff. Lett. 67, 55 (1981).
- 3 Mahesh K., Weng P. S., Furetta C. Thermoluminescence in Solids and Its Applications (Nuclear Technology Publisher, Kent (England), 1989).
- 4 Busuoli G., Sermenghi I., Rimondi O., Vicini G. Nucl. Instrum. Methods Phys. Res. 140, 385 (1977).
- 5 Prokic M. Nucl. Instrum. Meth. 175, 83 (1980).
- 6 Korepanov V.I., Lisitsyn V.M., Strezh V.V., Bochkanov A.V., Malyshev A.A. Transformation electronic excitation in KCl:J crystals // FTT. 1985. Vol. 27. No.10. pp. 3052-3056.
- 7 Osminin V. S., Plekhanov V. G., Silkin N. I. Zhurnal Prikladnoi Spektroskopii, 1974, Vol. 21, No.1, P. 88-91.
- 8 Kumar B. S., Kishan V. S., Acharyulu R., Sastry S. B. Emission Effects and Defects in Solids, 1993. V.127: 2-P. 215-224.
- 9 Lushchikand N.E., Meriloo I.A. Izv. Akad. NaukSSSR Ser. Fiz., 30, 1517 (1966).
- 10 Silkin N.I. Autoabstract of doctoral dissertation. Kazan, 2007.
- 11 Garifullina R.L., Krutikov V. F., Silkin N. I., Stepanov V. G. Fiz. Tverd. Tela, 14, 618 (1972).