Thallium-doped sulphate potassium crystals as materials for radiation detectors

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Luminescence characteristics of potassium sulphate (K_2SO_4) crystals doped with thallium were studied. Crystals were grown from water solution at slightly elevated temperature. The nature and properties of the luminescence centres in these crystals have been determined. The main monovalent thallium luminescence centres show the absorption peak at 216 nm and emission one peaking at 285 nm at room temperature. Thallium is substituting potassium which has two different positions in K_2SO_4 structure. Consequently, two different Tl^+ centers were found for thallium centers in these crystals and the third center includes an unspecified perturbation agent nearby. Tl^+ centers differ in radiative lifetime at low temperatures and in temperature dependence of decay times measured within 8–300 K.

Исследованы люминесцентные характеристики кристаллов сульфат калия (K_2SO_4), активированных таллием. Кристаллы выращены из водного раствора при комнатной температуре. Определены природа и свойства центров люминесценции в этих кристаллах. Основной одновалентный таллиевый центр люминесценции имеет при комнатной температуре поглощение при 216 нм и излучение при 285 нм. Таллий замещает калий, который имеет две различные позиции в структуре K_2SO_4. Определены два различных Tl^+-центра для таллиевых центров в этих кристаллах, а также третий центр, который включает в себя пока неизвестный агент возмущения поблизости. Tl^+-центры отличаются радиационным временем жизни при низких температурах и по температурной зависимости времени затухания, измеренных в диапазоне 8–300 К.

Особливості кристалів сульфату калію як матеріалів для детекторів випромінювань. *М.Мирзахмет, М.Нікл, В.Джері, Б.Далельхан, А.Жанабергенов.*

Досліджено люмінесцентні характеристики кристалів сульфату калію (K_2SO_4), активованих талієм. Кристали вирощено з водного розчину при кімнатній температурі. Визначено природу і властивості центрів люмінесценції в цих кристалах. Основний одновалентний талієвий центр люмінесценції має при кімнатній температурі поглинання при 216 нм і випромінювання при 285 нм. Талій замішає калій, який має дві різні позиції у структурі K_2SO_4. Визначено два різних Tl^+-центра для талієвих центрів в цих кристалах, а також третій центр, який включає поки невідомий агент обурення поблизу. Tl^+-центри відрізняються радіаційним часом життя при низьких температурах і по температурній залежності часу загасання, виміряних у діапазоні 8–300 К.

1. Introduction

One of the most widely used recent methods of synthesis of nanostructures are the so-called method of "soft chemistry" that allows to create a wide range of nanomaterials in solutions using controlled phase formation and crystallization processes (colloi-

dal synthesis, sol-gel method, synthesis in microemulsions) target self-assembly of nano-objects into ordered 2D and 3D assemblies (template synthesis aimed sedimentation, convection self-assembly) [1].

Such systems become demanding in the information processing. The development of technologies is required for manufacturing to broadcasting/excitation devices, photodetectors and light-controlled logic gates.

On the other hand, such nanomorphological systems can arise by self-organization, which is the case of naturally occurring material with properties of photonic crystal — precious opal. As a result of long-term research and experiments, carried out in various laboratories of the world, various methods for artificial synthesis of this mineral have been developed.

The technology of producing opal matrixes with regular packs is developed highly most fully for silicon dioxide (SiO_2). On this basis the three-dimensional characteristic nanocomposites with nanoscale structure are obtained. These structures provide a photonic material properties and formed a whole branch of research in the field of opal photonic crystals [2].

Nanocomposites using the precious opal host were created by filling its regular nanocavities by precious metals, nanocrystals of semiconductors and nanocrystals of crystalline phosphors on the basis of rare-earth ions [1]. So far the ionic nanocrystals with tetrahedrally-coordinated anions or cations have not been used for such a purpose. Tl-doped K_2SO_4 could be suitable for such a purpose, but before the manufacturing and study of such nanocomposites we report here the detailed study of Tl^+ emission center characteristics in potassium sulphate crystal host to have the material description in its bulk form. The Tl^+ luminescence centers in these crystals were briefly described in [19].

Potassium sulphate (K_2SO_4) at room temperature refers to the orthorhombic space group $D_{2h}^{16} = Pnma$ [3, 4], and at 587°C undergoes a phase transition to the hexagonal structure $D_{6h}^4 = P63/mmc$ [5]. The hexagonal high-temperature phase of the crystal is usually referred to as α-K_2SO_4, and the orthorhombic phase — as β-K_2SO_4. Similar phase transitions from α-type structure to β-type structure werefound for other crystals of the family (e.g., Na_2SO_4, $LiKSO_4$, K_2CrO_4 and K_2SeO_4) [6, 7]).

Another phase transition at 56 K is found by the authors [8]. The crystal symmetry of the low-temperature phase (γ-K_2SO_4) is monoclinic. However, the authors of [9] did not find any evidence in favor of a phase transition below room temperature.

In [10] it is shown that the phase transition between the β-K_2SO_4 and α-K_2SO_4 is a phase transition of the first kind. Pretransition effects lower than the temperature of phase transition are attributed to the water that is usually within the crystals grown from aqueous solutions. The authors [10] believe that the previous reports on such effects [11–13] should be treated with caution, because it is not clear whether these effects are related to the mobility of K^+ or SO_2^{-4}, or the mobility of extrinsic species like OH_3^+.

Undoped single crystals of potassium sulphate are transparent in a wide spectral range up to 8.0 eV [14] and show no absorption or fluorescence in the broad spectral range of 200–800 nm before and after X-ray irradiation of the samples [17].

Absorption spectra of thallium-activated K_2SO_4 crystals show bands with maxima at 5.7 and 7.3 eV, associated with transitions of the Tl^+-ion with a maximum of emission near 4.2 eV [15]. With an increase in concentration of thallium the additional 5.65 and 4.4 eV absorption bands arise the intensity of which changes linearly with the concentration of the impurity; the maximum of related emission band is at 3.5 eV. It is expected that the absorption bands of 5.75 and 7.35 eV and 4.2 eV emission band correspond to transitions in Tl^+-ions in $k1$ positions, while the absorption bands at 4.4 and 5.65 eV and 3.5 eV emission band correspond to transitions of Tl^+-ions in the $k2$ position.

When heating the irradiated crystals the intensive thermoluminescence in the 90–200 K range in the 2.35 eV emission band is observed. At high temperatures thermoluminescence spectra show bands with maxima at 4.2 and 3.5 eV coinciding with the intracenter luminescence of Tl^+-ions in $k1$ and $k2$ positions.

As it is shown in [16] by EPR method, X-ray radiation effectively creates the Tl^{2+}-centers. Authors [14] connect the luminescence of Tl^+-centers in thermoluminescence spectra with a recombination of Tl^{2+}-centers with electrons.

The potassium sulphate activated by thallium shows an absorption band in ultraviolet area with a maximum at 5.85 eV. After X-ray irradiation of crystals the intensity of this band decreases slightly, and the weak shoulder shows up in 5.5–5.6 eV region [17]. The emission spectra consist of
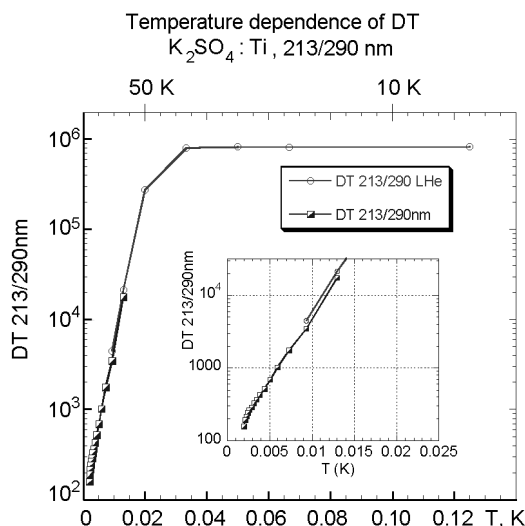
Fig. 1. The temperature dependence of the decay time of the emission band at 285 nm (at excitation in 213 nm, and the emission at 290 nm), obtained from a single-exponential approximation of decay curves. The inset shows enlarged the 70-500 K region.

Fig. 2. The temperature dependence of the decay time of the 330 nm band, obtained from a single-exponential approximation of the decay curves.

two bands: intensive 4.0 eV band and a weak band around 2.02–2.05 eV. The excitation spectra corresponding to these emission bands are similar. They have maximum at 5.4 eV and a shoulder at higher energy within 5.8–5.9 eV. Gamma irradiation of crystals does not give rise to any new excitation/emission bands.

For low irradiation doses the thermally stimulated luminescence shows three glow curve peaks with maxima at 340, 395 and 445 K. The low-temperature peak with an increase in a dose of radiation is overlapped by the second peak. There is a considerable afterglow after the usual doses of radiation. Spectral structures of afterglow, as well as thermoluminescence under various peaks, consist of two bands 2.04 eV and 4.0 eV. The low-energy band is quite weak at the room temperature and lower temperatures, but its intensity increases significantly at higher temperatures [17].

In the optical absorption spectra the C absorption band of Tl^+-ions is shown. The fluorescence shows emission of Tl^+ due to transitions from the $^3P_1$ and $^3P_0$ levels on $^1S_0$ level. Gamma irradiation causes a change in the valence of some of the Tl^+-ions. Tl^+ behaves during irradiation as an electronic trap. Formed Tl^0, evolving into Tl^+ at the time of recombination with the hole in the center of the heating time, and this causes the observed rec ombination thermoluminescence. The emission spectra of thermoluminescence contain the same band of Tl^+, as observed in the fluorescence [17].
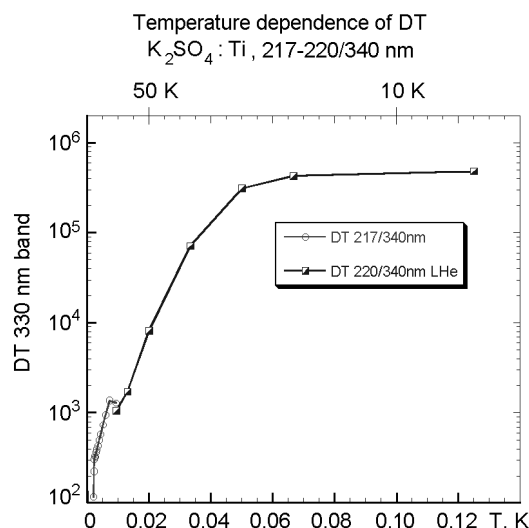
In [18] it is shown that radiation X-ray beams of crystals at a temperature of liquid nitrogen leads to the formation of the Tl^0 and Tl^{2+} centers. When heating crystals to room temperature the intensive thermoluminescence is observed associated with the decay of these centers.

For crystals of potassium sulphate, activated by thallium, a number of questions was not solved:

• uncertainty of a shape and position A-, B-, C-bands absorption of Tl^+-ions,

• difference in the optical properties of Tl^+-ions for two various positions of potassium which they replace,

• optical properties of Tl^+_2 pair centers in these crystals.

2. Experimental

Pure and thallium doped potassium sulphate crystals are grown in our laboratory from water solution by a method of slow evaporation at the room temperature. Measuring the optical properties of these crystals are carried out on the equipment of the Department of Optical Materials Institute of Physics of the Academy of Sciences of the Czech Republic in Prague [19]. Absorption of crystals was measured at the room temperature on the Shimadzu 3101PC spectrometer, luminescence spectra and decay kinetics were measured on HJY 5000M spectrofluorometer within 77–500 K.
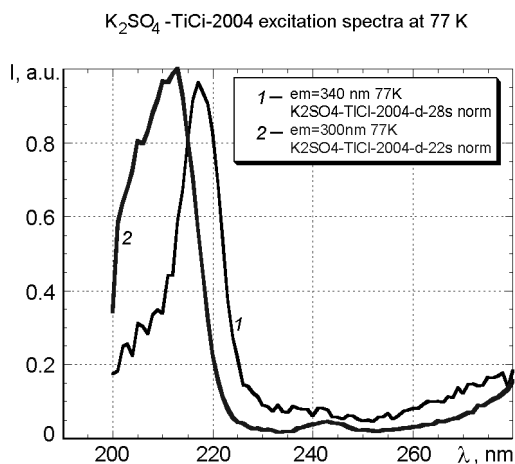
K$_2$SO$_4$-TiCi-2004 excitation spectra at 77 K

Fig. 3. Photoluminescence excitation spectra at 77 K, excited at 340 nm and 300 nm.

K$_2$SO$_4$-TiCi-2004 - D
Emission spectrum, ex = 243 nm   T = 77 K; Slits 8/6

Fig. 4. The photoluminescence spectrum at 77 K, excitation in 243 nm.

Temperature dependence of DT
K$_2$SO$_4$: Ti, 243/298 nm
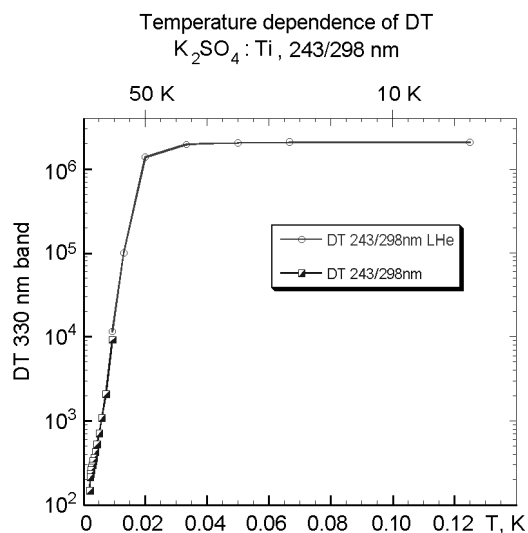
Fig. 5. Temperature dependence of the decay time values of the 296 nm band, excitation in 243 nm.

3. Results and discussion

In X-ray excited luminescence spectra the samples doped by thallium always showed a more intensive band of emission with various intensity (depending on a shape of a sample, the concentration of thallium, the quality of a material).

The absorption spectra of the samples with impurity of thallium *A*-band of Tl$^+$-ions with a maximum about 216 nm. Some of the undoped samples showed contamination by thallium and the same emission band, as in the Tl-doped samples.

Upon excitation in the *A*-band near 216 nm the emission band is observed with a maximum at 285 nm, which belongs to the Tl$^+$.

The excitation spectrum of the 285 nm band approximately copies the absorption *A*-band, some distortions arise likely due to high absorbance and resulting geometrical effects.

Thus, the luminescence centers in the crystals of potassium sulphate doped by thallium show absorption with a maximum at 216 nm and emission with a maximum at 285 nm at the room temperature. These centers belong to monovalent of thallium. Two different substitution sites show small effect in the luminescent characteristics.

Decay kinetic measurements complete further the descirption of the Tl$^+$ centers (Fig. 1). Measurement of KSO:Tl down to 8 K showed a plateau in the decay time of a dominating band at 285 nm (lower than 30 K), but for the decay time of a band at 330 nm we have growth up to 8 K, so in this case division of metastable and radiating levels of this center less authentically, then at a 285 nm band.
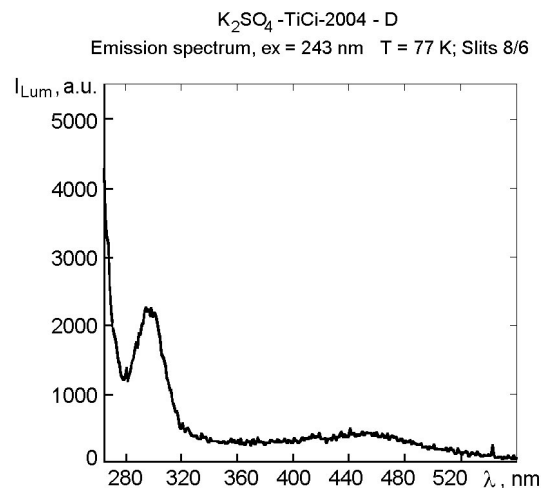
The temperature dependence of the decay time of the emission band at 330 nm is given in Fig. 2. In Fig. 3 and 4 the excitation and emission spectra are shown, respectively, demonstration of one more emission center is proved in a matrix of potassium sulphate with an emission about 296 nm and excitation near to 243 nm peaks.

Value of a radiative lifetime of the 296 nm band several times exceeds those of the other two bands described above. Furthermore, the temperature dependence of the decay time of the emission is different: the plateau extends to higher temperatures, and then drops sharply (Fig. 5).

Detailed measurements of temperature dependences of the decay times and carefully distinquished luminescence spectra clearly proved three emission centers associated with monovalent thallium. Two of them arise due to two positions of potassium ions in the structure of potassium sulphate, the third can be associated with the Tl$^+$ with a defect nearby.

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