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Recombination luminescence in alkali metal sulfates

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In this paper we present the results of investigation of the nature of intrinsic luminescence caused by photon excitation in a wide spectral range from 10.3 eV to 4 eV at a temperature of 15–300 K. It is shown that in alkali metal sulfates the main emission band formed after excitation by X-rays and photons with an energy of 9–11 eV and 4–7.5 eV at 15–300 K is located in the spectral range of 3.65–3.9 eV. When the sulfates are excited by 4–7.75 eV photons, in addition to the emission band at 3.65–3.9 eV the other effective long-wave band at 3.1–2.5 eV appears. It is assumed that the 3.65–3.9 eV radiation results from the recombination of electrons with unevenly located holes of SO_4^- type. The long-wave emission bands in the alkali metal sulfates may be connected with the formation of electron-hole trapping centers after irradiation by photons with energies above 4.4 eV.

1. Introduction

Studying of radiation of sulfates of alkali and alkaline-earth metals becomes increasingly important as they are widely used as active elements in dosimeters, scintillators and luminophores. As electron states responsible for absorption and emission in sulfates of alkali and alkaline earth metals have a complex structure, it is difficult to identify radiation bands in the wide spectral range of photon energies.

Identification of individual absorption and emission bands corresponding to certain electron transitions has a special practical value in selecting crystals for scintillators, dosimeters, detectors and luminophores.

It has been shown that the anion complex SO_4^{2-} plays a special role in the identification of radiation bands in sulfates. The electron configuration of the main sulfate anion state $2(a_1)^2$ $(2t_2)^6$ $(1e)^4(3t_2)^6$ $(1t_1)^6$, determines the energy state of the valence band [1]. The first unfilled molecular orbitals are free orbitals of the anion SO_4^{2-}, $3a_1^*$and $4t_2^*$determining the lower part of the conduction band [1]. The upper part of the conduction band is formed by free S – states of the cation (Na^+ and K^+) of the base.

Based on the measurements of the diffuse reflection spectrum of Na_2SO_4 and K_2SO_4 powders [2] and the analysis of theoretical calculations of the electron structure of the anion SO_4^{2-} [3,4], the authors [2] referred the reflection bands to two transition groups.

The first group of bands at 5.1 eV, 6.9 eV and 10.5 eV is associated with electron transitions from the molecular orbitals $1t_1$, $3t_2$, 1e, $2t_2$ of anion SO_4^{2-} to the conduction band of the matrix formed from the S state of Na^+ and K^+ cation. The second group of bands at 4.4eV, 6.0 eV and 9.8 eV is associated with intramolecular transitions from the molecular orbitals $1t_1$, $3t_2$, 1e, $2t_2$ to free orbitals $3a_1^*$and $4t_2^*$ of the same ion SO_4^{2-}. Thus, intrinsic luminescence of the alkali metal sulfate occurs as a result of transition of electrons from the excited state of the matrix to molecular $1t_1$, $3t_2$, 1e, and $3t_2$ orbitals of ion SO_4^{2-}.

In our previous works [5] a complex emission band with a few peaks was detected in Na_2SO_4 crystals after excitation by X-rays and photons. However, those emission bands were not identified. On the basis of the calculations made by the authors [6,7] the band gaps were estimated for $LiKSO_4$ and K_2SO_4 crystals, which were found to be 5.8 eV and 8–9 eV, respectively. The results of calculations are confirmed by the measurements of the absorption spectrum of $LiKSO_4$ crystal in the spectral range from 1.5 to 6.2 eV [8,9].

The research works on intrinsic luminescence of alkali metal sulfates show that when they are excited by X-rays, synchrotron radiation or ultraviolet photons, complex emission bands appear in the 2–4 eV spectral range.

Besides, in the irradiated sulfate, the basic electron transfers in

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the eigen-matrix may be superimposed by the transitions between the states of newly created electron-hole capture centers.

In this work we studied intrinsic luminescence of K_2SO_4 and $LiKSO_4$ crystals under the action of selective excitation by 4–11 eV photons at a temperature ranging from 15 K to 300 K.

2. Methods

The inorganic scintillator based on complex alkali metal sulfates, weight.%,: K_2SO_4 - 65.5, was prepared by dissolving these ingredients in water in the ratio 1: 1. As a result, a saturated aqueous solution of sulfates was formed, which was further heated to 38 °C. The crystals were synthesized by the method of isothermal evaporation. To provide initial nucleation and to stimulate crystal growth of a complex sulfate, 5–7 drops of sulfuric acid were added to the solution (to obtain pH 4–6). The resulting crystals of the inorganic scintillator hada form of 6–8 mm bipyramids.

Crystals of $LiKSO_4$ were grown at 40 °C from the aqueous solution of $LiSO_4$, KSO_4 and H_2O in the ratio of 1: 1: 1. The crystal growth started when a few drops of sulfuric acid were added to the initial solution. The crystals grown without impurities were colorless. The crystals had the shape of a bipyramid. To use them in the scintillation block (in combination with a photomultiplier tube) 5 mm-thick plates, 10–15 mm in diameter, were cut out from the crystal. The crystals were irradiated by the X-ray tube BSV-23 with a copper anti-cathode, tube current of 10 mA, voltage – 45 kV. The glow of the crystals was registered by FEU-62. The luminescence spectra were measured using a monochromator MDR-41 and spectrofluorimeter SOLAR CM2203. The excitation and luminescence spectra in the energy range 3–11.5 eV were measured on a vacuum monochromator assembled using the Seya-Namioka scheme. The source of ultraviolet radiation was a 200-Wt hydrogen lamp D 200VUV.

3. Experimental results analysis

3.1. Experimental results on studying intrinsic radiation for K_2SO_4 crystal

The studies of the authors [10,11] on fundamental properties of K_2SO_4 crystals showed that the band appears in the X-ray luminescence of K_2SO_4 crystal at 3.8 eV and the broad longwave band appears with 3.1, 2.6 and 2.3 maximum. Based on observation of excitation and temperature dependence spectrum of the radiation, the authors [10,11] assumed that short-wave band of 3.8 eV is due to radiative recombination of an exciton, and longwave radiation bands - induced defects of lattice. On the basis of experimental data on the reflection spectra [10,11] and theoretical calculations [7], the authors suggested that the width of the forbidden energy band for K_2SO_4 is 8–9 eV. In our previous works [12] it has been shown that excitation by synchrotron radiation resulted in wide shortwave band of the radiation with 3.9–4 eV maxima (Fig. 1, curve 1) and the excitation bands with 7, 8 and 9.4 eV maximum (Fig. 2, curve 1) at temperatures of 7–8 K. The results confirmed the hypothesis of previous authors [7,10,11], that the width of the forbidden zone of K_2SO_4 is about 8–9 eV.

As it was mentioned in the introduction of this work, the detailed study of crystal reflection spectra of K_2SO_4, Na_2SO_4 and $CaSO_4$ [2] showed that there are low-energy reflection bands 4.4, 5.1 and 6.0 eV in addition to the high-energy reflection bands (6.9, 9.8 and 10.5 eV).

This work covers the radiation spectrum of K_2SO_4 crystals when excited by photons in a wide energy range from 4 to 11 eV. Fig. 1, curve 2 shows the radiation spectrum of K_2SO_4 crystal upon excitation by ultraviolet photons (UVP) with an energy of 7.75 eV at

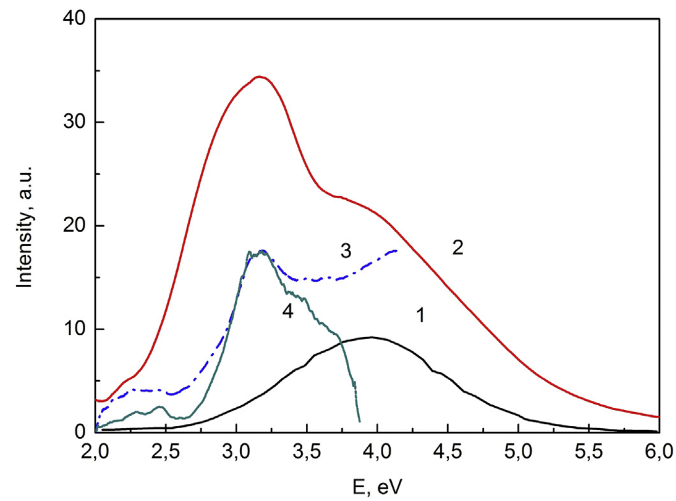

Fig. 1. Emission spectrum of the crystal K_2SO_4 at 8 K –80 K. 1 - Excitation by photons with an energy 9.3 eV, 2 - photons with an energy 7.75 eV, 3 - photons with an energy 5.5, photons with energies 4.0 eV.

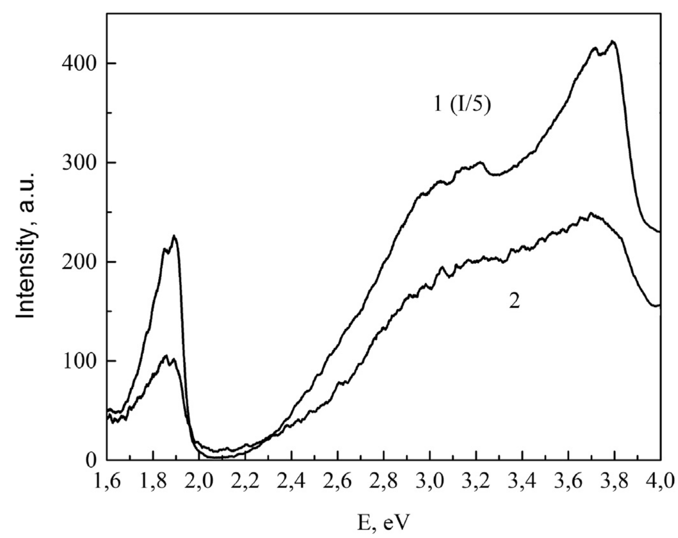

Fig. 2. X-ray spectrum of K_2SO_4 crystals: 1–80 K, 2–300 K.

15 K. As in our previous studies [12], the results has been a wide shortwave radiation band of 3–5 eV and long-wave radiation with several maximum. The occurrence of fundamental broad radiation bands with several maxima resulted in recombination of electrons with holes spaced not equivalent (SO_4^-) has been discussed in our works [13]. The same Fig. 1, curve 3 and 4 shows the radiation spectrum of K_2SO_4 crystal upon excitations by photons with energy of 4 and 5.5 eV, respectively, at 80 K. It can be seen that there are the same radiation bands as upon excitation by high-energy photons with energy of 7.75 eV and 9.4.

Fig. 3 shows the X-ray luminescence of K_2SO_4 crystal at a temperature of 298 K, curve 2 and 80 K (curve 1). It is evident that there are the same radiation bands as upon excitation by photon with energies from 4.4 to 11.3 eV.

Fig. 3, curve 2 presents the excitation spectrum of K_2SO_4 for radiation band of 3.5 eV in a wide spectral range of 3.5–12 eV. The figure shows that the short-wave band of intrinsic radiation 3.5 eV are excited by high-energy photons of 11.3 eV, 9.7 eV, 8.7 eV and 7.3 eV, as well as low-energy photons with an energy of 6.2–6.5 eV,

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