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Radiation defects in alkali metal sulfates irradiated by ultraviolet photons

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HIGHLIGHTS

- The capture of electrons and holes by anionic complexes form the defects in $LiKSO_4$.
- Excited electrons move from $1t_1$; $3t_2$; e; $2t_2$ orbitals of the valence band.
- $SO_3^- v_a^+ e^-$ and O_3^- centers are formed as a result of dissociation of the anionic complex.

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ABSTRACT

In the present paper the formation of defects in $LiKSO_4$ and K_2SO_4 crystals after excitation by 4–11 eV photons at the temperature of liquid nitrogen was studied by the methods of thermal activation and vacuum-ultraviolet spectroscopy. It is shown experimentally that electron-hole trapping centers are formed as a result of capture of electrons and holes by anion complexes SO_4^{2-} created by the transition of electrons from $1t_1$; $3t_2$; e; $2t_2$ orbitals in the valence band to the s-state of the cation in the conduction band. It is supposed that the formation of defects in $LiKSO_4$ and K_2SO_4 crystals is caused by the dissociation of excited anion complexes, created by the transition of electrons from $1t_1$; $3t_2$; e; $2t_2$ orbitals in the valence band to free, antibinding orbitals $4t_2^*$ and $3a_1^*$ in the conduction band. In this case, stable electron $SO_3^- v_a^+ e^-$ and hole O_3^- trapping centers are formed.

1. Introduction

Practical applications of many as scintillators, dosimeters, luminophors and other detectors are explained by high efficiency of transformation of the energy of primary ionizing radiation and particles in crystalline materials. In these systems, the primary energy of ionizing radiation and particles is transformed as follows. Primary ionizing radiation creates high-energy electron excitations in crystals, which are quickly transformed into a cascade of low-energy electron excitations, and each low-energy electron excitation may decay in two ways: (1) a radiative decay through direct recombination of electron-hole pairs or energy transfer to the impurities and their subsequent emission or (2) a non-radiative decay through recombination of electron-hole pairs with creation of radiation-induced defects. The energy of the primary ionizing radiation is transformed into defects of the crystal lattice.

Therefore in crystals used as scintillators and luminophors the energy of the primary ionizing radiation is transformed with a certain efficiency into the visible light, which can be detected. In crystals used as dosimeters the energy of the primary ionizing radiation may be stored in the form of defects, i.e. in the form of electron-hole capture centers, which in a certain period of time can decay radiatively emitting a certain fraction of the stored energy in the form of visible light.

Sulfates of alkaline metals are used as thermo-luminescent dosimeters, phosphors, etc. The sensitivity of dosimeters and luminophors depends on the concentration of active defects formed during transformation of the energy of primary radiation.

Crystals of K_2SO_4 and $CaSO_4$ are well-studied sulphates of alkaline metals. One of the methods used to detect defects generated by irradiation with X-rays and high-energy photons in K_2SO_4 crystal is measurement of peaks of thermally stimulated

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luminescence (TSL). TSL arises in the irradiated K_2SO_4 crystal with electron-hole capture centers. In ionic crystals peaks of TSL spectra are used to measure the band gap of the crystal, i.e., the photon energy creating an electron-hole pair. As a result of localization of free electron-hole pairs, trapping centersare formed. In (Tokbergenov et al., 1999) it was shown that the gap in K_2SO_4 is 8.5–9.0 eV. These experimental results (Tokbergenov et al., 1999) were confirmed by the other authors (Kityk et al., 1996).

In (Byberg, 1986) it was assumed that the electron-hole capture centers arise when holes and electrons are captured by anionic complexes as a result of the following reactions:

$$\left(SO_4^{2-}\right)^* \rightarrow SO_4^- + e^-; \quad SO_4^{2-} + e^- \rightarrow SO_4^{3-}, \tag{1}$$

SO_4^- hole (Alybakov et al., 1983) and electron SO_4^{3-} trapping centers (Byberg, 1986) were detected by EPR.

In the formation of the energy band of alkali metal sulfates a special role is played by the anionic complex SO_4^{2-}. The upper part of the valence band taking part in electron transitions is determined by orbitals of the sulfate-anion $(2a_1)^2(2t_2)^6(1e)^4(3t_2)^6(1t_1)^6$ (Alybakov et al., 1983; Sholokh et al., 1985; Höjer et al., 1976). The lower part of the conduction band consists of unfilled orbitals $3a_1^x$ and $4t_2^x$ of the anion of SO_4^{2-} matrix. The upper part of the conduction band is formed bys states of the base cation.

Based on the measurements of the diffuse reflection spectrum of polycrystalline powders Na_2SO4, K_2SO_4 and $CaSO_4$ (Sholokh et al., 1985), and an analysis of theoretical calculations of the electron structure of the anion SO_4^{2-} (Höjer et al., 1976; Barber et al., 1980) the authors of (Sholokh et al., 1985) referred the detected reflection bands to two transition groups. The first group of bands at 5.1 eV, 6.9 eV and 10.5 eV was referred to electronic transitions of the molecular orbitals $1t_1$, $3t_2$, 1e, $2t_2$of SO_4^{2-} anion to the conduction band of the matrix formed bys states of the cation K^+, Na^+, Ca^{2+}.

The second group of bands at 4.4 eV, 6.0 eV and 9.8 eV is associated with intramolecular transitions from orbitals $1t_1$, $3t_2$, 1e, $2t_2$to free antibinding orbitals $3a_1{}^*$ and $4t_2{}^*$ of the anion SO_4^{2-}. Thus, on the basis of these results it can be assumed that the bandgap in sulphates of alkali and alkaline earth metals is about 4.4–4.5 eV. According to the calculations of the authors (Kityk et al., 1994) and the experimental data on the absorption spectra (Madi et al., 1998; El-Muraikhi, 2001), the band gap in $LiKSO_4$ crystals can be estimated as 5.5–6 eV. According to the calculations [6.7] and the experimental data (Sholokh et al., 1985) free electron-hole pairs in the alkali metal sulfates can appear at photon energies of 5.1 eV, 6.9 eV and 10.5 eV. The results obtained in (Sholokh et al., 1985) do not contradict the experimental results obtained in (Tokbergenov et al., 1999). In this paper, we studied the formation of defects in $LiKSO_4$ and K_2SO_4 crystals upon excitation by ultraviolet photons with energies in the range of 4–6 eV at a temperature of liquid nitrogen.

2. Experiment

K_2SO_4 crystals were grown from the saturated aqueous solution by slow evaporation at a temperature of 50 °C. $LiKSO_4$ crystals were grown at 40 °C from the aqueous solution of Li_2SO_4, K_2SO_4 and H_2O in a ratio of 1:1:1. The crystal growth started when a few drops of sulfuric acid were added to the initial solution. 5 mm-thickplates, 10–15 mm in diameter, were cut from the crystals.

The samples were irradiated by a X-ray tube BSV-23 with a copper anti-cathode, tube currents 10 mA, and voltage 45 kV. The glow of crystals was registered using a photomultiplier FEU-62. The luminescence spectra were measured using a monochromator MDR-41 and spectrofluorimeter SOLAR CM2203. The excitation and luminescence spectra were measured in the energy range 3–11.5 eV on the vacuum monochromator using Seya-Namioka scheme. A 240 W hydrogen flow lamp was used as a source of ultraviolet radiation.

3. Discussion of the experimental results

The formation of electron-hole trapping centers in $PbWO_4$ and $ZnWO_4$ crystals under the action of low-energy photons was demonstrated experimentally (Byberg, 1986). A specific feature of tungstates as compared with sulfates of alkaline earth metals is generation of free electron-hole pairs under the intracenter excitation of the molecular anionic complex WO_4^{2-}. In this paper we show that electron-hole trapping centers are created as a result of intracenter excitation of molecular anionic SO_4^{2-} complex by 4–6 eV photons.

Fig. 1 shows the TSL spectrum of $LiKSO_4$ crystal irradiated by X-rays (1) and photons with energies 6–6.2 eV (2) at the temperature of liquid nitrogen. Fig. 1 shows that the TSL peaks at 140–170 K and 220–230 K appear after X-ray excitation. After excitation by photons with energies 6–6.2 eV, broad TSL peaks in temperature ranges 140–175 K and 185–240 K appear. The appearance of TSL peaks in the same temperature range after excitation by X-rays and photons with an energy of 6–6.2 eV means that in both cases electron-hole trapping centers are formed.

Fig. 2 shows the spectrum of TSL peaks of $LiKSO_4$ crystal irradiated by photons at the temperature of liquid nitrogen. The crystal was exposed to equal numbers of photons in the energy range from 6 eV to 11 eV at the temperature of liquid nitrogen and heated at a rate of 0.2 K/s.

The process of formation of TSL spectrum was studied using the following method. The energy of the emitted photon was changed in the interval from 6 eV to 11 eV with a step of 0.1 eV. After each irradiation by photons (6.1, 6.2, 6.3 … eV), the crystal was heated and the TSL intensity was measured. Fig. 2 shows the dependence of intensity of individual TSL peaks on the photon energy. It shows that TSL peaks at 160–165 K, 185–190 K and 220 K are formed by photons from the same energy intervals, i.e. 6–6.4 eV, 7.4–7.6 eV, 8.8–9 –10 eV and 9.8 eV. At these energies of photons, at the temperature of liquid nitrogen, free electron-hole pairs are formed in the $LiKSO_4$ crystal. These photon energies can somehow correlate with the reflection spectrum of alkali metal sulfates, measured by

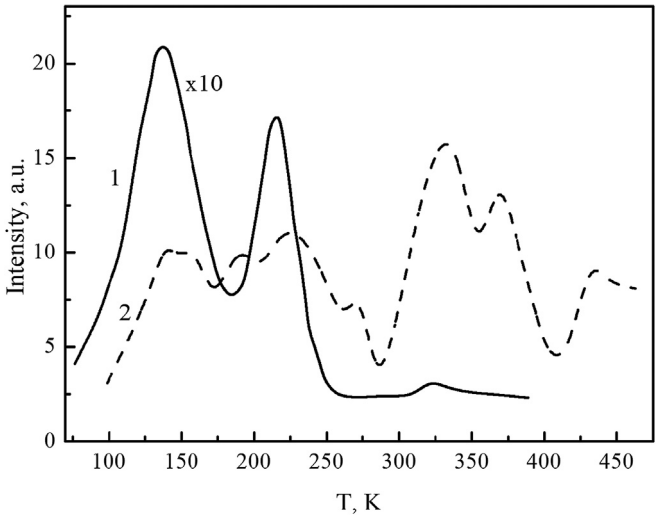

Fig. 1. TSL of $LiKSO_4$ crystal irradiated by X-rays(1) and 6–6.2eVphotons (2) at the temperature of liquid nitrogen.