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Review

Radiation defects in alkali metal sulfates

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HIGHLIGHTS

- The sulfates irradiated by energies 4–6.2 eV electron–hole capture centers are formed.
- TSL spectra in Na_2SO_4 and $KNaSO_4$ crystals confirms generation of electron–hole capture centers.
- Quantum chemical calculations modeling confirm the decay of the SO_4^{2-} anionic complex.

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ABSTRACT

Spectroscopic methods were used to investigate the mechanisms of formation of electron–hole capture centers in $KNaSO_4$ and $LiNaSO_4$ crystals by irradiation with ultraviolet (UV) light and photons with energies of 4–6.2 eV at 80 K and 300 K. We were the first who showed experimentally that the direct irradiation by photons with an energy of 4–6.2 eV at 80 K forms in $KNaSO_4$ and $LiNaSO_4$ crystals electron–hole capture centers registered in the measurements of TSL (thermo stimulated luminescence) and recombination radiation. During irradiation by photons, the electrons in $1t_1$, $3t_2$, 1e, $2t_2$ orbitals of SO_4^{2-}anion in the sulfate valence band are excited. From this state, the electrons recombine with the self-trapped hole (SO_4^{2-}) radiatively or with formation of defects. Quantum chemical calculations modeling the decay of the anionic complex confirm energy possibility of such processes.

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1. Introduction

In alkali metal sulfates irradiated by X-ray radiation, gamma radiation and ultraviolet (UV) photons with energies above 9 eV, the process of formation of radiation-induced defects is explained by subthreshold mechanisms. Such defects as SO_4^-, SO_3^-, SO_2^-, $O^-$and O_3^- are created during relaxation of intrinsic electron excitations. All these defects were detected in the irradiated alkali metal sulfates by the methods of electron paramagnetic resonance (EPR). It was assumed that the radicals SO_4^-, O_3^- and O^-refer to hole trapping centers (Hariharan and Sobhanadri, 1969; Alybakov et al., 1983; Sanyal et al., 2010; Nair et al., 1997). The nature of SO_3^- and SO_2^- radicals was not identified unambiguously. From the experimental results of (Hariharan and Sobhanadri, 1969; Alybakov et al., 1983; Sanyal et al., 2010; Nair et al., 1997; Nurakhmetov et al., 2006, 2014)it follows that the main intrinsic trapping centers are formed during radiolysis of the SO_4^{2-} ion in irradiated sulfates of alkali and alkaline earth metals. On the basis of theoretical calculations and

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experimental data on the measurement of reflection and absorption spectra in K_2SO_4 and $LiKSO_4$ crystals, the width of the energy gap was estimated (Nair et al., 1997; Nurakhmetov et al., 2006; Sholokh et al., 1985; Tokbergenov et al., 1999; Madi et al., 1998; El-Muraikhi, 2001).

For K_2SO_4 (Kityk et al., 1994, 1996) the width of the energy gap was about 9 eV, however, there are the experimental data (Sholokh et al., 1985) on measurement of the reflection spectra for K_2SO_4 powders where the band gap was about 4 eV. Calculated and experimental resultsfor the band gap for $LiKSO_4$ (Madi et al., 1998; El-Muraikhi, 2001; Kityk et al., 1996) gave practically the same values of about (5.8–6.2) eV. If defects are created as a result of decay of intrinsic electronic excitations, then defects in sulfates must be created by irradiation by UV photons.

In our previous works (Nurakhmetov et al., 2014; Tokbergenov et al., 1999) it was shown that excitation by ultraviolet photons with energies greater than 9 eV causes formation of electron–hole trapping centers in K_2SO_4 crystals. Experimental observation of thermally stimulated luminescence (TSL) in the K_2SO_4 crystal irradiated by UV photons at 80 K is explained by the mechanism of generation of electron–hole trapping centers.

On the basis of quantum-chemical calculations and measurements of the diffuse reflection in a number of alkali metal sulfates the authors of (Sholokh et al., 1985; Höjer et al., 1976; Tossell and Gibbs, 1977; Barber et al., 1980; Andriyevsky et al., 2009; Sholokh et al., 1986) assumed that the highest filled states (valence band) were $1t_1$ states and the lowest empty states were $4t_2^*$ states (in the conduction band) of the SO_4^{2-}ion. It means that SO_4^{2-}ions in states $1t_1$, $3t_2$ and $2t_2$ take part in the formation of the upper part of the valence band.

The bands are wide with a clearly pronounced anisotropy in different directions. The conduction band in sulfates is formed by $4t_2^*$ and $3a_1$ states of anions and s-states of cations. An analysis of the results of radiative decay in the irradiated alkali metal sulfates shows that formation of defects or creation of electron–hole trapping centers is caused by the decay of excited anionic SO_4^{2-}complexes or ionization according to the reactions:

$$\left(SO_4^{2-}\right)^* \to SO_3^- V_a^+ e^- + O^0 \tag{1}$$

We assume that this is the most probable mode of decay of the anionic complex. During irradiation, the anionic complex can be ionized creating an electron–hole pair

$$SO_4^{2-} \to SO_4^- + e^- \tag{2}$$

The electron may be captured by the anionic complex

$$SO_4^{2-} + e^- \to SO_4^{3-} \tag{3}$$

As a result, the hole SO_4^- and electron SO_4^{3-}capture centers will be formed (Byberg, 1986).

These reactions may cause formation of defects. To determine the mechanism of creation of trapping centers or intrinsic defects it is necessary to study kinetics of these processes. In alkali metal sulfates, it is possible to selectively create low-energy electronic excitations. When low-energy excitations are relaxed, defects may be formed and radiation is emitted. The process of relaxation of low-energy excitations can be observed experimentally. The aim of this work is to study the mechanisms of formation of radiation defects in several sulfates when they are excited by photons with energies up to 6.2 eV.

2. Materials and methods

$KNaSO_4$ crystals were grown by slow evaporation (isothermal method) at a constant temperature of 42 °C in a saturated aqueous solution. The ratio of salt to 100 g of the solvent was 66.7 g of Na_2SO_4 and 33.3 g K_2SO_4. To encourage the growth of crystals in solution is added sulfuric acid (to give pH = 2–3).Chemical analysis of the crystals showed that they contain sodium and potassium atoms in a ratio of moles of 1:1. For the experiment, samples were prepared in the form of a plane–parallel plate of optical quality in size 5 × 5 × 1 mm^3.

Used in the experiments $LiNaSO_4$ monocrystals were grown by slow evaporation at a temperature of 40 °C from a saturated aqueous solution containing 100 grams of 18.3 g and 14.7 g of Li_2SO_4 Na_2SO_4, which was added a few drops of sulfuric acid

The objects were irradiated in the X-ray tube BSV-23 with a copper anti-cathode and a tube current of 10 mA and 45 kV. The glow of crystals was registered by the photomultiplier tube FEU-62. Luminescence was measured using a monochromator MDR-41 and spectrofluorimeter SOLAR CM2203. Luminescence and excitation spectra in the energy range (5–11) eV were measured on a vacuum monochromator BMP-2, assembled by the Seya–Namiokas scheme in the Institute of Physics of the University of Tartu. As the UV light source, a 240 W flow-type hydrogen lamp was used. In this research, we studied radiation defects of $KNaSO_4$ and $LiNaSO_4$ crystals under excitation in the spectral range 4–6.2 eV.

3. Result and discussion

Based on theoretical calculations of the electron structure of the SO_4^{2-}anion (Höjer et al., 1976; Tossell and Gibbs, 1977; Barber et al., 1980) and measurements of reflection and absorption

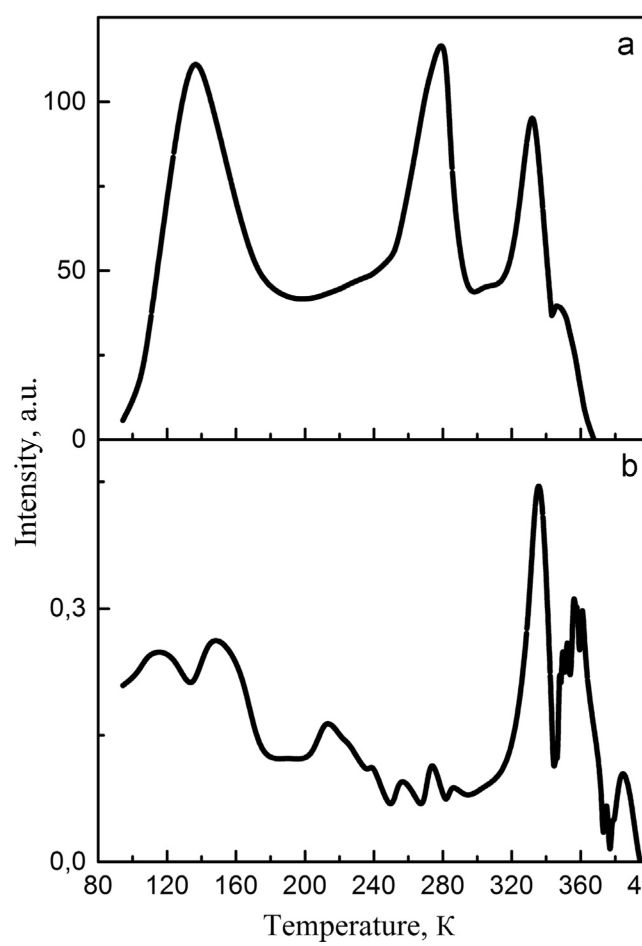

Fig. 1. TSL spectrum of $KNaSO_4$ crystal irradiated by X-rays (a) and photons with energy (6–6.2) eV (b) at a temperature of liquid nitrogen.