



ELSEVIER

Contents lists available at ScienceDirect

Journal of Luminescence

journal homepage: www.elsevier.com/locate/jlumin

Review

Intrinsic luminescence in alkali metal sulfates



T.N. Nurakhmetov, K.A. Kuterbekov, D.H. Daurenbekov*, Zh.M. Salikhodzha,
A.Zh. Kainarbay, A.M. Zhunusbekov, K. Bekmyrza

L.N. Gumilyov Eurasian National University, 13 Munaitpasov str., Astana 010000, Kazakhstan

ARTICLE INFO

Article history:

Received 29 July 2015

Received in revised form

26 October 2015

Accepted 30 October 2015

Available online 11 November 2015

Keywords:

Intrinsic luminescence

Ultraviolet photons

Thermally stimulated luminescence

Electron-hole trapping centers

ABSTRACT

For the first time, the nature of intrinsic luminescence of Na_2SO_4 and LiKSO_4 crystals at 80 and 300 K excited by ultraviolet photons with energy of (4–6.2 eV) is studied. During the excitation of sulfates by low-energy photons, the electrons on the bonds become excited. These electrons can be found in the conduction band formed from the free states of cations or $3a_1^*$ and $4t_2^*$ orbitals of SO_4^{2-} anion, also placed in the conduction band. As a result of the electrons transfer, holes are formed in the bonds or orbitals, which move from the valence band to the bandgap as SO_4^- radicals. Localized holes correspond to different local states. A special feature of this study is the appearance of several bands within the broad radiation band (4–2 eV), efficiently excited at photon energies (5.5–6.2 eV). It is supposed that the observed excitation spectra in spectral regions around 5, 5.5 and (6–6.2) eV of intrinsic luminescence of LiKSO_4 crystal correspond to transitions of electrons from e terms $1t_1$, $3t_2$, e, $2t_2$ of the ground state of the SO_4^{2-} ion. Intrinsic luminescence with several maxima occurs as a result of recombination of the excited electron in the conduction band with localized holes SO_4^- .

© 2015 Elsevier B.V. All rights reserved.

Contents

1. Introduction	9
2. Materials and methods	10
3. Experiment	10
4. Results and discussions	10
5. Conclusion	12
References	12

1. Introduction

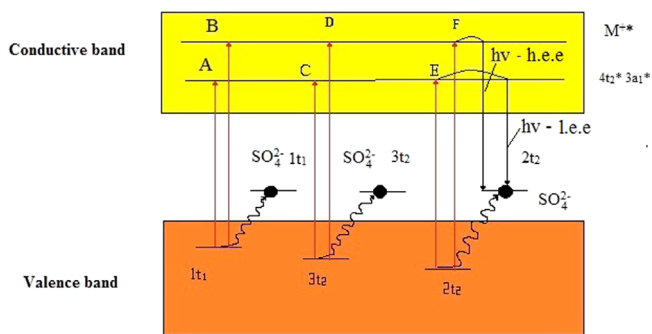
Research on self-radiation of alkali metal sulfates under the action of X-ray and synchrotron radiation has been addressed in a limited number of papers. Out of all ion-molecular crystals with tetrahedral anions most studied are sulfates of alkali and alkaline-earth metals (AEM). AEM activated by rare-earth ions are used as active elements in thermoluminescent dosimeters. In these systems, the nature of self-radiation transmitting energy from its own matrix to the radiator (impurity) is insufficiently studied. To understand the nature of self-radiation in alkali metal sulfates it is necessary to know not only their electron states but also their

absorption or reflection spectra over a broad spectral range. The electron configuration of the ground state of the sulfate anion SO_4^{2-} is $\dots 2(a_1)^2(2t_2)^6(1e)^4(3t_2)^6(1t_1)^6$ [1].

The first unfilled molecular orbitals, as it is described in [1], are free orbitals $3a_1^*$ and $4t_2^*$. The authors in [2] referred the reflection spectra to two groups of transitions, based on the measurements of the diffusion reflection of Na_2SO_4 and K_2SO_4 powders, theoretical calculations of the electron structure of the SO_4^{2-} anion [1,3,4] and the experimental data [5,6]. The first group of bands B (5.1 eV), D (6.8–6.9 eV) and F (10.5 eV) was referred to ionization of molecular orbitals $1t_1$; $3t_2$; $1e$; $2t_2$ of the SO_4^{2-} ion. These bands are caused by the electron transition from the molecular orbitals of the anion to the conduction band of the matrix formed by state Na^+ and K^+ cations. The second group of bands was referred to the following intra-molecular transitions: $3t_2 \rightarrow 4t_2$ $^*3a_1^*A$

* Corresponding author.

E-mail address: duke.ddx@yandex.ru (D.H. Daurenbekov).



Scheme 1. Band diagram where M^{**} are metal cations (Li^+ , K^+ , Na^+), ACE are levels of intramolecular on transitions, BDF are levels of ionized electrons of SO_4^{2-} , h.e.e is high energy emission, l.e.e is low energy emission.

(4.4 eV); $1e \rightarrow 4t_2^*C$ (6.0 eV); and $2t_2 \rightarrow 4t_2^*$, $3a_1^* - E$ (9.8 eV) in the SO_4^{2-} ion. In this case the reflection bands arise as a result of electron transition from $3t_2$, $1e$, $2t_2$ filled molecular orbitals of SO_4^{2-} to free $3a_1^*$ and $4t_2^*$ orbitals of the same SO_4^{2-} ion. Free orbitals $3a_1^*$ and $4t_2^*$ of SO_4^{2-} ion form the lower part of the conduction band of AEM (Scheme 1). Self-radiation of alkali metal sulfate should arise as a result of transition of electrons from the excited matrix state to molecular orbitals $1t_1$; $3t_2$; $1e$ or $2t_2$ of the SO_4^{2-} ion. Therefore, the spectra must have a broad emission band with several maxima.

The self-radiation of alkali metal sulfate in K_2SO_4 crystal at 4.2 K [6] was studied using a X-ray luminescence technique. A broad band emission with several maxima at 3.8, 3.1, 2.6 and 2.3 eV was registered. A shortwave band at 3.8 eV with the highest efficiency was observed in the area of fundamental absorption base. A long-wavelength luminescence with a rather high efficiency was observed in the area of the transparent base.

Calculations of the band structure made in [7,8] showed that the top of the valence band was formed by p-orbitals of oxygen. The upper part of the conduction band consisted of s-orbitals of the alkali metal cation, and the lower part of the conduction band was formed by unfilled oxygen p-states of $3a_1^*$ and $4t_2^*$ orbitals of SO_4^{2-} ion.

The authors in [7,8] estimated that the bandgap for crystal $LiKSO_4$ was about 5.8 eV, and for crystal K_2SO_4 it was equal to 8–9 eV. The results of calculations were confirmed by the measurement of the absorption spectra of the crystal in the spectral range from 6.2 eV to 1.5 eV [9,10]. A broad emission band with maxima at 3.9 eV after excitation by synchrotron radiation with photon energy of 9.3 eV was registered in K_2SO_4 crystals [11]. The authors measured the excitation spectrum of the emission band at 3.8 eV. The emission band at 3.8 eV was more efficiently excited at photon energy from 9 to 9.6 eV and less effectively excited in the photon energy range 6.4–7.8 eV. It is assumed that the emission band is formed as a result of recombination of an electron with a self-trapped hole [11,12].

The results of studying of intrinsic luminescence of alkali metal sulfates show that when they are excited by X-rays and synchrotron radiation with energies of 9–10 eV, a broad emission band with a maximum at 3.9 eV appears, which is excited in the fundamental domain of the matrix, where excitons or electron–hole pairs are created. Excitons or electron–hole pairs must be created as a result of ionization of molecular orbitals $1t_1$, $3t_2$ and $2t_2$ of the SO_4^{2-} anion.

In this research we studied the nature of intrinsic luminescence caused by the action of ultraviolet photons with energy of 4–6.2 eV. In this case $1t_1$, $3t_2$ and $2t_2$ molecular orbitals of SO_4^{2-} ion must be excited. We assume that these ultraviolet transitions transfer energy from its own matrix to emitters (impurities) in

dosimetry and scintillation materials. For example, the energy of excited states in alkali metal sulfates can be efficiently transferred to the admixtures of rare-earth ions Ce^{3+} , Dy^{3+} , Eu^{3+} in $SrSO_4$ and $CaSO_4$ crystals [13].

2. Materials and methods

The inorganic scintillator based on sulfates of alkali metals, having a composition in pts. wt: Na_2SO_4 - 65.5, is obtained by dissolving the latter ingredients in water in the ratio of 1:1. As a result, a saturated aqueous sulfate solution is formed, which is further heated to 38 °C. Crystals are synthesized at the same temperature by isothermal evaporation. To provide initial nucleation and stimulation of crystal growth of a complex sulfate, 5–7 drops of sulfuric acid (to obtain pH4–6) are added to the solution. Fabricated crystals of the inorganic scintillator of size (6–8 mm) had a form of bipyramids.

$LiKSO_4$ crystals were grown at temperature of 40 °C from the water solution of Li_2SO_4 , K_2SO_4 and H_2O in ratio of 1:1:1. The crystal growth begins after pouring of a few drops of sulfuric acid in the initial solution. The crystals grown without admixtures were colorless and had a form of bi-pyramids. For use in the scintillation block (in combination with a photomultiplier tube) plates of a thickness of 5 mm and (10–15 mm) in diameter (10–15 mm) were cut from the crystal.

3. Experiment

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 of (3–5.11 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 intrinsic luminescence spectra of Na_2SO_4 and $LiKSO_4$ under excitation in the spectral range of 4–6.2 eV.

4. Results and discussions

In the previous works [6,10–12,14–17] we and other authors studied self-radiation of the K_2SO_4 and Na_2SO_4 crystals under the illumination with X-ray, synchrotron and ultraviolet 6–11 eV radiation in a wide temperature range. In the present study, we investigated self-radiation of Na_2SO_4 and $LiKSO_4$ crystals after excitation by low-energy photons of energies in the range from 4 to 6.2 eV.

To confirm the fact that photoluminescence of studied sulfates is caused by its fundamental properties (rather than random impurities), we measured X-ray luminescence of the crystals at 80 K and 300 K and results are depicted in Fig. 1 (Na_2SO_4 crystal). Fig. 1 shows an asymmetric emission band consisting of short-wave and long-wave radiation (1 and 2, respectively).

Fig. 2 shows photoluminescence of Na_2SO_4 crystal excited by 5.5 eV photons at 300 K (curve 1) and 80 K (curve 2). The width of the photoluminescence band is almost the same as the bandwidth of X-ray luminescence. The intensity of individual bands within the wide radiation band changes depending on the temperature and energy of the excitation photon. When the crystal is excited by

Download English Version:

<https://daneshyari.com/en/article/5398667>

Download Persian Version:

<https://daneshyari.com/article/5398667>

[Daneshyari.com](https://daneshyari.com)