

PAPER • OPEN ACCESS

Radiation defects in sulfates of alkali and alkaline-earth metals creating at excitation by ultraviolet photons

To cite this article: T N Nurakhmetov *et al* 2018 *J. Phys.: Conf. Ser.* **1115** 052037

View the [article online](#) for updates and enhancements.

You may also like

- [Synthesis and Characterization of \$\text{Li}\(\text{Co}_{0.8}\text{Ni}_{0.2}\)\text{PO}_4\$ Cathode for Li-Ion Aqueous Battery Applications](#)
Manickam Minakshi, Neeraj Sharma, David Ralph et al.
- [Glycine-Assisted Sol-Gel Combustion Synthesis and Characterization of Aluminum-Doped \$\text{LiNiVO}_4\$ for Use in Lithium-Ion Batteries](#)
A. Sivashanmugam, R. Thirunakaran, Meijing Zou et al.
- [Amorphous Lithium Nickel Vanadate Thin-Film Anodes for Rechargeable Lithium Microbatteries](#)
Seung-Joo Lee, Heon-Young Lee, Tae-Seok Ha et al.



The Electrochemical Society
Advancing solid state & electrochemical science & technology

242nd ECS Meeting

Oct 9 – 13, 2022 • Atlanta, GA, US

Early hotel & registration pricing
ends September 12

Presenting more than 2,400
technical abstracts in 50 symposia

The meeting for industry & researchers in

BATTERIES
ENERGY TECHNOLOGY
SENSORS AND MORE!



ECS Plenary Lecture featuring
M. Stanley Whittingham,
Binghamton University
Nobel Laureate –
2019 Nobel Prize in Chemistry



Radiation defects in sulfates of alkali and alkaline-earth metals creating at excitation by ultraviolet photons

T N Nurakhmetov, B M Sadykova, Z M Salikhodzha, A M Zhunusbekov,
A Zh Kainarbay, D H Daurenbekov and K B Zhanylysov

L.N. Gumilyov Eurasian National University, 2 Saptayev Str., Astana, 010008,
Kazakhstan

E-mail: batsaiy_s@mail.ru

Abstract. X-ray luminescence, photoluminescence, and vacuum ultraviolet spectroscopy have been used to study the nature of intrinsic luminescence and the formation of electron-hole trapping centers in a LiNaSO₄ crystal in a broad spectral range at a temperature of 15-300 K. Based on the measurement of the spectrum of creation of intrinsic luminescence and recombination radiation at electron-hole trapping centers, the minimum energy of creation of electron-hole pairs is estimated, which determines the width of the band gap in the new model of the band structure, LiNaSO₄. It is assumed that the appearance of intrinsic luminescence and the formation of capture centers are associated with low-energy transitions from the 1t₁ orbitals of the valence band of the anionic complex to the s-state of the cation in the conduction band.

1. Introduction

Defect formation in irradiated sulfates of alkali and alkaline-earth metals is associated with the dissociation of the anionic complex SO₄²⁻ [1-3]. The main radiation defects are formed during the decay of the excited anionic complex SO₄²⁻ or in the localization of electrons and holes on anionic complexes. In the formation of the band structure of alkali and alkaline-earth metal sulfates, the electronic structure of the anion complex SO₄²⁻ plays a special role.

On the basis of measuring the reflection spectra [4, 5] and theoretical calculations [6-8] and experimental measurements of diffuse reflectance spectra in alkali metal sulfates, authors [9] have proposed electronic transitions corresponding to the reflection bands in the spectral range from 4 to 12 eV. In work [9] the band structure of alkali metal sulfates is proposed in the following way: the upper part of the valence band participating in the electronic transitions consists of the 1t₁, 3t₂, 1e, 2t₂ orbitals of the anionic complex SO₄²⁻, the conduction band consists of unfilled orbitals 3a₁^{*} и 4t₂^{*} of anions SO₄²⁻ and s-state of the cation. Depending on the energy of the exciting photons, transitions from the 1t₂, 3t₂, 1e, 2t₂ orbitals of the anion SO₄²⁻ to the s-state of the cation or from the 3a₁^{*} и 4t₂^{*} orbitals of the anion SO₄²⁻ into the conduction band. On the basis of the measured reflection spectra, the authors of [9] assumed that these bands correspond to two groups of transitions from the valence band to the conduction band. Reflection bands at 5.1 eV, 6.8 eV, and 10.5 eV are associated with electronic transitions from the molecular orbitals 1t₁, 3t₂, 1e, 2t₂ of the anion SO₄²⁻ to the sulfate conduction band. The next three reflection bands at 4.4 eV, 6.0 eV and 9.8 eV are attributed to intramolecular transitions in the anionic complex SO₄²⁻.



The nature of the intrinsic radiation and creation of electron-hole trapping centers in the irradiated crystals of *LiNaSO*₄ have not been adequately studied.

The thermoluminescence properties of *LiNaSO*₄-Eu crystals under irradiation with gamma rays and ⁷Li ions with an energy of 24 and 48 MeV were studied in works [10, 11]. During the heating, the created defects recombine and the released energy is transferred to the impurities Eu³⁺. Luminescent properties and defect formation processes were investigated by irradiating crystals with X-ray and γ -radiation. It is known that irradiation with high-energy photons in alkali metal sulfates is dominated by the formation of electron-hole capture centers. The intrinsic radiation in this case has a recombination character. A recombination process, for example, X-ray luminescence, arises when electrons are recombined from local states with self-localized holes. Therefore, in many cases in alkali metal sulfates, the spectral composition of TSL and phosphorescence from the spectral position coincide with the X-ray luminescence spectrum [12]. The study of intrinsic luminescence and of capture centers must be carried out under irradiation with UV photons, which are create only low-energy electron-hole pairs and excitons.

For the experimental justification of the new model [9] of the band structure of alkali and alkaline-earth metal sulfates, it is necessary to investigate:

- the bands of intrinsic radiation in *LiNaSO*₄ corresponding to the electronic transition from the 1t₂ orbital of the valence band to the s state of the conductivity band of cations under selective excitation by photons (5.1÷6.2 eV) producing low-energy electron-hole pairs;
- recombination processes on electron-hole trapping centers, leading to radiation.

2. Objects and methods of research

The crystals of *LiNaSO*₄ were grown from a saturated aqueous solution by slow evaporation at a temperature of 50 °C. From the crystal, plates 3 to 5 mm thick were cut out. We studied samples of crystals and powders of *LiNaSO*₄ with a purity of 99.99%.

Crystals and powders of *LiNaSO*₄ were studied by the methods of photoluminescence, X-ray luminescence, vacuum-ultraviolet and thermoactivation spectroscopy.

Irradiation of the objects of investigation was carried out from the X-ray tube BSV-23 with a copper anode, the tube current was 10 mA, the voltage was 40 kV. The energy of the X-ray photon was 10-15 keV. For excitation in the ultraviolet region of the spectrum, a deuterium lamp D200VUV (Heraeus Noblelight, Germany) with a photon energy of 6.2÷11.5 eV and a XBO 150W xenon lamp (OSRAM, Germany) with a photon energy of 1.5÷6.2 eV was used.

The spectrometer Solar SM 2203 was used to measure the emission and excitation spectra in the spectral range 1.5÷6.2 eV. Measurements of the excitation and emission spectra in the spectral region 4÷11.5 eV were carried out on a vacuum monochromator assembled according to the Seya-Namioka scheme in a wide temperature range of 15÷400 K. The radiation of the crystals was recorded through the MDR-41 monochromator using a photomultiplier tube 1P28 (Hamamatsu, Japan). The excitation spectrum is corrected for the spectral distribution of the intensity of the exciting radiation.

3. The experimental results and discussion

In our previous works [12] in *K*₂*SO*₄ и *Na*₂*SO*₄ crystals, emission bands at 3.65÷3.7 eV were detected. It was shown that these bands arise when electrons are recombined with self-trapped holes. In these crystals, longwave emission bands with several maxima in the spectral range from 2 to 3 eV were also found. It was assumed that these bands are associated with the creation of electron and hole trapping centers. Depending on the energy of the exciting radiation (X-ray and γ -rays, UV photons with energy 5÷11.5 eV) and the irradiation temperature, the maxima of the main emission band varied from 3.5 eV to 4.5 eV. In the same way, depending on the type and temperature of the irradiation, wide longwave emission bands with several maxima from 2 eV to 3 eV were created.

Figure 1 shows the emission spectrum of a *LiNaSO*₄ crystal measured at 300 K on a CM 2203 spectrofluorimeter. Under excitation by photons with an energy of 6.2 eV (figure 1, curve 1), a emission band appears with a maximum of 3.7÷3.8 eV and longwave emission bands 2.3÷2.4 eV,

2.6÷2.7 eV, 3.1 eV. It can be seen from figure 1 (curves 2, 3, 4, 5) that with a decrease in the energy of the exciting photon with the values of 5.9 eV, 5.6 eV, 5.4 eV, 5.1 eV and 4.96 eV, the intensity of the main emission band with a maximum of 3.7÷3.8 eV decreases several times.

At an energy of exciting photons of 4.96 eV, the emission band is almost not observed. According to the author's assumption [9], the minimum energy for creating electron-hole pairs in alkali metal sulfates was 5.1 eV (figure 1, curve 5). With a decrease in the intensity of the main emission band at 3.7÷3.8 eV, excitation in the energy range from 6.2 eV to 5.1 eV reduces in parallel the intensities of the long-wave emission bands at 3.1 eV, 2.6÷2.7 eV, 2.3÷2.4 eV. For the reliability of the obtained results, we investigated the pressed powders LiNaSO_4 with a 99.99% purity.

Figure 2 (curve 1) shows the emission spectrum of a pressed powder under photons excitation with an energy of 6.2 eV. It can be seen from figure 2 (curve 1) that an emission band with a maximum of 3.7÷3.8 eV and long-wave emission bands at 3.1 eV, 2.6÷2.7 eV and 2.3÷2.4 eV appears. With a decrease in the energy of the exciting photon from 6.2 eV to 5.1 eV, the intensity of the main emission band at 3.7÷3.8 eV decreases to a minimum. In parallel with the main band, the intensities of long-wave emission bands at 3.1 eV, 2.6÷2.7 eV and 2.3÷2.4 eV decrease. Thus, in particularly pure powder samples of LiNaSO_4 the following regularity is appear: the decreases intensity of the main band at 3.7÷3.8 eV, depending on the energy of the exciting photon from 6.2 eV to 5.1 eV.

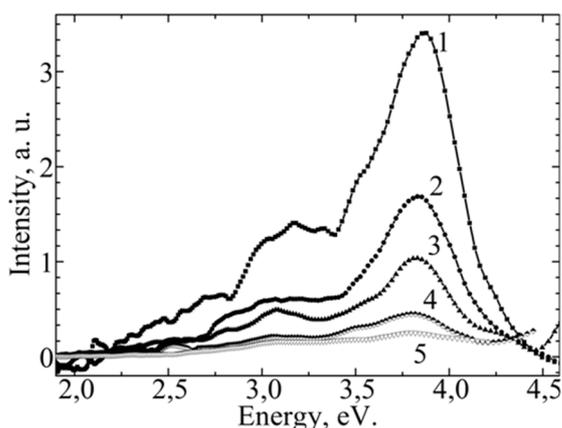


Figure 1. The emission spectrum of an irradiated crystal LiNaSO_4 at 300 K under excitation by photons with an energy: 1) 6.2 eV; 2) 5.9 eV; 3) 5.64 eV; 4) 5.4 eV; 5) 5.16 eV.

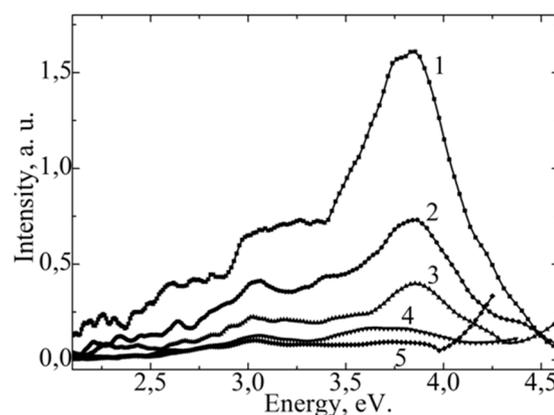


Figure 2. The emission spectrum of irradiated pressed powder LiNaSO_4 with a purity of 99.99% at 300 K under excitation by photons with an energy: 1) 6.2 eV; 2) 5.9 eV; 3) 5.64 eV; 4) 5.4 eV; 5) 5.16 eV.

Figure 3 shows the excitation spectrum of the main emission band at 3.7÷3.8 eV. Figure 3 (curve 1) shows that the emission band is effectively excited in the spectral range 5.4÷6.2 eV. Indeed, the main emission band begins to appear at an excitation photon energy of 5.4 eV. The longwave emission band 2.8÷3.1 eV is effectively excited in the spectral region 4.6–6.2 eV and 3.9÷4.2 eV (curve 2). The excitation spectrum of the long-wave emission band at 3.1 eV is represented by curve 3. It can be seen that this emission band 3.1 eV is excited with greater efficiency at a photon energy of 9–11.5 eV, and also at a photon energy of 5.2–7 eV.

Figure 4 (curve 3) shows the emission spectrum of LiNaSO_4 under excitation by photons with an energy of 4.1 eV. It can be seen from the figure that the emission band at 2.8÷3.1 eV is excited at photon energies of 4.1 eV. Emission at 2.8÷3.1 eV is excited in the transparency region of the LiNaSO_4 crystal. According to the authors' assumption [9], the minimum energy for creating electron-hole pairs in alkali metal sulphates should be 5.1 eV. The excitation of emission at 2.8÷3.1 eV in the

fundamental region $5.1\div 6.2$ eV should be associated with the creation of this electron-hole capture center during irradiation.

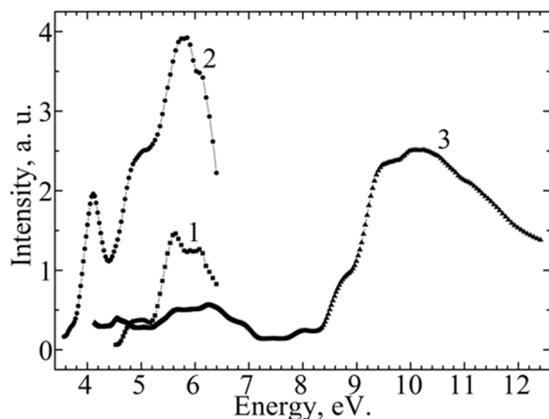


Figure 3. Excitation spectrum of the crystal LiNaSO_4 excitation spectrum for the emission band: 1) $3.7\div 3.8$ eV at 300 K; 2) 3.1 eV at 300 K; 3) 3.1 eV at 15 K.

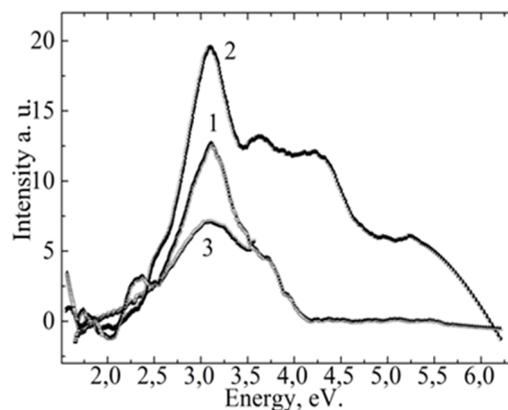


Figure 4. The emission spectrum of the crystal LiNaSO_4 . 1) X-ray luminescence at 80 K; 2) photoluminescence upon excitation by photons with an energy of 7.75 eV at 15 K; 3) photoluminescence upon excitation by photons with an energy of 4.1 eV at 300 K.

Figure 4 (curve 1) shows the X-ray luminescence of a LiNaSO_4 crystal at 80 K. It can be seen from the figure that the main emission band is $3.7\div 3.8$ eV does not release as a separate band. The total maximum of X-ray luminescence is 3.5 eV. In many cases, when the alkali metal sulfates excited by X-rays, the main $3.7\div 3.8$ eV and the longwave emission bands ($2.8\div 3.1$ eV) are not separately identified. In the case of X-ray excitation, when a high concentration of electron-hole pairs is created, the main part of the emission comes out under recombination of localized electron-hole pairs. In many sulphates, after stopping X-ray irradiation, we observed phosphorescence [12]. This means the creation of electron-hole trapping centers. In the same figure 4 (curve 2), the emission spectrum of a LiNaSO_4 crystal under excitation by photons with an energy of 7.75 eV. It can be seen from figure 4 (curve 2) that the contour of the emission band is similar to the contour of the X-ray luminescence band (curve 1). Primary emission at $3.7\div 3.8$ eV and long-wave emission with maxima at 3.1 eV and 2.6 eV is appeared (figure 4, curve 2).

On the basis of our experimental data, in accordance with the new model of the band structure of alkali and alkaline-earth metal sulfates, the appearance of the main emission bands and the formation of electron-hole trapping centers in LiNaSO_4 occurs as a result of the following electronic transitions:

- as a result of excitation by photons with an energy of $6.2\div 5.1$ eV, electrons transfer from the $1t_1$ orbitals of the valence band to the s orbitals of the cation in the conduction band, electron-hole pairs with a starting energy of $5.1\div 6.2$ eV should be created;
- as a result of the relaxation, emission appears at $3.7\div 3.8$ eV; with a decrease in the energy of the exciting photon, the emission intensity decreases at $3.7\div 3.8$ eV; at a photon energy of 5.1 eV, the process of creating electron-hole pairs stops, which is the new fundamental boundary of the forbidden band;
- at high energies excitation of 6.2 eV, generated electron-hole pairs create electron-hole trapping centers; with a decrease in the energy of the exciting photon to 5.1 eV, the emission intensity decreases at $3.1\div 2.8$ eV;
- under excitation by high-energy photons with an energy more than 7.75 eV, electronic transitions from the $1t_2$, $3t_2$, $1e$ orbitals of the valence band to the s orbitals of the conduction band should be

- performed. A large number of electron-hole pairs with high energy are created in the matrix; the efficiency of the formation of capture centers increases;
- therefore, under UV excitation or X-rays, the efficiency of formation of electron-hole trapping centers increases; this should lead to an increase in long-wave emission bands at 3.1 eV, 2.6 eV, and 2.3 eV;
 - we assume that creation of intrinsic emission that arise when electrons are recombined with localized holes, it is necessary to create low-energy electron-hole pairs with an optimal density.

4. Conclusions

On the basis of experimental studies of the nature of the intrinsic radiation and processes of creation of trapping centers for LiNaSO₄, the following results confirm the new model of band structure of alkali and alkaline earth metal sulfates:

- a joint change in the intensity of the intrinsic radiation and recombination radiation at the capture centers with a gradual decrease in the energy of the exciting photon from 6.2 eV to 5.1 eV indicates a unified nature of the appearance of intrinsic luminescence and the formation of trapping centers;
- a comparison of the intensity of recombination radiation 3.1 eV at the capture centers and intrinsic luminescence showed that when excited by X-ray and UV rays with an energy of 7.75 eV, the efficiency of the capture centers is greater than the intrinsic luminescence;
- it was established that for distinguishing intrinsic radiation it is necessary to excite a crystal with photons with an energy of 5.1÷6.2 eV with a lower density.

Acknowledgement

This work was supported by the Science Committee of Ministry of Education and Science Republic of Kazakhstan, Contract No.132, 12 marches 2018. AP05132165, AP05131725.

References

- [1] Danby R J, Boas J F, Calvert R L and Pilbrow J R 1982 *Phys. C: Solid State Phys.* **15** 2483
- [2] Sanyal B, Natarajan V, Chawla S and Sharma A 2010 *Radiation Measurements* **45** 899
- [3] Bakshi A, Bhaskar Sanyal, Joshi V, Bhide M, Natarajan V and Arun Sharma 2011 *Applied Radiation and Isotopes* **69** 254
- [4] Andriyevsky B, Kurlyak V, Romanyuk N and Ursul Z 1989 *Opt. Spectrosc* **66** 623
- [5] Andriyevsky B, Romanyuk M and Stadnyk V 2009 *Journal of Physics and Chemistry of Solids* **70** 1109
- [6] Kityk I, Kasperczyk J and Andrievskii B 1996 *Physics Letters A.* **216** 161
- [7] Höjer G, Meza-Höjer S and Hernández de Pedrero G 1976 *Chem.Phys.Lett.* **37** 301
- [8] Barber M, El-Issa B and Alan Hinchliffe J 1980 *Chem.Soc.Faraday Trans.* **2** 441
- [9] Sholokh V, Aleshkevich N, Syt'ko V, Perekalina Z, Baturina O and Brezina B 1986 *Prikladnoi Spektroskopii* **1** 70
- [10] Moharil S, Bodade S, Sahare P, Dhopte S, Muthal P and Kondawar V 1992 *Radiation Effects and Defects in Solids.* **127** 177
- [11] Salah N and Sahare P Awadhesh Prasad 2006 *Journal of Luminescence* **121** 497
- [12] Nurakhmetov T, Kuterbekov K, Salikhoja J, Kainarbay A, Zhunusbekov A, Pazylybek S and Bekmyrza K 2014 *Journal of Luminescence* **146** 243