

PAPER • OPEN ACCESS

Investigation of optical spectra of dielectric crystals

To cite this article: T A Koketay *et al* 2018 *J. Phys.: Conf. Ser.* **1115** 052005

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

Репозиторий КарГУ



IOP | ebooks™

Bringing you innovative digital publishing with leading voices to create your essential collection of books in STEM research.

Start exploring the [collection](#) - download the first chapter of every title for free.

Investigation of optical spectra of dielectric crystals

T A Koketay, A K Tussupbekova and E K Mussenova

Academician Y.A. Buketov Karaganda State University, 28 University Str.,
Karaganda, 100028, Kazakhstan

E-mail: katkargu@mail.ru

Abstract. Optical spectra of crystals oxyhalides of bismuth are investigated in this work. When measuring the transmission spectra of single crystals of oxyhalides of bismuth in the direction perpendicular to the layers, a large number of peaks associated with the occurrence of the interference pattern when light is reflected from the layers. The intense absorption band at 4.0 eV for BiOCl crystal has a doublet structure, in the case of the BiOBr crystal splitting is less pronounced. Upon excitation in the fundamental absorption region there photoluminescence spectra are investigated. The spectrum of luminescence of BiOCl crystal is not elementary and it consists of two bands of radiation. The presence in the excitation spectra and luminescence shortwave bands strongly depends on the degree of purity of the bismuth oxide is used in the synthesis oxyhalides of bismuth crystal. Thus, it allows to link the short-wave emission band with uncontrolled impurity, and long-wave – with its own glow crystal substrate.

1. Introduction

Two mechanisms are known for the formation of radiation defects in dielectric materials: electron and shock. The electronic mechanism of formation of radiation defects was developed in the 60's of the last century in the works [1, 2]. In oxide crystals (MgO, CaO, Al₂O₃, etc.), the electronic mechanism, as a rule, does not take place. In these materials, radiation defects are formed by the impact mechanism, which explains their high radiation resistance [3].

In complex sulfates, the mechanism of formation of radiation defects was considered in the works [4-6]. One of the first studies on the spectroscopy of impurity ions in crystals of ammonium halides and oxyhalides of bismuth and antimony was carried out at the Karaganda State University named after academician Y.A. Buketov under the guidance of T.A. Kuketayev and V. Yurov.

The Bi³⁺ and Sb³⁺ ions have an electronic configuration of the mercury atom and are related to mercury-like ions. In the homologous series, upon transition from Cl and Br, the absorption and emission spectra shift to the region of lower energies. This pattern is inherent in all mercury-like ions and is associated with an increase in the spin-orbit interaction upon transition to a heavier halogen. The oxyhalides of bismuth and antimony have tetragonal symmetry. The absorption spectrum should consist of three groups of bands corresponding to electronic transitions $^1S_0 \rightarrow ^3P_1$, $^1S_0 \rightarrow ^3P_2$ and $^1S_0 \rightarrow ^1P_1$. It is precisely this situation that is observed in our experiments. The splitting of the levels of the $3P_1$ state in a crystal field gives the experimentally observed doublet in the long-wave absorption spectrum [7].

At present, the optical properties of compounds containing ions with fn-configuration are widely studied in connection with the problem of stimulated emission. Questions arising in connection with



optical studies of crystals with f-ions are grouped around the following three directions: 1) the physicochemical conditions for the formation of activated crystals and the structure of activator centers; 2) energy schemes of activating ions in crystals; 3) processes occurring in the excited state [8].

A large number of studies around the world have been devoted to the study of calcium sulfate-based TLD. Calcium sulphate is used in many countries as a basis for thermoluminescent dosimetry (TLD) of the population. TLDs based on this compound have a record sensitivity at the moment to the level of background radiation.

Analysis of literature data showed that there is no clarity in the mechanisms of degradation processes of TLD based on calcium sulphate, therefore, we investigated the processes of recombination of charge carriers in such model dielectrics as potassium sulfate, ammonium halides, bismuth halide and antimony. From a brief review of earlier work and the current state of the issue, the first section outlines the tasks of the dissertation study [9].

2. Research Method

Growth of monocrystals of antimony oxyhalides was carried out by sublimation-condensation in closed vacuumed quartz ampoules. As a temperature sensor, platinum-platinum-rhodium thermocouples were used.

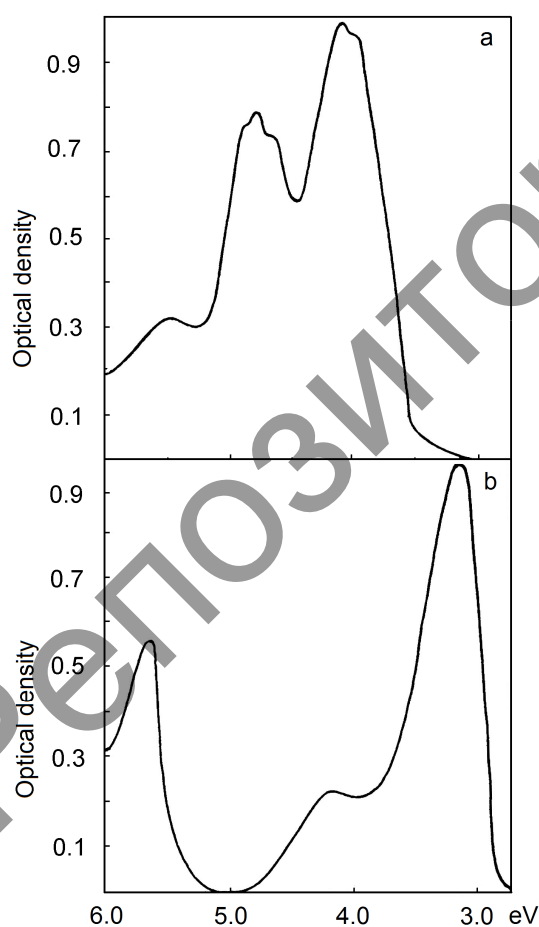


Figure 1. Absorption spectra of BiOCl (a) and BiOBr (b) at $T=300$ K.

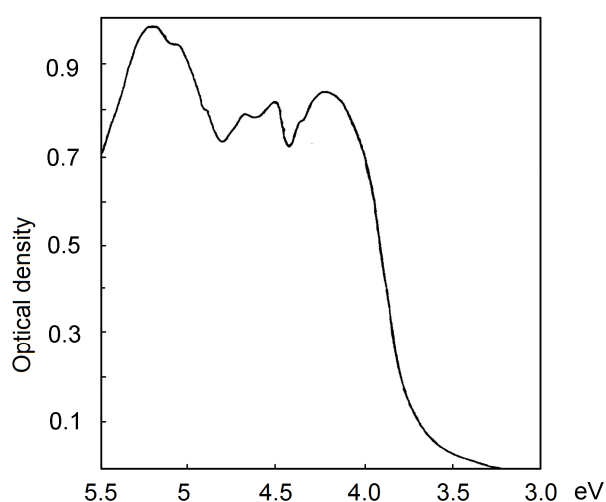


Figure 2. Absorption spectrum of $Sb_4O_5Cl_2$.

The temperature of the evaporation zone was from 500 to 550°C for oxychlorides and from 520 to 580°C for osbromide antimony. The temperature difference between the sublimation and growth zones was (20-25)°C. The growth time reached 5-6 days. Reducing the temperature difference to 20°C led to a decrease in the total number of crystals, an increase in their length to 3-5 mm, improved cutting and optical quality.

3. Result and Discussion

Figure 1 shows the absorption spectra of BiOCl and BiOBr. In the range 3.0-6.0 eV, in both cases, there are three absorption bands. The shape of these absorption bands is not elementary. The intense absorption band at 4.0 eV in BiOCl has a doublet structure. For a BiOBr crystal, the splitting of the absorption band at 4.0 eV is less pronounced.

When excited in the region of fundamental absorption of BiOCl and BiOBr crystals, photoluminescence arises [10]. The luminescence spectrum of BiOCl is non-elementary and consists of three bands. A shortwave band with a maximum of 3.1 eV does not disappear with an increase in temperature to 300-400 K, while the 2.4 eV band decays already at temperatures of 200-220 K. The excitation spectrum of the 2.4 eV band has a pronounced maximum at 3.75 eV. A short-wave band is excited in the region of 5 eV.

The presence in the excitation and luminescence spectra of the short-wave band depends strongly on the degree of purity of the bismuth oxide. Bismuth oxide is used in the synthesis of oxyhalides. In specially purified samples at low temperature, only a longwave band with a maximum of 2.4 eV is observed. Thus, the appearance of a short-wave luminescence band is associated with an uncontrolled impurity, and the long-wavelength luminescence band is associated with the intrinsic luminescence of the crystalline base.

The absorption spectrum of Sb₄O₅Cl₂ crystals is shown in figure 2. As in the case of bismuth oxyhalides in the energy range 3.0-6.0 eV, three non-elementary absorption bands are observed here.

On the decline of the long-wave absorption band, luminescence with a maximum of 2.54 eV and a maximum excitation band of 3.5 eV is effectively excited. The luminescence of Sb₄O₅Cl₂ crystals is already extinguished at $T=80$ K and completely damped at $T=180-200$ K.

4. Conclusion

Irradiation of bismuth oxyhalides with UV or X-ray quanta results in the appearance of a broad band in the decay of exciton absorption bands. Photostimulation in the band of induced absorption leads to the appearance of a luminescence band in the long-wavelength region of the spectrum. A change in temperature leads to broadening of the luminescence spectrum, however, the shift of the maximum of the band is insignificant.

References

- [1] Lushchik Ch B 1955 *Proc of the Inst of Phys and Astron of the Acad of Sci of the ESSR* 230
- [2] Lushchik Ch B, Vitol I K and Elango M A 1977 *UFN* **122** 223
- [3] Garlik G F and Gibson A F 1970 *Proc Ray Soc* **60** 574
- [4] Nurakhmetov T 2001 *Abstract of the thesis. fiz.-mat. Sci: 01.04.07* (Almaty: PhTI) p 23
- [5] Kim L M, Kuketayev T A and Orazbayev A Kh 1997 *Mater.of Intern. Conf. "Scientific and technological progress, the basis for the development of a market economy"* 15
- [6] Kuketayev T A, Murashova Z F, Kim L M and Sagyndykova G E 2003 *Book of abstracts. 12th International conf of the physics and chemistry of inorganic materials* 243
- [7] Perpetuo G I et al. 1991 *Phys Rev B* **45** 5163
- [8] Kudryavtseva I et al. 2015 *Physics of the Solid State* **57** 2191
- [9] Kim L M et al. 2009 *Eurasian physical technical journal* **1** 11
- [10] Koketai T A et al. 2014 *Book of abstracts. International conference of luminescence and optical spectroscopy of condensed matter* 39