Proceedings of the 15th Czech and Slovak Conference on Magnetism, Košice, Slovakia, June 17–21 2013

Anizotropy of Photoconductivity in BiOCl (X=Cl, Br, I) Single Crystals

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Oxyhalides of bismuth BiOX (X = Cl, Br, I) are very interesting materials which find various applications as X-ray luminescent screens, as anti-Stokes converters, photocatalyst, usual luminophors and as photoconductive analyzer of linear polarized radiation in the 0.24 – 1.2 μm spectral region. The great interest for these materials is strongly related to the influence of dimensionality on the behaviour of physical properties (they are 2D structured materials). Bismuth oxyhalides are one of the V-VI-VII group compound semiconductors belonging to the tetragonal system. The structure of BiOX is known to have a layered structure, which is constructed by the combination of the halide ion layer and the bismuth oxygen layer. We present results of the study of photoconductivity spectra anisotropy of the BiOX single crystals.

DOI: 10.12693/APhysPolA.126.274

PACS: 42.25.Ja, 42.70.Qs, 72.40.+w

1. Introduction

Oxyhalides of bismuth exhibit many intriguing and interesting properties such as photoluminescence, photoconductivity, and thermally stimulated conductivity [1]. The luminescent band at 1.6–2.2 eV is a result of capture of c-band free electrons by r-centres during recombination process. The shape of the absorption edge has been explained by the effect of the laminarity of these crystals. Previous investigations on the crystal structure and morphology of BiOX crystallites showed that they usually grow in the form of platelets with the c-axis normal to the platelets. Heat conductivity measurements as a function of temperature showed that the electronic component of heat conductivity is negligibly small, since the crystals are nearly insulators in the temperature range 90–300 K [1]. The BiOX single crystals are layered 2D structured materials.

2. Experimental details

The BiOX single crystals were grown by the chemical gas transport reactions method in the closed volume (typically of the order $10 \times 10 \times 0.5$ mm^3). The crystals exhibit tetragonal matlockite (PbFCl) type structure (space group $D_{4h}^7 - P\frac{4}{n}mm$; $Z = 2$). The trivalent Bi^{3+} ion is surrounded at one side by four oxygen ions and at the other side by five halide ions, four of which are in a plane, whereas fifth is situated on the fourfold axis. There is only one crystallographic site available for the trivalent ion and this site has C_{4v} symmetry.

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The lattice parameters of the crystals were determined by X-ray powder diffraction with a Si internal standard (high purity). The spectral dependences of the steady-state photocurrent (photoconductivity) were recorded using a LOMO MDR3 monochromator. Low temperatures were obtained by mounting the sample in an UTREKS continuous flow cryostat. The decay time measurements were performed using pulse UV-laser LGI-21 (pulse width 8-9 ns; excitation wavelength $\lambda = 0.337$ nm; filters UFS-2 and UFS-6 were used). The change in the intensity was done by a platinum reducer.

3. Results and discussion

The original specimens had a dark resistivity of $\rho_d = 10^{10}$ to 10^{11} Ω·cm and significant photosensitivity [1]. At a temperature 293 K the ratio ρ_d/ρ_{ph} (ρ_d is the resistivity in the dark, ρ_{ph} is the resistivity in the light) reached 10^3. When cooling the specimens to 90 K, there was a 3-4 orders increase in magnitude of the steady-state photocurrent with ratio $\rho_d/\rho_{ph} > 10^7$. The spectral dependence of the photoconductivity $\sigma_{ph}(h\nu)$ for a typical specimen of BiOCl recorded at 95 K (curve 1) and 293 K (curve 2) is illustrated in Fig. 1. In addition to the intrinsic maximum $h\nu_1 = 3.54$ eV (350 nm) which corresponds to the band gap of $E_g = 3.475$ eV at $T = 100$ K, a significant impurity photoconductivity is observed due to the transfer of an electron from the r-centre to the conduction band [1]. On heating, the main maximum is shifted towards the long-wave side at a rate of $dE_g/dT = -6.3 \cdot 10^{-4}$ eV/K, while the photoconductivity in both the impurity and intrinsic regions falls sharply. The depth of the level which produces the impurity photocurrent maximum was found to be $E_{cr}^0 = 2.2$ eV.

Next, we present results of the study of photoconductivity spectra anisotropy of the BiOX single crystals, obtained with the polarization of electrical vector $\boldsymbol{E}$ of the

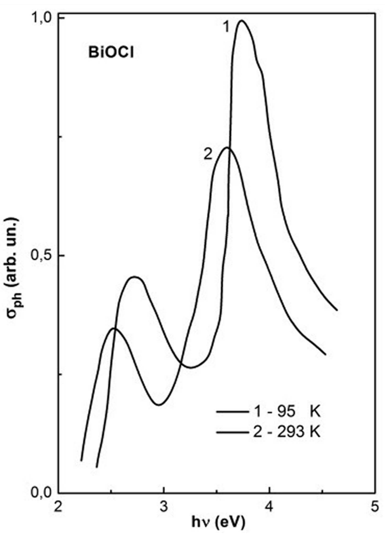

Fig. 1. The photoconductivity spectral dependencies of BiOCl single crystal.

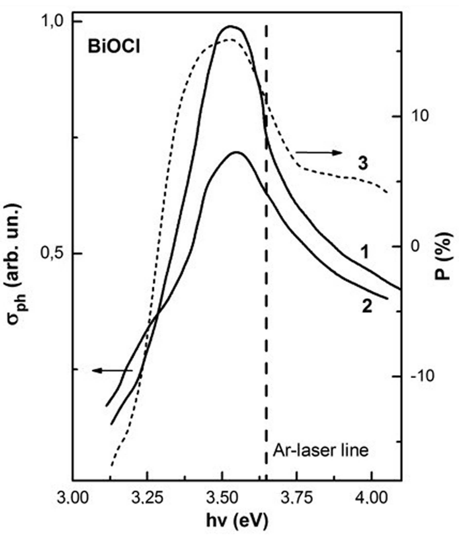

Fig. 2. Photoconductivity (1, 2) and photopleochroism (3) spectra of BiOCl single crystals at different light polarization and at temperature of 80 K.

electromagnetic wave parallel and perpendicular to each of the two axes ([100] or [010]) of the unit cell.

The BiOX compounds are broad-band (1.80 – 3.50 eV) photo-semiconductors. The maxima of their photoconductivity are in the interval of 0.24 – 1.2 mkm and their photosensitivities are $S = \sigma_{ph}/\sigma_d = 10^4$–$10^8$ (arb. units) at the temperature of 80 K (Fig. 2). The anisotropy of the photoconductivity spectra is believed to be the result of the layer matlockite-type (PbFCl) crystal structure of all bismuth oxyhalide compounds.

The coefficient of photopleochroism was calculated as

$$P = (I_{\parallel} - I_{\perp})/(I_{\parallel} + I_{\perp}) \cdot 100\%,$$

where $I_{\parallel}$ and $I_{\perp}$ are the photocurrent values at the $(E) \parallel [100]$ and $(E) \perp [100]$ light polarization, respectively.

The position of electrical vector $\boldsymbol{E}$ can be varied by rotating of the crystal. The change in light polarization at 90 degrees (from [100] to [010] crystallographic direction) leads to a change in the photoconductivity by approximately two orders of magnitude (Fig. 3).

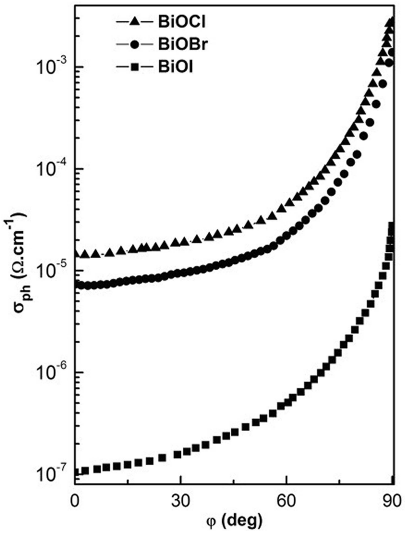

Fig. 3. Angular dependencies of photoconductivity of BiOX single crystals.

4. Conclusions

We investigated BiOX based photoresistors in the temperature range 80 – 400 K. We presented results of the study of photoconductivity spectra anisotropy of the BiOX single crystals. These materials are stable in air, and their parameters do not depend on the environment, which eliminates the need for sealing. The selectivity of BiOX spectral characteristics make them good radiation detectors of the nitrogen, argon and helium-cadmium lasers, as well as some of the semiconducting light-emitting diodes (LEDs). Crystal structure of the sample reduces the intrinsic noise of the radiation detector. Therefore, they can be used in optoelectronic circuits in conjunction with these lasers and LEDs.

Acknowledgments

This work was supported by the following projects: ERDF EU (European Union European regional development fond) grant under Contract No. 26220120005 and Development Agency contract No. APVV-0036-11.

References

[1] V. Bunda, S. Bunda, in: *Superconductors – properties, technology, and applications*, ISBN: 978-953-51-0545-9 Eds. Yu. Grigorashvili, InTech, Rijeka (Croatia) 2012, p. 323.