LIGHT DISPERSION IN BISMUTH GERMANATE CRYSTALS AND BISMUTH OXIDE FILMS

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The dispersion of light in \( \text{Bi}_4\text{Ge}_3\text{O}_{12} \) and \( \text{Bi}_{12}\text{GeO}_{20} \) single crystals and thin \( \text{Bi}_2\text{O}_3 \) films with a monoclinic structure was investigated in the visible spectral region. The parameters of a single-oscillator approximation have been found. It is established that in \( \text{Bi}_4\text{Ge}_3\text{O}_{12} \) crystals the absorption band caused by the \( \text{O}2\text{p}–\text{Bi}6\text{p} \) transitions makes the main contribution to the dispersion curve in the visible region, whereas in \( \text{Bi}_{12}\text{GeO}_{20} \) crystals this is made by transitions from the hybrid \( \text{O}2\text{p}–\text{Bi}6\text{p} \) states to the conduction band. The dispersion energy, the degree of the ionicity of binding, and the coordination number of the first coordination sphere of the \( \text{Bi}^{3+} \) cation have been determined.

Keywords: bismuth germanate, bismuth oxide, refractive index, dispersion.

Introduction. The interest shown in \( n\text{Bi}_2\text{O}_3–m\text{GeO}_2 \) compounds is motivated by their use in opto- and acoustoelectronics and also in recording ionizing radiation. The system contains a number of compounds, among which of greatest interest are compounds \( 2\text{Bi}_2\text{O}_3–3\text{GeO}_2 \) with a structure of the type of eulytine (4\( _3\text{m} \)) [1, 2] and \( 6\text{Bi}_2\text{O}_3–\text{GeO}_2 \) with a structure of the type of sillenite (23) [3, 4].

Although the optical properties of \( \text{Bi}_4\text{Ge}_3\text{O}_{12} \) and \( \text{Bi}_{12}\text{GeO}_{20} \) single crystals were investigated earlier (see, e.g., [5, 6]), the dispersion properties and their connection with the energy structure and crystal-chemical properties have not been studied in detail as yet. Investigation of these properties is rather urgent because it is known that the refractive index plays a decisive role in determining the resolving power of crystals, for example, in visualization of an ionizing radiation. Moreover, bearing in mind the wide application of these crystals, this study is not only of scientific but also of practical interest.

Since the optical-luminescent properties of bismuth germanates are mainly determined by the processes occurring in their constitutive parts, that is, bismuth-containing oxyanions [7], it is interesting to compare the results obtained with the results of investigation of \( \text{Bi}_2\text{O}_3 \). Since growing of \( \text{Bi}_2\text{O}_3 \) single crystals is a difficult problem, we used the results of investigation of thin \( \text{Bi}_2\text{O}_3 \) films, for purposes of comparison.

Experimental Technique. Bismuth germanate crystals with the structure of eulytine (\( \text{Bi}_4\text{Ge}_3\text{O}_{12} \)) and sillenite (\( \text{Bi}_{12}\text{GeO}_{20} \)) were grown by the Czochralskii method. Samples that were transparent up to 4.1 eV (\( \text{Bi}_4\text{Ge}_3\text{O}_{12} \)) and up to 3.2 eV (\( \text{Bi}_{12}\text{GeO}_{20} \)) and that had invisible defects were tested.

Thin \( \text{Bi}_2\text{O}_3 \) films of thickness 0.3–1.0 \( \mu \text{m} \) were obtained by the method of discrete evaporation in vacuum on fused quartz sublayers. After sputtering, the films were annealed in air and in vacuum at 500°C. As a result of \( x \)-ray diffraction investigations a polycrystalline monoclinic structure (\( \alpha–\text{Bi}_2\text{O}_3 \)) with predominant orientation in the (120), (223), and (033) planes has been revealed. Unannealed films had mainly an amorphous structure, relatively small transmission, and a blurred edge of the fundamental absorption.

The refractive indices \( n \) of the crystals investigated were determined on the basis of transmission spectra. The theoretical calculation in [8] showed that in this case the following relation is satisfied with rather high accuracy:

\[ n = 1 + \frac{\pi^2 \Delta \lambda^2}{\lambda^4} \]

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where $T_0$ is the transmission.

This formula allows one to calculate the value of $n$ from $T_0$ measured at the given wavelength. The transmission spectra of the Bi$_4$Ge$_3$O$_{12}$ and Bi$_{12}$GeO$_{20}$ crystals were measured on a Specord M40 two-beam spectrophotometer (Germany).

According to [9], for semiconducting and dielectric films, the Valeev method suggested in [8] is optimum for calculating the refractive index $n$, absorption coefficient $\alpha$, and film thickness $h$. It was used by us to determine the optical constant of thin Bi$_2$O$_3$ films. The transmission spectra of the films were also measured on a Specord M40 spectrophotometer.

**Results and Discussion.** The dispersion curves of the Bi$_4$Ge$_3$O$_{12}$ and Bi$_{12}$GeO$_{20}$ crystals are given in Fig. 1. The dependence of $(n^2 - 1)^{-1}$ on $\nu^2$ is presented in Fig. 2. It is seen that in the region with $\lambda > 400$ nm for the Bi$_4$Ge$_3$O$_{12}$ crystals and $\lambda > 500$ nm for the Bi$_{12}$GeO$_{20}$ crystals, the experimental results fall on a straight line.

The dispersion functions $n(\lambda)$ for thin Bi$_2$O$_3$ films of different thicknesses annealed in air and vacuum are given in Fig. 3. Figure 4 presents the dependence of $(n^2 - 1)^{-1}$ on $E^2$ for these films. In the spectral region of $\lambda = 600$ nm, the experimental points also fall well on a straight line. This indicates that the real part of the complex dielectric permeability $\varepsilon_1 = n^2$ in the region of transparency is described, with sufficient accuracy for both crystals and thin films, by a single-oscillator model [10]:

$$
\varepsilon_1(E) - 1 = \frac{E_0 E_d}{E_0^2 - E^2}.
$$

Here, $E_0$ is the energy of the absorption band which determines the course of the dispersion curve;

$$
E_d = \beta N_c Z_a n_e
$$

is a parameter called the dispersion energy; $\beta$ is a parameter depending on the degree of ionicity of the bond $f$, $\beta = 0.26$ (for ionic crystals) and 0.37 eV (for covalent ones); $N_c$ is the coordination number; $Z_a$ is the anion valency, and $n_e$ is the number of valence electrons per one formula unit.

Based on the found values of $n$ for the Bi$_2$O$_3$ films, we determined the density of packing of films $P$ as the ratio of the density of a film $\rho$ to the density of a bulk material $\rho_b$ [11]:

$$
P = \frac{\rho}{\rho_b} = \frac{n^2 - 1}{n^2 + 2 n_b^2 - 1},
$$