

MAGNETO-OPTICAL EFFECT IN $\text{Bi}_4\text{Ge}_3\text{O}_{12}$ SINGLE CRYSTALS DOPED WITH VANADIUM

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The results of magneto-optical effect measurements of undoped and vanadium doped $\text{Bi}_4\text{Ge}_3\text{O}_{12}$ (BGO) single crystals are presented. The absorption spectra of V-doped BGO samples, preliminarily illuminated with UV light as well as thermally annealed at 300°C, are compared. The modulation method with a vibrating polarizer was used to measure the magneto-optical rotation in the visible spectral range. The Verdet constant was calculated for all investigated samples, and plotted as a function of wavelength.

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1. Introduction

Bismuth Germanate crystals, known also as Eulytine, are colourless, transparent (from 300 to 6000 nm) and insoluble in water, with mechanical, chemical, thermal and radiation stability. They have found a wide range of applications such as scintillator materials for x-ray, γ -ray and particle detectors due to their room-temperature luminescence [1]; a solid state laser host matrix of rare-earth ions [2]; in opto-electronic devices as voltage and electric field sensors [3], as well as media for holographic data storage [4].

BGO crystals are isotropic and non-gyrotropic. They crystallize in $43m$ point group symmetry with a cubic structure, and have four chemical formula units in each cell. Each Ge^{4+} ion is coordinated by four oxygen ions arranged in a GeO_4 tetrahedron, and each Bi^{3+} ion is coordinated by six oxygen ions, forming a BiO_3 octahedron [5]. BGO has a large energy gap (4.14 eV), which appears to be a suitable matrix for extrinsic impurities such as transition metals or rare-earth elements. Furthermore, use of an appropriate dopant is an easy way to improve the photosensitivity and optimize the physical properties of BGO crystals for future practical applications.

In this paper we study the influence of vanadium on the optical properties and the magneto-optical effect in BGO crystals after preliminary thermal annealing or illumination treatments. Comparison with undoped BGO is also discussed.

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2. Experimental details

Nominally pure and V-doped BGO single crystals were grown by the Czochralski technique, using an automatic diameter-weight control method. Stoichiometric Bi_2O_3 and GeO_2 powders were mixed in the molar proportion 2:3. Vanadium was introduced into the melt as V_2O_5 oxide, and a doping element content of $7 \times 10^{18} \text{ cm}^{-3}$ was determined by atomic absorption spectroscopy.

Magneto-optical rotation was measured by the modulation method (φ -modulation) using a vibrating polarizer in the system Polarizer-Crystal-Analyzer (P-C-A). The transmitted signal through the P-C-A with φ -modulation depends linearly upon the angle between the P and the A, and the signal minimum can be exactly determined.

The magneto-optical rotation of undoped and V-doped BGO crystals is investigated in the vicinity of the absorption edge and in the transmission region where the ratio $\hbar\omega/E_0 \approx 0,1 - 1$ (E_0 is the edge energy) is valid. Therefore, the observed magneto-optical effect in BGO is determined principally by the interband rotation, conditioned by the dispersion at the fundamental absorption.

Since the photochromism in BGO crystals is associated mainly with the presence of dopants [6] (undoped BGO doesn't exhibit any measurable photochromic effect at room temperature), V-doped samples were studied in an annealed state (after thermal annealing at 300°C) and after a 15 minute exposure to a Hg lamp (we refer this state as a coloured state). The whole Hg spectrum was used, in order to take advantage of the maximum UV output. We limited our investigations to the saturation values of the coloration and the bleaching effects.

3. Results and discussion

Fig. 1 shows the optical absorption spectra of undoped and V-doped BGO crystals. The V-doped crystals were measured after illumination and after thermal annealing. The fundamental absorption edge is located at 4.1 eV, which corresponds to the inter-band transitions. As shown, vanadium addition shifts the optical absorption towards the visible spectral region in comparison with undoped BGO. Furthermore, the absorption coefficient for a V-doped crystal becomes larger after UV exposure (BGO:V - coloured state) and the effect is fully reversible - the sample recovered its transparency after thermal annealing (BGO:V - annealed state). We suppose that these absorption changes are probably due to the valence change transitions of vanadium ions $\text{V}^{2+/3+/4+}$ [7].

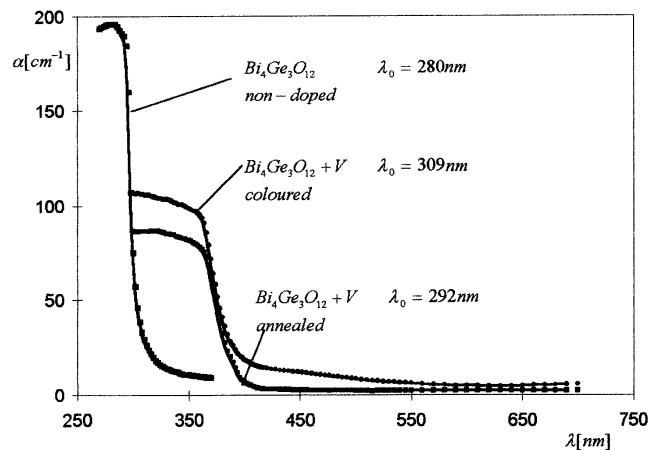


Fig. 1. Optical absorption spectra of undoped BGO and BGO:V in the annealed and coloured states.

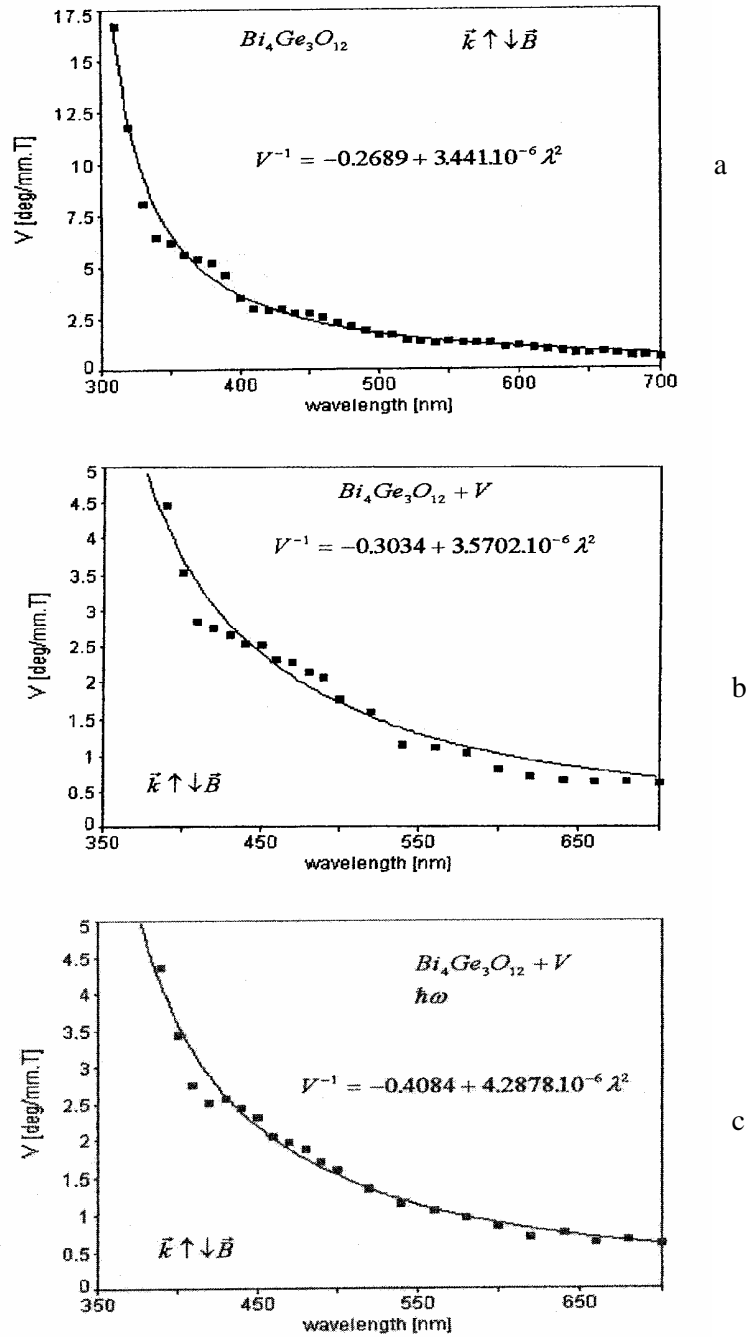


Fig. 2. Verdet constant as a function of wavelength. The symbols represent the experimental data, the solid lines are theoretical fits. (a) Undoped BGO; (b) BGO: V – annealed state;

(c) BGO:V - coloured state.

The results from the Faraday effect are analysed using the Bequerel formula [8]:

$$\varphi(\lambda) = \frac{A}{\lambda^2 - \lambda_0^2} \quad (1)$$

where A is a constant determined from the matrix elements of corresponding inter-band transitions, and λ_0 is the wavelength related to the inter-band transitions and corresponding to the natural frequency ω_0 of one harmonic effective oscillator. As seen from Fig.1, the λ_0 position for undoped BGO is located in the continuum 289-295 nm near to the absorption edge. However, in case of V-doping, the absorption edge is shifted to the longer wavelengths, which also causes the λ_0 shift. Furthermore, the λ_0 position depends on the initial state of the BGO:V crystals- $\lambda_{0 \text{ BGO:V coloured}} > \lambda_{0 \text{ BGO:V annealed}}$.

In addition, the Verdet constant as a function of the wavelength is calculated as

$$V = \varphi/B.d, \quad (2)$$

where d is the sample thickness and B the magnetic induction.

Figures 2 (a,b,c) show the dependence of the Verdet constant on the wavelength, where the symbols represent the experimental data and the solid lines are theoretical fits. As can be seen, the dependence is quadratic for all investigated samples. Deviations from the quadratic dependence (the step structure in the interval 350-450 nm for undoped and 400-500 nm for V-doped BGO) appear in the regions where the Urbach rule is fulfilled. We suppose that this step structure is probably due to exciton effects just before the absorption edge.

4. Conclusions

Undoped and V-doped bismuth germanate single crystals were successfully grown using the Czochralski technique, using the automatic diameter weight control method. Vanadium doping shifts the absorption edge to longer wavelengths in comparison with undoped BGO crystals. Furthermore, in the case of vanadium doping the optical behaviour depends on the initial state of the crystal. Magneto-optical rotation was precisely measured using the modulation method with a vibrating polarizer. The optical spectra were analysed and the wavelength of harmonic oscillator, due to the inter-band transitions, was determined. The spectral distribution of this oscillator depends on the initial state of the crystal: $\lambda_{0 \text{ BGO}} > \lambda_{0 \text{ BGO:V coloured}} > \lambda_{0 \text{ BGO:V annealed}}$. The Verdet constant was determined as a function of wavelength. The appearance of a step structure is assumed to be due to exciton effects just before the absorption edge.

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