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Optical and magneto-optical properties of $Bi_4Ge_3O_{12}$ doped with aluminium and manganese

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The magneto-optical effect and photochromism in Mn+Al co-doped $Bi_4Ge_3O_{12}$ single crystals are investigated in a wide spectral range. It is found that the photosensitivity of doped crystals is significantly shifted to the visible wavelengths. The Verdet constant is determined in two different states of the samples: the coloured state, obtained by exposure with ultraviolet (UV) light and the state developed after annealing at 400 ^oC. The spectra of the rotation angle are described by a sigmoidal function in the absorption range and by a quadratic function in the transmittance region. All doped crystals exhibit a strong photochromic effect at room temperature: this being fully reversible after thermal annealing or illumination with visible light. Annealing and UV exposure are used to modify the defect structure in the crystal lattice and thus influence the corresponding absorption bands.

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1. Introduction

Bismuth germanate $Bi_4Ge_3O_{12}$ (BGO) crystals (eulitine) are optically isotropic materials with a cubic structure (point group of symmetry *43m*). BGO crystals have attracted considerable attention due to the wide range of applications as holographic data storage materials [1,2], in opto-electronic devices as voltage and electric field sensors [3], as solid state laser host materials [4] as well as in dosimetry [5].

The properties of BGO crystals could be tailored for above applications by chemical modification using doping with different elements. For example, the transition metals occupy a special place among the impurities in eulitine because the BGO crystals doped with V, Mn, Co, acquire the properties of a photochromic material [6].

The influence of Mn+Al double doping on the optical and magneto-optical properties of BGO crystals after preliminary annealing and after ultraviolet (UV) exposure has been investigated in the present study.

2. Experimental

The pure and doped BGO single crystals were grown by a Cochralski technique, using the automatic diameter control method. Stoihiometric Bi_2O_3:GeO_2 powders were mixed in a molar proportion 2:3. Dopants were introduced to the melt solution during the crystal growth in the form of Al_2O_3 and MnO_2 oxides. The doping concentrations in the grown crystals were determined by inductively coupled plasma atomic absorption spectrometry as follows:

Mn = 5.10^{18} cm^{-3} ; Al = 7.10^{17} cm^{-3}.

The investigated crystals were about 1 mm thick and had double polished faces along the (100) direction. The transmittance spectra were measured from 210 nm to 1200 nm in the annealed state (after preliminary annealing to 400 ^oC) and the coloured state (after 30 min exposure to UV light) using a SPM-2 monochromator.

The magneto-optical rotation was measured using φ-modulation method in a wide spectral region. The φ-modulation was realized using a Polarizer-Crystal-Analyzer system with vibrating polarizer, i.e. (vP-C-A). P and A were placed in a crossed position before the beginning the P-vibration. The signal passing through the vP-C-A, for small angles between P and A, was a linear function. The rotation angle was measured by the minimum value of the signal. In this way the minimum could be determined by the crossing point of two straight lines [7]. The accuracy of the rotation angle determination using the φ-modulation was about ~0.1^o. The wave vector was antiparallel to the vector of the magnet induction ($\vec{k} \uparrow\downarrow \vec{B}$).

3. Results

3.1. Absorption

The spectra of the absorption coefficient measured from 210 nm to 1200 nm in the annealed and coloured states were calculated by the formula:

$$\alpha = \frac{1}{d} \ln \frac{I_0}{I} \quad (1)$$

where I_0 is the intensity of incident light on the crystal, I is the intensity of light that passed through the crystal and d is the sample thickness.

The absorption coefficient spectra shown in Fig.1. include part of the continuum (210-290 nm), the fundamental absorption edge (290-340 nm), the Urbach range (340-480 nm) and the transparent region (480-1200 nm).

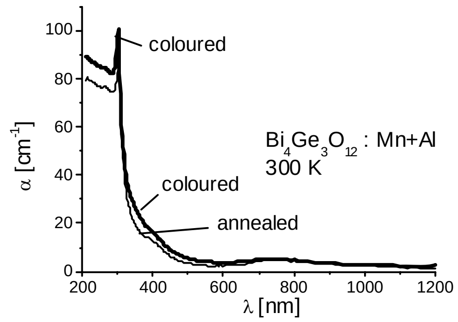

Fig.1. Spectrum of the absorption coefficient of Mn+Al co-doped BGO after illumination with UV light (coloured) and after heat treatment (annealed) state.

The coincidence of the absorption spectra in the coloured and annealed states shows that the photochromic effect is expressed in the continuum, at the absorption edge and in the Urbach range. Typical of the spectra of BGO doped with Mn+Al is a sharp peak at 300 nm. The knee which appears in the Urbach range at 400 nm can be related to the presence of Mn. Furthermore, the knee is weakly expressed in the spectrum in the coloured state. The maximum at about 750 nm is related to the Mn impurity [8].

3.2. Faraday rotation

The spectra of the magneto-optical rotation measured in the annealed and coloured states, using the φ-modulation method, are presented in Fig.2. The spectra contain part of the continuum, the absorption edge, plus the Urbach and the transparent range. As can be seen, considerable differences

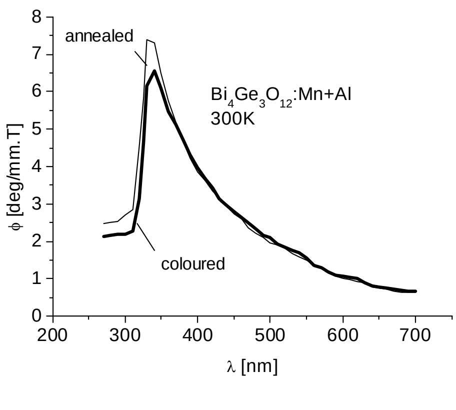

Fig.2. Spectrum of the rotation angle as a result of the magneto-optical effect in Mn+Al co-doped BGO in the coloured and annealed states

manifest themselves mainly in the absorption range. The investigation shows that the rotating angle reaches a maximum value in the Urbach range. The maximum value of the rotating angle divides the spectra into two sections: the absorption and the transparent section. The rotation angle in the absorption section is characterized by a value decreasing right at the fundamental edge and with a constant value in the continuum. This is a typical behaviour of the rotation angle in this section, as well as for doped and pure crystals [9]. The spectra of the rotation angle in the coloured and annealed states are described by a sigmoidal function (see Fig.3a, 4a).

The other section of the rotating angle spectra covers the transparent region. A quadratic dependence of the rotation angle on the wavelength is established in the transmission region, 380-700 nm (Fig.3b, 4b).

The section of the Urbach range from 340 nm to 380 nm cannot be interpreted in the framework of the above sigmoidal and quadratic dependences.

4. Discussion

It can be assumed that the sharp peak at 300 nm is conditioned by the Slater-Koster exciton which is localized around Mn^{+2} ions, and the knee at 400 nm is determined by absorption of the *3d* electrons of Mn.

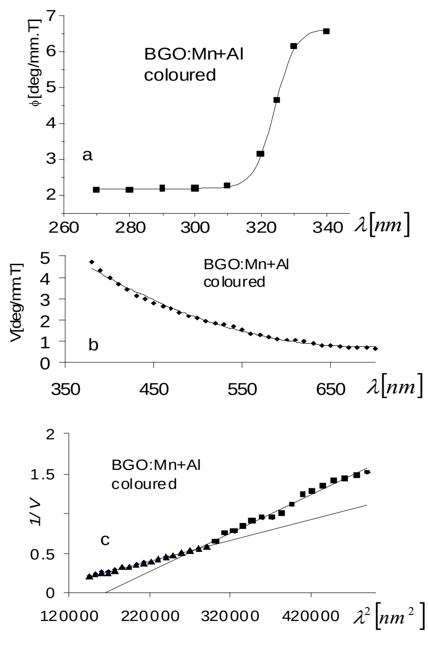

Fig. 3. Magneto-optical effect in coloured Mn+Al BGO crystal: a)Rotation angle in the absorption range described by a sigmoidal function in relation to λ;b) Verdet constant in the transparent region described by the quadratic function: $V = 4.10^{-5}\lambda^2 - 0.0538\lambda + 19.188$;
c) Linear sections in the dependence $V^{-1}(\lambda^2)$.

Faraday rotation manifests itself as a rotation of the polarization plane of the light passing through the sample in the presence of a magnetic field, and is characterized by the Verdet constant (V) of the crystal. The rotation angle φ can be expressed by the Bequerel formula:

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

where A is a constant determined from the matrix elements of the interband transitions, λ is the wavelength, and λ_o is the wavelength related to interband transitions and corresponding to the natural frequency ω_o of an effective harmonic oscillator.

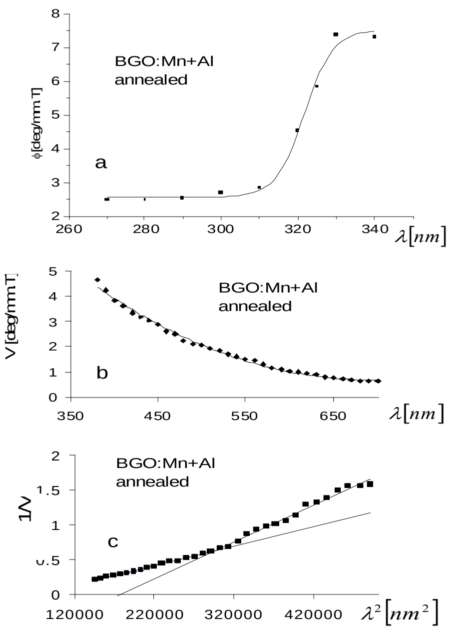

Fig. 4 . Magneto-optical effect in an annealed Mn+Al BGO crystal. a) Rotation angle in the absorption range described by a sigmoidal function in relation to λ; b) Verdet constant in the transparent region, described by the quadratic function: $V = 4.10^{-5}\lambda^2 - 0.0541\lambda + 19.176$ *; c)Linear sections in the dependence* $V^{-1}(\lambda^2)$.

The relationship between the rotation angle and the Verdet constant is:

$$V = \frac{\varphi}{B.d} \qquad (3)$$

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

The Verdet constant can be determined as a function of the wavelength only in the transparent spectral region, because there the rotation angle is conditioned by a magnet-induced circular birefringence, i.e. by induced magnetogyration.

The description of the Verdet constant of BGO: Mn+Al with a quadratic function (see Fig.3b, 4b) shows that the rotation angle in the transparent spectral region does not depend on the crystal state (coloured or annealed).

The dependence $V^{-1}(\lambda^2)$ is linear in the transmission region, in accordance with the Bequerel formula (1).

The linear sections, which are clearly demarcated in the curve in Figs. 3c and 4c can be associated with two effective harmonic oscillators corresponding to the two kinds of impurity in the crystal.

Faraday rotation in the transparent region is conditioned by the presence of free carriers. The concentration of the free carriers increases and reaches maximum value with approaching of the absorption edge.

The rotating angle in the absorption spectral range can be characterized as a combined effect strongly influenced by the absorption, i.e. by the interband electron transitions between the valence and conduction band.

Faraday rotation at the absorption edge, where band-band transitions occur, drops almost abruptly. This behaviour is unexpected.

5. Conclusions

The absorption spectra of $Bi_4Ge_3O_{12}$:Mn+Al crystals in coloured and annealed state have been measured from 210nm to 1200nm.

Spectra of the rotation angle in a magnetic field have been measured from 270nm to 700nm, using the φ-modulation method.

The spectra of the Verdet constant in the transmission spectral range were analysed using the Bequerel formula.

It was established that the spectra of the rotation angle in the range of the absorption edge and the continuum can be described using a sigmoidal function.

It was proved that differences in the Verdet constants for crystals in the coloured and annealed states cannot be observed in the transparent spectral region. The differences in the Faraday effect for both states manifest themselves only in the absorption range.

With the measured spectra of the Faraday rotation at the absorption edge and in the continuum of BGO (pure and Al+Mn co-doped), preconditions are created for an explanation of the influence of the interband transitions and the free electrons in the conduction band on the magneto-optical effect.

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