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## **Faraday Effect of BSO and BTO Crystals Doped with Cr, Mn and Cu**

The influence of both photochromic doping and photochromic transitions on the effect of magneto-optical rotation (Farady effect - FE) of undoped and doped with Cr, Mn and Cu  $\text{Bi}_{12}\text{SiO}_{20}$  (BSO) and  $\text{Bi}_{12}\text{TiO}_{20}$  (BTO) crystals is studied. The present results show, that Cr, Mn and Cu increase the FE. The influence of Cr, whose affect on the optical activity (OA) of BSO is most significant, here is too negligible (Verdet coefficient ( $V$ ) increases only with 1-2 % in the range 700 - 590 nm). The Mn-doping of BSO led to a  $V$ -increase with about of 11 % in the range 400 - 700 nm, as at 460 nm the relative increase of  $V$  reaches to about 30 %. The influence of Cu on FE in BSO (likely the case of the natural optical rotation) is again significant. Thus, the influence of  $V$  in the case of BSO:Cu is about 18 % in the range 700 - 480 nm as reaches 28 % in the shortwave region at 480 nm. However, in BTO:Cu (0.02 mol.% Cu) the influence of Cu is opposite in respect of both effects. Now the values of  $V$  increase with 21 % at 630 nm, 22 % at 590 nm, 42 % at 520 nm, and 73 % at 480 nm in comparison to BTO-undoped.

Keywords: faraday effect, photochromic, doping,  $\text{BiSiO}$ ,  $\text{BiTiO}$

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### **1. Introduction**

The sillenites with the structure of  $\text{Bi}_{12}\text{MO}_{20}$  (BMO - M: Si, Ge, Ti) are well known photorefractive materials (ARIZMENDI, CABRERA, AGULLO-LOPEZ; BOROWIEC). Their unique properties soon led to many applications in various technical areas: in surface acoustic wave (SAW) devices, in non-linear integral optics as reverse holographic recording elements (KEISSLIN, WENKE), phase-conjugated spatial-time light modulators (CASASANT, CAIMI, KHOMENKO), as correlators, photodetectors, optical interconnections and fork-joint on dynamic gratings, laser resonators (RAJBENBACH, HUIGNARD), etc.

Among the main sillenite's properties are the observed strong photochromic (TANGUAY et al.; BEREZKIN, KRASINKOVA; WARDZINSKI et al.; BOROWIEC, WARDZINSKI et al.) and magneto-optical (Faraday) effect (FE) (FELDMAN, BROWER, HOROWITZ). The first of them consists in the appearance of additional absorption bands at 410, 480, 530 and 850 nm after illumination with light with  $l < 540$  nm (MALINOVSKII, GUDAEV, GUSEV, DEMENKO). That additional absorption could be totally eliminated by heat treatment of the sample at 350 K, or (up to 95 %) by illumination at  $l > 540$  nm (the so-called "bleaching effect"). The second (Faraday) effect is related to the polarization plane rotation of a linear polarized light beam passes cross the crystal if a longitudinal (to the light beam) magnetic field is applied. Investigating both the natural optical and the magneto-optical rotation (FELDMAN, BROWER, HOROWITZ; BOER) establish a positive (in right direction) Faraday rotation in the sillenites. They show that the Faraday rotation is about 30% part from the natural optical activity of the

samples. Also, that the Wiedemann rule (FELDMAN, BROWER, HOROWITZ) (that treats the independence of the ratio “Faraday rotation/natural optical rotation”) holds only in the range of 20 %. The later authors (BURKOV, V., KRASILOV, YU et al.) investigate some other related materials as  $\text{Bi}_8\text{TiO}_{24}$ ,  $\text{Bi}_{48}\text{GaO}_{75}$  and  $\text{Bi}_{48}\text{ZnO}_{73}$ . They clarify the kind of the dispersion curves of the Verdet coefficient  $V$  in the spectral range 200 - 600 nm and establish that the differences in the values  $V$  for all studied materials (including BSO, BGO and BTO) are in the range of 8%. Working in room temperatures, the same authors obtain a better agreement between experimental data and theoretical calculations (1% differences) assuming that the nature of the Faraday effect in the sillenites is mainly diamagnetic one. Recently, some papers (BRIAT, TOPA et al.; MOYA, ZALDO et al.; RAMAZ, HAMRI et al.) studying the magnetic circular dichroism in sillenites, doped with photochromic dopands appeared.

Really, Mn, Cu and, especially, Cr strongly affect on the absorption spectra of BMO (PETROVA GOSPODINOV, SVESHTAROV). The doped crystals grow dark in colour and the absorption shoulder shifts to the long wavelength range of the spectra.

On the other hand, the influences of the illumination and annealing procedures are more expressive and the transmission spectra changes could be explained by charge transfer related to the dopant atom. However, the assumptions of the different authors are too contradictory. For instance (BEREZKIN, KRASINKOVA) and (WARDZINSKI, LUKASIEWICZ, ZMIJA) accept that the illumination of BSO:Cr provokes the transfer  $\text{Cr}^{3+}$  a  $\text{Cr}^{2+}$ , while (BOROWIEC, WARDZINSKI, LUKASIEWICZ, ZMIJA) find as acceptable the  $\text{Cr}^{4+}$  a  $\text{Cr}^{3+}$  transfer. On the other hand, by high accurate methods (magnetic circular dichroism and optical absorption) the authors (BRIAT, TOPA, LAULAN BODY, LAYNAY) find in BGO:Cr only  $\text{Cr}^{5+}$  and  $\text{Cr}^{4+}$  ions on Ge-sites. In the case of BMO:Mn the photochromic changes after illumination are attributed to the charge transfers  $\text{Mn}^{4+} \cdot \text{Mn}^{5+}$  (WARDZINSKI et al.; BOROWIEC, WARDZINSKI et al.; LIANG et al.),  $\text{Mn}^{4+}$  a  $\text{Mn}^{3+}$  (PANCHENKO, TRUSEEVA) or  $\text{Mn}^{2+}$  a  $\text{Mn}^{3+}$  a  $\text{Mn}^{4+}$  (VOLKOV, EGORISHEVA, KARGIN, SCORIKOV). At BMO:Cu the researchers (BOROWIEC; CHEVRIER et al.) accept as responsible for the crystal coloration (after illumination) mainly the charge transfer  $\text{Cu}^{2+}$  a  $\text{Cu}^+$ .

The illumination and annealing procedures also must be related to the appearance and disappearance of the paramagnetic centers  $[\text{BiO}_3+\text{h}]^3$  (h - hole), discussed in a previous our paper.

This article presents results on study of the Faraday effect in doped with photochromic Cr, Mn, Cu, bismuth silicate and titanate crystals. The influence of the illumination and the thermal treatment of the samples is investigated too. Some discussions about the magneto-optical rotation nature in the sillenites are made.

## 2. Experiment

Large BSO crystals with diameters up to 40 mm and length up to 60 mm are grown from melt by the Czochralski (CZ) method. The colour of the crystals from yellow (for the undoped BSO) became red for BSO:Cr, slight red (rose) for BSO:Cu and green for BSO:Mn. The obtained crystals are high optical homogeneous as the refraction index gradient  $\Delta n$  is smaller than  $10^{-4} \text{ cm}^{-1}$ . The concentration of the dopants Mn, Cu and Cr within the crystals is estimated by chemical absorption and emission spectral analyses with an accuracy of 5 %. The cut (perpendicular to the growth axis [100]) samples with thickness 1 mm are two-side polished, as plane parallel plates.

As a light source in the scheme a 250 W halogen lamp is used. After a modulator, the light beam enters a monochromator with diffraction grating of reciprocal dispersion of  $0.5 \text{ nm.mm}^{-1}$ . The exit beam is collimated and turned to the photodetectors, as consecutively

passes through polarizer, the measured sample, mirror and analyzer (extinction coefficients of the polarizers - 50 dB, aperture 8°). The samples is place between the poles of electro-magnet which creates longitudinal magnetic field with induction about 0.5 T. The analyzer devides the incoming beam into two beams with mutually orthogonal polarization, that turn to 2 Si-photodetectors (current in dark - 10 nA). The differential method and 45°-polarization scheme are preferred. The signal is amplified and registered by sensitive *lock-in amplifier*. Further, the signal inputs into computer, which is responsible for the work of the system and the calculations of the obtained data.

The spectral dependencies of the Verdet coefficient  $V$  is studied in the spectral range 480 - 1180 nm in undoped BSO, BGO and BTO crystals, also in BSO:Mn (0.8 mol %), BSO:Cr (0.03 mol %), BSO:Cu (0.02 mol.%) and BTO:Cu (0.02 mol.%). The ratio "signal/noise" is about  $6.5 \times 10^3$  and the relative error at measuring of the angle of the plane polarization rotation is about  $1.5 \times 10^{-2}$  %, respectively.

### 3. Results

#### 3.1 FE in undoped crystals

The magneto-optical rotation measurements in undoped BSO, BGO and BTO crystals show, that the values of  $V$  are in a very good agreement with the earlier works (FELDMAN et al.; BURKOV, KRASILOV et al.). The dispersion curves of  $V$  are too like to that ones of the optical rotatory power. They are very closed one of the other as the larger differences between  $V_{BTO}$ ,  $V_{BSO}$  and  $V_{BGO}$  are observed only in the shortwave region from 480 to 750 nm (Fig.1).

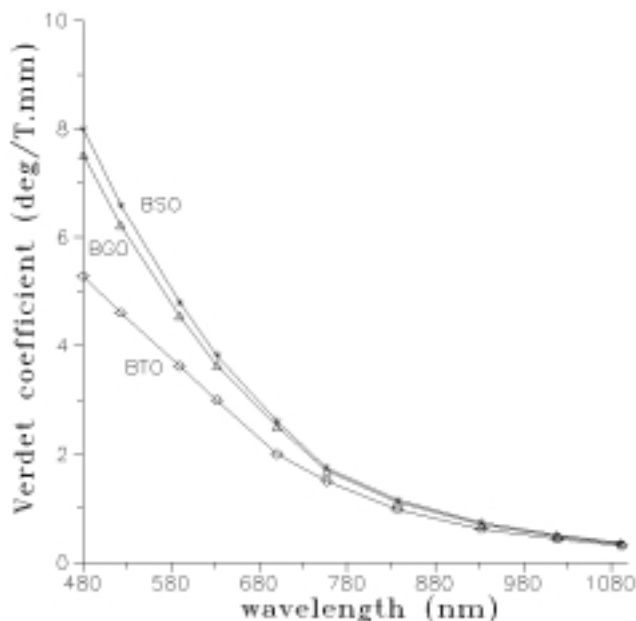


Fig. 1: Spectral dependence of the Verdet constant  $V$  of undoped  $\text{Bi}_{12}\text{SiO}_{20}$  (●),  $\text{Bi}_{12}\text{GeO}_{20}$  (Δ) and  $\text{Bi}_{12}\text{TiO}_{20}$  (○) crystals.

For instance, at 480 nm  $V_{BTO}$  is about 69% of  $V_{BGO}$  and 65 % of  $V_{BSO}$ . At 632 nm the percentages are 82 % and 78 %, at 932 nm - 88 % and 85%, and at 1100 nm - already they are 95 % and 92 %. Likely the case of the natural optical rotation,  $V_{BSO} > V_{BGO}$ , as in the whole studied range  $V_{BGO}$  is about 95 % of  $V_{BSO}$ .

### 3.2 FE in photochromic doped crystals

As a previous our study (TASSEV, GOSPODINOV, VELEVA) showed the photochromic dopands strongly influence on the natural optical rotation of the sillenites. The present results show, that Cr, Mn and Cu at the mentioned concentrations, as whole, increase the FE. The influence of Cr, whose affect on the optical activity (OA) of BSO is most significant, here is too negligible ( $V$  increases only with 1-2 % in the range 700 - 590 nm). Regretfully, below 590 nm the large absorption does not permit any measurement to be carry out. The Mn-doping of BSO led to a  $V$ -increase with about of 11 % in the range 400 - 700 nm, as at 460 nm the relative increase of  $V$  reaches to about 30 %.

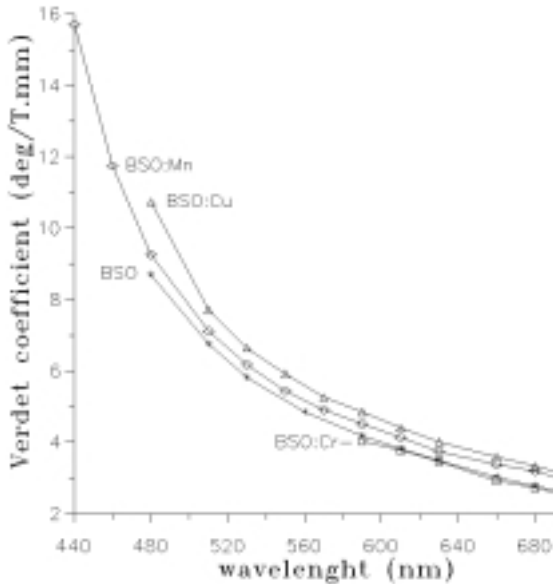


Fig. 2: Spectral dependences of the Verdet constant  $V$  of  $\text{Bi}_{12}\text{SiO}_{20}$  crystals, doped with Cr (0.03 mol %) ( ), Mn (0.8 mol %) (o) and Cu (0.02 mol.%) ( $\Delta$ ), in comparison with the undoped sample (.

The influence of Cu on FE in BSO (likely the case of the natural optical rotation) is again significant. Thus, the influence of  $V$  in the case of BSU:Cu is about 18 % in the range 700 - 480 nm as reaches 28 % in the shortwave region at 480 nm. However, in BTO:Cu (0.02 mol.% Cu) the influence of Cu is opposite in respect of both effects. Now the values of  $V$  increase with 21 % at 630 nm, 22 % at 590 nm, 42 % at 520 nm, and 73 % at 480 nm in comparison to BTO-undoped.

material	studied in the range [nm]	influence on $V$	relative $\Delta V/V$ aver.	changes [%] max./at
BSO	700 - 460	↑	5.3	1.0 / 460
BSO:Cr	700 - 550	↑	6.7	8.9 / 590
BTO:Cu	700 - 480	↑	0.9	5.6 / 480
BSO:Mn	700 - 510	↓	8.2	13.6 / 510
BSO:Cu	700 - 480	↓	1.4	5.0 / 530

Table 1: Influence of the annealing and the illumination on  $V$

### 3.3. Influence of the annealing and the illumination

Because of the great significance of the previous treatment of the material, initially,  $V$  is measured immediately after the sample annealing. An illumination with white light for about 20 min and a second measurement at constant other conditions followed (table 1).

The summarized results show that: (I) The illumination provokes increase of  $V$  of the undoped and Cr-doped BSO and BTO:Cu but it decreases  $V$  of BSO:Mn and BSO:Cr, as the influence is strongest for BSO:Mn and BSO:Cr and it is negligible at BTO:Cu and BSO:Cu (ii) The maximum changes of  $V$  are mainly at the short-wave region.

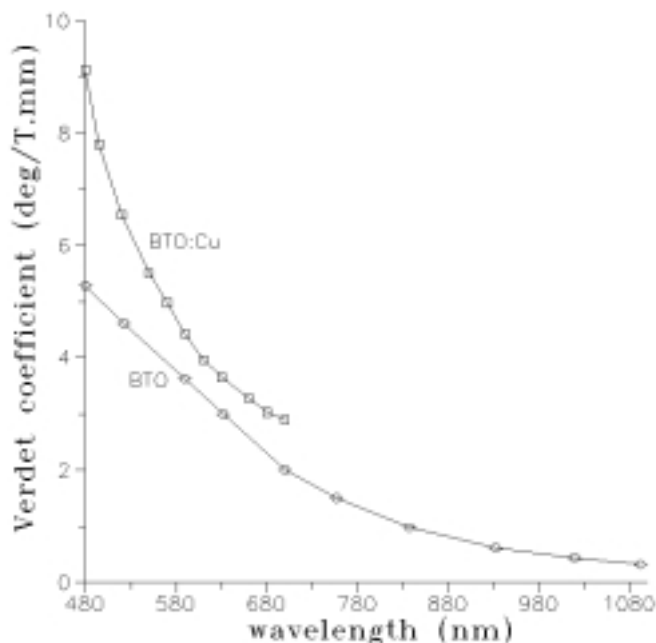


Fig. 3: Spectral dependences of the Verdet constant  $V$  of  $\text{Bi}_{12}\text{Ti}_{20}$  crystals, doped with Cu (0.02 mol.%), in comparison with the undoped sample (o).

## 4. Discussion and Conclusion

It is known (ABRAHAMS, JAMIESON, BERNSTEIN; PETROVA, GOSPODINOV, SVESHTAROV) that BSO possesses a cubic symmetry I23 including 99 different atoms in their cell, that are organized in two main structural units in the cell:  $\text{MO}_4$ -tetrahedra, that are placed in the apexes and in the center of the cube and connected by  $\text{BiO}_7$ -polyhedra as each tetrahedron is surrounded from 12 such polyhedra (BURKOV, VOLKOV, KARGIN). That means that two - Bi - O and M - O - oscillators are possible.

As our previous results showed (TASSEV, DIANKOV, GOSPODINOV) the Wiedemann's rule (FELDMAN, BROWER, HOROWITZ) (that treats the independence of the ratio "Faraday rotation/natural optical rotation" on the wavelength) holds well (in the range of 5 - 10 %) for undoped samples. At the doped crystals, it holds relatively well, only, in the case of BSO:Cr (in the range of about 30 %). This rule does not hold, especially, in the cases of Fe-doped crystals. These facts permit for explanation of the Faraday effect in the sillenite the so-called two-oscillator model to be accepted as more suitable. In that, the share of the Bi - O oscillator is accepted to be more determinative than the one of the M - O oscillator. However, the doping considerably changes the influence of the M - O oscillator. That

concerns, especially, the cases of BTO:Cu, BSO:Cu and BSO:Mn. The results show, that Cr (where the Wiedemann's rule holds relatively well) almost does not change the magneto-optical rotation of BSO. Hence, the conclusion, that the share of the Cr - O oscillator is not larger, or at least not much different from the share of the Si - O oscillator.

The results show that all dopants in the studied BSO samples increase  $V$ . That means, that any other M - O oscillators (excepting the Si - O oscillator) is more effective, with respect to the increase of FE in BSO.

Like the case of OA, the illumination of the undoped samples provokes a decrease of FE in these materials. However, the influences on the optical activity and the Faraday effect of some of the photochromic dopants (Mn, Cu) are opposite. That suggests a different share of the relevant photochromic transition in the forming of these optical rotation effects.

The measurements are carried out at room or close to room temperatures, in which the Zeeman splitting (whose result is the FE) is  $\Delta E \gg kT$ . Thus, at the mentioned temperatures, the nature of the magneto-optical rotation may be considered as mainly diamagnetic, as many other authors (BURKOV, KRASILOV et al.) accept, too. The studied influence of the annealing and illumination in air (with and without the paramagnetic center  $(Bi^{3+}O_3h)^3-$  (h-hole)) confirmed this conclusion. Really, as a previous our study showed the paramagnetic rotation is only about 3-5 % from the total FE in BSO.

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