Proceedings of the International Conference on Oxide Materials for Electronic Engineering (OMEE 2021)

Dispersion of Optical Activity of $Ca_3Ga_2Ge_4O_{14}$ Crystals

N. Ftomyn[a,*] and Y. Shopa[b]

[a] *Ivan Franko National University of Lviv, Drahomanov 19, 79005 Lviv, Ukraine*
[b] *Cardinal Stefan Wyszyński University in Warsaw, Dewajtis 5, 01-815 Warszawa, Poland*

Doi: 10.12693/APhysPolA.141.361 *e-mail: nazar.ftomyn@lnu.edu.ua

A high accuracy polarimetric method was used for measuring the values of the gyration tensor component g_{11} of $Ca_3Ga_2Ge_4O_{14}$ for various wavelength of light. A calculation technique based on the polarizability theory of optical activity was applied to determine the dispersion of the optical rotatory power for investigated crystals in a wide spectral region.

topics: optical activity, polarimetry, polarizabilities

1. Introduction

The $Ca_3Ga_2Ge_4O_{14}$ (CGG) crystals attract great interest from researchers as materials with a unique combination of physical properties such as dielectric, elastic, piezoelectric and luminescence [1, 2]. These crystalline systems belong to the space symmetry group $P321$ (the point group 32), with a single molecule per unit cell [3]. At the same time, a significant feature of these crystals is the disordering of their structure ($1a$ and $3f$ Wyckoff positions are partially occupied by Ga and Ge atoms) [3]. They are optically positive ($n_e > n_o$, with n_e and n_o being respectively the extraordinary and ordinary refractive indices) and optically active (the gyration tensor g_{ij} is diagonal, with two independent components $g_{11} = g_{22}$ and g_{33}) [2].

As a matter of fact, the dispersion of the optical activity (OA) in the direction that coincides with the optical axis of these systems is widely investigated (see, e.g. [2]) in contrast to information about optical rotation in the direction perpendicular to the optical axis (the spectral dependence and g_{11} tensor component are expressed in [2] only for $La_3Ga_5SiO_{14}$ and Cr-doped $Sr_3Ga_2Ge_4O_{14}$ crystals, which have the same type of the structure as CGG). The value of the gyration tensor component g_{11} for pure CGG crystals have been measured in [4] for wavelength of light $\lambda = 780$ nm using the HAUP-related (HAUP — High accuracy universal polarimeter) polarimetric method. In addition, the HAUP method is the precise and convenient technique for solving the mentioned crystal optics problems (see, e.g. [5, 6]).

It is well known that the OA should certainly be associated with structural properties of crystals, peculiarities of the orientation of the molecules, etc. [7]. As a result, the aim of the present work is to measure optical rotation in the direction perpendicular to the optical axis for 532 and 635 nm wavelengths of the CGG by means of high accuracy polarimetric measurements and calculate it using the calculus method [8]. Furthermore, the dispersion of the optical rotation could be obtained and analyzed.

2. Measuring and calculus methods

A single-wavelength laser polarimeter built on the basis of a PSA (polarizer–specimen–analyzer) system was used for our experiments. The resolution of a stepping motor-driven system used for rotating polarizer and analyzer was $\approx 1.34 \times 10^{-3}$ deg. Two high-quality Glan prisms served as polarizers. The light sources were the approximately 10 mW two lasers with wavelengths of light 532 and 635 nm. The intensity of light transmitted through the PSA system was measured with a low-noise photodiode using a 24-bit digital-to-analog converter. Making use of a thermo–optical effect and corrections for the specimen thickness, we could provide any desired phase difference for the fixed light wavelength in a wide temperature range (approximately 20–100°C). The temperature stabilization of our crystal specimen was better than 0.01 K. The absolute error of determination of the temperature was smaller than 0.5 K. A colorless CGG crystal plate of high optical quality had a thickness of 0.88 mm in our experiment.

The three characteristic azimuthal angles θ_0, θ_1, θ_2 of the incident light have been measured in the PSA system as functions of temperature. Then the differences $\Delta\theta_{ij}$ $(i, j = 0, \ldots, 2;\ i \neq j)$ have been

analyzed in order to determine the unknown optical parameters. The relation commonly used for the characteristic differences $\Delta\theta_{ij}$ can be expressed rigorously as [9, 10]

$$\Delta\theta_{01}\left(1-\cos(\Gamma)\right) = -2\Delta\theta_{12} = \left(2k-\gamma\right)\,\tan\left(\frac{\Gamma}{2}\right) - \delta\chi, \tag{1}$$

$$2\Delta\theta_{02}\,\tan\left(\frac{\Gamma}{2}\right) = -2\Delta\theta_{12}\,\cot\left(\frac{\Gamma}{2}\right) = 2k-\gamma-\delta\chi\,\cot\left(\frac{\Gamma}{2}\right). \tag{2}$$

Here $\Gamma = (2\pi/\lambda)\,d\Delta n$ denotes the phase difference of the light eigenwaves, d is the specimen thickness, Δn is the linear birefringence (LB), and λ is the light wavelength. The eigenwave ellipticity k is linked with the scalar gyration parameter $G{=}g_{ij}l_il_j$ ($l_{i,j}$ being the directional cosines and $g_{11}{=}2k\Delta n\,\bar{n}$, where $\bar{n}$ is the mean refractive index). Next is $\gamma = p - q$, where p and q are the parasitic ellipticities of the polarizer and analyzer, respectively. The angular systematic error is denoted by $\delta\chi$.

Notice that the characteristic azimuthal angles have been measured for the two specimen orientations in the PSA system, the second of which differs from the first by the rotation of the crystal by 90° around the direction of the beam propagation. This rotation of the specimen ensures a sign reversal for the Γ and k parameters [11].

In contrast, the computation method based on the classical polarizability theory of OA [8] can be successfully applied to determine the gyration and refractive parameters of inorganic, molecular, and ionic crystals. Optical rotatory power (ORP) can be calculated using the data of the structure of crystals and electronic polarizability volumes α' (i.e., $\alpha' = \alpha/(4\pi\varepsilon_0)$, where α — electronic polarizability, ε_0 — permittivity of free space) of individual atoms. As a result, the ORP $\rho(\boldsymbol{k})$ as a function of the wave vector $\boldsymbol{k}$ may be obtained using [8]

$$\rho(\boldsymbol{k}) = -\frac{e_{rij}k_r}{2nv}\,\mathrm{Im}\left(\sum_{SS'}(C_{SS'})_{ij}\right). \tag{3}$$

Here e_{rij} denotes the Levi–Civita symbol for $i,j,r = 1,2,3$, and n denotes the refractive index, v is the unit-cell volume, δ_{ij} means the Kronecker symbol, $C_{SS'}$ is complex tensors, and S is the index referring to different atoms in the crystalline structure.

We have created and applied software of our own for calculating the optical rotation of the investigated crystals, in contrast to well-known WinOPTACT [12]. The information about the electronic polarizability volumes of CGG crystals, as well as the data about the structures of the two enantiomorphic forms of these materials, have been expressed in [3, 4].

3. Experimental results

The temperature dependence of the $\Delta\theta_{01}$, $\Delta\theta_{02}$ and $\Delta\theta_{12}$ differences are displayed in Fig. 1 for $\lambda = 532$ and $\lambda = 635$ nm, respectively.

The experimental dependence of the function $\Delta\theta_{01}(1-\cos(\Gamma))$ on $\tan(\Gamma/2)$ measured at two different wavelength of light for two specimen settings in the PSA system are shown in Fig. 2a and b, respectively. The easiest way to determine the unknown k, γ, and $\delta\chi$ parameters is to apply the linear regression analysis to these data (the ellipticity k can be considered as independent of the temperature in the temperature region from 290 to 350 K) according to function in (1).

As can be seen in Fig. 2a and b, the angular systematic error changes its sign due to the rotation of the specimen in the PSA system. The average absolute values of these errors are presented in Table I. Finally, one can calculate the unknown parameters k and γ (Table I) from the slopes of lines for two angular positions of specimen (see (1) and Fig. 2). Furthermore, the error parameter $\Delta_{\mathrm{err}} = \Delta\theta_{01}\,(1-\cos(\Gamma)) + 2\Delta\theta_{12}$ in determining the differences between characteristic values (see (1)) is insignificant (see Fig. 2a, b).

As a result, applying data of the spectral studies of refractive indices [1, 2], i.e., $n_{\mathrm{e}} = 1.8307$, $\Delta n = 0.0240$, $\bar{n} = 1.8186$ (λ=532 nm) and $n_{\mathrm{e}} = 1.8198$, $\Delta n = 0.0244$, $\bar{n} = 1.8076$ (λ=635 nm)

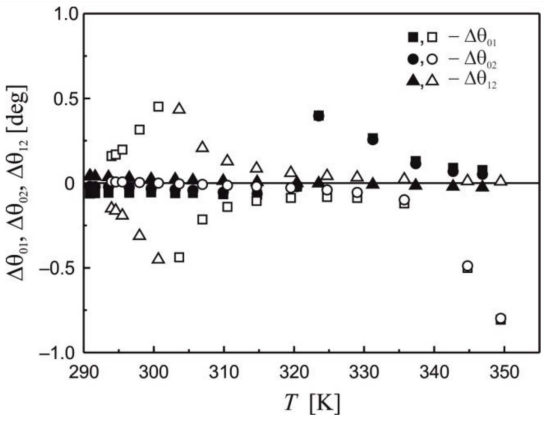

Fig. 1. Temperature dependence of characteristic differences for the CGG crystals as measured for one of the orientations of the specimen in the PSA system at 532 nm (open symbols) and 635 nm (solid symbols).

TABLE I

Experimental results of CGG crystals for two wavelengths of light.

Light wavelength [nm]	$\delta\chi$ ($\times10^{-5}$)	γ ($\times10^{-5}$)	k ($\times10^{-5}$)
532	10.9 ± 3.6	2.1 ± 0.9	70.7 ± 0.5
635	13.7 ± 0.8	5.2 ± 0.9	57.8 ± 0.5

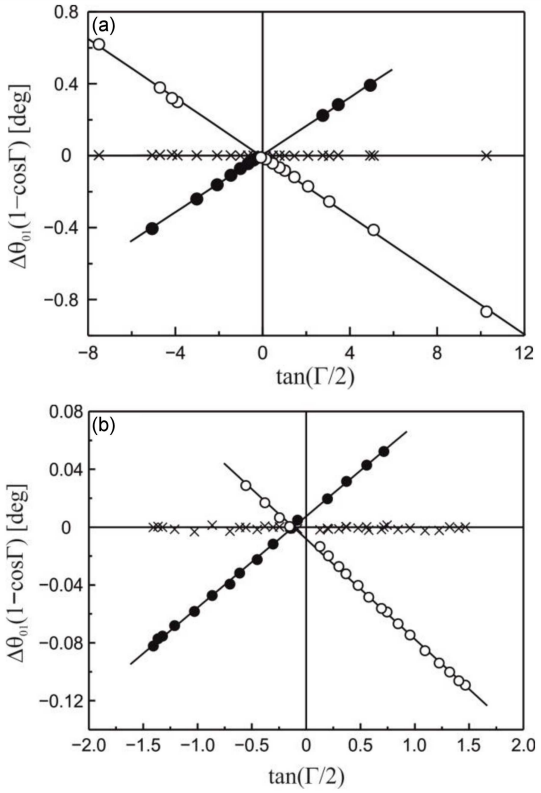

Fig. 2. The dependence of the function $\Delta\theta_{01}(1-\cos(\Gamma)$ $(\circ, \bullet)$ and $\Delta_{\rm err}$ $(\times)$ vs $\tan(\Gamma/2)$ for CGG crystals: (a) $\lambda = 532$ nm, (b) $\lambda = 635$ nm. There are two crystal orientations in the PSA system: $\circ$ — 0° setting, $\bullet$ — 90° setting. Solid lines represent the best linear fits to the experimental data.

we derive $g_{11} = 6.17 \times 10^{-5}$ (for green wavelength) and $g_{11} = 5.10 \times 10^{-5}$ (for red wavelength). Using the relation for the ORP perpendicular to optic axis ($\rho_\perp = \pi g_{11}/(\lambda n_{\rm e})$) we get the values $\rho_\perp = 11.4$ deg/mm and $\rho_\perp = 7.95$ deg/mm for 532 and 635 nm wavelength, respectively. The values of gyration parameters of the CGG for 780 nm wavelength are as follows: $g_{11} = 2.5 \times 10^{-5}$ and $\rho_\perp = 3.2$ deg/mm [4].

4. Dispersion of the optical activity

Let us consider the results of calculations performed for CGG crystals. The electronic polarizability volumes α'_S of individual atoms have been determined in [4] for CGG using the structure data [3] of laevorotatory crystal (with negative optical rotation in the direction of the optical axis). The calculated optical rotation in the directions both parallel and perpendicular to the optical axis was $\rho_{||} = -12.3$ and $\rho_\perp = 5.5$ deg/mm ($\lambda = 632.8$ nm), respectively [4]. The Lorentz–Lorenz equation [13] has been used to estimate the wavelength dependence of the optical rotatory power $\rho_\perp$ in the spectral region from 500 to 800 nm. The same method of the determination of both $\rho_{||}$ and refractive indices dispersion has early successfully been applied in [4].

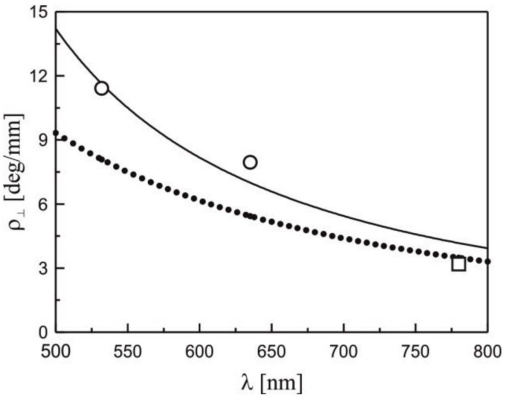

Fig. 3. Wavelength dependence of the ORP of CGG crystals (◯ — experimental data, □ — result obtained in [4], ••• — calculated values). The dispersion of the $\rho_\perp$ is calculated using (4) and expressed by solid line.

Finally, Fig. 3 displays wavelength dependence of both the calculated and experimentally obtained values of the optical rotation of CGG crystals. The analysis of experimental data was carried out (as, for example, in [14] for KDP crystals) on the basis of the Drude-type formula [15]

$$\rho = \frac{A}{\lambda^2 - \lambda_0^2}, \tag{4}$$

where $A = 2.1 \times 10^{-3}$ deg μm and $\lambda_0 = 0.32$ μm are the fit parameters of the curve (solid line in Fig. 3). In addition, the value of the obtained λ_0 correlates with the bands positions in the circular dichroism spectrum of the CGG crystals [16].

5. Conclusions

The application of the high-accuracy polarimetric method allowed us to measure the optical activity along the light propagation direction perpendicular to the optic axis in the CGG crystals. Since the magnitudes of systematic errors were commensurated to OA, the $\delta\chi$ and γ were taken into account and eliminated. The value of gyration tensor component g_{11} was obtained for 532 and 635 nm wavelength of light.

The spectral dependence of the $\rho_\perp$ of CGG crystal was experimentally obtained and calculated in the wide spectral region (from 500 to 800 nm) using the polarizability theory of optical activity. The dispersion of the optical rotation was satisfactorily described by the Drude-type formula.

References

[1] A. Kaminskii, L. Aminov, V. Ermolaev et al., *Physics and Spectroscopy of Laser Crystals*, Nauka, Moscow 1986 (in Russian).

[2] K. Kaldybaev, A. Konstantinova, Z. Perekalina, *Gyrotropy of Uniaxial Absorbing Crystals*, ISPIN, Moscow 2000 (in Russian).

[3] B.V. Mill, A.A. Klimenkova, B.A. Maximov, V.N. Molchanov, D.Yu. Pushcharovsky, *Crystallogr. Rep.* **52**, 785 (2007).

[4] Ya. Shopa, N. Ftomyn, *Opt. Appl.* **XLIII**, 217 (2013).

[5] J. Kobayashi, Y. Uesu, *J. Appl. Crystallogr.* **16**, 204 (1983).

[6] A. Takanabe, H. Koshima, T. Asahi, *AIP Adv.* **7**, 025209 (2017).

[7] A. Martin, S. Nichols, V. Murphy, B. Kahr, *Chem. Commun.* **57**, 8107 (2021).

[8] V. Devarajan, A.M. Glazer, *Acta Cryst. A* **42**, 560 (1986).

[9] Y.I. Shopa, *J. Phys. Stud.* **5**, 70 (2001).

[10] M. Shopa, N. Ftomyn, Ya. Shopa, *J. Opt. Soc. Am.* **34**, 943 (2017).

[11] J.R.L. Moxon, A.R. Renshaw, *J. Phys. Condens. Matter* **2**, 6807 (1990).

[12] A.M. Glazer, *J. Appl. Cryst.* **35**, 652 (2002).

[13] M. Born, E. Wolf, *Principles of Optics*, 2nd Ed., Nauka, Moscow 1970 (in Russian).

[14] M. Shopa, Ya. Shopa, M. Shribak, E. Kostenyukova, I. Pritula, O. Bezkrovnaya, *J. Appl. Cryst.* **53**, 1257 (2020).

[15] S.S. Kotsur, I.V. Stasyuk, *Phys. Stat. Sol (b)* **149**, 347 (1988).

[16] V.I. Burkov, E.P. Perederei, E.V. Fedotov, B.V. Mill, Yu.V. Pisarevskii, *Crystallogr. Rep.* **53**, 843 (2008).