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Optical activity of $Ca_3Ga_2Ge_4O_{14}$ crystals: experiment and calculus

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Using a highly accurate polarimetric method, we determine the gyration tensor component g_{11} for $Ca_3Ga_2Ge_4O_{14}$ (CGG) crystals. For this aim we employ a single-wavelength high-accuracy polarimeter and eliminate the main systematic errors of our polarimetric measurements. A calculation technique based on the polarizability theory for optical activity (OA) is applied to derive optical rotatory power (ORP) for the CGG. A comparison of the observed and calculated OA parameters confirms the validity of our theoretical calculations. Dispersions of both the ordinary and extraordinary refractive indices and the ORP are calculated.

Keywords: langasite, optical activity, polarimetry, polarizabilities.

1. Introduction

$Ca_3Ga_2Ge_4O_{14}$ crystals, abbreviated hereafter as CGG, belong to a large family of langasite $La_3Ga_5SiO_{14}$. They attract great interest of researchers as materials with a unique combination of physical properties such as dielectric, elastic, piezoelectric and luminescence ones which, in particular, enable generation of laser light [1, 2]. The structural studies [1, 3] have demonstrated that the crystalline systems under interest belong to the space symmetry group $P321$ (the point group 32), with a single molecule per unit cell. At the same time, a significant feature of the langasite-family crystals is disordering of their structure which, in particular, is characteristic of $Ca_3Ga_2Ge_4O_{14}$ (CGG), $Sr_3Ga_2Ge_4O_{14}$ (SGG) and $La_3Ga_5SiO_{14}$ (LGS) compounds (the occupations of the $1a$, $3f$ and $2d$ Wyckoff positions by Ga/Ge, Ga/Si atoms are different) [1, 3]. The results on optical properties of the crystals available in the literature indicate they are optically uniaxial and optically positive ($n_e > n_o$, with n_e and n_o being respectively the extraordinary and ordinary refractive indices). Moreover, they are acentric and reveal an optical activity effect. Their gyration tensor g_{ij} is diagonal, with two independent components ($g_{11} = g_{22}$ and g_{33}).

Unlike widely known α-SiO_2 crystals, which crystallize in the same point symmetry group, the compounds of Ca-gallogermanate structural type have no screw axes. Therefore, the OA of the CGG should certainly be associated with some peculiarities of its structural units, *e.g.*, the 1*a* octahedron (there is a deviation from the rotation angle of 60° for the opposite faces of this octahedron) [4, 5].

Spectral studies of OA of the langasite-family crystals have earlier been performed for the cases of light propagation in crystals both along and perpendicular to the optic axis (see [2]). In order to measure simultaneously the OA and a linear dichroism (LD) effect in the pure and doped LGS, CGG, SGG and some other compounds, the authors [2] have applied a method based on the analysis of oscillations of polarization azimuth for the output light, which has been implemented for different phase differences between the normal light waves.

As a matter of fact, a high-accuracy universal polarimeter (HAUP) [6] is already widely known as a technique for measuring optical effects, which manifests the highest sensitivity and accuracy. It can be applied for the studies of OA and linear birefringence (LB) for arbitrary anisotropic directions of crystals. Furthermore, this technique has been successfully extended to simultaneous measurements of the OA, LB, LD and a circular dichroism (CD) in dichroic crystals [7–9]. It is worthwhile to notice that the technique takes into account important systematic polarimetric errors associated with parasitic ellipticities of both polarizer and analyzer, and an angular systematic error. This makes the HAUP-related methods the most preferable tool in case of any practical measurements.

Theoretical techniques used for calculations of the refractive indices and the OA (see, *e.g.*, [10]) are usually based on the dipole–dipole interaction theory [11]. Nowadays they are a subject of ever increasing attention. This is because the calculation technique suggested in the work [10] is rather simple and purely classical. It has been successfully utilized, in particular, in the crystal optical studies [12–16]. For this reason we have chosen the method for calculating optical parameters of the langasite-family crystals and, first of all, the CGG compound.

The aim of the present work is to determine crystal optical parameters of the CGG by means of HAUP-related polarimetric measurements and calculate them theoretically basing on the method suggested in the study [10]. A further comparison of the data obtained experimentally and theoretically could be of great importance for better characterization of the above compounds.

2. Experiment

The $Ca_3Ga_2Ge_4O_{14}$ single crystal was grown from high-purity (at least 99.99%) raw materials $CaCO_3$, Ga_2O_3 and GeO_2. We used a Czochralski technique, an argon atmosphere with the admixture of oxygen, and a platinum crucible. A colourless crystal plate of a high optical quality had the thickness of 0.88 mm. It was cut parallel to the optic axis and then mechanically polished.

A single-wavelength laser polarimeter built on the basis of 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 approximately

1.34×10^{-3} deg. Two high-quality Glan prisms served as polarizers. The light source was a 10 mW semiconductor laser diode (the wavelength of 780 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 desirable 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.

It is well-known that non-activated crystals of the Ca-gallogermanate structural type [17], including the CGG, contain some amount of structural defects formed during the process of growth. This conclusion has been inferred from the dispersion of the birefringence and the LD and CD spectra measured in the region 270–370 nm. Following from the analysis of optical transmission and CD spectra in the region of 285–500 nm, the authors of the work [18] have studied the nature of these defect centers. It has been shown that there exist defects which are formed by cation vacancies and excessive oxygen atoms in optically active positions. These defect centers form a number of spectral bands of the CD (closely associated with the OA effect) at the wavelengths less than 500 nm. Since we use single-wavelength measurements at 780 nm, these defects cannot be of a real importance in our studies.

The pure CGG crystals are transparent for the light wavelength used in our polarimeter and there are no considerable LD and CD bands in the range from 500 to 3200 nm [17, 18]. Therefore we applied the method for measuring the OA [19] valid for purely birefringent crystal sections far from the optic axes. In this way, the gyration tensor component g_{11} of the CGG crystals has been determined. This is quite different from the studies of the doped CGG crystals [20, 21], where both the LD and the CD have been taken into account. 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 $\Delta\theta_{ij}$ $(i, j = 0, ..., 2; i \neq j)$ 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 [19]

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

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

$$\Delta\theta_{12}\cot\left(\frac{\Gamma}{2}\right) = -2k+\gamma+\delta\chi\cot\left(\frac{\Gamma}{2}\right) \tag{3}$$

Here, $\Gamma = (2\pi/\lambda)\Delta n\,d$ denotes the phase difference of the light eigenwaves, d the specimen thickness, Δn the LB, λ the light wavelength in vacuum, k the ellipticity of the eigenwaves linked with the scalar gyration parameter $G = g_{ij}l_il_j$ ($l_{i,j}$ being the directional cosines and $g_{11} = 2k\Delta n\bar{n}$), $\bar{n}$ the mean refractive index, $\gamma = p - q$, p and

q the parasitic ellipticities, respectively, of the polarizer and analyzer, and $\delta\chi$ the angular systematic error.

Notice that the characteristic azimuthal angles have been measured for the two specimen orientations in the PSA system, the second of which differing from the first by rotating the crystal by 90° around the beam propagation direction. This rotation of the specimen ensures a sign reversal for the Γ and k parameters [22].

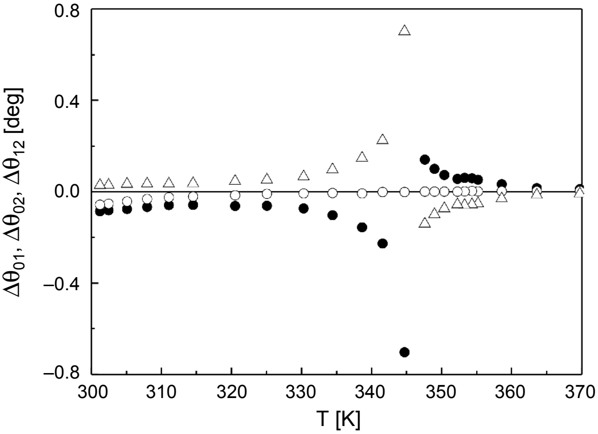

Fig. 1. Temperature dependences of differences among the characteristic azimuthal angles $\Delta\theta_{01}$ (●), $\Delta\theta_{02}$ (○), $\Delta\theta_{12}$ (△) for the CGG crystals as measured for one of the orientations of specimen in the PSA system at 780 nm.

The temperature dependences of the $\Delta\theta_{ij}$'s are displayed in Fig. 1. Now let us analyze the differences among the characteristic azimuthal angles measured in the PSA system. As evident from Fig. 1, the dependences obtained by us are typical of optically active birefringent crystals (see, *e.g.*, [23]). It is instructive to compare our results with those obtained for dichroic samples [21]. In Fig. 1, one cannot observe specific peculiarities of the $\Delta\theta_{ij}$ dependences typical of the dichroic crystals [21]. It is to be noted that the accuracy of θ_i ($i = 0, ..., 2$) depends notably on the phase difference Γ. In particular, the precision of the azimuth θ_1 becomes worse in the vicinity of the point $\cos(\Gamma) \to -1$ (observed in this experiment at 346 K), in contrast to the θ_0 and θ_2 parameters, whereas the most unfavourable situation occurs if $\cos(\Gamma) \to 1$. This is because all of the characteristic azimuths are functions of $\sin(\Gamma)$, $\cos(\Gamma)$, $\tan(\Gamma/2)$, *etc.* [23], and singularities of the $\Delta\theta_{01}$, $\Delta\theta_{12}$ differences happen at the points mentioned above (see Fig. 1). As a consequence, only the $\Delta\theta_{02}$ difference has been used while determining the crystal optical parameters of the CGG.

Figure 2 shows dependence of the $\Delta_{02} = 2\Delta\theta_{02}\tan(\Gamma/2)$ parameter upon $\cot(\Gamma/2)$ for the two orientations of specimen in the PSA system. The easiest way to extract the $\delta\chi$, k and γ parameters is to apply the linear regression analysis of the data shown in Fig. 2 and find the slope and the intercept of the linear function appearing in Eq. (2).

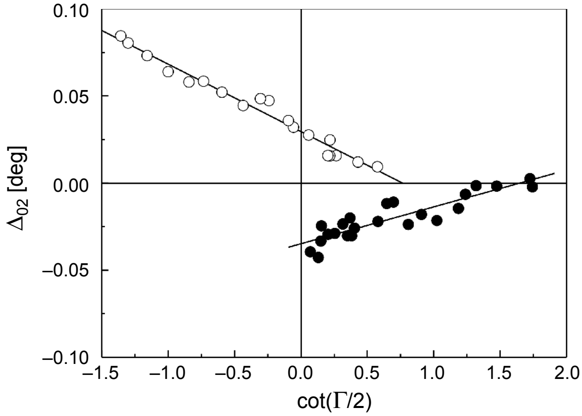

Fig. 2. Plots of the parameter Δ_{02} versus cot(Γ/2) for the CGG crystals. The two plots correspond to alternative specimen orientations as obtained before (○) and after (●) rotating the specimen by 90° around the light beam direction. Solid lines represent the best fit to Eq. (2).

Even visual inspection of the behavior of the experimental parameters (see Fig. 2) testifies that the data could be fairly well fitted to Eq. (2). Then the ellipticity k of the eigenwaves can be considered as independent from temperature in the overall temperature region. Since the two linear dependences $\Delta_{02}(\cot(\Gamma/2))$ reveal different slopes, the angular systematic error should change its sign due to rotation of specimen in the PSA system. The average absolute value of this systematic error typical of our polarimeter is $\delta\chi = 5.2\times10^{-4}$. Finally, one can calculate the unknown ellipticity k and the parasitic ellipticity difference γ from the intersections of lines with the ordinate axis taken for the two angular positions of specimen (see Eq. (2) and Fig. 2). Since, according to our analysis, we have $\gamma = 0.4\times10^{-4}$, the γ value adds little to the ellipticity $2k = 5.6\times10^{-4}$ (approximately 7 percent).

The procedure of determination of the gyration tensor component g_{11} still requires information about the mean refractive index $\bar{n}$ and the LB Δn. The spectral studies of the refractive indices have been accomplished in the works [1, 2]. For the wavelength of 780 nm the parameters under interest are equal to $n_o = 1.7867$, $n_e = 1.8114$, $\bar{n} = 1.7990$, and $\Delta n = 0.0247$. Hence, we derive $g_{11} = 2.5\times10^{-5}$. Finally, using the relation $\rho_\perp = \pi g_{11}/\lambda n_e$ for the optical rotatory power (ORP) perpendicular to the optic axis, we get the value $\rho_\perp = 3.2$ deg/mm.

3. Calculation of optical activity

3.1. Calculation technique

Below we consider the problem of calculating the OA [10] basing upon the dipole–dipole interaction theory [11]. It should be noticed that the calculation method described in the work [10] could be applied to inorganic molecular and ionic crystals. It is valid only for the visible spectral region where there is no absorption and no LD or CD edges [10]. In particular, the studies [10] have been successfully extended to determine the parameters of electrogyration, electrooptic and second-harmonic generation effects, using the model called as dipole electron shifting (DES) [13–16]. In general, the calculations need correct and very precise data on the crystalline structure (*i.e.*, the coordinates $\mathbf{r}_S$ of the S atoms in the crystalline lattice) and the electronic polarizabilities α_S of the individual atoms (*e.g.*, the electronic polarizability volume $\alpha' = \alpha/4\pi\varepsilon_0$, with ε_0 being the permittivity of free space).

Let us now recite the main working relationships of the technique described in [10]. The ORP $\rho(\mathbf{k})$ as a function of the wave vector $\mathbf{k}$ and the optical dielectric constants ε_{ij} may be calculated using the formulae

$$\varepsilon_{ij} = \delta_{ij} + \frac{1}{v}\sum_{SS'}(C_{SS'})_{ij} \tag{4}$$

$$\rho(\mathbf{k}) = -\frac{e_{rij}k_r}{2nv}\,\mathrm{Im}\sum_{SS'}(C_{SS'})_{ij} \tag{5}$$

Here e_{rij} denotes the Levi–Civita symbol, n the refractive index, v the unit-cell volume, δ_{ij} the Kronecker symbol, $C_{SS'}$ complex tensors, and S the index referred to different atoms in the crystalline structure.

The $C_{SS'}$ tensors are in general defined as functions of the electronic polarizability volume [10]. The most convenient way to calculate these complex tensors is using the special equations of the model (see [10, 13, 14]) and the information about precise crystalline structure (for the CGG crystals see the work [3]).

There is well-known WinOPTACT software for solving these problems [24]. Nonetheless, we have created software of our own for calculating the optical parameters of the CGG. A comparison of our data with those reported in the study [10] shows that our software yields almost the same ORP and refractive index values (the errors do not normally exceed 4% for the ORP and 0.1% for the refractive indices) and essentially the same ORP sign. We have performed the corresponding verifications for SiO_2, HgS, $AlPO_4$, $LiIO_3$, $NaClO_3$, $NaBrO_3$ and some other crystals. For all of those crystals, we have taken the electronic polarizability volumes identical to those used in the calculations [10] (the absolute structures of the compounds have been reported, *e.g.*, in the work [12]).

3.2. Determination of polarizability volumes

One of the main peculiarities of the calculation method [10] is determination of electronic polarizabilities of the atoms in crystal. In this respect we should mention that different approaches for solving of the problem exist. According to [14], one can choose the ways that comprise making use of different tabular values, *e.g.*, the isotropic electronic polarizability volumes taken from the study by TESSMANN *et al.* [25]

(republished, *e.g.*, in the works [26, 27]) or from the work by BATSANOV [26] (the crystal refractions of ions), the applied isotropic polarizability volumes scaled to the Fourier peaks of the atoms (proportional to the atomic electron densities), and anisotropic polarizability volume tensors calculated from the diagonal thermal coefficients U_{ii}

$$\alpha_{ii} \sim \frac{3U_{ii}^{-1}}{\sum_{i=1}^{3} U_{ii}^{-1}}$$

Notice that the method [10] also enables calculations of so-called "effective" electronic polarizabilities (tensors of a rank two). Furthermore, an inversely proportional dependence between the thermal coefficients U_{ij} and the electronic polarizability tensors α_{ij} is observed [12].

The first method has been used while determining the isotropic electronic polarizabilities in our case. That is why the values of the polarizability volumes vary within a large though limited range. In other words, one should assume that the correct unknown α' parameter is situated inside the intervals, of which boundaries correlate with the tabular values [25–27]. As a result, the ORP can be calculated using the imaginary parts of the $C_{SS'}$ tensors (see Eq. (5)), provided that a good agreement between the calculated (see Eq. (4)) and the experimental refractive indices is observed for the fixed light wavelength taken in the calculations.

3.3. Calculation results for the CGG crystal

Preliminary absolute structural data for a number of langasite-family crystals are known from the literature [1]. According to most recent study [3], the crystal lattice parameters of the left-handed CGG are $a = 8.075(1)$ Å and $c = 4.9721(6)$ Å, and there is also information about the coordinates of the basic atoms needed for the calculations. The experimental refractive indices and the ORP along the optic axis for the CGG used in our calculations are as follows: $n_o = 1.7965$, $n_e = 1.8204$ [1, 2], and $\rho_{||} = 12.51$ deg/mm [28] ($\lambda = 632.8$ nm).

The following intervals for the electronic polarizability volumes $\alpha'_{S'}$ of Ca^{2+}, Ga^{3+}, Ge^{4+} and O^{2-} ions have been considered during our calculations: $\alpha'_{Ca} = 0...1.2$ Å^3, $\alpha'_{Ga} = 0...1.2$ Å^3, $\alpha'_{Ge} = 0...1.2$ Å^3, and $\alpha'_{O} = 0.5...3$ Å^3. Since the CGG belongs to disordered materials, the polarizability volumes of the both Ga and Ge atoms occupying mixed 1*a* and 3*f* Wyckoff positions have been determined via the relations 0.4Ga + 0.6Ge and 0.53Ga + 0.47Ge [3]. Besides, all the calculations have been performed in the orthogonal coordinate system. Configuration of the Cartesian coordinate system has been determined according to recommendations for the space group symmetry *P*321 [29]: *OX* axis should coincide with **a** axis and *OZ* axis with **c** one, where **a** and **c** are the basic vectors of the direct lattice.

Let us consider the results of the calculations performed for the CGG at the wavelength of 623.8 nm (see Table 1). Issuing from the electronic polarizability volumes

T a b l e 1. Crystal optical parameters calculated for the left-handed (upper row) and right-handed (lower row) CGG crystals at 632.8 and 780 nm.

Light wavelength [nm]	n_o	n_e	$\rho_{\|\|}$ [deg/mm]	$\rho_{\perp}$ [deg/mm]
632.8	1.798	1.820	–12.3	5.5
	1.798	1.821	12.4	–5.6
780	1.788	1.810	–7.8	3.5
	1.788	1.810	7.9	–3.6

$\alpha'_{\mathrm{Ca}} = 1.139$ Å^3, $\alpha'_{\mathrm{Ga}} = 0.266$ Å^3, $\alpha'_{\mathrm{Ge}} = 0.244$ Å^3 and $\alpha'_{\mathrm{O}} = 1.659$ Å^3, the calculated crystal optical parameters are as follows: $n_o = 1.798$, $n_e = 1.820$, and $\rho_{||} = -12.3$ deg/mm (for the optic axis direction). It is comforting that the values obtained for the electronic polarizability volumes match the experimental ones very well. A negative ORP sign is obtained for the left-handed CGG. The $\rho_{\perp}$ value calculated for the direction perpendicular to the optic axis is 5.5 deg/mm. This parameter has the opposite sign, when compared to $\rho_{||}$. At the same time, the results of calculations for the right-handed CGG are almost the same: $n_o = 1.798$, $n_e = 1.821$, $\rho_{||} = 12.4$ deg/mm, and $\rho_{\perp} = -5.6$ deg/mm.

Besides, we have a good agreement of the calculated and experimental results for the selected polarizability volumes [1, 2, 28]. What is also of primary importance, our calculations make possible correct determination of the OA sign along the optic axis direction, *i.e.*, the ORP signs derived for the two enantiomorphic forms of the CGG crystals turn out to be the opposite. The $\rho_{\perp}$ parameter calculated for the light propagation direction perpendicular to the optic axis has the opposite sign, when compared with the $\rho_{||}$ parameter for the direction that matches the optic axis.

3.4. Calculation of optical activity dispersion

This subsection deals with the spectral dependences of crystal optical parameters of the CGG crystal. In fact, the relation between the refractive indices *n* and the electronic polarizabilities α in the visible range is given by the Lorentz–Lorenz formula [30], known also as the Clausius–Mossotti relation. Then, one can estimate the OA dispersion, as has earlier been done, *e.g.*, for the $\mathrm{SiO_2}$ crystals [10]. Moreover, in calculating the wavelength dependences of the crystal optical parameters, the light wavelength λ does not represent the only changeable parameter. Besides, one should consider additional changes in the electronic polarizabilities dependent on λ [10]. In general, one can determine the dispersion of the total electronic polarizability volume α' for the CGG, using the additivity rule $\alpha' = 3\alpha'_{\mathrm{Ca}} + 2\alpha'_{\mathrm{Ga}} + 4\alpha'_{\mathrm{Ge}} + 14\alpha'_{\mathrm{O}}$ and the complete set of spectral data for the refractive indices (for the case of the CGG crystals see the results [2]).

The principal feature of the algorithm [10] suggested for estimating the OA dispersion is determining a proportionality coefficient κ that links the total electronic polarizability volume α' with the average refractive index $\bar{n}$ according to the Lorentz–Lorenz equation. Here we write out the formula in the same form as in the work [10]:

$$\frac{\bar{n}^2 - 1}{\bar{n}^2 + 2} = \kappa\alpha' \tag{6}$$

Using the calculated electronic polarizability volumes α'_{Ca}, α'_{Ga}, *etc*., and the mean refractive index at $\lambda = 632.8$ nm, one can calculate the κ parameter from Eq. (6). As a result, the total electronic polarizability volume is then recalculated from Eq. (6) for the fixed light wavelength, basing on the dispersion data for the refractive indices of the CGG crystals and the calculated proportionality coefficient κ. Furthermore, the separate components (α'_{Ca}, α'_{Ga}, *etc*.), which are necessary for evaluating the OA at different wavelengths, are calculated using the same percentage ratios (*e.g.*, $3\alpha'_{\mathrm{Ca}}/\alpha'$, $2\alpha'_{\mathrm{Ga}}/\alpha'$, *etc*.) as obtained at $\lambda = 632.8$ nm. Figure 3 presents the calculated dispersion of the ordinary and extraordinary refractive indices of the CGG and the results of earlier experimental studies. A good agreement of theoretically calculated and experimentally obtained refractive indices is clearly seen.

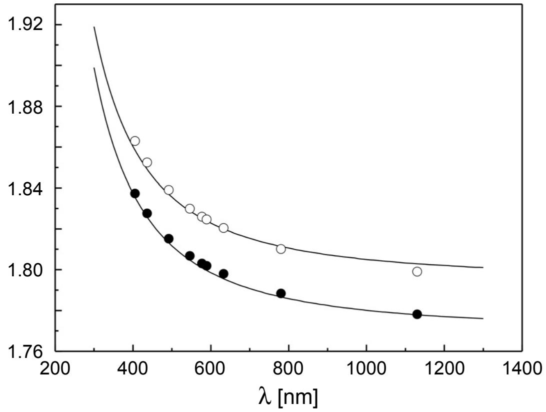

Fig. 3. Dispersions of the ordinary (●) and extraordinary (○) refractive indices calculated for the CGG crystals: lines represent the experimental results [1, 2].

Using the wavelength dependences of the electronic polarizability volumes, one can calculate the OA dispersion. Figure 4 displays dispersion of the absolute $\rho_{||}$ value calculated for the left-handed CGG crystal. As seen from Fig. 4, the correlation between the theoretical and experimental results is excellent.

The experimental and calculated ORP values at 780 nm for the propagation direction perpendicular to the optic axis in the CGG crystals are compared in Table 1. The calculated ORPs are $\rho_{\perp} = 3.5$ deg/mm and -3.6 deg/mm, where plus and minus correspond to the left- and right-handed crystals, respectively. The electronic po-

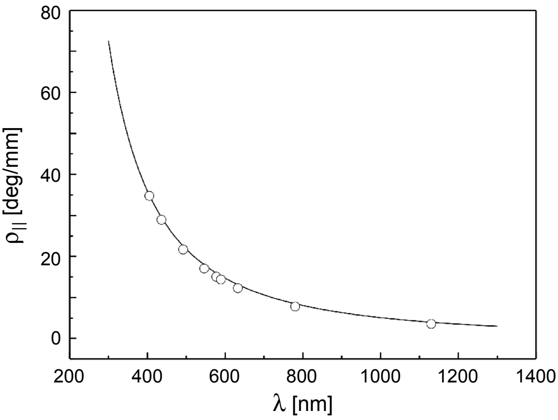

Fig. 4. Calculated dispersion of the absolute value of $\rho_{||}$ parameter for the CGG crystals: line represents the experimental results [1, 2].

larizability volumes we have used as follows: $\alpha'_{\mathrm{Ca}} = 1.129$ Å^3, $\alpha'_{\mathrm{Ga}} = 0.264$ Å^3, $\alpha'_{\mathrm{Ge}} = 0.242$ Å^3, and $\alpha'_{\mathrm{O}} = 1.645$ Å^3. Issuing from the data reported in Section 2, one can see a good correlation between the experimental and theoretical values of the OA for the propagation direction perpendicular to the optic axis.

4. Conclusions

Let us summarize the main results obtained in the present work. We have measured the OA along the light propagation direction perpendicular to the optic axis in the CGG crystals, using the high-accuracy polarimetric methods. This has allowed obtaining the value of the gyration tensor component g_{11}. The systematic errors γ and $\delta\chi$ of the polarimetric setup have been accounted for and eliminated, thus providing correct determination of the gyration component mentioned above.

The OA of CGG crystals has been calculated in the frame of the dipole–dipole interaction model. While selecting in a relevant way the electronic polarizability volumes of the ions, we have achieved a good agreement of the calculated and experimental optical anisotropy parameters for the light wavelengths $\lambda = 632.8$ and 780 nm. In addition, using dispersion of the electronic polarizability volumes calculated with the Lorentz–Lorenz formula, we have calculated the spectral dependences of the ORP and the refractive indices. Good correlation between the experimental and calculated parameters for the visible spectral region is reported. Finally, application of the above calculation technique has enabled determination of the correct ORP sign for the two enantiomorphic forms of the CGG crystals.

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