

Proceedings of the International Conference on Oxide Materials for Electronic Engineering, May 29–June 2, 2017, Lviv

Calculation of Linear Electro-Optic Coefficients in $\text{La}_3\text{Ga}_5\text{SiO}_{14}$ Crystals

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The values of electronic polarizabilities of La^{3+} , Ga^{3+} , Si^{4+} , O^{2-} ions are specified using new experimental data about optical activity of $\text{La}_3\text{Ga}_5\text{SiO}_{14}$ crystals. A calculation technique based on the dipole electron shifting model is applied to estimate linear electrooptic coefficients for the $\text{La}_3\text{Ga}_5\text{SiO}_{14}$. Wavelength dependences of the both linear electro-optic tensor components r_{11} and r_{41} are calculated.

DOI: [10.12693/APhysPolA.133.933](https://doi.org/10.12693/APhysPolA.133.933)

PACS/topics: 78.20.Jq, 32.10.Dk, 78.20.Ek, 61.50.Ah

1. Introduction

Langasite ($\text{La}_3\text{Ga}_5\text{SiO}_{14}$) crystals abbreviated hereafter as LGS attract great interest of researchers as materials with a unique combination of physical properties such as dielectric, elastic, piezoelectric, and luminescence [1, 2]. The structural studies [3] have demonstrated that the crystalline system under interest belongs 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 crystals is disordering of their structure ($2d$ Wyckoff positions are partially occupied by Ga and Si atoms) [3]. They are optically uniaxial optically positive ($n_e > n_o$, with n_e and n_o being respectively the extraordinary and ordinary refractive indices) and optically active. Their gyration tensor g_{ij} is diagonal, with two independent components ($g_{11} = g_{22}$ and g_{33}) [2].

As a matter of fact, the linear electro-optic effect is widely investigated in this system [4–8] and can generally be described by equation [9]:

$$\Delta a_{ij} = \sum_k r_{ijk} E_k. \quad (1)$$

Here $\Delta a_{ij} = a_{ij} - a_{ij}^0$, a_{ij} denotes polarization tensor, r_{ijk} — the linear electro-optic tensor of the third rank, E_k — the k -th component of the applied electric field and index 0 refers to polarization tensor without electric field.

The aim of present work is to theoretically calculate the linear electro-optic parameters of the LGS by means of the method suggested in studies [10, 11]. A further comparison of the data obtained experimentally and theoretically could be of great importance for better characterization of the above compounds.

2. Calculus method

It is well known that calculus method based on classical polarizability theory of optical activity [10] can be

extended to determine the parameters of electrogyration, electro-optic and second-harmonic generation effects [11]. There is so-called dipole–dipole interaction electron-cloud shifting (DES) model of calculations. The results of applications of the DES available in literature [11, 12] indicate validity of theoretical calculations based on this approach.

In DES model the virtual shift x_i of i -atom is calculated using its electronic polarizability α ($x_i = (4\pi_0/e) \sum_j \alpha'_{ij} E_j^{loc}$, where e is the electron charge, ϵ_0 — the permittivity of free space, $\alpha' = \alpha/4\pi\epsilon_0$ the electronic polarizability volume), after determination of the value of the so-called local electric field E^{loc} ($E^{loc} = \left(\frac{2+\epsilon'}{3}\right) E^{ext}$ with ϵ' and E^{ext} being respectively the effective relative dielectric constant and the external electric field) [11]. As a result, the r_{ijk} coefficients could be determined via relation: $a_{ij}(E_k^{ext}) - a_{ij}(0) = \sum_k r_{ijk} E_k^{ext}$ [11].

There is well-known WinOPTACT software for calculating the optical activity and refractive indices of crystals [13]. Nonetheless, we have created software of our own for calculating the optical rotation, refractive indices and electro-optic parameters of the crystals. A comparison of our data with those reported in the study [11, 12] shows that our software yields almost the same r_{ijk} and tensor components. We have performed the corresponding verifications for NaClO_3 , D-mannitol ($\text{C}_6\text{H}_{14}\text{O}_6$), etc. For all of those crystals, we have taken the electronic polarizability volumes and effective relative dielectric constant identical to those used in the calculations [12] (the absolute structures of the compounds have been reported, e.g., in the works [11, 12]).

3. The electronic polarizability volumes refinement of LGS crystals

The electronic polarizability volumes α'_s of individual atoms have been determined in [14] for LGS using the structure data [3] of right-handed crystal (with positive optical rotation). The calculated optical rotation in the direction of the optical axis was $\rho_{\parallel} = 3.0$ deg/mm

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($\lambda = 635$ nm) [14]. On the other hand, using those values of electronic polarizabilities we obtained $\rho_{\perp} = 1.1$ deg/mm for direction perpendicular to optical axis. Unfortunately, this result is inaccurate because of the ρ_{\parallel} and ρ_{\perp} should be opposite in sign (according to gyrotropic properties of crystals with point symmetry group 32 [15]). That is why the values of α'_S should be recalculated for LGS.

Let us consider the new results of calculations performed for LGS crystals at $\lambda = 635$ nm. The following refinement values of polarizability volumes are obtained during our calculations: $\alpha'_{La} = 1.580 \text{ \AA}^3$, $\alpha'_{Ga} = 0.330 \text{ \AA}^3$, $\alpha'_{Si} = 0.570 \text{ \AA}^3$, $\alpha'_O = 1.750 \text{ \AA}^3$. The calculated values of optical rotations and refractive indices are as follows in this case: $\rho_{\parallel} = 3.0$ deg/mm, $\rho_{\perp} = -0.88$ deg/mm and $n_o = 1.877$, $n_e = 1.912$. In addition, the x -cut of the gyration surface is expressed in Fig. 1. It is interesting to note that there is good correlation between obtained data and the experimental results of optical activity measurements for LGS $\rho_{\parallel} = -3.3$ deg/mm and $\rho_{+} = 0.73$ deg/mm [14, 16, 17]. Finally, the experimental refractive indices (calculated using the parameters of the Sellmeier equation for LGS at $\lambda = 635$ nm) are as follows: $n_o = 1.8998$, $n_e = 1.9109$ [1, 2].

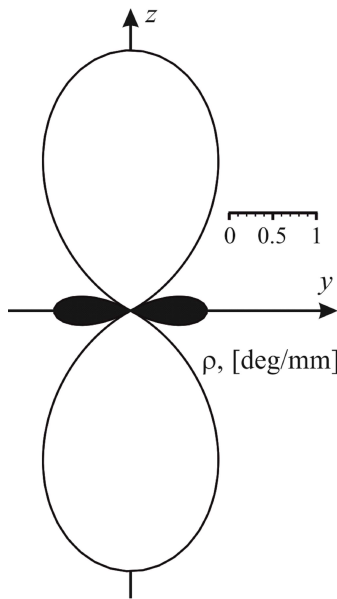


Fig. 1. The x -cut of calculated gyration surface for LGS crystals (black and white colors correspond to negative and positive optical rotation, respectively).

4. Linear electro-optic effects in LGS crystals

Since the point symmetry group of LGS crystals is 32, there are only two nonzero independent components of r_{ijk} tensor i.e., $r_{11} = -r_{21} = -r_{62}$, $r_{41} = -r_{52}$ [9] (the contracted indices are used 1 = (11), 2 = (22), 3 = (33), 4 = (23) = (32), etc.).

It is known that information about low frequency dielectric constant is still needed for DES calculations. In

our case there are $\varepsilon_{11} = \varepsilon_{22} = 19$ and $\varepsilon_{33} = 51$ [4], respectively. Using these data of the ε_{ij} , as well as calculated polarizabilities we obtained the next values of r_{ij} coefficients: $r_{11} = -2.8$ pm/V, $r_{41} = 0.16$ pm/V. It is necessary to note that linear electro-optic tensor components obtained by means experimental measuring are e.g., $r_{11} = -2.68$ pm/V, $r_{41} = 1.22$ pm/V [5] and $r_{11} = 2.62$ pm/V, $r_{41} = 1.20$ pm/V [7]. Good agreement of theoretically calculated and experimentally obtained r_{11} component is clearly seen. On the other hand, the value of calculated r_{41} coefficient is approximately 8 times smaller than experimental ones. It may probably be explained by the affect of the optical inhomogeneity of crystals on the experimentally obtained linear electro-optic tensor components [7] (e.g., the value of the measured r_{41} coefficient varies from 0.69 to 1.44 pm/V in the same sample). In addition, the theoretical calculations [10, 11] significantly depend on the structure peculiarities of crystals under the test e.g., disordering. Otherwise, the simple approach [14] in calculating the polarizabilities of Ga and Si atoms occupying mixed 2d Wyckoff positions (the polarizability have been determined via the relation depends on site occupancy factor [3] i.e., 0.5Ga + 0.5Si) may probably another reason of the inaccuracy in calculations of the r_{41} coefficient.

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 [18], known also as the Clausius–Mossotti equation. Then one can estimate the wavelength dependence of the electro-optic coefficients, as has earlier been done for optical rotatory power and refractive indices (see e.g., results for SiO_2 , $\text{Ca}_3\text{Ga}_2\text{Ge}_4\text{O}_{14}$, $\text{La}_3\text{Ga}_{5.5}\text{Ta}_{0.5}\text{O}_{14}$ crystals [10, 19, 20]). In general, one can determine the dispersion of the total electronic polarizability volume α' for the LGS, using the additivity rule $\alpha' = 3\alpha'_{La} + 5\alpha'_{Ga} + \alpha'_{Si} + 14\alpha'_O$ and the complete set of spectral data for the refractive indices (for the case of the LGS crystals see the results [1, 2]). Using the calculated electronic polarizability volumes α'_{La} , α'_{Ga} etc., and the mean refractive index at $\lambda = 635$ nm, one can calculate the κ parameter from equation $(\bar{n}^2 - 1) / (\bar{n}^2 + 2) = \kappa\alpha'$ [10] (here \bar{n} is mean refractive index, κ — the proportionality coefficient). As a result, the total electronic polarizability volume is then recalculated from this equation for the fixed light wavelength, basing on the dispersion data for the refractive indices of the LGS crystals and the calculated proportionality coefficient κ . Furthermore, the separate components (α'_{La} , α'_{Ga} , et al.), which are necessary for evaluating the optical parameters at different wavelengths, are calculated using the same percentage ratios (e.g., $3\alpha'_{La}/\alpha'$, $5\alpha'_{Ga}/\alpha'$, etc.) as obtained at $\lambda = 635$ nm. Finally, Fig. 2 displays wavelength dependences of the both calculated r_{11} (absolute value) and r_{41} coefficients, respectively. It is interesting to note that the same regularity on the λ -dependence of the electro-optic coefficient r_{11} are observed for e.g., α -quartz (has the same space symmetry group as LGS) [21].

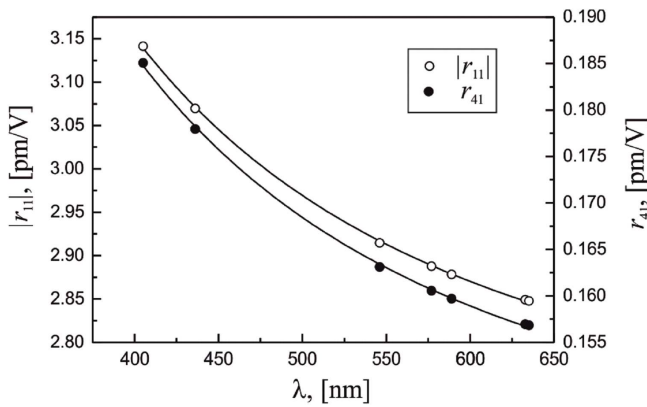


Fig. 2. Wavelength dependences of the electro-optic r_{11} and r_{41} coefficients (the coordinates of the points \circ , \bullet have been determined using the experimental spectral dependences of the refractive indices [1, 2]). Lines represent the best fit of the calculated values.

5. Conclusions

Let us summarize the main results obtained in the present work. The linear electro-optic coefficients of LGS crystals have been calculated in the frame of the DES model. While selecting in a relevant way the electronic polarizability volumes of the ions, we have achieved satisfied agreement of the calculated and experimental optical anisotropy parameters for the light wavelengths $\lambda = 635$ nm. In addition, using dispersion of the electronic polarizability volumes calculated with the Lorentz–Lorenz formula, we have calculated the spectral dependences of the electro-optic coefficients.

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