

NONLINEAR OPTICAL EFFECTS IN CRYSTALS OF LANGASITE FAMILY

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A calculation technique based on the Dipole Electron Shifting model is applied to investigate the nonlinear optical properties of the crystals of langasite family. The d_{11} component of nonlinear optical susceptibility tensors is determined for $\text{La}_3\text{Ga}_5\text{SiO}_{14}$, $\text{Ca}_3\text{Ga}_2\text{Ge}_4\text{O}_{14}$, $\text{La}_3\text{Ga}_{5.5}\text{Ta}_{0.5}\text{O}_{14}$, $\text{La}_3\text{Ga}_{5.5}\text{Nb}_{0.5}\text{O}_{14}$ crystals. The results of the calculations are compared with the experimental ones, described in literature.

Key words: nonlinear optics, polarizabilities, langasite.

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I. INTRODUCTION

In recent years, researchers have become increasingly interested in investigating new nonlinear optical (NLO) materials effective in the wide spectral region. The crystals of langasite family ($\text{La}_3\text{Ga}_5\text{SiO}_{14}$, $\text{Ca}_3\text{Ga}_2\text{Ge}_4\text{O}_{14}$, $\text{La}_3\text{Ga}_{5.5}\text{Ta}_{0.5}\text{O}_{14}$, $\text{La}_3\text{Ga}_{5.5}\text{Nb}_{0.5}\text{O}_{14}$, etc) are promising in the application in the midinfrared region (they are transparent up to $7\ \mu\text{m}$) [1]. They also attract great interest as systems with unique physical properties, e.g., dielectric, elastic, piezoelectric, etc [2, 3]. The structural studies [4–6] have demonstrated that the crystalline systems under interest belong to the space symmetry group $P321$ ($Z = 1$). 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}). The optical activity of the some of these crystals are studied in [3, 7–11].

Nonlinear optical properties of crystals of the langasite family were widely investigated and reported in the works [1, 12–14]. The second harmonic generation effect is observed and d_{11} coefficients were measured for $\text{La}_3\text{Ga}_5\text{SiO}_{14}$, $\text{Ca}_3\text{Ga}_2\text{Ge}_4\text{O}_{14}$, $\text{La}_3\text{Ga}_{5.5}\text{Ta}_{0.5}\text{O}_{14}$, $\text{La}_3\text{Ga}_{5.5}\text{Nb}_{0.5}\text{O}_{14}$ e.g., in [12] ($d_{11} = 1.7 \times 10^{-12}$ m/V for $\text{La}_3\text{Ga}_5\text{SiO}_{14}$). It is necessary to note that there are no possibility to obtain the phase-matching conditions for $\text{La}_3\text{Ga}_5\text{SiO}_{14}$ crystals in the range from 500 to 2500 nm [14] (in contrast, the directions of the phase-matching were investigated and experimentally determined in [13] for $\text{La}_3\text{Ga}_{5.5}\text{Ta}_{0.5}\text{O}_{14}$ materials).

It is well known that for nonlinear crystals the polarization \mathbf{P} can be expressed as [15]:

$$P_i = \varepsilon_0 \chi_{ij} E_j + 2d_{ijk} E_j E_k + \dots + \quad (1)$$

Here E_j denotes the j th component of the electric field, χ_{ij} the linear susceptibility, d_{ijk} the second-order nonlinear optical susceptibility, ε_0 the permittivity of free space.

The aim of our work is to calculate the NLO parameters (NLO susceptibility tensor components) of some crystals of the langasite family by using the method expressed in [17].

II. CALCULATION METHOD

It is well known that the calculation method based on the classical polarizability theory of optical activity [16] can be extended to determine the parameters of NLO effects (electrogyration, electro-optic effect and second-harmonic generation) [17]. There is the so-called DES (Dipole–dipole interaction electron-cloud shifting) model of calculations. The results of the applications of the DES available in literature [17–20] indicate the validity of the theoretical calculations based on this approach.

In the DES model, the virtual shift \mathbf{x} of the electron cloud of the selected atom is directly proportional to its electronic polarizability α ($x_i = (8\varepsilon_0/e) \sum_j \alpha'_{ij} E_j^{\text{Light}}$,

where e is the electron charge, $\alpha' = \alpha/4\pi\varepsilon_0$ the electronic polarizability volume, $\mathbf{E}^{\text{Light}}$ the field of light wave) [18]. As a result, the coefficients d_{ijk} of NLO susceptibility tensor could be determined via relation [18]:

$$\varepsilon_{ij}(E^{\text{Light}}) - \varepsilon_{ij}(0) = 2 \sum_k d_{ijk} E_k^{\text{Light}}. \quad (2)$$

Here ε_{ij} denotes relative dielectric constants, E_k^{Light} the k th component of the field of light wave, and 0 refers to relative dielectric constants without electric field.

We have created our own software (the C++ programming language was used) for calculating the electro-optic [22] and NLO susceptibility tensor components. In addition, our program was tested, in particular, for SiO_2 , D-mannitol ($\text{C}_6\text{H}_{14}\text{O}_6$), and KH_2PO_4 (KDP) crystals (we have obtained almost the same values of d_{ijk} tensor components, as expressed in [17, 18]). The errors of the calculations did not normally exceed 5% for the d_{ijk} . In contrast, there is the



WinOPTACT software [21] for calculating the refractive and gyrotropic parameters of crystals based on the polarizability theory of optical activity [16].

III. THE ELECTRONIC POLARIZABILITY VOLUMES AND RESULTS OF THE CALCULATION

Let us consider the results of the calculations performed for $\text{La}_3\text{Ga}_5\text{SiO}_{14}$, $\text{Ca}_3\text{Ga}_2\text{Ge}_4\text{O}_{14}$, $\text{La}_3\text{Ga}_{5.5}\text{Ta}_{0.5}\text{O}_{14}$ and $\text{La}_3\text{Ga}_{5.5}\text{Nb}_{0.5}\text{O}_{14}$ crystals, respectively. The values of electronic polarizability volumes have been determined for these materials in [7, 8, 22] using the good correlation between the calculated and observed refractive indices and optical rotation in the direction of the optical axis. It is necessary to note that excellent agreement between the calculated and measured [7, 9] (the high-accuracy polarimetry method has been applied) optical rotation in the direction perpendicular to the optical axis for $\text{Ca}_3\text{Ga}_2\text{Ge}_4\text{O}_{14}$ and $\text{La}_3\text{Ga}_5\text{SiO}_{14}$ crystals is reported.

The Lorentz–Lorenz equation [23] has been used to obtain the α' for the wavelength of light $\lambda = 1064$ nm (this wavelength of light is typically used in the second harmonic generation experiments). This method of determining the wavelength dependence of electronic polarizability volumes has earlier been used for e.g., SiO_2 [16], $\text{La}_3\text{Ga}_5\text{SiO}_{14}$, $\text{Ca}_3\text{Ga}_2\text{Ge}_4\text{O}_{14}$, $\text{La}_3\text{Ga}_{5.5}\text{Ta}_{0.5}\text{O}_{14}$ [7, 8, 22]. As a result the following values of α' are estimated: $\alpha'_{\text{La}} = 1.557 \text{ \AA}^3$, $\alpha'_{\text{Ga}} = 0.325 \text{ \AA}^3$, $\alpha'_{\text{Si}} = 0.561 \text{ \AA}^3$, $\alpha'_{\text{O}} = 1.725 \text{ \AA}^3$ ($\text{La}_3\text{Ga}_5\text{SiO}_{14}$), $\alpha'_{\text{Ca}} = 1.121 \text{ \AA}^3$, $\alpha'_{\text{Ge}} = 0.262 \text{ \AA}^3$, $\alpha'_{\text{Ge}} = 0.240 \text{ \AA}^3$, $\alpha'_{\text{O}} = 1.633 \text{ \AA}^3$, ($\text{Ca}_3\text{Ga}_2\text{Ge}_4\text{O}_{14}$), $\alpha'_{\text{La}} = 1.996 \text{ \AA}^3$, $\alpha'_{\text{Ga}} = 0.412 \text{ \AA}^3$, $\alpha'_{\text{Ta}} = 0.902 \text{ \AA}^3$, $\alpha'_{\text{O}} = 1.731 \text{ \AA}^3$ ($\text{La}_3\text{Ga}_{5.5}\text{Ta}_{0.5}\text{O}_{14}$), $\alpha'_{\text{La}} = 1.941 \text{ \AA}^3$, $\alpha'_{\text{Ga}} = 0.428 \text{ \AA}^3$, $\alpha'_{\text{Nb}} = 1.022 \text{ \AA}^3$, $\alpha'_{\text{O}} = 1.742 \text{ \AA}^3$ ($\text{La}_3\text{Ga}_{5.5}\text{Nb}_{0.5}\text{O}_{14}$), respectively. Because the considered systems belong to disordered materials, the polarizability volumes of the atoms occupying mixed $1a$, $2d$ and $3f$ Wickoff positions have been determined via the relations depending on site occupancy factors [4–6]: $0.5\text{Ga} + 0.5\text{Si}$ ($2d$, $\text{La}_3\text{Ga}_5\text{SiO}_{14}$), $0.4\text{Ga} + 0.6\text{Ge}$ and $0.53\text{Ga} + 0.47\text{Ge}$ ($1a$ and $3f$, $\text{Ca}_3\text{Ga}_2\text{Ge}_4\text{O}_{14}$), $0.55\text{Ga} + 0.45\text{Ta}$ ($1a$, $\text{La}_3\text{Ga}_{5.5}\text{Ta}_{0.5}\text{O}_{14}$) $0.48\text{Ga} + 0.52\text{Nb}$ ($1a$, $\text{La}_3\text{Ga}_{5.5}\text{Nb}_{0.5}\text{O}_{14}$).

Since the point symmetry group of the investigated crystals is 32, the NLO susceptibility tensor can be written [15]:

$$d_{ij} = \begin{pmatrix} d_{11} & -d_{11} & 0 & d_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & -d_{14} & -d_{11} \\ 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix}. \quad (3)$$

Here contracted indices are used: $1 = (11)$, $2 = (22)$, $3 = (33)$, $4 = (23) = (32)$, etc. As a result, there are only two d_{11} and d_{14} nonzero independent components, respectively.

The calculated d_{11} components for $\text{La}_3\text{Ga}_5\text{SiO}_{14}$, $\text{Ca}_3\text{Ga}_2\text{Ge}_4\text{O}_{14}$, $\text{La}_3\text{Ga}_{5.5}\text{Ta}_{0.5}\text{O}_{14}$, $\text{La}_3\text{Ga}_{5.5}\text{Nb}_{0.5}\text{O}_{14}$ crystals are shown in Table 1.

As can be seen from the data in the Table 1, the results of the calculations are in excellent agreement with the experimental ones for $\text{La}_3\text{Ga}_5\text{SiO}_{14}$ and $\text{Ca}_3\text{Ga}_2\text{Ge}_4\text{O}_{14}$ crystals, in contrast to $\text{La}_3\text{Ga}_{5.5}\text{Ta}_{0.5}\text{O}_{14}$ and $\text{La}_3\text{Ga}_{5.5}\text{Nb}_{0.5}\text{O}_{14}$ (the value of the calculated d_{11} coefficients are approximately 4 times smaller). It may probably be explained by the application of the unsatisfactory sets of electronic polarizability volumes of the ions for these materials. In addition, the α' of ions for $\text{La}_3\text{Ga}_5\text{SiO}_{14}$ and $\text{Ca}_3\text{Ga}_2\text{Ge}_4\text{O}_{14}$ were determined using the experimental results of the optical activity in the direction parallel and perpendicular to the optical axis. As a result, the complete information about the gyrotropic properties of investigated materials is necessary for the correct calculation of the parameters of NLO effects in DES approach.

| Crystal | $d_{11}, 10^{-12} \text{ m/V}$ | Experimental results |
|--|--------------------------------|--------------------------------|
| | | $d_{11}, 10^{-12} \text{ m/V}$ |
| $\text{La}_3\text{Ga}_5\text{SiO}_{14}$ | 1.48 | $1.7^a, 1.86^b$ |
| $\text{Ca}_3\text{Ga}_2\text{Ge}_4\text{O}_{14}$ | 0.82 | 0.9^a |
| $\text{La}_3\text{Ga}_{5.5}\text{Ta}_{0.5}\text{O}_{14}$ | 0.60 | $2.3^a, 2.4^c$ |
| $\text{La}_3\text{Ga}_{5.5}\text{Nb}_{0.5}\text{O}_{14}$ | 0.61 | 2.6^a |
| a [12], b [1], c [13] | | |

Table 1. Results of calculations

IV. CONCLUSIONS

1. Components of the nonlinear optical susceptibility tensor of some crystals of the langasite family have been calculated using the dipole–dipole interaction model. Good correlation between the experimental (expressed in literature) and calculated parameters is reported for $\text{La}_3\text{Ga}_5\text{SiO}_{14}$ and $\text{Ca}_3\text{Ga}_2\text{Ge}_4\text{O}_{14}$ crystals.
2. The values of the calculated d_{11} coefficients are approximately four times smaller than the experimental ones for both $\text{La}_3\text{Ga}_{5.5}\text{Ta}_{0.5}\text{O}_{14}$ and $\text{La}_3\text{Ga}_{5.5}\text{Nb}_{0.5}\text{O}_{14}$ crystals. It may be explained by the application of the unsatisfactory sets of electronic polarizability volumes of the ions for these materials.
3. To obtain correct values of the nonlinear optical susceptibility, the magnitude of the electronic polarizabilities should be determined according to complete information about the optical activity of the investigated material.

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НЕЛІНІЙНО ОПТИЧНІ ЕФЕКТИ В КРИСТАЛАХ РОДИНИ ЛАНГАСИТІВ

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Розрахунковий метод, що базується на DES-моделі (Dipole Electron Shifting), використано для дослідження нелінійно-оптичних властивостей кристалів родини лангаситів. У межах цього підходу також можна розраховувати параметри таких оптичних ефектів, як електрогірація, електрооптичний ефект тощо.

Визначено d_{11} -компоненту тензорів нелінійно-оптичної сприйнятливості кристалів $\text{La}_3\text{Ga}_5\text{SiO}_{14}$ (1.48×10^{-12} м/В), $\text{Ca}_3\text{Ga}_2\text{Ge}_4\text{O}_{14}$ (0.82×10^{-12} м/В), $\text{La}_3\text{Ga}_{5.5}\text{Ta}_{0.5}\text{O}_{14}$ (0.60×10^{-12} м/В), $\text{La}_3\text{Ga}_{5.5}\text{Nb}_{0.5}\text{O}_{14}$ (0.61×10^{-12} м/В) з використанням інформації про їхню кристалічну структуру та електронні поляризованості. Оскільки досліджувані об'єкти є розупорядкованими, електронні поляризованості йонів у кристалографічних позиціях $1a$, $2d$ та $3f$ розраховували згідно зі статистикою їх заповнення ($2d$: $0.5\text{Ga} + 0.5\text{Si} - \text{La}_3\text{Ga}_5\text{SiO}_{14}$, $1a$: $0.4\text{Ga} + 0.6\text{Ge}$ та $3f$: $0.53\text{Ga} + 0.47\text{Ge} - \text{Ca}_3\text{Ga}_2\text{Ge}_4\text{O}_{14}$, $1a$: $0.55\text{Ga} + 0.45\text{Ta} - \text{La}_3\text{Ga}_{5.5}\text{Ta}_{0.5}\text{O}_{14}$, $1a$: $0.48\text{Ga} + 0.52\text{Nb} - \text{La}_3\text{Ga}_{5.5}\text{Nb}_{0.5}\text{O}_{14}$) для відповідних кристалів. Крім того, для обчислення величин поляризованостей для довжини хвилі 1064 нм використовували співвідношення Лорентц-Лоренца.

Визначені в цій роботі величини d_{11} порівняли з експериментальними даними, наявними в літературі. Для кристалів $\text{La}_3\text{Ga}_5\text{SiO}_{14}$ та $\text{Ca}_3\text{Ga}_2\text{Ge}_4\text{O}_{14}$ отримано достатньо добре узгодження між результатами розрахунків та експериментом. Натомість для $\text{La}_3\text{Ga}_{5.5}\text{Ta}_{0.5}\text{O}_{14}$ та $\text{La}_3\text{Ga}_{5.5}\text{Nb}_{0.5}\text{O}_{14}$ обчислені компоненти тензорів нелінійно-оптичної сприйнятливості суттєво відрізняються від літературних (розраховані значення d_{11} приблизно в чотири рази менші). Цю особливість можна пояснити вибором неточних величин електронних поляризованостей для цих об'єктів, оскільки інформація про оптичну активність у напрямках, відмінних від оптичної осі, для цих кристалів відсутня.

Ключові слова: нелінійна оптика, поляризованості, лангасити.