New nonlinear crystal LiGa(Se$_x$S$_{1-x}$)$_2$ for near-IR radiation frequency conversion

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For the first time, coefficients of the Sellmeier dispersion equations for the new promising nonlinear mixed crystals like LiGa(Se$_x$S$_{1-x}$)$_2$ ($0 \leq x < 1$;) belonging to mm2 point group have been found for different ratios of x mixing. The phase matching diagrams for the second harmonic generation and optical parametric oscillation for the principal crystal plane have been calculated and plotted. Tuning curves for optical parametric oscillator pumped by Nd:YAG laser cover the entire long-wave part of the crystal transparency spectrum up to 13.2 μm. The spectral dependences of acceptable variations of the x mixing ratios have been found.

Introduction

When solving practical problems related with highly effective laser radiation frequency conversion in nonlinear crystals, the latter have to meet a number of strong requirements. For the infrared, where the availability of nonlinear crystals is very limited,[1] the task of searching and producing suitable nonlinear materials with high optical quality, great nonlinearity, and high damage threshold is of high importance. Recently, the interest to Li-containing sulfides and selenides as nonlinear optical media, first of all LiInS$_2$, LiInSe$_2$, LiGaS$_2$, and LiGaSe$_2$ noticeably increased.[2–5]

However, all these crystals, in general case, do not meet the condition of non-critical phase matching at any preset pumping wavelength. One of the ways to optimize characteristics of nonlinear elements is application of solid solution crystals, in which a possibility of optical parameter variation appears due to changing chemical composition. Triple chalcogenide crystals with high nonlinear quadratic susceptibility are used in the radiation frequency conversion between visible and mid-infrared range, as well as in pico- and femtosecond laser instrumentation. It was shown earlier that solid solutions of two semiconductor crystals of A^{I}B^{III}C$_2^{VI}$ (Ref. 6) or A^{IV}B$_2^{VI}$ and A^{I}B^{III}C$_2^{VI}$ (Ref. 7) types are promising in producing crystals with a wide range of transparency and controlled birefringence. Among crystals of non-centrosymmetrical sulfides and selenides, many pairs of isostructural compounds are also known, capable of forming solid solutions at a partial replacement of S for Se.[8]

These crystals also allow realization of the non-critical phase matching through selecting the mixing ratio. It was informed earlier about constructing different laser instruments using the non-critical phase matching in the crystals CdGe(As$_x$P$_{1-x}$)$_2$, AgGa$_x$In$_{1-x}$S$_2$,[9] and AgGa$_x$In$_{1-x}$Se$_2$.[10] The dispersion

properties of the mixed crystal LiGa(Se$_x$S$_{1-x}$)$_2$, which is a solid solution of crystals LiGaS$_2$:LiGaSe$_2$, are studied in this paper.

1. Physical properties

Crystals LiGaS$_2$ and LiGaSe$_2$ have the C$_{2V}$ (mm2) point symmetry and a structure of wurtzite type. The grid parameters of LiGaS$_2$ are: $a = 652$, $b = 787$, and $c = 624$ pm; they differ by data of different authors.[5,11] The grid parameters of LiGaSe$_2$ are[12]: $a = 683$, $b = 824$, and $c = 654$ pm. Greater parameters of the LiGaSe$_2$ elementary cell as compared to LiGaS$_2$ are connected with replacement of anion S^{2-} with a larger anion Se^{2-}. A fragment of the crystal grid is shown in Fig. 1, the principal elements of the LiGaS$_2$ and LiGaSe$_2$ structures are tetrahedrons LiS$_4$(Se$_4$) and GaS$_4$(Se$_4$). Like LiInS$_2$ together with LiInSe$_2$,[13] LiGaS$_2$ and LiGaSe$_2$ form a set of isostructural compounds capable of forming solid solutions with different S/Se ratios.

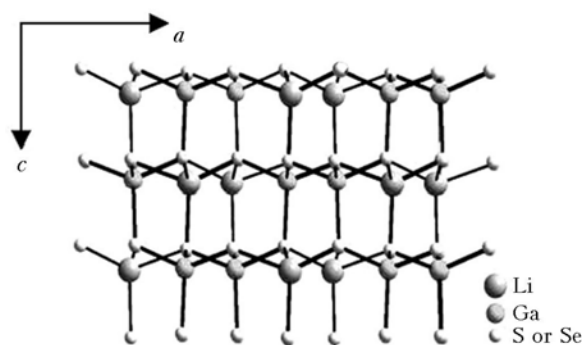**Fig. 1.** Crystal structure of the compounds LiInS$_2$ or LiInSe$_2$.

Optical transmission ranges measured by the level of absorption α = 5 cm^{-1} are 0.32–11.6 μm for LiGaS$_2$ and 0.37–13.2 μm for LiGaSe$_2$,

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respectively.[5,12] As the fraction of selenium (a heavier element than sulfur) increases, the short-wave boundary of the transmission spectrum shifts to longer wavelengths. It should be expected, because the considered compounds are semiconductors with the widths of forbidden zones $E = 3.76$–4.15 eV in LiGaS$_2$[5,11] and 3.34–3.65 eV in LiGaSe$_2$.[12,14]

The nonlinear coefficients estimated at $\lambda = 2.53$ μm with respect to the coefficient $d_{36} = 13.9$ pm/V for AgGaS$_2$ are equal to 5.8–10 pm/V for LiGaS$_2$ and 9.9–18.2 pm/V for LiGaSe$_2$, respectively.[12] This parameter for LiGaSe$_2$ is a quarter higher than for LiInS$_2$, but 20% less than for LiInSe$_2$.[13] It should be expected, because it is well-known that, for example,
on replacing sulfur atoms by selenium or tellurium in triple chalcogenides, the transparency range shifts to the long-wave spectral part, and the nonlinear susceptibility increases as the chalcogen mass increases.[15] The formulas for the effective nonlinear coefficient for initial and mixed crystals coincide and have the form $d_{\text{eff}}(eo\text{-}e) = -(d_{24}\sin^2\varphi + d_{15}\cos^2\theta)$ in the plane XY, $d_{\text{eff}}(oe\text{-}o) = -d_{24}\sin\theta$ in the plane YZ, $d_{\text{eff}}(oo\text{-}e) = -d_{31}\sin\theta$, and $d_{\text{eff}}(eo\text{-}e) = d_{15}\sin\theta$ in the plane XZ, respectively.

2. Phase matching conditions

Phase matching of waves interacting according to the type $(oo \rightarrow e)$ is reached at simultaneous fulfillment of the conditions

$$\frac{1}{\lambda_1} + \frac{1}{\lambda_2} = \frac{1}{\lambda_3},$$

$$\frac{n_1^o}{\lambda_1} + \frac{n_2^o}{\lambda_2} = \frac{n_3^e(\theta)}{\lambda_3} = \frac{n_3^o n_3^e}{\lambda_3 \sqrt{(n_3^o \sin\theta)^2 + (n_3^e \cos\theta)^2}}, \quad (1)$$

which are, in the essence, the energy and quasi-momentum conservation laws; similar expressions can be also written for other interaction types. Here λ_i are the wavelengths of interacting radiations, μm, n_i is the refractive index at λ_i, θ is the angle of matching.

The dispersion dependences of the LiGaS$_2$ and LiGaSe$_2$ refractive indices n_y and n_z were measured in three main planes.[12] Note that the main values of n_y and n_z are very close and have the crossing points at $\lambda = \sim 6.5$ μm for LiGaS$_2$ and ~ 8 μm for LiGaSe$_2$. Following the generally accepted convention,[16] assume that $n_x < n_y < n_z$, then the optical axes lie in the main plane XZ, and the optical coordinate system relates to the crystallographic system as $XYZ \leftrightarrow bac$. The refractive indices of solid solutions can be determined by the formula

$$n_i(x) = [(n_i^A)^2 x + (1 - x)(n_i^B)^2]^{1/2}, \quad i = X, Y, Z. \quad (2)$$

Here A is for LiGaSe$_2$ and B is for LiGaS$_2$. Then the obtained data were approximated in the range 0.5–

11.5 μm using the method of least squares by the Sellmeier equations of the type

$$n^2 = A + B/(\lambda^2 - C) - D\lambda^2. \quad (3)$$

Constants determined in such a way are presented in the Table. Besides, the Sellmeier coefficients were found by the method of proportional averaging the respective coefficients for the initial crystals LiGaS$_2$ and LiGaSe$_2$. The results practically coincide in the both cases.

Sellmeier coefficients for LiGa(Se$_x$S$_{1-x}$)$_2$

x	n	A	B	C	D
0	n_x	4.32683	0.103091	0.030988	0.003702
	n_y	4.47891	0.120426	0.034616	0.003512
	n_z	4.49388	0.117745	0.033700	0.003777
0.2	n_x	4.46118	0.10810	0.06083	0.00343
	n_y	4.62533	0.13108	0.05297	0.00324
	n_z	4.64036	0.12865	0.05140	0.00349
0.4	n_x	4.59533	0.11704	0.07431	0.00316
	n_y	4.77143	0.14379	0.06305	0.00296
	n_z	4.78655	0.14139	0.06126	0.00320
0.5	n_x	4.66224	0.12250	0.07853	0.00302
	n_y	4.84441	0.15055	0.06654	0.00282
	n_z	4.85958	0.14813	0.06469	0.00305
0.6	n_x	4.72903	0.12776	0.08181	0.00289
	n_y	4.91736	0.15749	0.06938	0.00267
	n_z	4.93258	0.15503	0.06750	0.00291
0.8	n_x	4.86252	0.13930	0.08659	0.00261
	n_y	5.06319	0.17174	0.07372	0.00239
	n_z	5.07853	0.16919	0.07179	0.00261
1	n_x	4.99592	0.15130	0.08989	0.00233
	n_y	5.20896	0.18632	0.07687	0.00211
	n_z	5.22442	0.18365	0.07493	0.00232

The degenerated case of three-frequency interactions is the second harmonic generation (SHG). The matching curves for SHG at different content of S/Se in main planes XY and XZ are shown in Fig. 2; the birefringence in the plane YZ is very small, and SHG is possible in narrow wavelength ranges: 2.1–2.3 and 4.8–7.81 μm.

As it follows from Fig. 2, through varying mixing ratio, SHG can be realized in the range 2.1–7.81 μm in the plane XY ($\varphi = 43$–$90°$) and 1.5–11.72 μm in the plane XZ ($\theta = 0$–$57°$). It is also possible to attain the wavelength-conversable non-critical ($90°$) phase matching through selecting the mixing ratio. The optical parametric oscillation (OPO) in LiGa(Se$_x$S$_{1-x}$)$_2$ at pumping by Nd:YAG-laser radiation is of especial interest.

To estimate general tendencies in the behavior of the angular conversion curves of the optical parametric oscillation, we calculated the dependences of excited frequencies (wavelengths) on the angle between the pumping wave vector and the optical axis (Fig. 3).

The conversion curves have no breaks and allow obtaining OPO in the long-wave range of the crystal transparency: 1.2–13 μm ($\varphi = 30$–$90°$) for plane XY; 1.2–13 μm ($\theta = 40$–$55.8°$) for plane XZ; 1.98–2.8 μm ($\theta = 0$–$90°$) for plane YZ.
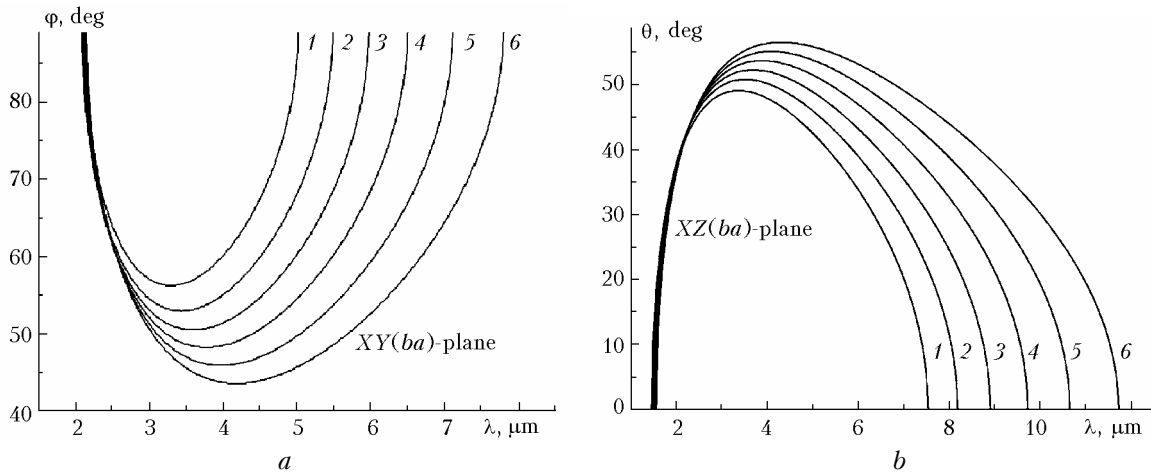
Fig. 2. Phase matching curves for SHG in LiGa(Se$_x$S$_{1-x}$) at $x = 0$ (curve *1*), 0.2 (*2*), 0.4 (*3*), 0.6 (*4*), 0.8 (*5*), 1./0 (*6*) in main planes *XY* (*a*) and *XZ* (*b*).
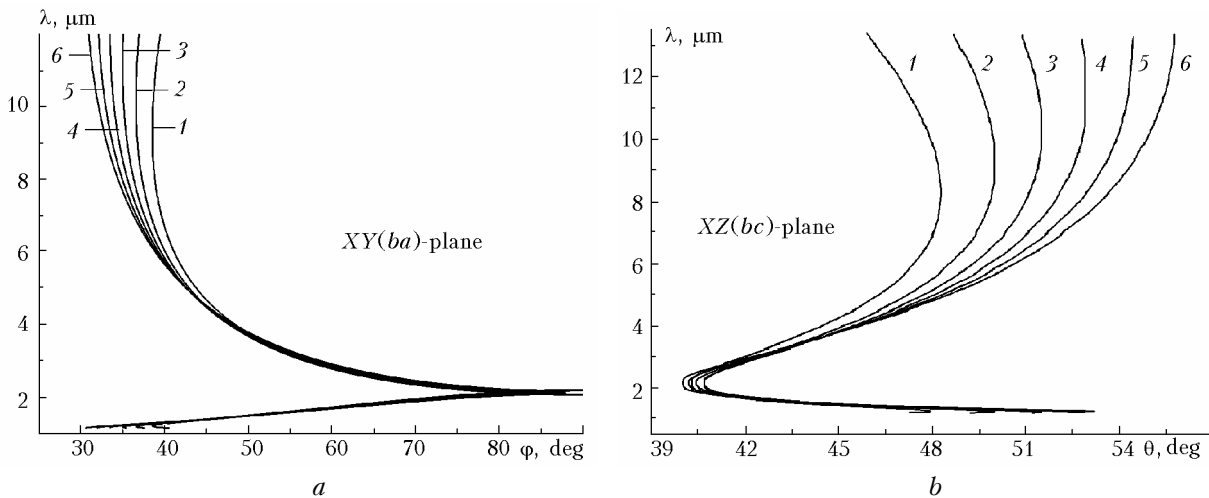
Fig. 3. Conversion curves of phase matching for OPO with pumping by radiation at $\lambda_p = 1.06$ µm at $x = 0$ (curve *1*), 0.2 (*2*), 0.4 (*3*), 0.6 (*4*), 0.8 (*5*), 1.0 (*6*) in main planes *XY* (*a*) and *XZ* (*b*).

3. Admissible variations of the mixing ratio

It is impossible to reach exact phase matching in real frequency converters, i.e., to fulfill the condition $\Delta k = 0$ for interacting waves, therefore, the angular $\Delta\theta$, spectral $\Delta\lambda$, and temperature ΔT matching widths should be known. They allow one to estimate the admissible radiation divergence, spectral width of the pumping source line, as well as random or systematic changes in the crystal (frequency converter) temperature. Besides, there appears a necessity to take into account primarily variations of the mixing ratio x in mixed crystals along the propagation direction, because the mixing ratio can strongly change in the process of the crystal growth in the growth direction.[17] Then, in the linear approximation, Δk can be represented in the form of expansion

$$\Delta k = \frac{\partial(\Delta k)}{\partial(\delta\theta)}\delta\theta + \frac{\partial(\Delta k)}{\partial\lambda}\Delta\lambda + \frac{\partial(\Delta k)}{\partial T}\Delta T + \frac{\partial(\Delta k)}{\partial x}\Delta x; \quad (4)$$

where

$$\frac{\partial(\Delta k)}{\partial x} = \frac{2\pi}{\lambda_1}\frac{\partial n_1}{\partial x} + \frac{2\pi}{\lambda_2}\frac{\partial n_2}{\partial x} - \frac{2\pi}{\lambda_3}\frac{\partial n_3}{\partial x}, \quad \lambda_1 \geq \lambda_2 > \lambda_3; \quad (5)$$

k is the wave vector; $\delta\theta$ is the angular mismatching from the matching direction; T is temperature.

Double decrease of the converted radiation power occurs at wave mismatching $\Delta k = 0.886\ \pi/L$,[1] where L is the crystal length. Taking into account this fact, the estimate of the respective matching widths is possible

$$\Delta\theta = 1.772\pi\left\{L\frac{\partial(\Delta k)}{\partial(\delta\theta)}\right\}^{-1}, \ \Delta\lambda = 1.772\pi\left\{L\frac{\partial(\Delta k)}{\partial\lambda}\right\}^{-1},$$

$$\Delta T = 1.772\pi\left\{L\frac{\partial(\Delta k)}{\partial T}\right\}^{-1}, \ \Delta x = 1.772\pi\left\{L\frac{\partial(\Delta k)}{\partial x}\right\}^{-1}. \quad (6)$$

In this work, we are mainly interested in the spectral behavior of admissible variations of the mixing ratio Δx^+ and Δx^-, i.e., those, which lead to

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50% losses in the conversion efficiency. The results of corresponding calculations for the 1 cm long crystal in its main plane XY are shown in Fig. 4.

a

b
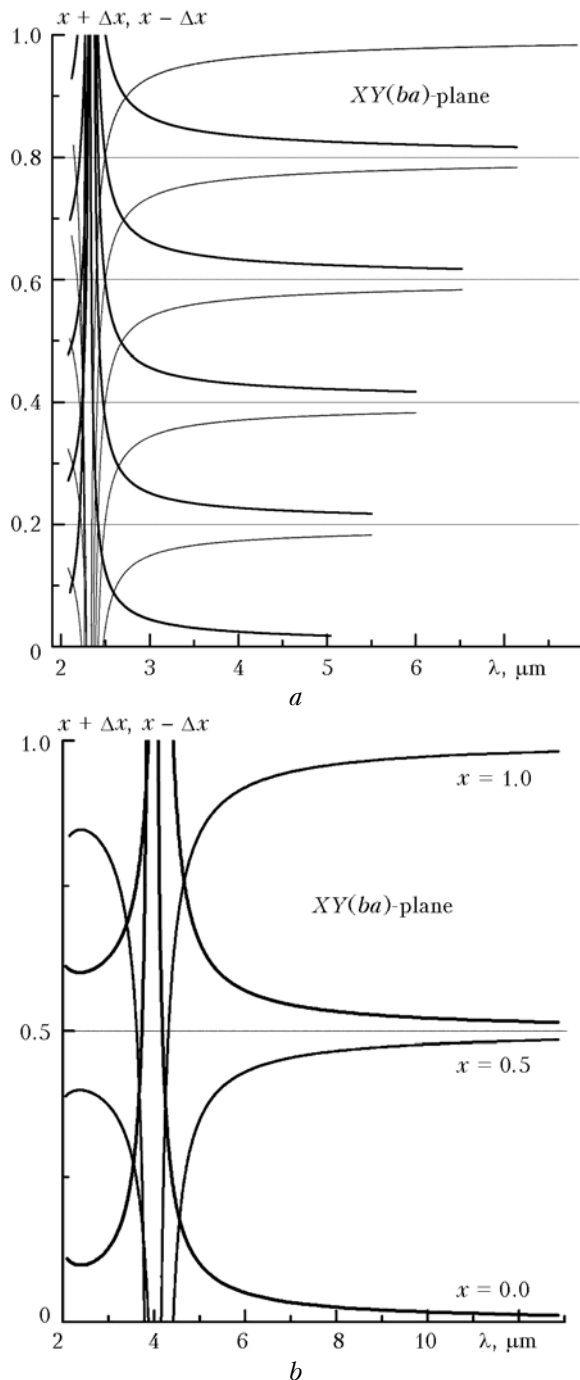
Fig. 4. Spectral dependences of the mixing ratio width causing 50% losses of effectiveness of SHG (*a*) and OPO (*b*) pumped by Nd:YAG-laser in the plane XY.

It is seen (Fig. 4*a*) that in case of SHG the wavelength of 2.45 μm is non-critical to variations of the mixing ratio, which completely corresponds to the results shown in Fig. 2. The behavior of the admissible mixing ratio spectral dependence in case of OPO (Fig. 4*b*) with pumping at $\lambda = 1.06$ μm is

similar to SHG and contains a non-critical point at $\lambda = 4.1$ μm. Thus, the acceptable range of variations of the mixing ratio is determined by the structure of phase matching curves and the pumping wavelength.

The group length L_g is the most important efficiency parameter for frequency conversion of super-short pulses. Its increase is proportional to the decrease of group mismatching of the participating pulses. The group length of interaction L_g for SHG was determined by the formula $L_g = \tau_p / |\Delta u^{-1}|$, where $\Delta u^{-1} = u_1^{-1} - u_2^{-1} = c^{-1}(n_1 - \lambda_1 \partial n_1 / \partial \lambda_1 - n_2 + \lambda_2 \partial n_2 / \partial \lambda_2)$ is the group mismatching, τ_p is the pulse width, $u_{1,2}$, $n_{1,2}$, and $\lambda_{1,2}$ are the group velocities, refractive indices, and wavelengths of pumping and second harmonic, respectively.[18] In spite of the fact that $L_g \to \infty$ only at fixed wavelengths, $LiGa(Se_xS_{1-x})_2$ crystals with finite but quite long group lengths (several millimeters) can be used for practical realization of femtosecond frequency converters.

Conclusion

Based on the conducted investigations and systematization of the known data, coefficients of the Sellmeier dispersion equations for the mixed nonlinear crystals $LiGa(Se_xS_{1-x})_2$ are determined for the first time. Phase matching conditions are found for any three-frequency interactions, OPO pumped by solid-body lasers, and SHG as function of the selenium and sulfur percentage. In some cases, the matching close to non-critical can be attained through varying mixing ratio x. Thus, the radiation shift effect is excluded, and, hence, the conversion efficiency increases. When pumping by femtosecond lasers ($\lambda = 0.7-1.32$ μm) in the direction of phase matching, the group velocity matching conditions are also fulfilled. Comparative analysis of the known physical characteristics of crystals for nonlinear optical interactions in the IR shows that $LiGa(Se_xS_{1-x})_2$ crystals belong to most promising nonlinear media for creation of optical parametric oscillators pumped by solid-body near-IR lasers and for frequency conversion of the femtosecond radiation to the IR.

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