Fulfillment of phase-matching conditions and optical characteristics of lithium thioindat nonlinear crystals

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The paper describes the results of investigation of linear and nonlinear-optical characteristics as well as the radiation stability for biaxial $LiInS_2$ crystal. The Sellmeier equation coefficients for the spectral range of 0.45–11.5 μm and the values of coefficients of a nonlinear susceptibility tensor are determined. Calculations have been carried out of phase-matching conditions for different problems in the frequency conversion, namely, angular and frequency tuning dependences. A possibility has been demonstrated of realizing group matching in a wide range of wavelengths when generating the sum and difference frequencies. The paper describes the spectral dependences of group-velocity matching calculated in a direction of phase matching, whence a possibility of creating frequency converters of 3 μm femtosecond lasers follows.

It is known that the remote laser sensing of the atmosphere is of great importance in evaluating the changes occurring in the Earth's atmosphere. In the case that these changes are accompanied by the appearance of toxic gas components, their detection by use of IR sources becomes very desirable. This depends upon the fact that most of molecules have the vibration-rotation transitions in the middle infrared range (2–12 μm). To detect the absorption gases at these transitions, a frequency-tunable source with a narrow radiation line is required, which can be tuned to definite characteristic absorption lines.

The development of such systems was limited because of the lack of corresponding infrared nonlinear-optical materials for frequency conversion of the effective lasers, above all, CO_2 laser. The preparation of effective crystal frequency converters can not only greatly enlarge the number of the problems to be solved but also can improve the parameters of existing systems. A good example of the aforesaid are the doublers of 9 μm radiation band extending the number of gases controlled with a lidar based on CO_2 lasers.[1,2] Such crystals as silver selenogallate ($AgGaSe_2$), silver thiogallate ($AgGaS_2$), gallium selenide (GaSe), zinc germanium phosphide ($ZnGeP_2$), cadmium germanium arsenide ($CdGeAs_2$) were used in the middle infrared range for harmonic generation, generation of combination frequencies, parametric generation and amplification.[3] Selection of the most attractive crystal depends on a series of parameters. The most important parameters are the transmission range, nonlinear coefficient, and damage threshold.

However, selection of a nonlinear crystal even for a particular problem, e.g., the CO_2 laser second harmonic generation, is not clear. If we proceed only from the value of the nonlinear susceptibility coefficient, $CdGeAs_2$ crystal is in the lead, but its operating conditions are fulfilled at cryogenic temperatures and in crystal growing it is difficult to obtain high-quality crystals of a large size. The other materials have their own disadvantages. This paper presents the results of the investigation of a promising nonlinear lithium thioindat crystal, which is poorly known.

In spite of a wide transmission range, a sufficiently high nonlinear susceptibility, and satisfactory birefringence, the semiconductor nonlinear $LiInS_2$ crystals[4–6] did not attract the attention of specialists. Being second to oxide crystals in the visible and near infrared ranges in radiation stability and being second to many crystals of the middle infrared range in the value of the nonlinear susceptibility coefficient, the semiconductor nonlinear $LiInS_2$ crystals are unlikely to seek leadership even though in one spectral range. The difficulties of a growing qualitative crystal of acceptable size are an additional restricting factor. The difficulties did not enable one to evaluate practically the advantages of $LiInS_2$ crystals as compared with crystals of the middle IR range, which can give the presence of more light Li cations. However, the technological advances in recent years[7,8] have stimulated the investigations and have made it possible to study the physical characteristics, to determine the role of $LiInS_2$ crystals in nonlinear optics, the prospects for the development of applied devices on the crystal basis.

In our investigations we used the transparent or slightly yellowich samples of crystals of size to

4×4×4 mm and of relatively high optical quality grown at the Kuban State University, using the Bridgman–Stockbarger method. The biaxial negative $LiInS_2$ crystals refer to the mm2 point symmetry group; they are not hygroscopic, their density is 3.5 g/cm^3, the melting point is 880°C, the Moos hardness is 3–4.[1]

To determine the transmission spectra in the visible and near infrared ranges, we used an optical Shimadzu UV-3101PC spectrophotometer with a blind of diameter 2 mm and a polarization attachment. In the middle infrared range the spectra were determined by means of Specord 75IR and Specord 80 spectrophotometers. The transmission range of colorless 3.6 mm crystals at a level of 0.1 lies in the range 0.4–12.5 μm, and at a level of 0.25 the crystals are transparent in the range 0.5–11 μm (Fig. 1).

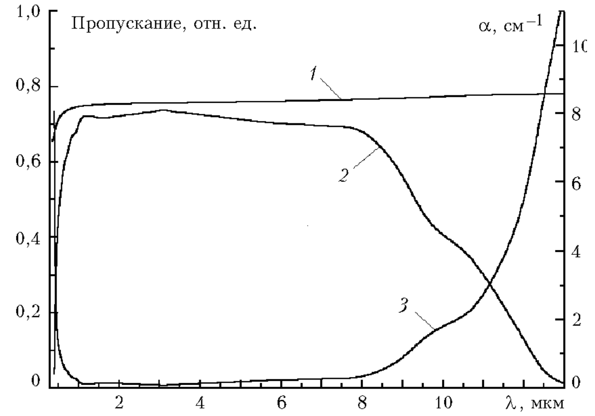


Fig. 1. The level of Fresnel's losses (*1*), the transmission spectrum (*2*), and the absorption coefficient (*3*) of $LiInS_2$ monocrystal of 3.6 mm length.

In the range of maximum transmittance from 0.1 to 8.0 μm, the coefficient of optical losses $a \approx 0.1$–0.25 cm^{-1}, and at CO_2 laser wavelengths 9.2–10.8 μm – from 1.1 to 2.3 cm^{-1}. The shortwave boundary of the transmittance spectrum for a 3.5 mm crystal of a comparable composition and quality at the level $a = 200$ cm^{-1} is determined as 330–334 nm at a temperature of 80 K and 342–343 nm at 300 K for different polarization of optical radiation.[7] The longwave boundary at the same level can be determined as close to 13.2 μm.

The dispersion dependences of the refraction indices were determined by the method of the least deviation using prisms. Figure 2 shows the experimental dispersion curves $n_x < n_y < n_z$, which were approximated with an accuracy of $\leq 10^{-3}$ using the Sellmeier equation

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

The values of coefficients are given in Table 1 for the range 0.45–11.5 μm in the crystal-optical coordinate system.

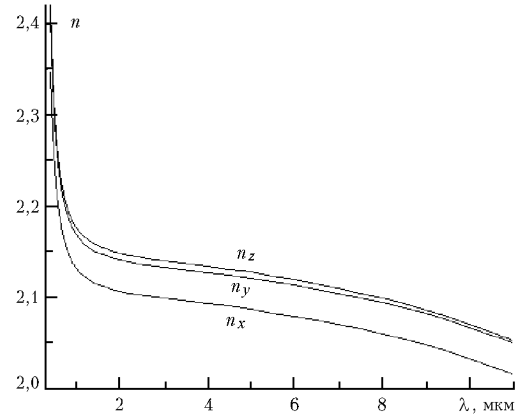


Fig. 2. Dispersion dependences of the key values of refraction indices.

Drastic distinctions between the measured and described in Ref. 4 refraction indices were not detected.

The values of coefficients of tensor of nonlinear susceptibility of the second order $d_{31} = 6.2$, $d_{32} = 5.4$, and $d_{33} = 9.8$ pm/V (correct to ±15%) are 80% lower than the corresponding known values.[4,8] These values were obtained from the comparative measurements of the SHG efficiency using the method of slender wedge (5°) by the procedure from Ref. 4 with the use of a pulse-periodic CO laser. The coefficients $d_{14} = d_{36}$ of the reference wedges from $ZnGeP_2$ were taken equal to 75 pm/V. Note that the measured and calculated phase-matching angles agreed accurate to no less than 0.3° determined by the measurement error.

Table 1. Table of the Sellmeier coefficients

Coefficients	*Y*	*X*	*Z*
A	4.418222	4.559534	4.59206
B	0.1254461	0.1403701	0.1410887
C	0.0657432	0.069233	0.069287
D	0.0028850	0.0028731	0.0030589

The damage threshold was determined for 36 ± 2 ns pulses of TEA CO_2 laser radiation (9.55 μm) formed by TEM_{00} mode, containing no less than 85% of total pulse power. The destruction threshold is 120–130 MW/cm^2.

According to the modern practice of classification of types of interaction, when transforming the radiation in biaxial crystals, the following types of interaction occur: ssf (slow-slow-fast), sff (slow-fast-fast) and fsf (fast-slow-fast); the last letter corresponds to the smallest wavelength. The relations between the values and signs of the coefficients of tensor of nonlinear susceptibility show that for ssf-type of interaction the effective nonlinear coefficient differs from zero in the plane *xz* at $\theta < V_z$ (V_z is the angle to optical axis). For sff- and fsf-types the effective nonlinear coefficient differs from zero in the plane *xz* at $\theta > V_z$ and in the planes *xy* and *yz*. The maximum value of the coefficient of effective nonlinearity takes place for the second type of interaction along y axis.

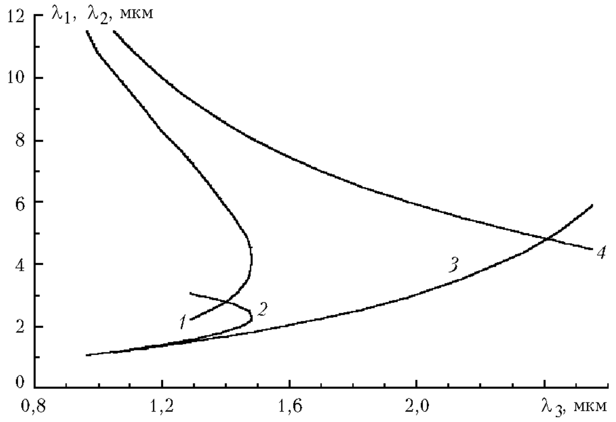
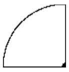
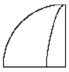
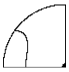
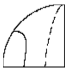
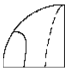
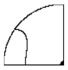
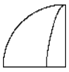
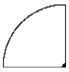


Fig. 3. Spectral dependence of group velocity matching of waves s_1–f_3 (*1*), s_2–f_3 (*2*), f_1–f_3 (*3*) and f_2–f_3 (*4*) for sff-type (*1*, *4*) and fsf-type (*2*, *3*) of interaction.

Table 2. Table of transitions using the diagram of directions of SHG phase-matching

Transition	Diagram	λ, nm	
		ssf	sff
00–10		1573.5 (y)	–
10–30		1731.9 (z)	–
30–31		–	2294.8 (y)
31–33		–	2638.3 (z)
33–31		–	5104.7 (z)
31–30		–	5785.7 (y)
30–10		7945.2 (z)	–
10–00		8498.5 (y)	–

The SHG phase-matching characteristics for $LiInS_2$ crystal are conveniently expressed by the diagram of directions of phase matching in biaxial crystals.[9] Table 2 gives the numbers corresponding to the transitions from one projection to another using the diagram,[9] that is, to those cases that the direction of phase matching coincides with one of the optical axes. Table 2 gives also the wavelengths of basic radiation, at which this transition occurs, and designation of the axes.

Each of the stereographic projections in Table 2 shows the angular distribution of phase-matching directions for ssf (solid line) and sff-types (dashed lines) of interaction. Depending on the dispersion of birefringence of a crystal (on the difference between basic values of refraction indices) and the variation of the dispersion when varying a wavelength of basic radiation, the type of angular distribution is changed converting from one projection to another. At such a transition the position of a point of intersection of a phase-matching curve with the main crystal planes (xy, xz or yz) is changed.

From these results it follows that the phase matching along a direction to x axis is not realized at any wavelengths. A "loop" character of transitions based on the diagram of directions of phase matching, when changing a wavelength, indicates that phase matching must exist in the crystal, that is not critical in relation to the wavelength, and its special case, group velocity matching.

Figure 3 shows the dependences of wavelengths λ_1 and λ_2 on the wavelength λ_3 ($\lambda_3^{-1} = \lambda_1^{-1} + \lambda_2^{-1}$), for which the condition of group velocity matching is fulfilled in a direction of phase matching of the fsf-type and sff-type in the plane xy. These results indicate that the frequency conversion (SHG, SFG, DFG) of femtosecond pulses can be performed within a wide wavelength range. In particular, $LiInS_2$ crystals are the only known crystals for the frequency conversion of femtosecond lasers of 3 μm range. The wavelength-tuned characteristics in the xy plane at different values of the angle ϕ are given in Fig. 4, and the spectral dependence of group velocity matching along the phase-matching direction for the ssf type of interaction is shown in Fig. 5.

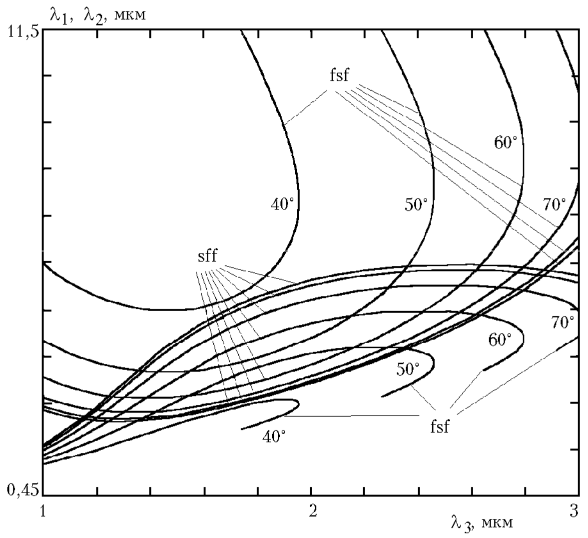


Fig. 4. The wavelength-tuned characteristics in the xy plane.

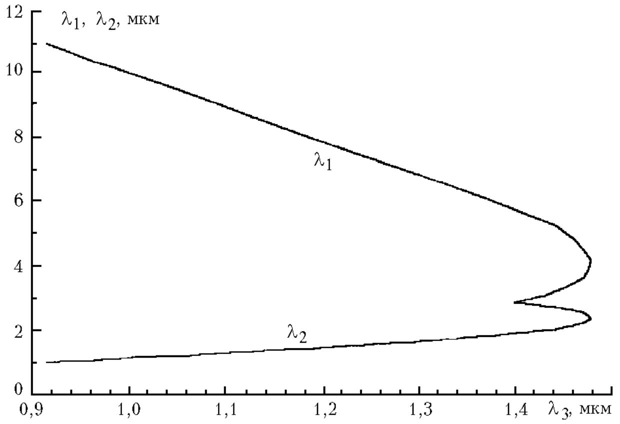


Fig. 5. Spectral dependence of group velocity matching of s_1–f_3 for the ssf-type of interaction (along the direction of phase matching).

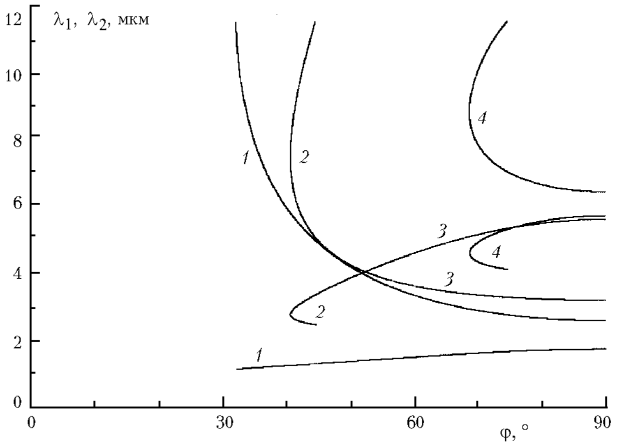


Fig. 6. The angle ϕ-tuned characteristics in the *xy*-plane at λ_3 = 1 μm (*1*), 2 μm (*2*, *3*) and 3 μm (*4*) for the fsf (*1*, *2*, *4*) and sff (*3*) types of interaction.

Figure 6 gives the angle ϕ-tuned dependences for the sff and fsf types of interaction at pumping wavelengths λ_3 = 1 μm, 2 μm, and 3 μm. The type of tuning curves counts in favor of a possible advantage of 3 μm lasers among other known crystals for a set of parameters at the second harmonic generation.

In conclusion it should be noted that the transmission spectrum, nonlinear characteristics, and birefringence of $LiInS_2$ monocrystals allow us to consider them as promising ones for the frequency conversion of femtosecond 3-μm Er lasers. The calculated results on phase-matching conditions were obtained with the use of the LID-SHG information-computing program complex (www.bmstn.ru/~lid).

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