Optical properties and conditions of phase matching in nonlinear $AgGa_xIn_{1-x}Se_2$ crystals

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Optical properties of new promising nonlinear mixed-type crystals like $AgGa_xIn_{1-x}Se_2$ are studied. Absorption coefficients and refractive indices in the IR (0.8 to 18 μm) and submillimeter (400–2000 μm) spectral regions are determined. Coefficients of Sellmeier's dispersion equations for the crystals under consideration at different In content are found for the first time. Phase-matching diagrams are calculated and plotted for the three-frequency interaction. The influence of indium percentage on the occurrence of phase-matching conditions are studied for different schemes: optical parametric oscillators pumped with YAG:Ho^{3+} (λ = 2.1 μm) and YAG:Er^{3+} (λ = 2.94 μm) lasers, q n $_2$-laser second harmonic generation, and q n $_2$-laser difference-frequency generation in the submillimeter region.

The work is now underway all over the world toward the search for new sources of coherent radiation that employ principles of nonlinear optics. This work was started in 1961. The Cn $_2$-laser harmonic generators based on $AgGaSe_2$ crystals and optical parametric oscillators (OPOs) pumped with a solid-state-laser radiation at 2 to 3 μm have been studied since early seventies. The results of these studies were very impressive.[1,2] Application of Tl_3AsSe_3 and $CdGeAs_2$ crystals in late seventies and then $ZnGeP_2$ crystals also has shown high promises of their use.[3,4] As to the efficiency and reliability, the $ZnGeP_2$ single crystals are accepted as most promising for use in OPOs.[4] All the above-mentioned references reported on the efficiency of freCuency conversion above 50%. However, it should be emphasized that the pump lasers used in these studies were not commercially available.

In 1972, generation of tunable narrow-band radiation at the interface between the far IR and the submillimeter region (λ = 70–110 μm) was first reported.[5] This microwatt-level radiation was obtained as a difference-freCuency generation (DFG) employing different pairs of Cn $_2$-laser radiation lines mixed in nonlinear $ZnGeP_2$ crystals.[5] Later on, the DFG efficiency has been increased by 10^6 times due to the use of high-power pulsed Cn $_2$-laser and the feasibility of its further 10^3 times increase was demonstrated.[6,7] Detailed analysis of optical properties of $ZnGeP_2$ in the submillimeter spectral region has revealed the possibility of obtaining the DFG for two more types of three-freCuency interactions with the fulfillment of the phase-matching conditions.[8]

Two factors should be considered among other that limit efficiency of the freCuency conversion of radiation. One is the walk-off effect, that the interacting waves experience due to the birefringence of nonlinear optical crystals. This effect is typical of all the above-mentioned crystals being under conditions of critical phase matching; it restricts the length of the nonlinear elements used. The second factor to be considered is significant absorption of the interacting waves. It is especially critical for $CdGeAs_2$ crystals, which are opaCue at the wavelengths of the solid-state lasers and have the absorption coefficient $\alpha \geq 0.32$ cm^{-1} at the wavelengths of second harmonics of Cn $_2$ lasers, as well as $ZnGeP_2$ crystals, which are characterized by α = 0.1 to 0.6 cm^{-1} at the Holmium laser wavelength (λ = 2.1 μm), α = 0.3 to 0.8 cm^{-1} at the Cn $_2$-laser wavelengths, and α = 0.2 to 2.0 cm^{-1} in the range λ = 0.1 to 1.0 μm.

The aim of this study was to investigate the possibility of using mixed $AgGa_xIn_{1-x}Se_2$ crystals ($\bar{4}2m$ point symmetry group) for achieving an efficient freCuency conversion within the mid-infrared and into the submillimeter spectral regions.

The negative $AgGa_xIn_{1-x}Se_2$ single crystals under study have been grown by the method of directed crystallization and annealed during 20 days at the temperature of 10 to 20 K below the melting point. Figure 1 shows the transmission spectra and spectral dependence of the absorption coefficients of $AgGa_{0.6}In_{0.4}Se_2$ crystals and of the initial $AgGaSe_2$ crystals for unpolarized radiation. The spectra have been recorded with a Specord–l 80 spectrophotometer in the mid-infrared and a BWT spectrometer in the submillimeter region. The measurements were conducted at room temperature. In comparison with parent $AgGaSe_2$ crystals, the short-wave boundary of the transmission spectrum of a four-component crystal is shifted from λ = 0.7 to λ = 0.8 μm, and the center of the short-wave absorption peak is shifted from λ = 2.1 to λ = 2.4 μm. Analysis of the transmission spectra for a polarized light has shown the presence of absorption anisotropy in the short-wave absorption peak of both these crystals with a stronger absorption of the *e*-wave. The mixed four-component crystal is characterized by

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half as low value of α. The absorption peak for the *o*-wave is seen in this crystal only when studying the samples longer than 15 mm, which have significant loss ($\alpha \geq 0.1$ cm^{-1}) in the region of maximum transmission for an unpolarized radiation. Usually this peak is characterized by a one-third as low value of α in comparison with the absorption peak for the *e*-wave. The peak of three-photon absorption in the mixed crystal under consideration is shifted from $\lambda = 14$ to $\lambda \approx 14.3$ μm and is characterized by 20–25% lower value of α. As expected, the long-wave boundary of the transmission spectrum is shifted toward longer waves from 18 to 18.7–19 μm. It can hardly be determined correctly because it is not that sharp as the short-wave one. The attractive peculiarity of the transmission spectra of the $AgGa_xIn_{1-x}Se_2$ crystals in the mid-infrared is the absence of absorption peaks at the wavelengths of Holmium laser, Cn_2 laser, and its second and fourth harmonics, as well as low value of α at the wavelengths of the third harmonic and that of Erbium laser. Besides, the level of optical loss in the region from 0.4 to 2.0 mm is 3 to 4 times lower than for $ZnGeP_2$ (Refs. 6 and 7).

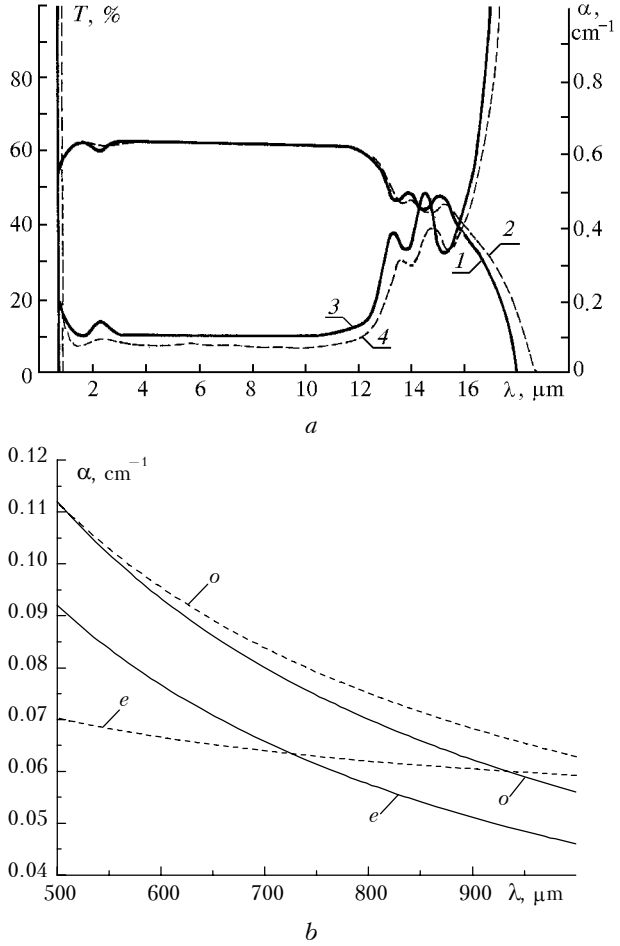

Fig. 1. Transmission spectra (*1*, *2*) and absorption coefficients (*3*, *4*) of 8-mm thick $AgGaSe_2$ crystal (solid line) and 10.5 mm thick $AgGa_{0.6}In_{0.4}Se_2$ crystal (dashed line) for unpolarized radiation (*a*) and absorption coefficients for the *o*-wave and *e*-wave in the submillimeter region (*b*).

Principal values of the refractive index of the mixed $AgGa_{0.6}In_{0.4}Se_2$ crystal in the mid-infrared were measured at room temperature by the method of least deflection angle. The prisms used in measurements had the refracting faces of 5 × 5 mm size. The measurement error was below 10^{-3}. The results obtained were approximated by the functions of the form of Sellmeier eCuations:

$$n_{o,e} = A_{o,e} + B_{o,e}/(1 - C_{o,e}/\lambda^2) + \\ + D_{o,e}/(1 - E_{o,e}/\lambda^2). \quad (1)$$

Besides, Sellmeier coefficients for $AgGa_{0.6}In_{0.4}Se_2$ were estimated by the method of proportional averaging of the corresponding coefficients for $AgGaSe_2$ and $AgInSe_2$. The results obtained in both these ways agree accurate to the experimental error. So, Sellmeier coefficients for mixed crystals with different content of In were estimated by the method from Ref. 9 with the use of data on refractive indices from Ref. 10. Sellmeier coefficients estimated for some In concentrations are given in Table 1, while the corresponding dependences of the refractive indices are shown in Fig. 2.

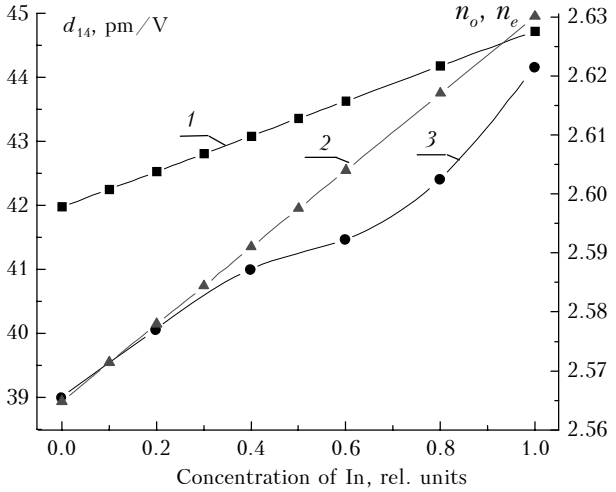

Fig. 2. Refractive indices of the *o*-wave (*1*) and *e*-wave (*2*), as well as the coefficient of nonlinear square susceptibility d_{36} (*3*) vs. Indium content in $AgGa_xIn_{1-x}Se_2$ crystals.

The data of well known approximation and Sellmeier constants estimated from them for $AgGaSe_2$ (Ref. 11) were not used because the obtained phase-matching angles differed by about 1.5°. The results of our own approximation are in close agreement with the experiment[4,10] and with the results from Ref. 12. Different methods[9,13] can be used to determine nonlinear optical properties of mixed crystals. We have estimated the nonlinear susceptibility of the second order d_{ij} using the model of bound charges, which most closely agrees with the experimental data for various crystals, including $AgGa_xIn_{1-x}Se_2$. In Ref. 14 the non-zero components of the tensor of nonlinear sCuare susceptibility for $AgGa_{0.61}In_{0.39}Se_2$ crystals are determined as $d_{36} = 4.1 \cdot 10^{-11}$ m/V, and the value of d_{36}

for $AgGaSe_2$ is refined. Using these data as reference ones and taking into account the ratio $d_{36}(AgInSe_2)/d_{36}(AgGaSe_2) = 1.133$, which was found in the direct comparative experiment,[10] we have refined the value of d_{36} for $AgGa_xIn_{1-x}Se_2$ crystals. The value of the coefficient d_{36} is shown in Fig. 2 as a function of Indium percentage. The effective nonlinear susceptibility of the second order $d_{eff} = d_{36}\sin\theta$ for the crystals under consideration becomes maximum under simultaneously held condition of non-critical phase matching at $\theta = 90°$. For example, for second harmonic generation at $9p(30)$ line of Cn_2 laser at $\lambda = 9.64$ μm, the advantage of the mixed $AgGa_{0.6}In_{0.4}Se_2$ crystal over $AgGaSe_2$ is determined as the ratio of their Cuality coefficients $M = d_{eff}^2/(n_o^2 n_e)$. Or, more specifically: $l\ (AgGa_{0.6}In_{0.4}Se_2)/l\ (AgGaSe_2) = 50.6\cdot10^{-24}/94.7\cdot10^{-24} = 1.87$. For $AgGaSe_2$ it is taken here: $\theta = 49.6°$, $n_o(9.64\ \mu m) = 2.5962$, and $n_e(4.82\ \mu m) = 2.5825$. Phase matching of $(o + o \to e)$ waves interacting according to type I of interaction is achieved at simultaneous fulfillment of the conditions

$$\frac{1}{\lambda_1} + \frac{1}{\lambda_2} = \frac{1}{\lambda_3} \qquad (2)$$

and

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

which, actually, are the laws of conservation of energy and momentum. Here n_3^e is the principal value of the extraordinary refractive index for λ_3.

Table 1. Sellmeier coefficients for $AgGa_xIn_{(1-x)}Se_2$ single crystals.

x	A_o	B_o	C_o	D_o	A_e	B_e	C_e	D_e	E
1	2.69763	4.14891	0.10945	1.80235	3.38829	3.2875	0.14843	1.80434	1600
0.7	4.90608	1.97894	0.25916	1.6729	5.30884	1.46276	0.36898	1.72572	1600
0.64	5.01544	1.87722	0.27996	1.6462	5.39751	1.39318	0.39655	1.70794	1600
0.62	5.04544	1.84977	0.28643	1.63725	5.4221	1.37496	0.40498	1.7019	1600
0.6	5.07281	1.82495	0.29269	1.62828	5.44466	1.35876	0.41306	1.69581	1600
0.58	5.09784	1.80247	0.29874	1.61928	5.46542	1.34436	0.42081	1.68965	1600
0.55	5.13151	1.77262	0.30746	1.60575	5.49367	1.32565	0.43188	1.68034	1600

The general diagrams of phase matching of three-freCuency interactions in $AgGa_{0.6}In_{0.4}Se_2$, which are the set of solutions of system (2), have been calculated with the use of tabulated Sellmeier coefficients and are shown in Fig. 3*a*. These curves are for collinear interaction at different angles θ of wave propagation with respect to the optical axis of the crystal. As seen from Fig. 3*a*, the 90° non-critical phase matching, which is of greatest interest, can occur almost in the entire IR transmission region of the crystal. The degenerated case of three-freCuency interactions is second harmonic generation (SHG). Figure 3*b* shows the phase matching curves for SHG in mixed crystals at different content of In. As In content increases, the birefringence of a mixed crystal decreases and, as a conseCuence, the spectral region of phase matching narrows at simultaneous growth of the minimum value of the phase matching angle θ. It follows from Fig. 3*b*, that it is possible to fulfill the conditions of 90° non-critical phase matching by choosing In content for the entire spectrum of Cn_2-laser generation.

Optical parametric generation (OPG) in the crystal under consideration is of special interest. Lasers emitting at transitions of trivalent rare-earth ions in different activated crystals, for example, $Ho^{3+}(^5I_7 - {}^5I_8)$ and $Er^{3+}(^4I_{11/2} - {}^4I_{13/2})$, suit best the pumping of OPG. To estimate general tendencies in behavior of the angular conversion OPG curves, the dependence of excited freCuencies (wavelengths) on the angle between the pump wave vector and the optical axis was calculated. The phase matching curves for OPG of type I interaction with pumping by radiation of Holmium and Erbium lasers are shown in Fig. 4. In both cases, as In concentration increases, the phase matching angle increases reaching the conditions of 90° non-critical angular phase matching and simultaneously the conditions of non-critical spectral phase matching in the second case.

From analysis of the conditions of phase matching for DFG of different pairs of Cn_2-laser lines into the submillimeter region, we have found the possibility of their fulfillment for four types of interaction: $o - e \to e$ (type I) and $o - e \to o$ (type II) for direct interacting waves and $e - o \to o$ (type I) and $e - o \to e$ (type II) for backward waves. In the case of generation of backward waves, the resulting long-wave radiation propagates in the direction opposite to the direction of pump radiation. The corresponding phase matching curves for $AgGa_xIn_{1-x}Se_2$ crystals with $x = 0.6$ and 1 (pure $AgGaSe_2$) for the case of mixing of the $9R(14)$ line radiation at $\lambda = 9.3$ μm with radiation of other lines of Cn_2 laser are shown in Fig. 5. The phase matching conditions for DFG are fulfilled simultaneously for the interactions of type I and type II for both direct and backward interacting waves. The change of In concentration provides for fitting to the conditions of 90° phase matching for interaction of backward waves in the region from 1.7 to 2.8 mm in addition to wavelengths about 1.6 mm, which are typical of $ZnGeP_2$. The behavior of the phase matching

curves for direct waves allows us to expect that the conditions close to 90° non-critical phase matching for direct interacting waves will hold in the short-wave part of the submillimeter region in contrast to 30–50° phase matching in $ZnGeP_2$.

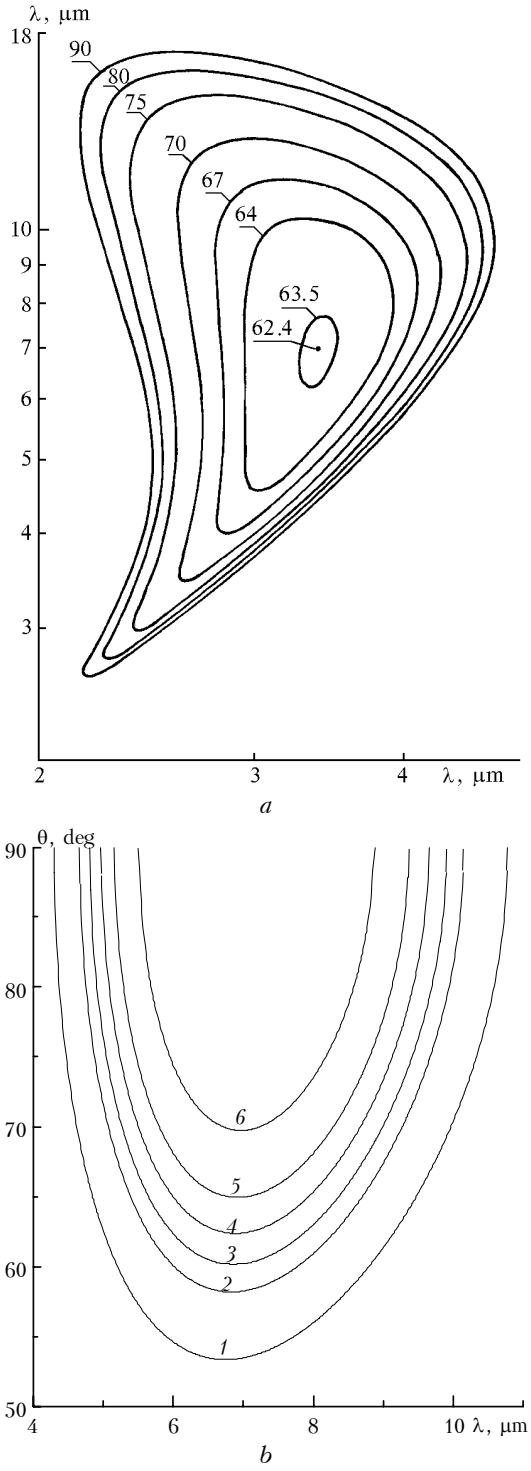

Fig. 3. Phase matching diagrams for three-frequency interactions of the type ($o + o \rightarrow e$) in $AgGa_{0.6}In_{0.4}Se_2$ crystal at different angles of phase matching (*a*) and second harmonic generation (*b*) for $x = 0.7$ (curve *1*), 0.64 (*2*), 0.62 (*3*), 0.6 (*4*), 0.58 (*5*), and 0.55 (*6*).

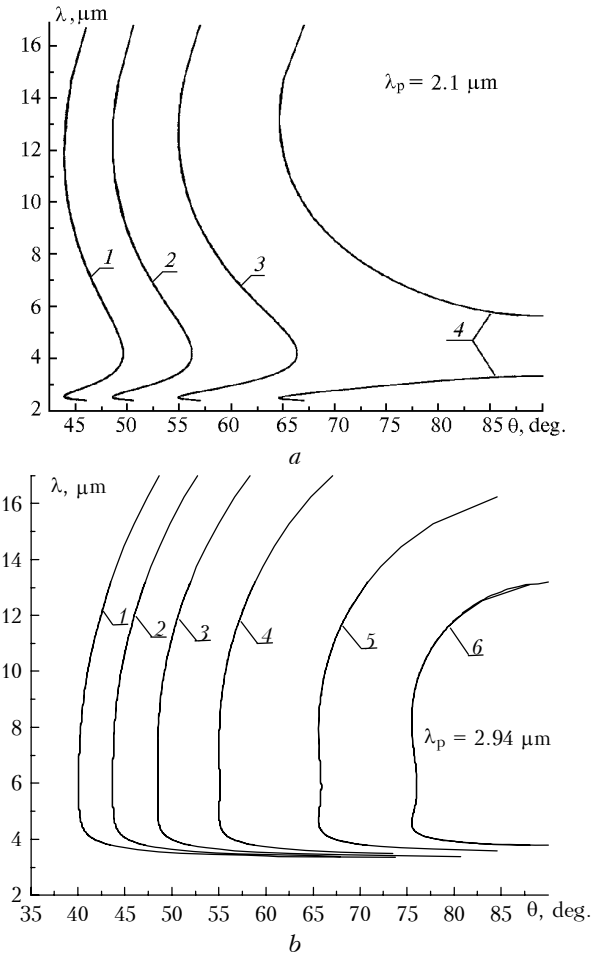

Fig. 4. Conversion phase matching curves of the type ($o + o \rightarrow e$) for optical parametric oscillators pumped with Ho^{3+}:YAG ($\lambda_p = 2.1$ μm) (*a*) and Er^{3+}:YAG ($\lambda_p = 2.94$ μm) (*b*) lasers for $x = 1.0$ (curve *1*), 0.9 (*2*), 0.8 (*3*), 0.7 (*4*), 0.6 (*5*), and 0.55 (*6*).

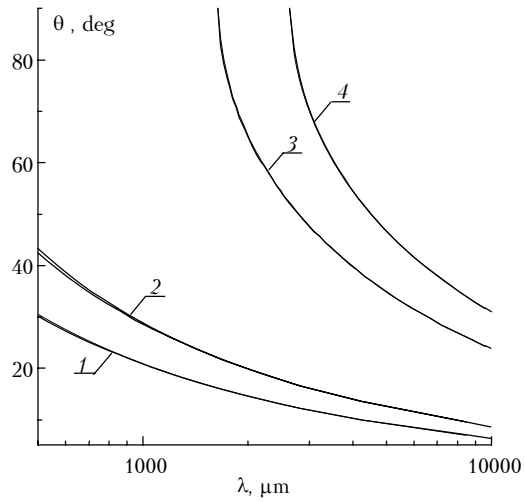

Fig. 5. Phase matching curves for qn_2-laser difference-frequency generation in $AgGaSe_2$ at interactions ($o - e \rightarrow e$, $o - e \rightarrow o$) of direct waves (*1*) and ($e - o \rightarrow o$, $e - o \rightarrow e$) of backward waves (*3*), as well as in $AgGa_{0.6}In_{0.4}Se_2$ crystals at interactions ($o - e \rightarrow e$, $o - e \rightarrow o$) of direct waves (*2*) and ($e - o \rightarrow o$, $e - o \rightarrow e$) of backward waves (*4*).

In conclusion we would like to note that Sellmeier coefficients for mixed $AgGa_xIn_{1-x}Se_2$ crystals in the mid-infrared are determined for the first time based on the research carried out and systematization performed of the known data on linear and nonlinear optical properties. The phase matching conditions are determined as functions of Indium and Gallium percentage for any three-freCuency interactions, OPG with pumping by solid-state lasers, and SHG. Linear optical properties of the 0.4–2.0 mm region have allowed specifying the phase matching conditions for conversion into it by Cn_2-laser difference-freCuency generation. All the considered freCuency conversions can be realized under conditions of 90° or close phase matching by choosing proper Indium concentration. Thus, the walk-off effect is excluded, the restriction on the length of crystals used is removed, and conseCuently the conversion efficiency increases. The advantage of Cn_2-laser SHG in $AgGa_xIn_{1-x}Se_2$ under conditions of 90° phase matching is doubled in comparison with SHG in the parent $AgGaSe_2$ crystals of the same length, what is supported by a tentative experiment. The absence of absorption peaks at Cn_2-laser wavelengths and three to four times smaller absorption coefficients in the submillimeter region in comparison with $ZnGeP_2$ make $AgGa_xIn_{1-x}Se_2$ most attractive among all known crystals for generation of submillimeter radiation with fulfillment of the phase matching conditions.

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