Phase matching and group-velocity matching conditions in nonlinear mixed AgGa(Se$_{1-x}$S$_x$)$_2$ crystals

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The coefficients of Sellmeier dispersion equations for the new promising nonlinear mixed crystals AgGa(Se$_{1-x}$S$_x$)$_2$ are found for the first time. The phase matching diagrams for three-frequency interactions are calculated and plotted. The dispersion of group-velocity matching for second harmonic generation is determined. The influence of the mixing ratio on the phase-matching conditions is studied for different schemes: optical parametric oscillators pumped with YAG:Ho^{3+} ($\lambda = 2.1$ μm) and YAG:Nd^{3+} ($\lambda = 1.064$ μm) lasers, CO$_2$ laser second harmonic generation. The surface damage threshold is estimated.

Introduction

Generation of frequency tunable coherent radiation by the methods of nonlinear optical frequency mixing is now a well-developed technique. After advent of lasers, numerous nonlinear materials were discovered for their use in different laser devices operating in the UV, visible, and IR spectral regions. For laser systems operating in the mid-IR, high optical quality ZnGeP$_2$ and AgGaSe$_2$ crystals are now available. However, because of significant absorption in the short-wave transparency range, pump sources for these crystals should have the wavelength longer than 1.5 μm. Investigations aimed at seeking and production of suitable nonlinear materials with high optical quality, strong square-law nonlinearity, and high damage threshold are still in progress.

Reference 1 reported the creation of a CsGeCl$_3$ crystal having a wide transparency range in both infrared and visible regions (0.4−20 μm). However, this crystal is yet insufficiently studied; it is available only in the form of laboratory samples. The LiInS$_2$ crystal transparent in the region of 0.4−12.5 μm has low nonlinearity ($d_{31} = 6.2$, $d_{32} = 5.4$, and $d_{33} = 9.8$ pm/V) [Refs. 2, 3]. However, in the general case all the above-mentioned crystals do not guarantee fulfillment of the noncritical phase matching conditions for any pre-selected pump wavelength.

To solve this problem, it is worth considering mixed crystals of chalcogenide or chalcopyrite structures. Triple chalcogenide crystals with high nonlinear square-law susceptibility find their use in conversion of the radiation frequency from the visible to the mid-IR region, in particular, in pico- and femto-second laser systems. Earlier it was shown that production of solid solutions of two semiconductor crystals like A^{I}B^{III}C$_2^{VI}$ (Ref. 4) or A^{IV}B$_2^{VI}$ and A^{I}B^{III}C$_2^{VI}$ (Ref. 5) is a promising method for obtaining crystals with a wide transparency range and controllable birefringence.

These crystals possess noncritical phase matching achievable by the proper selection of the mixing ratio x for the pre-selected wavelength. Development of various laser devices employing noncritical phase matching in CdGe(As$_x$P$_{1-x}$)$_2$, AgGa$_x$In$_{1-x}$S$_2$ (mid-IR, Ref. 4) and AgGa$_x$In$_{1-x}$Se$_2$ (near and middle IR, Refs. 6 and 7) has already been reported.

This paper considers optical properties of a mixed AgGa(Se$_{1-x}$S$_x$)$_2$ crystal[8] being a solid solution of the initial AgGaS$_2$ and AgGaSe$_2$ crystals.

1. Linear optical properties

Negative AgGaS$_2$ and AgGaSe$_2$ crystals of the point symmetry group $\overline{4}2m$ have a wide transparency range, zero-level transmittance of (0.47−13 μm) and (0.71−19 μm), respectively.[9] We had thin 2-mm plates of the AgGa(Se$_{1-x}$S$_x$)$_2$ crystal for $x = 0.2$, 0.5, and 0.75 grown by the Bridgeman−Stockbarger method. Point chemical microanalysis conducted with a Jeul electronic spectrophotometric microscope (Japan) revealed that 5% variations of the composition are possible in local volumes of about 1×1 mm in the area and 50 Å in depth.

To determine dispersion of the absorption coefficients of the studied crystals, the transmittance $T(\lambda)$ of the plates was measured in the non-polarized light in the range of 0.5–1.0 μm. An analog signal from the spectrophotometer receiving system was converted into the digital code and then processed on a computer. Since the radiation was incident normally on the plate, the absorption coefficients $\alpha(\lambda)$ were determined from the experimental data on $T(\lambda)$ by the equation

$$T(\lambda) = \frac{[1 - R(\lambda)]^2 \exp[-\alpha(\lambda)d]}{1 - R^2(\lambda)\exp[-2\alpha(\lambda)d]},$$

where $R(\lambda) = [n(\lambda) - 1]^2/[n(\lambda) + 1]^2$ is the reflection coefficient for the air-crystal interface; d is the plate thickness. The measured results are depicted in Fig. 1.
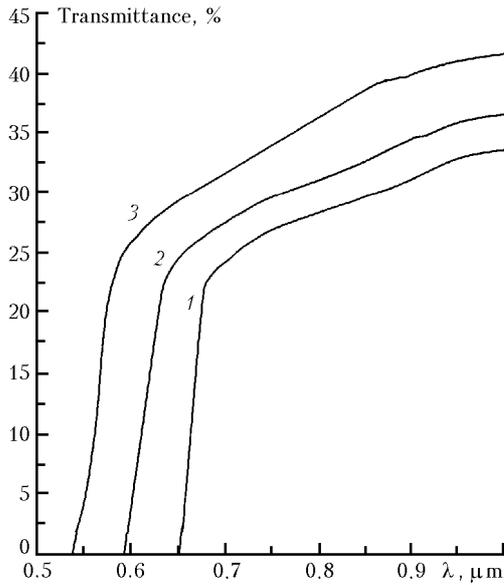
Fig. 1. Spectral dependence of the transmittance of AgGa(Se$_{1-x}$S$_x$)$_2$ crystal 2 mm thick for $x = 0.2$ (curve *1*), 0.5 (*2*), and 0.75 (*3*).

It can be seen from Fig. 1 that as the relative content of selenium, as a heavier than sulfur element, increases, the short-wave boundary of transparency shifts toward longer waves. This was to be expected, because the width of the forbidden zone almost linearly varies from 1.72 eV (AgGaSe$_2$) to 2.59 eV (AgGaS$_2$) [Ref. 4]. Although the transmittance in the mid-IR was not measured, it would be expected that the long-wave boundary of transparency also should shift toward longer waves with the increasing selenium content.

Measurements of the main values of the refractive indices of the crystals in the mid-IR were conducted at room temperature on prisms by the method of the least deflection angle. The measurement error did not exceed 10^{-3}. The dispersion dependences were estimated by the weighted mean method[10] using the equation

$$n^2_{o,e}[\text{AgGa}(\text{Se}_{1-x}\text{S}_x)_2] =$$

$$= xn^2_{o,e}[\text{AgGaS}_2] + (1-x)n^2_{o,e}[\text{AgGaSe}_2].$$

The data obtained were then fitted by the least squares method to the Sellmeier equations of the form

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

the corresponding constants are tabulated below. In addition, the Sellmeier coefficients were determined by the method of proportional averaging of the corresponding coefficients for AgGaSe$_2$ and AgGaS$_2$.

The results obtained in both of these cases were practically identical.

2. Nonlinear optical properties

In ternary chalcogenides, as sulfur atoms are replaced by selenium or tellurium atoms, the transparency range shifts toward longer waves and the nonlinear susceptibility also increases with the increase of the chalcogenide mass.[11,12]

Different methods can be used for determining nonlinear optical properties of mixed crystals.[10,13] This paper presents the second-order nonlinear susceptibility d_{ij} estimated using the bound charge model, which provides for the closest agreement with the experiment for various crystals, including AgGa(Se$_{1-x}$S$_x$)$_2$. For the AgGa(Se$_{0.8}$S$_{0.2}$)$_2$ crystal, nonlinear components of the tensor of nonlinear square-law susceptibility were determined: $d_{36} = (33.5 \pm 2) \cdot 10^{-12}$ m/V with regard for the refined value $d_{36} = (39 \pm 2) \cdot 10^{-12}$ m/V for AgGaSe$_2$. For AgGaS$_2$ the value of d_{36} was taken equal to $(12 \pm 1) \cdot 10^{-12}$ m/V (Ref. 9). Using these data as reference ones, we determined the values of d_{36} for the AgGa(Se$_{1-x}$S$_x$)$_2$ crystals. The equations for the effective nonlinear coefficient for the initial and mixed crystals coincide and have the form $d_{\text{eff}}(oo-e) = d_{36}\sin\theta\sin2\varphi$, $d_{\text{eff}}(eo-e) = d_{36}\sin2\theta\cos2\varphi$. The conversion efficiency is directly proportional to the nonlinear figure of merit $M_{\text{eff}} = d^2_{\text{eff}}/n^3$, whose calculated spectral dependence for the SHG case is shown in Fig. 2. It is interesting to note that for the case of second harmonic generation by the $eo-e$ type, in spite of the fact that d_{36} in the mixed crystals is smaller than in AgGaSe$_2$, at $x = 0.2$ and 0.4 the figure of merit may be higher in the mixed crystals due to the smaller refractive indices and optimal matching angles (Fig. 2*b*.).

3. Phase matching and group-velocity matching conditions

Phase matching in negative crystals interacting by the I type ($o + o \rightarrow e$) is achieved at simultaneous fulfillment of the following conditions:

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

$$\frac{n^o_1}{\lambda_1} + \frac{n^o_2}{\lambda_2} = \frac{n^e_3(\theta)}{\lambda_3} = \frac{n^o_3 n^e_3}{\lambda_3\sqrt{(n^o_3\sin\theta)^2 + (n^e_3\cos\theta)^2}},$$

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

x	A_o	B_o	C_o	D_o	A_e	B_e	C_e	D_e	$E_{o,e}$
0.10	2.08892	0.50478	0.15396	0.23261	2.21393	0.34882	0.22881	0.24038	1000
0.20	2.077	0.49936	0.15008	0.25802	2.19861	0.34171	0.22335	0.26424	1000
0.40	2.04832	0.4832	0.1404	0.31026	2.16354	0.33132	0.20899	0.3134	1000
0.50	2.03026	0.48393	0.13427	0.33713	2.14238	0.32942	0.19935	0.33873	1000
0.60	2.00816	0.48496	0.12697	0.36454	2.117	0.33153	0.1873	0.36458	1000
0.75	1.96217	0.49901	0.11303	0.40668	2.06372	0.34947	0.16243	0.40435	1000

Fig. 2. Spectral dependence of the nonlinear figure of merit for SHG of the $oo-e$ type (a) and $eo-e$ type (b) in AgGa(Se$_{1-x}$S$_x$)$_2$ for $x = 1$ (curve 1), 0.75 (2), 0.6 (3), 0.5 (4), 0.4 (5), 0.2 (6), and 0.0 (7).

being, in fact, the laws of conservation of energy and quasi-momentum. Using the measured and published[9] refractive indices for AgGaSe$_2$ and AgGaS$_2$, we have analyzed possible nonlinear three-frequency processes in these crystals.

The phase matching diagrams of three-frequency interactions in AgGa(Se$_{0.5}$S$_{0.5}$)$_2$, being a set of solutions of the mentioned system of equations, are calculated using the tabulated Sellmeier coefficients and depicted

in Fig. 3. The curves are drawn for collinear interaction at different angles of wave propagation with respect to the crystal optical axis. It can be seen from Fig. 3 that noncritical 90° phase matching that is of greatest interest can be realized in a wide spectral range.
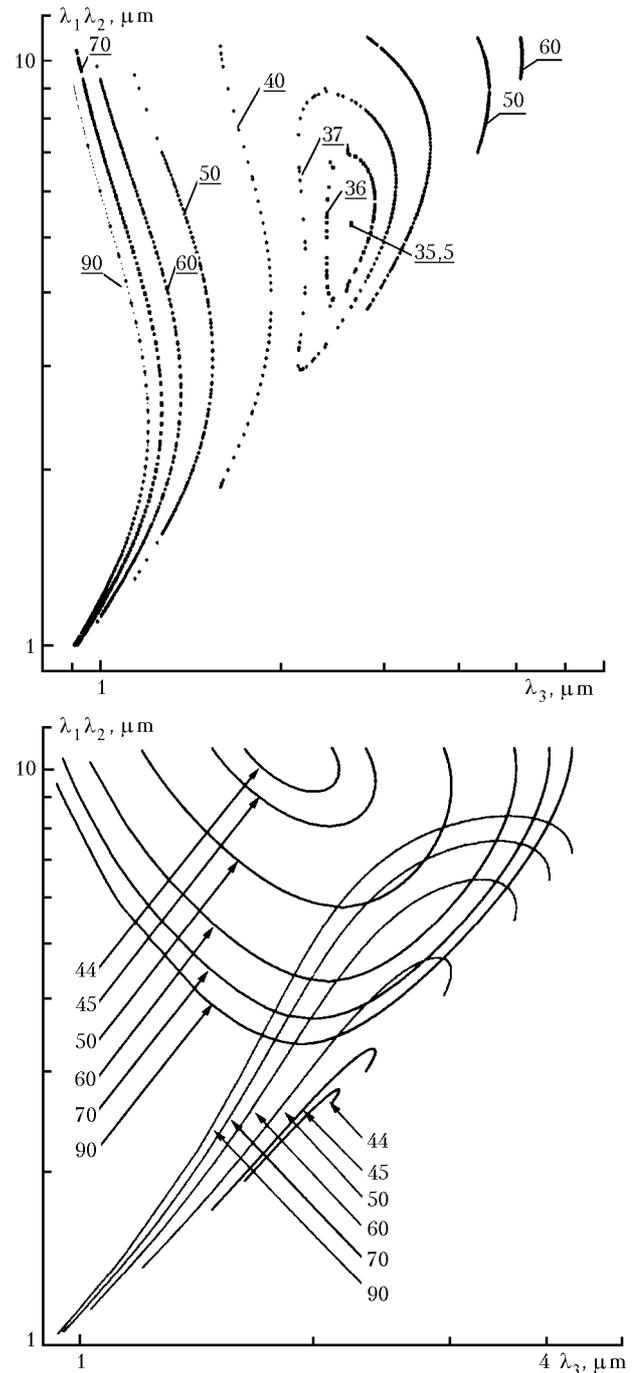
Fig. 3. Diagrams of phase matching of three-frequency interactions of type I ($o + o \rightarrow e$) (a) and II ($e + o \rightarrow e$) (b) in the AgGa(Se$_{0.5}$S$_{0.5}$)$_2$ crystal at different phase matching angles.

The degenerated case of three-frequency interactions is the second harmonic generation. Figure $4a$ shows phase matching curves for SHG at different Se content.

As the Se content increases, birefringence of the mixed crystal decreases and, as a consequence, the spectral range of phase matching becomes narrower, while the minimum value of the phase matching angle increases.

a

b
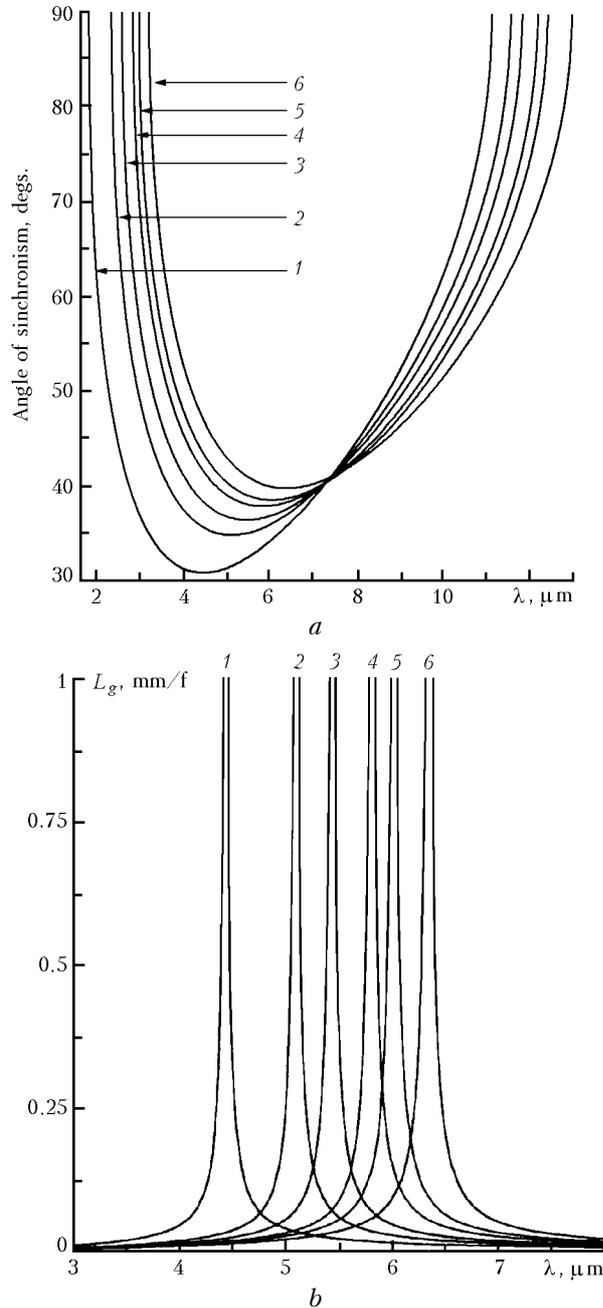
Fig. 4. Phase matching curves (*a*) and dispersion of group-velocity matching (*b*) for SHG by the type I (*oo–e*) interaction in AgGa(Se$_{1-x}$S$_x$)$_2$ at $x = 1.0$ (curve *1*), 0.6 (*2*), 0.4 (*3*), 0.2 (*4*), 0.1 (*5*), and 0.0 (*6*).

For frequency conversion of femtosecond pulses, the key parameter determining the efficiency is the group length L_g, whose increase is proportional to the decrease of the mismatch among the group velocities taking part in the pulse interaction. The group length of the interaction L_g was determined by the equation

$$L_g = \tau_p / |\Delta u^{-1}|,$$

where

$$\Delta u^{-1} = u_1^{-1} - u_2^{-1} =$$

$$= c^{-1}\left(n_1 - \lambda_1 \frac{\partial n_1}{\partial \lambda_1} - n_2 + \lambda_2 \frac{\partial n_2}{\partial \lambda_2}\right)$$

is the group detuning; τ_p is the pulse duration; $u_{1,2}$, $n_{1,2}$, and $\lambda_{1,2}$ are the group velocities, refractive indices, and wavelengths of the pump wave and the second harmonic.[14,15] The calculated results are shown in Fig. 4*b*. In spite of the fact that $L_g \to \infty$ only at fixed wavelengths it is possible, for practical realization of femtosecond frequency converters, to use crystals with finite, but rather large group lengths.

In reality, it is never possible to reach exact phase matching, that is, to meet the condition $\Delta k = 0$ for the interacting waves, and therefore it is necessary to know the angular spectral and the temperature width of phase matching. They allow estimation of the acceptable divergence and spectral width of the pump source line, as well as random or systematic variation of the temperature of a crystal — frequency converter. In the linear approximation for Δk we have

$$\Delta k = \frac{\partial(\Delta k)}{\partial(\delta\theta)}\delta\theta + \frac{\partial(\Delta k)}{\partial\lambda}\Delta\lambda + \frac{\partial(\Delta k)}{\partial T}\Delta T.$$

The power of the converted radiation halves at the wave mismatch $\Delta k = 0.886\pi/L$ (Ref. 9), where L is the crystal length. Taking this into account, we can estimate the corresponding phase-matching widths:

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

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

Temperature widths were not calculated because of the lack of data on temperature dependences of the refractive indices. For the second harmonic generation by the type I interaction in negative crystals, the phase mismatch Δk has the form

$$\Delta k = 2\left[\frac{2\pi n_1^o}{\lambda_1}\right] - \frac{2\pi n_2^e(\theta)}{\lambda_2}.$$

After differentiation of this equation with the prior substitution of the equation for $n_2^e(\theta)$ and the Sellmeier equation for the main values of the refractive indices, we obtain

$$\frac{\partial\Delta k}{\partial\theta} = \frac{2\pi}{\lambda_2}\left\{(n_2^e(\theta))^3\cos\theta\sin\theta\left[\frac{1}{(n_2^o)^2} - \frac{1}{(n_2^e)^2}\right]\right\},$$

$$\frac{\partial\Delta k}{\partial\lambda} =$$

$$= \frac{2\pi}{\lambda_2}\left\{\frac{1}{2}\left[\frac{(n_1^o)^3}{(n_2^o)^3}\cos^2\theta\frac{\partial n_2^o}{\partial\lambda_2} + \frac{(n_1^o)^3}{(n_2^o)^3}\sin^2\theta\frac{\partial n_2^e}{\partial\lambda_2}\right] - \frac{\partial n_1^o}{\partial\lambda_1}\right\}.$$

Figure 5 depicts the calculated spectral and angular phase-matching widths.
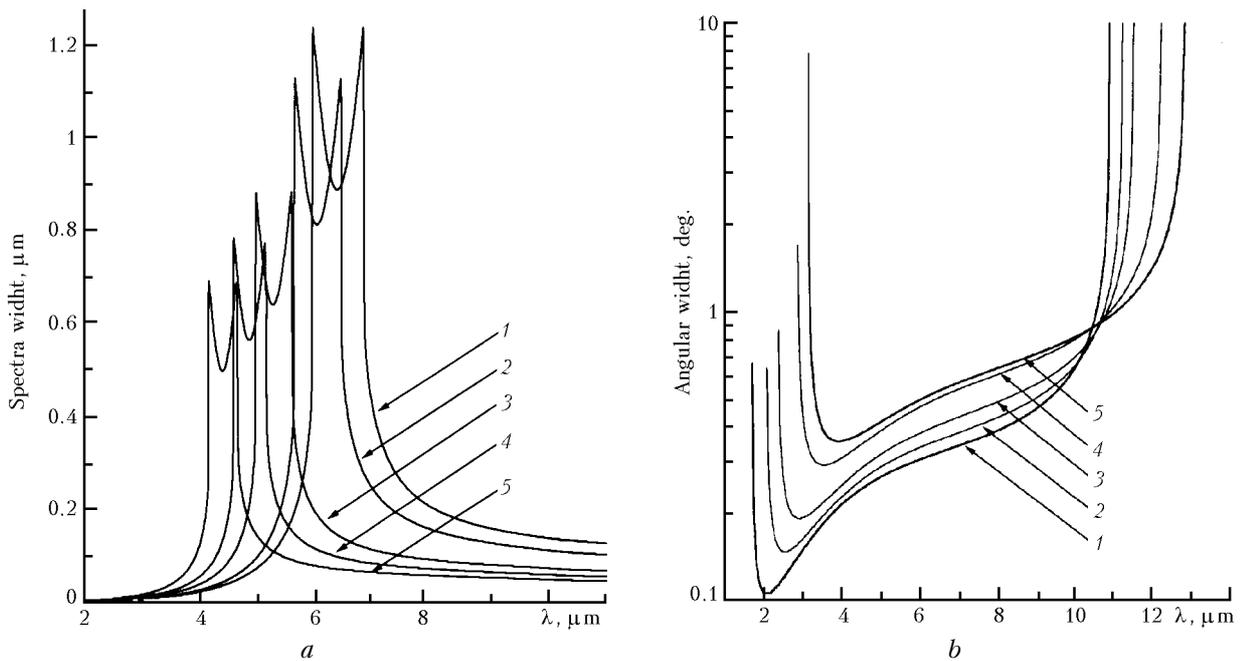
Fig. 5. Spectral (*a*) and angular (*b*) phase-matching widths for second harmonic generation in AgGa(Se$_{1-x}$S$_x$)$_2$ for x = 1 (curve *1*), 0.75 (*2*), 0.5 (*3*), 0.1 (*4*), and 0.0 (*5*).
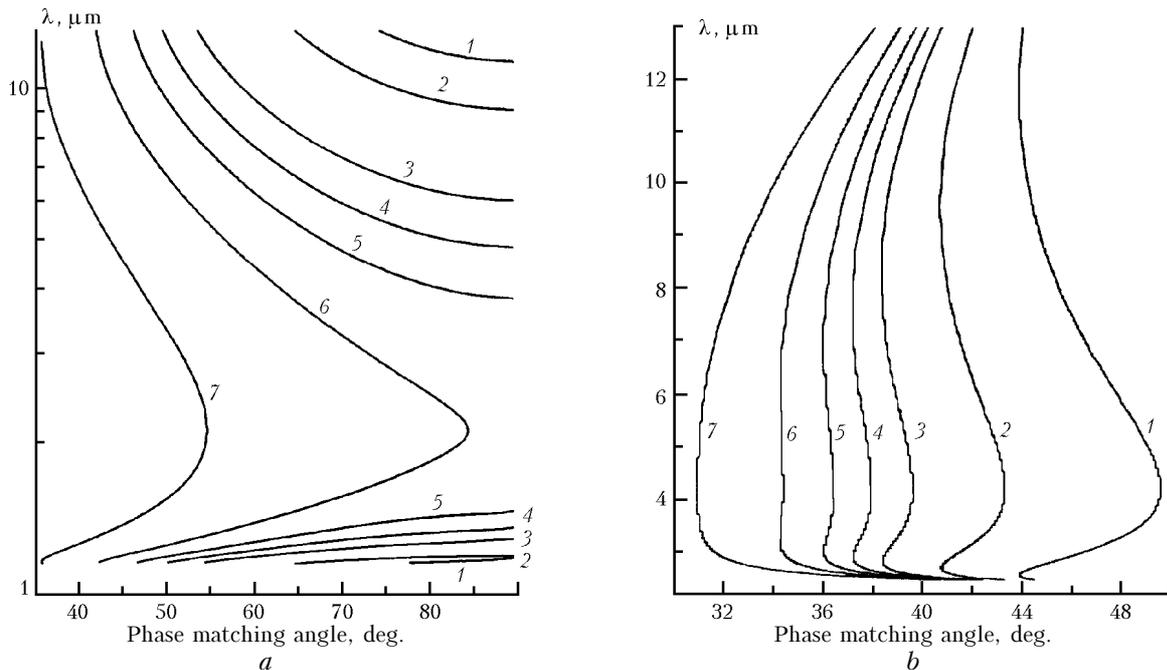
Fig. 6. Phase-matching curves of type ($o + o \rightarrow e$) for optical parametric oscillators pumped by Nd:YAG (λ_p = 1.064 μm) (*a*) and Ho:YAG (λ_p = 2.1 μm) (*b*) laser radiation for x = 0.0 (curve *1*), 0.2 (*2*), 0.4 (*3*), 0.5 (*4*), 0.6 (*5*), 0.75 (*6*), 1.0 (*7*).

Optical parametric oscillation in AgGa(Se$_{1-x}$S$_x$)$_2$ crystals is of particular interest. To evaluate the general tendencies in the behavior of OPO angular tuning curves, we have calculated the dependences of the excited frequencies (wavelengths) on the angle between the pump wave vector and the optical axis.

Lasers of 1–2 μm range, first of all, Nd:YAG and Ho:ILF lasers are most suitable for OPO pumping in this crystal. Phase matching curves for OPO of

type I interaction pumped by Nd and Ho laser radiation are shown in Fig. 6.

In both cases, as the Se concentration increases, the phase matching angle grows approaching the conditions of noncritical spectral phase matching.

The optical damage threshold was measured by the standard technique described, for example, in Ref. 16. Under the exposure to a TEA CO$_2$ laser pulse of a typical shape (half-amplitude duration of 150–200 ns

and a microsecond tail bearing about a half of the pulse energy), surface damages were observed at the power density of $40-50$ MW/cm^2.

Note that for the initial AgGaSe$_2$ and AgGaS$_2$ crystals, the damage threshold was within the same limits and depended on the quality of pre-processing of the crystal surface. It should be expected that for the formed pulse (without a tail) having the duration of about 30 ns, the damage threshold increases up to $150-160$ MW/cm^2 (Ref. 16).

Conclusion

Based on the results obtained and systematization of the known data on the linear and nonlinear optical properties, the coefficients of Sellmeier dispersion equations are determined for the first time for the mixed AgGa(Se$_{1-x}$S$_x$)$_2$ single crystals.

The possibility of using this crystal for conversion of femtosecond pulses is demonstrated. The phase matching conditions are determined for any three-frequency interactions, OPO pumped by solid-state lasers, and SHG as a function of the selenium and sulfur percentage. Realization of all considered frequency conversions under conditions of noncritical or close phase matching is possible.

Thus, the radiation walk off effect is excluded, restriction on the length of the crystals used is removed, and, as a consequence, the conversion efficiency increases.

References

1. G.-Q. Tian, F.C. Shui, S. Wei, W.-X. Wen, and P.-Q. Wei, J. Cryst. Growth **225**, 501–504 (2001).

2. L. Isaenko, I. Vasilieva, A. Yelisseyev, S. Labanov, V. Malakhov, L. Dovlitova, J.J. Zondy, and I. Kavun, J. Cryst. Growth **218**, 313–322 (2000).

3. Yu.M. Andreev, L.G. Geiko, P.P. Geiko, and S.G. Grechin, Quant. Electron. **34**, No. 7, 647–648 (2001).

4. J.C. Mikkelsen and H. Kildal, J. Appl. Phys. **49**, No. 1, 426–431 (1978).

5. Yu.M. Andreev, P.P. Geiko, V.V. Badikov, G.C. Bhar, S. Das, and A.K. Chaudhury, Nonlinear Optics **29**, No. 1, 19–27 (2002).

6. Yu.M. Andreev, I.V. Baturin, P.P. Geiko, and A.I. Gusamov, Quant. Electron. **32**, No. 1, 66–70 (1999).

7. P.P. Geiko, A.I. Gusamov, and Yu.M. Andreev, Atmos. Oceanic Opt. **12**, No. 7, 582–586 (1999).

8. Cheng Gan Chao, Yang Lin, Wu Haixin, and Cheng Ning, Acta Opt. Sin. **15**, No. 3, 375–377 (1995).

9. V.G. Dmitriev, G.G. Gruzadyan, and D.N. Nikogosyan, *Handbook of Nonlinear Optical Crystals* (Springer Verlag, New York; Berlin; Heidelberg, 1999), 413 pp.

10. L.K. Samanta, D.K. Ghosh, and G.C. Bhar, Phys. Rev. B **33**, No. 6, 4145–4148 (1986).

11. P.G. Schunemann, S.D. Setzler, T.M. Pollak, M.C. Ohmer, J.T. Goldstein, and D.E. Zelmon, J. Cryst. Growth **211**, 242–246 (2000).

12. M.C. Ohmer, J.T. Goldstein, D.E. Zelmon, A.W. Saxler, S.M. Hegde, J.D. Wolf, P.G. Schunemann, and T.M. Pollak, Appl. Phys. **86**, No. 1, 94–99 (1999).

13. G.C. Bhar, S. Das, O. Chatterjee, P.K. Datta, and Yu.M. Andreev, Appl. Phys. Lett. **63**, No. 10, 1316–1318 (1993).

14. S.A. Akhmanov, V.A. Vysloukh, and S.A. Chirkin, *Optics of Femtosecond Laser Pulses* (Nauka, Moscow, 1988), 310 pp.

15. A.A. Lukashev, S.A. Magnitskii, and V.I. Pryalkin, Izv. Ros. Akad. Nauk, Ser. Fiz. **59**, No. 12, 123–129 (1995).

16. Yu.M. Andreev, V.V. Badikov, V.G. Voevodin, L.G. Geiko, P.P. Geiko, M.V. Ivashchenko, A.I. Karapuzikov, and I.V. Sherstov, Quant. Electron. **34**, No. 12, 1075–1078 (2001).