Orthorhombic nonlinear crystals of Ag$_x$Ga$_{1-x}$Ge$_1$Se$_2$ for the mid-infrared spectral range

Valeriy Badikov a, Konstantin Mitin b, Frank Noack c, Vladimir Panyutin a, Valentin Petrov c,*, Alexander Seryogin b, Galina Shevyrdyaeva a

a High Technologies Laboratory, Kuban State University, 149 Staromolodovskaya Street, 350040 Krasnodar, Russia
b FSUE ‘SPA Astrophysica’, 55 Volokolamskoe Chaussee, 125424 Moscow, Russia
c Max-Born-Institute for Nonlinear Optics and Ultrafast Spectroscopy, 2A Max-Born-Street, D-12489 Berlin, Germany

**A R T I C L E  I N F O**

Article history:
Received 21 December 2007
Received in revised form 18 June 2008
Accepted 19 June 2008
Available online 6 September 2008

PACS:
42.65.Ky
42.70.Mp
PACS:

**A B S T R A C T**

We study the birefringence and nonlinearity of quaternary semiconductors of the type AgGaGe$_x$Se$_{2x(n+1)}$ solid solutions in the system AgGaSe$_2$–nGeSe$_2$. The birefringence, e.g. $n_a - n_e$, at 1064.2 nm, increases from 0.114 for $n = 2$ (AgGaGe$_2$Se$_6$) to 0.149 for $n = 5$ (AgGaGe$_5$Se$_{12}$) which substantially exceeds the birefringence of the uniaxial AgGaSe$_2$ ($-0.022$). The parent compound in the limit $n = 0$, Sellmeier equations valid in the 0.6–11.5 μm range are constructed for the solid solutions with $n = 2...5$. All four quaternary compounds are optically negative biaxial crystals. The calculated second-harmonic generation (SHG) limit (minimum fundamental wavelength) is $\approx 1470$ nm for AgGaGe$_2$Se$_6$ and $\approx 1240$ nm for AgGaGe$_5$Se$_{12}$, for type-I interaction and propagation along the $Y$ principal optical axis. These limits are much lower than the $\approx 3120$ nm limit for type-I interaction in AgGaSe$_2$. Thus, the AgGaGe$_x$Se$_{2x(n+1)}$ orthorhombic crystals can be used for SHG down to their band-edge. The results for the nonlinear coefficients of AgGaGe$_x$Se$_{2x(n+1)}$ ($n = 3, 4$ and 5), obtained from phase-matched SHG, indicate weak dependence on the composition. On the average, the larger nonlinear coefficient $d_{31}$ is very close to $d_{32}$ of AgGaSe$_2$ ($\approx 30$ pm/V) while $d_{32}$ is roughly two times smaller.

© 2008 Elsevier B.V. All rights reserved.

**1. Introduction**

Several recent studies were devoted to the linear and nonlinear optical properties of the quaternary Ag$_x$Ga$_{1-x}$Ge$_1$Se$_2$ or AgGaGe$_x$Se$_{2x(n+1)}$ (in the system AgGaSe$_2$–nGeSe$_2$) crystals with orthorhombic symmetry mm2, for $n = 1...5$. The results and all the literature that has appeared on this family of sulfide materials for nonlinear optics in the mid-IR can be found in a review book chapter which appeared in 2008 [1]. Much less attention has been paid to the selendie analogs of this series, although the first publication, including the first publication, solid solutions in the system AgGaSe$_2$–nGeSe$_2$ exist only in a limited range for the parameter $x$, and their properties are related to a much lesser extent to the properties of AgGaSe$_2$ and GeSe$_2$. While the chalcopyrite AgGaSe$_2$ with point group 42m has mature growth technology and is a well established and characterized nonlinear optical crystal, GeSe$_2$ exhibits several polymorphic forms. It can be assumed that the relevant phase of GeSe$_2$ is the centrosymmetric monoclinic one [6] with space group $C$_2h–F$_21/c$ (point group 2/m) in analogy with the sulfide compounds [1,5,7]. The structure of the Ag$_x$Ga$_{1-x}$Se$_2$ solid solutions results from the substitution of Ge$x$ by Ga$^{1-x}$ in the GeSe$_2$ cation sublattice. The valence deficiency is compensated by Ag$^+$ ions filling the tetrahedral vacancies. On the basis of the structural studies, it can be assumed that the $β$-phase quaternary selenium...
compounds have the same \( \cdot \) space group (point group mm2) as the corresponding sulfides [2]. Note that the existence of the AgGaSe\(_4\) compound (an analog of AgGaS\(_4\)), \( x = 0.5 \) or \( n = 1 \), although mentioned in previous literature, was not confirmed in these studies. The symmetry of polycrystalline AgGaSe\(_4\) samples was indicated before to be tetragonal [8–10], and single crystals grown by chemical transport reaction showed indeed defect chalcopyrite structure [11].

The birefringence of the quaternary Ag\(_{3}\)Ga\(_{3}\)Ge\(_{5}\)Se\(_{12}\), Se\(_2\) compounds increases with \( n \), reaching a value of \( \approx 0.43 \) for \( n = 9 \) near 700 nm [2], which provides a unique possibility for engineering the phase-matching capability. This property will be reconsidered here. If compared to other mixed crystals like AgGaIn\(_{1} \)Se\(_2\) it should be outlined that with Ag\(_{3}\)Ga\(_{3}\)Ge\(_{5}\)Se\(_{12}\) the desired uncritical phase-matching is achieved in combination with higher (relatively to AgGaSe\(_2\)) and not lower birefringence which results in an extended potential for applications at shorter wavelengths.

In fact, until now only one selenide compound, AgGaGe\(_5\)Se\(_{12}\), has been thoroughly studied as a nonlinear crystal, on one hand estimating its nonlinear coefficients from phase-matched second-harmonic generation (SHG) and on the other hand demonstrating some advantages with respect to difference-frequency mixing to produce femtosecond pulses in the mid-IR [12]. The material was resistant to damage at least up to 80 GW/cm\(^2\) for 50 fs pulses at 1400 nm. This stimulated further research on its growth and characterization: High scattering losses (of the order of 10 cm\(^{-1}\)) were observed in as grown crystals [13]. The nonlinear coefficients of AgGaGe\(_5\)Se\(_8\) were also determined using phase-matched SHG [14]. It was shown that doping with Cu improves the transparency of the Ag\(_{3}\)Ga\(_{3}\)Ge\(_{5}\)Se\(_{12}\) compounds in the visible and near-IR [15]. With 10 ns pulses at 1064 nm, damage was observed at 75 MW/cm\(^2\) [15].

Here, we present a systematic study of the birefringence and the nonlinearity of the orthorhombic solid solutions AgGaGe\(_{5}\)Se\(_{2(n+1)}\), focusing on four representatives, \( n = 2 \ldots 5 \). It is based on older measurements of the index of refraction, a refinement using phase-matched SHG to derive Sellmeier equations, and estimations of the nonlinear coefficients also from phase-matched SHG.

2. Dispersion, birefringence, and effective nonlinearity

As their sulfide counterparts, the quaternary AgGaGe\(_{5}\)Se\(_{2(n+1)}\) compounds are grown by the Bridgman–Stockbarger method [2]. All measurements described in this work were performed on samples cut from single crystals grown at the High Technologies Laboryatory, after annealing. The specified x-values correspond to the charge. Fig. 1 shows boules of grown AgGaGe\(_5\)Se\(_{12}\).

Characteristic average rates for the growth of high optical quality AgGaGe\(_{5}\)Se\(_{2(n+1)}\) crystals range from 2 to 8 mm/day for the different compounds. The present state of the art permits the growth of single crystals as large as 60–80 mm in length and 22 mm in diameter (Fig. 1) with an optical homogeneity of \( \Delta n < 1 \times 10^{-4} \) cm\(^{-1}\) achieved after post growth thermal annealing in a furnace for 30 days. The homogeneity of the crystals, both along the growth and in the radial directions, was tested by monitoring the orientation of the two optic axes C1 and C2 in dependence on the position. Oriented wedged plates with a diameter of 1–2 cm and an angle between the normal and the C1 or C2 axis of 10°–15° were scanned across their surface with a step of 4–5 mm using a spot size of about 2 mm. This angle was found to be constant within the accuracy of the measurement (10°–20°) which leads to a maximum variation of the \( x \) parameter of the order of 0.002.

Table 1 summarizes some important properties of the studied compounds. The lattice parameters are from the first publication [2]; other data appeared in the literature only on AgGaGe\(_{5}\)Se\(_{8}\) [7]. It can be seen that with increasing \( n \) the two optic axes C1 and C2 move from the \( a \) crystallographic plane to the \( c \) plane. Note that per definition they lie in the XZ principal optical plane. The values for the angle between these axes and the X principal optical axis in the table are from the present work. The calculated angles are very close to the measured ones at 633 nm, see Fig. 2a. All four compounds are optically negative biaxial crystals, compare Table 1 and Fig. 2b.

The starting point for fitting of two-pole Sellmeier equations were the measured in the beginning of the 1980s [16], but unfortunately unpublished refractive indices from 0.6 to 11.5 µm, included in Table 2. The same table shows the values calculated by the derived here Sellmeier equations as well as the differences \( \Delta n = n_{\text{calc}} - n_{\text{meas}} \) for the three refractive indices \( n_\alpha \), \( n_\beta \), and \( n_\gamma \). Note that according to the conventions \( n_\alpha \leq n_\beta \leq n_\gamma \).

For refinement of the Sellmeier equations, we used the measured angles between the two optic axes (see Fig. 2a) and (only for \( n = 3, 4, \) and 5) SHG data obtained from two different experimental set-ups. The first system was based on optical parametric amplifiers (OPAs) pumped at 800 nm by a 1-kHz femtosecond Ti:sapphire regenerative amplifier. At 2.3 µm we used the idler output of a commercial \( \beta \)-BaB\(_2\)O\(_4\) (BBO) based OPA (TOPAS, Light Conversion Ltd.). At longer wavelengths we used home-made OPAs which were seeded at the signal wavelength by the frequency-doubled idler output of the same BBO OPA. Depending on the idler wavelength which ranged from 2.8 to 4.5 µm, either KTIOPO\(_4\) (3 mm thick) or MgO:LiNbO\(_3\) (2 mm thick) or KNbO\(_3\) (4 mm thick) were employed in the seeded OPA. In all cases the energy at the fundamental used in the SHG experiments amounted to several microjoules. The pulse duration ranged from 120 to 160 fs (increasing with the wavelength). At 10.6 µm (fundamental) we used a TEA CO\(_2\) laser. It operated at 10 Hz in the TEM00 mode and provided 120 ns long pulses with energy of up to 100 mJ. For the SHG measurements, thin plates of 0.5 mm thickness were used, except at 10.6 µm where the thickness was \( \approx 3 \) mm but the cut was the same.

The Sellmeier equations of the type \( n^2 = A_1 + A_2/(\lambda^2 - A_3) + A_4/(\lambda^2 - A_5) \), where \( \lambda \) is in microns, are summarized for the four AgGaGe\(_{5}\)Se\(_{2(n+1)}\) compounds (\( n = 2, 3, 4, \) and 5) in Table 3. Previously such equations were published only for AgGaGe\(_{5}\)Se\(_{8}\) [12]; the coefficients in Table 3 for this case represent a refinement.

The refractive index \( n_\alpha = n_\beta \) is substantially smaller than \( n_\beta \) which are rather close but do not cross within the transparency range, except for AgGaGe\(_{5}\)Se\(_{12}\). As already mentioned the increased birefringence, relative to one of the parent compounds AgGaGe\(_{5}\), is
one of the main characteristic properties of the quaternary AgGaGe1−nSe2 compounds. This is illustrated in Fig. 3a by plotting the difference between two of the refractive indices \( n_2 - n_1 \). It can be seen that for all compounds the birefringence is much larger in comparison to AgGaSe2. This means that much shorter wavelengths can be produced by SHG. The difference with AgGaSe2 is due not only to the larger birefringence but also to the qualitatively different wavelength dependence of the birefringence which remains almost constant with wavelength while in AgGaSe2 it exhibits an isotropic point near 813 nm.

The different correspondence between the crystallographic and principal optical axes leads to different expressions for the effective nonlinearity \( d_{\text{eff}} \). In the principal planes it is given for \( n = 4 \) and 5 by:

\[
d_{\text{eff}}(\text{oo-e}) = d_{32} \sin \phi \quad \text{in the } XY \text{ plane} \tag{1}
\]

\[
d_{\text{eff}}(\text{ee-o}) = d_{32} \sin^2 \theta + d_{31} \cos^2 \theta \quad \text{in the } YZ \text{ plane} \tag{2}
\]

\[
d_{\text{eff}}(\text{oo-o}) = d_{31} \cos \theta \quad \text{in the } XZ \text{ plane (} \theta < 90^\circ - V_1 \) \tag{3}
\]

An interesting phenomenon can be observed in Fig. 3b for the compound AgGaGe2Se6 (\( n = 3 \) or \( x = 0.25 \)). The minimum fundamental wavelengths for SHG along the \( a \) and \( b \) crystallographic axes differ by only \( \sim 0.4 \) nm. This composition corresponds to anomalously small in the dependence of the unit cell volume. The point corresponds to coinciding maxima of the solidus and liquidus curves in the phase diagram [5], which means that AgGaGe2Se6 can be regarded as a separate compound, with special position among the solid solutions in the AgGaSe2−nGeSe2 system. Therefore, even in the presence of slight deviations in the charge composition, it can be expected that this particular compound will grow with constant composition. It should be outlined that such a compound does not exist within the AgGaS2−nGeS2 system.

3. Nonlinear coefficients

The first estimation of the nonlinear coefficients of AgGaGe2Se6 was based on SHG using femtosecond pulses, as described earlier in relation to the refinement of the Sellmeier equations. Using samples of \( \sim 0.5 \) mm thickness, cut at \( \theta = 61^\circ \) (XZ plane) and \( \phi = 18^\circ \) (XY plane) the result obtained at 3400 nm (fundamental) was: \( d_{31} = 2.08d_{36}(\text{AgGaS2}) \) and \( d_{32} = 1.07d_{36}(\text{AgGaSe2}) \) [12]. For the present work we performed a number of such measurements for several wavelengths and three different compositions with \( \sim 0.5 \) mm thick samples cut in the XZ and XY planes.

### Table 1

Properties of the studied AgGaGe\(_6\)Se\(_{2(n+1)}\) compounds for \( n = 2, 3, 4, \) and 5

<table>
<thead>
<tr>
<th>Nonlinear crystal</th>
<th>AgGaGe(_2)Se(_6)</th>
<th>AgGaGe(_3)Se(_6)</th>
<th>AgGaGe(<em>4)Se(</em>{10})</th>
<th>AgGaGe(<em>5)Se(</em>{12})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compound</td>
<td>( n = 0.333 )</td>
<td>( x = 0.025 )</td>
<td>( x = 0.2 )</td>
<td>( x = 0.1667 )</td>
</tr>
<tr>
<td>Space (point) group symmetry</td>
<td>( C_4 ) (mm2)</td>
<td>( C_3 ) (mm2)</td>
<td>( C_2 ) (mm2)</td>
<td>( C_1 ) (mm2)</td>
</tr>
<tr>
<td>Lattice constants [( \AA )]</td>
<td>( c = 7.06 )</td>
<td>( c = 7.12 (7.15) )</td>
<td>( c = 7.21 )</td>
<td>( c = 7.26 )</td>
</tr>
<tr>
<td>Cations/anions ratio in unit cell</td>
<td>( n: m = 8/12 )</td>
<td>( n: m = 7.5/12 )</td>
<td>( n: m = 7.2/12 )</td>
<td>( n: m = 7/12 )</td>
</tr>
<tr>
<td>Two-fold polar axis</td>
<td>( Y )</td>
<td>( X )</td>
<td>( Y )</td>
<td>( Y )</td>
</tr>
<tr>
<td>Correspondence principal optical/crystallographic axes</td>
<td>( Z \rightarrow a \rightarrow b \rightarrow c \rightarrow a \rightarrow b \rightarrow c )</td>
<td>( Z \rightarrow a \rightarrow b \rightarrow c \rightarrow a \rightarrow b \rightarrow c )</td>
<td>( Z \rightarrow a \rightarrow b \rightarrow c \rightarrow a \rightarrow b \rightarrow c )</td>
<td>( Z \rightarrow a \rightarrow b \rightarrow c \rightarrow a \rightarrow b \rightarrow c )</td>
</tr>
<tr>
<td>Optic axes ( C_1, C_2 ) plane and exp. (calc.) value of the angle ( V_n ) with the c-axis [(^\circ)] at 633 nm</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Fig. 2. (a) Measured angle \( V_n \) between the optic axes \( C_1, C_2 \) and the c-axis of AgGaGe\(_{6}\)Se\(_{2(n+1)}\) at 633 nm in dependence on the x-parameter (solid triangles) and calculated values (open triangles). The transition between the two crystallographic planes is illustrated assuming a different sign of this angle \( V_n \). (b) Principal optical axes and types of interaction in a biaxial crystal. The two optic axes lie per definition in the \( ZX \) plane. \( V_n \) is the angle they make with the \( Z \)-axis, \( V_2 = 90^\circ - |V_n| \). For \( n = 2,3, \) \( XYZ = cbc \) holds and for \( n = 4,5, \) \( XYZ = abc \) holds, see Table 1.
In the small signal limit, the relative measurements were based on plane wave analysis with corrections only for the Fresnel losses and the index of refraction dependence of the SHG efficiency. No linear losses were taken into account for these thin samples. The dependence on the composition was within the experimental error. This situation is similar to the one observed with the sulfide compounds [1]. Hence, we estimated average values of the two nonlinear coefficients. The result (at a fundamental of 3500 nm) is $d_{31} = 1.9d_{36}(\text{AgGaS}_2)$ and $d_{32} = 0.78d_{36}(\text{AgGaS}_2)$ with relative errors of the order of 5%. Hence, $d_{31}/d_{32} = 2.4 \pm 0.2$. Using $d_{36}(\text{AgGaS}_2) = 13.15 \text{pm/V}$ [17], a value transformed to 3500 nm using Miller’s rule, one arrives at $d_{31} = 25 \text{pm/V}$ and $d_{32} = 10.3 \text{pm/V}$. 

### Table 2

Measured ($n_{\text{exp}}$) and calculated ($n_{\text{calc}}$) refractive indices of AgGaGe$_{7-x}$Se$_x$ compounds for $x = 2, 3, 4$, and $5$

<table>
<thead>
<tr>
<th>$\lambda$ [nm]</th>
<th>$n_{\text{exp}}$</th>
<th>$n_{\text{calc}}$</th>
<th>$\Delta n$</th>
<th>$n_{\text{exp}}$</th>
<th>$n_{\text{calc}}$</th>
<th>$\Delta n$</th>
<th>$n_{\text{exp}}$</th>
<th>$n_{\text{calc}}$</th>
<th>$\Delta n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>600</td>
<td>1.940</td>
<td>1.940</td>
<td>0.000</td>
<td>1.940</td>
<td>1.940</td>
<td>0.000</td>
<td>1.940</td>
<td>1.940</td>
<td>0.000</td>
</tr>
<tr>
<td>700</td>
<td>2.450</td>
<td>2.450</td>
<td>0.000</td>
<td>2.450</td>
<td>2.450</td>
<td>0.000</td>
<td>2.450</td>
<td>2.450</td>
<td>0.000</td>
</tr>
<tr>
<td>800</td>
<td>2.960</td>
<td>2.960</td>
<td>0.000</td>
<td>2.960</td>
<td>2.960</td>
<td>0.000</td>
<td>2.960</td>
<td>2.960</td>
<td>0.000</td>
</tr>
<tr>
<td>900</td>
<td>3.470</td>
<td>3.470</td>
<td>0.000</td>
<td>3.470</td>
<td>3.470</td>
<td>0.000</td>
<td>3.470</td>
<td>3.470</td>
<td>0.000</td>
</tr>
<tr>
<td>1000</td>
<td>3.980</td>
<td>3.980</td>
<td>0.000</td>
<td>3.980</td>
<td>3.980</td>
<td>0.000</td>
<td>3.980</td>
<td>3.980</td>
<td>0.000</td>
</tr>
</tbody>
</table>

### Table 3

Sellmeier coefficients for the AgGaGe$_{7-x}$Se$_x$ compounds ($x = 2, 3, 4$, and $5$)

<table>
<thead>
<tr>
<th>$n$</th>
<th>$A_1$</th>
<th>$A_2$</th>
<th>$A_3$</th>
<th>$A_4$</th>
<th>$A_5$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.6–1.15 \mu m</td>
<td>6.233430</td>
<td>0.1207668</td>
<td>0.2887427</td>
<td>519.06</td>
<td>151.5253</td>
</tr>
<tr>
<td>0.6–1.15 \mu m</td>
<td>7.563806</td>
<td>0.1188860</td>
<td>0.3479427</td>
<td>1044.74</td>
<td>1217.077</td>
</tr>
<tr>
<td>0.6–1.15 \mu m</td>
<td>7.381058</td>
<td>0.1383535</td>
<td>0.3458227</td>
<td>947.69</td>
<td>872.9966</td>
</tr>
<tr>
<td>0.6–1.15 \mu m</td>
<td>6.299683</td>
<td>0.1315100</td>
<td>0.2514435</td>
<td>698.27</td>
<td>349.5382</td>
</tr>
<tr>
<td>0.6–1.15 \mu m</td>
<td>8.358085</td>
<td>0.1279484</td>
<td>0.3301877</td>
<td>1535.63</td>
<td>3049.823</td>
</tr>
<tr>
<td>0.6–1.15 \mu m</td>
<td>7.327939</td>
<td>0.1188178</td>
<td>0.3597997</td>
<td>997.63</td>
<td>968.4704</td>
</tr>
</tbody>
</table>

V. Badikov et al. / Optical Materials 31 (2009) 590–597
Thus $d_{31}$ is roughly three times larger than the corresponding coefficient in the sulfide compounds [1].

The nonlinear coefficients of AgGaGe₃Se₈ were measured also by SHG at 10.6 µm, using the CO₂ laser described before and the same ~3 mm thick samples, under the same assumptions as with the femtosecond system. The reference sample of similar thickness was AgGaSe₂ in this case. The results of the measurements are shown in Fig. 4.

The analysis of the SHG data gave at this wavelength $d_{31} = (1.14 \pm 0.02) d_{31}$(AgGaSe₂) and $d_{32} = (0.67 \pm 0.05) d_{32}$(AgGaSe₂). The ratio $d_{31}/d_{32} = 1.7 \pm 0.3$ obtained here is much closer to the one observed in the sulfide compounds [1]. Having in mind the much closer second harmonic energies measured at 10.6 µm for the two AgGaGe₃Se₈ samples, it can be expected that this ratio and hence the value of the lower nonlinear coefficient are more reliable from the measurement using the CO₂ laser. Using $d_{31}$(AgGaSe₂) = 29.3 pm/V [18], a value corrected to 10.6 µm using Miller’s rule, one arrives at $d_{31} = 33.4$ pm/V and $d_{32} = 19.6$ pm/V. Obviously, the difference in the larger nonlinear coefficient $d_{31}$ is quite significant in the two SHG measurements. Note that this coefficient is more important for any applications because as we shall see the phase-matching properties in the two planes XY and XZ are quite similar. Unfortunately, the comparison of the two values is complicated by the great scatter in the data on the reference materials, although these are the two most established nonlinear crystals for the mid-IR spectral range. Thus, the value of $d_{31}$(AgGaSe₂) at 10.6 µm varies in the literature by almost a factor of 3 [19]. Hence, the same factor of uncertainty holds for the ratio $d_{31}$(AgGaSe₂)/$d_{31}$(AgGaS₂). The only work where the nonlinear coefficient $d_{31}$(AgGaSe₂) was measured relative to $d_{31}$(AgGaS₂) gave a ratio of only 1.19 at 10.6 µm which is too low [20]. The values of $d_{31}$(AgGaSe₂) and $d_{31}$(AgGaSe₂) that we used in the above evaluation of the nonlinear coefficients of the quaternary selenide compounds [17,18], give a ratio of 2.42 at 3500 nm and 2.66 at 10.6 µm. We tried to estimate this ratio using 0.5 mm thick plates for SHG at 3500 nm with the femtosecond system. The result, 2.09, was lower than the latter values but still much higher than obtained in the previous direct comparison [20]. With this in mind, the deviation of the $d_{31}$ values obtained in the present work for the AgGaGe₃Se₈ compounds by two different set-ups is within the experimental uncertainty.

4. SHG phase-matching characteristics

The most important feature of the SHG phase-matching curves calculated in Figs. 5 and 6 for AgGaGe₃Se₈ and in Figs. 7 and 8 for AgGaSe₂ (selected for its special position), is the nearly symmetric behavior in the XY and XZ planes due to the close values of the indices $n_Y$ and $n_Z$. In the YZ plane where the tunability is very limited, the interaction is quasi-angle-noncritical which ensures large angular acceptance and small walk-off angle. This is much more pronounced for AgGaSe₂ as could be expected from the previous discussion. On the opposite, in the XY and XZ planes, there are regions of quasi-wavelength-noncritical phase-matching. The chosen presentation of the inverse group velocity mismatch, GVM, is equivalent to the spectral acceptance ($|\Delta l| = 0.888/|\Delta \lambda|)$ but contains the sign as additional information. Vanishing $\Delta \lambda$ means large spectral acceptance for SHG of short pulses where the second derivative of the wave-mismatch comes into play. The internal angular acceptance is calculated as FWHM in the small signal limit using analytical expressions analogous to those well-known for uniaxial crystals and critical phase-matching, i.e. only the first derivative of the wave-mismatch with respect to the angle is taken into account. The walk-off angle was calculated also using the simplified formalism valid for uniaxial crystals. Positive value of the walk-off angle means that the Poynting vector is at an angle larger than the phase-matching angle and vice versa. The three parameters $\rho_1 = (\rho_2, \rho_3)$ designate the walk-off at the corresponding wave $\lambda_1, (\approx \lambda_2, \lambda_3)$. Note, that in contrast to the older
Sellmeier equations for AgGaGe_{5}Se_{12} [12], the new ones do not predict propagation along the X-axis.

The angular acceptance is calculated in Figs. 6 and 8 using only the linear approximation in the expansion of the wave-mismatch in order to preserve the scalability with the crystal thickness. This approximation is not valid in the vicinity of the principal optical axes and that is why the curves are interrupted in these regions. The effect is strongly pronounced in the case of AgGaGe_{3}Se_{8} for the YZ plane (Fig. 8). In fact, the angular acceptance along the Y and Z axes of this crystal, calculated using the next, quadratic approximation but then for a given crystal thickness of say 1 cm, amounts to 1.13 rad, which coincides with the limits chosen for presenting Fig. 8. It is obvious that in this case more critical will be the angular acceptance in the other planes: Thus, using the second order approximation for a crystal thickness of 1 cm one obtains almost equal limiting angular acceptance of ~0.029 rad.

\[ \Delta_{31} = \frac{1}{v_{1} - v_{2}}, \quad \Delta_{32} = \frac{1}{v_{1} - v_{3}} \]
both in the XY plane for propagation along the Y axis and in the XZ plane for propagation along the Z axis. This value is used as a limit for the corresponding curves in Fig. 8. Similarly, the limits of the acceptance angle curves in Fig. 6 correspond to the values for AgGaGe\textsubscript{5}Se\textsubscript{12} along the Y and Z axes in the three respective principal planes, calculated using the second order derivatives for a crystal length of 1 cm.

One of the parent compounds, AgGaSe\textsubscript{2}, is normally the crystal of choice for frequency doubling of 10.6 \textmu m radiation. Unfortu-
could be a subject of future research include the thermo-mechanical and thermo-optical properties.

5. Conclusion

In conclusion, we characterized the birefringence and the nonlinearity of the orthorhombic solid solutions AgGaGe$_n$Se$_{(n+1)}$ for $n = 2...5$ using phase-matched SHG. Two-pole Sellmeier equations were constructed for these four quaternary compounds and SHG was then analyzed in terms of angle tuning, spectral and angular acceptance, and spatial walk-off in the three principal planes. We confirmed previous assumptions concerning the exceptionally large birefringence which enables SHG down to the absorption edge. The larger nonlinear coefficient of these crystals is independent of the exact composition and comparable to $d_{36}$ of AgGaSe$_2$, one of the parent compounds. The compound AgGaGe$_3$Se$_8$ ($n = 3$) occupies a special position in this family of mid-IR crystals and deserves further attention especially in relation to its composition stability in the growth process.

Acknowledgment

This research leading to these results has received funding from the European Community's Seventh Framework Programme FP7/2007-2011 under grant agreement n° 224042.

References