Acoustic anisotropy of $AgGaGe_3Se_8$ crystals and their acoustooptic applications

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Abstract. We present the studies of anisotropy of acoustic wave (AW) propagation in $AgGaGe_3Se_8$ crystals. Complete matrices of mechanical stiffness and compliance coefficients are determined basing on the experimental values of AW velocities. Cross sections of AW velocity surfaces by the principal crystallographic planes are obtained. We have found that the velocities of quasi-transverse and quasi-longitudinal AWs propagating in the $AgGaGe_3Se_8$ crystals can be very low, thus facilitating potentially high acoustooptic figures of merit.

Keywords: acoustooptics, chalcogenide crystals, acoustic wave velocities, elastic properties

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1. Introduction

Acoustooptic (AO) control of optical radiation in the mid-infrared (mid-IR) spectral range is one of important topics of optoelectronics [1, 2]. Progress in this field is stipulated by the well-known needs of IR spectroscopy, in particular the measurements of absorption spectra of the atmospheres of solar-system planets [3] and gas concentration [4], as well as controlling CO_2-laser radiation [5]. Mercury-containing crystalline compounds [6–8] or chalcogenide crystals and glasses are usually utilized for these aims [9]. Many of the chalcogenide crystals appropriate for AO applications in the mid-IR range, e.g. Tl_3AsSe_3 and Tl_3AsS_4 [4, 5], contain thallium and so are toxic and not environment-friendly. The same is true of mercury-containing crystals (e.g., Hg_2Cl_2 [1] or Cs_2HgCl_4 [2, 3]). At the same time, optically isotropic chalcogenide glasses still reveal a restricted diversity of promising AO interactions [10]. The goal of the present work is to begin with large-scale AO studies of the crystalline chalcogenides containing no toxic chemical elements. The first candidate is $Ag_xGa_xGe_{1-x}Se_2$ compound.

Semiconductor $AgGaGe_3Se_8$ represents a novel group of quaternary crystalline materials belonging to Ag–Ga–Ge–Se system [11, 12]. In the group of crystals with the general chemical formula $Ag_xGa_xGe_{1-x}Se_2$, the compound that corresponds to $AgGaGe_3Se_8$ crystals ($x = 0.25$) occupies a special position. It deserves a great attention, at least in relation to its composition stability during the growth process [13]. The compound has orthorhombic structure (the spatial symmetry group *Fdd2* and the point group *mm2*). Its unit cell parameters are $a = 12.4423$, $b = 23.82036$ and $c = 7.14034$ Å [14]. The $AgGaGe_3Se_8$ crystals are optically biaxial and negative [3]. Their refractive indices are equal to $n_a = 2.799$, $n_b = 2.791$ and $n_c = 2.627$ at $\lambda = 600$ nm

[3]. The main bulk of the data obtained for the $Ag_xGa_xGe_{1-x}Se_2$ crystals has been devoted to the electronic band structure [4], the absorption spectra [15], and the laser-induced phenomena [16–19]. Moreover, the crystals have been thoroughly investigated from the viewpoint of their nonlinear optical properties, which may prove promising for the optical frequency doubling. The earlier studies on the quaternary crystals $Ag_xGa_xGe_{1-x}Se_2$ [3, 20] and, in particular, on $AgGaGe_3Se_8$ have testified that the above materials may find their applications in the mid-IR nonlinear optics, since they reveal a remarkable optical transparency (0.60–16 μm) [1] and good optical properties [21].

It is known [22] that the efficiency of AO interactions is governed by an AO figure of merit (AOFM) defined as $M_2 = n^6 p_{ef}^2 / \rho v_{ij}^3$. This quantity depends on the constitutive material parameters: the acoustic wave (AW) velocities v_{ij} (with i denoting the direction of propagation and j the polarization of the AW), the effective elastooptic coefficient p_{ef}, the refractive index n, and the material density ρ. As mentioned above, the refractive indices of $AgGaGe_3Se_8$ are relatively high, thus resulting in potentially high AOFM values. The density equals to 4834.9 kg/m^3 [8]. As far as we know, the elastooptic coefficients and the AW velocities for $AgGaGe_3Se_8$ have not yet been determined, although those parameters dominate the AOFM of the AO materials [23]. Below we present the first relevant results associated with the AW anisotropy for the $AgGaGe_3Se_8$ crystals.

2. Experimental methods and calculation procedures

Single crystalline $AgGaGe_3Se_8$ samples were grown from the melt using a standard Bridgman–Stockbarger method as specified in Ref. [17]. High-purity elemental components (at least 99.999 wt. %) were used. The growth process was performed in a two-zone furnace by lowering a specially-shaped quartz container containing the melt along a constant temperature profile of the furnace. The temperature of the growth zone was 1250 K, and that of the annealing zone 720 K, thus making the temperature gradient of 3.5 K/mm at the solid–melt interface. The lowering rate of the container in this experiment was 3 mm/day. Upon complete crystallization, the crystal was transferred into an annealing zone (annealing duration 150 h), and then cooled down to the room temperature at the rate of 50 K/day. The single-crystalline boule obtained under these conditions (dark red in the passing light) was 40 mm in length and 18 mm in diameter.

The samples prepared for the acoustic velocity studies had almost cubic shapes, with the typical dimensions ~ 5×5×5 mm^3 and the surfaces perpendicular to the directions <100> and <110>. The AW velocities were measured with a pulse-echo overlap technique [24]. We exited the AWs in the samples using $LiNbO_3$ transducers (the resonance frequency $f = 10$ MHz, the bandwidth $\Delta f = 0.1$ MHz, and the acoustic power $P_a = 1-2$ W). Hereafter the acoustic velocities are denoted with respect to the principal crystallographic axes, using the notations $a = 1$, $b = 2$ and $c = 3$.

There are 9 nonzero independent elastic stiffness coefficients $C_{klmn} = C_{ij}$ for orthorhombic crystals (i, j = 1–6; 1 = 11, 2 = 22, 3 = 33, 4 = 23, 5 = 13 and 6 = 12): C_{11}, C_{22}, C_{33}, C_{44}, C_{55}, C_{66}, C_{12}, C_{13}, and C_{23}. These coefficients have been calculated following from the known AW velocities and the relations

$$\begin{aligned} &C_{11} = \rho v_{11}^2, C_{22} = \rho v_{22}^2, C_{33} = \rho v_{33}^2, C_{44} = \rho v_{23}^2, C_{55} = \rho v_{13}^2, C_{66} = \rho v_{12}^2, \\ &C_{12} = 0.5\sqrt{(4\rho v_{66}^2 - C_{11} - C_{22} - 2C_{66})^2 - (C_{11} - C_{22})^2} - C_{66}, \\ &C_{13} = 0.5\sqrt{(4\rho v_{55}^2 - C_{11} - C_{33} - 2C_{55})^2 - (C_{11} - C_{33})^2} - C_{55}, \\ &C_{23} = 0.5\sqrt{(4\rho v_{44}^2 - C_{33} - C_{22} - 2C_{44})^2 - (C_{22} - C_{33})^2} - C_{44}. \end{aligned} \tag{1}$$

The elastic compliances S_{ij} have been determined basing on the elastic matrix C_{ij} and the formulae

$$\begin{aligned} &S_{11} = (C_{22}C_{33} - C_{23}^2)A^{-1}, \quad S_{12} = (C_{13}C_{23} - C_{12}C_{33})A^{-1}, \quad S_{44} = 1/C_{44}, \\ &S_{22} = (C_{11}C_{33} - C_{13}^2)A^{-1}, \quad S_{23} = (C_{12}C_{13} - C_{11}C_{23})A^{-1}, \quad S_{55} = 1/C_{55}, \\ &S_{33} = (C_{22}C_{11} - C_{12}^2)A^{-1}, \quad S_{13} = (C_{12}C_{23} - C_{22}C_{13})A^{-1}, \quad S_{66} = 1/C_{66}, \end{aligned} \tag{2}$$

where

$$A = \begin{vmatrix} C_{11} & C_{12} & C_{13} \\ C_{12} & C_{22} & C_{23} \\ C_{13} & C_{23} & C_{33} \end{vmatrix}. \tag{3}$$

The angle between the AW vector and the group velocity vector (the so-called 'obliquity angle') is an important parameter that characterizes a practice of AO applications of the anisotropic materials. The obliquity angle has been calculated using the relation (see Ref. [25])

$$\Delta_i = \arctan \frac{1}{v(\phi_i)} \frac{\partial v(\phi_i)}{\partial \phi_i}. \tag{4}$$

Here $v(\phi_i)$ denotes a function of the acoustic velocity that depends on the angle ϕ_i between the AW vector and the corresponding axis of the crystallographic coordinate system, with the subscript *i* referring to the axis perpendicular to the geometric plane under consideration.

Another important characteristic of AO materials is the angle of deviation of the acoustic polarization from purely longitudinal or transverse types. It has to be properly accounted when deriving phenomenological relations for the effective elastooptic coefficients. We have calculated this angle basing on the Christoffel equation [26]:

$$\zeta_1 = \frac{1}{2}\arctan \frac{(C_{23} + C_{44})\sin 2\phi_1}{(C_{22} - C_{44})\cos^2\phi_1 + (C_{44} - C_{33})\sin^2\phi_1}, \tag{5}$$

$$\zeta_2 = \frac{1}{2}\arctan \frac{(C_{31} + C_{55})\sin 2\phi_2}{(C_{55} - C_{11})\cos^2\phi_2 + (C_{33} - C_{55})\sin^2\phi_2}, \tag{6}$$

$$\zeta_3 = \frac{1}{2}\arctan \frac{(C_{11} + C_{66})\sin 2\phi_3}{(C_{11} - C_{66})\cos^2\phi_3 + (C_{66} - C_{22})\sin^2\phi_3}. \tag{7}$$

Eqs. (5)–(7) are concerned respectively with the *bc*, *ac* and *ab* planes. Here ϕ_1, ϕ_2 and ϕ_3 are the angles between the AW vector and the *b*, *a* and *a* axes, respectively. The corresponding non-orthogonality of the quasi-transverse AWs may be, in principle, calculated with the same formulae. The only difference is that the factor $90°$ should be added to the right-hand sides of Eqs. (5)–(7).

3. Results and discussion

The AW velocities measured for the propagation directions parallel to the principle crystallographic axes and the bisectors of these axes are presented in Table 1.

Table 1. AW velocities found experimentally for the $AgGaGe_3Se_8$ crystals.

Indices v_{ij}	Wave propagation direction i	Approximate acoustic displacement direction j	Velocity, m/s	AW type*
v_{11}	[100]	[100]	3314±9	PL
v_{22}	[010]	[010]	3465±9	PL
v_{33}	[001]	[001]	2513±9	PL
v_{23}	[010]	[001]	1275±8	PT
v_{13}	[100]	[001]	1950±8	PT
v_{12}	[100]	[010]	1740±8	PT
v_{44}	[011]	[011]	2695±9	QL
v_{55}	[101]	[101]	3417±9	QL
v_{66}	[110]	[110]	3249±9	QL

*PL and PT denote respectively purely longitudinal and purely transverse modes, and QL implies a quasi-longitudinal mode.

As seen from Table 1, some of the transverse AWs reveal sufficiently low velocities. In particular, the velocity of the AW v_{23} is equal to 1275±8 m/s. Among the longitudinal AWs, the slowest is the v_{33} mode propagating with the velocity 2513±9 m/s. Notice that those AW velocities may still turn out to be not the lowest, owing to acoustic anisotropy in the $AgGaGe_3Se_8$ crystals. The cross sections of the AW velocity surfaces can be obtained on the basis of the elastic module matrix. Using Eqs. (1), we have determined all the stiffness coefficients (see Table 2). All of the compliance coefficients have been calculated using Eqs. (2) and (3).

Table 2. Elastic stiffness and compliance coefficients calculated for the $AgGaGe_3Se_8$ crystals.

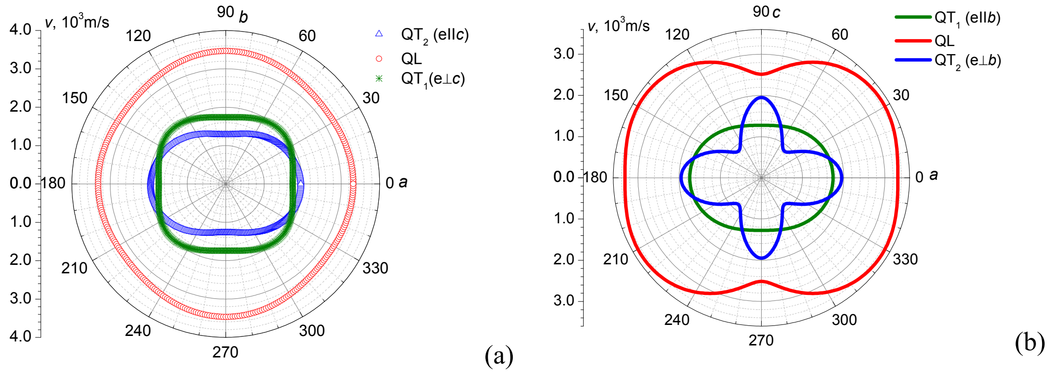
Indices ij	C_{ij}, 10^9 N/m^2	S_{ij}, 10^{-11} m^2/N	Indices ij	C_{ij}, 10^9 N/m^2	S_{ij}, 10^{-11} m^2/N
11	53.11±0.29	6.96±0.79	66	14.64±0.14	6.83±0.07
22	58.05±0.31	2.09±0.08	12	17.09±0.67	–1.56±0.25
33	30.52±0.21	11.06±1.27	13	33.08±0.72	–7.34±1.01
44	7.86±0.10	12.72±0.16	23	3.875±0.85	1.42±0.32
55	18.39±0.16	5.44±0.05			

Basing on the Christoffel equation and the data presented in Table 2, we have constructed the cross sections of the AW velocity surfaces by the crystallographic planes.

It seen from Fig. 1, the AW velocities for the $AgGaGe_3Se_8$ crystals manifest essential spatial anisotropy. For example, the slowest AW is the quasi-transverse wave propagating in the *ac* plane at the angle of 49 deg with respect to the *a* axis (the velocity 853 m/s). The polarization vector of this AW belongs to the crystallographic plane *ac*. The slowest quasi-longitudinal AW propagates in the *bc* plane at the angle of 62 deg with respect to the *b* axis (the velocity 2411 m/s).

As mentioned above, the very slow transverse AWs (1275 m/s) also propagate along the *c* (or *b*) axis with the polarization parallel to the *b* (or *c*) axis. Notice that, for the latter waves, the obliquity angles remain zero (see Fig. 2). The obliquity angle is equal to zero for the slowest quasi-transverse wave, too. Nonetheless, the obliquity angle is high enough in the close vicinity of the propagation directions for the slowest AWs: we have ~ 58 deg for the propagation angles 57.5 and

65 deg with respect to the *a* axis (see Fig. 2b). The obliquity angle for the quasi-longitudinal AW acquires its maximum value (~ 30 deg) when this wave propagates in the *bc* and *ac* planes. Finally, the obliquity angle remains close to zero for the slowest quasi-longitudinal AW.



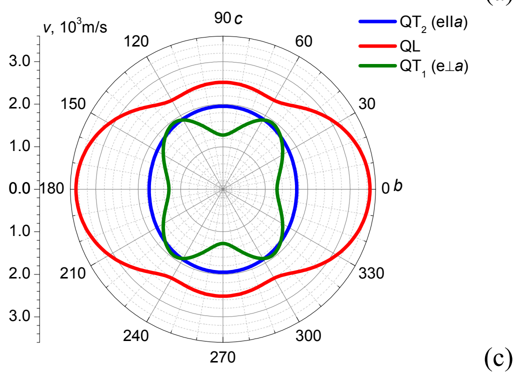
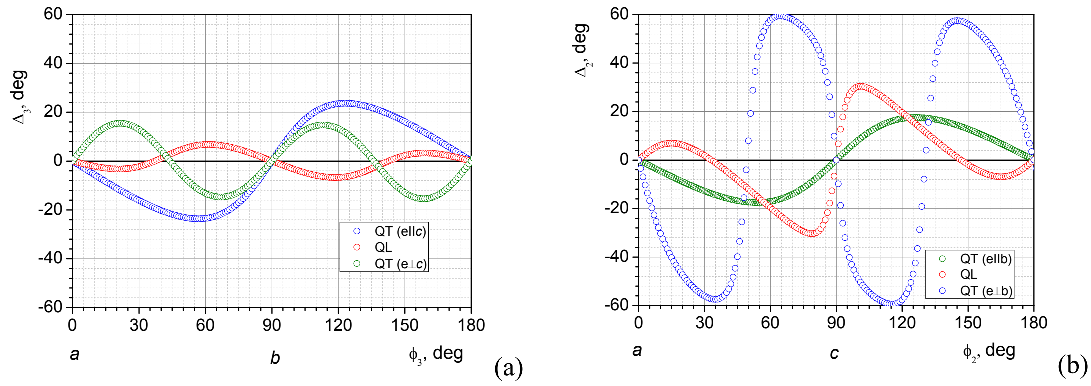


Fig. 1. Cross sections of AW velocity surfaces by the *ab* (a), *ac* (b) and *bc* (c) planes for the $AgGaGe_3Se_8$ crystals. *e* is acoustic displacement vector.



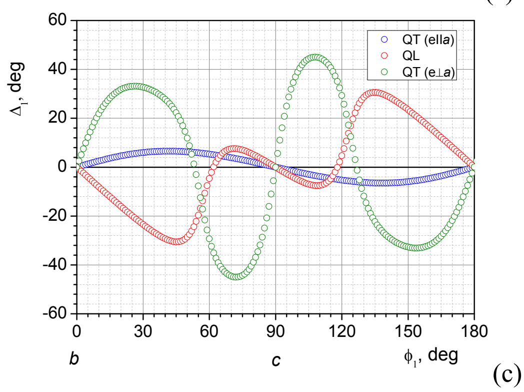


Fig. 2. Obliquity angle Δ_i calculated for the *ab* (a), *ac* (b) and *bc* (c) planes in the $AgGaGe_3Se_8$ crystals.

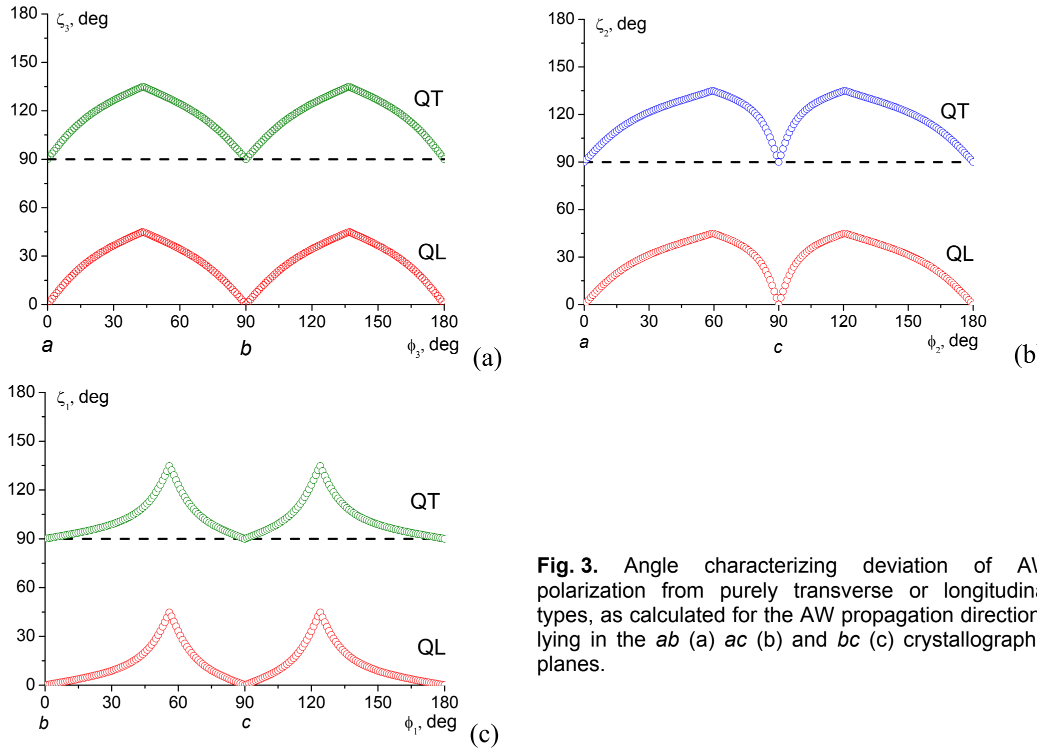


Fig. 3. Angle characterizing deviation of AW polarization from purely transverse or longitudinal types, as calculated for the AW propagation directions lying in the *ab* (a) *ac* (b) and *bc* (c) crystallographic planes.

As seen from Fig. 3, the angle of deviation of the AW polarization from the purely transverse or longitudinal types can be as large as ~ 45 deg for some propagation directions. The polarization of the slowest quasi-transverse AW, which propagates in the crystallographic plane *ac*, deviates by 40.5 deg from the purely transverse type. Similarly, the polarization of the slowest quasi-longitudinal AW propagating in the *bc* plane deviates by 27.9 deg from the purely longitudinal type. These large deviations need to be necessarily accounted if one derives phenomenological relations for the effective elastooptic coefficients, which characterize the AO interactions with the slowest AWs.

4. Conclusions

In the present work we have studied the spatial anisotropy of AW propagation in the $AgGaGe_3Se_8$ crystals. The complete matrices of the stiffness and compliance coefficients have been determined on the basis of experimental data for the AW velocities. The cross sections of the AW velocity surfaces by the principal crystallographic planes have been obtained. The acoustic obliquity and the deviation of AW polarization from the purely longitudinal and transverse types have been analyzed.

We have found that the velocity of the quasi-transverse acoustic mode can reach very low values (853 m/s). Then the AW propagates in the *ac* crystallographic plane under the angle 49 deg with respect to the *a* axis and has its polarization perpendicular to the *b* axis. Such a low AW velocity is comparable with the velocities of AWs known for the best AO materials such as TeO_2 or Tl_3AsS_4 crystals [22]. If the effective elastooptic coefficient is somewhere in the region of 0.01–0.2, one can expect that the corresponding AOFM for the $AgGaGe_3Se_8$ crystals can be as high as $16\times10^{-15} - 6.4\times10^{-12}\ s^3/kg$. In particular, for the case of AO interaction with the slowest quasi-longitudinal AW, the AOFM can reach the value of 280×10^{-15} s^3/kg, whenever the effective elastooptic coefficient is equal to ~ 0.2. Issuing from these potential AOFM values, one can expect that the $AgGaGe_3Se_8$ crystals may turn out to be the best AO material for the IR spectral range. Nonetheless, the values of all of the elastooptic coefficients are needed for any comprehensive analysis of the AO efficiency. The studies of those coefficients will be the aim of our forthcoming work.

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Анотація. *У роботі представлено результати досліджень анізотропії поширення акустичних хвиль у кристалах* $AgGaGe_3Se_8$*. На основі експериментального вивчення швидкостей поширення акустичних хвиль визначено повні матриці коефіцієнтів жорсткості і податливості цих кристалів. Побудовано перетини поверхонь швидкостей акустичних хвиль головними кристалографічними площинами. Виявлено, що швидкості поширення квазі-поперечних і квазі-поздовжніх акустичних хвиль сягають низьких значень, що повинно привести до великих коефіцієнтів акустооптичної якості кристалів* $AgGaGe_3Se_8$.