Acoustic and elastic anisotropies of acoustooptic $AgGaGeS_4$ crystals

[1] Martynyuk-Lototska I., [2] Parasyuk O. and [1] Vlokh R.

[1] Vlokh Institute of Physical Optics, 23 Dragomanov Street, 79005 Lviv, Ukraine, vlokh@ifo.lviv.ua
[2] Department of Inorganic and Physical Chemistry, Eastern European National University, 13 Voli Ave., 43025 Lutsk, Ukraine

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Abstract. We have experimentally studied the acoustic and elastic anisotropies of $AgGaGeS_4$ crystals. Basing on the acoustic wave velocities measured, we have determined the complete matrices of elastic stiffnesses and compliances. We have found that the orthorhombic unit cell of $AgGaGeS_4$ is only slightly distorted with respect to the prototypical tetragonal lattice. We have revealed a quite rare effect in $AgGaGeS_4$ crystals, an equality of the velocities of quasi-transverse and quasi-longitudinal waves. When propagating along the direction of a so-called longitudinal-transverse 'acoustic axis', these waves become 'half-transverse' and 'half-longitudinal'. It has been found that the quasi-transverse acoustic wave that propagates in the crystallographic plane *ac* with the velocity 1570 m/s is the slowest wave in $AgGaGeS_4$. The acoustooptic figure of merit for our crystals calculated following from the velocity of the slowest acoustic wave and rough estimation of the elastooptic coefficient can reach 500×10^{-15} s^3/kg. This suggests that $AgGaGeS_4$ can be a promising material for acoustooptic applications in the mid-IR spectral range.

Keywords: $AgGaGeS_4$ crystals, elastic properties, acoustic wave velocities.

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1. Introduction

$AgGaGeS_4$ (AGGS) is a quaternary halcogenide wide-band semiconductor [1, 2]. This crystal belongs to the acentric orthorhombic point symmetry group mm2 (the space group Fdd2) [1, 3] and can be regarded as a representative of solid solutions $Ag_xGa_xGe_{1-x}S_2$ at x = 0.5 [1]. According to the X-ray studies [1], the unit cell parameters of AGGS are equal to a = 12.028 Å, b = 22.918 Å and c = 6.874 Å (Z = 12). A transparency of AGGS in the mid-IR spectral range (0.5–11.5 μm, with the bandgap E_g = 2.78 eV) [3,4] and high enough second-order optical susceptibilities (d_{31} = 15 pm/V, d_{32} = 8 pm/V and d_{33} = 8 pm/V [1]) make the material attractive for various nonlinear optic applications, in particular for parametric oscillators [1, 5–7]. Moreover, the studies of its radiation resistance [4] have shown that the laser damage threshold for AGGS is high enough (250 MW/cm^2 for the pulses with the duration 30 ns and the wavelength 1.064 μm).

The earlier studies of optical anisotropy for the AGGS crystals have revealed interesting dispersion behaviour of the refractive indices n [8]. Namely, the refractive index n_c corresponding to the polar (two-fold symmetry) axis is smaller than n_a and n_b, whereas n_a and n_b are very close (e.g., we have n_c = 2.3706, n_b = 2.4355 and n_a = 2.4362 at 0.6 μm) and become exactly equal at 548 and 7565 nm. Both of the optic axes belong to the *ac* plane in the region limited by the two

wavelengths mentioned. Exactly at 548 and 7565 nm, AGGS becomes optically uniaxial, while below 548 nm and above 7565 nm the optic axes belong to the *bc* plane. To the best of our knowledge, the other optical properties of the AGGS crystals have not yet been studied, except for our recent work on the Faraday rotation (see *Adamenko D. et al, 2016. Ukr. J. Phys. Opt. 17: 105*). On the other hand, due to its high enough refractive indices, this compound can be interesting, e.g., from the viewpoint of its acoustooptic applications in the mid IR-spectral range.

To examine such possibilities, one has to determine the acoustooptic figure of merit (AOFM). It is given by the known formula $M_2 = n^6 p_{ef}^2 / \rho v^3$, where p_{ef} denotes the effective elastooptic coefficient, v the acoustic wave (AW) velocity, and ρ the density. In its turns, this needs the values of the AW velocities and the elastooptic coefficients. The aim of the present work is to make the first step in verifying the prospects of acoustooptic applications of the AGGS crystals, i.e. to study the anisotropies of AW velocities and elastic properties.

2. Experimental procedures

The AGGS crystals were grown using a Bridgman–Stockbarger technique (see *Adamenko D. et al, 2016. Ukr. J. Phys. Opt. 17: 105*). For the AW velocity studies, we prepared samples, which had nearly cubic shapes, with the dimensions ~ 5×5×5 mm^3. The sample surfaces were perpendicular to the directions <100> and <110>. The AW velocities were measured with a pulse-echo overlap technique [9]. We excited the AWs in the samples using $LiNbO_3$ transducers with the resonance frequency $f = 10$ MHz, the bandwidth $\Delta f = 0.1$ MHz and the acoustic power $P_a = 1-2$ W. The acoustic velocities were denoted using the indices associated with the crystallographic axes, with a standard notation $a = 1$, $b = 2$ and $c = 3$.

There are 9 nonzero independent elastic stiffness coefficients $C_{klmn} = C_{ij}$ in the 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 were calculated following from the known AW velocities and the relations

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

where $\rho = 3.80\times10^3$ kg/m^3 [1]. The elastic compliances S_{km} were determined from the matrix of elastic stiffness coefficients C_{ij} and the relations

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

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 so-called obliquity angle between the acoustic group velocity direction and the AW vector was calculated using the formula (see Ref. [10])

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

Here $v(\phi_i)$ denotes a function of the acoustic velocity depending upon the angle ϕ_i between the wave 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.

The angle of deviation of the acoustic polarization from a purely longitudinal type is also a very important characteristic of acoustooptic materials. It has to be properly accounted for when deriving the phenomenological relations for the effective elastooptic coefficients. We calculated this angle basing on the Christoffel equation [11] as

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

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

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

The above relations refer respectively to 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 quasi-transverse (QT) waves may, in principle, be calculated with the same formulae. The only difference is that the additive factor 90 deg should be added to the right-hand sides of formulae (5)–(7).

3. Results and discussion

The AW velocities obtained experimentally are collected in Table 1. The velocities of the longitudinal and transverse waves belong to the intervals 3389–4256 and 1570–2406 m/s, respectively. Basing on the AW velocities, we have determined the complete matrices of the elastic stiffness and compliance coefficients (see Table 2). As seen from Table 2, AGGS reveals rather high elastic anisotropy. For example, the coefficient C_{33} is approximately 1.5 times smaller than C_{11} and C_{22}, while the coefficients C_{11} and C_{22} are almost the same. The same is true of the elastic compliance tensor components. Notice that the above effect is similar to that observed in optics. As stated above, the refractive indices n_a and n_b are also very close. Thus, the peculiarities observed in both optical and elastic properties testify that the orthorhombic distortion of AGGS lattice is weak enough and the unit cell is close to tetragonal. This conclusion agrees well with the fact that two of the lattice constants are also very close to each other (see Introduction).

Table 1. AW velocities of AGGS crystals.

Directions of propagation and polarization	Velocity v_{ij}, m/s	Directions of propagation and polarization	Velocity v_{ij}, m/s
[100], [100]	4147±12	[110], [110]	4048±12
[010], [010]	4256±13	[100], [010] or [010], [100]	2183±12
[001], [001]	3389±12	[100], [001] or [001], [100]	1570±20
[011], [011]	3461±30	[010], [001] or [001], [010]	2406±12
[101], [101]	3787±13		

Table 2. Elastic stiffness and compliance coefficients for AGGS crystals.

C_{ij}, 10^9 N/m^2	C_{ij}, 10^9 N/m^2	S_{km}, 10^{-11} m^2/N	S_{km}, 10^{-11} m^2/N
C_{11} = 65.35±0.95	C_{66} = 18.11±0.31	S_{11} = 6.35±0.80	S_{66} = 5.52±0.07
C_{22} = 68.83±0.99	C_{12} = 21.19±1.22	S_{22} = 4.06±0.08	S_{12} = –3.91±0.25
C_{33} = 43.64±0.66	C_{23} = –19.70±1.92	S_{33} = 9.88±1.27	S_{23} = 4.92±0.32
C_{44} = 22.0 ±0.37	C_{13} = 34.43±1.19	S_{44} = 4.55±0.16	S_{13} = –6.80±1.01
C_{55} = 9.37±0.27		S_{55} = 10.67±0.05	

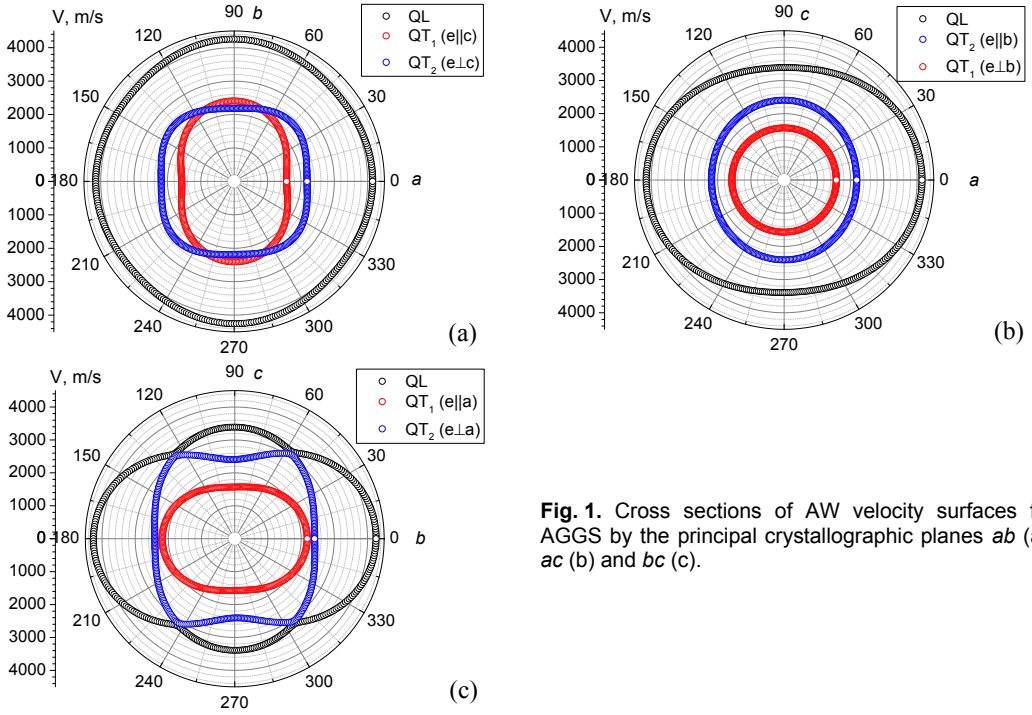

Fig. 1. Cross sections of AW velocity surfaces for AGGS by the principal crystallographic planes *ab* (a), *ac* (b) and *bc* (c).

Using the elastic stiffness matrix thus determined and the Christoffel equation, we have constructed the cross sections of the AW velocity surfaces by the principal crystallographic planes. As seen from Fig. 1, the AW QT_1 that propagates in the crystallographic plane *ac* and is polarized in the same plane is the slowest. Notice that, within this plane, the velocity of the wave QT_1 does not depend on the propagation direction (see Fig. 1b). Moreover, this wave reveals no obliquity of the energy flow (see Fig. 2b). Notice that the non-orthogonality of this wave becomes equal to 45 deg when the wave propagates at the angle 52 deg with respect to the *a* axis in the *ac* plane (see Fig. 3b). In other terms, this AW acquires 'by half' the features of the longitudinal wave.

Among the longitudinal AWs, the slowest one propagates in the *bc* plane at the angles 58 or 124 deg with respect to the *b* axis, with the velocity being equal to 3154 m/s (see Fig. 1c). These propagation directions are characterized by a following rare physical phenomenon: the propagation velocities of the QT wave QT_2 and the quasi-longitudinal (QL) wave become equal to each other. Thus, these directions are nothing but acoustic axes for the longitudinal and transverse waves. As far as we know, such a phenomenon has been observed only in paratellurite crystals [10]. The matter is that the velocities of the longitudinal AWs are usually much higher than those of the transverse waves. As seen from Fig. 2c, the obliquity of the energy flow for this propagation direction of the waves QL and QT_2 is equal to zero. However, the angular dependence of the

obliquity is very sharp in the vicinity of this direction. It is also interesting that, for the directions mentioned above, the non-orthogonality of the wave QT_2 and the deviation from the purely longitudinal state of the wave QL both reach the same value, 45 deg (see Fig. 3c). Thus, both of these waves become 'half-transverse' and 'half-longitudinal'.

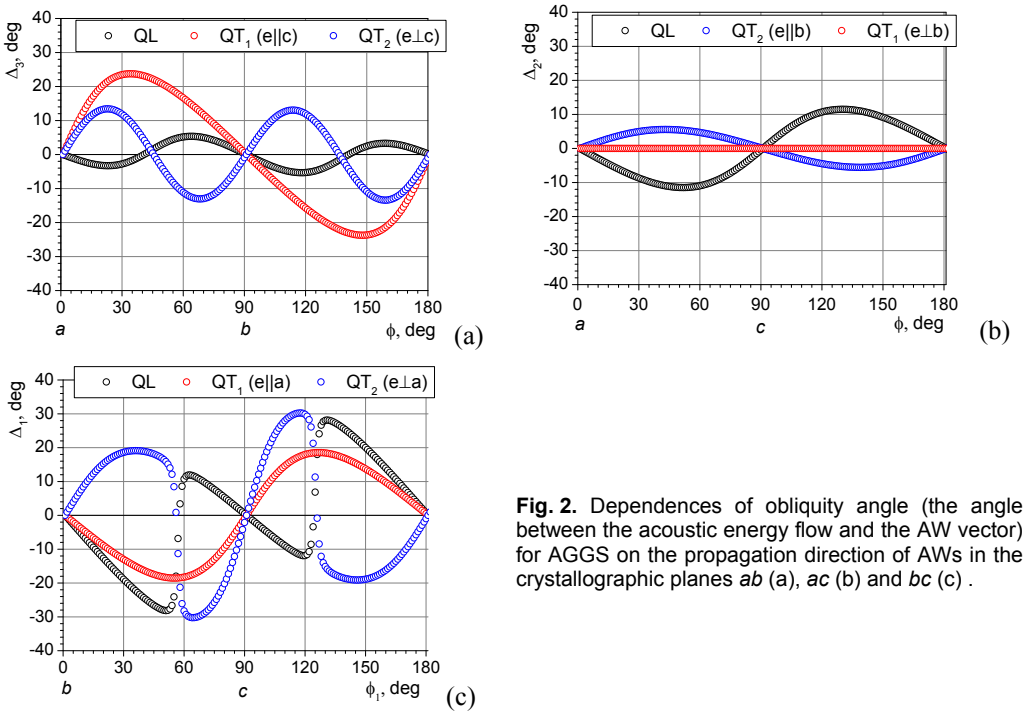

Fig. 2. Dependences of obliquity angle (the angle between the acoustic energy flow and the AW vector) for AGGS on the propagation direction of AWs in the crystallographic planes *ab* (a), *ac* (b) and *bc* (c) .

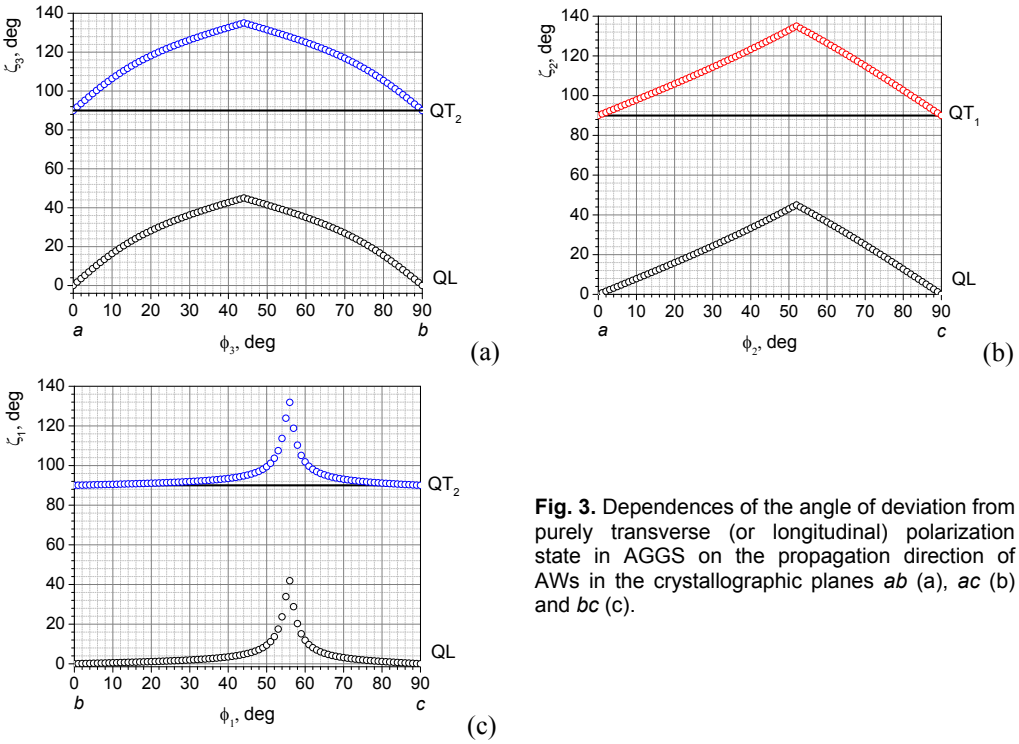

Fig. 3. Dependences of the angle of deviation from purely transverse (or longitudinal) polarization state in AGGS on the propagation direction of AWs in the crystallographic planes *ab* (a), *ac* (b) and *bc* (c).

The acoustic axes are also observed for the transverse AWs in AGGS. In particular, the velocities of the waves QT_1 and QT_2 become the same (2300 m/s) when the AWs propagate at the angles 70 or 110 deg with respect to the *a* axis in the *ab* plane.

Unfortunately, one cannot calculate the exact AOFM value without the exact data for the elastooptic coefficients. However, one can roughly estimate the AOFM for the AGGS crystals after recalling that the effective elastooptic coefficient usually lies in the range 0.01–0.2. Using the mean refractive index value $\overline{n} = 2.4141$ and the velocity of the slowest AW (1570 m/s), one can find a rough AOFM value. Our calculations have yielded in the estimations $\leq 500\times10^{-15}$ s^3/kg. Thus, the AGGS crystals can be assumed to be a promising acoustooptic material for the mid-IR spectral range. Of course, to make thorough conclusions on this subject matter, one has to determine reliably the complete elastooptic matrix. The latter will be the aim of our forthcoming work.

4. Conclusions

We have studied experimentally both the acoustic and elastic anisotropies of the AGGS crystals. In particular, we have measured the AW velocities and, on their basis, determined the complete matrices of elastic stiffness and compliance coefficients. Using the data obtained and the elastic symmetry principles, we have found that the orthorhombic lattice distortion in the AGGS crystals is rather small, i.e. the crystals are close to tetragonal.

We have also revealed a rare effect, the equality of the velocities of QT and QL waves. The corresponding longitudinal-transverse acoustic axes belong to the *bc* plane. The effect appears whenever the waves mentioned above propagate at the angles 58 or 124 deg with respect to the *b* axis. The corresponding velocity is equal to 3154 m/s. The oblique angle of the QL and QT_2 waves along this propagation direction is equal to zero. The non-orthogonality of the QT_2 wave and the deviation from the purely longitudinal state of the QL wave propagating along these directions reach the same value, 45 deg, so that the both waves become 'half-transverse' and 'half-longitudinal'. The acoustic axes in AGGS can also be observed for the transverse AWs, although in the *ab* plane.

We have found that the slowest AW in AGGS is the QT wave propagating in the crystallographic plane *ac* with the velocity 1570 m/s. Using the roughly evaluated elastooptic coefficient and the velocity of the slowest AW, we have obtained the estimation for the AOFM ($\leq 500\times10^{-15}$ s^3/kg). These supposed values suggest that the AGGS crystals can be promising for different acoustooptic applications in the mid-IR optical range.

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Анотація. *Експериментально досліджено акустичну і пружну анізотропію кристалів $AgGaGeS_4$. На основі виміряних швидкостей акустичних хвиль визначено повні матриці коефіцієнтів пружних жорсткостей і податливостей. Виявлено, що орторомбічність кристалів $AgGaGeS_4$ представляє собою слабку дисторсію прототипної тетрагональної ґратки. В кристалах $AgGaGeS_4$ виявлено рідкісний ефект, що полягає в рівності швидкостей поширення квазіпоперечної та квазіпоздовжньої хвиль. При поширенні в напрямку поздовжньо-поперечної акустичної осі обидві згадані хвилі стають напівпоздовжніми і напівпоперечними. Встановлено, що найповільнішою хвилею в кристалах $AgGaGeS_4$ є квазіпоперечна хвиля, яка поширюється в кристалографічній площині ac зі швидкістю 1570 м/с. Значення коефіцієнта акустооптичної якості для кристалів $AgGaGeS_4$, розраховане з використанням швидкості поширення найповільнішої акустичної хвилі і грубої оцінки пружнооптичного коефіцієнта, може досягати значення 500×10^{-15} $с^3$ / кг . Це говорить про те, що кристали $AgGaGeS_4$ можуть виявитися перспективним акустооптичним матеріалом для використання в середній ІЧ-області спектру.*