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Dispersion properties of GaS studied by THz-TDS

Cite this: *CrystEngComm*, 2014, 16, 1995J. F. Molloy,^a M. Naftaly,^a Yu. M. Andreev,^{bc} G. V. Lanskii,^{bc} I. N. Lapin,^c A. I. Potekaev,^c K. A. Kokh,^{cde} A. V. Shabalina,^c A. V. Shaiduko^{bc} and V. A. Svetlichnyi^cReceived 1st November 2013,
Accepted 7th December 2013

DOI: 10.1039/c3ce42230e

www.rsc.org/crystengcomm

High optical quality centimeter sized GaS crystals are grown using a modified vertical Bridgman method with heat field rotation of the growth melt. Ordinary and extraordinary wave refractive index dispersions are studied by THz time-domain spectroscopy (THz-TDS). New dispersion equations are designed to be suitable for estimating dispersion properties of solid solution GaSe_{1-x}S_x crystals from the near IR through the mid-IR and further into the THz range.

Introduction

Gallium sulfide (GaS) is one of a group of isostructural A^{III}B^{VI} compounds with a GaSe-type layered structure. GaS crystals grown using the conventional vertical Bridgman method crystallize invariably in the centrosymmetric β -polytype (β -GaS). This is in contrast to GaSe which crystallizes predominantly in the acentrosymmetric ϵ -polytype (ϵ -GaSe) and can contain an admixture of other (β , δ or γ) polytypes.¹ ϵ -GaSe is transparent at wavelengths from the visible through to the mid-IR (0.62–18 μm) and further into the THz (≥ 50 μm) range, making it usable for both mid-IR and THz generation and detection.^{2,3} However, poor mechanical properties caused by the layered structure have so far restricted its practical applications. In this regard, the relatively wide band gap of β -GaS of 2.8 eV at 300 K (shortwave edge at 0.45 μm) and its longwave transmission extending to 14 μm (ref. 4) make this crystal very useful for growing ϵ -polytype acentrosymmetric solid solution crystals ϵ -GaSe_{1-x}S_x (mixing ratio, $x \leq 0.5$), whose structure and basic physical properties are similar to those of ϵ -GaSe.^{5–7} ϵ -GaSe_{1-x}S_x crystals are characterized by wide band transparency, possess large nonlinearity, and exhibit birefringence intermediate to that of ϵ -GaSe and ϵ -GaS crystals. Due to significantly improved mechanical properties, as well as optical and other physical properties that are responsible for frequency conversion efficiency, ϵ -GaSe_{1-x}S_x crystals are becoming popular for

frequency conversion into mid-IR and THz ranges,^{5,7–12} and appear to be useful for field applications.¹³

Successful design of ϵ -GaSe_{1-x}S_x crystals for nonlinear applications calls for adequate data on dispersion *versus* mixing ratio of the ordinary (n_o) and extraordinary (n_e) wave refractive indices over the entire transparency range. Dispersion in solid solution crystals grown from structurally identical parent crystals can be estimated by using the well-known relation from ref. 14, adapted to the case of ϵ -Ga(Se,S) as

$$n_{o,e}^2(\epsilon\text{-GaSe}_{1-x}\text{Se}_x) = (1-x) \cdot n_{o,e}^2(\epsilon\text{-GaSe}) + x \cdot n_{o,e}^2(\epsilon\text{-GaS}). \quad (1)$$

Clearly, in order to apply eqn (1), the dispersion properties of parent ϵ -GaSe (hereinafter GaSe) and ϵ -GaS crystals have to be known. For this purpose, dispersion equations for GaSe in ref. 15 have been found to be suitable for estimating phase matching (PM) over the whole transparency range.³ However, the optical properties of bulk ϵ -GaS crystals are not available since to the best of our knowledge crystals of such a polytype have not yet been grown and similarly studied. The only available experimental data reported in ref. 5 present mid-IR dispersions for β -GaS. On the other hand, it is well known that physical properties of polytypes differ negligibly.^{16,17} Thus, it can be proposed that dispersion properties for β -GaS are close to that for ϵ -GaS (hereinafter both polytypes are labeled as GaS) and applied for estimating the dispersions of ϵ -GaSe_{1-x}S_x (hereinafter GaSe_{1-x}S_x) by using eqn (1).

Mid-IR dispersion equations for GaS were designed *via* a nonlinear method,¹⁸ using our own experimental data on phase matching in GaSe_{1-x}S_x and dispersion data for GaSe from ref. 15. By the same method, dispersion equations for GaS were also designed by using known experimental data for phase matching in GaSe_{1-x}S_x and GaSe.¹⁹ It should be noted that in utilizing a nonlinear method, it has to be borne in mind that some of the published experimental data on mid-IR and THz dispersions in selected ϵ -GaSe_{1-x}S_x crystal

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compositions appear to be in disagreement.^{5,7,20–25} To estimate phase matching data for the low doped solid solution crystal $\epsilon\text{-GaSe}_{0.91}\text{S}_{0.09}$ in the THz range, dispersion equations for pure GaSe were successfully used in ref. 9. Nevertheless, reported dispersion equations for GaS have not been analyzed in comparison for mid-IR applications; validity range and applicability for the THz range have not been studied.

In the present work, we report for the first time to our knowledge THz-TDS measurements of dispersions of o- (n_o) and e-wave (n_e) refractive indices for GaS crystals which were grown using a modified vertical Bridgman method with heat field rotation to improve the crystal uniformity. New dispersion equations are designed for the entire transparency range of GaS from the near IR through to the mid-IR and further into the THz range.

Experimental procedure

Preparation of polycrystalline material

The modified material synthesis and vertical Bridgman method²⁶ were employed to grow a single crystal GaS. The starting materials for the synthesis were Ga 99.9997% and S 99.99% which were additionally purified by remelting in a continuously evacuated ampoule. Weighing was performed with an accuracy of ± 0.1 mg. All growth and synthesis ampoules were evacuated to a residual pressure of $\sim 10^{-4}$ torr. After several hours of melt homogenization during the synthesis process, the temperature was slowly decreased to 40 K below the melting point of 1238 K of the compound at a rate of ~ 10 K h^{-1} . The synthesised large-grain polycrystalline material is shown in Fig. 1a.

Crystal growth of GaS

For the growth process, the polycrystalline material was loaded into a single wall ampoule. The internal wall had a layer of pyrolytic carbon which protected the melt from reaction with quartz. The unseeded crystal growth was realized using the vertical Bridgman method, with heat field symmetry change and rotation described in detail in ref. 27. The sealed growth ampoule was loaded into the furnace having a temperature gradient of ~ 15 K cm^{-1} at the estimated level of crystallization front. After homogenization of the melt at a temperature 30 K above the melting point, the ampoule was mechanically lowered at a speed of 10 mm per day. An external view of the grown boule is presented in Fig. 1b.

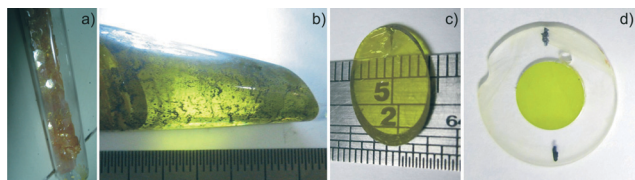


Fig. 1 External view of (a) an ampoule section with a synthesized GaS compound, (b) a section of as-grown boule, (c) an as-cleaved single crystal disk and (d) an orthogonally ($\theta = 90^\circ$) cut and polished sample in a colorless polymer holder.

Two types of GaS samples were fabricated for the present study. The first type was c-cut, *i.e.* had faces orthogonal to the c -axis, so that a traversing beam travelled parallel to the c -axis. This type of sample (Fig. 1c) was exfoliated from the as-grown single crystal boule. The second type of sample was cut so that a traversing beam travelled orthogonally to the c -axis. To make this type of sample (Fig. 1d), a section of the GaS boule was first immersed in a monomer (polymethyl acrylate) mixed with a thermoinitiator and placed in an oven for polymerization. Once set, the boule section was cut perpendicular to the growth layers ($\perp c$) and then polished with fine $0.8\text{--}1.2$ μm Al_2O_3 powder. The resulting samples of both types were free from precipitates, voids or microbubbles, or other visual defects. Samples of GaSe crystals, grown and prepared using similar techniques, were used in the study for comparison.

Crystal characterisation

The physical properties of the samples were characterized at room temperature. Scanning electron microscopy (SEM) (SEM Quanta 200 3D (FEI, Netherlands) microscope) was performed to study surface morphology. This microscope, equipped with an EDAX ECON VI microanalyzer, was also used to measure Ga and Se contents and to study structural properties. An X-ray diffractometer (Shimadzu XRD 6000 (Japan)) and a transmission electron microscope (TEM) (CM12 (Philips, Netherlands)) used for the measurements in the SAED method were also employed in analyzing structures. UV-visible-near-IR transmission spectra were recorded using a Cary 100 Scan (Varian Inc.) spectrophotometer over the spectral range $190\text{--}900$ nm with a spectral resolution of $\Delta\lambda$ $0.2\text{--}4$ nm and wavelength accuracy of ± 1 nm. The measurements of linear optical properties at $0.2\text{--}4$ THz were performed at room temperature using THz-TDS described elsewhere.^{28,29} The terahertz time-domain spectrometer used a standard configuration incorporating a femtosecond laser, four off-axis parabolic mirrors, a biased GaAs emitter, and electro-optic detection with a (110) ZnTe crystal and balanced Si photodiodes. The frequency resolution was 2 GHz. The THz beam was horizontally polarized.

GaS samples were placed in the focused THz beam such that they interacted with the incident radiation in either $E^- \perp c$ (o-wave) or $E^- \parallel c$ (e-wave) configuration, where E^- is the electric field vector of the incident light and c is the optical axis of the crystal, which is perpendicular to the cleavage plane.

Results and discussion

Sample quality

The cleaved GaS (001) surface is automatically flat with roughness as low as ≤ 0.06 nm (Fig. 2a). Fig. 2b shows a typical surface micrograph of a cut and polished sample of over 1 mm length. Measured surface roughness: $R_a = 0.095$ μm for GaS and 0.22 μm for GaSe. It can be seen in Fig. 2c that the surface finish of these very easily cleaved crystals is suitable for THz-TDS study.

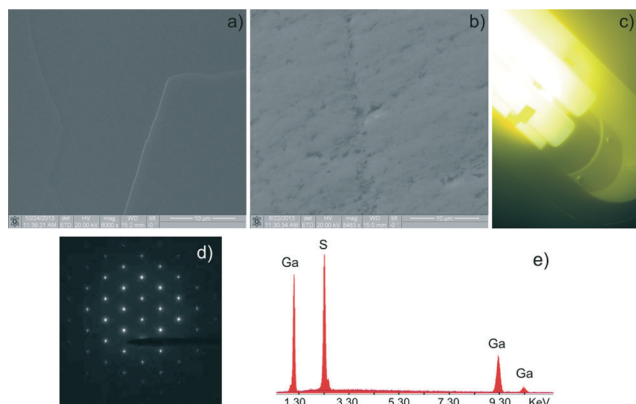


Fig. 2 SEM micrographs of a fracture of (a) a cleaved surface with a broken layer, and (b) a cut and polished surface of a 2 mm plate with 10 μm resolution; (c) the view through the polished crystal backlit by a white light lamp; (d) SAED patterns observed by TEM; and (e) an uncalibrated EDAX spectrum of GaS qualitatively revealing its chemical composition.

Regions of local defects were observed on the polished surfaces of samples with about 1 mm thickness. Thinner samples had high concentration of defects and were useless for the study. The diffraction patterns in Fig. 2d clearly confirm the high quality of the crystalline structure. Fig. 2e depicts the EDAX spectrum for GaS. Only Ga and S peaks were observed, indicating the fine purity of the product. EDAX spectra recorded during the surface scanning confirm the highly uniform distribution of the GaS composition. The analysis showed that the average atomic ratio Ga : S = 50.35 : 49.75, which indicates that the average chemical formula is $\text{GaS}_{0.986}$ or approaching the stoichiometric one with small Ga excess.

Fig. 3a shows the short-wave cut-off edge of the cleaved GaSe crystal, which lies at $0.62 \mu\text{m}$ and corresponds well to the known band-gap absorption edge.¹⁵ The short-wave cut-off edge of the cleaved GaS crystal is at about $0.45 \mu\text{m}$. The GaSe edge shows a well known exciton absorption peak at $\sim 0.615 \mu\text{m}$ (ref. 38) and etalon oscillations of the GaSe wafer.

We found that in unpolarised light, the absorption coefficient α for both GaS and GaSe crystals does not exceed 0.05 cm^{-1} within their maximal transparency range, although it is undoubtedly smaller for GaS than for GaSe. Absorption spectra recorded by THz-TDS (smoothed in post-processing)³¹ are shown in Fig. 3b. The o-wave absorption coefficient (α_o) spectra of GaSe agree well with known data in both spectral structure and magnitude.^{32–35} The strong and narrow absorption peak of the $E^{(2)}$ rigid phonon mode at 0.59 THz reflects its high optical quality.³⁶ Fig. 3b again demonstrates that GaS possesses higher transparency for o-wave than does GaSe. Furthermore, absorption in GaS is strongly anisotropic, with the e-wave absorption coefficient at least a factor of 2 to 3 lower than that for o-wave in the range $>2.15 \text{ THz}$. The good match between the published and measured data for GaSe together with fine optical properties of the grown crystals form a basis for confidence in the accuracy of the measured dispersion properties of GaS.

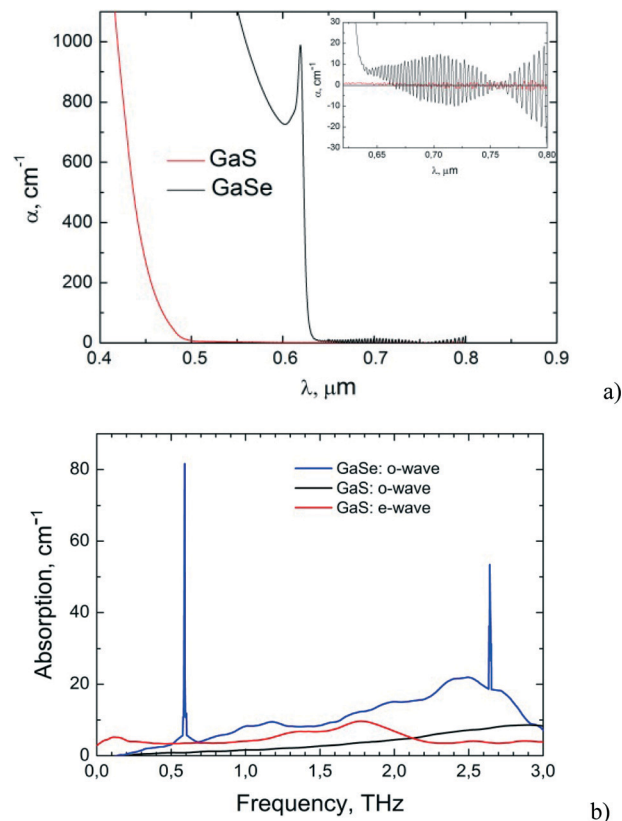


Fig. 3 (a) Short-wave absorption spectra in unpolarized light (scaled-up GaS and GaSe edges are shown in the inset) and (b) THz polarized light of 1 mm thick crystals.

THz dispersions

Fig. 4a presents GaS and GaSe dispersions measured *via* THz-TDS for comparison.

The measured n_o and n_e dispersions of GaSe indicate spectral features including the weak peak of abnormal n_e dispersion at about 1.1 THz, similar to experimental data.^{32–35} In Fig. 4a, it is also seen that n_o dispersions for both cleaved and cut and polished GaS samples are coincident within the measurement accuracy. The close agreement between the measured and published data on absorption and refractive indices of GaSe gives confidence in the accuracy of the measured data for GaS, including dispersion data, over the entire transparency range.

Dispersion equations in ref. 5, claimed valid at $0.63 \leq \lambda \leq 20 \mu\text{m}$, are as follows:

$$n_o^2 = -\frac{0.03485}{\lambda^4} + \frac{0.6305}{\lambda^2} + 6.556 - 0.001304\lambda^2 - 0.00000203\lambda^4,$$

$$n_e^2 = -\frac{0.03544}{\lambda^4} + \frac{0.3355}{\lambda^2} + 4.954 - 0.0008844\lambda^2 - 0.00001115\lambda^4.$$
(2)

The dispersion of n_o calculated from eqn (2) shows an abnormal trend at wavelengths exceeding $20 \mu\text{m}$, in contrast to the n_e curve which has a quite reasonable spectral position

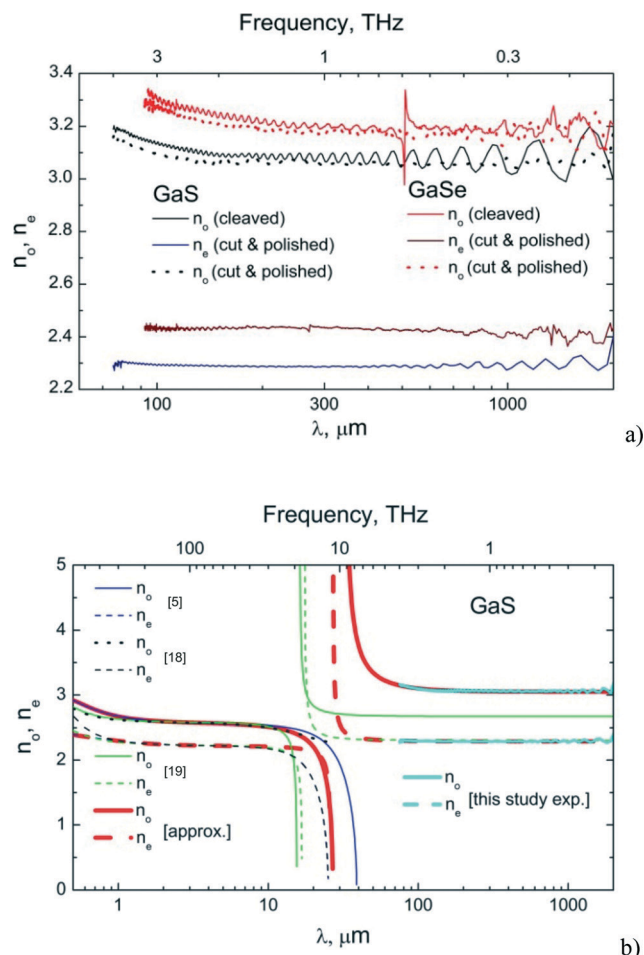


Fig. 4 (a) GaS and GaSe dispersions obtained by THz-TDS and (b) GaS dispersions calculated by using dispersion equations from ref. 5, 18, 19, the experimental (exp.) data in this study and its approximations (approx.).

of the fundamental phonon absorption peak (Fig. 4b). It can be proposed that both n_o and n_e dispersions are overestimated in the region from 0.6 or 0.8 μm up to 1.4 μm , which evidently lies within the maximal transparency range and should be characterized by slow changes with an almost invariable gradient. Fig. 4b also displays dispersion curves calculated using equations from ref. 18

$$\begin{aligned} n_o^2 &= \frac{0.0211305}{\lambda^4} + \frac{0.206623}{\lambda^2} + 6.62346 - 0.004058\lambda^2 \\ &\quad + 0.0000028447\lambda^4, \\ n_e^2 &= \frac{0.073448}{\lambda^4} + \frac{0.262196}{\lambda^2} + 4.94284 - 0.00102111\lambda^2 \\ &\quad - 0.0000107464\lambda^4 \end{aligned} \quad (3)$$

that were designed for GaS using a nonlinear method. Measured experimental data for CO₂ laser SHG phase matching in solid solution GaSe_{1-x}S_x crystals, dispersion equations for GaSe crystal from ref. 15 and relation (1) were used in designing this equation. It can be seen that dispersion n_o

becomes more reasonable at a short wavelength range in contrast to that obtained from ref. 5. However, it was found that neither set of dispersion equations^{5,18} is useful for THz applications.

Dispersion equations for GaS in ref. 19 are as follows:

$$\begin{aligned} n_o^2 &= 7.12996 + \frac{0.26073}{\lambda^2 - 0.04627} + \frac{127.335}{\lambda^2 - 258.431}, \\ n_e^2 &= 5.30813 + \frac{0.20852}{\lambda^2 - 0.05251} + \frac{101.479}{\lambda^2 - 302.223}. \end{aligned} \quad (4)$$

Eqn (4) was designed *via* the nonlinear method using the available experimental phase matching data for GaSe_{1-x}S_x and the recent data for GaSe, which provided a good reproduction of the phase-matching conditions for type 1 SHG.⁷ Dispersions calculated from eqn (4) appear to be more consistent than those obtained from ref. 5, 18 at least at short wavelengths (Fig. 4b). Moreover, these equations produce reasonable results for THz applications, although it may be expected that THz birefringence should be larger than in the mid-IR. It should be noted that up till now, there has been an extreme scarcity of data from direct measurements of n_o and n_e , which are available for very few GaSe_{1-x}S_x compositions in the mid-IR at 0.6–20 μm (ref. 5) and 0.633–10 μm .¹¹ This is because the widely used wedge method of sample preparation is of limited utility for these crystals due to their relatively poor mechanical properties. Thus, in addition to experimental data,¹¹ the nonlinear method allows one to estimate dispersions in GaS that are of practical interest in the solid solution GaSe_{1-x}S_x technologies, as well as other applications, but only in a limited part of the mid-IR.

In this study, new dispersion equations were designed for the entire transparency range of GaS by the best fit method using only experimental data, including that obtained by THz-TDS (Fig. 4b) and the accepted data for mid-IR dispersions.⁵ Eqn (1)⁵ is unsuitable for direct use in the fitting process due to a lack of a term responsible for the input of TO phonon modes into dielectric response.³⁷ To address this problem, we included in eqn (1) the necessary terms in the form $A\lambda^2/(\lambda^2 - B)$, where A and B are constants, and then approximated it by using the best fit method to account for this study's results. The new dispersion equations designed are as follows:

$$\begin{aligned} n_o^2 &= -\frac{0.01129}{\lambda^6} + \frac{0.03648}{\lambda^4} + \frac{0.51402}{\lambda^2} + 6.59624 + \frac{2.71047\lambda^2}{\lambda^2 - 1025.42116}, \\ n_e^2 &= \frac{0.0113}{\lambda^6} + \frac{0.10569}{\lambda^4} - \frac{0.44573}{\lambda^2} + 4.92144 + \frac{0.315\lambda^2}{\lambda^2 - 720.12225}. \end{aligned} \quad (5)$$

As illustrated in Fig. 4b, eqn (5) matches well the experimental data as reported⁵ across the validity range 0.63–20 μm , as well as those recorded in this study in the spectral range from 0.25 to 4 THz. Older experimental data^{30,38} are found to be in serious disagreement with relation (5), as they involve

approximations in ref. 19 in the short wavelength range up to 1.4 μm . Therefore, the approximations (5) need to be improved in this range by using improved experimental data. Estimations made using relation (1), eqn (5) and those for GaSe^{15} describe well phase matching in $\text{GaSe}_{1-x}\text{S}_x$ in the mid-IR. Their usefulness for THz requires experimental verification due to widely scattered experimental data from a limited number of compositions. Finally, it can be concluded that designed dispersion equations for GaS are valid at least within 0.8–20 μm and for the first time have been adapted for applications between 0.2 and 4 THz. In future studies, special attention has to be paid to determining dispersions at 0.45–0.8 μm (shortwave abnormal refraction range) and 20–50 μm (fundamental phonon absorption) and to verify experiments at longer wavelengths.

Conclusion

High optical quality centimeter-sized GaS crystals are grown using a modified vertical Bridgman method with heat field rotation. For the first time, anisotropy of ordinary and extraordinary refractive index dispersions is studied *via* THz time-domain spectroscopy (THz-TDS). New dispersion equations are designed for GaS crystals suitable for application through the entire transparency range from the visible to the THz range and capable of providing phase matching estimations in $\text{GaSe}_{1-x}\text{S}_x$ crystals with $0 \leq x \leq 0.5$.

Acknowledgements

Work at the National Physical Laboratory was supported by the National Measurement Office of U.K. and by the Engineering and Physical Sciences Research Council through the Industrial Doctoral Center at Heriot-Watt University, Edinburgh, U.K. This work was also supported in part by RFBR, project no. 12-08-00482-a, 12-02-33174, and 13-02-00667; Presidium SB RAS, MIPFI no. 46 and VIII.80.2.4.

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