# $BaGa_4S_7$: wide-bandgap phase-matchable nonlinear crystal for the mid-infrared


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**Abstract**: We report measurements of the transparency, nonlinear coefficients and damage threshold of $BaGa_4S_7$ grown by the Bridgman-Stockbarger technique. We also present calculations showing that this crystal is phase-matchable for down conversion into the mid-IR starting from a pump wavelength of 1064 nm.





**OCIS codes:** (160.4330) Nonlinear optical materials; (190.4410) Nonlinear optics, parametric processes.


## References and links


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## 1. Introduction

Only few non-oxide nonlinear optical crystals exist that are transparent above ~5 µm in the mid-IR and simultaneously possess sufficiently wide band-gap to be pumped at relatively short wavelengths, e.g. by Nd:YAG lasers at 1064 nm, without two-photon absorption, for efficient down-conversion and high powers in the mid-IR [1]. The chalcopyrite $AgGaS_2$ (AGS) is the only such crystal that is commercially available while the related defect chalcopyrite $HgGa_2S_4$ is extremely difficult to grow. The orthorhombic $LiGaS_2$, $LiInS_2$, $LiGaSe_2$ and $LiInSe_2$ also exhibit band-gaps corresponding to wavelengths shorter than 532 nm but their nonlinearities are modest and the residual losses are still quite high. The recently developed chalcopyrite $CdSiP_2$, which exhibits exceptionally high nonlinearity and can be non-critically phase-matched, unfortunately transmits only up to ~6.5 µm [1].

The non-centrosymmetric orthorhombic *mm*2 structure of $BaGa_4S_7$ (BGS) was identified as early as 1983 [2]. More recently, the BaS-$Ga_2S_3$ binary phase diagram was studied [3]. Single crystals of BGS were grown by the Bridgman-Stockbarger technique in [4] and the SHG effect was confirmed by the Kurtz powder test. The bandgap was estimated in [4] to correspond to ~350 nm (3.54 eV) and the transparency to extend up to 13.7 µm at the 0-level. In [5] we measured the three refractive indices of BGS in the 0.42-9.5 µm spectral range and


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constructed the first set of Sellmeier equations. The correspondence between the dielectric (principal optical) axes *xyz* and the crystallographic axes *abc* in the orthorhombic BGS crystal, in which *c* coincides with the two-fold symmetry axis, is *xyz* = *cab* if the convention $c_0<a_0<b_0$ is used for the lattice parameters and $n_x<n_y<n_z$ [5]. Furthermore, the angle $\Omega$ between the optic axes and the *z*-principal (dielectric) axis was measured to be $\Omega = 45.6°$ at 633 nm [5]. Here we report on the calculated phase-matching properties of BGS for down-conversion processes and experimental measurements of the transparency, nonlinear coefficients and the damage threshold at 1064 nm.

## 2. Crystal growth and transparency

We grew BGS by the Bridgman-Stockbarger method using raw materials with high purity, 6Ns for Ga and S, and 99% for Ba. Because of the pronounced chemical activity of Ba, the synthesis took place in glass-carbon containers, evacuated to a residual pressure of $2 \times 10^{-5}$ torr. The temperature in the synthesis furnace was initially raised to 1150°C at 200°C/h and the charge was held at this temperature for a few hours in order to homogenize it, after that the oven was switched-off to cool the charge down to room temperature. Then the charge was loaded into quartz ampoules of $\phi 18 \times 150$ mm size which were evacuated again to residual pressure of $2 \times 10^{-5}$ torr and inserted into the heating zone of the growth furnace. The temperature was raised to 1130-1140°C and after 3 h the ampoule was lowered into the crystallization zone. In order to avoid the contact between the melt and the quartz, the inner wall of the ampoule was with carbon fettling.

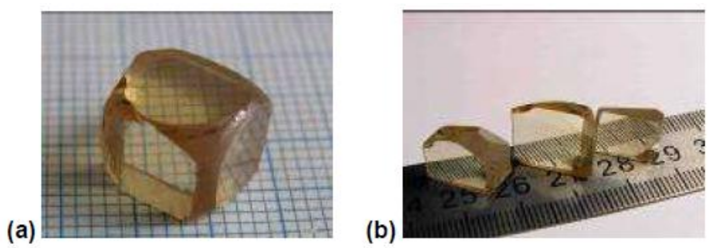


Fig. 1. (a) Cube and (b) prisms of BGS prepared for determination of the two-fold axis and refractive indices, respectively, see [5].

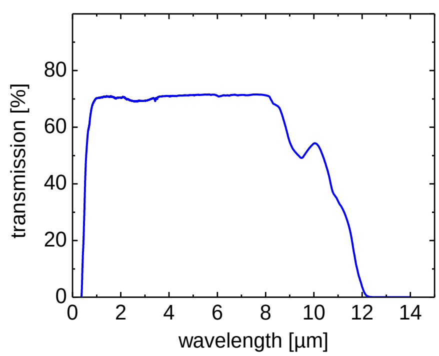


Fig. 2. Unpolarized transmission spectrum of BGS measured with a 10.9 mm thick *y*-cut plate.

The optimum parameters for the crystal growth were derived from several preliminary experiments by assessing the optical quality of the grown crystals. The optimum crystallization rate is in the 7 ± 2 mm/day range, the temperature gradient in the crystallization zone is 15 ± 2 °C/cm and the characteristic growth time is 12-15 days. The as-grown crystals are colorless (Figs. 1(a) and 1(b)). The good transmission limits for such initial samples,

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estimated at an absorption level of 0.3 $cm^{-1}$ from unpolarized transmission spectra, are 0.545-9.4 µm (Fig. 2).

## 3. Phase-matching configurations for down conversion

Figure 3 shows the calculated phase-matching configurations for down conversion in BGS (difference-frequency generation, optical parametric generation, amplification and oscillation) using the Sellmeier equations from [5]. The configurations correspond to three-wave interactions in the principal planes that have non-vanishing effective nonlinearity $d_{eff}$ taking into account that *x* corresponds to the two-fold symmetry axis. With respect to down conversion of high-power radiation from 1064 nm to the mid-IR, BGS is phase-matchable in the *x-y* plane (oo-e) for idler wavelengths only up to 5.42 µm where $d_{eff}$ vanishes. In the *y-z* plane, phase-matching (ee-o) is possible up to 6.23 µm at which wavelength the non-critical configuration is combined with non-zero nonlinearity. Most promising seems oo-e interaction in the *x-z* plane, where phase-matching is possible at idler wavelengths starting from 6.23 µm in the non-critical configuration and with maximum $d_{eff}$ up to the mid-IR transmission cut-off of BGS. Wavelengths near 6.45 µm, interesting for medical applications, could be possibly achieved by temperature tuning in the non-critical configuration. In this plane also type-II (oe-o) interaction is possible but it starts from idler wavelengths of 8.05 µm where $d_{eff}$ is vanishing and this nonlinearity remains small within the entire possible idler tuning range.

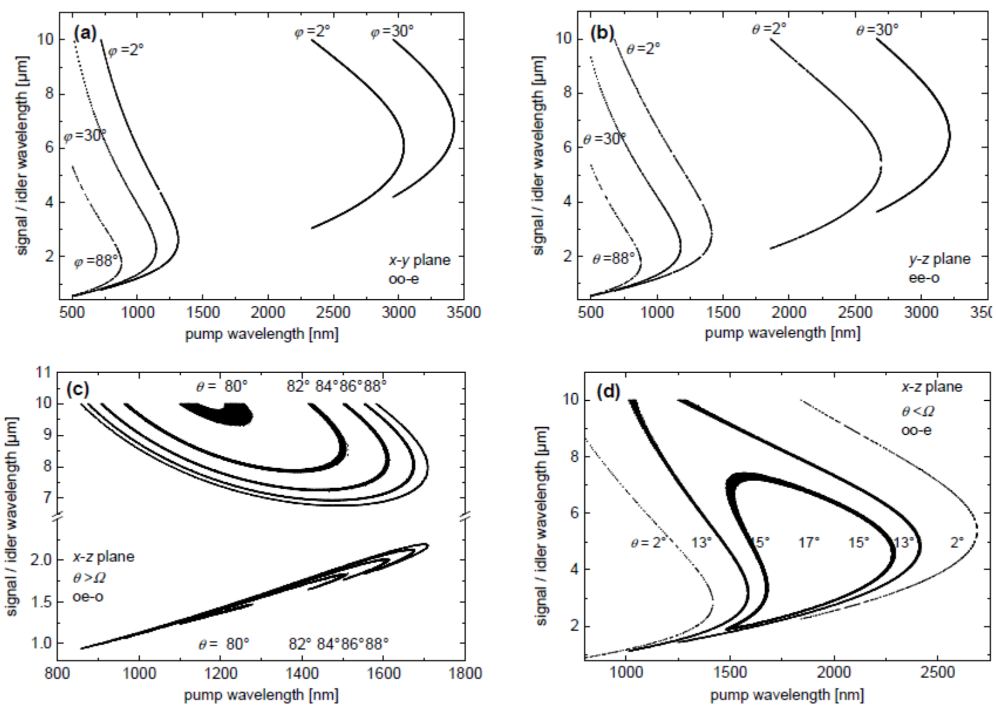


Fig. 3. Phase-matching for down-conversion in BGS (a) in the *x-y* plane (oo-e negative type-I), (b) in the *y-z* plane (ee-o positive type-I), (c) in the *x-z* plane for $\theta>\Omega$ (oe-o positive type-II) and (d) in the *x-z* plane for $\theta<\Omega$ (oo-e negative type-I).

## 4. Nonlinear coefficients

The expressions for the effective nonlinearity of the orthorhombic BGS read in the principal planes of the dielectric frame (Kleinman symmetry condition assumed, $d_{15} = d_{31}$, $d_{24} = d_{32}$):

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$$\text{plane } x-y,\ \text{oo}-\text{e}, d_{\text{eff}} = d_{32}\sin\varphi, \quad (1a)$$

$$\text{plane } y-z, \text{ee}-\text{o}, d_{\text{eff}} = d_{32}\sin^2\theta + d_{31}\cos^2\theta, \quad (1b)$$

$$\text{plane } x-z, \theta < \Omega,\ \text{oo}-\text{e}, d_{\text{eff}} = d_{31}\cos\theta, \quad (1c)$$

$$\text{plane } x-z, \theta > \Omega, \text{oe}-\text{o}, d_{\text{eff}} = d_{15}\cos\theta. \quad (1d)$$

Note that the tensor components $d_{\text{il}}$ are defined traditionally in the *abc* crystallographic frame.

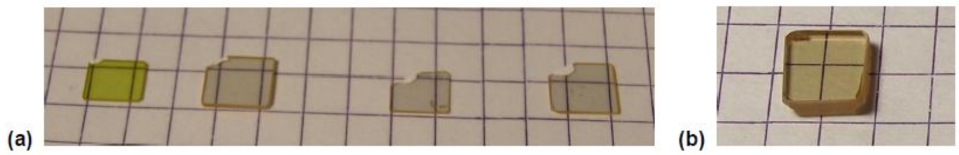


Fig. 4. (a) AGS (left) and 3 BGS samples used for determination of the nonlinear coefficients, and (b) BGS damage test plate.

The two components of the *d*-tensor, $d_{32}$ and $d_{31}$, were measured relative $d_{36}$(AGS) by second harmonic generation (SHG) with the set-up described in [1]. A femtosecond source based on a Ti:sapphire femtosecond amplifier operating at 1 kHz repetition rate was employed. The fundamental wavelength was 2260 nm (BBO type-II optical parametric amplifier) and 4620 nm ($KNbO_3$ optical parametric amplifier). The three thin plates of BGS shown in Fig. 4(a) were used: two of them were ~0.40 mm thick with orientation $\varphi$ = 35.5°, $\theta$ = 90° and $\varphi$ = 90°, $\theta$ = 38.4° for oo-e type SHG in the *x-y* plane and ee-o type SHG in the *y-z* plane, respectively. The experiments with these two plates were performed at 2260 nm and the SHG efficiency was compared to that obtained with an AGS crystal of 0.2 mm thickness, also shown in Fig. 4(a), cut at $\varphi$ = 45°, $\theta$ = 45° for oo-e type interaction. Thus the calculated spectral acceptances were very close (within 10%) for the test and reference samples; this was important in this case because both values were comparable to the spectral bandwidth of the femtosecond fundamental pulses. Finally, the third BGS sample was 0.815 mm thick and cut at $\varphi$ = 0°, $\theta$ = 15.5° for oo-e type SHG in the *x-z* plane ($\theta<\Omega$). At the fundamental wavelength of 4620 nm this sample was compared with an additional, 0.85 mm thick AGS plate cut at $\varphi$ = 45°, $\theta$ = 32° again for oo-e type interaction. At this wavelength the spectral acceptances of both samples, though different, were much larger than the bandwidth of the femtosecond fundamental pulses. Taking into account the beam size and the focusing properties of the lens, in all cases there was also an excess of angular acceptance and the birefringence walk-off could be neglected. The incident pulse energy was limited to few microjoules and the internal conversion efficiency was below 10%. This justifies the plane wave approximation and the effective nonlinear coefficient was estimated by correcting the relative SHG efficiency only for the different Fresnel losses and index of refraction. The results, scaled by Miller's rule to 2260 nm and assuming $d_{36}$(AGS) = 13.9 pm/V at this wavelength [6], read:

$$d_{31} = (0.37 \pm 0.02) d_{36} = (5.1 \pm 0.3) \text{ pm/V}, \quad (2a)$$

$$d_{32} = (0.41 \pm 0.02) d_{36} = (5.7 \pm 0.3) \text{ pm/V}, \quad (2b)$$

where $d_{31}/d_{32} > 0$.

### 5. Surface damage threshold

Damage tests of BGS were performed with 14-ns and 1-ns long pulses at 1.064 μm at repetition rates of 100 and 500 Hz, respectively.

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An uncoated unoriented BGS plate with a thickness of 2 mm, Fig. 4(b), was placed in the far field zone of the Q-switched Nd:YAG laser, emitting 14-ns pulses. The laser beam of a diameter of 3.8 mm was additionally focused with a 25-cm lens and the test plate was placed behind the focus where the spot size amounted to ~$3 \times 10^{-2}$ $cm^2$ at intensity level of $e^{-2}$. The energy incident on the plate was varied by a system of half-wave plate and Glan polarizer. The BGS test plate was exposed to laser radiation for a period of 1 min (6000 pulses) and the time interval between two successive exposures was 2 min. We started at a level of 0.6 $J/cm^2$ (incident peak-on-axis energy fluence) increasing it with a step of 0.2 $J/cm^2$. The damage threshold was determined as the arithmetic average between the last measurement without any visible changes in the test plate (at 3.6 $J/cm^2$) and the energy at which first signs of damage were observable (3.8 $J/cm^2$), i.e. we obtained 3.7 $J/cm^2$ of incident peak-on-axis energy fluence (or 264 $MW/cm^2$ of peak-on-axis intensity) as a characteristic damage threshold. The damage observed was a crater on the rear surface of the plate.

The beam from the regenerative amplifier providing 1 ns pulses at 500 Hz repetition rate had a diameter of 3 mm and was also focused with a 25-cm lens. The same plate was tested behind the focus where the beam cross section was measured to be $1.46 \times 10^{-3}$ $cm^2$ at intensity level of $e^{-2}$. Similar tests were performed as described above, starting from 0.6 $J/cm^2$ of incident peak-on-axis energy fluence with a step of 0.2 $J/cm^2$. The exposure time was 12 sec (6000 pulses) and the time interval between two exposures was 1 min. The damage threshold obtained in the same manner amounted to 2.9 $J/cm^2$ of incident peak-on-axis energy fluence (or 2.9 $GW/cm^2$ of peak-on-axis intensity). The damage observed was again a crater on the rear surface of the plate.

## 6. Conclusion

In conclusion, we presented first data on the nonlinear coefficients and the damage threshold of BGS, a new wide-bandgap nonlinear crystal phase-matchable for frequency down conversion from the 1 µm spectral range to the mid-IR. In accordance with the expectation from a bandgap lying in the UV, the nonlinear coefficients are modest and comparable to some oxide crystals. However, the damage threshold measured (3.7 $J/cm^2$) is exceptionally high for a non-oxide nonlinear crystal transparent in the mid-IR. This is promising for optical parametric oscillation starting with a pump wavelength of 1064 nm where no two-photon absorption in BGS is expected.


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