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$BaGa_4S_7$: Wide-Bandgap Phase-Matchable Nonlinear Crystal for the Mid-Infrared

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Abstract: The orthorhombic biaxial crystal $BaGa_4S_7$ has been grown by the Bridgman-Stockbarger technique in large sizes with good optical quality. Refractive indices have been measured and Sellmeier equations fitted to analyze the phase-matching configurations.

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

Only few non-oxide nonlinear 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. Nd:YAG laser 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 bang-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 structure of $BaGa_4S_7$ (BGS) was identified as early as 1983 [2]. Recently, single crystals of BGS were grown by the Bridgman-Stockbarger technique and the SHG effect was confirmed by the Kurtz powder test [3]. While the bandgap was estimated in [3] to correspond to ~350 nm (3.54 eV) and the transparency to extend up to 13.7 μm at the 0-level, no information exists on the dispersive properties of BGS. Here we report on refractive index measurements of BGS, present the constructed Sellmeier equations and analyze the possible phase-matching configurations for frequency down-conversion.

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 2×10^{-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 ϕ18×150 mm size which were evacuated again to residual pressure of 2×10^{-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. We estimated a melting temperature of 1105±5°C. 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 (Fig. 1a,b). The good transmission limits for such initial samples, estimated at an absorption level of 0.3 cm^{-1} from unpolarized transmission spectra, are 0.545-9.4 μm.

(a)


(b)


(c)
Sellmeier coefficients of BGS (0.42-9.5 μm):

$n^2=A_1+A_3/(\lambda^2-A_2)+A_5/(\lambda^2-A_4)$ where λ is in μm.

n	A_1	A_2	A_3	A_4	A_5
n_x	7.090307	0.019272	0.172059	858.223	1748.013
n_y	7.812188	0.015907	0.182439	990.979	2653.548
n_z	7.907286	0.015853	0.184081	981.884	2630.008

Fig. 1. (a) Cube and (b) prisms of BGS prepared for determination of the two-fold axis and refractive indices, respectively; (c) Sellmeier equations of BGS constructed by fitting the refractive index data.

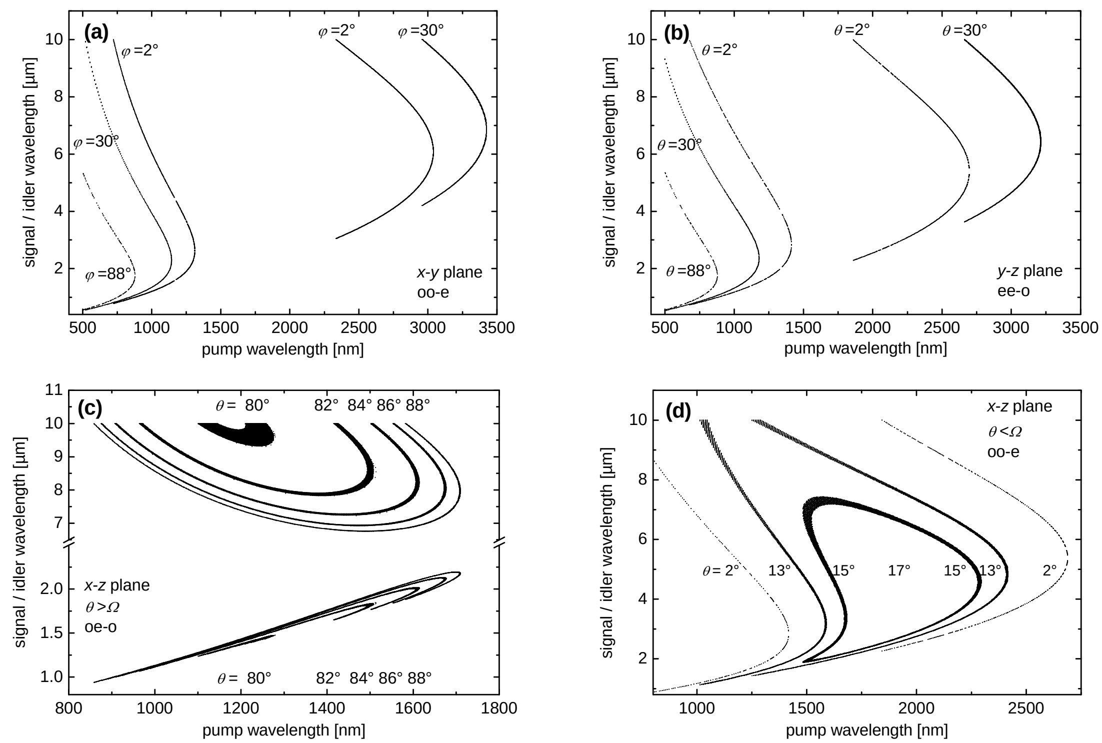

Fig. 2. Phase-matching for down-conversion in BGS (a) in the *x-y* plane (oo-e negative type-I), (b) in the *y-z* plane (ee-o positive type-I), (c) in the *x-z* plane for $\theta>\Omega$ (oe-o positive type-II) and (d) in the *x-z* plane for $\theta<\Omega$ (oo-e negative type-I).

The biaxial BGS is orthorhombic (*mm*2 point group) and the orientation of the dielectric frame (optical ellipsoid) and the two optic axes was determined from conoscopic pictures at 633 nm. Three prisms were prepared for index of refraction measurements using the auto-collimation method with the reflecting face always coinciding with one of the principal planes (Fig. 1b). The principal refractive index measurements were performed in the 0.42-9.5 µm spectral range and two-pole Sellmeier equations were then fitted to the experimental data (Fig. 1c). These equations reproduced rather well the angle Ω between the optic axes and the *z*-principal (dielectric) axis (under the convention $n_x<n_y<n_z$): Ω=46.3° while the experimental value was Ω=45.6°. The computed refractive indices at 1064.2 nm are n_x=2.28153, n_y=2.30104 and n_z=2.32175. The maximum birefringence at this wavelength is ~0.04. The two-fold axis of BGS was determined to coincide with the *c*-crystallographic axis from non-phase-matched SHG generation using amplified femtosecond pulses at 1300 nm and propagation along the three principal axes in the cube shown in Fig. 1a. The correspondence *xyz*=*cab* holds for BGS if the convention $c_0<a_0<b_0$ is used for the lattice parameters.

Figure 2 shows the calculated phase-matching configurations for down conversion in BGS (difference-frequency generation, optical parametric generation, amplification and oscillation). 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.

Currently we are evaluating the nonlinear coefficients of BGS by phase-matched SHG using femtosecond pulses and the damage threshold with nanosecond pulses at 1064 nm; the results will be reported at the conference.

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