physica status solidi

wileyonlinelibrary.com

reprints

www.pss-rrl.com

www.pss-c.com

www.pss-b.com

www.pss-a.com

WILEY-VCH

REPRINT

Phys. Status Solidi RRL **5**, No. 1, 31–33 (2011) / **DOI** 10.1002/pssr.201004425

pss +++rapid research letters+++
www.pss-rapid.com

Phase-matching properties of $BaGa_4S_7$ and $BaGa_4Se_7$: Wide-bandgap nonlinear crystals for the mid-infrared

Valeriy Badikov[1], Dmitrii Badikov[1], Galina Shevyrdyaeva[1], Aleksey Tyazhev[2], Georgi Marchev[2], Vladimir Panyutin[2], Valentin Petrov[*, 2], and Albert Kwasniewski[3]

[1] High Technologies Laboratory, Kuban State University, 149 Stavropolskaya Str., 350040 Krasnodar, Russia
[2] Max-Born-Institute for Nonlinear Optics and Ultrafast Spectroscopy, Max-Born-Str. 2A, 12489 Berlin, Germany
[3] Leibniz Institute for Crystal Growth, Max-Born-Str. 2, 12489 Berlin, Germany

Received 6 October 2010, revised 26 October 2010, accepted 26 October 2010
Published online 29 October 2010

Keywords chalcogenide crystals, nonlinear crystals, mid-infrared, frequency conversion, phase-matching

[*] Corresponding author: e-mail petrov@mbi-berlin.de, Phone: +49 30 6392 1272, Fax: +49 30 6392 1289

Biaxial $BaGa_4S_7$ and $BaGa_4Se_7$ crystals transparent in the mid-IR have been grown by the Bridgman–Stockbarger technique in sufficiently large sizes and with good optical quality to measure the refractive indices and analyze phase-matching properties.

Non-oxide nonlinear crystals can be used for frequency conversion of high-power solid-state laser systems operating near 1 µm (e.g. Nd:YAG at 1064 nm) to the mid-IR above ~5 µm, the upper wavelength cut-off limit of oxide materials. In order to avoid two-photon absorption, the bandgap of such crystals should correspond to <532 nm, a condition which is met by only few chalcogenide compounds. The most prominent of them is the commercially available chalcopyrite type $AgGaS_2$ (AGS). Other crystals with relatively wide bandgap are the related defect chalcopyrite $HgGa_2S_4$, which is extremely difficult to grow, the orthorhombic $LiGaS_2$, $LiInS_2$, $LiGaSe_2$ and $LiInSe_2$ which exhibit relatively low nonlinearities, the recently developed chalcopyrite $CdSiP_2$, which is highly nonlinear and noncritically phase-matchable but transparent only up to ~6.5 µm, as well as some solid solutions whose composition is almost impossible to control during growth [1, 2]. Two new compounds can be now added to this short list, $BaGa_4S_7$ (BGS) and $BaGa_4Se_7$ (BGSe), and as it will be shown here, both exhibit phase-matching capability to cover the mid-IR spectral range by down-conversion of 1064 nm laser radiation.

The acentric orthorhombic structure of BGS was identified as early as in 1983 [3]. More recently, the $BaS–Ga_2S_3$ binary phase diagram was studied [4] and single crystals of BGS were grown by the Bridgman–Stockbarger technique [5]. The SHG effect was confirmed by the Kurtz powder test [5]. The bandgap is at ~350 nm (3.54 eV) and the transparency extends up to 13.7 µm at the 0-level [5] but no information exists on the dispersive properties of BGS.

We successfully grew BGS and for the first time its selenide analogue, BGSe, by the Bridgman–Stockbarger method in sizes sufficiently large to measure the dispersion of the refractive indexes, a prerequisite for the prediction of the phase-matching properties. The raw materials used to synthesize the charge were with high purity, 6 Ns for Ga, S and Se, and 99% for Ba. Ba is chemically active, hence glass-carbon containers, evacuated to a residual pressure of 2×10^{-5} torr, were used for the synthesis. 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 for homogenization, after that the oven was switched-off to cool the charge down to room temperature. Then the charge was loaded into quartz ampoules of ∅ 18 × 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 (BGS) and 1070–1080 °C (BGSe) and after 3 h the ampoule was lowered into the crystallization

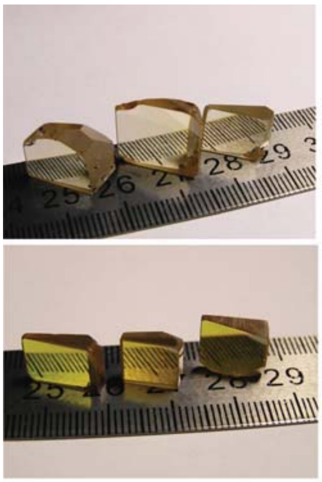

Figure 1 (online colour at: www.pss-rapid.com) Prisms of (a) BGS and (b) BGSe prepared for refractive index measurements.

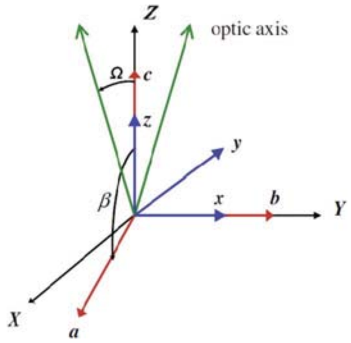

Figure 2 (online colour at: www.pss-rapid.com) Crystallographic (*abc*), crystallo-physical (*XYZ*) and dielectric (*xyz*) frames of BGSe. All frames are right-handed. The *b*-axis is normal to the *a*–*c* plane and the *a*–*c* plane contains the $y \equiv -X$ axes. The two optic axes (green arrows) lie in the *x*–*z*-plane.

zone. In order to avoid the contact between the melt and the quartz, the inner wall of the ampoule was with carbon fettling. Melting temperature of 1105 ± 5 °C was estimated for BGS and 1050 ± 5 °C for BGSe. The optimum crystal growth parameters were derived from several preliminary experiments by assessing the optical quality of the grown crystals: crystallization rate in the 7 ± 2 mm/day range and temperature gradient in the crystallization zone of 15 ± 2 °C/cm. The characteristic growth time is then 12–15 days.

The as-grown crystals are colorless in the case of BGS (Fig. 1a) and light-yellow in the case of BGSe (Fig. 1b). 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 (BGS) and 0.776–14.72 µm (BGSe). As for BGS [5], the short wave limit of BGSe is red-shifted with respect to the bandgap which is at 469 nm (2.64 eV). Thus in both crystals no two-photon absorption should be expected at 1064 nm.

Both crystals are biaxial but while BGS is orthorhombic (*mm*2 point group), BGSe is monoclinic (*m*-point group). We determined the orientation of the dielectric frames (optical ellipsoids) from conoscopic pictures using 633 nm laser light. The three principal dielectric axes and the two optic axes were identified. For both compounds, three prisms were prepared for refractive index measurements by the auto-collimation method with the reflecting face always coinciding with one of the principal planes. The accuracy in the orientation of this face was <0.5°, the aperture was >10 × 12 mm^2 and the refraction angles were in the 10–14° range. Using three instead of two prisms helps to estimate the error in the principal refractive index measurements: <0.003 in the 1–2 µm wavelength range. Measurements were performed in the 0.42–9.5 µm spectral range for BGS and between 0.48 µm and 10.4 µm for BGSe, and used to fit two-pole Sellmeier equations (Table 1). These equations reproduced rather well the angle Ω (at 633 nm) between the optic axes (see the green arrows in Fig. 2) and the *z*-principal (dielectric) axis (under the convention $n_x < n_y < n_z$): $\Omega = 46.3°$ (BGS) and $\Omega = 25.5°$ (BGSe) while the experimental values were $\Omega = 45.6°$ (BGS) and $\Omega = 26.3°$ (BGSe). BGSe is an optically positive biaxial crystal while BGS is one of the rare examples of equidistant refractive indices in a biaxial crystal. The computed refractive indices at 1064.2 nm amount to $n_x = 2.28153$, $n_y = 2.30104$ and $n_z = 2.32175$ for BGS, and $n_x = 2.48615$, $n_y = 2.50245$ and $n_z = 2.55872$ for BGSe. Hence, the maximum birefringence at this wavelength (~0.04 for BGS and ~0.07 for BGSe) is obviously sufficient for phase-matching.

In order to determine in which principal planes phase-matched processes exhibit non-vanishing effective nonlinearity d_{eff}, it is imperative to identify the two-fold axis of BGS and the correspondence between the dielectric (*xyz*) and crystallographic (*abc*) axes in both crystals. 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. The correspondence in the orthorhombic BGS crystal is *xyz* = *cab* if the convention $c_0 < a_0 < b_0$ is used for the lattice parameters. In monoclinic crystals one of the principal axes always coincides with the *b*-crystallographic axis and from X-ray measurements we established that for BGSe $x \equiv b$. At

Table 1 Sellmeier coefficients of BGS and BGSe: $n^2 = A_1 + A_3/(\lambda^2 - A_2) + A_5/(\lambda^2 - A_4)$ where λ is in µm.

crystal	n	A_1	A_2	A_3	A_4	A_5
BGS	n_x	7.090307	0.019272	0.172059	858.223	1748.013
0.42–	n_y	7.812188	0.015907	0.182439	990.979	2653.548
9.5 µm	n_z	7.907286	0.015853	0.184081	981.884	2630.008
BGSe	n_x	7.410040	0.051215	0.293340	1265.119	1896.441
0.48–	n_y	7.323096	0.052725	0.292889	1182.324	1573.474
10.4 µm	n_z	7.764197	0.069734	0.326812	1297.079	1975.857

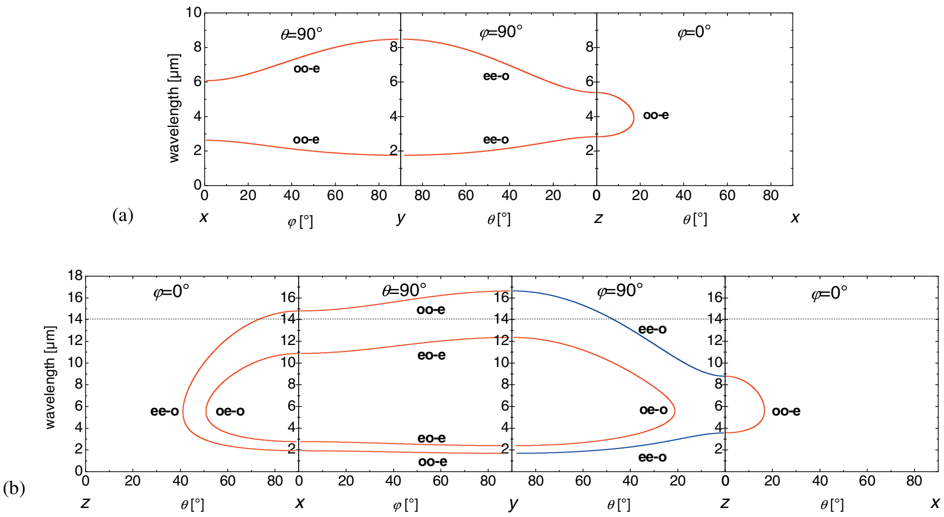

Figure 3 (online colour at: www.pss-rapid.com) SHG in the three principal planes of (a) BGS and (b) BGSe for interactions with non-vanishing d_{eff} (red lines). Blue lines in (b) are for vanishing d_{eff} while the dashed line is an upper limit for the BGSe clear transparency and validity of the calculations.

633 nm, the y-principal axis of BGSe, within ±0.5° uncertainty, is antiparallel to the X-crystallo-physical axis, and $z \equiv c \equiv Z$ (assuming $c_0 < a_0$ for monoclinic crystals). Note that the crystallo-physical frame XYZ, an orthogonal frame for reporting tensor properties, has two axes coinciding per definition with the crystallographic b- and c-axes (see Fig. 2). It is interesting that for the BGSe crystal the tensor elements of the second-order nonlinear susceptibility, d_{il} can be defined and measured directly in the xyz frame since it coincides with the crystallo-physical frame XYZ.

The calculated second-harmonic generation (SHG) phase-matching curves for BGS, fundamental wavelength versus phase-matching angle, are shown in Fig. 3a for the three principal planes. Depicted are only type-I interactions, negative (oo-e) in the x–y and x–z planes and positive type (ee-o) in the y–z-principal plane, which possess $d_{eff} \neq 0$.

With respect to down conversion of high-power radiation from 1064 nm to the mid-IR using three-wave interactions, 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 d_{eff}. 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. Wavelengths ~6.45 µm, interesting for medical applications, could be possible 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 $d_{eff} = 0$ and the effective nonlinearity remains small within the entire possible idler tuning range.

The calculated SHG phase-matching curves for BGSe are shown in Fig. 3b for the three principal planes. As can be seen, more polarization configurations exist due to the lower symmetry, and only type-I (ee-o) interaction in the y–z plane is with vanishing d_{eff}. Thus SHG is possible in the entire transparency range of BGSe with few non-critical configurations along the three principal dielectric axes. All non-critical configurations for propagation along the x-axis exhibit $d_{eff} \neq 0$ while for propagation along the y-axis this is only type-II interaction. Among the fundamental wavelengths that could be possibly non-critically phase-matched by temperature tuning is also the CO_2 laser wavelength at 10.6 µm. Down conversion from 1064 nm is possible also with BGSe, covering its entire transmission range in the mid-IR. Radiation at 6.45 µm, e.g. can be generated by oe-o interaction in the y–z plane or ee-o and oe-o interactions in the x–z plane. In any case, the best configuration will depend on the values of the nonlinear coefficients. Under Kleinman symmetry, there are four, instead of only two as for BGS, non-zero non-diagonal elements d_{il} for the monoclinic BGSe and the measurement of d_{il} for BGS and BGSe will be the main focus of our future work.

In conclusion, we grew the wide bandgap nonlinear crystals BGS and BGSe, and established that these two new compounds possess attractive phase-matching properties for down conversion of 1064 nm radiation into the mid-IR.

Acknowledgement The research leading to these results has received funding from the European Community's Seventh Framework Programme FP7/2007–2011 under grant agreement n°224042.

References

[1] D. N. Nikogosyan, Nonlinear optical crystals: A complete survey (Springer, 2005).
[2] V. Petrov et al., Proc. SPIE **7197**, 71970M (2009).
[3] B. Eisenmann et al., Rev. Chim. Miner. **20**, 329 (1983).
[4] C. Hidaka et al., J. Cryst. Growth **275**, e439 (2005).
[5] X. Lin et al., Cryst. Growth Des. **9**, 1186 (2009).