

GaS_xSe_{1-x} compounds for nonlinear optics

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Abstract: We measure the nonlinearity and transparency of mixed GaS_xSe_{1-x} crystals and show that GaS_{0.4}Se_{0.6} is a promising nonlinear material for mid-IR (>5 μm) OPO operation without two-photon absorption for a pump wavelength of 1064 nm.

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The nonlinear optical properties of mixed GaS_xSe_{1-x} crystals with x=0.2 and 0.4 were studied as early as 1982 [1]. A Q-switched CO₂ laser operating at 130 Hz, with a peak power of ~400 W, was used for SHG and relative measurements of the efficiency gave $d_{22}(x=0.2)=(0.525 \pm 0.05) d_{22}(\text{GaSe})$ and $d_{22}(x=0.4)=(0.31 \pm 0.05) d_{22}(\text{GaSe})$ for the nonlinear coefficients. In addition, the authors of [1] demonstrated difference-frequency generation from 7 to 12.5 μm with GaS_{0.2}Se_{0.8}. The observed reduction of the nonlinear coupling constant with increasing S content and the deterioration of the crystal quality in comparison to the two parent compounds, GaS and GaSe, typical for solid solutions, especially with respect to the anionic sub-lattice, obviously contributed to the lacking interest in further investigation of mixed GaS_xSe_{1-x} crystals. Only very recently the phase-matching properties of a series of solid solutions with x ranging from 0.04 to 0.412 were measured for SHG of 2.79 μm (Er:YSGG laser) and 9.58 μm (CO₂ laser) radiation [2]. The phase-matching angle varied only little with the composition but these authors speculated that the conversion efficiency with GaS_{0.09}Se_{0.91} is 2.4 times higher than that of pure GaSe.

Two essential advantages can be expected from adding S to the well known nonlinear crystal GaSe: increase of the band-gap value or the short wave cut-off limit [3,4] and increased hardness which is one of the basic limitations of GaSe [5]. Note that while In-doping could also be useful for improvement of the opto-mechanical properties of GaSe, such mixed crystals do not show extended transparency [6]. A microhardness of 40 kg/mm² was found in [5] for a composition of GaS_{0.4}Se_{0.6} and even stronger dependence on the composition (increase from 7-8 to 15 kg/mm² with x from 0 to 0.09) has been reported in [6], which, extrapolated, gives again about 40 kg/mm² for a composition of Ga S_{0.4}Se_{0.6}. In the Moh's scale these values are in the 2-3 range, above NaCl and close to NaF. Here we present measurements of the nonlinear coefficient of GaS_xSe_{1-x} in the 0≤x≤0.4 range and the transmission of such crystals. The motivation for this work is the expectation that around x=0.4 a number of characteristics such as band-gap, transparency, effective nonlinearity, damage threshold and microhardness will make this solution suitable for nanosecond pumping of an OPO at 1064 nm without the onset of two-photon absorption, a nonlinear process for which only a few suitable chalcogenide compounds exist, all of them with modest nonlinearity.

GaS_xSe_{1-x} crystals were grown for compositions x = 0.0, 0.05, 0.10, 0.40 in the charge. The elemental purity was Ga (99.9999%), Se(99.999%) and S(99.999%). The measured melting temperatures for these compounds were (960 ± 10)°C. Single crystals were grown by the Bridgman-Stockbarger method in quartz ampoules with a diameter of 14 mm. The crystallization front velocity was 3 mm/day and the whole growth process took 20-25 days. Uniform single crystals up to 60 mm in length were grown. Interestingly, it was observed that for the composition with x=0.4 the crystals grow without any "cap" at the top of the boule. This means that the charge and crystal compositions are identical, which is normally not the case even for pure GaSe for which a nominal Ga:Se ratio in the charge equal to 1:1 leads to a crystal composition of say Ga:Se=0.92:1.08 [7]. This observation could possibly mean congruent melting character which is equivalent to the existence of a separate compound in the system of solid solutions.

Table 1. Room temperature band-gap parameters of GaS_xSe_{1-x} crystals versus composition.

composition	sample thickness [μm]	$E_{g,dir}$ [eV]	λ_g [nm]	$\alpha=3 \text{ cm}^{-1}$ @ λ [nm]
x=0	310	1.976 (1.986)	628	636
x=0.05	80	2.015 (2.018)	616	625
x=0.1	570	2.026 (2.051)	612	620
x=0.4	125	2.307 (2.276)	538	567

For measurement of the visible absorption edge and estimation of the band-gap, thin plates with a thickness between 50 and 600 μm were cleaved from the different crystals. Characteristic unpolarized spectra corresponding to the o-wave are shown in Fig. 1. They were used to compute the absorption coefficients $\alpha(h\nu)$ and $\alpha(\lambda)$ near the band-edge. The value of the direct band-gap was obtained from the linear fit to the $(\alpha h\nu)^2$ dependence on $h\nu$. There is good agreement with the results from [4] which are included in brackets in Table 1.

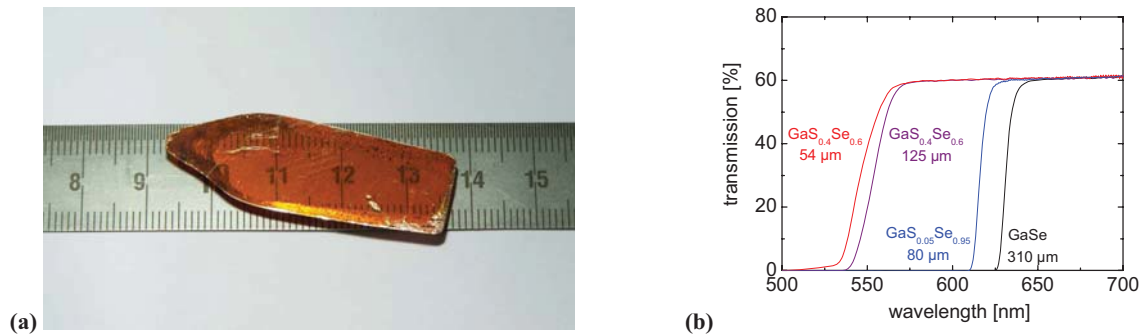


Fig. 1. Cleaved plate from an as grown crystal of $\text{GaS}_{0.4}\text{Se}_{0.6}$ with a thickness of 3.5 mm (a) and transmission of some $\text{GaS}_x\text{Se}_{1-x}$ mixed crystals.

The nonlinear coefficient of the mixed compounds was measured by comparing the second harmonic conversion efficiency to that of pure GaSe. A KNbO_3 femtosecond optical parametric amplifier was used as a laser source, operating at 4.65 μm at a repetition rate of 1 kHz. With a 6-mm long KNbO_3 crystal the idler pulses were about 350 fs long with a spectral FWHM of the order of 100 nm. All $\text{GaS}_x\text{Se}_{1-x}$ samples were cleaved with faces perpendicular to the c -axis and their thickness varied from 0.27 to 0.77 mm. Care was taken to have sufficient spectral and angular acceptance. For a fundamental energy of 3-4 μJ , the spot size was selected large enough so that spatial walk-off was negligible and the internal energy conversion efficiency remained below 10% (small signal approximation). Since the observed phase-matching angles for the different samples were very close we assumed the same index of refraction and the relative values obtained for the conversion efficiency were just square rooted in order to estimate the nonlinear coefficients. For $x=0, 0.05, 0.1$ and 0.4, two different samples of each kind were measured but the deviation for d_{22} was less than $\pm 2\%$. For each sample the result was an average of 6 measurements rotating it about the c -axis (angle φ) with steps of 60° according to the symmetry ($d_{\text{ooe}}=d_{22}\cos\theta\sin 3\varphi$ for type-I phase-matching). Note that the second harmonic signal, scanned with a step of 2° in φ , fell to zero between these angles which suggests that the symmetry of GaSe ($\bar{6}m2$) is preserved or the d -coefficient which is independent of the azimuthal angle φ (in 3m symmetry) has a negligible contribution. Thus, the results can be summarized as $d_{22}(\text{GaS}_{0.05}\text{Se}_{0.95})=0.9 d_{22}(\text{GaSe})$, $d_{22}(\text{GaS}_{0.1}\text{Se}_{0.9})=0.88 d_{22}(\text{GaSe})$, and $d_{22}(\text{GaS}_{0.4}\text{Se}_{0.6})=0.83 d_{22}(\text{GaSe})$.

The main conclusion from the present work is that mixed crystals of $\text{GaS}_x\text{Se}_{1-x}$ show very high effective nonlinearity, comparable to that of pure GaSe. This contradicts both the underestimations in [1] and the obviously overestimated value given in [2] without details. The high nonlinearity of $\text{GaS}_{0.4}\text{Se}_{0.6}$, together with the improved thermo-mechanical properties and the increased band-gap make this crystal attractive for mid-IR OPO operation above 5 μm with 1064 nm pumping. Further investigations of the crystal structure, exact composition and two-photon absorption of this crystal are under way and will be reported at the conference.

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