Erbium doped GaSe crystal for mid-IR applications

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Abstract: We reported a type-I difference-frequency generator (DFG), based on erbium doped GaSe (Er:GaSe) crystals as a coherent infrared source tunable from 2.4 μm to 28 μm. The two mixing beams used for the DFG are a tunable near infrared output (1.1-1.8 μm) from an optical parametric amplifier (OPA) and the fundamental beam of a picosecond Nd:YAG laser at 1.064 μm. The system can produce a maximum output pulse energy of 5 μJ at wavelength of 3.5 μm, corresponding to a photon conversion efficiency of 8 % at a pump intensity of 1.7 GW/cm^2. The nonlinear coefficient (d_{eff}) of 0.5 atom % erbium doped GaSe crystal was found to be 55.3 pm/V or 24 % higher than that of a pure GaSe crystal. The improvement of d_{eff} is attributed to the substitutive and interstitial doping of Er ion in GaSe unit cell. The optical properties of GaSe influenced by the erbium doping are also presented.

OCIS codes: (190.4400) Nonlinear optics, materials; (190.2620) Frequency conversion; (320.7110) Ultrafast nonlinear optics, (320.7100) Ultrafast measurements

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1. Introduction

Generation of broadly tunable coherent mid-infrared (mid-IR) pulses via parametric three-photon processes are of considerable interest in many disciplines ranging from molecular spectroscopy, bio-medical diagnostics, to remote sensing of atmospheric trace constituents. The core of optical parametric devices is a nonlinear optical (NLO) crystal with high figure of merit d_{eff}^2 / n^3, which is proportional to the squared second-order nonlinear coefficient d_{eff} of the crystal. NLO crystals such as $ZnGeP_2$, $AgGaSe_2$, Tl_3AsSe_3, CdSe, and GaSe have been used to produce mid-IR radiation [1, 2, and 3]. Among these NLO crystals, the layered crystal GaSe exhibits a fairly high d_{eff} with a reported value of 54 pm/V at 10.6 μm and a wide transparency range from 0.62 μm to 20 μm [4]. Most importantly, the figure of merit of GaSe is about four, nine, and fifteen times higher than those of $AgGaSe_2$, CdSe, and $AgGaS_2$, respectively. Although surface damage threshold of GaSe, which was measured to be 121 MW/cm^2 with a 30 ns pulsed CO_2 laser at 9.55 μm, is similar to that of CdSe (127 MW/cm^2) [5], GaSe crystal is more suited for high power application owing to its high thermal conductivity of 0.162 W/cm . K. In spite of its many attractive features, GaSe crystal is difficult to be cut and polished along some arbitrarily chosen directions. For laser applications, further improvement in the optical and mechanical properties of GaSe crystal is highly desirable.

The doping of the GaSe crystals seems to be the most economic way to improve its optical and mechanical properties. Recent developments in crystal growth technology indicated that GaSe can be doped with elemental indium to strengthen the structural properties without altering its optical characteristics. As a result, indium doped GaSe can be cut and polished at arbitrary angles [6]. An improvement in the optical nonlinearity of GaSe crystal with doping of silver gallium selenide or sulphur has also been reported [7, 8]. Recently, we reported the electrical and optical characteristics of erbium doped GaSe (Er:GaSe) crystals [9, 10]. The two acceptor levels were found to originate either from the substitution of one Er^{3+} for one pair of Ga^{2+} or interstitial insertion of one Er^{3+} at interlayer sites. In this paper, we report the

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optical properties of Er:GaSe crystals and explore further its potential in the generation of mid-IR radiation.

2. Experimental methods

The GaSe crystals used in this study were grown with the Bridgman method. Pure erbium (99.95%) was introduced into the melt to 0.2 or 0.5 atom %. Raw materials were enclosed in a well-cleaned quartz tube and then the quartz tube was pumped down to below 10^{-6} Torr. The crystal growth was carried out under a thermal gradient of 30 ^{o}C/cm with a growth rate of 2 cm/day. The resulting pure and Er:GaSe crystals exhibit the characteristic appearance of hexagonal layered structure of (001) plane. At this doping level, the crystal still can not be cut and polished at other orientations. This drawback may be remedied with higher doping levels to increase the number of Er^{3+} ions at interlayer sites to yield a higher interlayer binding energy. The compositions of these crystals were determined by electron-probe X-ray microanalysis method [9]. The crystal qualities of these home-made crystals were evaluated by measuring the X-ray rocking curve of the diffraction peak from the (008) plane. The optical transmission in the mid-IR region was characterized with a Fourier-transform infrared spectrometer (FTIR, Bomem DA8.3).

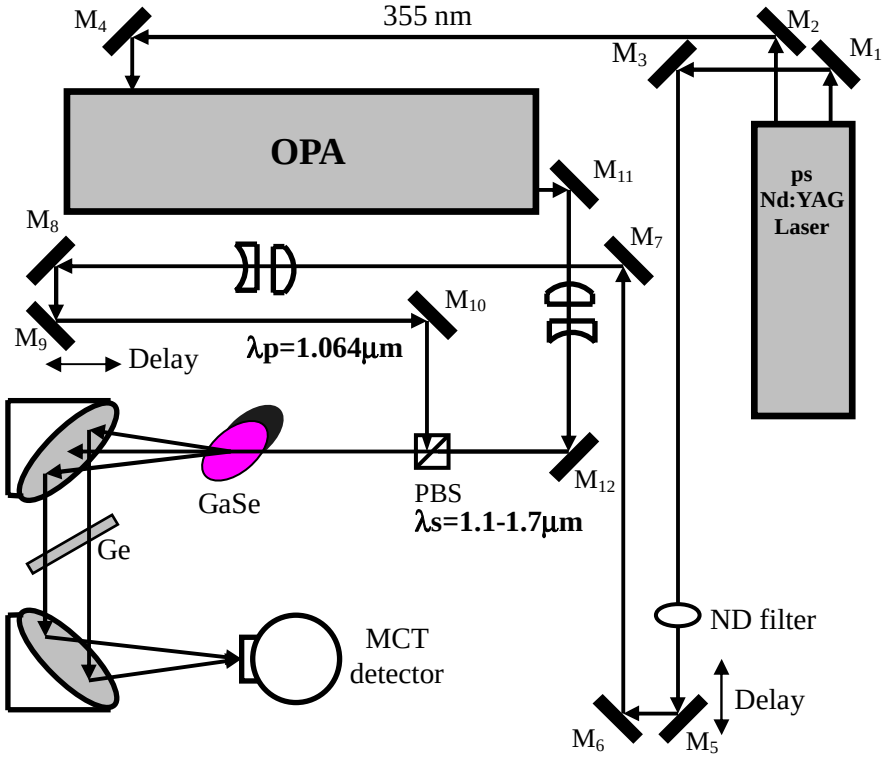

Fig. 1. Schematic of the experimental setup for generating tunable mid-IR radiation based on a Er:GaSe DFG crystal. Here M_1-M_{12} are the dichroic mirrors.

The experimental arrangement for difference-frequency generation (DFG) is shown schematically in Fig. 1. Type-I (o+o→e) phase-matching geometry was chosen in view of the higher conversion efficiency comparing with that of the type-II geometry. The pump and the signal beam of DFG are from a Nd:YAG laser at 1.064 μm and a β-BaB_2O_4 (BBO)-based optical parametric amplifier (OPA). The fundamental beam of the Nd:YAG laser has a pulse duration of 20 ps with a repetition rate of 10 Hz. The OPA, which was pumped by the

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355-nm output of the Nd:YAG laser, can generate an idler output with a pulse duration of 5 ps and wavelength tunable in the range of 1.1-1.8 μm. The typical pulse energy of the 1.064 μm pulse used is about 750 μJ and the pulse energy of the OPA is varied between 35 and 50 μJ in front of the DFG device. The spot size of the pump beam was measured to be about 1.6 mm, corresponding to a maximum peak intensity of 1.7 GW/cm^2 on the GaSe crystal. The idler beam of the OPA was combined with the pump beam in a collinear configuration by a polarizing beam splitter. The polarization directions of the pump and the idler beam were arranged to be the e-ray and o-ray of the GaSe DFG, respectively. Their temporal overlap was carefully adjusted with an optical delay line. The GaSe DFG crystal was mounted on a rotation stage for fine angular tuning. GaSe and the Er:GaSe crystals used in this study have a nominal thickness of 6.5 mm. The major and minor axes of the cleaved elliptical face of the crystals are 15 and 10 mm, respectively. There are no antireflective coatings on these crystals. The generated mid-IR radiation was detected with a cryogenically cooled mercury cadmium telluride (MCT) detector and a silicon bolometer. The residual pump radiation was blocked with a germanium (Ge) filter. The absolute pulse energies of the generated mid-IR radiation were determined with a calibrated pyroelectric detector. The pulse energies obtained are corrected for the losses from Fresnel reflection and transmittance of the Ge filter.

In order to determine the effective nonlinear coefficients of the pure and Er:GaSe crystals, second harmonic generation (SHG) in a second GaSe crystal was carried out by using 5 ps IR pulse at a wavelength of 6 μm with a pulse energy of 1 μJ from DFG system described above. The 6 μm excitation beam is horizontally polarized to meet the type-I SHG phase-matching condition.

3. Results and discussion

The X-ray rocking curves of the pure and 0.5% Er:GaSe crystals are shown in Fig. 2.

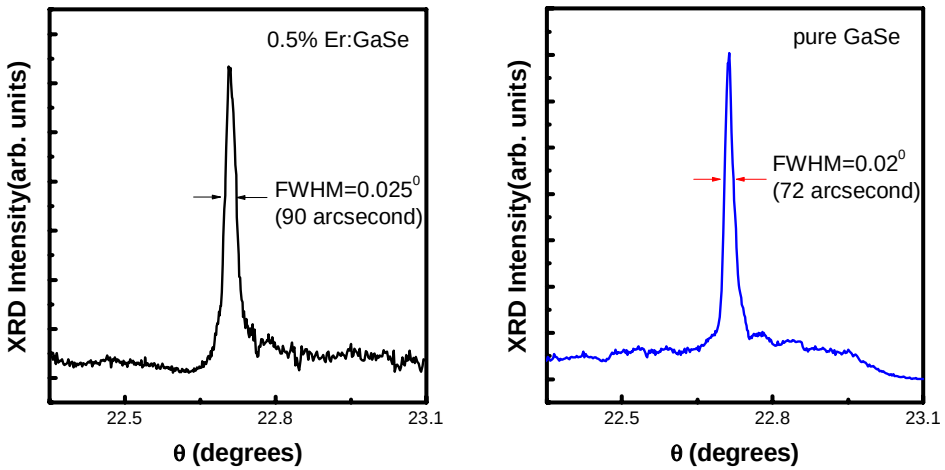

Fig. 2. X-Ray rocking curves of the diffraction peak from the (008) plane of the pure GaSe and 0.5% Er:GaSe crystals.

The diffraction peak from the (008) plane does not reveal any sign of peak splitting, indicating that large-angle grains do not exist in these crystals. The full-width-at-half-maximum (FWHM) widths of the (008) diffraction peaks were estimated to be about 0.02° and 0.025° for the pure and the 0.5% Er:GaSe crystals, respectively. The results show that crystal qualities of the pure and the 0.5% Er:GaSe crystals to be similar and are much better than that reported by Singh, *et al* [11].

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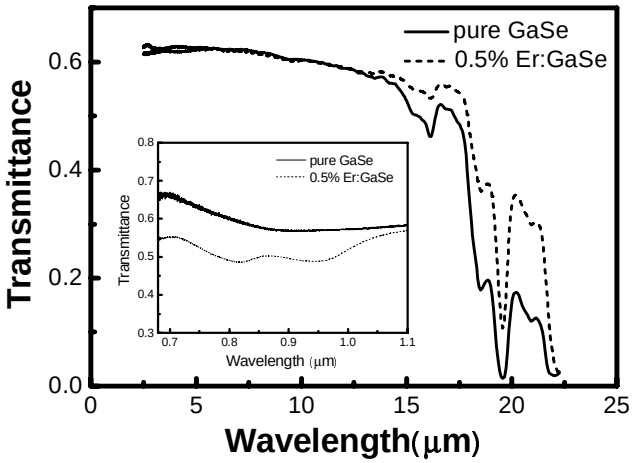

Fig. 3. Infrared transmission spectra of the pure and 0.5% Er:GaSe crystals. Inset, optical transmission spectra of the pure and 0.5% Er:GaSe crystals at near infrared region.

The optical transmission characteristics of the pure and 0.5 % Er:GaSe crystals are presented in Fig. 3. It can be seen that the optical transmission in the range of 2-15 μm is not affected by erbium doping. However, as the wavelength goes beyond 15 μm, we observe increased optical transmission for the 0.5 % Er:GaSe crystal. The IR absorption peaks near 16 μm, 19 μm, and 22 μm are attributed to the overtone absorptions of the IR active phonon modes A1', E'(LO), and E'(TO) modes, respectively. It has been known that some metal atoms can replace the Ga atoms in the lattice of GaSe and they can also occupy the voids between the layers. The impurities modify the lattice vibration in the doped crystals and produce local and resonance modes [12]. In our case, one Er^{3+} can substitute one pair of Ga^{2+} in the 0.5 % Er:GaSe crystal. Since GaSe lattice can be well represented as a linear chain of Se-Ga-Ga-Se–Se-Ga-Ga-Se [13], the vibration frequencies of the erbium doping induced vacancy or substitutional impurity in GaSe crystal can be shifted to lower frequencies. As a result, the heights of overtone absorption peaks at 16 μm, 19 μm, and 22 μm, which are from the unperturbed part of GaSe lattice, are reduced. In the inset of Fig. 3, the near-IR transmission spectrum of the 0.5 % Er:GaSe is presented. The two absorption dips, which are identified as the $4I_{9/2} \rightarrow 4I_{15/2}$ and $4I_{11/2} \rightarrow 4I_{15/2}$ transitions of the crystal-field perturbed Er^{3+} ion. This further confirms successful doping of erbium into the GaSe crystal.

The phase-matching curve of the 0.5 % Er:GaSe was examined with a collinear DFG configuration. Figure 4 shows the external phase-matching angle as a function of the idler wavelength for a pump wavelength of 1.064 μm. The external angle can be varied from 34° to 80° for our crystal, corresponding to a tuning range of DFG from 2.4 to 28 μm. The open symbols in Fig. 4 indicate the experimental data, and the solid-line is the calculated result by using the Sellmeier equation reported by Vodopyanov *et al*. [14]. We find good agreement between the experimental and the theoretical curves. This indicates that the refractive index of GaSe crystal dose not change significantly with the erbium doping up to 0.5 atomic %. In the near and mid-infrared (2.4-28 μm), the dispersion relations of GaSe given in Ref. [14] are still applicable for our Er:GaSe crystals.

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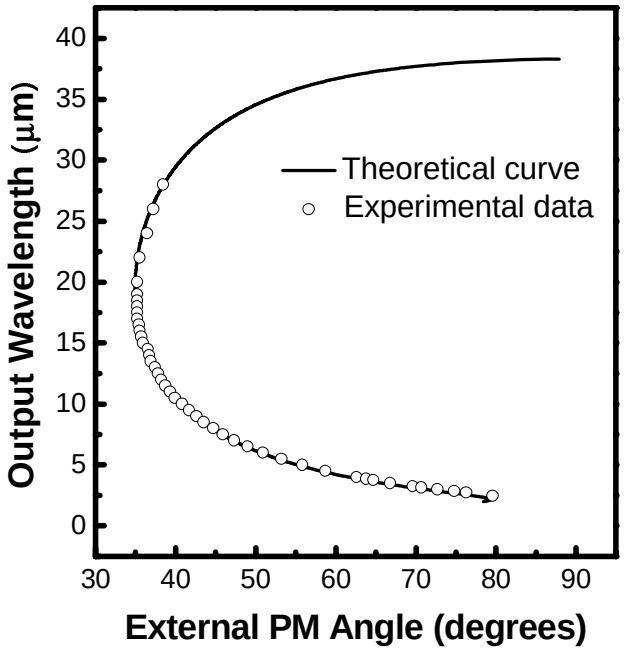

Fig. 4.Type-I phase matching wavelength versus external angle for 0.5% Er:GaSe crystal.

The high nonlinearity of GaSe allows efficient generation of mid-infrared radiation. The measured infrared pulse energies at different wavelengths by DFG in the pure GaSe, 0.2%, and 0.5% Er:GaSe crystals with an equal crystal length of 6.5 mm are shown in Fig. 5. The three GaSe crystals yield similar output energy of about 5 μJ around the wavelength of 3.5 μm. At longer infrared wavelengths, however, DFG in the Er:GaSe crystals exhibit a broader tuning range and higher conversion efficiency. The improvements become more significant for GaSe doped with higher concentration of erbium. A photon conversion efficiency greater than 8 % can be achieved at 3.5 μm. This is higher than the Dahinten's result of 2 % [15], but still lower than the maximum efficiency of 50 % reported by Finsterbusch *et al*. [16]. After taking into account the losses from reflection and linear absorption, the maximum conversion efficiency of our GaSe DFG remains significantly lower than 50%. The difference may be attributed to two-photon absorption (TPA), which occurs when photon energy of the pump laser used is larger than half of the band gap of GaSe crystal. The TPA coefficient of GaSe has been reported to be $\beta=6.3\times10^{-9}$ cm/W at 1.064 μm [17]. Thus the nonlinear absorption losses in GaSe need to be taken into account when the intensity of incident beam is in the order of GW/cm^2.

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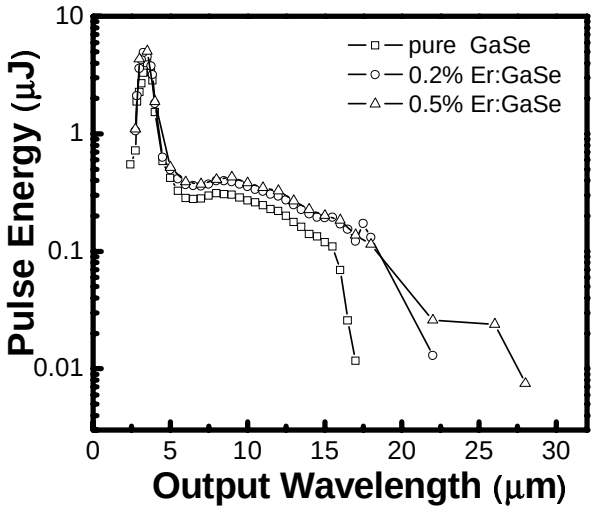

Fig. 5. Output pulse energy versus wavelength for type-I DFG.

Although the Er:GaSe crystals can generate higher output pulse energy in the long wavelength region than the pure GaSe does, the improved nonlinear conversion efficiency does not necessarily imply a higher optical nonlinearity in Er:GaSe for a collinear DFG. The difficulty is due to that in DFG two input beams are employed and the influences from beam misalignment and different beam divergence for pump and signal beams are difficult to remove. In this regard, a more reliable method for measurement of the effective optical nonlinearity is SHG in view that an accurate SHG theory for a focused input beam is available. Therefore, to evaluate the effective optical nonlinearity of the crystals we employ the infrared pulses from the DFG setup for SHG in pure and Er:GaSe crystals.

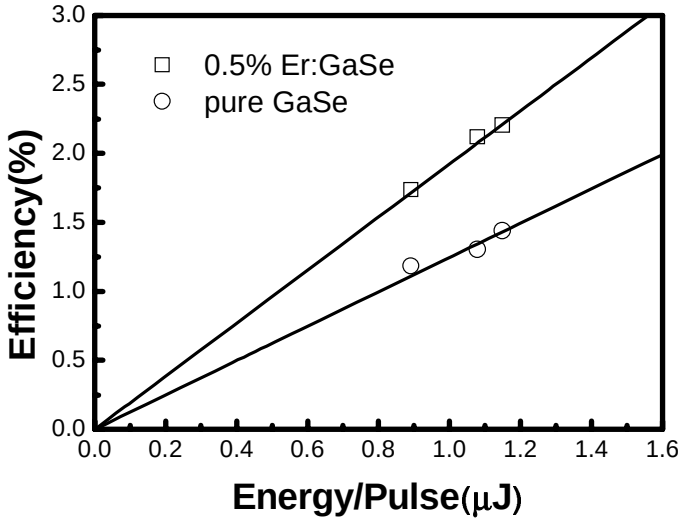

Fig. 6. Comparison of the SHG conversion efficiencies of pure and 0.5% Er:GaSe crystals with identical crystal length.

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The output from the DFG system at a wavelength of 6 μm is chosen as the pump of the SHG crystals. Type-I ($o+o \rightarrow e$) phase-matching condition can be satisfied with an external phase-matched angle of 30.18°. The measured SHG conversion efficiency as a function of the input pump energy for the pure and Er:GaSe crystals are presented in Fig. 6. The slopes of the SHG conversion efficiency curves were then used to deduce the effective optical nonlinearity of the crystals by using the focused Gaussian beam theory of Boyd and Kleinman [6]. The effective nonlinear coefficient d_{eff} of the pure and 0.5% Er:GaSe crystals were determined to be 44.5 pm/V and 55.3 pm/V, respectively. The difference could be ascribed to either crystal quality [6] or doping-induced effect [7]. The structural analysis of our GaSe crystals shown in Fig. 2 suggests that these crystals have similar crystal quality. Therefore, the increased effective nonlinear coefficient of Er:GaSe must originate from the doping effect with erbium. A plausible interpretation could be that the substitution of one Er^{3+} ion for one pair of Ga^{2+} and insertion of one Er^{3+} interstitial ion at interlayer sites in the unit cell could result in a favorable local structural alteration with better optical nonlinearity. Note that an 20 % increase in optical nonlinearity by impurity substitution was also observed recently in $YCa_4O(BO_3)_3$ crystal [18] doped with Yb at a fairly high doping level of 20%. The increase in optical nonlinearity was attributed to the more covalent nature of Yb, which causes large delocalization of the π-electrons in the BO conjugate ring. Based on these two experimental studies, doping indeed seems to be an effective way to improve the optical properties of nonlinear optical crystals.

4. Conclusions

We reported a type-I DFG, based on Er:GaSe crystals as a coherent infrared source tunable from 2.4 μm to 28 μm. The two mixing beams used for the DFG are a tunable near infrared output (1.1-1.8 μm) from an optical parametric amplifier (OPA) and the fundamental beam of a picosecond Nd:YAG laser at 1.064 μm. The system can produce a maximum output pulse energy of 5 μJ at wavelength of 3.5 μm, corresponding to a photon conversion efficiency of 8 % at a pump intensity of 1.7 GW/cm^2. The nonlinear coefficient (d_{eff}) of 0.5 atom % erbium doped GaSe crystal was found to be 55.3 pm/V or 24 % higher than that of a pure GaSe crystal. The improvement of d_{eff} is attributed to the substitutive and interstitial doping of Er ion in GaSe unit cell. The optical properties of GaSe influenced by the erbium doping are also presented.

Acknowledgments

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