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Optical properties and application of GaSe:$AgGaSe_2$ crystal

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Abstract: The nonlinear optical crystal grown from the melt GaSe:$AgGaSe_2$ (10%, mass percent) is identified as acentrosymmetric ε-GaSe:Ag ($\leqslant$0.04%, mass percent) and is used for phase matched frequency conversion. The silver presence results in 30% increase in microhardness, which allows the crystal to be cut and polished at arbitrary direction. The optical properties from visible to mid-IR and further THz ranges are studied in detail. It demonstrates that the absorption coefficient of GaSe:Ag ($\leqslant$0.04%, mass percent) crystal is twice that of a pure GeSe, and the CO_2 laser Second Harmonic Generation (SHG) efficiency is about 1.7 times that of $ZnGeP_2$ crystal.

Key words: GaSe:$AgGaSe_2$ crystal; optical property; mid-infrared; THz range; Second Harmonic Generation (SHG)

GaSe:$AgGaSe_2$ 晶体的光学性能及应用

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摘要:从 GaSe:$AgGaSe_2$熔体(质量掺杂浓度为10%)中生长的非线性光学晶体 ε-GaSe:Ag 晶体(质量掺杂浓度≤0.04%)是一种非中心对称晶体,可用于相位匹配频率转换。Ag 的掺入使 GaSe 晶体的显微硬度提高了30%,从而使其可以在任意方向上进行切割和抛光。本文研究了 GaSe:$AgGaSe_2$晶体在可见、中红外及太赫兹波段的光学性能。实验证明:GaSe:$AgGaSe_2$晶体的吸收系数是纯 GaSe 晶体的2倍,其 CO_2 激光倍频效率是 $ZnGeP_2$ 晶体的1.7倍。

关 键 词:GaSe:$AgGaSe_2$晶体;光学特性;中红外波段;THz 波段;二次谐波振荡
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1 Introduction

In the early 80s, Allakhverdiev[1] *et al*. had shown that S-doping in GaSe resulted in the decrease of the nonlinearity coefficient d_{22}. For the first time 84% improvement in the efficient nonlinearity in GaSe doped with In was reported by Suhre *et al*[2]. and confirmed in Ref. [3]. It is ascertained that the increase is caused by the improvement in the crystal optical quality. Later Hsu *et al*.[4] reported that doping with 0.5% (mass percent) heavier erbium led to 24% increase in intrinsic nonlinearity. Besides, in spite of the nonlinearity decreasing[1], it was established that the set of modified physical properties of S-doped GaSe yielded 2.4-fold increase in CO_2 laser Second Harmonic Generation (SHG) efficiency[5].

The intricate ternary compounds $AgGaSe_2$ and $AgGaS_2$ with $\bar{4}2$ m point group symmetry were also used as the doping agents in the GaSe crystals of $\bar{6}2$ m point group. In 1999, Singh *et al*. grew the crystal from the GaSe:$AgGaSe_2$ (10.1%, mass percent) melt with the highest nonlinearity among the doped GaSe crystals[6], which generates twice larger efficient figure of merit "d^2/n^3" than that of $ZnGeP_2$. However, there is still no further information about the real composition, optical properties, and phase matching in this crystal. Recently, the crystal was grown from the melt of GaSe:$AgGaS_2$ (10.6%, mass percent)[7] whose nominal charge composition of $Ag_{0.05}Ga_{0.95}Se_{0.9}S_{0.1}$ is close to that described in Ref. [6]. Grown crystal was identified as GaSe:S (2%, mass percent) and almost identical in CO_2 laser SHG efficiency to GaSe:S (2% mass percent) crystal grown by conventional S-doping technology[8-17].

In this research chemical composition, crystal structure, optical properties of the crystal grown from the GaSe:$AgGaSe_2$ melt (10%, mass percent) are studied for the first time.

2 Crystal growth and characterization

2.1 Crystal growth

Pure GaSe crystals were grown in a two-zone vertical Bridgman furnace in evacuated quartz ampoules with 10 mm in diameter by conventional technique similar to that described elsewhere[8-17]. The starting materials for the GaSe synthesis were Ga (99.999 9%) and Se (99.999 9%). As a dopant, 10% (mass percent) of stoichiometric $AgGaSe_2$ was added to a charge of pre-synthesized GaSe. The temperature gradient at the crystallization front was 10 ℃/cm and the crystal pulling rate was 10 mm/d. For doped crystals, a heat field rotation during crystal growth was used[16]. All *z*-cut specimens studied were cleaved from the nose part of the as-grown ingot and used without any additional treatment.

2.2 Composition

The composition of the crystals grown was estimated by Electron Probe Microanalysis (EPMA) with aver-

aging over an area 100 μm × 100 μm that reveals clear signal of sulphur (S) and gallium (Ga), and no signal related to the silver (Ag) in GaSe:$AgGaSe_2$ (10% mass percent). Silver content determination was provided by atomic-absorption spectrometry with Z-8000 Hitachi spectrometer (air-acetylene flame) and sulphur content by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) with spectrometer iCAP 6500, thermo scientific after dissolution of sample weights in nitric acid. In that case, the composition is identified as GaSe:Ag with Ga (44.59%, mass percent), Se (55.37%, mass percent) and Ag (≤0.04%, mass percent) both in NCTU, Hsinchu, Taiwan, China and TSU, Tomsk, Russia. As it was reported, low miscibility gap in the Ag_2Se and GaSe phase-diagram resulted in Ag-precipitation[6] that was not so evidently observed in this study.

2.3 Crystal structure

Structural properties of the crystals were observed by Transmission Electron Microscopy (TEM) with TESLA BS-513A microscope at an electron accelerating voltage of 100 kV. Only ε-GaSe crystalline phase was detected by TEM. The electron diffraction patterns confirm the high quality of pure GaSe lattice that reflexes are round and symmetrically disposed circles. The electron diffraction patterns for GaSe:Ag ingot are evidently attributed to ε-GaSe structure. Diffraction patterns of GaSe:Ag (≤0.04%, mass percent) are something deformed (polar splitting angle is ~0.3°) due to Ag presence.

The ε-polytype structure of the observed specimens was also identified by proposed non linear method through the φ-angle dependence of CO_2 laser type SHG signal[18]. For all crystals, CO_2 laser SHG signal versus φ-angle was clear six-petal-flower type similar to that in ε-GaSe, as it goes from the relation for efficient nonlinear susceptibility coefficient $d_{\text{eff}} = d_{22}\cos\theta\sin 3\varphi$ for the I type of interaction.

2.4 Hardness

The crystal hardness was measured by CSEM Nano Hardness Tester. It is established that GaSe:Ag (≤0.04%, mass percent) hardness in 10.6 kg/mm^2 is 30% higher than that of GaSe in 8 kg/cm^2. It is possibly due to Ga vacancy occupation and substitution, interstitials and the intercalation between the growth layers. Due to improved hardness the crystal can be cut and polished at arbitrary direction.

2.5 Visible to mid-IR absorption

UV-visible optical density of the specimens observed was recorded by Cary 100 Scan (Varian, Inc., Austria) spectrometer. The wavelength range is 190 – 900 nm, spectral resolution is 0.2 – 4 nm, wavelength deviation is ±1 nm (see Fig. 1(a)).

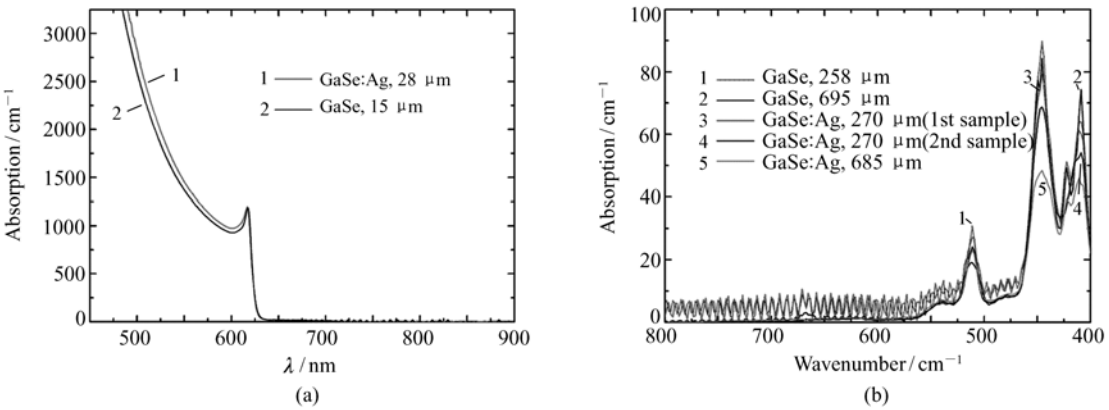

Fig. 1　Optical density spectra of GaSe and GaSe:Ag (≤0.04%, mass percent) crystals at short-wavelength (a) and long-wavelength ends of the transmission range (b). The crystal thicknesses are identified in the figure insets.

Mid-IR optical density was recorded by FTIR Nicolet 6700 (Thermo Electron Corp.) spectrometer. The operation wavelength range is 11 000 – 375 cm^{-1}, spectral resolution is 0.09 cm^{-1}. Selected spectra are displayed in Fig. 1(b).

The absolute value of attenuation coefficients at maximal mid-IR transparency range $\alpha = 0.2$ cm^{-1} was measured at chosen points on the crystal face with a low power ϕ1.0 mm beam at a wavelength of 9.6 μm CO_2 laser band to minimize the influence of surface defects on the measurement results.

2.6 Optical properties in THz range

The absorption coefficient in Terahertz range and n_o spectra in the crystals were determined by a home-made THz-TDS spectrometer with a 50 fs Ti:sapphire laser system (797 nm) described elsewhere[15]. THz beam was normally incident to the crystal face. THz absorption spectra are shown in Fig. 2. Ordinary refractive index (n_o) determined at normal incidence of the THz beam on the grown *z*-cut crystal surface was presented in Fig. 3(a) and Fig. 3(b). Scattering in the determined n_o dispersions in the grown and different origin crystals were also studied in comparison (see Fig. 3(c) and Fig. 3(d)).

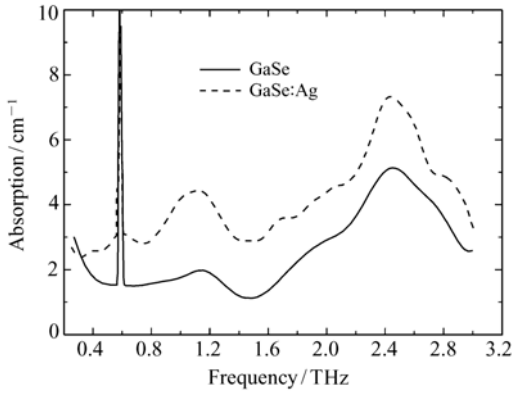

Fig. 2 Absorption spectra of GaSe and GaSe:Ag (≤ 0.04%, mass percent).

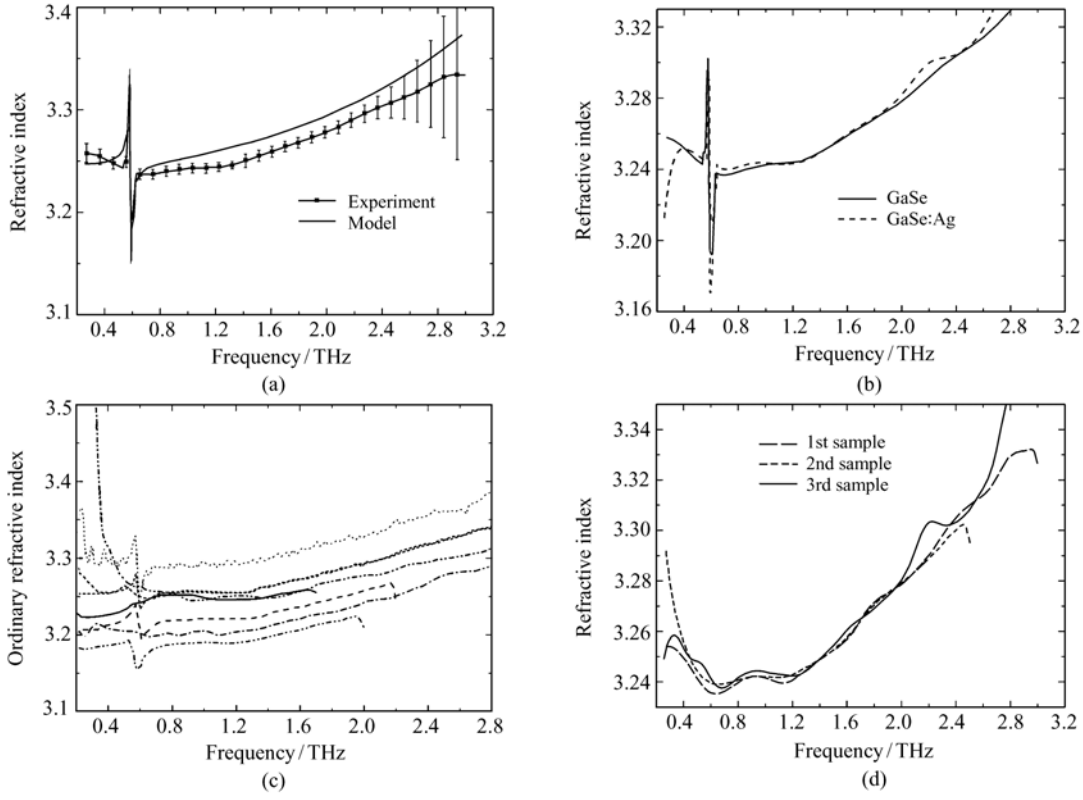

Fig. 3 Measured and calculated n_o dispersions in grown GaSe (a), grown GaSe and GaSe:Ag (0.04%, mass percent) (b), different origin GaSe (c) and three samples GaSe:Ag (≤0.04%, mass percent) in comparison (d).

Then modified method as described below was used to measure both n_o and n_e dispersions in GaSe and GaSe: $AgGaSe_2$ (≤0.04%, mass percent) crystals (see Fig. 4).

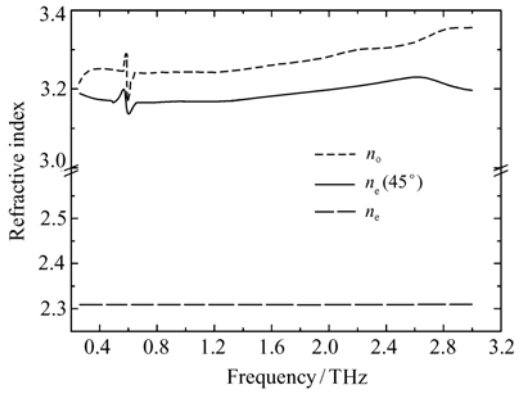

Fig. 4　n_o, n_e and $n_e(45°)$ dispersions in GaSe: Ag(≤ 0.04%, percent).

When n_o is determined (see Fig. 2) in the same measurement manner, but for an inclined incident THz beam, dispersions $n_e(\theta)$ has to be determined. Further, n_e is calculated by using well known relation[19] between n_o and n_e : $n_e(\theta) = n_o n_e / \sqrt{(n_e^2\cos^2\theta + n_o^2\sin^2\theta)}$. The modified method was first tested by application to a pure GaSe crystal for check and then to GaSe: Ag(≤0.04%, mass percent) through measurement at an incident angle of 45° (see Fig. 4).

2.7　CO_2 laser SHG

The CO_2 laser SHG efficiency was studied by using GaSe and two GaSe: Ag(≤0.04%, mass percent) specimens that were cleaved from the beginning and middle parts of the grown ingot. Optical faces of every specimen were cleaved for giving close interaction lengths of (2 ± 0.02) mm. 2 mm long $ZnGeP_2$ crystals ($\alpha \leq 0.1$ cm^{-1} at the maximal transparency range of 2.5 – 8.5 μm, about 1 cm^{-1} at CO_2 laser wavelength) was also applied in the experimental study.

Low pressure tunable CO_2 laser with electronically controlled pulse repletion rate was used as a pump source. The laser emits highly-stabilized 250 ns and 5 kW peak power pulses with a pulse repletion rate up to 1 kHz in the ϕ6 mm smooth-energy-distribution beam. SHG pulses were recorded by RT pyroelectric detector MG-30, Russia ($D = 7 \times 10^8$ cm · $Hz^{1/2}$/W at the range of 2 – 20 μm) with selective nanovoltmeter Unipan-237, Poland (1 or 10 Hz spectral bandwidth) and displayed with TDS 3052 oscilloscope (see Fig. 5).

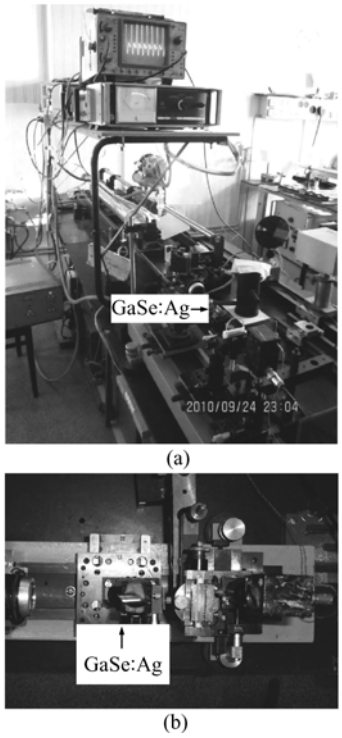

Fig. 5　External view on CO_2 laser SHG facility (a) and SHG nod (b).

3　Results and discussion

Crystal grown from the GaSe: $AgGaSe_2$ melt (10%, mass percent) is identified as ε-polytype low silver doped GaSe: Ag(≤0.04%, mass percent) that is useful for nonlinear applications. The lattice quality of the sample is close to that of the pure GaSe crystal. So, the growth technology from the melt of GaSe with 62 m point group and $AgGaSe_2$ with 42 m point group is the new doping technology in fact.

GaSe: Ag(≤0.04%, mass percent) is characterized by 30% improved hardness to that in the

pure GaSe and can be cut and polished at arbitrary direction. It is also characterized by 2-fold absorption coefficient both in mid-IR and THz(see Fig. 2) ranges and nevertheless demonstrated about 1.7-fold CO_2 laser SHG efficiency of that in $ZnGeP_2$ that is in coincidence with data in Ref. [2]. It looks like it is simply due to still much lower absorption losses at the range of 9 – 11 μm.

Measured and estimated n_o dispersions are in reasonable agreement(see Fig. 3(a)) and it is much better for n_e dispersions. No sample-to-sample variations in dispersions are found in grown crystals(see Fig. 3(d)) in difference to significant variation in different origin GaSe crystals(see Fig. 3(c)). n_o dispersion properties in GaSe:Ag(≤0.04%, mass percent) are identical to that in GaSe(see Fig. 3(b)). Proposed modified method allows every body to measure both n_o and n_e dispersions in *z*-cut pure and doped GaSe crystals.

4 Conclusion

Acentrosymmetric ε-GaSe:Ag crystal is grown from the melt GaSe:$AgGaSe_2$. The chemical composition, crystal structure and optical properties of GaSe:Ag crystals are studied. The silver presence resulted in 30% increase in microhardness. The absorption coefficient of GaSe:Ag crystal is twice that of a pure GaSe crystal and the CO_2 laser SHG efficiency is about 1.7 times that of $ZnGeP_2$ crystal.

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