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Structural characterization of pure and doped GaSe by nonlinear optical method

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ABSTRACT

In this study angular dependencies of type-I and type-II phase matching in pure and doped GaSe were applied for efficient identification of their polytype structure and structural features. In turn the express analysis of optical uniformity is performed by crystal incorporation into the SHG scheme as an attenuator of the pump beam.

1. Introduction

Pure and doped GaSe crystals are of great potential for nonlinear applications as efficient frequency converters from near-IR into mid-IR and further into the THz-range [1]. Due to its layered structure, GaSe crystallizes into four (ε, γ, δ and β) polytypes. Therefore, in a general case a mixture of all polytypes may be found in one crystal. Another point is to identify twinning and other defects affecting optical quality of the prepared samples.

Identification of different polytypes and analysis of their relative contents and locations in a sample are quite difficult with X-rays, since 2θ angles of the most intensive diffraction lines are very close (Fig. 1). Moreover, if nondestructive characterization by X-ray reflection from the surface of the sample is necessary, it possible to analyze only a thin layer of the sample. That is why other nondestructive and low-price methods to determine polytype structure are required.

The nonlinear optical method (NLOM) is known to provide more accurate results than X-ray analysis in the case of investigation of surface structure of light absorbent crystals [2,3].

In this work, the NLOM was applied to nondestructive analysis of optical homogeneity and polytype structure inside the whole volume of pure and doped GaSe crystals.

2. Experimental

A CO_2 laser SHG scheme described elsewhere [4] was realized. Due to good transparency of GaSe crystals in the range of CO_2 lasers, type-I and type-II SHGs of the most efficient and stable 10.6 μm emission line were chosen for the NLOM. All samples used in this study were cleaved from the grown ingots parallel to the *c*-plane. No additional treatment or polishing of the samples was performed. The samples were mounted on a step-motor-drive computer-controlled rotational stage (RSA100, Zolix Instruments Co. Ltd., China) with positioning accuracy of 18″. The residual CO_2 laser radiation was blocked by two LiF plates of 4 mm thickness, which are close to the nonlinear crystal and the detector. A pyroelectric detector (MG-30, Russia) with $D \geq 7\times10^8$ cm Hz$^{1/2}$/W at a $2-20$ μm range was applied to measure SHG pulses over 1000 averaging pulses.

Characterization of optical homogeneity was performed using another variety of NLOM. SHG of the Nd:YAG laser with a uniform beam was being applied in this case. A sample of GaSe was incorporated into the SHG scheme as an attenuator between the pump beam and the frequency doubler ($KTiOPO_4$ crystal). A doubled-frequency beam was projected onto a sheet of white paper for a visual study or was detected using a digital camera for optical property estimation.

3. Results and discussion

Table 1 presents crystallographic point groups and corresponding expressions of effective nonlinear coefficients d_{eff} [5] of GaSe polytypes. The variation between phase matching conditions may be used for discrimination of different polytypes. And due to the transparency of GaSe in the chosen wavelength range, it is possible to investigate the whole volume of the sample.

The absence of phase matching conditions in the type-I and type-II parametric frequency conversions (for SHG in this study) reveals the β-polytype of GaSe. The δ-polytype shows a phase matching versus θ angle only in the type-I interaction at any φ angle. In ε-GaSe the term sin 3φ provides a remarkable six-petal dependence of d_{eff} versus φ angle (Fig. 2a). In this case the θ angle should not be equal to 90° or 270°. Almost the same six-petal relationship is provided by the γ-polytype for type-II interactions

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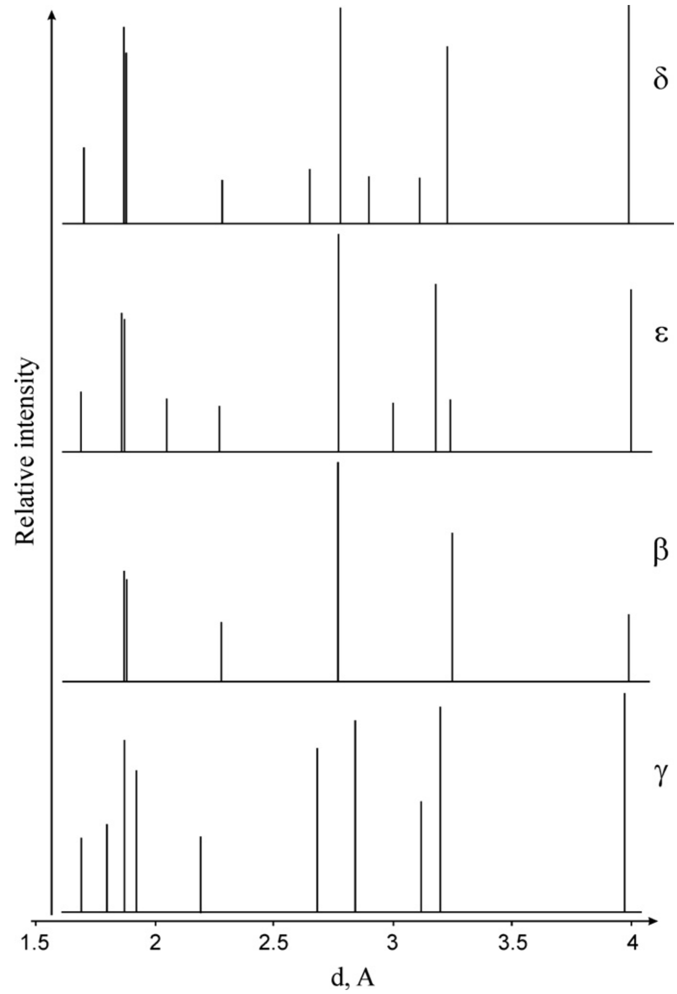

Fig. 1. X-ray powder diffraction data of δ-, ε-, β- and γ-GaSe according to the JCPDS, card nos. 29-0628, 80-2271, 65-3508 and 81-1971, respectively.

Table 1
Effective nonlinear coefficients $d_{eff}(\theta, \varphi)$ of polytypes of GaSe crystal.

Polytype	Point group	Type-I interactions	Type-II interactions
ε	$\bar{6}m2$	$d_{22}\cos\theta\sin3\varphi$	$d_{22}\cos^2\theta\sin\varphi$
γ	3m	$d_{15}\sin\theta - d_{22}\cos^2\theta\sin3\varphi$	$d_{22}\cos^2\theta\sin3\varphi$
δ	6mm	$d_{15}\sin\theta$	0
β	6/mmm	0	0

due to $\cos 3\varphi$. Nevertheless, the γ-polytype is still phase-matchable in type-I interactions at a θ angle equal to 90° or 270°.

During investigations of phase matching in pure GaSe, solid solutions of $GaSe_{1-x}S_x$, $x \leq 0.412$ and $Ga_{1-x}In_xSe$, $x \leq 0.27$ showed that the majority of either is single crystals that have ε-polytype structure. If the length of the crystal sample is significantly greater than the coherence length or if sensitivity of the system is high enough, a specific six-petal dependency of type-I SHG efficiency versus φ angle appears (Fig. 2a, solid line). Six maxima in the plot are due to the presence of the $\sin 3\varphi$ member in the relation for d_{eff}. The remaining part of the grown crystals was polycrystalline blocks and few a ε-polytype twins with 6.5–7° disorientation.

Another point in the NLOM is its ability to provide information on uniformity of crystallographic orientation of the whole sample. If any defects provide disorientation of the atomic layers with a width greater than the length of coherence, it may be clearly defined by the change in dependency of the SHG intensity. For instance, Fig. 2b illustrates the phase matching versus θ angle in a 2.49 mm sample of the $Ga_{0.97}In_{0.03}Se$ crystal with two blocks (possibly twins) disoriented at 6.5°.

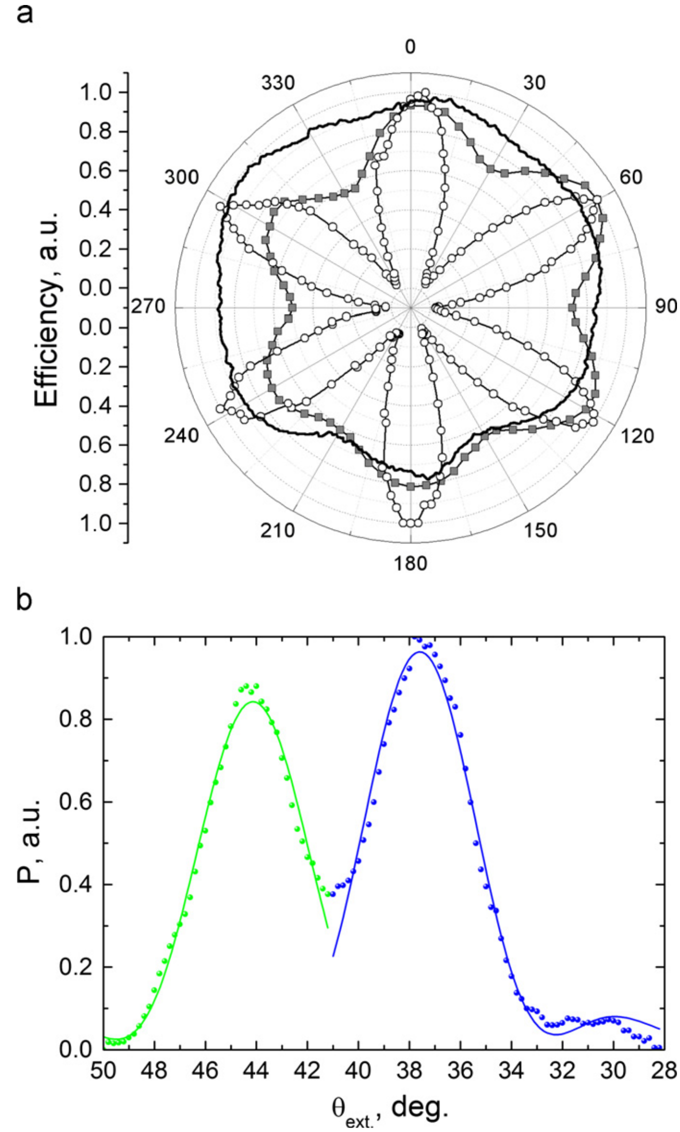

Fig. 2. Normalized efficiency of CO_2 laser type-I SHG versus (a) phase matching angle φ when the length of the ε-GaSe sample is significantly greater (circles), insignificantly greater (squares) and less (solid line) than coherence length and (b) versus θ angle at optimal φ angle in 2.49 mm $Ga_{0.97}In_{0.03}Se$ crystal.

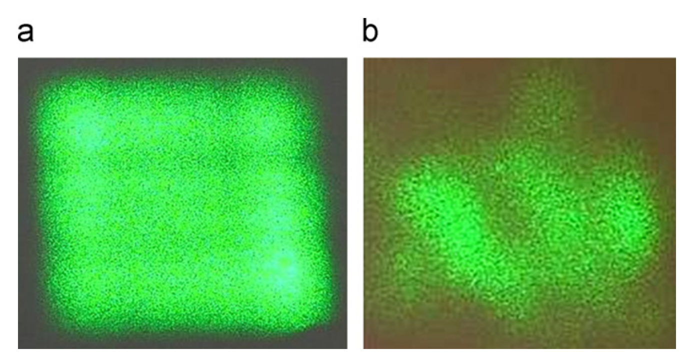

Fig. 3. Distributions of SHG of the Nd:YAG laser (a) without and (b) with the sample of GaSe incorporated into SHG scheme as an attenuator between the pump beam and the frequency doubler ($KTiOPO_4$ crystal).

Fig. 3 presents the distributions of Nd:YAG laser SHG intensity projected on a sheet of white paper. The difference between the patterns is the result of light propagation through the sample of GaSe crystal. Therefore optical uniformity of the crystal may be examined. It should be mentioned that due to exponential absorption of light (Beer–Lambert law) and quadratic dependence of the SH power versus pump beam power [6], the inhomogeneities of the test sample produce contrast traces in the distribution of the SH beam.

4. Conclusion

For nondestructive analysis of structural features and optical homogeneity of the NLO crystals the nonlinear optical method (NLOM) was successfully applied in this study. It is shown that by pump beam scanning of the crystal surface, localization of some structural defects in the sample volume can be determined. Optical uniformity is tested by crystal incorporation into the SHG scheme as an attenuator of the pump beam.

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References

[1] B. Raton, Terahertz spectroscopy: principles and applications, CRC Press, 2008 пользован.

[2] L. Kylyuk, V. Miravitskii, E. Arushanov, V. Tezlevan, M. Leon, E. Mishina, N. Shevstyuk, T. Dumouchel, E. Fovtin, Th. Rasing, Structure investigation of $CuIn_5Se_8$ single crystals by optical second harmonic generation, elippsometry, and photoluminescence, Appl. Phys. Lett. 89 (2006) 151915–151918.

[3] K. Pedersen, O. Keller, Nonlinear optical methods in the nondestructive testing of metal surfaces, NDT Int. 21 (1988) 411–414.

[4] Zhi-Hui Hong-Zhi Zhang, Yun Kang, Jin-Yue Jiang, Feng-Guanf Gao, Zhi-Shu Wu, Yu.m. Feng, G.V. Andreev, A.N. Lanskii, E.I. Morozov, S. Sachkova, Yu. Sarkisov, SHG phase matching in GaSe and mixed $GaSe_{1-x}S_x$, $x \leq 0.412$, crystals at room temperature, Opt. Express 16 (2008) 9951–9957.

[5] F.J. Duarte, Tunable Lasers Handbook, Academic Press Inc, 1995.

[6] V.G. Dmitriev, G.G. Gurzadyan, D.N. Nikogosyan, Handbook For Nonlinear Optical Crystals, Springer, 1999.