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GaSe 及相关晶体的历史、现状与未来:具有特异非线性光学特性的层状材料

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摘要:概述了高度各向异性的,尤其是无掺杂和掺杂的层状半导体 GaSe 和相关晶体 InSe、GaS 和 GaSe-GaS(固溶液)的结构特性、光学特性和非线性光学特性的实验研究结果,同时概述了由共焦拉曼和光致发光显微镜研究得到的结果和由声波降解法和激光消融技术得到的 GaSe 纳米粒的光学性质。重点讨论了 ε-GaSe 的性质,指出其具有最大的光学二阶非线性系数 χ,并可结晶成 4 种不同的多型体(ε,γ,β,δ),且每个晶胞有以不同数目和排列方式的层状结构。研究认为,在红外和太赫兹光谱波段,GaSe 可以被看作是最有应用前景的非线性晶体之一。已发表的 1700 多篇关于材料物理性质的论文也指出,在 THz 波段,GaSe 是一种具有特异非线性光学特性的材料。通过共焦拉曼显微镜的实验研究,讨论了晶体的域结构和非线性光学性质。除了探讨这些材料最重要的物理性质,还进一步研究了在主边缘附近的光吸收,在红外和太赫兹波段的光致发光、非线性光学性质以及它们的纳米物理性质,这些研究对理解二维晶体结构和其物理性质之间的联系是必要的。由于 GaSe 及 GaSe 型晶体具有包含 - Se-Ga-Ga-Se-共价键的单一四层结构,因而它们的纳米粒表现出一些特殊的性质。一些 GaSe 型晶体(InSe, GaTe)的带隙宽度在 1.2~1.5 eV 之间,这使得它们及其纳米粒很适合用作光伏材料。

关 键 词:低维材料;纳米粒;共焦拉曼光谱;硒化镓;晶体改性
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Past, present and future of GaSe and related crystal-layered materials with outstanding nonlinear optical properties

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Abstract: The experimental and studied results of the structural, optical and nonlinear optical properties on the highly anisotropic especially un-doped and doped layered semiconductor GaSe (gallium selenide) and related crystals, InSe, GaS and GaSe-GaS (solid solutions) are overviewed. It includes also the investigation results on optical properties performed by confocal Raman and photoluminescence

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(PL) microscopy. Some experimental results on optical properties of GaSe nanoparticles obtained via ultrasonication and laser ablation methods are considered also. The properties of ε-GaSe is emphasized, which has one of the highest coefficient $\chi^{(2)}$ of optical second-order nonlinearity and are crystallized into four different polytypes (ε, γ, β, δ), containing different number and arrangement of layers per unit cell. It is shown that GaSe may be considered as one of the best crystals for nonlinear applications in the IR range. More than 1 700 papers describe the physical properties of the GaAs and indicate that it is an outstanding material for applications to the teraherz (THz) spectral range. The domain structure of the crystal in connection with the Nonlinea Optical(NLO) properties is discussed by confocal Raman microscopy experiments. In spite most important physical properties of these materials are mainly investigated, further studies of optical absorption near the fundamental edge, PL, NLO properties in the IR and THz ranges as well as physical properties of their nanoparticles are necessary to understand the connection between the 2-D crystal structure and the physical properties. It is known that the nanoparticles of GaSe and GaSe- type crystals are highly interesting because they have a single tetra layer structure consisting of covalently bond - Se-Ga-Ga-Se- tetra layers. Some of GaSe-type crystals have band gaps in the range of 1.2—1.5 eV (InSe, GaTe) which make them and their nanoparticles suitable for photovoltaic applications.

Key words: low-dimensional materials; nanoparticles; confocal Raman spectroscopy; SeGa; crystal modification

1 Introduction

GaSe, GaS, InSe and mixed $GaSe_{1-x}S_x$ ($0 \leqslant x \leqslant 1$) compounds belong to a class of layered chalcogenide semiconductors which are characterized by strong covalent bonds within thin layers and weak interactions of mainly van-der-Waals type between them. The absorption edge varies among about 1 000 nm in InSe, 630 nm in GaSe and 490 nm in GaS at room temperature. With increasing temperature it shows a pronounced red shift in all compounds[1-2]. The crystals usually occur in several polytypes which differ in the arrangement of the layers and their number per elementary cell. Four modifications have been described for GaSe[2]: (i) centrosymmetric β-type consists of 2 layers per unit cell and has the centrosymmetric space group (SG) D_{6h}^4; (ii) noncentrosymmetric ε-modification is the main component obtained from the melt, SG D_{3h}^1, contains 2 layers; (iii) the simplest modification is γ, SG C_{3v}^5, contains one layer; (iv) the δ-type grows from the vapor phase, contains 4 layers, SG C_{6v}^4. Existence of a new 8-layer polytype was suggested[3], but not proved by structural and optical investigations. Only one centrosymmetric modification (SG D_{6h}^4, two layers per unit cell) was described for GaS, whereas for InSe ε-, and γ-type was described[2,7]. $GaSe_xS_{1-x}$ solid solutions are formed in whole range of $0 \leqslant x \leqslant 1$[2,7]. The most thoroughly studied material of this class is GaSe[2-12]. ε-polytype of GaSe is characterized by a very high nonlinear optical susceptibility of second order. Other polytypes such as γ-GaSe and δ-GaSe are typically present as inclusions in grown crystals and exist as extended stacking faults in the layer plane (across to crystal *c*-axis). The nonlinear-optical coefficient for ε-polytype has only one independent tensor element, d_{22},[13] for which a non-resonant value of $(2.0 \pm 0.4) \times 10^{-7}$ esu or (86 ± 17) pm/V was measured from second-harmonic generation (SHG) of CO_2 laser light (10.6 μm)[4,8]. Since GaSe has, in addition, a very wide transparency range between about 0.65 and 18 μm, a high threshold for optical damage, and the possibility of phase matching,[11,14-15] it is of great interest

for nonlinear frequency conversion in the near-, to mid IR and THz range of spectra. The comprehensive reviews see Ref. [10,14,16-17].

Recently, GaSe was investigated at room temperature by a confocal Raman micro-spectrometer equipped with a HeNe laser as excitation source[18-19]. While photon's energy of the HeNe laser line of 632.8 nm falls below the direct band gap of the crystal at 295 K, the intense PL bands on the anti-Stokes side were detected. Moreover, blue shifted PL showed a quadratic signal dependence on laser intensity within two orders of laser power. This effect can not be understood in the field of linear optics and it was attributed to SHG of light in the laser focus followed by excitation of electrons into the conduction band and luminescence emission from direct-gap Wannier excitons[18-19]. The assignment to SHG was attained since the reported data of two-photon absorptiom (TPA) coefficients β for below band gap energies in GaSe are not sufficiently large to explain band to band carrier generation[20-21]. The TPA coefficient of GaSe was measured at different wavelengths with different nano-, pico-, and femtosecond lasers[20,22-24] with wavelengths of 700 and 626 nm and values of (6±1.2) cm/GW[22] and 0.3 cm/GW,[23] respectively, were reported at room temperature. In low temperature measurements between 75 and 240 K, the authors of Ref. [24]found that the TPA coefficient increases strongly (by a factor of 5～10 at 75 K) in a narrow spectral region of width 1/4 kBT around the excitation energy of the indirect exciton.

A novel coherent THz source based on collinear phase-matched *DFG* in GaSe which is continuously tunable in the wide range of 56.8－1 618 μm (0.18－5.27 THz) was reported[25]. The generation of backward THz waves in GaSe was demonstrated by mixing two coherent IR beams in two GaSe crystals[26]. With one 47 mm long crystal, the output wavelength was tuned in the wide range of 167.6 to 2 060 μm (0.146 to 1.79 THz) with a peak output power of ～217 W. A high-power tunable (0.53－3 THz) radiation source based on nonlinear difference-frequency mixing of CO_2 laser lines was reported[27]. THz generation using GaSe crystals with different carrier densities in the near IR and THz frequency region has been reported by Japanese groups[28-29]. Optical properties of pure and doped GaSe∶In, GaSe∶S, GaSe∶Te and mixed GaSe∶$AgGaS_2$ crystals as well as THz geneartion are actively investigated by Prof. Yu. M. Andreev *et al.*, and Prof. Luo Chinwei *et al.*[30]. Some other groups in Russia as well as in China actively started to investigate the nonlinear properties of layered crystals in far IR and THz range of spectra[30].

Besides its outstanding NLO properties, GaSe has attracted interest as a 2-D semiconductor (including investigations under high hydrostatic pressure, in particular for exploring pressure-induced structural phase transitions associated with the disappearance of the layered structure[31-34]), concerning the crossover between direct and indirect gap[35-36], as an effective laser light modulator[37-39], detector of radiation[40-47], and Li^+ intercalation matrix[48-51].

Well-defined nanoparticles of GaSe were obtained from vapor-phase thermolysis of heterocubane molecules under CVD conditions[52]. GaSe nanoparticles grown at 335 ℃ have pseudo-spherical shapes with a mean particle diameter of 42 nm and a standard deviation of 13 nm. Layered feature leads to relatively simple method of preparation nanoparticles of GaSe and related crystals by solvent intercalation and subsequent crystal shattering (splitting) at the nanometer level. Taking this peculiarity into consideration, the authors used powder as well as single crystals of GaSe in methanol to sonicate under ambient conditions[53]. The spectra of crystallites with a diameter of 20 nm and less turned out to be blue-shifted. A second-harmonic signal generated with the 1.064 nm line of a mode-locked

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The synthesis of GaSe nanoparticles with sizes in the range of 2－6 nm by using a method based on the reaction of trimethyl gallium with trioctyl phopshine selenium in a high temperature solution of trioctyl phosphine and trioctyl phosphine oxide was described, and it was shown that the particles are emissive (360 to 450 nm) with emission quantum yields of ～10%[54].

The formation of strongly interacting aggregates of GaSe nanoparticles and their spectra were studied and it was shown that although a significant fraction of the excitons in the aggregates are delocalized more than one nanoparticle, the average coherence length is short, one or two monomers, which makes these types of aggregates unique among semiconductor nanoparticles[55]. A group of the University of California, Merced, USA, is optimistic to develop nanoparticles of GaSe which have just the appropriate size for applications in solar cells. These particles may absorb all the visible light and nothing in the spectral range of near IR, which would reduce the voltage. GaSe nanoparticles were obtained also via laser ablation, and the experimental results of optical absorption, Raman scattering, photoluminescence and IR absorption were discussed in relation to the particle size[56].

The paper is organized as follows. In Sec. II, we present the results of crystal growth, crystal structure, band structure calculations and the lattice dynamics of GaSe and related crystals. In section III, the Sellmeier equations for the refractive indices and the NLO properties in the mid-IR and THz range are given, whereas in section IV the properties of nanoparticles of GaSe and the confocal Raman and PL spectra of bulk crystals are considered. Summary and Outlook are given in Sec. V.

2　Crystal growth, structure, band structure and lattice dynamics of GaSe and related crystalsIntroduction

The first record of the synthesis of GaSe seems to have been published by Klemm *et al*.[57]. The vapor growth method was described by Terhell *et al*.[58]. The melt growth provides large single crystals sufficiently homogeneous and free of defects. Growth conditions for melt-grown GaSe crystals were published in different articles[59-63]. At present time the reproducible technology is developed to grow by the Bridgman method big enough and high optical quality of GaSe and GaSe-type crystals.

GaSe crystals have a dark red colour. When adding S (sulfur) the color of crystals change to orange (at S content nearly about 2 weighted) and yellow (when 100% of Se atoms are substituted by S atoms). Most physical properties of GaSe and related crystals were studied on slabs or plates cleaved from crystals which have the *c*-axis perpendicular to the cleavage face (usually referred to as *z*-cut, $\boldsymbol{E} \perp c$, where $\boldsymbol{E}$ is the electric-field vector of the incident electromagnetic wave).

Over the last few years, Allakhverdiev *et al*. developed a simple but effective technology with which optical-quality cutting and polishing of GaSe and GaSe-type crystals at an angle arbitrary to the *c*-axis can be achieved[64]. As a result of this technology, they were able to measure the optical properties of both the o (ordinary) and e (extraordinary) rays[64]. It is worth to mention the technology described in Ref. [64] is applicable also to other representatives of layered $A^{\mathrm{III}}B^{\mathrm{IV}}$ crystals and their solid solutions.

Taking into consideration the selection rules deduced from the band structure and the ellipsometric measurements[2,65,66], we can summarize: a) the direct band gap of ε-GaSe (hereafter

GaSe) is located at the Γ point; b) the second-lowest band edge in energy is observed near ~3.8 eV; c) the valence and conduction bands are not degenerate at the band edge; d) an optical transition in the vicinity of the direct edge is allowed only for $\boldsymbol{E}//c$, and the $\boldsymbol{E}\perp c$ component is attributed to intervalence-band mixing between the valence and conduction bands due to spin-orbit interaction; e) the intralayer bond energy in GaSe is ~1 eV/atom, whereas between the layers it is ~1 meV/atom.

GaSe exhibits strong excitonic effects both in emission and absorption at room and, especially, at low temperatures. It is obvious that, because of the uniaxial anisotropy of GaSe, the charge carriers have different effective masses for motions // and $\perp$ to the c-axis. Data of the strong anisotropy in the absorption spectra and anisotropies in the thermal and electronic properties for two directions of thermal-wave propagation in GaSe were reported[2].

The available lasers, Raman, IR equipments, and neutron scattering facilities allowed researchers to obtain reliable experimental data on the vibrational properties of GaSe. Theoretical calculations of the lattice dynamics are also available[2]. Decompositions of the normal vibrations for different polytypes of GaSe at the center of the Brillouin zone may be found in Ref. [2]. The symmetries of the 24 vibrational modes of the ε-type (point group D_{3h}) at $k=0$ are:

$$\Gamma=4A_1'+4A_2''+4E'+4E'', \qquad (1)$$

of which $A_2''+E'$ are the acoustic modes. There are 11 non-degenerate Raman-active $4E''$, $4A_1'$, $3E'$ modes and 6 IR-active $3A_2''$ and $3E'$ modes. The Raman- and IR-active modes co-exist simultaneously. The vibration properties of ε-GaSe have been mostly investigated as compared with the other polytypes[2]. The major differences which occur when comparing the Raman spectra of the different polytypes of GaSe are described in Ref. [3].

The lattice dynamics of GaSe and related crystals were interpreted in terms of a linear-chain model that included the interlayer and intralayer force constants[2]. Vibration frequencies of the impurity atoms in GaSe were calculated in the approximation of isolated impurity atoms[67].

An overview of the vibration properties of pure and doped GaSe crystals as well as the frequencies and the type of impurity vibrations (gap, local, or resonance) is given in Ref. [3].

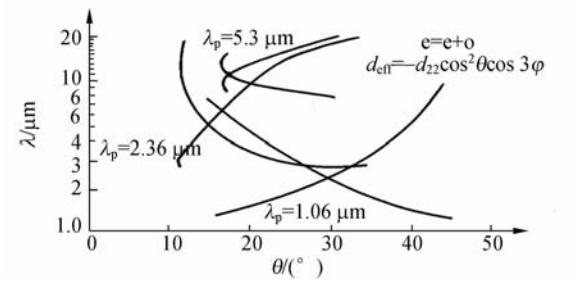
3 Sellmeier equations and NLO properties in the IR and THz range

First results of the NLO properties of GaSe were reported by scientists of the former USSR in 1972 in the frame of a joint research project between the Institute of General Physics of the Russian Academy of Sciences, Moscow, Russian Federation, and the Institute of Physics of the Azerbaijan National Academy of Sciences, Baku, Azerbaijan Republic[4]. GaSe was one of the first efficient NLO crystals grown, investigated, and suggested for SHG and optical frequency mixing in the former USSR. Since 1972, a large number of articles have been published on this matter. It was shown that GaSe is an outstanding material for NLO applications and has a number of exciting properties which can be summarized as follows: a) negative uniaxial crystal, $n_o-n_e\approx 0.28$($\lambda=1\,060$ nm); b) symmetry class $\bar{6}\,m^2$; c) wide transparency range of 0.65−18 μm with the absorption coefficient less than $\alpha\leqslant 0.3$ cm^{-1}; d) nonlinearity in the phase-matched direction: $d_{eff}=-d_{22}\cos\theta\sin 3\varphi$ (e=o+o), $d_{eff}=d_{22}\cos^2\theta\sin 3\varphi$ (e=e+o) (where θ is the angle between the wave vector $\boldsymbol{K}$ of the pump radiation and the optical c-axis and φ is the angle between the crystal planes XZ and KZ); e) very high NLO coefficient d_{22}(10.6 μm)=(86±17) pm/V, corresponding to (2.0±0.4)×10^{-7} esu; f) phase-matching angle θ for the second harmonic at the pump wavelength $\lambda=2.36$ μm is $\theta=18°40'$

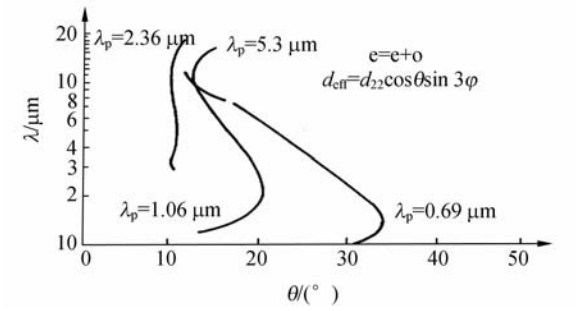
$\pm 10'$; $\theta(\lambda=5.3\ \mu m)=10°10'\pm 20'$; $\theta(\lambda=10.6\ \mu m)=12°40'\pm 20'$; g) high power threshold for optical damage of $\approx 2\times 10^7$ W/cm^2 ($\lambda=0.694\ \mu m$, $\tau_p=25$ ns), $\approx 3.5\times 10^7$ W/cm^2 ($\lambda=1.06\ \mu m$, $\tau_p=10$ ns), ≈ 25 MW/cm^2 ($\lambda=9.3$ mm, $f=20$ Hz); ≈ 100 W/cm^2 ($\lambda=800$ nm); h) high value of the TPA coefficient ($\approx 10^{-7}$ cm/W at $\lambda=1.06\ \mu m$).

Fig. 1 represents the curves of angle versus wavelength for collinear parametric interaction with the pump wavelengths of 0.69, 1.06, 2.36, and 5.3 μm[49]. By illuminating the *z*-cut surfaces of GaSe with giant pulses from a $CaF_2:Dy^{2+}$ laser, the authors established that the surface of the crystal becomes damaged at power densities >5 MW/cm^2[4].

Dispersion relations for n_o and n_e of GaSe were published in a number of articles and the results presented were obtained by indirect methods using the Brewster angles at different laser lines and interference fringe patterns.



(a)



(b)

Fig. 1　Wavelength as a function of angle of parametric radiation for different pump wavelengths in GaSe[4]

Allakhverdiev *et al*.[68] measured the room-temperature refractive indices of GaSe in the 0.7 −1.4 and 2.4−5 μm ranges using the method of minimum deviation of light through a prism with polarization either parallel (n_e) or perpendicular (n_o) to the crystal *c*-axis. The birefringence (Δn) at 300 K has been measured directly using polarized-light interference in transmittance from 1.73 to 4.97 μm. The n_o, n_e, and Δn values determined from the positions of fringe maxima were compared to those obtained from the prism measurements in the mid-IR and with previously published data. It was found that the prism method and interference fringe method resulted in values of n_o, n_e, and Δn accurate to ±0.003 and ±0.006, respectively. The corrected Sellmeier equations for GaSe presented in Ref. [68] are as follows:

$$n_o^2=-0.054\ 78/\lambda^4+0.385\ 29/\lambda^2+7.389\ 94-1.1\cdot 10^{-3}\lambda^2-9.3\cdot 10^{-7}\lambda^4, \quad (2)$$

$$n_e^2=5.774\ 1+0.262\ 88/(\lambda^2-0.214\ 57)-1.1\cdot 10^{-3}/\lambda^2. \quad (3)$$

Intense subpicosecond laser pulses tunable by subsequent down conversion in GaSe provided pulses of 0.7 ps duration tunable in the range of 4 − 20 μm, as was reported by Bayanov *et al*.[69]. Tunable SHG of CO_2 laser radiation and tunable up-conversion of IR radiation from a CO_2 laser was performed in GaSe and it was shown that GaSe crystals are useful for the detection of low IR signals[70]. 2.8 μm-laser-pumped type Ⅰ (e=o+o) and type Ⅱ (e=e+o) travelling-wave optical parametric generation in GaSe in the range of 3.5−14 μm were reported by Vodopyanov *et al*.[11]

Doping of GaSe with a small amount of indium improves the mechanical properties and does not alter the efficiency of SHG. It was shown that the surface of the crystal remains stable under CO_2 laser irradiation of 60 kW/cm^2 at 30 kHz. Northrop Grumman Corporation performed the theoretical and experimental studies to synthesize, grow and characterize the optical

and NLO properties of GaSe[14,30].

The highly efficient NLO properties of GaSe found useful practical applications. The tunable mid-IR difference-frequency generator (DFG) (7-17 μm) as well as fully automated mid-IR DFG spectrometer with a spectral resolution below 70 MHz pumped by a pair of conventional room-temperature 800－900 nm diode lasers was built. 0.1 μW of tunable CW radiation was produced from incident diode laser powers of 120 and 75 mW. Due to the large tuning range, the spectrometer has the potential to detect any trace gas that has an acceptably strong absorption line. A mid-IR optical parametric generator with wide tunability in the range of 3－19 μm was reported. This spectrometer is a very useful tool for the NLO spectroscopy of intersubband transitions of conduction-band electrons confined in semiconductor quantum wells, as well as for the study of intersubband-based resonantly enhanced $\chi^{(2)}$ effects in quantum wells. A tunable coherent IR source between 5 and 16 μm based on difference-frequency mixing in In-doped GaSe crystals was also described[14].

Femtosecond generation of coherent optical phonons in GaSe was reported[71-72].

The third-order optical nonlinearity of GaSe and refractive-index changes after picosecond laser irradiation and optical switching caused by the nonlinearities, coherence and dephasing were observed in GaSe[2].

The following concluding remarks concerning the NLO properties of GaSe can be made: a) large second-order NLO coefficient d_{22} (10.6 μm) = (86 ± 17) pm/V; b) adequate birefringence $\Delta n \approx 0.28$ (at $\lambda = 1\,060$ nm); c) negative birefringence as preferred for nonlinear materials; d) appropriate change in birefringence with temperature; e) availability of large crack-free single crystals; f) availabilty of ultra-pure elemental ingredients; g) extreme transparency with low absorption coefficient (0.65－18 μm, $\alpha < 0.25$ cm^{-1}); h) high thermal conductivity (0.162 W/cm·K); i) high environmental stability; j) large laser damage threshold (121 MW/cm^2) which is almost the same as for CdSe (127 MW/cm^2) as measured with a TEA CO_2 laser at 9.55 μm which has 30 ns pulses with 90% of the total pulse energy in the leading edge; k) very good performance in different laser systems; l) commercial availabilty. It is, however, necessary to note some disadvantages of GaSe: a) weak mechanical stability; b) relatively high cost. Deficiency may be overcome by doping with In, S, Tl, and other elements.

Fig. 2 represents the nonlinear figure of merit d_{eff}^2/n^3 for different NLO crystals. It is seen that the value of GaSe is about 4, 8, and 9 times higher than that of $AgGaSe_2$, CdSe, and $AgGaS_2$, respectively, and slightly below that of $ZnGeP_2$.

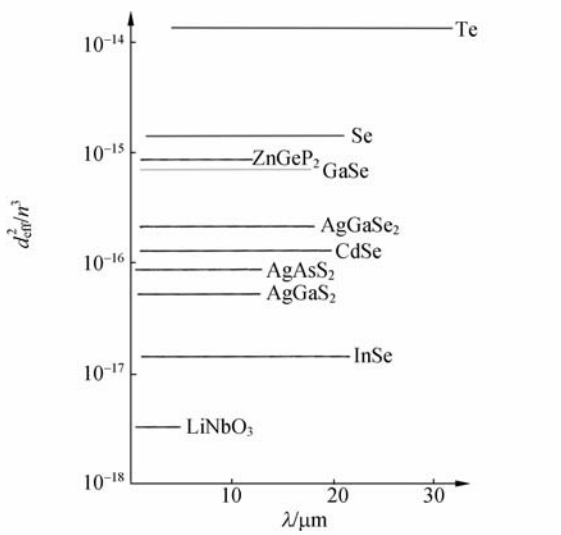


Fig. 2 Quality coefficient for different NLO crystals

GaSe appears to be one of the most promising materials for THz generation and tuning. A novel coherent THz source based on collinear phase-matched DFG in GaSe which is continuously tunable in the wide range of 56.8－1 618 μm (0.18－5.27 THz) was reported in Ref. [25]. The generation of backward THz waves in GaSe was demonstrated by mixing two coherent IR beams in two GaSe crystals[26]. With a 47

mm long crystal, the output wavelength was tuned in the wide range of 167.6 to 2 060 μm (0.146 to 1.79 THz) with a peak output power of ~217 W. A high-power tunable (0.53－3 THz) radiation source based on nonlinear difference-frequency mixing of CO_2 laser lines was reported[27]. THz generation using GaSe crystals with different carrier densities in the near IR and THz frequency region has been reported by Japanese groups[28-29].

4 Nanoparticles, confocal Raman and PL spectroscopy

Well-defined nanoparticles of GaSe were obtained from vapor-phase thermolysis of heterocubane molecules under CVD conditions[52]. GaSe nanoparticles grown at 335 ℃ have pseudospherical shapes with a mean particle diameter of 42 nm and a standard deviation of 13 nm.

Layered feature leads to a simple method of preparing nanoparticles of GaSe by solvent intercalation and subsequent crystal shattering (splitting) at the nanometer level. Taking this peculiarity into consideration, the authors used powder as well as single crystals of GaSe in methanol to sonicate under ambient conditions[66]. The spectra of crystallites with a diameter of 20 nm and less turned out to be blue-shifted. A second-harmonic signal generated with the 1.064 nm line of a mode-locked Nd:YAG laser was observed from particles which have been spin-coated onto a glass substrate from solution, and this finding opens up a new perspective to use GaSe crystallites in NLO applications[53].

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Three groups (Bayreuth University, Germany; TÜBİTAK MRC MI, Turkey, and the Institute of Physics ANAS, Azerbaijan) have started investigations of the optical properties of bulk GaSe by confocal Raman and PL spectroscopy[18-19]. The PL spectra excited with an unpolarized HeNe laser (λ=632.8 nm, 15 mW, focused to a spot size of ~5 μm) is characterized by three broad and intense bands, which are mainly located to the blue of the laser line[18]. The PL signals showed a quadratic dependence on excitation intensity. In an external electric field the PL showed a strong increase and a quadratic red-shift, whose magnitude is consistent with the Franz-Keldysh mechanism. This was interpreted as SHG in the laser focus followed by the excitation of electrons into the conduction band and PL emission from direct-gap Wannier excitons. The three bands were tentatively ascribed to three crystal modifications of GaSe (ε, γ, and β) and their lateral intensity distributions were mapped with a confocal microscope[18,19].

The room-temperature Raman spectra of

single crystals of GaSe, GaS, and mixed compounds $GaSe_{1-x}S_x$ with $0.02 < x < 0.8$ were measured with a HeNe laser in confocal configuration[19]. The changes in the spectra indicate changes of the crystal structure. The spectra of pure GaSe and its mixed compound with $x=0.02$ show pronounced PL signals blue-shifted from the laser line, whereas these signals do not appear for higher sulfur content. Their origin was again interpreted as SHG in the laser focus causing the formation and radiative decay of Wannier excitons. TPA was ruled out, since the effect was absent in the centrosymmetric crystals with $x>0.02$. With a green laser whose photon energy is larger than the band gap, strong PL was also observed in crystals with higher sulfur content indicating a high PL quantum yield for all crystals.

5 Summary and Outlook

GaSe and GaSe -type crystals are outstanding materials for linear and nonlinear optical applications. In spite of the fact that most of the important physical properties of GaSe have been investigated, further studies of the optical absorption near the fundamental edge, Raman and PL spectra, NLO properties in the THz range as well as physical properties of nanoparticles are necessary in order to understand the connection between the 2-D crystal sructure and the physical properties. Further optical confocal (Raman and PL) experiments (including the influence of electric fields) are required to clarify the spatial distribution of the polytypes in real crystals and its influence on the total NLO properties.

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●下期预告

应用于特殊环境下的光纤光栅温度压力传感器

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针对现有高温高压油井下实时长期监测的要求,设计了温度补偿式光纤光栅温度压力双参量传感系统。首先,根据传感器的使用环境,优选了恒弹性合金。接着,采用优选后的恒弹性合金做为基底材料设计了圆筒与圆形膜片组合式传感器结构,圆形膜片是整体加工成型的。最后,对传感器进行相关实验测试。实验测试与误差分析的结果为:传感器实现了温度和压力的大量程、传感特性的单值线性、温度补偿一体化封装;温度线性检测范围为0～350 ℃,温度灵敏度为0.020 1 nm/℃,温度测量的静态误差为0.029%;压力线性检测范围为0～60 MPa,压力灵敏度为0.013 6 nm/MPa,压力测量的静态误差为0.046%。上述指标能够满足实际工程的要求。