Linear and NLO spectroscopy of GaSe and InSe nanoparticles formed via laser ablation

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ABSTRACT

Nanoparticles of layered GaSe, InSe were fabricated by laser ablation (LA) method (KrF laser, λ = 248 nm, 50 Hz, maximum energy 200 mJ, τ = 4 ns) and characterized by: XRF, GDOES, SEM and TEM, UV-, VIS-, and IR-absorption; Raman and PL spectroscopy (also in confocal geometry). Results are discussed in relation to the particle size. Absorption spectra of particles with diameter 20 nm and less turned out to be blue shifted and is consisted with a weak confinement effect on Wannier-Mott type excitons. It is shown, that with decreasing the particle size the energy position of the low-frequency Raman active phonons in both compounds are shifted to lower frequencies (21 and 18 cm⁻¹ in bulk GaSe and InSe and 8 and 7 cm⁻¹ in particles with sizes 5 and 7 nm, respectively). From the low frequency Raman data, decrease of the force constants ca. 25 % (for GaSe) due to the formation of the nanoparticles are estimated, and the origin is suggested. Second harmonic generation (SHG) with 1064 nm line of a mode locked Nd : YAG laser was observed for nanoparticles ablated on different substrates. Potential for using these structures for laser light visualizers are discussed.

Keywords: Nanoparticles, layered crystals, gallium selenide, indium selenide, Raman scattering, PL, SHG, absorption

1. INTRODUCTION

Semiconductor nanostructures are promising building blocks for future electronic and photonic devices. Nanostructures based on layer-type semiconductors, such as GaSe-type (GaS, InSe, GaTe) are of particular interest in terms of the optical, non-linear optical (NLO), solar, X-ray and particles detection applications. GaSe and InSe have two main advantages over other semiconductors (GaAs, CdS, CdSe etc.), i.e. the large exciton binding energy (19.5 and 16.9 meV at 300 K, for GaSe and InSe, respectively) and the availability to perform the van der Waals homo-, and hetero- epitaxy growth for highly lattice-mismatched system.

Reduced dimensionality has a profound effect on the electronic, optical and NLO properties of material. The strong bonding inside the layers is thought to be covalent, with some ionic contribution. At the same time the inter-layer bonding is much weaker, and is mainly of the van der Waals type. Because of this, easy cleavage occurs parallel to layers (perpendicular to the direction of the optical c-axis) into plane parallel slabs with mirror like surfaces.

The hierarchy of weak forces and the ability of these materials for easy cleavage together with the low density of electronic states on freshly cleaved surfaces (does not exceed ~ 10¹⁰ cm⁻², water absorbs on a surface without any reaction and forms 3-D clusters on the (0001) planes)) and existence of different polytypes and other unique properties is one of the main reason why GaSe-type layered semiconductors were extensively investigated about since 1960th up to the present time. Both in GaSe and InSe all polytypes have the same stacking unit of the covalently bonded Se – Ga(In) – Ga(In) – Se layer with average thickness of 0.797 nm (GaSe) and 0.669 nm (InSe). Difference between different polytypes are the stacking sequence and/or the stacking periodicity. For GaSe and InSe 4 and 3 polytypes were reported, respectively: GaSe- β (D₃h), γ (C₃v), ε (D₆h); δ (C₃v) and InSe- β (D₆h); γ (C₃v); ε (D₆h). For both compounds the noncentrosymmetric ε-modification is the main component obtained from melt. It contains 2 layers per unit cell. The indirect 1.96 eV (1.2 eV for InSe) and the direct 2.1 eV band gaps (1.32 eV for InSe) have been reported for GaSe single crystals. Melting points of GaSe and InSe Tm = 960 °C and Tm = 600 °C, respectively (density: InSe 5.80 g/cm³ and GaSe 5.03 g/cm³).
To our knowledge, first data on the formation of metastable phases of gallium and indium selenide have been reported by using metal organic chemical vapor deposition (MOCVD). Well-defined nanoparticles of GaSe and InSe were obtained from the vapor phase thermolysis of heterocubane molecules under CVD conditions. GaSe particles grown at 335 °C consist of pseudo-spherical nanoparticles with the mean particle diameter of 42 nm, with a standard deviation of 13 nm. However, unlike the InSe films, GaSe apperas as "string of pearls" (fiber with rounded structure), which retain their connectivity and remain intact after being floated from the grown substrate (KBr). It was noted that the films of GaSe grown onto the Si substrate are mirror-like and adhere well to the substrate.

Due to a weak interlayer van der Waals bonding in both compounds, one dimension (i.e., in the direction of c-axis) of small particles will be integral values of the fundamental layer thickness. This feature leads to a simple method of preparing nanoparticles of GaSe- type semiconductors by solvent intercalation and subsequent crystal splitting at the nanometer level. Taking this peculiarity into consideration, Allakhverdiev et al. used powder as well as single crystal of GaSe in methanol to sonicate under ambient conditions (same has been made with InSe). After filtration or centrifugation a mixture were obtained which contained particles with diameters less that 30 nm. The optical absorption spectra of crystallites with a diameter of 20 nm and less turned out to be blue shifted. These results are consistent with a perturbation of GaSe and InSe band structure due to carrier confinement, resulting in widening of the forbidden gap. A second harmonic generation generated with the 1.064 nm line of a mode-locked Nd:YAG laser was observed in particles which have been spin-coated onto a glass substrate from solution and this finding opened a new perspective to use GaSe and InSe crystallites in NLO.

Theoretical study of the structural and electronic properties of GaSe nanotubes were reported and the strain (deformation) energy of GaSe nanotubes was found to be comparable to existing carbon nanotubes. Besides, it was shown that the energy gap of GaSe nanotubes should be less than the bulk value as the nanotubes get smaller. Theoretical analysis showed that the energy requirement for the formation of GaSe nanotubes should allow tubes with radii between 40 - 48 Å. Synthesis of GaSe nanoparticles with sizes in the range of 2 - 6 nm by using the method based on the reaction of trimethyl gallium with trioctyl phosphshine selenium in a high temperature solution of trioctyl phosphshine 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%. Later on, the relaxation dynamics in photoexcited GaSe nanoparticles were studied and it was shown that GaSe nanoparticles emit intense, polarized emission and several dynamical processes depolarize and attenuate the intensity of this emission at 480 nm. All models used are based on the energetics of bulk GaSe, subjected to the large quantum confinement shifts observed in nanoparticles.

The electron and hole transitions in GaSe particles with the diameters ranging from 4 to 9 nm was studied by femtosecond transient absorption spectroscopy. The results showed that the transient absorption spectrum in the 500-700 nm region has a size-independent peak at about 600 nm. Formation of strongly interacting aggregates of GaSe nanoparticles and their spectroscopy were studied and it was shown that although a significant fraction of the excitons in the aggregates are delocalized over more than one nanoparticle, an average coherence length is short, (one or two monomers), which make these types of aggregate unique among semiconductor nanoparticles.

Exciton dynamics of GaSe nanoparticle aggregates were described. Nanotubes of GaSe with an inner diameter of 5 nm and an outer diameter of 20 nm were formed and characterized and it was shown that thermal exfoliation of GaSe yields scrolls, nanotubes, and nanoflowers. Transitions from parabolic to ring-shaped valence band maximum in few-layer GaS, GaSe, and InSe was reported. More results concerning the properties of GaSe nanoaggregates may be found.

Well defined nanoparticles of InSe (mean ∅ of 88 nm with standard deviation (s.d) of 30 nm) and GaSe (mean ∅ of 42 nm with s.d. of 13 nm) were obtained from the vapor phase thermolysis of heterocubane molecules ([EtMe2C]InSe)4 for InSe, ([′BuGaSe]4 for GaSe) and possible controlling mechanism were discussed by the authors. Memory device using InSe nanowire as programmable resistive element was fabricated and its resistive switching property was studied as functions of electrical pulse width and voltage magnitude. It was shown that the nanowire memory can be repeatedly switched between high-resistance and low-resistance states which are attributed to amorphous and crystalline states, respectively. This observation suggests that the nanowire can be programmed into two distinct states with a large on-off resistance ratio for nonvolatile information storage. The growth methods and properties of InSe nanoaggregates are presented also by the authors of Refs.

Surface-phonon-dispersion curves of the (001) surfaces of the GaSe and InSe films epitaxially grown on the Si(111) surface have been investigated by high-resolution inelastic helium-atom scattering. No difference has been found between the surface and bulk phonons of these two compounds, as expected due to weak interlayer interaction forces.
For the last years our research groups at the National Aviation Academy of Azerbaijan, Scientific-Research Institute of Transport and Aviocosmic Problems, and the TÜBITAK, Marmara Research Centre, Materials Institute have been focused on layered semiconductors, specifically, GaSe and InSe due to increasing interest of their NLO and other applications (photovoltaics, particle detection etc.). We used the LA (Laser Ablation) method to obtain the nanoparticles of GaSe and InSe with a given size and to examine elemental content (XRF- X-ray Fluorescence, GDOES- Glow Discharge Optical Emission Spectroscopy ), structural (X-ray, TEM- Transition Electron Microscopy, and SEM- Scanning Electron Microscopy), optical (absorption in VIS- Visible, near-, and mid- IR- Infrared, PL (photoluminescence) also in confocal geometry), vibrational (Raman and confocal Raman spectroscopy) and NLO (SHG) properties. The properties of nanoparticles ranging from 100 nm to several nanometers are strongly size dependent, due to quantum size effects. We were primarily interested in using above mentioned effects to control the properties of obtained nanoparticles and optimize these properties for different practical applications, including visualization of near-IR laser radiations. In this paper detailed description will be presented for GaSe, due to comparatively wider practical applications (mainly in laboratories) of this crystal in comparing with InSe. The results obtained for InSe are qualitatively similar to those of GaSe.

The paper is organized as follows. In Section 2 the methods of crystal and nanoparticle growth and characterization they properties are presented. Section 3 represents the results and discussions. Summary and outlook are presented in Section 4.

2. METHODOLOGY

The starting materials were prepared by mixing quantities of high-purity (99.999%) gallium (indium) and selenium powder. Powder was obtained by grinding the single crystal plates in an agate grinder. Then the powder was pressed into a form of pellets and used as a target in the LA experiments.

Equipment, facilities and methods used for characterization of bulk crystals and nanoparticles are as follows: •XRD- (Shimadzu XRD-600); •XRF- (Philips PW 2404); •GDOES- High Resolution HR 10000 Glow Discharge Profiler (Jobin Yvon); •home made confocal Raman and PL microspectrometer equipped with a He:Ne 632.8 nm (12 mW) and second harmonic of Nd:YAG lasers at 530 nm (50 mW) lines; •every small drops of samples were dropped onto carbon support film coated copper TEM grids. JEOL-2100 HR TEM operating at 200 kV (LaB₆ filament) and equipped with an Oxford Instruments 6498 EDS system; •JEOL-JSM-6335F FEG-SEM equipped with Oxford EDS system, operated at 20 kV and INCA software; •IR Fourier transform spectrometers- Perkin Elmer Spectrum 1 FTIR and Bomem DA-3; •1064 nm line of a mode-locked Nd:YAG laser- Continuum PY61C, repetition rate 20 Hz, pulse duration 100 ps and Nd:YVO₄ laser with a wavelength of 1064 nm, repetition rate of 81 MHz and a pulse duration of 10 ps. The SHG signal generated form GaSe and InSe (bulk crystals and nanoparticles) passed through a low-resolution spectrometer and was detected by a photomultiplier. Besides, the SHG signal might be also observed by eyes; •Raman scattering- using the 514.5 nm of an Ar⁺ laser (NEC Corp.) and a double-pass spectrometer (Jobin Yvon U-1000) with the photon counting system equipped with a photomultiplier (RCA-C31034) and a multichannel analyzer (Canberra Series 40). The measurements were made in the back scattering geometry using a cylindrical lens for focusing the laser beam on the sample surface, and the excitation power of the laser at the sample was set to be less than about 3 mW to avoid local heating of the sample. No change in optical properties due to laser irradiation could be observed under the conditions of our measurements. This setup was mainly used for high resolution measurements in the low-frequency range (less than ~ 100 cm⁻¹) with the aim to control the spectral position of the rigid layer mode (RLM). This is a mode (at ~ 21 cm⁻¹ for GaSe and at ~ 18 cm⁻¹ for InSe) corresponding to the vibration of a whole layer Se – Ga(In) – Ga(In) – Se as a rigid unit against each other (Raman measurements with confocal setup in the range below ~ 100 cm⁻¹ were not possible due of the Notch Filter which cuts the spectral lines below ~ 100 cm⁻¹). The accuracy of measurements was better than ± 1 cm⁻¹. The wavenumber peak positions and the full width at half maximum (FWHM) of phonon modes were determined by fitting Lorentzian lines shapes to the experimental data.

From the boules (Ø 20 mm), slabs of different thickness were easily cleaved with a razor blade for further preparation of powder. Powder was obtained by grinding the single crystal plates in an agate grinder. Then the powder was pressed into a form of pellets and used as a target in the LA experiments.
Nanoparticles were grown by home built LA apparatus during stay of Prof. K. Allahverdiyev at the Institute of Material Sciences, Tsukuba University, Tsukuba, Japan (Prof. K. Allahverdiyev are indebted to Prof. S. Onari for his hospitality during stay at Tsukuba University). KrF Excimer laser at 248 nm (COHERENT COMPex 201), with the repetition frequency \( f = 10 \) Hz and pulse duration \( \tau = 10 \) ns, 25 mJ and 200 mJ pulses were used and the particles were deposited at different gas pressures. The laser light was focused to a point onto the pellet surface with either a 100 mm f. 1 or 150 mm f. 1 Suprate quartz lens. The spot size of the focused laser beam was 1 - 4 mm
\(^2\). The laser light hit the target at the angle of 45\(^\circ\). The pellets were mounted on the shaft of a rotary motion feedthrough with an adjustable nylon coupler, which is slowly rotated (~ 6 rpm) to perform uniform ablation. The distance between the pellet and substrate was ~ 25 mm. When the fluence of the laser light became about 1.5 - 2.5 J/cm
\(^2\) per pulse, the focused form of the light on the target was a spot with the diameter of 1.5 - 2 mm. The plume was adjusted in size to have the top just below the substrate for obtaining homogeneous film. Ar and He was used in the pressure range of 0.1 - 2.2 Torr and 0.1 - 4.0 Torr, respectively. As a substrate quartz, Si, GaSe, InSe and GaS single crystal plates were used at 77 K (when the substrate was at 300 K a polycrystalline films with a grain sizes more than ~ 300 \( \mu \)m thick were obtained). In the present paper the results only for nanoparticles deposited onto the quartz plates will be presented and discussed for both crystals.

The average size of grown GaSe and InSe nanoparticles were controlled by a change in the pressure of the noble gases and the laser energy. The size of grown particles was estimated by direct observation with a TEM operated at 200 kV. All measurements were carried out at room temperature. The diameter \( d \) of synthesized particles used in our experiment was in the range of 4 - 60 nm. The relationship between the gas pressure and the mean diameter of nanoparticles obtained in the present work indicated the average of GaSe and InSe nanoparticles which was made in each gas pressure. To obtain these dependences we enlarged TEM image pictures and measured by hand the size of each nanoparticle. We choose about 200 nanoparticles as specimens. From these data we obtained the average size of nanoparticle. Then we built histograms (dependences of number of particles in \( \% \) versus the size of particles obtained at different pressures under fixed laser pulse energy). The accuracy of this method is in dependence on choices which we get nanoparticles as specimen, and we choose nanoparticles which were considerable easily measurable.

3. RESULTS

Growth from the melt provides large single crystals sufficiently homogeneous and free of defects which allows the fabrication of samples destined for optical or transport phenomena measurements (GaSe, and GaSe-type crystals can be grown from the vapor phase in closed quartz ampoules by employing either the iodine chemical transport process, or the sublimation technique\(^1,2,44\). A little thin slice of single-crystal sample was ground into powder and its XRD pattern was recorded. The results showed the presence of diffractions characteristic of hexagonal phase for GaSe and InSe. The XRD pattern indicated that the as-prepared products have high crystallinity. The cell parameters for GaSe is calculated to be \( a = b = 3.69 \) Å, \( c = 15.73 \) Å, which are in agreement with the values \( a = b = 3.75 \) Å, \( c = 15.81 \) Å reported\(^1\). The cell parameters for InSe is calculated to be \( a = b = 4.87 \) Å, \( c = 16.85 \) Å, which are in agreement with \( a = b = 4.95 \) Å, \( c = 16.93 \) Å presented in Ref.\(^1\).

Elemental content analysis of grown crystals are as follows: the results obtained by the GDOES confirmed nearly stoichiometry content (49.7 at % of Ga and 49.4 at % of Se for GaSe and and 49.8 at % of In and 49.5 at % of Se for InSe. XRF measurements performed on series of InSe crystals showed the next content of the initial components in pure crystals: In in the range from 49.3 at % (Se 49.1 at %) to 49.9 at % (49.3 at %), which are in reasonable agreement with the results obtained by the GDOES. Due to relatively high resistivity- it was not possible to perform reliable XRF measurements for GaSe. Energy dispersive X-ray spectrometer (EDS) analysis indicated only presence of O (oxygen) element in the spectrum, indicating the high purity of grown crystals.

The size of nanoparticles was successfully controled by: • the selection of experimental parameters of rare gas species of Ar or He; • pulse laser power; • the distance between the target and substrate. The results given below are for the next parameters: the laser source is KrF at \( \lambda = 248 \) nm with pulse energy 200 mJ/pulse, pulse duration \( \tau = 10 \) ns, repetition frequency \( f = 10 \) Hz; the quartz substrate is at 77 K and the distance between the target and the substrate is 30 mm.

Series of experiments allowed us to built the output in size distribution (\%) versus gas pressure (histogram) which are shown for GaSe in Fig. 1 (a) and 1 (b) for Ar and He gases, respectively. Using the histograms shown in Fig. 1 (a) and (b) the dependences of mean diameter of synthesized particles versus the gas pressure for Ar and He gases were obtained (these dependences are shown in Fig. 1 (c)) and may be used for obtaining the particles of GaSe with a
preferable given size). As shown in Fig. 1 (c) the size of of ablated particles first decreases with increasing the pressure up to ~ 0.2 Torr and 1.5 Torr for Ar and He gas, respectively) and then increases with pressure. The values obtained for

Figure 1. Histograms for number of ablated GaSe particles (%) versus size (mean diameter in nm) at different pressure for Ar (a) and He (b) gases. GaSe was ablated by using a KrF laser (λ = 248 nm, repetition rate f = 10 Hz, pulse energy P = 200 mJ/pulse, pulse duration τ = 10 ns, number of shorts 100). The distance from source to substrate is ~ 25 mm. The laser light hit the target at the incidence angle of 45°. The particles were grown onto the quartz substrate at 77 K. Lower Fig. (at the middle) represents the size of nanoparticles versus gas pressure at a fixed laser power (derived from the dependences shown in (a) and (b)).

InSe are as follows: the size of ablated particles decreases from ~ 25 nm at pressure ~ 0.05 Torr to ~ 12 nm at ~ 0.2 Torr and then slightly increases with pressure to ~16 nm at 0.5 Torr. For both compounds the results of visual observation of the shape of formed plasma are in good agreement with the results of TEM. It was established that at low pressures (lower than 0.05 Torr and 0.5 Torr for Ar and He gases, respectively) only polycrystalline films are formed. In this case the shape of plasma is feebly marked. With increasing the pressure to 0.05 Torr and 0.5 Torr (for Ar and He gases, respectively) shape of the plasma becomes pronounced and TEM analysis show presence of film and nanoparticles. Further increasing the pressure of the gas leads to formation of strongly pronounced plume having shape close to theoretical one (like an ampoule lump) and there are only nanoparticles onto the quartz substrate. Respective photos are shown in Fig. 2 for He gas (for GaSe). Optimal growing conditions to obtain the output of ~ 30 % particles with minimal sizes are: the gas pressure 0.15 and 1.5 Torr for the particles with sizes 5 nm and 7 nm using Ar and He gases,
respectively. Experiments described above were performed also for InSe. Obtained results are as follows: optimal growing conditions to obtain the output of \(\sim 30\%\) particles with minimal sizes (5 - 10 nm) (for KrF laser \(f = 10\) Hz, pulse duration \(\tau = 10\) ns., pulse energy 200 mJ/pulse, quartz substrate at 77 K) are: Ar and He gas pressure 0.11 and 1.2 Torr, respectively.

Figure 2. Shape of plume formed during ablation in dependence on the gas pressure (less than 0.05 Torr- upper left; 0.5 Torr- middle; 1.5 Torr- right). Lower 3 pictures represent the TEM of GaSe particles ablated at different He gas pressure.

Spectral dependences of optical density of grown particles versus gas pressure (Ar and He) for GaSe and InSe particles for different laser powers were built, analyzed and by using these data absorption gap versus gas pressure were built. It was established that characteristic feature of these dependences is that with increasing gas pressure optical density shifts to lower energies. Absorption gap versus gas pressure (Ar, He) for GaSe particles at different energy of laser pulses (upper dependences), and absorption gap of nanoparticles versus gas pressure at different distances between GaSe pellet and substrate are presented in Fig. 3. It is seen that absorption gap increases with increasing pressure up to about 0.6 Torr (He gas, laser pulse power 200 mJ and He gas, laser pulse power 25 mJ) and then decreases. Nearly same dependences are for Ar gas at laser pulse power 25 and 200 mJ, but in this case particle gaps start to decrease at about 0.1 - 0.15 Torr. With increasing the distance between the target and substrate gas pressure value from which the gap of particles start to decrease and shifts to higher gas pressure (at \(\sim 0.1 - 0.15\) Torr at distance 30 mm and at \(\sim 0.25\) Torr at distance 60 mm for GaSe (for InSe these values are 0.2 - 0.25 and \(\sim 0.35\), respectively)).

We associate the blue shift in the optical absorption spectra of GaSe and InSe with decreasing the particle sizes to the presence of nanocrystals in the quantum size regime (nearly same as it was reported earlier\(^\text{10}\)). According to Brus\(^\text{45}\) an analytical expression for the first excited electronic state of the quantum particle is:

\[
E = \frac{\hbar^2 \pi^2}{2 R^2} \left[ \frac{1}{m_e^*} + \frac{1}{m_h^*} \right] - \frac{1.8 e^2}{\epsilon R} + \text{polarization terms}
\]

(1)

where: the first term is the quantum energy of localization; the second term is the Coulomb attraction; the third term (smaller term) arises from Coulomb interaction in the presence of a crystalline surface; \(R\) is the radius of the particle; \(m_e^*\) and \(m_h^*\) are the effective masses of electron and hole, respectively, and \(e\) is the charge of an electron, \(\epsilon\) is the dielectric constant at the optical frequency. The value of \(E\) represents the energy shift with respect to the value of the band gap for bulk crystal. In Table 1 we present the results of calculation the values of the first 2 terms for different particle sizes neglecting the polarization terms and using the values given in Ref.\(^\text{1}\) for GaSe \((m_e^* = 0.24\) \(m_o, m_h^* = 0.5\) \(m_o, \epsilon = 6.0\), where \(m_o\) is the rest mass of an electron, \(m_o = 9.11 \times 10^{-28}\) gr) and \((m_e^* = 0.14\) \(m_o, m_h^* = 0.5\) \(m_o, \epsilon = 5.0\) for InSe (the...
values for the effective masses and the dielectric susceptibilities were averaged between the corresponding values for the directions perpendicular and parallel to the optical c-axis). The results for GaSe given in Table 1 are in reasonable agreement with those published in Ref.10. It is seen that for nanoparticles of GaSe and InSe the combination of Coulomb term and relatively large effective masses (compared to GaAs, InSb etc.) keeps the excited state energy near the bulk forbidden gap for diameters larger than approximately 20 nm. It was rather difficult to make a comparison of the results of optical absorption experiments (Fig. 3) with the results given in Table 1 (to do this comparison one needs to calculate a value for the absorption coefficient and the effective band gap45. This was out of our interest in the present paper (such a calculations can be performed using a method described in Ref.46).

PL intensity, peak energy and FWHM versus particle size (GaSe) have been investigated also in the present work. It was established that PL intensity is nearly independent on the gas pressure up to ~ 1 Torr (~ 1.5 Torr for InSe) and then increases with increasing pressure up to about 6 Torr (same for InSe). Nearly same behavior was observed for PL peak energy and PL peak FWHM for InSe particles.

![Figure 3. Absorption gap versus gas pressure (Ar, He) for GaSe particles at different energy of laser pulses (upper dependences). Lower dependences represent the absorption gap of nanoparticles versus gas pressure at different distances between the pellet and substrate.](image)

Table 1. Numerical results of the energy terms from eq. (1) for GaSe and InSe nanoparticles of different radii R.

<table>
<thead>
<tr>
<th>R, nm</th>
<th>2</th>
<th>4</th>
<th>5</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kinetic term (GaSe), eV</td>
<td>0.58</td>
<td>0.15</td>
<td>0.09</td>
<td>0.01</td>
</tr>
<tr>
<td>Coulomb term (GaSe), eV</td>
<td>-0.20</td>
<td>-0.10</td>
<td>-0.09</td>
<td>-0.01</td>
</tr>
<tr>
<td>Total shift (GaSe), eV</td>
<td>0.38</td>
<td>0.05</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Kinetic term (InSe), eV</td>
<td>0.52</td>
<td>0.12</td>
<td>0.07</td>
<td>0.03</td>
</tr>
<tr>
<td>Coulomb term (InSe), eV</td>
<td>-0.20</td>
<td>-0.10</td>
<td>-0.07</td>
<td>-0.03</td>
</tr>
<tr>
<td>Total shift (InSe), eV</td>
<td>0.32</td>
<td>0.02</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

Decomposition of the normal vibrations for different polytypes of GaSe (InSe) at the center of the Brillouin zone may be found1. The symmetries of the 24 vibrational mode of the ε-GaSe (InSe) at \( \mathbf{k} = 0 \) are1-3,47

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*Note: The image contains a graph and a table.*
\[
\Gamma = 4A1' + 4A2'' + 4E' + 4E''
\]  
(1)

of which \(A_2'' + E'\) are the acoustic mode; there are 11 non-degenerate Raman active \(4E''\), \(4A_1\), \(3E\) modes and 6 IR active \(3A_2'' + 3E\) modes. The Raman and IR active modes co-exist simultaneously as the crystals do not have an inversion symmetry. RLM is expected in the low-frequency range in which the layers vibrate as rigid units against each other and that there is no relative displacement of the Ga (In in case of InSe) and Se atoms within a layer. Existing data for the Raman spectra show that for \(\beta\)-GaSe only 7 of the 11 theoretically predicted phonons were observed at 19 cm\(^{-1}\) (\(E\)), 59 cm\(^{-1}\) (\(E''\)), 134 cm\(^{-1}\) (\(A_1\)), 209 cm\(^{-1}\) (\(E''\)), 213 cm\(^{-1}\) (\(E'(TO)\)), 253 cm\(^{-1}\) (\(E(LO)\)), and 308 cm\(^{-1}\) (\(A_1\)), where LO and TO are for the longitudinal and transverse optical phonons, respectively (frequencies of Raman active phonons obtained in the present work for bulk GaSe crystals are nearly same. See Table 2).

For bulk crystals of \(\beta\)-InSe we observed 5 Raman active phonon modes at 18 cm\(^{-1}\) (\(E\)), 41 cm\(^{-1}\) (\(E''\)), 113 cm\(^{-1}\)(\(A_1\)), 172 cm\(^{-1}\) (\(E''\)), and 223 cm\(^{-1}\) (\(E\)) (see Table 3), which are in accordance with previously published in Ref. 48. We observed also low frequency phonon band at 18 cm\(^{-1}\) in the IR absorption spectra. Latter allowed us to assign the symmetries of phonon bands for bulk InSe on the basis of \(\beta\)-InSe (due of the fact that the line at 17 cm\(^{-1}\) is simultaneously Raman and IR active, which is excluded for centrosymmetric \(\beta\)- modification. It is worth to mention that in previous publication the assignment of Raman active modes for InSe have been made by supposing \(\beta\)- polytype\(^{49}\). In the present work, we observed 5 Raman active modes for GaSe nanoparticles (also 5 for InSe). Symmetry, energy position of Raman bands versus particle size for GaSe and InSe are presented in Table 2 and Table 3, respectively. Characteristic feature of all Raman bands for both compounds is that- small geometrical dimensions of the scattering particles lead to a downshift (shifting to lower frequency) and broadening of Raman bands. Relative shift (\(\omega_{\text{bulk}} - \omega_{\text{part}})/\omega_{\text{bulk}}\), where \(\omega_{\text{bulk}}\) and \(\omega_{\text{part}}\) is for phonon in bulk crystal and nanoparticles with given sizes, respectively) is more pronounced for the low frequency range phonons (21, 60 cm\(^{-1}\) (GaSe) and 18, 41 cm\(^{-1}\) (InSe)). Fig. 4 represents the size dependence frequency position for the RLM of GaSe measured at room temperature. It is seen that with decreasing the particle size the energy position of the low-frequency RLM shifts to lower frequency. Observed behavior may be qualitatively explained taking into account that tensile and compressive stress affect the Raman line by a redshift and a blue shift respectively, while spherical microcrystals smaller than 1000 nm lead to downshift and broadening\(^{40}\), which is typical for the results obtained in the present work.

\[
\begin{align*}
\text{Intensity (arb. units)} & \\
\text{Raman Shift (cm}^{-1}\text{)}
\end{align*}
\]

Figure 4. Particle size dependence for the low-frequency RLM of GaSe. Spectra were excited at room temperature by the 514.5 nm of an Ar\(^+\) laser and a double-pass spectrometer (Jobin Yvon U-1000) with the photon counting system equipped with a photomultiplier (RCA-C3 1034) and a multichannel analyzer (Canberra Series 40). The measurements were made at room temperature in the back scattering geometry.

From the low frequency Raman data for GaSe, decrease of the force constant for the RLM ~ 25 % (in a frame of linear chain model for the lattice dynamics of GaSe, developed by Wieting\(^{41}\) due to formation of nanoparticles were estimated in the present work. This conclusion was obtained by using the data presented in Ref\(^{51}\): the shearing interlayer force

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constant for the low-frequency RLM of GaSe (19.1 cm⁻¹) is $C_s = 1.61 \times 10^3$ dyn/cm. Assuming linear dependence of the RLM frequency on the force constant we get $C_s = 1.22 \times 10^3$ dyn/cm at a frequency of 16 cm⁻¹ (the particle with size 16 nm. See Table 2), which is ~25% less than for bulk crystal. The origin of this may be connected with decreasing amount of ionic contribution to the interlayer forces (it is only theoretically supposed occurrence of pure Van der Waals forces between the layers. In reality some ionic contribution takes place also from surrounding atoms).

Table 2. Symmetries and frequencies of Raman active phonons for GaSe nanoparticles versus particle sizes $\varnothing$ (nm).

<table>
<thead>
<tr>
<th>Symmetry</th>
<th>GaSe (bulk), cm⁻¹</th>
<th>GaSe, $\varnothing$ 30nm, cm⁻¹</th>
<th>GaSe, $\varnothing$ 15 nm, cm⁻¹</th>
<th>GaSe, $\varnothing$ 10nm, cm⁻¹</th>
<th>GaSe, $\varnothing$ 5 nm, cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E'$</td>
<td>21</td>
<td>19</td>
<td>18</td>
<td>17</td>
<td>16</td>
</tr>
<tr>
<td>$E''$</td>
<td>60</td>
<td>57</td>
<td>53</td>
<td>50</td>
<td>47</td>
</tr>
<tr>
<td>$A_1$</td>
<td>135</td>
<td>133</td>
<td>130</td>
<td>126</td>
<td>123</td>
</tr>
<tr>
<td>$E$</td>
<td>254</td>
<td>252</td>
<td>249</td>
<td>247</td>
<td>245</td>
</tr>
<tr>
<td>$A_1$</td>
<td>310</td>
<td>308</td>
<td>306</td>
<td>302</td>
<td>299</td>
</tr>
</tbody>
</table>

Table 3. Symmetries and frequencies of Raman active phonons for InSe nanoparticles versus particle sizes $\varnothing$ (nm).

<table>
<thead>
<tr>
<th>Symmetry</th>
<th>InSe (bulk), cm⁻¹</th>
<th>InSe, $\varnothing$ 35nm, cm⁻¹</th>
<th>InSe, $\varnothing$ 18 nm, cm⁻¹</th>
<th>InSe, $\varnothing$ 12nm, cm⁻¹</th>
<th>InSe, $\varnothing$ 7 nm, cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E'$</td>
<td>18</td>
<td>16</td>
<td>15</td>
<td>12</td>
<td>13</td>
</tr>
<tr>
<td>$E''$</td>
<td>41</td>
<td>37</td>
<td>32</td>
<td>29</td>
<td>27</td>
</tr>
<tr>
<td>$A_1$</td>
<td>113</td>
<td>109</td>
<td>106</td>
<td>102</td>
<td>99</td>
</tr>
<tr>
<td>$E''$</td>
<td>172</td>
<td>169</td>
<td>166</td>
<td>163</td>
<td>160</td>
</tr>
<tr>
<td>$E$</td>
<td>223</td>
<td>220</td>
<td>218</td>
<td>216</td>
<td>213</td>
</tr>
</tbody>
</table>

We used developed method of nanoparticles growth for preparation of laser radiation converters using the nanoparticles of GaSe. As a result we converted pulsed and continuous IR (900 - 1360 nm) laser radiation into the visible spectral range (450 - 680 nm) using a transparent substrate covered with the nanoparticles of GaSe. Based on the physical phenomenon of SHG in nonlinear media the device structures prepared convert pulsed and continuous IR laser radiation (900 - 1360 nm) into a spectral range which can be detected by human eyes in transmission or reflection geometry as a visible spot corresponding to the real size of the incident laser beam (commercial laser light visualizators do not show this peculiarity). In conjunction with a photomultiplier these device structures can be used for detecting the IR signals from high power lasers operating up to 2000 nm. At pulse energy less or equal 69 µJ (wavelength 1053 nm) commercially available visualizators (sensors) showed weak SHG signal, whereas our device structures showed already well noticeable and intensive green signal. Low energy limit for visualization of the IR laser pulses using our structures are: between 2.1 - 1.0 µJ at 1200 nm; 5.3 - 1.1 µJ at 1300 nm and 11.0 - 7.0 µJ at 1360 nm (in comparing with the same parameters for bulk crystals (3.2 - 1.3 µJ at 1200 nm; 6.8 - 1.5 µJ at 1300 nm and 12.9 - 7.6 µJ at 1360 nm) and for polycrystals of GaSe (4.6 - 2.1 µJ at 1200 nm; 8.4 - 2.6 µJ at 1300 nm and 14.4 - 8.1 µJ at 1360 nm). The device structures prepared in the present work may be used: • for optical alignment and visualization of the near IR lasers; • for checking if the laser is emitting; • for visualization of the distribution of the intensity of laser radiation over the cross of the beam; • for investigation of content of the laser radiation; • in the area which uses the diode lasers for optical and telecommunications systems etc. It is worth to mention that we do not interpret the origin of Raman active mode near ~ 230 cm⁻¹ and IR active mode near ~ 275 cm⁻¹ for bulk GaSe as possible surface phonon modes (it was mentioned in our Abstract submitted to the AMPL XII). This idea came from the fact that more detailed experiments performed in large amount of bulk crystals revealed that these modes are not characteristic for all bulk GaSe crystals studied. To reveal a nature of these modes additional investigations are necessary including temperature dependences of IR spectra.
4. CONCLUSIONS

Several conclusions are as follows:

1. High quality NLO crystals of GaSe and InSe were grown by the Bridgman-Stockbarger method having a size of 20 mm in diameter and 60 mm in length. The crystals were characterized using XRD, XRF, GDOES analysis, Raman and IR spectroscopy. It was shown that both compound belong to the hexagonal non-centrosymmetric \( \varepsilon \)-modification (space group \( D_{3h}^\infty \), two layers per primitive unit cell) and have nearly stoichiometry content: Ga in the range from 49.3 at\% (Se 50.7 at\%) to 47.7 at\% (Se 51.3 at\%) for GaSe, and In in the range from 49.3 at\% (Se 49.1 at\%) to 49.9 at\% (Se 49.3 at\%) for InSe (XRF results for InSe crystals. Nearly same results were obtained by GDOES analysis). Five Raman active phonons were recorded for bulk crystals of each compound.

2. The nanoparticles of GaSe and InSe have been synthesized using LA method. The size of nanoparticles was successfully controlled by selection of the experimental parameters of rare gas species of Ar or He (for GaSe): at pressures lower than 0.1 Torr the particles with diameter more than 12 nm were obtained. Increasing the gas pressure more than 0.1 Torr results to formation of particles with diameter 7 nm and less (at gas pressure 1 Torr). Further increasing the pressure leads to increasing the particle sizes (10 nm at 4 Torr). For InSe these parameters are as follows: the size of ablated particles decreases from \( \sim 25 \) nm at pressure \( \sim 0.05 \) Torr to \( \sim 12 \) nm at \( \sim 0.2 \) Torr and then slightly increases with pressure to \( \sim 16 \) nm at 0.5 Torr.

3. Blue shift in the optical absorption spectra of GaSe and InSe with decreasing the particle sizes was explained by presence of nanocrystals in the quantum size regime. These results are consistent with a perturbation of GaSe and InSe band structure due to carrier confinement, resulting in a widening of the forbidden gap.

4. Five Raman bands were observed for nanoparticles of both compounds. The long-wavelength shift of the position of each band and they broadening are qualitatively explained taking into account that tensile and compressive stress affect the Raman line by a redshift and a blue shift respectively, while spherical crystals smaller than 1000 nm lead to downshift and broadening.

5. It is shown, that with decreasing the particle size the energy position of the low-frequency phonon modes in both compounds are shifted to lower frequencies (21 and 18 cm\(^{-1}\) in bulk GaSe and InSe and 8 and 7 cm\(^{-1}\) in particle with sizes 5 and 7 nm, respectively). From the low frequency Raman data, decrease of the force constants ca. 25 % (for GaSe) due to nanoparticles formation are estimated. The origin of this qualitatively explained (for GaSe) by supposing decreasing amount of ionic contribution to the interlayer forces with decreasing the size of the particles.

6. GaSe nanoparticles grown in the present work have been used for preparation of laser radiation converters. As a result it became possible to converted pulsed and continuous IR (900-1360 nm) laser radiation into the visible spectral range (450 – 680 nm) by using a transparent substrate covered with the nanoparticles of GaSe. Low energy limit for visualization of the IR laser pulses using our structures are: between 2.1 - 1.0 \( \mu J \) at 1200 nm; 5.3-1.1 \( \mu J \) at 1300 nm and 11.0-7.0 \( \mu J \) at 1360 nm (in comparing with the same parameters for bulk crystals (3.2 - 1.3 \( \mu J \) at 1200 nm; 6.8 - 1.5 \( \mu J \) at 1300 nm and 12.9 - 7.6 \( \mu J \) at 1360 nm) and for polycrystals of GaSe (4.6 - 2.1 \( \mu J \) at 1200 nm; 8.4 - 2.6 \( \mu J \) at 1300 nm and 14.4 - 8.1 \( \mu J \) at 1360 nm ). The device structures prepared in the present work have wide range of applications, including the area which uses the diode lasers for optical and telecommunications systems etc.

REFERENCES


