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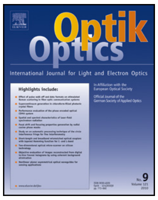

Original research article

Optical and non-linear optical properties of the solid solutions $AgGaGe_{3(1-x)}Si_{3x}Se_8$

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ABSTRACT

Solid state solution $AgGaGe_{3(1-x)}Si_{3x}Se_8$ in the range of x = 005–030 were synthesized and absorbance, FTIR, Raman spectroscopy, second harmonic generation measurements has been performed to explore linear and non-linear optical features The measured SHG intensity demonstrate significant dependence of non-linear optical properties from silica content. Analysing of Urbach's energy and Raman spectra allowed to determine the degree of defect depending on the chemical composition and temperature.

1. Introduction

Single crystals and polycrystalline metal mixed due to wide window of transparency up to several micrometers are used as active part of many optical devices operating in IR spectral range [1]. The unique crystal structure of the chalcogenide compounds give opportunity partial or complete substitution of cation or anion groups, and finally resulting significantly improve desired properties of pure compounds [2,3].

The significant field of applications metal chalcogenide compounds is nonlinear optics in infrared spectral range [1–3]. In particular, an effective method of searching for new materials is a changing the chemical composition: systematic substitution of one type of ion by another isovalent ion, possess differ ion radius. The strains of the crystallographic network introduced by this method (substitution Ge by Si) and at the same appearance of defects strongly affect non-linear optical properties [4].

Solid state solution $Ag_xGa_xGe_{1-x}Se_2$ in the range of 64–90 mol.% $GeSe_2$ were synthesized during the investigation of the $AgGaSe_2$–$GeSe_2$ phase diagram [5]. The composition of $AgGaGe_3Se_8$ ($x = 0.333$) corresponds to the melting point maximum.

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These crystals are already quite extensively studied [6,7] having proved itself a promising nonlinear optical [8] and piezoelectric material [9]. Efforts to improve its properties led to the discovery of solid solutions with cation (Ag → Cu [10], Ga → In [11], Ge → Sn [12], Ge → Si [13]) and anion (Se → Te [14] Se → S [15]) substitutions.

The studies of the crystals doped with Cu, In, Sn, Te were performed in [10,14]. The solid solution range was determined by plotting phase diagrams for the systems of $AgGaGe_3Se_8$ and another, hypothetical, compound with a completely substituted element (e.g. $AgGaGe_3Se_8$–'$AgInGe_3Se_8$'). The extent of the solid solutions in these systems is quite narrow and does not exceed 12–15 mol.% in the case of Ga → In [11] or Ge → Sn [12], or even smaller for the substitutions Ag → Cu [10] and Se → Te [14]. The uniform effect of the substitute element was studied in [10,14] using crystals with 5 mol.% dopant for the starting batch composition. But the study of the effect of the dopant concertation on the $AgGaGe_3Se_8$ parameters is also of interest, especially for the practical applications for the spectrally operated nonlinear optical devices. The solid solutions $AgGaGe_{3(1-x)}Si_{3x}Se_8$ that forms in the $AgGaGe_3Se_8$–'$AgGaSi_3Se_8$' system was selected as it has the widest region of solid solubility ($0 < x < 0.33$) for the cation substitutions. Earlier [13] we presented the results of the investigation of piezoelectric properties. Here we report the study of the dependence of optical properties in visible and IR regions, and second harmonic generation (SHG) versus Si content in the crystals of the $AgGaGe_{3(1-x)}Si_{3x}Se_8$ solid solutions for $x = 0.05$; 0.1; 0.2; 0.3.

The main goal of the present work is to explore linear and second order non-linear optical features $AgGaGe_{3(1-x)}Si_{3x}Se_8$ compounds. We will study the corresponding features at different temperatures for the fundamental absorption The FTIR and Raman spectra were studied. The second harmonic generation (SHG) was carried out versus the angle for samples with different composition for different light polarization and was spectrally separated using the interferometric filters.

2. Experimental

The growth and quality control of the investigated crystals was described elsewhere [13]. Optical spectra studies in the visible spectrum were performed using an MDR-206 monochromator with a silicon-based photosensor. Temperature measurements were performed in a nitrogen cryostat equipped with a Utrecs K41-3 thermo-regulator with 0.1 K accuracy. Optical absorption spectra in the intrinsic transition region were studied using thin parallelepiped samples (0.08–0.10 mm thickness) with optical-quality, parallel-plane surfaces.

IR transmission spectra were investigated using Spectrum Two^{TM} FTIR Spectrometer (PerkinElmer) with spectra resolution 1.5 nm. SHG studies at a pulse laser 1064 nm wavelength with pulse duration 7 ns, pulse frequency repetition 10. . .20 Hz. The output signal was connected with the photomultiplier with relaxation 1 ns connected with oscilloscope Tektronix (1 GB0).

The Raman spectra were obtained using in Via micro Raman (Renishaw) spectrometer. The continuous wave He-Ne laser ($\lambda = 633$ nm) was used as an excitation light source. The measurements were carried out in the backscattering configuration using Leica DM 2500 M microscope equipped with 50x lens magnification, which give 1,0 μm of a laser spot size. The data were collected at low energies (about 0.12 mW) and 10 s of exposure time, within the range of 50–1000 cm^{-1} and 2 cm^{-1} spectral resolution.

3. Results and discussion

Single crystals of the $AgGaGe_{3(1-x)}Si_{3x}Se_8$ solid solutions, like the original $AgGaGe_3Se_8$, possess high concentrations of defects, prevailingly silver vacancies [6], and their properties approach those of disordered systems [15] as confirmed by the investigations of the frequency dependence of the fundamental absorption edge.

Energy dependence of the absorption coefficient of the $AgGaGe_{2.4}Si_{0.6}Se_8$ crystal ($x = 0.2$) in the temperature range 100–300 K is presented in Fig. 1a. The spectra of other studied crystals have similar shapes, differing only in the exact energy position of the spectral curves. Bandgap energy of the crystals was estimated for $\alpha = 280\ cm^{-1}$. The results of the E_g evaluation are plotted in Fig. 2.

The band gap at ambient temperature decreases from 2.11 to 2.07 eV with increase of x from 0.05 to 0.30. This E_g decrease is clearly consequence of the partial substitution of Ge^{4+} by Si^{4+} possessing smaller ionic radii (0.044 nm and 0.039 nm, respectively) [16]. Such dependence is common feature other multinary chalcogenide crystals [17]. An additional contribution to the band gap decrease can also be provided by vacancy-type defects which these crystals are rich in [6,18].

Temperature dependence of the band gap energy of the solid solution in the temperature range of 100–300 K is linear (Fig. 2). Calculated thermal coefficient of the band gap variation is equal to $\beta = dE_g/dT = -9{\cdot}10^{-4}$ eV/K, and is almost the same for all crystals. The negative sign of the coefficient suggests [19] that the contribution of the electron-phonon interaction with increasing temperature is greater than the contribution from the thermal expansion of the lattice.

The absorption edge of the studied crystals is described well by the exponential dependence (Fig. 1b) known as Urbach's rule [20]: $\alpha = \alpha_0 \exp\left(\frac{h\nu - E_0}{E_U}\right)$.

The reasons for such behavior of the absorption edge are explained in [21,22] that suggest that such dependence results from the fluctuation of band angles and lengths; in energy terms, tailing results from the transitions between the localized states at the edges of the bands.

The calculated parameters of Urbach's energy ($E_U = k_B/\sigma(T)$ where k_B is Boltzmann constant, $\sigma(T)$ is the parameter of the slope of the absorption edge) are equal to 54; 58; 60; 73 meV for the crystals with $x = 0.05$; 0.10; 0.20; 0.30 respectively. The