Evolution of $GaSe_{1-x}S_x$ phonon absorption peaks with S-doping studied by THz-TDS

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***Abstract*—A dense set of solid solution crystals $GaSe_{1-x}S_x$ is examined using THz-TDS. Evolution of phonon absorption peaks with the increase of S content is shown to have complex transformation, which should be considered in the design of dispersion equations for THz applications.**

I. Introduction

Efficiency of laser frequency conversion in layered nonlinear GaSe crystals increases with heavy S-doping, also described as solid solution crystals GaSe:GaS or $GaSe_{1-x}S_x$, where x is the mixing ratio [1]. At the optimal S-doping of between 2 and 3 mass.%, the frequency conversion efficiency of $GaSe_{1-x}S_x$ is up to 3 times higher than that of GaSe under identical pumping conditions and up to 15 times higher at limit pump intensity [2,3]. This increase is due to the outstanding optical properties of the parent GaSe and GaS crystals, to the lower number of defects and stacking faults, as well as to the modification of some other physical properties [1]. Successful growth and use of $GaSe_{1-x}S_x$ crystals for laser frequency conversion calls for adequate data on the ordinary (n_o) and extraordinary (n_e) wave dispersions.

Dispersion properties for the full transparency range of $GaSe_{1-x}S_x$ can be estimated quite accurately by using the available dispersion data for parent crystals [4], or for one parent and the selected solid solution crystal [5]. On the other hand, to date there have been very few direct measurements of $n_{o,e}$ in the THz range. Recently dispersion properties in the THz range were studied in detail by using samples cut parallel and orthogonal to the optical axis, but no detailed attention was given to the analysis of phonon structure, peak profile transformation or spectral shift with S-doping [6,7]. This new data confirms some of the previous results [8], but differs from others, which did not observe new phonon peaks and their transformation due to doping [9]. The presence and transformation of profiles of phonon absorption peaks resulting in transformation of relative input in the dielectric responce (ranges of abnormal dispersion) should be taken into account in designing dispersion equations, as has been done for the well-known rigid phonon peak in GaSe at 0.59 THz [10].

In this study, the transformation of phonon structure and peak parameters with sulphur doping was studied by THz time-domain spectroscopy (THz-TDS) and FTIR between 0.2-4 THz, and was analysed in detail for a range of different compositions high optical quality $GaSe_{1-x}S_x$ crystals (x=0.002, 0.006, 0.014, 0.046, 0.09, 0.103, 0.133, 0.175, 0.216, 0.294, 0.406, 0.412, 0.44) grown by modified technology with heat field rotation [11].

II. Results

It has been established that the intensity of the rigid phonon mode $E'^{(2)}$ at 0.59 THz in o-wave spectrum for GaSe decreases with increasing S-doping (Fig.1) till collapsing, similarly to that for Te-doping [8].

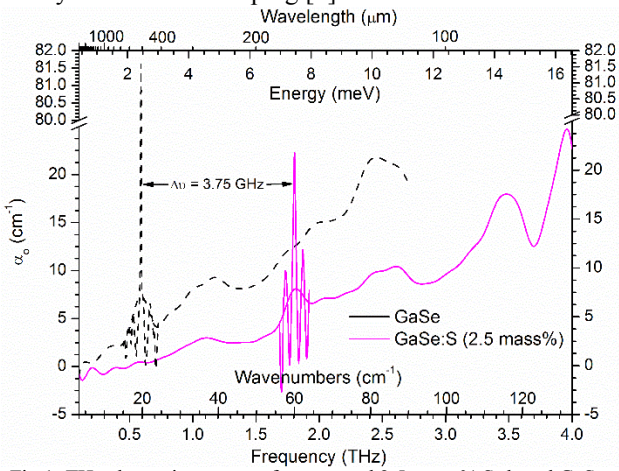
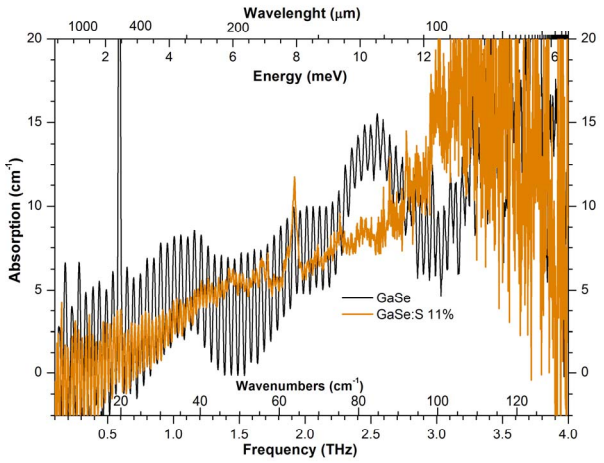


Fig.1. THz absorption spectra for pure and 2.5 mass.% S-doped GaSe.

In Fig.1 it is seen that $E'^{(2)}$ phonon peak completely disappears at optimal 2.5 mass% S-doping. It was also found clearly in e-wave spectrum (in difference to data in [9]) that the $E''^{(2)}$ phonon mode at 1.7 THz grows with S-doping and shifts to higher frequencies at a gradient of 17 GHz/1 mass%, confirming conclusions reported in [7].



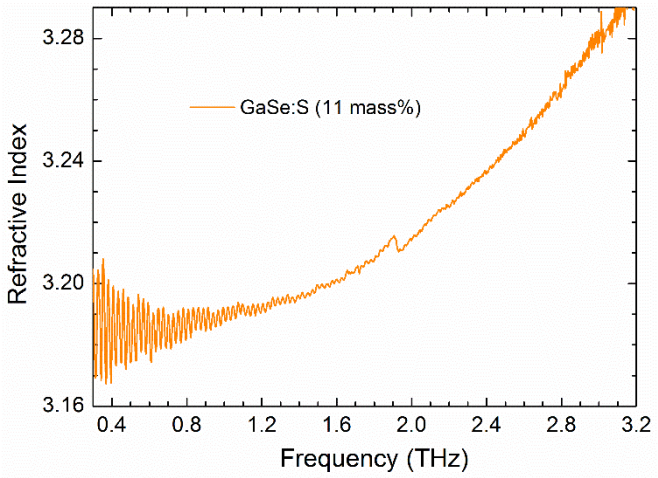


Fig.2. (A) Absorption spectra for o-wave in pure and e-wave in 11 mass% S-doped GaSe, (B) e-wave dispersion in 11 mass% S-doped GaSe.

For the first time, arising and frequency-shifting of other phonon peaks (forexample at 1.9 THz (Fig.2A) were also clearly observed in e-wave absorption spectrum of heavily (11 mass%) S-doped GaSe that resulted in arising of abnormal dispersion region (Fig.2B).

The intensity and spectral width of the phonon absorption peaks was also found to be dependent on S-doping and crystal temperature. Fig. 3 presents shifts in phonon peak as recorded by THz-TDS.

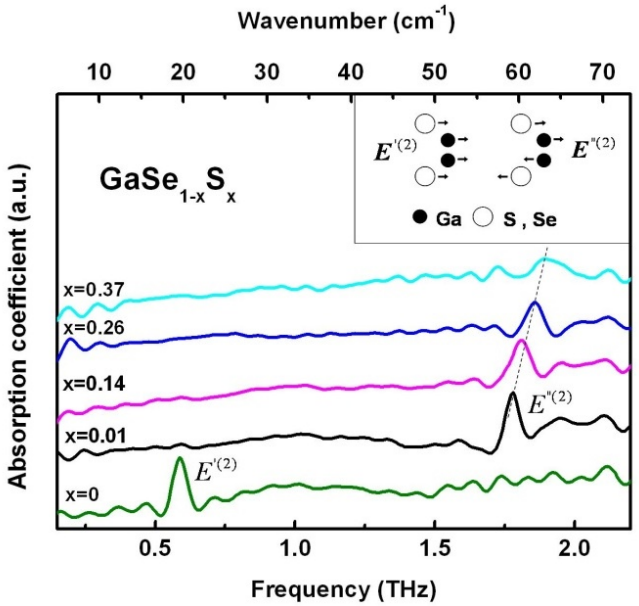


Fig. 3. The spectral shift of 1.7 THz phonon absorption peaks with S-doping.

Moreover, it was established that spectral measurements with frequency resolution better than 3 GHz are necessary to determine the nonlinear dependence of the phonon linewidth on dopant concentration, and to apply it in designing dispersion equations (Fig.4).

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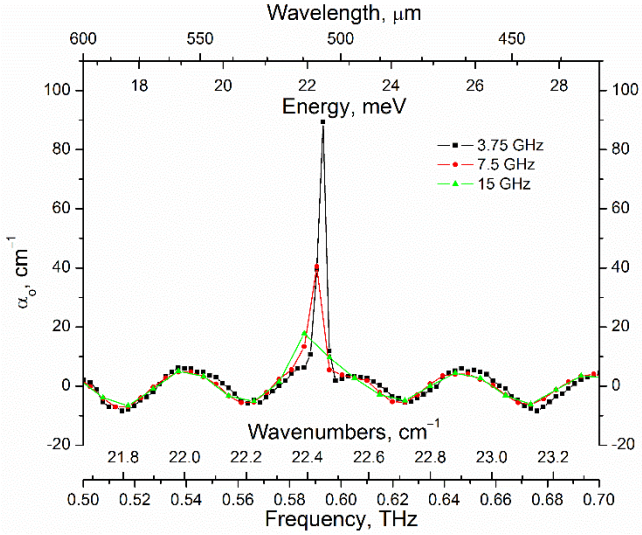

Fig.4. Effect of THz-TDS spectral resolution on phonon amplitude.

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