We present the systematic study of the structure and elastic properties of the metastable crystalline and amorphous ternary (GaSb)$_{1-x}$Ge$_x$ and (InSb)$_{1-x}$Ge$_x$ solid solutions with composition varied nearly over all concentrations of components. The high-pressure technology for synthesis of these metastable substances as bulk amorphous samples consist in the complete solution of the components under pressure in the region of stability of the metallic high-pressure phases of Ge, GaSb, and InSb (at $P>8$ GPa) with subsequent solid-state amorphization to semiconductor phase upon compression. The metastable crystalline (GaSb)$_{1-x}$Ge$_x$ solid solutions are in turn obtained by room-pressure crystallization of the corresponding amorphous compounds before their decay into an eutectic mixtures. By the way the whole set of the synthesized samples provides a controllable variation of the configurational and topological disorder in tetrahedrally-bonded semiconductors. For (GaSb)$_{1-x}$Ge$_x$ solid solutions, it is found that elastic moduli for crystalline phases are systematically higher than those for amorphous counterparts or comparable at all Ge concentrations $x$. The both amorphous (GaSb)$_{1-x}$Ge$_x$ and (InSb)$_{1-x}$Ge$_x$ solutions have elastic moduli considerably below a potential linear interpolation between the corresponding characteristics of crystalline Ge and GaSb or InSb. Particularly, for the (GaSb)$_{1-x}$Ge$_x$ solid solutions, it is found that the moduli of crystalline phases initially decrease with Ge concentration, falling down to minimum values at 20 to 30 % of Ge. The minimal values of elastic moduli for amorphous samples are observed at 50 to 60 % of Ge. Using experimental data, we argue that elastic softening of tetrahedrally-bonded solid solutions, both amorphous and crystalline, is related to the degree of geometrical disorder, which in turn includes contributions of configurational (or chemical) and topological disorder.

**Introduction**

Firstly, amorphous tetrahedrally bonded semiconductors (IV group elements, such as Si and Ge, as well as III-V compounds, GaAs, GaSb, InSb, etc.) were obtained in the form of thin films by different methods, like evaporation, sputtering, etc. ($d=1000$ Å) [1-3]. Such geometrical form of samples essentially restricts the experimental possibility to study mechanical and elastic properties. Method of high-pressure solid-state amorphization allowed one to synthesize the bulk samples of amorphous tetrahedral semiconductors [4-7]. The basic idea of the high-pressure technology for synthesis of these metastable substances as bulk samples consists in the complete solution of the components under pressure in the region of stability of the metallic high-pressure phases of semiconductors (Ge, GaSb, and InSb in the current case, where pressure should exceed 8-10 GPa) with subsequent solid-state amorphization to semiconductor phase upon compression.
The high-pressure solid state amorphization technique is applicable for synthesis of amorphous ternary solid solutions between IV-group elements and III-V compounds, particularly, \(a-(\text{GaSb})_{1-x}\text{Ge}_{2x}\) alloys [7-9]. In turn, the metastable crystalline \(c-(\text{GaSb})_{1-x}\text{Ge}_{2x}\) solid solutions can be obtained as bulk samples by room-pressure crystallization of the corresponding amorphous compounds before their decay into an eutectic mixtures [8,9]. Although the crystalline \((\text{GaSb})_{1-x}\text{Ge}_{2x}\) solid solutions, as well as crystalline \((\text{GaAs})_{1-x}\text{Ge}_{2x}\), have been studied both experimentally [10-17] and theoretically [18-31], the elastic properties of the such type tetrahedrally bonded ternary solid solutions was not practically studied to date [32,33]. Moreover, the information on elasticity on the pseudobinary ternary solid solutions formed by III and V elements is also rather scanty [32,33].

In this respect, the existence of the bulk samples provides new opportunity to study in detail their macroscopic properties, including mechanical and elastic characteristics. The first ultrasonic study of the amorphous GaSb and \((\text{GaSb})_{1-x}\text{Ge}_{2x}\) \((x=0.27)\) semiconductors prepared by the high-pressure solid state amorphization technique evidenced that their elastic moduli were less than those for the crystalline counterparts, while densities for amorphous and crystalline samples were almost the same [34]. This result was intriguing, but could not still clarify general relations driving the elasticity of complicated and partially disordere tetrahedrally bonded semiconductor compounds.

The systematic study of the elastic shear \(G\) and bulk \(B\) moduli in metastable ternary \((\text{GaSb})_{1-x}\text{Ge}_{2x}\) (amorphous and crystalline) and \((\text{InSb})_{1-x}\text{Ge}_{2x}\) (amorphous) solid solutions with compositions varied over all Ge concentrations is presented in this paper. The variation of Ge in the solid solution leads to a change of average covalence in the system and to a variation of the chemical and, so, the geometrical disorder, because of covalent bonds between different atoms have different length. Comparison of amorphous and crystalline solid solutions provides the possibility to extract the role of topological disorder in elasticity of amorphous tetrahedral semiconductors. By the way the whole set of the synthesized samples provides a controllable variation of the configuration and topologic disorder in tetrahedrally bonded semiconductors.

**Experimental**

\(a-(\text{GaSb})_{1-x}\text{Ge}_{2x}\) and \(a-(\text{InSb})_{1-x}\text{Ge}_{2x}\) samples were synthesized by the method of solid-state amorphization [4-9] in the toroid-type high pressure chamber [35]. In \(a-(\text{GaSb})_{1-x}\text{Ge}_{2x}\) the Ge concentration was varied from 0 to 75 %, since at higher Ge concentration the crystalline solid solutions with structures of BC-8 or ST-12 type are formed [6-9]. As for \(a-(\text{InSb})_{1-x}\text{Ge}_{2x}\) the Ge concentration was initially varied from 0 to 100 %. Unfortunately, these samples contained admixtures of crystalline phases, and an efficient concentration of Ge in amorphous component, as well as the portion of amorphous fase in the samples will be discussed later. The crystalline solid solutions \(c-(\text{GaSb})_{1-x}\text{Ge}_{2x}\) were obtained by annealing of the corresponding amorphous samples [8,9]. The structure of the samples was determined by X-ray diffraction (Cu \(K_{\alpha}\) and Mo \(K_{\alpha}\)). Density of the specimens was determined by the picnometric method. The hardness of samples was investigated by the Vickers method. The ultrasonic measurements were carried out on the "Akustomer-1" [36] and consisted in determination of the flight time of 10 MHz ultrasonic pulses generated by either shear or compression wave piezoelectric transducers. The pulse flight times in the sound line with or without a sample were determined to an accuracy of few nanoseconds. The faces of samples were polished to be parallel within few microns. Elastic moduli were determined from the sound wave velocities in the approximation of isotropic medium, using equations \(\rho V_{L}^{2}=B+4/3G\) and \(\rho V_{T}^{2}=G\), where \(\rho\) is density and \(V_{L}\) and \(V_{T}\) are the longitude and transverse sound wave velocities, respectively.
The typical x-ray diffraction data for $a$-(GaSb)$_{1-x}$Ge$_{2x}$ are shown in Fig. 1. Only at low Ge concentrations ($x<10\%$) we observed admixture of crystalline solid solutions in accordance with [37]. Experimentally it has been established that the densities of amorphous and crystalline (GaSb)$_{1-x}$Ge$_{2x}$ counterparts with the same concentrations are very close to each other and with experimental accuracy corresponds to the Vegard’s law for lattice constants of crystalline alloys. Experimental data on Vickers’ hardness of the both amorphous and crystalline (GaSb)$_{1-x}$Ge$_{2x}$ solid solutions are presented in Fig. 2. The hardness values for amorphous and crystalline (GaSb)$_{1-x}$Ge$_{2x}$ samples are sufficiently close and increase with Ge concentration. It is naturally to assume that such behavior related to the growth of the covalence in the system and increasing of the average bond energy per atom, since the plastic deformation of the covalent materials during indentation is accompanied by numerous breaking of the covalent bonds.

Fig. 3 shows the results of systematic study of the elastic moduli in amorphous and crystalline metastable ternary solid solutions (GaSb)$_{1-x}$Ge$_{2x}$ with composition varied over all Ge concentrations. The bars in figures correspond to scattering of the repeated measurements for the same sample. At the same time the scattering of experimental points over different concentrations show real uncertainty of experimental data and probably related to the synthesis conditions uncertainty, possible concentration heterogeneity in the samples, influence of the small sample size on the ultrasonic measurements, etc.

For (GaSb)$_{1-x}$Ge$_{2x}$ solid solutions, it is found that elastic moduli for crystalline phases are systematically higher than those for amorphous counterparts or comparable at all Ge concentrations $x$. The difference amounts to 40\%, whereas at 20–30\% Ge the both values are rather close. The densities of amorphous and crystalline phases with the same compositions coincide with accuracy of 5\%. At the same time, the moduli of crystalline
phases initially decrease with Ge concentration, falling down to minimum values at 20–30 % Ge. The increasing of the Ge concentrations \( x \) (up to 10–20 % Ge) in amorphous solid solutions \( a-(\text{GaSb})_{1-x}\text{Ge}_x \) initially leads to the growth of elastic moduli, and then the moduli remarkably decrease. The minimal values of elastic moduli for amorphous samples are observed at 50–60 % Ge, i.e., with some shifts with respect to the corresponding minima on the dependences for the crystalline solutions.

### \( a-(\text{InSb})_{1-x}\text{Ge}_x \) solid solutions

Fig. 4 shows the example of X-ray diffraction pattern for \( a-(\text{InSb})_{0.6}(\text{Ge}_2)_{0.4} \) sample. All the diffraction patterns are similar and demonstrate the existence of small volume fraction (5–15 % for different samples) of crystalline phase. The positions of crystal peaks indicate on existence only pure or nearly pure crystalline InSb. So we may recalculate the effective Ge concentration \( x^\text{eff} \) in the amorphous phase, taking into account that x-ray scattering is proportional to the average square of atomic number (number of electrons \( <z^2> \)). Depending on the crystal phase content the effective Ge concentration slightly increases.

The Vickers’ hardness for \( a-(\text{InSb})_{1-x}\text{Ge}_x \) either increase but the character of growth of more drastic and at 50 % Ge reaches the satiation (Fig. 5). Fig. 6 presents the results of study of the elastic moduli in amorphous \( (\text{InSb})_{1-x}\text{Ge}_x \) solid solutions. The behavior of the elastic
constants vs Ge concentration differ from those in \( a-(GaSb)_{1-x}Ge_x \), but it should note the similarity of \( B \) and \( G \) modulii dependences. The increasing of the effective Ge concentration till 50% leads to the remarkable growth of elastic moduli. Then the elastic constants slightly fall down forming not large maximum. Here it is important to note that samples with high Ge concentrations contain near 15% of crystalline InSb, which is the significantly softer material with respect to amorphous Ge. One can suppose that decrease of mechanical characteristics at high Ge concentration can be related to morphology effects of the presence of the soft material with concentration nears the volume percolation threshold [37]. At intermediate Ge concentrations, the share of crystalline admixtures is less (~5%).

**Fig. 5.** Vickers' hardness vs Ge concentration for amorphous InSb-Ge solid solutions.

**Fig. 6.** Concentration dependences of shear \( G \) and bulk \( B \) elastic moduli in amorphous (●) InSb-Ge solid solutions. * - tabulated value of elastic moduli for crystalline InSb-Ge.
Discussion and conclusions

The Fig. 2 shows monotonously increasing dependence of hardness of amorphous and crystalline \((\text{GaSb})_{1-x}\text{Ge}_x\) samples in the whole interval of concentration. However, the obtained data specify a non-monotonic behavior of elastic constants. Elastic softening in both the amorphous and crystalline solid solutions \((\text{GaSb})_{1-x}\text{Ge}_x\) is anomalous because increasing of germanium concentration \(x\) corresponds to the increase of the covalence degree in the system. Possibly, abnormal behavior of elastic modules is connected with occurrence of distortions in the tetrahedral short range order structure. Such assumption directly proves to be true at comparison of compressibility of the whole amorphous network of \(a\)-GaSb with an effective average value of compressibility of separate bonds, that illustrates, that additional compressibility of the amorphous tetrahedrally ordered phase in comparison to the crystalline counterpart is directly connected to additional average distortions of tetrahedrons from the ideal shape [38]. Thus, it is possible to assume, that the degree of the geometrical and topological disorder is a key factor in abnormal behaviour of elastic modules of crystalline and amorphous \((\text{GaSb})_{1-x}\text{Ge}_x\).

In covalent solid solutions the bond length is defined by type of atoms and very weekly depends on component concentration. In [39] by means of EXAFS spectroscopy, it has experimentally been received, that coordination number and bond lengths of the certain type do not change in amorphous and crystalline solid solutions \((\text{GaSb})_{1-x}\text{Ge}_x\) with a variation of concentration Ge. Presence of different bond types leads to a deviation of atoms from average effective positions in a correct effective sphalerite/diamond lattice in solid solution, i.e. to the configurational disorder and a deviation of bond angles from ideal in ideally ordered diamond-like lattice. In amorphous phases appears additional softening because of the topological disorder. Thus average deviations of bond angles from ideal values \((\approx 109^\circ\) in the regular tetrahedron) arise and average fluctuations of bond lengths increase.

In solid solutions \((\text{A}^{I\text{II}}\text{B}^{III})_{1-x}(\text{C}^{IV})_{2x}\) at some concentration phase transition from sphalerite to diamond structure is observed. For the description of structural phase transition sphalerite-diamond which it is possible to consider in terms of order-disorder, parameter of order \(M\) is used which is distinct from zero in a sphalerite phase and it is equal to zero in a diamond phase since in it there is no distinction between cation and anion sublattice:

\[
M = \left( P_{Ga}^c - P_{Ga}^a + P_{Sb}^a - P_{Sb}^c \right) / 2,
\]

where \(P_{Ga}^c\) - probability for Ga to take place in nominal cation sublattice (index \(a\) corresponds to anion sublattice). The rate of a geometrical disorder may be connected with a system configurational entropy. According to results [13] it is possible to express configurational entropy through parameter of order and concentrations of components (fig. 7):

\[
S = -\frac{1}{2}(1-x+M)\ln[\frac{1}{2}(1-x+M)] - \frac{1}{2}(1-x-M)\ln[\frac{1}{2}(1-x-M)] - x\ln(x).
\]

The received dependence has a strongly pronounced maximum at critical concentration Ge near 30 %. It is necessary to assume, that the maximum of entropy corresponds to the maximal disorder leading to the minimum of elastic

![Fig. 7](image-url)
modules, that we observed experimentally.

The increasing of the topological disorder in amorphous samples leads to falling down of elastic modules in system for a significant interval of concentration Ge. Upon amorphization the topology of a lattice is broken and in an amorphous network five- fold and seven- fold ring of bonded atoms should be appeared. In this case nominally cation and anion sublattice are absent. It is possible to assume, that the maximal geometrical disorder in amorphous solid solutions will be observed at the equal concentration of the components (~50 %), that also corresponds to the experimental observations.

The dependences observed for \( a-(\text{InSb})_{1-x}\text{Ge}_{2x} \) are more complicated for interpretation, since these samples contain admixtures of crystalline InSb. As we mentioned in the Section with results on this system, the decrease of mechanical characteristics at high Ge concentration can be related to morphology effects of the presence of the soft crystalline InSb with concentration nears the volume percolation threshold. Still, we have not observed the concentration minimum at ~50 % Ge for elastic modulii. Nevertheless, this result doesn’t reject the previous discussion for \((\text{GaSb})_{1-x}\text{Ge}_{2x}\) solid solutions. In the case of disordered covalent network the previous arguments on role of configurational and topological disorder should be valid only for component with relatively close interatomic distances, like for GaSb and Ge. It is not true for InSb-Ge alloys, since Ge atoms have radii rather smaller than atoms of InSb. This can result in preferred (not random) arrangement of Ge between atoms In and Sb. It is reasonable that Ge atoms can tend to position to softer part of InSb amorphous network with additional free volume. Such non-random rearrangement of Ge during amorphization can make amorphous network more rigid. Indeed, we observe experimentally the strong increase of mechanical characteristics of \( a-(\text{InSb})_{1-x}\text{Ge}_{2x} \) with the Ge concentration. But the elasticity of amorphous \((\text{InSb})_{1-x}\text{Ge}_{2x}\) solid solutions is still considerably softer with respect to values of crystalline InSb and Ge (Fig. 6).

Finally, using experimental data, we argue that elastic softening of tetrahedrally-bonded solid solutions, both amorphous and crystalline, is related to the degree of geometrical disorder, which in turn includes contributions of configurational (or chemical) and topological disorders. However the correlation between concentration dependences of elastic constants and topological disorder is clearly interpreted only for systems with atoms with rather close covalent radii. The both amorphous \((\text{GaSb})_{1-x}\text{Ge}_{2x}\) and \((\text{InSb})_{1-x}\text{Ge}_{2x}\) solutions have elastic moduli considerably below a potential linear interpolation between the corresponding characteristics of crystalline Ge and GaSb or InSb.

**Acknowledgements**

The work was supported by the Russian Foundation for Basic Research (project Nos. 04-05-16308 and 05-02-165969), by the Grant of the President of Russian Federation “The Leading Scientific Schools” (project No. NSh-307.2003.2), and by the Russian Foundation for the Support of National Science.

**Literature**


