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Local atomic ordering in bulk amorphous $(GaSb)_{1-x}Ge_{2x}$

Andrei Sapelkin,[a]* Susan Bayliss,[a] Alexandr Lyapin,[b] Vadim Brazhkin[b] and Andy Dent[c]

[a]Solid State Research Centre, De Montfort University, Leicester, LE1 9BH, England, [b]Institute for High Pressure Physics, Russian Academy of Sciences Troitsk, Moscow region, 142092, Russia, and [c]CCLRC Daresbury Laboratory, Warrington, Cheshire, WA4 4AD, England. E-mail: sapelkin@dmu.ac.uk

The local structure of bulk amorphous $(GaSb)_{1-x}Ge_{2x}$ produced by solid state amorphization has been studied using EXAFS and neutron diffraction. Measurements have been made at the Ga, Ge and Sb K edges. The results show the dominating role of bond angle distortions in the amorphous nature of the samples. All samples are found to be four-fold coordinated with structure possibly close to c − GaSb zinc-blende phase. The partial distances R_{Ga-Sb}, R_{Ge-Sb}, R_{Ge-Ga}, R_{Ga-Ge}, R_{Sb-Ga} and R_{Sb-Ge} are shown to be independent of Ge concentration and defined by the covalent radii of the components. The nature of local ordering in the amorphous material is such that Ge seems to substitute mainly for Sb at lower Ge concentration ($x < 30 - 40$ at. %), aiding relief of stress inserted during amorphization of the material.

1. Introduction

The macroscopic properties of disordered tetrahedral semiconductors prepared by solid state amorphization (SSA) under high pressures (Demishev *et al.*, 1987; Brazhkin *et al.*, 1992) have been extensively studied (Brazhkin *et al.*, 1993; Sidorov *et al.*, 1994; Brazhkin *et al.*, 1996; Lyapin *et al.*, 1996; Brazhkin *et al.*, 1997). However, these properties are defined by the microscopic nature of the materials, and understanding of this can provide deeper insight into the structure of materials prepared by SSA. Recently, a number of papers was presented on the local structure and long range structural correlations in SSA a − GaSb and its solid solutions with Ge (Brazhkin *et al.*, 1996; Sapelkin *et al.*, 1997; Barkalov *et al.*, 1996). At the same time no structural technique at present can uniquely describe the structure of an amorphous solid. This is because of the loss of the periodicity in disordered materials and, as a consequence, the relation between structure and symmetry. Therefore the structure of such substances can only be described in terms of mean values (of e.g. distances, nearest neighbours numbers, Debye-Waller factors) or, at best, distributions. Thus the structural description of an amorphous solid is a challenging task even in the case of monoatomic substances. The situation becomes even more complicated for binary or polyatomic materials. The ability of EXAFS to yield significant structural information for binary amorphous materials has been recently demonstrated for a range of sputtered amorphous materials (Elgun *et al.*, 1992; Baker *et al.*, 1993; Baker *et al.*, 1996) and for bulk amorphous GaSb prepared by SSA (Sapelkin *et al.*, 1997).

Although the possible influence of Ge on macroscopic and structural properties was discussed previously (Sidorov *et al.*, 1994; Brazhkin *et al.*, 1996), to our knowledge there is only one paper (Brazhkin *et al.*, 1993) which describes local structure of a − $(GaSb)_{1-x}Ge_{2x}$. In that paper, a − $(GaSb)_{1-x}Ge_{2x}$ studied using x-ray diffraction showed anomalies in the behavior of coordination numbers and shell distances determined. It was found that the radius of the first coordination sphere increases with increase of Ge content, in contrast with what would be expected for GaSb dopped with Ge since the covalent radius of Ge (1.22 Å) is smaller than covalent radii of Ga (1.26 Å) and Sb (1.32 Å). This increase in bond length and also the change in ratio N_2/N_1 from 2.7 to 3 were ascribed to a transition from a highly strained amorphous network (with some crystalline impurities of Ge and GaSb) into the homogeneous amorphous solid solution. However, from the point of view of our recent investigations of the local structure of a − GaSb using EXAFS, (Sapelkin *et al.*, 1997) the conclusion about anomalous increase of bond length with introduction of Ge seems less well founded.

In this paper we present the results of an investigation of local structure of these materials by EXAFS at all K absorption edges (Ga, Ge, Sb) and by neutron diffraction. Using the advantages of EXAFS for studies of local structure we have been able to extract partial (not averaged as in the case of (Brazhkin *et al.*, 1993)) structural parameters (R_{Ga-Sb}, R_{Ge-Sb}, R_{Ga-Ge}, $R_{Sb-Ga,Ge}$, etc.). This allowed us to obtain important additional information and demonstrate more complex role of Ge in a − $(GaSb)_{1-x}Ge_{2x}$ than was suggested in (Brazhkin *et al.*, 1993).

2. Experiment

Amorphous $(GaSb)_{1-x}Ge_{2x}$ was prepared by the high pressure solid state amorphization technique described earlier (Demishev *et al.*, 1987; Demishev *et al.*, 1991). Note that samples of a − GaSb normally contain up to 1-3% of c − GaSb. The experimental procedure of collection and analysis of EXAFS spectra are described in detail elsewhere (Sapelkin *et al.*, 1997). Experiments were carried out at ambient conditions on stations 7.1 (Ga and Ge K edges) 9.2 (Ga, Ge and Sb K edges) and at low temperature on station 9.3 (Ge and Ga K edges) at CCLRC Daresbury Laboratory synchrotron radiation source. Neutron diffraction experiments have been carried out on Liquids and Amorphous Diffractometer at ISIS (Rutherford Appleton Laboratory, UK). Samples were loaded in thin vanadium containers for neutron experiments. The LAD description and parameters for different detector banks can be found at http://www.isis.rl.ac.uk/disordered/ladspec.htm.

3. Experimental Results

The concentration x dependencies of the numbers of nearest neighbours extracted from EXAFS data are presented in Fig. 1. Broken lines represent the case of random substitution of Ge for Ga and Sb in the solution (see, for example (Stern *et al.*, 1985)). Sb K edge first shell coordination numbers were fitted assuming either Ge or Ga neighbours. This procedure is valid due to the essentially similar scattering power of Ge and Ga atoms and therefore their equivalence from the point of view of EXAFS. This can be seen in Fig. 1 — both fitting procedures give the same result. For the same reason Ge and Ga K edge coordination numbers other then Sb were obtained assuming either Ga and Ge neighbours respectively (no Ga-Ga and Ge-Ge bonds). We can see that experimental points fall out of these dependencies in the concentration range of Ge below $x < 30 - 40$ at. %. One can also see that at higher values of x the line tends to follow the behaviour of an homogeneous solid solution as it was suggested in (Brazhkin *et al.*, 1993). However,

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EXAFS results allow us to suggest that there is observable change in the dependence of N_{Sb} versus x at both Ge and Ga edges. Such a change was not observed in (Brazhkin *et al.*, 1993) due to the intrinsic limitations of diffraction in the case of amorphous multicomponent materials when an average coordination is calculated. A similar behavior of the number of nearest neighbours versus Ge concentration was observed in $c-(GaSb)_{1-x}Ge_{2x}$ studied by EXAFS (Stern *et al.*, 1985). In that paper the effect was ascribed to Ge preferably substituting for Sb at the grain boundaries, thus relaxing possible stresses. One can also see that the number of nearest neighbours in the material at all concentrations of Ge stays close to four. This suggests that the structure of the material is close to that of c – GaSb (Zn-blende) or c – Ge (diamond).

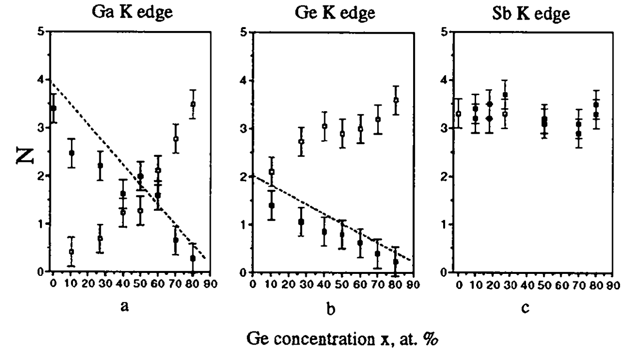

Figure 1
The concentration dependence of nearest neighbours coordination numbers around Ga (a) and Ge (b) centers in $a-(GaSb)_{1-x}Ge_{2x}$. Ga K edge (a): solid squares — N_{Ga-Sb}, open squares — N_{Ga-Ge}. Ge K edge (b): solid squares — N_{Ge-Sb}, open squares — N_{Ge-Ga}. Sb K edge (c): solid squares — $N_{Sb-Ge(Ga)}$, open squares — N_{Sb-Ga}. Sb K edge was fitted assuming either Ga or Ge neighbours. It does not make any difference from the point of view of EXAFS since the scattering power of Ge and Ga are essentially the same. This can be seen in the figure.

The next figure (Fig. 2) presents the concentration dependencies of nearest neighbour distances at all edges studied. Here we can see that all the distances are essentially independent of concentration of Ge. Note that neutron scattering experiments (Barkalov *et al.*, 1996) also indicate that the bond length in a – GaSb does not noticeably change from that of c – GaSb. The results of this paper and the ones published recently on EXAFS (Sapelkin *et al.*, 1997) and neutron diffraction (Barkalov *et al.*, 1996) suggest that there exist significant distortions of bond angles in $a-(GaSb)_{1-x}Ge_{2x}$ and not in nearest neighbours distances.

Our EXAFS results are also confirmed by neutron diffraction performed on samples of a – GaSb and $a-(GaSb)_{0.73}Ge_{0.27}$ (see total correlation function, Fig. 3). One can see that first and second shell distances are higher for a – GaSb (R_1 = 2.65(2) Å and R_2 = 4.32(5) Å) than those for $a-(GaSb)_{0.73}Ge_{0.27}$ (R_1 = 2.61(2) Å and R_2 = 4.23(5) Å) indicating no anomalous increase of average bond length as found in (Brazhkin *et al.*, 1993). The result for a – GaSb (Fig. 3, a) is in agreement with that from (Barkalov *et al.*, 1996). We can also determine the value of the bond angle ϕ for $a-(GaSb)_{0.73}Ge_{0.27}$ from the first and second peak positions in $T(r)$ (Fig. 3) and $\phi_{a-(GaSb)_{0.73}Ge_{0.27}} = 108(1)^\circ$, while $\phi_{a-GaSb} = 110(1)^\circ$ and $\phi_{c-GaSb} = 109.47^\circ$. Thus all the angles are close to the ideal tetrahedral value found in c - GaSb.

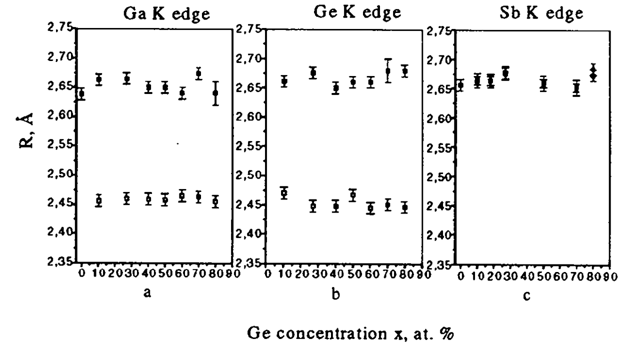

Figure 2
The nearest neighbour distances around Ga (a) and Ge (b) centres in $a-(GaSb)_{1-x}Ge_{2x}$ versus concentration of Ge x. Ga K edge (a): solid squares — R_{Ga-Sb}, open squares — R_{Ga-Ge}. Ge K edge (b): solid squares — R_{Ge-Sb}, open squares — R_{Ge-Ga}. Sb K edge (c): solid squares — $R_{Sb-Ge(Ga)}$, open squares — R_{Sb-Ga}.

4. Discussion

The role of Ge in a – GaSb can be understood if we recall that III-V semiconductors in general and GaSb in particular are understood to be slightly ionic in character. This means in the case of GaSb negative charge transfers from Ga to Sb. This charge transfer could make Ga-Sb-Ga and Sb-Ga-Sb angles in general different. This difference can be observed in the low temperature EXAFS measurements (Sapelkin *et al.*, 1997) at Sb and Ga K edges. While nearest neighbours Debye-Waller (DW) factors are the same at both edges 0.0044(4) Å^2, the second neighbour DW factors are not (0.012(1) Å^2 at Ga K edge and 0.009(1) Å^2 at Sb K edge). The stress inserted on a – GaSb during amorphization would make the bond angles even more different. This difference could well be responsible for Ge substituting for Sb at lower x because such substitution would lower the ionicity of a bond, thus increasing the stability of the structure. Thus we can suggest that introduction of Ge leads to the relaxation of stresses related to angle distortions in a – GaSb. This would not significantly affect the nearest neighbour distances, and we can see from EXAFS that it does not — distances are not notably affected by introduction of Ge. Strain relief would also explain the increase in high pressure transition pressure with increase of Ge concentration observed in our earlier experiments (see (Brazhkin *et al.*, 1996)). Overall, the Ge concentration $x \approx 30 - 40$ at. % indicates the region where the balance between the two modes of substitution takes place — from Ge atoms which preferably substitute for Sb to Ge as a homogeneously distributed impurity.

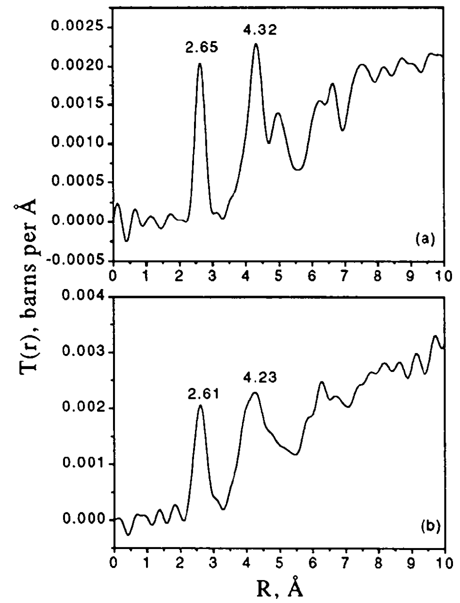

Figure 3
Total correlation functions for a − GaSb (a), and for a − $(\mathrm{GaSb})_{0.73}\mathrm{Ge}_{0.27}$ (b).

In general, Ge seems to act as a stress relief agent in GaSb, lowering the total energy of the solution compared to that of a − GaSb, mainly substituting for Sb in the areas of maximum stress at lower concentration. This follows from the analysis of the distribution of numbers of nearest neighbours (Fig. 1). At higher concentrations the distribution tends to follow the case of the homogeneous solution. The a − $(\mathrm{GaSb})_{1-x}\mathrm{Ge}_{2x}$ seems to have a structure close to that of c − GaSb I phase (tetrahedral), with the number of nearest neighbours in the first coordination shell close to four.

The exact microscopic description of the mechanism of Ge incorporation in GaSb is still to be established. Also a model needs to be built of a − $(\mathrm{GaSb})_{1-x}\mathrm{Ge}_{2x}$ in terms of atomic positions, and the information collected to date on the local structural properties of these solutions could be extremely valuable in this respect. A theoretical model that would explain preference of angle over the bond length distortions has still to be built. It would also be useful to compare the local structure of a − $(\mathrm{GaSb})_{1-x}\mathrm{Ge}_{2x}$ with that of c − $(\mathrm{GaSb})_{1-x}\mathrm{Ge}_{2x}$.

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