

Nuclear quadrupole resonance study of local structure of the Ge–As–Se ternary chalcogenide glasses

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Abstract

The local bonding structure in the Ge–As–Se ternary glassy system has been investigated by ⁷⁵As nuclear quadrupole resonance (NQR) at 77 K. For the compositions with average coordination number $\bar{r} = 2.2, 2.4, 2.54$ the NQR measurements yield no evidence for the presence of As–As homopolar bonds. For the composition Ge₂As₂Se₅ ($\bar{r} = 2.67$) the NQR lineshape exhibits two peaks corresponding to arsenic sites with zero (or three) and two As–As bonds. High Ge and As content leads to formation of microclusters, where the predominant structural units are, possibly, As₄Se₄ molecules or partial molecules with As–As bonds. The NQR spectrum for the composition Ge_{0.33}As_{0.12}Se_{0.55} ($\bar{r} = 2.78$) shows a weak peak corresponding to an arsenic site with zero (or three) homobonds and two resolved peaks in the high frequency region. Such behavior is consistent with an increase in inhomogeneity in the local structure and perhaps nanoscale phase separation.

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1. Introduction

Chalcogenide glasses have some unique properties, such as low phonon energy, high values of refractive indexes and transparency in middle and far infrared parts of the electromagnetic spectrum, that make them attractive for different applications in optoelectronics and photonics. Glasses in the Ge–As–Se ternary system (undoped and doped with rear-earth elements) are under intensive investigation as promising materials for active media in optoelectronics [1–4] and ultrafast all-optical switches in telecommunication systems [5,6]. However, the local structure of these amorphous materials is not well understood.

It is believed that the local structure of the Ge_xAs_ySe_{1-x-y} glasses contains Ge–Se and As–Se covalent bonds. Each element has a coordination number corresponding to eight minus its group number ($8 - N$ rule [7]) in the periodic table of elements, while the average coordination number for the entire glass is expressed as

$$\bar{r} = r_A x + r_B y + r_C (1 - x - y), \quad (1)$$

where A , B , and C are the constituent elements, respectively. Glasses in this system occur over a broad glass-forming region with average coordination number ranging from $\bar{r} = 2$ for pure selenium to 3.3 for compositions with high concentrations of As and Ge. Since selenium is the main glass former in these glasses, it is convenient to consider local structure of the ternary system on the basis of structural units of the corresponding binary systems, Ge–Se and As–Se.

In this work we investigate the local structural ordering and its dependence on the average coordination number.

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Nuclear quadrupole resonance (NQR) spin-echos of ^{75}As in glasses with $\bar{r} = 2.2, 2.4, 2.54, 2.67$, and 2.78 are reported.

2. Experimental details and technique

All the samples were grown by the standard melt quenching technique. Proper amounts of the initial elements (Ge, As and Se) with 6 N purity were sealed under vacuum (with residual pressure 10^{-6} torr) in quartz ampoules, heated up to 900°C , rocked overnight and quenched in ice water. Bulk samples then were crushed into small chunks and placed in plastic or pyrex tubes to fit inside the NQR coil. The glasses were checked by X-ray diffraction and no sharp peaks were observed.

NQR studies the interaction between the quadrupole moment of a nucleus and the electric field gradient at the nuclear site, which is created predominantly by external (bonding) electrons. NQR is one of the most powerful methods to investigate local bonding in amorphous solids. The first application of pure NQR (i.e. NQR in absence of or in low magnetic field) to amorphous systems was made in the glassy As_2Se_3 and As_2S_3 binary systems [8].

The experimental setup and procedure are similar to those described in [9].

3. Results

According to the formal valence shell (FVS) model [10], atoms with the greatest number of valence electrons form the anion sublattice in most cases. Thus in the $\text{Ge}_x\text{As}_y\text{Se}_{1-x-y}$ system the preferred bonds are Ge–Se and As–Se. Compositions where only these bonds are pres-

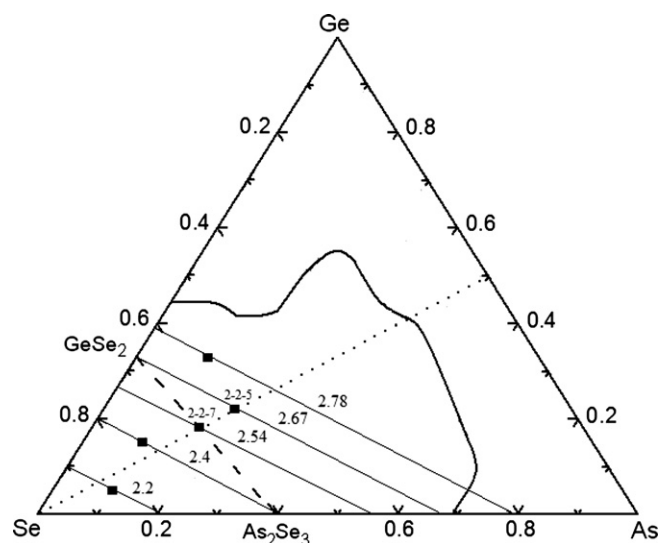


Fig. 1. Compositional diagram for Ge–As–Se ternary glassy system. Squares are the compositions studied in this work. The solid lines across the diagram represent compositions with different average coordination numbers and the dashed line displays ternary glasses consisting of stoichiometric compositions of corresponding binary glasses. $\text{Ge}_x\text{As}_y\text{Se}_{1-x-y}$ compositions and the glass-forming region are shown as the dotted line and the curved line, respectively.

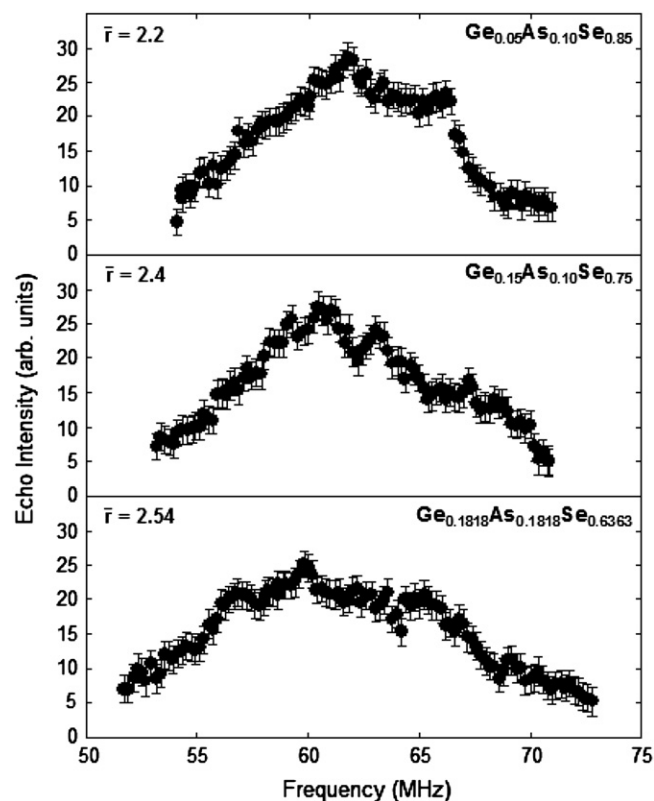


Fig. 2. The ^{75}As NQR spectra at 77 K in $\text{Ge}_x\text{As}_y\text{Se}_{1-x-y}$ glassy system. The average coordination numbers corresponding to each composition are also shown.

ent can be located along a specific line in the phase diagram (the dashed line in Fig. 1). This line can be expressed as $(\text{GeSe}_2)_x(\text{As}_2\text{Se}_3)_{1-x}$.

Fig. 2 represents the spectral dependence of the intensity of the spin echo for the compositions with \bar{r} changing from 2.2 to 2.54. As is apparent from the figure, each composition exhibits a broad spectrum with one peak with no pronounced features. Such broad spectra are typical for amorphous solids, where due to the absence of long range order the resonance line is broadened in frequency. Fig. 3(a) and (b) represents the NQR spectra of $\text{Ge}_2\text{As}_2\text{Se}_5$ and $\text{Ge}_{0.33}\text{As}_{0.12}\text{Se}_{0.55}$, respectively. The first one consists of a broad peak centered around 71 MHz and a narrower and less intense, partially resolved peak near 59 MHz. Two peaks in high frequency region are clearly resolved in the case of $\text{Ge}_{0.33}\text{As}_{0.12}\text{Se}_{0.55}$. These spectra are completely different from those in Fig. 2.

4. Discussion

In the part of the compositional triangle (Fig. 1) bounded by Se– GeSe_2 – As_2Se_3 for the case of a random and homogeneous distribution of Ge and As atoms in the glassy network and with only Ge–Se and As–Se bonds there are no Ge–Ge and As–As homopolar bonds. In this Se-rich region Ge and As atoms form tetrahedral and pyramidal structural units, respectively, which produce

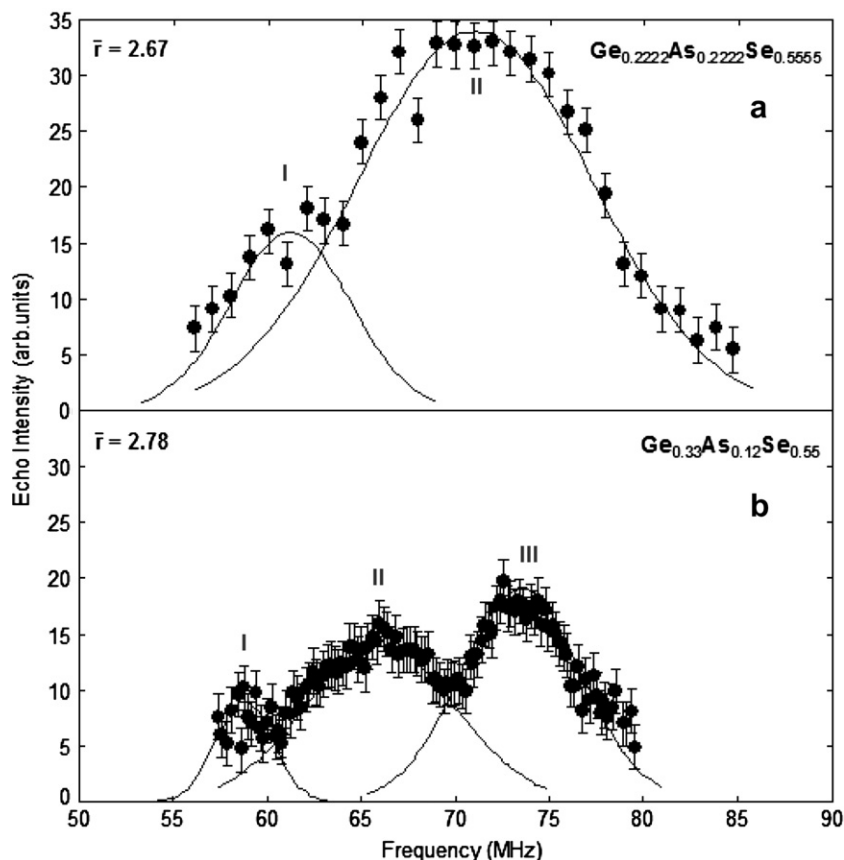


Fig. 3. The ^{75}As NQR spectra at 77 K in $\text{Ge}_x\text{As}_y\text{Se}_{1-x-y}$ glassy system: (a) for the $\text{Ge}_{0.2222}\text{As}_{0.2222}\text{Se}_{0.5555}$, and (b) for the $\text{Ge}_{0.33}\text{As}_{0.12}\text{Se}_{0.55}$. The solid curves denote arsenic sites with different number of As–As bonds.

‘branching’ and ‘cross-linking’ between Se chains [11]. The ^{75}As NQR experimental data support this representation. The spectra for compositions with $\bar{r} = 2.2, 2.4$, and 2.54 are similar to those for the $\text{g-As}_x\text{Se}_{1-x}$ binary system with $x \leq 0.4$ [9]. In both cases the spectra are located near 60 MHz and the positions of the peaks shift towards lower frequencies with increasing \bar{r} . This similarity suggests that in the given region of compositions (to the left of the dashed line in Fig. 1) of the Ge–As–Se system there are no homopolar As–As bonds. Each As atom is bonded to three Se atoms. This conclusion is based on the fact that the NQR spectrum of the crystalline stoichiometric composition, $\text{c-As}_2\text{Se}_3$, has two resonant frequencies at 56.07 and 60.25 MHz [12].

In compositions to the right of the dashed line on the compositional diagram (Fig. 1) there are not enough free selenium atoms to satisfy all Ge and As bonding requirements, and Ge–Ge and As–As homopolar bonds are unavoidable [11]. For the binary system $\text{As}_x\text{Se}_{1-x}$ with $x > 0.4$ three peaks occur on the NQR lineshapes at ~ 59 , 71 and 81 MHz, which can be assigned to As sites with zero (or three), two and one As–As bonds, respectively [9]. In the case of the Ge–As–Se system one observes different behavior. As shown in Fig. 1, we have considered two compositions to the left of the $(\text{GeSe}_2)_x(\text{As}_2\text{Se}_3)_{1-x}$ tie line ($\text{Ge}_{0.05}\text{As}_{0.10}\text{Se}_{0.85}$ and $\text{Ge}_{0.15}\text{As}_{0.10}\text{Se}_{0.75}$), two compositions to the right ($\text{Ge}_{0.2222}\text{As}_{0.2222}\text{Se}_{0.5555}$ ($\text{Ge}_2\text{As}_2\text{Se}_5$) and

$\text{Ge}_{0.33}\text{As}_{0.12}\text{Se}_{0.55}$) and the last one located on the tie line ($(\text{GeSe}_2)_x(\text{As}_2\text{Se}_3)_{1-x}$ ($\text{Ge}_{0.1818}\text{As}_{0.1818}\text{Se}_{0.6363}$ ($\text{Ge}_2\text{As}_2\text{Se}_7$)). The $\text{Ge}_2\text{As}_2\text{Se}_7$ and $\text{Ge}_2\text{As}_2\text{Se}_5$ compositions are, in addition, located on the center line (dotted line on Fig. 1) where Ge and As atoms occur in equal proportion.

In the NQR spectra for the $\text{Cu}_x(\text{As}_{0.4}\text{Se}_{0.6})_{1-x}$ glassy system, besides the peak typical for $\text{As}_{0.4}\text{Se}_{0.6}$ (at about 58 MHz), an additional peak begins to appear in the high frequency region (78 MHz) with increasing x . This peak is related to arsenic sites with one homopolar bond [13]. At the highest Cu concentration ($x = 0.23$) only a single peak (centered around 71 MHz) is observed, while the first two peaks disappear. Such behavior indicates that the increase in concentration of fourfold coordinated Cu atoms leads to the formation of more Cu–Se bonds, which are energetically more preferred, thereby reducing the number of Se atoms available for As–Se bonds. By comparison with spectra in the $\text{As}_x\text{Se}_{1-x}$ system, the location of the peak near 71 MHz shows that there are two As–As bonds at each arsenic site. One can expect similar behavior in the Ge–As–Se system in compositions located on the compositional triangle near the As–Se pseudobinary line (Fig. 1). However, for the compositions located along the center line, with increasing of average coordination number, the number of Se atoms participating in heteropolar bonds decreases faster due to equal concentrations of Ge and As atoms. When compositions reach $\text{Ge}_2\text{As}_2\text{Se}_7$ all the Se atoms are bonded to Ge

or As atoms and further increasing \bar{r} leads to the occurrence of Ge–Ge and As–As bonds and clustering effects become more pronounced. Thus, the observed peak in the $\text{Ge}_2\text{As}_2\text{Se}_5$ NQR lineshape near 71 MHz can be plausibly assigned to the arsenic site with two As–As bonds. Such an increase in the concentration of homopolar bonds can result in the formation of microclusters, consisting of molecules such as As_4Se_4 or partial molecules with one or two As–As bonds, as a major component.

Of special interest is the spectrum for $\text{Ge}_{0.33}\text{As}_{0.12}\text{Se}_{0.55}$ (Fig. 3(b)), which is known commercially as AMTIR. The spectrum consists of two intense peaks (II and III) located at ~ 66 and 73.4 MHz, and a possible weaker peak (I) at ~ 58.8 MHz (although there is a marked decrease in the signal-to-noise ratio in this region). The latter can be assigned to an arsenic site with no As–As bonds. However, the frequencies of the first two peaks do not match any frequency mentioned above. These peaks are of special interest. Arsenic content in the composition is 12 at.%, however, due to the high Ge content, the average coordination number of the glass is high ($\bar{r} = 2.78$). By comparison of the spectra in Fig. 3(a) and (b) one can conclude that the NQR peak II for $\text{Ge}_2\text{As}_2\text{Se}_5$ splits into two peaks II and III for $\text{Ge}_{0.33}\text{As}_{0.12}\text{Se}_{0.55}$. The sum of the areas under the peaks II and III in Fig. 3(b) is the same as the area under peak II in Fig. 3(a). Thus, one can suggest that peaks II and III correspond to As sites with two and one As–As bonds, respectively. Such behavior can be interpreted as due to clustering effects, which lead to nanoscale phase separation. This explanation is supported by NQR relaxation time measurements, which have revealed different spin–spin relaxation times for these two peaks. Although, the underlying mechanism is not clear, one could assume that the shift in peak frequencies is due to the high Ge content. These results are consistent with temperature modulated differential scanning calorimetry (MDSC) measurements [14], according to which, the $\text{Ge}_{0.33}\text{As}_{0.12}\text{Se}_{0.55}$ glass is located in the nanoscale-phase-separation region of the compositional triangle.

5. Summary

^{75}As NQR spectra at 77 K in the $\text{Ge}_x\text{As}_y\text{Se}_{1-x-y}$ glasses with $\bar{r} = 2.2, 2.4$, and 2.54 consist of a single broad line

and show no resolved features. This corresponds to the absence of the arsenic homopolar bonds in these compositions. The spectra for compositions with $\bar{r} = 2.67$ and 2.78, however, consist of several peaks, which have been analyzed to correspond to As sites with different numbers of As–As bonds. Such behavior has been interpreted as due to clustering effects, which lead to nanoscale phase separation. The observed shifts in peak frequencies for the $\text{Ge}_{0.33}\text{As}_{0.12}\text{Se}_{0.55}$ composition from the observed in As–Se glasses may be due to the high concentration of Ge atoms.

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