Vibrational Relaxation in the GeAsSe Glass Series as Probed by IR Laser Techniques

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Abstract—When chalcogenide glasses are doped with molecular impurities containing hydrogen, inhomogeneously broadened vibrational bands appear. We have used the techniques of persistent IR spectral hole burning and IR saturation spectroscopy to probe the relaxation dynamics of simple molecules in the chalcogenide glass alloy series GeAsSe, where the chemical composition of the glass can be readily varied. This comprehensive experimental study of different but related glasses demonstrates that network topology, and not chemical composition of the glass, is correlated with a number of dynamical properties of the molecules including the vibrational lifetimes.

1. INTRODUCTION

From persistent spectral hole burning studies of organic and inorganic glass in the visible region [1–3], it is still not clear how much of the underlying behavior is controlled by chemical bonding and how much by glass structure. Chalcogenide glasses provide a way to address this question. It is energetically favorable for a chalcogen atom such as Se to have two covalent bonds per atom. Elemental Se glass is thus made up of chains of Se atoms, each Se within a chain covalently bonded to two others, and weak van der Waals interactions providing the only coupling between chains. The result is a loose, nonrigid structure. This structure can be modified by replacing some of the Se atoms with As or Ge atoms, which prefer to be threefold and fourfold coordinated, respectively. The result of adding these higher coordination atoms is to cross-link the Se chains, adding rigidity to the structure.

Phillips [4], using constraint counting arguments to explain the strong glass-forming tendency of certain alloy compositions, first suggested that the network connectivity could be parameterized by simply using an average atomic coordination number, $\langle r \rangle$, which for a GeAsSe alloy is simply calculated from the concentration of the three constituents according to $\langle r \rangle = 4[\text{Ge}] + 3[\text{As}] + 2[\text{Se}]$. The idea is then to replace the real network structure consisting of a variety of atoms of different coordination numbers, with a network of identical virtual atoms, all having the coordination number $\langle r \rangle$. The distinguishing feature of this approach is that it permits nonintegral coordination numbers and recognizes the topological relevance of such a concept. This mean coordination number concept has been refined by Thorpe *et al.* [5, 6] and Tanaka [7] who proposed that as $\langle r \rangle$ is increased, rigid regions form in the "floppy" structure of pure Se glass, growing in size and number until at some critical value of $\langle r \rangle$ the rigid regions become connected throughout the network, i.e., a "rigidity percola-

tion" transition occurs from an underconstrained "floppy" structure to an overconstrained rigid structure.

Since small molecules can be doped into these chalcogenide glasses and their vibrational modes can be excited (in the electronic ground state) and monitored using IR laser techniques, they provide ideal high-Q mechanical oscillators with which to monitor the mechanical relaxation properties of these systems. Because a given value of the average coordination number $\langle r \rangle$ can be realized with a continuous range of chemical compositions, purely topological effects can be distinguished from chemical effects. We review here some of the IR experiments which have demonstrated that the network topology of the glass rather than its chemical composition influences the vibrational lifetime of the impurity molecule.

2. PERSISTENT IR SPECTRAL HOLE BURNING

2.1. Spectral Holes

Persistent IR spectral hole burning in the electronic ground state was first observed with Pb-salt diode lasers for SH in As_2S_3 glass [8]. The technique was then applied to other molecules in chalcogenide glasses [9] since they all are transparent in the infrared region of the spectrum. During the past few years, a combined persistent IR spectral hole burning and pump–probe study has been employed to examine the low-temperature vibrational lifetimes of molecules resulting from the H_2 and H_2O doping of chalcogenide glasses. Typical infrared absorption spectra showing the inhomogeneous absorption bands produced by melting the chalcogenide glass in H_2 gas are displayed in Fig. 1 for a-Se (solid line) and As_2Se_3 (dashed line). In each case, the result of doping is a broad asymmetric absorption band at the chalcogen–hydrogen stretch vibrational frequency. The asymmetry of the inhomogeneous band results from the large variety of bonding sites in the

glass [10]. As was initially observed [8] for the SH center in As_2S_3, hole widths in these hydrogen-related centers show a remarkably strong dependence on the burn frequency. The symbols plotted in Fig. 1 show the hole width at 1.5 K in the short burn time limit as a function of burn frequency for each of these systems. In each case, the hole width increases with decreasing burn frequency from a minimum of less than 1 GHz at the high-frequency limit of the band to values at least an order of magnitude greater at the lowest burn frequencies attempted.

2.2. Persistent Spectral Hole Filling

In monitoring the time evolution of the spectral hole after burning ceases, one is in effect monitoring the relaxation among the glassy configurations involved in the hole burning. Experiments of this type have been performed by many workers on a variety of amorphous systems, both organic and inorganic [11–13]. The one qualitative feature universal to all these systems is the highly nonexponential nature of the hole relaxation, indicating the existence of a broad distribution of relaxation rates for each system.

By studying hole filling as a function of time for a single molecular impurity in the GeAsSe glass series we have found that large variations in the hole relaxation behavior do occur [13]. To investigate a possible structural origin for this variation, the 1.5 K relaxation of spectral holes burned in the 4.5-μm SeH absorption band was studied as a function of network connectivity for a number of glass compositions in this series. It was found that the dominant rate characterizing the nonexponential relaxation increases monotonically by over three orders of magnitude as the average atomic coordination number of the host is increased from 2.0 to 2.8. These results from the 1.5 K hole-relaxation experiment for ten different GeAsSe compositions are presented in Fig. 2. The compositions were chosen so that there are two having $\langle r \rangle = 2.2$, four having $\langle r \rangle = 2.4$, two having $\langle r \rangle = 2.6$, and one composition each for $\langle r \rangle = 2.0$ and 2.8. The hole depth, plotted as a function of the time t after burning ceases, is normalized to unity at $t = 0$ for each composition. Note that the hole relaxation behavior in these glasses appears to be determined solely by network connectivity considerations, independent of chemical composition. Throughout the composition range studied here, the overall hole relaxation rate increases monotonically with $\langle r \rangle$, with holes at $\langle r \rangle = 2.8$ decaying over three orders of magnitude faster than those at $\langle r \rangle = 2.0$.

2.3. Dependence of the Hole Width on the Mean Coordination Number

A useful measurement is that of the zero temperature hole width since its value may be directly related to the vibrational lifetime. However, experiments show that the hole width increases with increasing burn time,
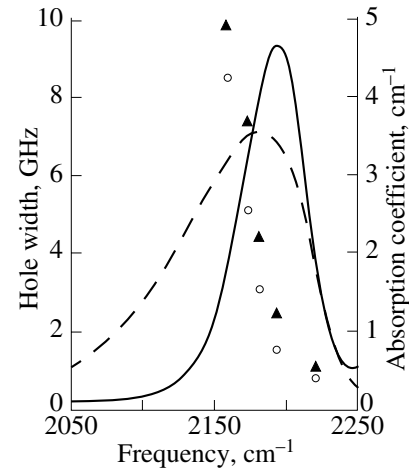

Fig. 1. IR absorption spectra and 1.5 K hole width as a function of burn frequency for hydrogen-related centers in As_2Se_3 and a-Se. Absorption spectra and 1.5 K hole widths for SeH in As_2Se_3 (dashed line, triangles) and in glassy a-Se (solid line, circles). Hole widths (FWHM) are in the short burn limit. IR spectra taken with a FTIR at 1 cm^{-1} resolution. (After [9].)
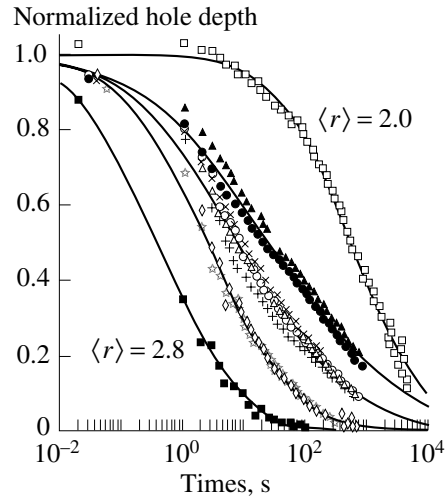

Fig. 2. Spectral hole refilling at 1.5 K for the SeH absorption in GeAsSe glasses. Data points show the hole depth, normalized to unity at $t = 0$, as a function of time t after burning ceases for ten different compositions burned and probed under identical conditions. The laser frequency is 2227 cm^{-1} and the intensity at the sample is roughly 200 mW/cm^2. The initial hole in each sample is burned for 2 minutes. The average atomic coordination numbers $\langle r \rangle$ and compositions of the ten samples, listed in order of decreasing relaxation time, are as follows: $\langle r \rangle = 2.0$, glassy Se (open squares); $\langle r \rangle = 2.2$, $As_{0.2}Se_{0.8}$ (solid triangles), $Ge_{0.089}As_{0.022}Se_{0.889}$ (solid circles); $\langle r \rangle = 2.4$, $Ge_{0.15}As_{0.10}Se_{0.75}$ (x), As_2Se_3 (open circles), $Ge_{0.1}As_{0.2}Se_{0.7}$ (open triangles), $Ge_{0.133}As_{0.133}Se_{0.733}$ (+); $\langle r \rangle = 2.6$, $Ge_{0.1}As_{0.4}Se_{0.5}$ (open diamonds), $Ge_{0.2}As_{0.2}Se_{0.6}$ (open stars); $\langle r \rangle = 2.8$, $Ge_{0.3}As_{0.2}Se_{0.5}$ (solid squares). Solid lines are fits, for each set of compositions having a given value of $\langle r \rangle$, to a Gaussian distribution of tunneling parameters (After [13].)
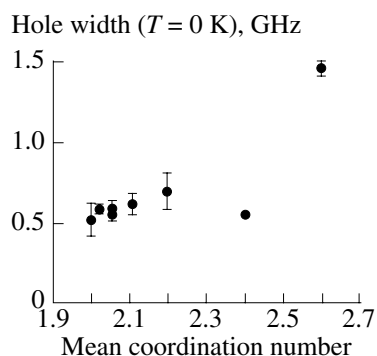
Fig. 3. Dependence of the low-temperature homogeneous hole width of the SeH molecule on the mean coordination number $\langle r \rangle$. Solid circles with error bars: hole width extrapolated to zero temperature. (After [15].)
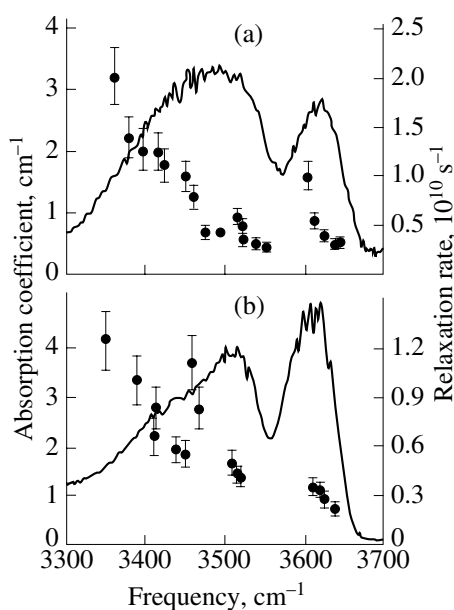

Fig. 4. Absorption spectrum and frequency dependence of the relaxation rate for H_2O-doped Ge–As–Se glasses at $T = 5$ K. The solid lines go with the left ordinates and solid dots go with the right ordinates: (a) $Ge_{0.177}As_{0.146}Se_{0.677}$ with $\langle r \rangle = 2.5$, (b) $Ge_{0.78}As_{0.144}Se_{0.778}$ with $\langle r \rangle = 2.3$. (After [17].)

so it is necessary to measure the hole width as a function of burn time and intensity and extrapolate to zero burn time to eliminate saturation effects. In the work of Völker [14] it was found that the hole width depends on the fluence (the product of intensity and burn time) only but this is not the case for these chalcogenide glasses. Instead, there exists a linear relationship between hole width and hole area for all our experimental data measured for different burn times at the same intensity [15].

Figure 3 shows the dependence of the low-temperature hole width on the mean coordination number. This width grows from about 0.5 to 1.5 GHz as the mean coordination number increases from 2.0 to 2.6. Only

the data point at $\langle r \rangle = 2.4$ does not follow the increasing tendency but indicates a minimum at this value. (Note that the rigidity transition is expected to occur in the Ge–As–Se system with this average number of bonds per atom.) Although the persistent spectral hole burning linewidth provides information about the total dephasing time only, if one makes the additional assumptions that there are no other dynamical processes such as spectral diffusion [16] and that the energy relaxation time determines the homogeneous linewidth at low temperatures then the corresponding lifetime T_1 of the SeH vibration is determined. It varies from 0.3 to 0.1 ns.

3. IR PUMP–PROBE MEASUREMENTS

3.1. Dependence of the Lifetime on the Position in the Band

To check whether or not the persistent hole burning measurements at low temperature give a true measure of the energy decay time, fast laser measurements are required. The method of picosecond infrared pump–probe saturation spectroscopy has been used to determine the energy relaxation time T_1 of the vibrationally excited molecules [10]. In such experiments, an intense IR picosecond pump pulse ($I_p \geq 1$ GW/cm^2) excites a fraction of the oscillators to the first excited $n = 1$ vibrational state and bleaching occurs because the second excited state $n = 2$ is not resonant with the laser radiation due to anharmonicity. After the excitation the population returns to its equilibrium value due to the relaxation of the excited state with a time constant T_1. A second weak picosecond pulse probes the change in transmission as a function of the time delay between the pump and probe pulse.

The results of frequency-dependent measurements of the relaxation rates across the inhomogeneously broadened lines for two samples in the region of the stretching modes are shown in Fig. 4 together with the absorption coefficient [17]. Figures 4a and 4b represent the results for $Ge_{0.177}As_{0.146}Se_{0.677}$ with $\langle r \rangle = 2.5$ and for $Ge_{0.078}As_{0.144}Se_{0.778}$ with $\langle r \rangle = 2.3$, respectively, both measured at 10 K. The unusually complex frequency dependence consists of at least two components: (1) the superposition of the vibrational spectrum of two different molecular species and (2) the decrease in the vibrational lifetime with decreasing frequency due to increased coupling of the molecule to the host. Another feature represented here is that even the longest lifetimes of the three vibrational modes (OH and H_2O) are short. Following the relaxation rate for each band in Fig. 4a to its smallest value (and hence the molecules weakest coupling to the host) gives lifetimes shorter ~400 ps in each case.

3.2. Dependence of the Relaxation Rate on Mean Coordination Number

In this investigation H_2O molecules in 14 different compositions in the GeAsSe series were examined cov-
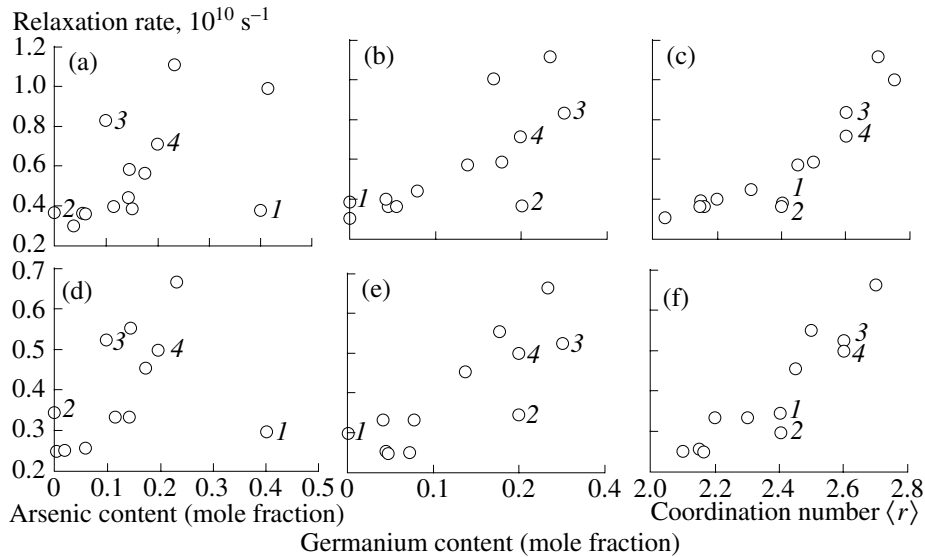
Fig. 5. (a–c) Low-temperature relaxation rate of the H_2O symmetrical stretching mode at $\nu_1 = 3515$ cm^{-1}, and (d–f) of the H_2O asymmetrical stretching mode at $\nu_3 = 3612$ cm^{-1}, in the Ge–As–Se glass series versus different parameters: (a and d) as a function of the arsenic content in mole fraction, (b and e) the germanium content in mole fraction, (c and f) the mean coordination number $\langle r \rangle$. The sample temperature is $T = 10$ K. The following samples are identified in the figure by numbers: (*1*) $\langle r \rangle = 2.4$: $As_{0.4}Se_{0.6}$, (*2*) $\langle r \rangle = 2.4$: $Ge_{0.2}Se_{0.8}$, (*3*) $\langle r \rangle = 2.6$: $Ge_{0.25}As_{0.10}Se_{0.65}$, (*4*) $\langle r \rangle = 2.6$: $Ge_{0.2}As_{0.2}Se_{0.6}$. (After [18].)

ering the range from $\langle r \rangle = 2.038$ to 2.75. The relaxation rates of the H_2O symmetrical stretching mode at $\nu_1 = 3515$ cm^{-1} and of the H_2O asymmetrical stretching mode at $\nu_3 = 3612$ cm^{-1} were measured [17, 18]. About a factor of three increase in the relaxation rates with increasing $\langle r \rangle$ was found at both frequencies. In order to determine whether the chemical composition or average network properties play a key role in the systematics of the relaxation mechanism, we plot the experimentally determined relaxation rates in three different ways in Figs. 5a and 5d versus the arsenic content, Figs. 5b and 5e versus the germanium content, and Figs. 5c and 5f versus the mean coordination number. These plots demonstrate that the scatter of the data in Figs. 5c and 5f is much smaller than that in Figs. 5a, 5b, 5d, and 5e. The samples with the same coordination number but different composition are particularly significant because they are topologically the same but chemically very different. These samples are labeled 1 and 2 with $\langle r \rangle = 2.4$ and samples 3 and 4 with $\langle r \rangle = 2.6$ in the figure. These results indicate that the mean network does play a role in the energy relaxation process.

4. CONCLUSION

Persistent infrared spectral hole burning and infrared picosecond pump–probe experiments have been carried out on the inhomogeneously broadened vibrational modes of SeH, OH, and H_2O defects in GeAsSe glasses. In both kinds of experiments the sample compositions were varied to systematically investigate the influence of the mean coordination number. The H_2-doped glasses have revealed a clear dependence of the hole

burning and refilling process of the Se–H vibrational mode on the mean coordination number $\langle r \rangle$ and yield a range of lifetimes of the Se–H vibration. This result provides the first indication that the mechanical relaxation of the vibrational mode depends on $\langle r \rangle$. Time-resolved measurements confirmed that for both the symmetric and asymmetric stretch modes of H_2O, the average coordination number of the glass plays the same special role in determining the short time dynamical relaxation properties as was observed for the (long time scale) persistent IR hole burning experiments. The monotonic dependence of the relaxation rate on the mean coordination number and not the chemical composition demonstrates the influence of the topological environment on the energy transfer. All of these findings suggest that the microscopic topology of the glass plays a significant role in determining the vibrational mode relaxation dynamics.

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