Role of Network Topology on the Vibrational Lifetime of an H_2O Molecule in the Ge-As-Se Glass Series

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The relaxation of a vibrationally excited H_2O molecule in glasses of the Ge-As-Se series is studied at low temperatures by means of time resolved infrared saturation spectroscopy. This experimental study of fourteen different glasses demonstrates that the network topology of the glass is correlated with the vibrational lifetime even though the local bonding of the molecule sets the ps time scale.

The role of the microscopic topology of disordered solids and glass-forming compounds on their physical properties has attracted considerable interest in recent years [1–10]. In constraint-counting arguments attempting to explain the strong glass-forming tendency of certain alloy compositions, Phillips [1] first suggested that the network connectivity could be parametrized by simply using an average atomic coordination number $\langle r \rangle$. Later this concept was refined by Thorpe *et al.* [3–5] who predicted, for this mean-field case, a sudden rise in bulk modulus as the composition passes through the rigidity percolation threshold at $\langle r \rangle = 2.4$. One of the best suited systems for the study of the influence of the mean coordination number on physical properties is the ternary Ge-As-Se system [8]. The fact that all three components are from the same row of the periodic table brings out the covalent character of the binding, resulting in a very broad glass-forming region. Experimentally the mean coordination number in these alloys, which is given by $\langle r \rangle = 4X_{Ge} + 3X_{As} + 2X_{Se}$ (where X is in mole fraction), can be varied from $\langle r \rangle = 2.0$ up to values of $\langle r \rangle = 3.2$. The same values of $\langle r \rangle$ can be realized for a continuous range of different chemical compositions allowing one to distinguish between pure chemical and topological effects. With the technique of persistent IR spectral hole burning [8] on SeH molecules in Ge-As-Se, it was already shown that the network topology has a major influence on the low-temperature persistent spectral hole relaxation. The spontaneous hole refilling rate was found to increase by over 3 orders of magnitude as the mean coordination number varies from 2.0 to 2.8. Over the composition range studied the quantitative form of the nonexponential hole relaxation depends solely on the average coordination number, independent of the chemical composition. In addition, the temperature dependence of the hole width [11] is found to follow a power law with an increasing temperature exponent with increasing mean coordination number. On the other hand, a detailed study of the vibrational density of states (VDOS) in Ge-As-Se glasses [12] shows that the appearance of the highest frequency peak (about 38 meV) in the VDOS is associated with the germanium content of the glass. Glasses with the same coordination number, around $\langle r \rangle = 2.4$, but different

compositions have different VDOS at the highest frequencies indicating that these high frequency modes depend on the chemical composition of the glass. Because nonradiative relaxation is usually associated with an energy gap law which involves the highest frequency modes and hence, in this case, depends on the chemical composition of the glass, the opportunity exists to separate topological from chemical contributions in the vibrational energy decay.

Our systematic experimental study with the ps pump-probe technique of the influence of the average coordination number on the vibrational lifetime of the H_2O modes in a variety of different samples for the Ge-As-Se series indicates that topological considerations are important. We show here that the energy gap law [13], usually used to describe the relaxation of impurity molecules in host crystals or glasses, is not consistent with our experimental results.

The chalcogenide glasses are quite transparent in the IR with a window extending from about 800 to $12\,000$ cm^{-1} making them ideal hosts in which to explore the dynamical properties of molecules in their electronic ground states [14]. When such glasses are doped with molecular impurities inhomogeneously broadened vibrational bands appear due to the bonding or trapping of the molecules in different network surroundings. Previously the techniques of persistent IR spectral hole burning [14,15] and saturation spectroscopy [16] both have shown that the SH stretch mode lifetime in vitreous As_2S_3 at low temperatures varies from 350 ps on the high frequency side of the inhomogeneously broadened absorption band to about 60 ps on the low frequency side, demonstrating a site dependence relaxation rate in which the larger the redshift of the molecular frequency, the stronger the bonding to the host glass. A temperature dependent study at a fixed frequency has been interpreted as the SH stretch mode relaxing through a multivibrational decay into modes of the glassy host compatible with an energy gap law decay scheme.

We have doped sixteen different Ge-As-Se glasses with H_2O covering the range of the mean coordination numbers from $\langle r \rangle = 2.038$ to 3.0. The samples are bulk-melt quenched glass ingots prepared by first synthesizing the binary and ternary alloy glasses from their chemical constituents [7]. The doping of each sample with H_2O is

achieved by heating the samples together with a small amount of pure water in a sealed quartz tube well above its glass temperature. Continuously rocking for 30 min followed by a rapid quenching in either air or liquid nitrogen [14] ends the doping process. For optical quality of the surfaces the samples are cut and polished using standard techniques.

Figure 1 shows a typical mid-IR H_2O induced absorption spectrum for $\langle r \rangle = 2.6$. The peak positions of the vibrational modes are the same for all compositions in the intermediate range of $\langle r \rangle = 2.2$ to 2.8. For glasses in this intermediate range three strong absorption bands are observed to be associated with this dopant. The highest and lowest frequency lines in the figure are readily assigned to H_2O: the bending mode (ν_2) with the peak of absorption at 1585 cm^{-1} and the asymmetric stretching mode (ν_3) with the peak absorption at 3625 cm^{-1}. The broad middle band in Fig. 1 is composed of the symmetric stretching mode (ν_1) of H_2O with a peak frequency of 3510 cm^{-1} and the stretching mode of OH with a peak absorption at 3460 cm^{-1} [17].

For high coordination numbers ($r > 2.8$) only one absorption line at 3460 cm^{-1} associated with the OH stretch mode is found. Glasses with low coordination numbers ($r < 2.2$) have softening temperatures below 100 °C. Besides the "isolated" molecules with the absorption bands described above these samples contain H_2O clusters or small water droplets which generate additional bands at lower frequencies.

We use the method of ps infrared pump-probe saturation spectroscopy to determine the energy relaxation time T_1 of the vibrationally excited molecules at low temperatures. An intense IR ps pump pulse ($I_p \geq 1$ GW/cm^2) excites a fraction of the oscillators to the first excited state of the anharmonic energy level ladder so bleaching occurs. After
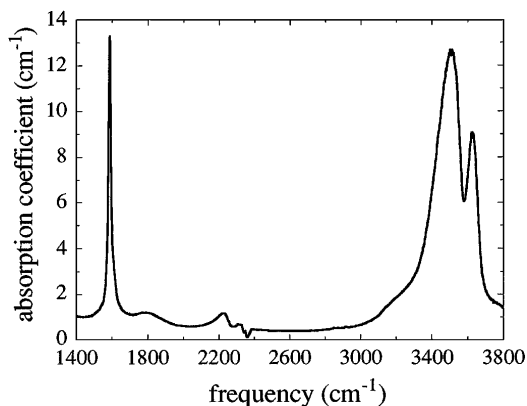
the excitation the population returns to its equilibrium value due to the relaxation of the excited state with a time constant T_1. A second weak ps pulse probes the change in transmission as a function of the time delay between the pump and probe pulse. A detailed description of the experimental setup is given in Ref. [16]. For all measurements the linewidth of the laser has been adjusted to be less than 10 cm^{-1} so only a small fraction of the molecules in the inhomogeneously broadened bands are excited. Within the experimental uncertainties the intensity of the probe pulse behind the sample does follow a simple exponential decay. Denoting the intensity of the transmitted probe pulse as a function of the time delay $I(\Delta t)$ and the transmitted probe intensity I_0, the relation between the transmitted probe intensity and the relaxation time is [18]

$$\ln\left(\frac{I(\Delta t)}{I_0}\right) \propto \exp\left(-\frac{\Delta t}{T_1}\right). \quad (1)$$

From a best fit including the convolution of the temporal width of the laser pulses ($\sigma = 20$ ps), the vibrational lifetime T_1 is determined.

The relaxation rate and the absorption coefficient in the region of the OH and H_2O stretching modes are shown in Fig. 2. Frame (a) represents the results for $Ge_{0.177}As_{0.146}Se_{0.677}$ with $\langle r \rangle = 2.5$ and (b) for $Ge_{0.078}As_{0.144}Se_{0.778}$ with $\langle r \rangle = 2.3$, both measured at 10 K. The unusually complex frequency dependence of

FIG. 1. Absorption spectrum of a H_2O doped chalcogenide glass. Three absorption bands are associated with the dopant in the $Ge_{0.25}As_{0.10}Se_{0.65}$ glass with $\langle r \rangle = 2.6$: the bending mode $\nu_2(H_2O) = 1585$ cm^{-1}, the asymmetric stretching mode $\nu_3(H_2O) = 3625$ cm^{-1}, and the broad middle band with two components composed of the symmetric stretching mode $\nu_1(H_2O) = 3510$ cm^{-1}, and the stretching mode of OH centered at $\nu(OH) = 3460$ cm^{-1}.
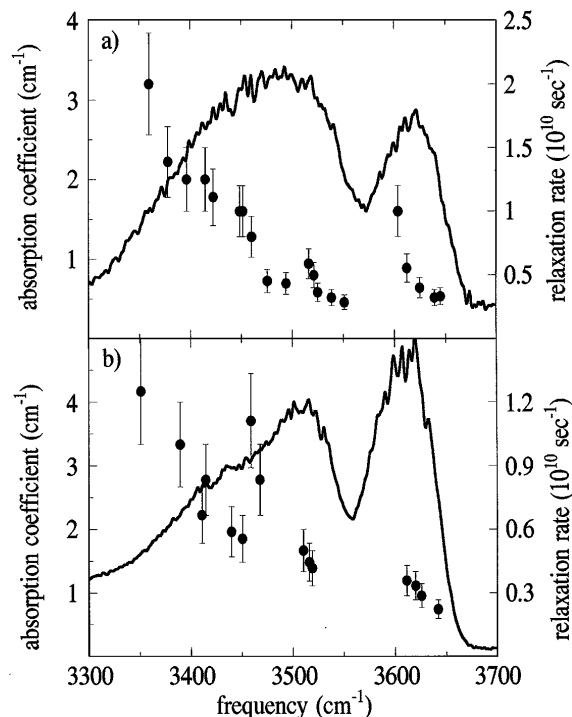

FIG. 2. Absorption spectrum and frequency dependence of the relaxation rate for H_2O doped Ge-As-Se glasses at $T = 5$ K. The solid lines go with the left ordinates and solid dots go with the right ordinates. (a) $Ge_{0.177}As_{0.146}Se_{0.677}$ with $\langle r \rangle = 2.5$, (b) for $Ge_{0.078}As_{0.144}Se_{0.778}$ with $\langle r \rangle = 2.3$.

the lifetime consists of at least two different contributions: (1) the superposition of the vibrational spectrum of three different modes from two different molecular species and (2) the increase in the vibrational relaxation rate with decreasing frequency due to increased coupling of the molecule to the host [14,16]. Another feature displayed here is that all three vibrational modes (OH and H_2O) have short lifetimes. Following the relaxation rate for each band in Fig. 2(a) to its smallest value (and hence the molecules weakest coupling to the host) gives lifetimes ~400 ps for both OH and H_2O.

To determine whether local host or average host properties play a key role in the vibrational lifetime mechanism, we have made similar measurements with other compositions of the Ge-As-Se series covering the range from $\langle r \rangle = 2.038$ to 2.75. Fourteen samples have been studied and the relaxation rate results for H_2O are summarized in Fig. 3. These measurements were made at two differ-
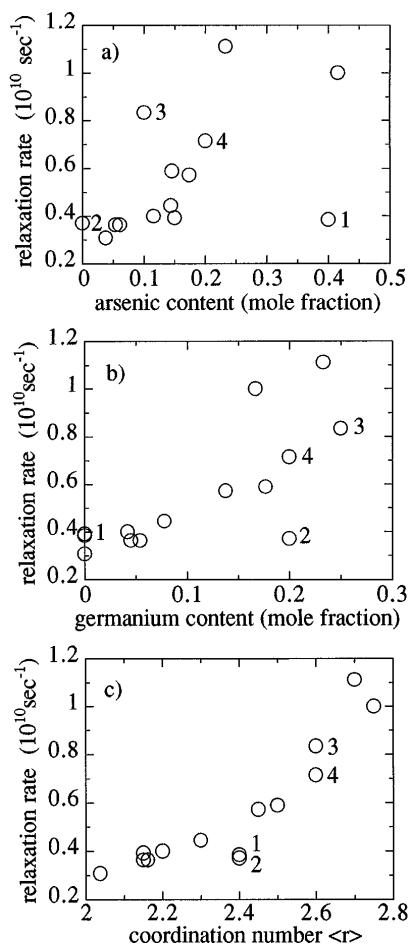
ent frequencies, one centered on the symmetric stretching mode at $\nu_1 = 3515$ cm^{-1} and the other centered on the asymmetric stretching mode at $\nu_3 = 3612$ cm^{-1}. We find an increase of the relaxation rates with increasing $\langle r \rangle$ of about a factor of 3 at both frequencies. No such measurements were possible on OH over this series of glasses because in some ranges the concentration of these molecules was too small.

In order to determine whether the chemical composition or average network properties play a key role in the relaxation mechanism, we plot the experimentally determined relaxation rates in three different ways in Fig. 3: (a) versus the arsenic content, (b) versus the germanium content, and (c) versus the mean coordination number. These plots demonstrate that the scatter of the data in Fig. 3(c) is much smaller than that in Fig. 3(a) or 3(b). 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 support the network interpretation.

There is another possible interpretation which needs to be considered. Figure 3(b) shows that the relaxation rate also increases with increasing Ge concentration as does the high frequency tail of the VDOS [12]; hence it might be argued that the energy gap law could account for the change in the vibrational lifetime. However, this approach cannot explain the same relaxation rates found for samples with the same $\langle r \rangle$ but different Ge content, for example, the two samples labeled 1 and 2 in Fig. 3(b) with $\langle r \rangle = 2.4$: As_2Se_3 and $GeSe_4$, respectively, which have completely different compositions but show the same relaxation rates. In this case the energy gap law fails and the influence of the network topology is apparent.

There is additional evidence that the energy gap law does not work for this molecule-glass system since there is no difference between the relaxation rate of the diatomic molecule OH and the triatomic molecule H_2O. For H_2O there is the additional internal anharmonic energy decay channel from the stretching modes to the bending mode and then from the bending mode into modes of the glassy host, a less strongly forbidden process than for vibrational energy transfer from the OH stretch mode into modes of the glassy host.

One surprising feature is that nearly the same lifetime is found for the ν_3 mode and the ν_1 mode, showing that there is no measurable internal relaxation of the H_2O ν_3 mode to the ν_1 mode via a one phononlike process. This is in contrast to the behavior of H_2O molecules in liquids observed by Graener and Seifert [19] who found at room temperature a fast (~5 ps) internal relaxation towards an equilibrium population of these H_2O stretching modes in liquid solutions.

In conclusion, time resolved measurements demonstrate a site-dependent relaxation rate for the vibrational modes of OH and H_2O in a chalcogenide glass series at low

FIG. 3. Low temperature relaxation rate of the H_2O symmetrical stretching mode at $\nu_1 = 3515$ cm^{-1} in the Ge-As-Se glass series vs different parameters: (a) as a function of the arsenic content (mole fraction), (b) the germanium content (mole fraction), and (c) the mean coordination number $\langle r \rangle$. The sample temperature is 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) $\langle r \rangle = 2.6$, $Ge_{0.2}As_{0.2}Se_{0.6}$.

temperatures. We found similar lifetimes for OH and H_2O, in disagreement with the energy gap law. The main discovery of this vibrational lifetime investigation on the symmetric and asymmetric stretch modes of the H_2O molecule across the Ge-As-Se glass series is a simple monotonic dependence of the relaxation rate on the mean coordination number $\langle r \rangle$ and not the chemical composition. This finding also contradicts an energy gap law interpretation and demonstrates that the vibrational lifetime of the guest molecule depends not only on the local bonding but also on the topological environment.

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