Anomalously large decoupling of rotational and shear relaxation in a molecular glass

E. L. Gjersing and S. Sen

Department of Chemical Engineering and Materials Science, University of California at Davis, Davis, California 95616, USA

P. Yu

Solid State NMR Facility, University of California at Davis, Davis, California 95616, USA

B. G. Aitken

Glass Research Division, Corning, Inc., Corning, New York 14831, USA (Received 18 October 2007; published 13 December 2007)

 31 P NMR spectroscopy is used to study the nature of the molecular dynamics in a P-doped molecular As sulfide glass in the region of glass transition. Isotropic tumbling of the constituent molecules in the glass is observed even at ~70 K below glass transition temperature, indicating an anomalously strong decoupling of this motion from viscosity and diffusion. The presence of such dynamic orientational disorder at temperatures where the positional disorder is likely to be nearly frozen in is unusual in molecular glass formers and may have important implications in understanding the thermodynamic vs dynamic origin of glass transition.

DOI: 10.1103/PhysRevB.76.214202

PACS number(s): 64.70.Pf, 61.43.Fs, 76.60.-k

I. INTRODUCTION

A liquid, if it does not crystallize on cooling, can undergo "glass transition," a falling out of equilibrium in terms of motion and rearrangement of its molecular constituents. The rapid increase in viscosity of a glass-forming liquid by more than 10 orders of magnitude on cooling and its divergence near and below the glass transition temperature T_g transform the flowing liquid into a rigid solid without the long-range order characteristic of crystals. The glass transition has been the subject of extensive thermodynamic, kinetic, and structural investigation and modeling at the molecular level.^{1–4} In spite of this, the dynamic and thermodynamic nature of the glass transition remains one of the most fascinating and unsolved scientific problems to date.^{3–6}

The structural changes that accompany the cooling of a glass-forming liquid have been found to be small.^{1,6} Therefore, the key ingredients in all modern theories of glass transition are the temperature-dependent changes in the nature and time scale of the atomic or molecular dynamics in a supercooled glass-forming liquid. Recent spectroscopic work on molecular glass-forming liquids has indicated that the correlation times associated with translational and rotational diffusion of the constituent molecules are intimately related to the shear and structural relaxation time scales.⁷ Strong evidence for spatiotemporal heterogeneities in these dynamical processes near T_g has also been reported.⁸⁻¹⁰ However, the origin of the slowdown of the translational and rotational molecular motions remains controversial, and theoretical arguments based on both thermodynamic (volumetric and entropic) and dynamic transitions have been proposed in the literature.^{1–4}

Previous experimental studies of molecular dynamics in the glass transition region have entirely been limited to organic glass formers primarily due to the fact that inorganic molecular glass formers are extremely rare. We have recently reported the finding of molecular arsenic sulfide glasses consisting of isolated cagelike As_4S_3 molecules that are held together by van der Waals forces, with $Ge_3As_{52}S_{45}$ being a

representative composition.^{11,12} These molecules consist of a three-membered As₃ ring surmounted by an AsS₃ pyramid with each S atom being bonded to an As atom in the As₃ ring that is directly below it (Fig. 1). The small amount of Ge doping is necessary in stabilizing this As-rich sulfide glass from devitrification.¹¹ This glass, owing to its molecular nature, displays unusual physical properties including highly fragile behavior in the temperature dependence of viscosity, unusually low T_g (~312 K), and high thermal expansion coefficient (96 ppm/K).¹¹ It is interesting to note that, to the best of our knowledge, the only other predominantly molecular inorganic glass that has been reported in the literature belongs to the P-Se binary system and consists of isolated P_4Se_3 molecules that are conformationally similar to the As_4S_3 molecules.^{13,14} We report here the results of a variable-temperature ³¹P nuclear magnetic resonance (NMR) spectroscopic study of the tumbling dynamics of similar cage



FIG. 1. (Color online) Ball-and-stick model of the structure of As_4S_3 molecule. S and apical and basal As atoms are shown in green, red, and yellow, respectively. P doping results in the replacement of apical As (red) with P.

molecules in a glass of composition $Ge_3P_{1.3}As_{50.7}S_{45}$ in the glass transition region.

II. EXPERIMENT

A. Sample preparation

The glass was synthesized by melting a mixture of the constituent elements (\geq 99.9995% purity, metals basis) in an evacuated (10⁻⁶ Torr) fused silica ampoule and by subsequently quenching the ampoule in cold water. In this glass, a small amount of As (1.3 at. %) from the original composition has been replaced with P such that ³¹P NMR spectroscopy can be used as a probe for studying the molecular dynamics.¹⁶

B. ³¹P NMR spectroscopy

All ³¹P NMR spectra were collected with a Bruker Avance 500 solid-state spectrometer equipped with a 11.74 T wide bore magnet (³¹P Larmor frequency of 202.45 MHz). Crushed glass samples were taken in ZrO₂ rotors. A 4 mm and a 7 mm Bruker cross-polarization magic-angle spinning (CPMAS) probe were used for static NMR experiments at temperatures above and below ambient, respectively. The sample temperature in all experiments was controlled to within ± 2 K using hot or cold N₂ gas. Pb(NO₃)₂ was used as an external standard to calibrate the sample temperature against the temperature of the exhaust N₂ gas. The temperature calibration was performed using the well-known temperature dependence of the 207Pb chemical shift of $Pb(NO_3)_2$.¹⁵ The static spectra were collected with pulse lengths adjusted to yield a magnetization tip angle of 60° at all temperatures. A recycle delay of 15-30 s was used and 100-200 transients were averaged to obtain each spectrum. The ambient temperature magic-angle spinning (MAS) spectrum was collected with a 4 mm Bruker CPMAS probe and the crushed sample was spun at a rate of 14.5 kHz. A magnetization tip angle of 60° (1 μ s pulse duration) and a recycle delay of 30 s were used, and 32 transients were averaged to obtain the MAS spectrum. The ³¹P chemical shift was externally referenced to 85% H₃PO₄ in all experiments.

III. RESULTS AND DISCUSSION

P atoms at such small doping levels are known to preferentially replace the apical As atoms in the molecules to form the top PS₃ pyramid in PAs₃S₃ molecules as shown in Fig. 1.¹⁶ This atomic environment for the P atoms is corroborated by the ³¹P MAS NMR spectrum (Fig. 2) that shows a single sharp peak at a chemical shift of ~126 ppm, consistent with a phosphorus atom bonded to three nearest-neighbor sulfur atoms.^{17,18}

The static ³¹P NMR spectrum of this glass at T=231 K shows a typical powder pattern for a spin-1/2 nuclide that can be simulated well with three principal components of the chemical shift tensor: $\sigma_{11}=66$ ppm, $\sigma_{22}=113$ ppm, and $\sigma_{33}=199$ ppm (Figs. 2 and 3). This chemical shift tensor indicates a distortion of the ideally uniaxial site symmetry of the P nuclides in PS₃ pyramidal environment in the PAs₃S₃ cage



FIG. 2. (a) ³¹P static NMR powder spectrum of $Ge_3P_{1.3}As_{50.7}S_{45}$ glass at T=231 K. (b) ³¹P MAS NMR powder spectrum of the same glass at ambient temperature.

molecules (Fig. 1). This static ³¹P line shape does not show any significant change upon lowering the temperature to 222 K. In contrast, the line shape changes rapidly with increasing temperature above 240 K until it finally collapses to a single narrow Lorentzian peak at the isotropic chemical shift at $T \ge 301$ K, indicating rapid tumbling motion of the PAs₃S₃ (and thus As₄S₃) molecules (Fig. 3). These dynamical changes in the ³¹P line shape are found to be completely



FIG. 3. Experimental ³¹P static NMR spectra of $Ge_3P_{1.3}As_{50.7}S_{45}$ glass and supercooled liquid at temperatures indicated (left) and corresponding simulated spectra (right). Note the effect of motional narrowing on the line shape with increasing temperature. See text for details of the simulation procedure.



FIG. 4. Comparison between τ_{NMR} (squares) and τ_{shear} (circles) for Ge₃P_{1.3}As_{50.7}S₄₅ glass and supercooled liquid at different temperatures. The average shear relaxation times τ_{shear} at temperatures $T \ge T_g$ have been calculated from the shear viscosities η of the Ge₃P_{1.3}As_{50.7}S₄₅ supercooled liquid reported in the literature (Ref. 11) using the Maxwell's relation $\tau_{\text{shear}} = \eta/G_{\infty}$, where G_{∞} represents the infinite frequency shear modulus which is nearly independent of temperature and can be treated as a constant $\sim 3 \times 10^{10}$ Pa, for a wide variety of glass formers (Refs. 1 and 2). The arrow pointing upward marks T_g , while the arrow pointing downward marks the temperature (T=302 K) across which the activation energy of τ_{NMR} changes from \sim 35 kJ/mol at lower temperatures to \sim 50 kJ/mol at higher temperatures.

reversible upon cooling. The ³¹P NMR spectral line shapes in Fig. 3 have been simulated over the entire temperature range 231 K $\leq T \leq$ 319 K using a model of reorientational exchange of PAs₃S₃ molecules among N different orientations under the rigid molecule ($T \leq 231$ K) powder pattern via isotropic tumbling. The analytic expression for the resulting line shape is given by the real part of $g(\omega)$, where $g(\omega) = (1/N)L/[1 - (L/\tau_{\text{NMR}})]$ and $L = \sum_{j=1,N}[i(\omega - \omega_j) + 1/T_{2j}]$ $+N/\tau_{\rm NMR}$]⁻¹, where ω_i is the frequency, T_{2i} is the reciprocal of the intrinsic linewidth corresponding to the orientation j, and $1/\tau_{\rm NMR}$ is the frequency of the reorientational exchange or tumbling frequency of the PAs₃S₃ molecules. In this analysis, the frequencies ω_i corresponding to 400 orientations (N) were generated by taking that many angular steps through the expression for the uniaxial powder pattern.¹⁹ The value of T_{2i} has been kept constant as 0.3 ms for all orientations in all of the simulations. A single average temperature-dependent tumbling frequency $\tau_{\rm NMR}^{-1}$ is found to be sufficient for simulation of all spectra.

The time scale τ_{NMR} of the molecular tumbling is compared with that of the macroscopic shear relaxation process τ_{shear} derived from the viscosity data in an Arrhenius plot in Fig. 4. At temperatures above T_g , the two time scales tend to converge, indicating a coupling between the two processes. However, τ_{shear} diverges and strongly decouples from τ_{NMR} below T_g by several orders of magnitude (Fig. 4). This strong decoupling is in sharp contrast with the results obtained in previous studies on organic molecular glass-forming liquids. In the latter, the rotational diffusion time scales remain strongly coupled to viscosity, while the translational diffusion time scales become faster and decouple near the glass transition region. Previous studies have shown that this apparent violation of the Stokes-Einstein and Debye predictions can be accounted for when the dynamical heterogeneity is taken into consideration.⁷⁻⁹ Clearly, significant diffusive motion of the constituent molecules in this chalcogenide glass is not expected at temperatures below T_o , and the positional disorder of these molecules in the structure is expected to be frozen in at the experimental time scale. In contrast, the frequency of rotational reorientation of these molecules is found to remain surprisingly fast ($\sim 2 \text{ kHz}$) even at ~ 70 K below T_g . Hence, dynamically, the glass behaves like a system where the molecules reorient relatively freely over a time scale during which their average positions remain fixed in space. It is interesting to note that such dynamics is somewhat similar to the molecular dynamics encountered in plastic crystals where the molecules reorient while their positions remain fixed at the lattice sites of the structure. In fact, high-temperature polymorphs of As₄S₃ and P_4S_3 are examples of such plastic crystalline phases.^{20–23} Since plastic crystals can form orientational glasses on quenching, the similarity in the molecular dynamics between plastic crystals and a structural glass as observed here may imply fundamental mechanistic similarities between glass transition processes in orientational and structural glasses. It should be noted here that the temperature dependence of the rotational dynamics and the associated heat capacity changes in molecular plastic crystals are similar to those of the main or α relaxation in structural glasses.^{24,25} On the other hand, the temperature dependence of the molecular dynamics observed here has similarities with that of the slow (Johari-Goldstein) β processes in glass formers.^{26,27} However, recent NMR studies have shown that the slow β processes in molecular glasses are fundamentally different in that they involve highly restricted reorientation of the molecules and not isotropic rotational tumbling as has been observed here.²⁷

Finally, the temperature dependence of $\tau_{\rm NMR}$ in the Arrhenius plot in Fig. 4 shows a break in the slope at $T \sim 302$ K, a temperature near T_g . The corresponding activation energies are found to be ~50 and 35 kJ/mol, above and below $T \sim 302$ K, respectively (Fig. 4). The weak coupling of $\tau_{\rm NMR}$ with glass transition accompanied by an increase in the activation energy above $T \sim T_g$ may be indicative of the effect of the onset of significant long-range diffusion of the molecules on the tumbling process.

The anomalously large decoupling between the time scales of rotational reorientation and shear relaxation in a molecular glass as observed here may have important implications in understanding the nature of the glass transition process. As the heat capacity of a supercooled liquid is larger than that of the stable crystals, extrapolation of the entropy vs temperature curves of these two phases below T_g results in an intersection of the two curves at a positive temperature T_K , known as the Kauzmann temperature.^{3,28} A further extrapolation would lead to an entropy for the supercooled liquid that is less than that of the crystal. Since the entropy of a crystal goes to zero as $T \rightarrow 0$ K, a lower value for the supercooled liquid would necessitate a negative value of entropy, in direct violation of the third law of thermodynamics. This

phenomenon is known as the Kauzmann catastrophe that can be avoided if the supercooled liquid forms an ideal glass with a unique configuration at $T \sim T_K$.³ According to the thermodynamic model of glass transition, the observed glass transition is a kinetically masked manifestation of a true second-order thermodynamic phase transition at T_K .

Previous studies have shown that the value of the constant T_0 obtained from fitting the viscosity vs temperature data of a supercooled glass-forming liquid with the Tammann-Vogel-Fulcher (TVF) equation $(\log_{10} \eta = A + B/T - T_0)$, where η is viscosity and A, B, and T_0 are constants) corresponds closely to the calorimetrically determined T_K . This correspondence is within 10% for fragile glass formers such as the molecular chalcogenide glass studied here, characterized by a fragility index m of ~102, where m is given by²⁹ m $= d \log_{10} \langle \tau \rangle / d(T_g/T) |_{T=T_g}$. A TVF fit to the viscosity data of the chalcogenide glass results in a T_0 value of ~268 K (Fig. 3). At this temperature, the stable crystalline polymorph of α -As₄S₃ does not exhibit any rotational reorientation of the constituent molecules, while the ³¹P NMR line shape of the glass at similar temperatures indicates a relatively rapid tumbling motion of the PAs₃S₃ and As₄S₃ molecules with $\tau_{\rm NMR} \sim 10^{-4}$ s (Figs. 2 and 3). Therefore, at $T \sim T_K$, this glass is expected to have nonzero rotational configurational entropy. This observation raises the question of whether the corresponding supercooled liquid would display similar behavior if it could be equilibrated at T_{K} . If so, then such unusual molecular dynamics that continues down to the Kauzmann temperature may have important consequences in understanding the connection between dynamics and thermodynamics in a glass-forming liquid and the Kauzmann catastrophe.

IV. SUMMARY

To summarize, ³¹P NMR spectroscopy has been employed to study the tumbling dynamics of the constituent molecules in a chalcogenide glass. A comparison between the time scales for isotropic rotational reorientation and that for shear relaxation indicates large decoupling of the two time scales below T_g , a phenomenon that is unexpected in a simple molecular glass. The results imply that the positional disorder of the constituent molecules is largely frozen below T_g , while the orientational disorder remains sufficiently rapid (several kilohertz or faster) at least down to ~ 70 K below T_{g} . Although the characteristics of strong decoupling from shear relaxation and near-Arrhenius temperature dependence of the dynamics observed here are similar to those of Johari-Goldstein-type β processes, dynamically they are distinct. The β process primarily involves highly restricted rotational jumps of molecules in contrast with the isotropic molecular tumbling motion observed in this study.

ACKNOWLEDGMENTS

This work was supported by the NSF Grant No. DMR-0603933 for S.S. The authors wish to thank S. C. Currie for sample preparation.

- ¹G. N. Greaves and S. Sen, Adv. Phys. **56**, 1 (2007).
- ²C. A. Angell, K. L. Ngai, G. B. McKenna, P. F. McMillan, and S. W. Martin, J. Appl. Phys. 88, 3113 (2000).
- ³P. G. Debenedetti and F. H. Stillinger, Nature (London) **410**, 259 (2001).
- ⁴E. Donth, *The Glass Transition: Relaxation Dynamics in Liquids and Disordered Materials* (Springer-Verlag, Berlin, 2001).
- ⁵P. W. Anderson, Science **267**, 1615 (1995).
- ⁶M. D. Ediger, Science **287**, 604 (2000).
- ⁷S. F. Swallen, P. A. Bonvallet, R. J. McMahon, and M. D. Ediger, Phys. Rev. Lett. **90**, 015901 (2003).
- ⁸M. D. Ediger, Annu. Rev. Phys. Chem. **51**, 99 (2000).
- ⁹M. T. Cicerone and M. D. Ediger, J. Chem. Phys. **104**, 7210 (1996).
- ¹⁰K. Schmidt-Rohr and H. W. Spiess, Phys. Rev. Lett. 66, 3020 (1991).
- ¹¹B. G. Aitken, J. Non-Cryst. Solids 345-346, 1 (2004).
- ¹²S. Sen, S. Gaudio, B. G. Aitken, and C. E. Lesher, Phys. Rev. Lett. **97**, 025504 (2006).
- ¹³D. J. Verrall and S. R. Elliott, Phys. Rev. Lett. **61**, 974 (1988).
- ¹⁴R. T. Phillips, D. Wolverson, M. S. Burdis, and Y. Fang, Phys. Rev. Lett. **63**, 2574 (1989).
- ¹⁵T. Takahashi, H. Kawashima, H. Sugisawa, and T. Baba, Solid State Nucl. Magn. Reson. **15**, 119 (1999).
- ¹⁶B. H. Christian, R. J. Gillespie, and J. F. Sawyer, Acta Crystallogr., Sect. C: Cryst. Struct. Commun. C43, 187 (1987).

- ¹⁷C. Rosenhahn, S. Hayes, G. Brunklaus, and H. Eckert, in *Phase Transitions and Self-Organization in Electronic and Molecular Networks*, edited by J. C. Phillips and M. Thorpe (Kluwer Academic, Dordrecht/Plenum, New York, 2001), pp. 123–141.
- ¹⁸B. G. Aitken, R. E. Youngman, and C. W. Ponader, J. Non-Cryst. Solids **284**, 34 (2001).
- ¹⁹M. Mehring, *Principles of High Resolution NMR in Solids* (Springer-Verlag, Berlin, 1983).
- ²⁰R. Tycko, G. Dabbagh, R. M. Fleming, R. C. Haddon, A. V. Makhija, and S. M. Zahurak, Phys. Rev. Lett. **67**, 1886 (1991).
- ²¹ A. Loidl and R. Böhmer, in *Disorder Effects in Relaxational Processes*, edited by R. Richert and A. Blumen (Springer-Verlag, Berlin, 1994), pp. 659–696.
- ²²T. K. Chattopadhyay, E. Gmelin, and H. G. von Schnering, J. Phys. Chem. Solids **43**, 925 (1982).
- ²³T. K. Chattopadhyay, E. Gmelin, and H. G. von Schnering, J. Phys. Chem. Solids **43**, 277 (1982).
- ²⁴F. Affouard, J.-F. Willart, and M. Descamps, J. Non-Cryst. Solids 307-310, 9 (2002).
- ²⁵F. Affouard and M. Descamps, Phys. Rev. E **72**, 012501 (2005).
- ²⁶M. Paluch, C. M. Roland, S. Pawlus, J. Ziolo, and K. L. Ngai, Phys. Rev. Lett. **91**, 115701 (2003).
- ²⁷M. Vogel and E. Rössler, J. Chem. Phys. **114**, 5802 (2001).
- ²⁸W. Kauzmann, Chem. Rev. (Washington, D.C.) 43, 219 (1948).
- ²⁹C. A. Angell, Physica D **107**, 122 (1997).