PHYSICAL REVIEW B **77**, 020201(R) (2008)

Viscoelastic relaxation in molten phosphorus pentoxide using photon correlation spectroscopy

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(Received 16 November 2007; revised manuscript received 11 December 2007; published 16 January 2008)

A study of the viscoelastic relaxation in anhydrous liquid P_2O_5 is reported. Properties of the time decay of the dynamic structure factor, including the average structural relaxation time and the stretching exponent, were obtained for temperatures from 850 °C to near the glass transition (T_g=419 °C) using photon correlation spectroscopy. Analysis indicates that P_2O_5 is a strong glass-forming liquid but one that exhibits an abnormally nonexponential relaxation near T_g. The viscoelastic behavior of P_2O_5 is compared with that of its alkali-metal-modified metaphosphate counterparts $NaPO_3$ and $LiPO_3$, as well as with the mechanical relaxation of chalcogenide glasses, to demonstrate common patterns in dynamical behavior presumably arising from changes in the average connectivity of the glass structure.

DOI: 10.1103/PhysRevB.77.020201 PACS number(s): 64.70.P−, 78.35.+c, 66.20.−d, 78.40.−q

Phosphorus pentoxide (P_2O_5) ranks third among the top network-forming oxides (behind SiO_2 and B_2O_3) in terms of its commercial use in glass products, and it is an important chemical compound in many other materials. P_2O_5 is a major component in aluminophosphate glasses, whose large thermal expansion is advantageous for special glass-to-metal seals, and in biocompatible calcium phosphate glasses and glass ceramics used to promote the regeneration of bone tissue.[1] It is also the material of choice for hosting optically active rare earth ions as a lasing medium in ultrahigh-power lasers.[2]

Over the years, several studies have focused on the *structural* properties of phosphate glasses and two excellent reviews are available.[1,3] However, far less work has been done to elucidate the *viscoelastic* behavior of this commercially signifcant oxide glass former. Indeed, while there are numerous studies[4,5] on the glass transition in simple molecular liquids like glycerol, salol, and orthoterphenyl, which are liquids at ambient temperatures, there have been far fewer investigations of the more commercially relevant, network-forming oxides like SiO_2, B_2O_3, and P_2O_5, whose liquid state requires refractory temperatures. Nevertheless, the few studies of molten oxide glasses that have appeared in the literature[6–10] reveal a strikingly different dynamical signature near the glass transition in comparison with the molecular liquids. As Angell pointed out some years ago,[11] the viscosity (or equivalently, the structural relaxation time) of supercooled liquids increases near the glass transition in a manner that is highly non-Arrhenius-like for what are termed "fragile" glass-forming molecular liquids, but nearly Arrhenius-like for the "strong" network-forming oxides.

These differences between fragile and strong are believed to reflect differing levels of cooperativity in the structural relaxation of the liquid.[12] The cohesion of a fragile liquid involves isotropic van der Waals interactions in which many molecules collectively respond to an applied stress, each individually making minor adjustments to accommodate macroscopic flow. In the strong network-forming oxides, viscous flow is thought to be far less cooperative. Rather, it is believed to be the product of a "tear and repair" process wherein individual covalent bonds are discretely broken and reformed under applied stress.[13]

These differences in the cooperativity of the microscopic relaxation are also thought to be responsible for the degree in which the structural relaxation displays a nonexponential decay. The decay of quantities such as the dynamic structure factor (associated with density fluctuations of wave vector q) is often modeled by a stretched exponential of the form

$$S_q(t) \propto \exp[-(t/\tau)^{\beta}], \quad 0 < \beta < 1. \tag{1}$$

The smallness of β is a measure of the width in the corresponding distribution of relaxation times present in the decay. It is also referred to as the heterogeneity parameter,[4] as it is thought to provide a measure of the diversity of microscopic processes that collectively contribute to the macroscopic structural relaxation. Support for this interpretation derives from a literature survey by Boehmer *et al.*,[14] who demonstrated a general correlation of β with fragility. Strong glass-forming oxides display most nearly exponential relaxation (β between 0.7 and 1), while β decreases with increasing fragility.

Phosphorus pentoxide is a challenging liquid to study. First, it is a volatile fluid, exhibiting an unusually high vapor pressure upon melting, and so must be investigated in a sealed container. Second, it is highly hygroscopic. In fact, it is widely used as an aggressive desiccant. Studies of vitreous P_2O_5 conducted over the years attest to the difficulty in obtaining an anhydrous sample. This is evident in the values for the glass transition temperature T_g, which have increased, chronologically, from 260 °C reported in 1971,[15] to 319 °C reported in 1986,[16] to the most recent value of 380 °C reported in 1993. In this most recent study,[17] an anhydrous sample was produced by sublimation of P_2O_5 together with continuous isolation in a dry atmosphere.

To our knowledge, the only previous study of the viscoleastic behavior of molten P_2O_5 is the 1963 study[18] wherein a falling sphere method was employed to estimate the viscosity over a limited (1.5 decade) range for temperatures from 545 to 655 °C. These limited data led Martin and Angell[16] to conclude that P_2O_5 behaves like a strong liquid, similar to SiO_2. However, as these same data extrapolate to a glasslike viscosity at T_g=260 °C, one must concede that these measurements are not representative of a truly anhydrous sample.

In this paper, we report measurements of the structural relaxation in anhydrous liquid P_2O_5. Our dynamic light scattering technique is able to track the structural relaxation time over six orders of magnitude and exhibits a fragility similar to that of other strong glass formers like SiO_2, GeO_2, and As_2O_3. Interestingly, we observe that the shape of the relaxation function evolves with temperature and that the heterogeneity parameter (β) decreases considerably on approach to T_g. In comparing these results with similar measurements conducted on metaphosphate glasses, we demonstrate that the heterogeneity parameter displays a variety of temperature dependencies; decreasing on approach to T_g for P_2O_5 while increasing for the metaphosphates. Comparison of these dynamics with those in chalcogenide systems suggests a common dependence on the bond connectivity of the covalent network.

Anhydrous P_2O_5 with a purity greater than 99.99% (Sigma-Aldrich) was handled only in a dry argon environment. A carefully cleaned (10% HF wash followed by drying on a vacuum line) quartz ampoule (8 mm outer diameter, 6 mm inner diameter) was loaded with P_2O_5 and fitted with a vacuum-tight valve. This was then attached to a vacuum line ($\approx$30 mTorr) and the lower portion of the ampoule was inserted into a vertical tube furnace. The P_2O_5 was slowly sublimed at around 330 °C and collected into an upper portion of the ampoule. While still under vacuum, the lower section of the ampoule containing the residue was torched off and the ampoule was then flame sealed above the sublimed material. A small quartz rod was attached for maneuvering the ampoule within the optical furnace.

Other details of our photon correlation spectroscopy technique can be found elsewhere.[9] All measurements were performed at a 90° scattering angle and only the vertically polarized scattering was analyzed owing to the abnormally low scattering intensity. In our experience[7,9,19] with other oxide liquids (B_2O_3 and As_2O_3) a distinct beam of scattered light was visible to the naked eye and could be confidently separated from stray parasitic elastic scattering. This was not the case for P_2O_5 and as a result of its weak scattering (I_S) relative to the parasitic elastic light (I_{LO}), only heterodyne detection could be achieved. In this instance, the intensity-intensity autocorrelation function that we measure is approximately[20] related to the dynamic structure factor, $S_q(t)$ as

$$C_{\mathrm{het}}(t) \approx 1 + 2f_{\mathrm{coh}}\frac{I_S}{I_{\mathrm{LO}}}S_q(t). \tag{2}$$

No attempt was made to determine either I_S or I_{LO} and so the actual amplitude of $S_q(t)$, the so-called nonergodic level,[9] could not be estimated.

In analyzing the spectra, $S_q(t)$ was fitted to the stretched exponential of Eq. (1) to obtain the heterogeneity parameter (β) and the average relaxation time[5] $\tau_{\mathrm{av}}=[\Gamma(\beta^{-1})/\beta]\tau$. The temperature variation of the average relaxation time is presented in Fig. 1, while that of the heterogeneity parameter is displayed in the inset. In Fig. 1 we see that the relaxation time is approximately Arrhenius-like for temperatures below 650 °C, but it is non-Arrhenius-like overall. A common approximation for the non-Arrhenius-like temperature dependence is the Vogel-Fulcher function[4] $\tau_{\mathrm{av}}=\tau_0 \exp[DT_0/(T-T_0)]$. When fitted to this expression, we obtain $\tau_0=4.5\times10^{-10}$ s, $D=7.6$, and $T_0=422.0$ K.

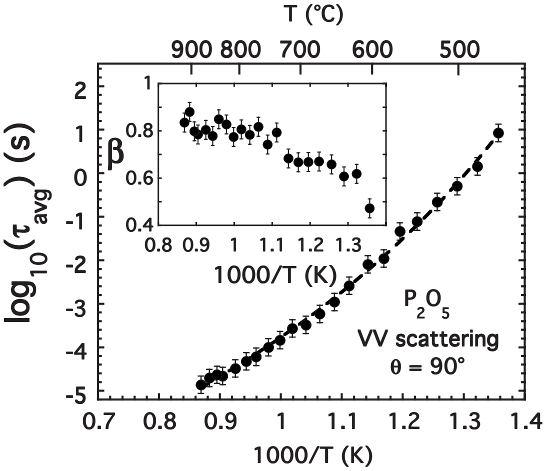

FIG. 1. Average structural relaxation time of liquid P_2O_5 against reciprocal temperature. The dashed line indicates the Vogel-Fulcher curve fit discussed in the text. Inset shows corresponding plot of the stretching parameter, showing how the heterogeneity increases on approach to T_g.

In the inset, we observe that the relaxation is nearly exponential ($\beta\approx0.85$) at the highest temperatures but becomes increasingly nonexponential with decreasing temperature. The value of the heterogeneity parameter at T_g is smaller than that reported for other strong oxide glass formers (Boehmer *et al.*[14] report that β at T_g ranges from 0.7 for SiO_2 to 1 for GeO_2), and it is in fact more typical of a fragile liquid.

An estimate for the glass transition temperature of our sample can be obtained by extrapolating to an average relaxation time of 100 s where $T_g=419\pm10$ °C. This temperature is slightly higher than that reported by Hudgens and Martin[17] but reaffirms the low water content of our sample. In any event, the 40 K discrepancy is not unusual for strong glasses and it could be readily accounted for by differences in how T_g is defined.

Armed with T_g we can now construct a fragility plot;[11] that is, a plot of $\log_{10}(\tau_{\mathrm{av}})$ against reciprocal temperature scaled to T_g. Figure 2(a) shows our data for P_2O_5 plotted in this manner (albeit rotated by 90° from its normal orientation) together with data taken for two metaphosphate liquids.[19] From the slope of the data near T_g, we find that P_2O_5 is a strong glass-forming liquid with a fragility index[14] of $m=20\pm2$. This value is identical to that reported[14] for SiO_2 and GeO_2 and only slightly more fragile than As_2O_3 ($m\approx18\pm2$).[8,9]

These fragility values are near the $m=16$ limit[14] for strong glass formers, and their nearly Arrhenius-type temperature dependence would suggest that viscous flow occurs predominantly through a tear and repair process. By comparison, the two metaphosphate liquids possess a polymeric structure consisting of PO_3 chains that are more weakly cross linked by alkali-metal ions.[1] Here the fragility index is approxi-

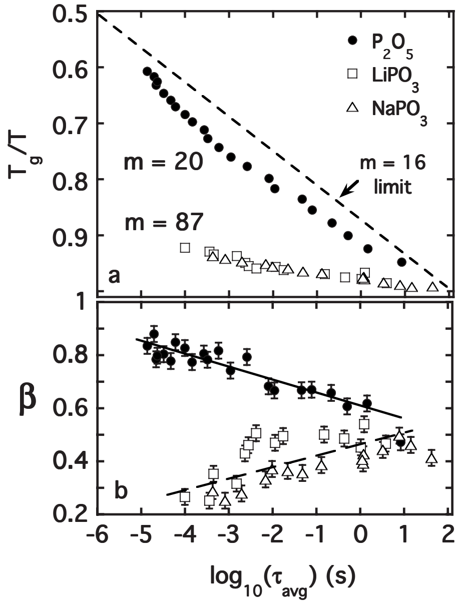

FIG. 2. (a) Fragility plot for P_2O_5, $LiPO_3$, and $NaPO_3$. Values of the fragility index are indicated. The dashed line references the extreme of strong behavior with a limiting fragility index of $m=16$. (b) Corresponding plot of the stretching exponents for the same oxide glasses against the average structural relaxation time. Lines are only guides to the eye.

mately $m \approx 90(\pm 5)$,[19] suggesting that viscous flow in these liquids more resembles that of organic polymer melts.

Shown in Fig. 2(b) is the variation of the heterogeneity parameter for these same oxide glasses on approach to T_g. Ignoring the temperature dependencies for the moment, an overall general agreement with the correlation of Boehmer *et al.*[14] is seen in that β is generally smaller for the more fragile liquids. However, once again, there is a stark contrast among these oxide liquids in terms of the temperature dependence for the heterogeneity. For P_2O_5 the heterogeneity parameter decreases as T_g is approached, while the two (polymeric) metaphosphates exhibit an anomalous increase in the heterogeneity parameter with decreasing temeperature. For $NaPO_3$, the increase of β shown in Fig. 2(b) is monotonic while $LiPO_3$ exhibits a slightly abrupt increase near $\tau_{\mathrm{av}} \approx 3$ ms.

The origin of this anomalous trend seen in the metaphosphates is unknown, but might be related to unique structural changes observed in both $LiPO_3$ and $NaPO_3$ by x-ray diffraction.[21] In studies conducted on both monovalent (Li, Na) and divalent (Mg, Ca) metaphophate glasses and liquids, a so-called first sharp diffraction peak (FSDP) was absent for all the glasses below T_g, but developed only in $NaPO_3$ (and to a lesser extent in $LiPO_3$) in the liquid above T_g. The FSDP in $NaPO_3$ intensified with increasing temperature and was attributed to the thermally induced dilation of the coordination sphere surrounding the alkali-metal ion.[21] The increased ion mobility associated with the dilation could potentially alter the nature of the cooperative relaxation so as to produce the unusual temperature dependence for β that we observe.

Evident in Fig. 2 are sharply contrasting dynamics that have arisen from the addition of an alkali metal into the phosphate network. The effect of this chemical change on the structure of the covalently bonded phosphate network is well understood.[1,2] P_2O_5 is composed of a three-dimensional network of PO_4 tetrahedra connected by three bridging oxygen bonds (one oxygen is double bonded). As alkali-metal oxides are added, one of the bridging oxygen bonds is ruptured. This "depolymerization" increases with increasing alkali-metal content in such a manner that all the PO_4 tetrahedra eventually become connected by only two bridging oxygen bonds at the metaphosphate composition.[1] Thus the metaphosphates are polymeric, consisting of two-dimensional chains.

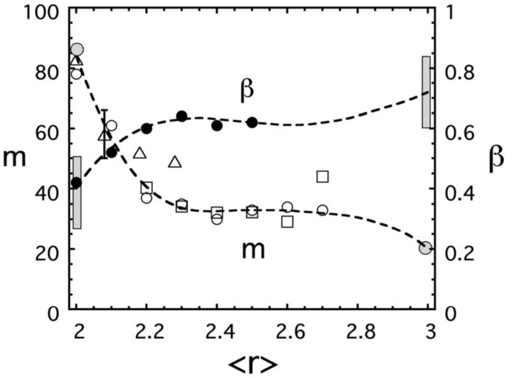

FIG. 3. Fragility (open circles) and heterogeneity parameter (solid circles) reported (Ref. 25) for $As_xGe_xSe_{1-2x}$ as functions of the average bond connectivity. Fragility values (open squares) for $Ge_xSb_{10}Se_{90-x}$ are also included (Ref. 24). Also included are values of the fragility (hashed circles) and range of heterogeneity parameters (hashed rectangles) observed for P_2O_5 (at $\langle r \rangle = 3$) and for the two metaphosphates (at $\langle r \rangle = 2$) as well as fragility values (open triangles) estimated from viscosity data of mixed alkali-metal ultraphosphates (Ref. 31). The two dashed lines are only guides to the eye.

The changes in the covalently bonded network of the ultraphosphate brought on by alkali-metal addition are not unlike the changes occurring in chalcogenide glasses, such as $As_xGe_ySe_{1-x-y}$, as a function of composition. Several studies[22–26] have examined the elastic and mechanical properties of chalcogenide glasses in response to changes in the average bond coordination $\langle r \rangle$. Impetus for these chalcogenide studies lies partly in theoretical considerations[27] regarding glass-forming stability in relationship to an optimal balance between bond constraints and the degrees of freedom. A mean-field theory of bond constraints[28,29] suggests that stability is maximum near a critical connectivity $\langle r \rangle = 2.4$, where "rigidity percolation" occurs. Glasses with $\langle r \rangle < 2.4$ are "underconstrained" and possess a large fraction of "floppy" modes. Glasses above the critical threshold are "overconstrained" and characterized by percolation of "rigid" modes throughout the network.

Studies of mechanical relaxation in this same ternary chalcogenide system have been recently carried out by Bohmer and Angell.[25] Results for the fragility index and heterogeneity parameter obtained on glasses along the tie line $As_xGe_xSe_{1-2x}$ are shown in Fig. 3 as a function of the average connectivity. For the underconstrained Se glass, a fragility of $m \approx 77$ and $\beta(T_g) \approx 0.42$ were reported, and these rapidly changed to $m \approx 33$ and $\beta(T_g) \approx 0.62$ for $\langle r \rangle \geqslant 2.3$. Also included in the figure are values for the fragility obtained from viscosity studies by Senapti and Varshneya[24] on a comparable chalcogenide system ($Ge_xSb_{10}Se_{90-x}$).

Important similarities can be seen between the dynamic behavior of these chalcogenides and that of the phosphate glasses. For the ultraphosphates, the comparable quantity to characterize the overall connectivity of the oxide network would be the average number of bridging oxygen bonds per PO_4 tetrahedron.[30] Thus, for P_2O_5, the network is overconstrained with $\langle r \rangle = 3$, while for the metaphosphates it is underconstrained with $\langle r \rangle = 2$. In Fig. 3, the fragility values for the phosphate glasses examined here have been included together with values estimated from limited viscosity data available in the literature for mixed alkali-metal ultraphosphates.[31] The fragility of the metaphosphates agrees closely with that of the amorphous Se at $\langle r \rangle = 2$, and the fragility of P_2O_5 is not inconsistent with the chalcogenide trend. Also in the figure, we have plotted shaded regions to represent the temperature-dependent range observed for the heterogeneity parameter for both P_2O_5, at $\langle r \rangle = 3$, and for the metaphosphates at $\langle r \rangle = 2$. Again, the results are consistent with those of the chalcogenides.

In summary, the primary result of our study is embodied in Fig. 1: an investigation of the viscoelastic response of anhydrous P_2O_5. We find that P_2O_5 exhibits strong ($m = 20$) glass-forming behavior, but with a large degree of heterogeneity in the relaxation. But we also see sharply contrasted behaviors in the dynamics of P_2O_5 as compared with its alkali-metal-modified counterparts. Not only are the modified glasses more fragile than P_2O_5, but they display something of an anomaly in that the heterogeneity parameter in metaphosphate liquids increases with decreasing temperature. Despite this anomalous temperature dependence in the metaphosphates, a common pattern is demonstrated for the fragility and the heterogeneity parameter for both chalcogenides and oxide glasses as a function of the bond connectivity of the covalent network.

The authors gratefully thank S. Martin and R. Brow for helpful discussions. This work is supported by the Petroleum Research Fund (Grant No. 43743-GB10).

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