Observation of a Reentrant Structural Transition in an Arsenic Sulfide Liquid

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Abstract

A fundamental and much-debated issue in glass science is the existence and nature of liquid-liquid transitions in glass-forming liquids. Here we report the existence of a novel reentrant structural transition in a S-rich arsenic sulfide liquid of composition $As_{2.5}S_{97.5}$. The nature of this transition and its effect on viscosity are investigated *in situ* using a combination of differential scanning calorimetry and simultaneous Raman spectroscopic and rheometric measurements. The results indicate that, upon heating significantly above its glass transition temperature (261K), the constituent $[S]_n$ sulfur chains in the structure of the supercooled liquid first undergo a $[S]_n \rightleftharpoons S_8$ chain-to-ring conversion near ~383K, which is exothermic in nature. Further heating above 393K alters the equilibrium to shift in the opposite direction towards an endothermic ring-to-chain conversion characteristic of the well-known λ-transition in pure sulfur liquid. This behavior is attributed to the competing effects of enthalpy of mixing and conformational entropy of ring and chain elements in the liquid. The existence of reentrant structural transitions in glass-forming liquids could provide important insight into the thermodynamics of liquid-liquid transitions and may have important consequences for harnessing novel functionalities of derived glasses.

I. Introduction

The structural and thermodynamic nature of phase transitions in the liquid state remain a highly controversial topic in condensed matter science.[1,2] As density serves as the principal order parameter, it is not surprising that the majority of the experimental studies in the literature focused on the existence of transitions between the low- and high- density phases in the liquid state, or in the amorphous state in glasses derived from these liquids.[1,2] Some of the unambiguous experimental observations of the existence of such transition have been made on network glass-formers such as SiO_2 and Y_2O_3-Al_2O_3 as well as on molecular glass-formers including H_2O, elemental P, triphenyl phosphite and chalcogenides such as elemental S and As_4S_3.[3–13] Perhaps the most prominent examples of a liquid-liquid transition (LLT) are those observed in elemental P and S.[4,8] In both cases a molecular low-density liquid transforms into a polymerized high-density liquid with increasing pressure. This structural transformation is similar to the well-known λ-transition in liquid S.[14] The λ-transition involves polymerization of a predominantly molecular liquid containing S_8 ring molecules at $T< T_\lambda$ to one containing a large concentration of $[S]_n$ polymeric chains at $T > T_\lambda$.[15–17] This dynamic polymerization of liquid S occurs at ambient pressure, at a temperature $T_\lambda \approx 432K$ that is significantly above its melting point $T_m \approx 388K$ and the relative concentration of the polymeric chains reaches a maximum of ~ 65-70% near 573 K.[16] As temperature approaches T_λ from below, this structural transformation results in an endothermic event that is accompanied by a relatively abrupt increase in the viscosity of molten sulfur by several orders of magnitude as well as concomitant sharp changes in density, electrical and optical properties and in specific heat.[18–23] However, in the vast majority of the cases the average structure of a glass-forming liquid changes in an approximately continuous fashion across a LLT and experimental observation of the effect of the transition on the bulk transport properties such as viscosity becomes experimentally challenging.[24] Simultaneous measurements of the pressure and temperature dependent evolution of the atomic structure and the transport properties of the liquid across the transition may provide unique information in this regard. Such measurements are particularly important as, in the absence of structural and thermodynamic data, the existence of LLTs was erroneously postulated in the past in a number of liquid polymers on the basis of kinetic (e.g. viscoelastic and dielectric loss processes) data alone.[25,26] This body of work was subsequently criticized by Plazek and coworkers[27–30] as they pointed out that the observation of temperature dependent kinetic phenomena alone may not be sufficient to establish the existence of LLTs. Instead, any such claim needs to be validated by direct observation of clear thermodynamic and structural transition in the liquid.

Recently we have modified a rheometer in our laboratory (see Supplementary Materials for details) in order to enable simultaneous measurements of the shear viscosity and the Raman spectrum of a liquid to establish direct connection between its structural evolution and viscous flow as a function of temperature. Here we present the first results of an *in situ* simultaneous Raman spectroscopic and viscometric study of a liquid of composition $As_{2.5}S_{97.5}$ (liquidus temperature ~ 388K) using this probe. These results directly demonstrate the presence of a novel reentrant liquid-liquid transition in a glass-forming liquid for the first time. We find that in spite of its chemical similarity with elemental S, the $As_{2.5}S_{97.5}$ liquid shows a rather different behavior owing to the coexistence of $[S]_n$ chains and S_8 rings in its structure compared to the structure of liquid S consisting solely of S_8 rings at temperatures below the λ-transition.

II. Experimental

A. Synthesis and Differential Scanning Calorimetry

The $As_{2.5}S_{97.5}$ glass was synthesized from a 10g batch via the conventional melt-quench method. Elemental arsenic (Sigma-Aldrich, 99.999%) and sulfur (Alfa Aesar, 99.999%) were mixed and taken in an evacuated (10^{-4} Torr) silica ampoule and loaded into a rocking furnace. The ampoule was heated to 923K over 13 h, and subsequently held and rocked at this temperature for 24 h to ensure homogeneity. The melt was subsequently quenched by dipping the ampoule in ice-water to obtain the glass sample. Approximately 12 mg of $As_{2.5}S_{97.5}$ glass was loaded in a hermetically sealed 40 μL aluminum crucible and differential scanning calorimetric (DSC) scans were acquired using a Mettler-Toledo DSC1 STAR calorimeter under a constant flow of nitrogen and a heating rate of 10 K/min heating rate.

B. Raman spectroscopy and Rheometry

Simultaneous *in situ* Raman spectroscopic and viscosity measurements were carried out using a rheometer (Anton-Paar MCR92) modified (see Supplementary Materials for a detailed description of the setup) to connect with a Fourier transform (FT) Raman spectrometer (Brucker RFS 100/S). Prior to the viscosity measurements the glass sample was heated above the softening point to 393K in a flowing nitrogen environment inside the rheometer and trimmed between an 8 mm diameter stainless steel upper plate and a 55 mm diameter quartz bottom plate to form a sandwich-like geometry with a thickness of ~ 1 mm. The Newtonian viscosity in a range of ~ 10^2 – 10^6 Pa.s was measured using steady shear, where the viscosity was determined as the ratio of stress and strain rate at various shear rates $\dot{\gamma}$ ranging between 0.0005 s^{-1} and 0.05 s^{-1}. The upper plate was used to apply the strain while the non-removable lower plate remained stationary. The corresponding stress response was recorded using a torque transducer. The variable temperature unpolarized Raman spectra were collected in backscattering geometry with a Bruker RFS 100/s

FT Raman spectrometer equipped with a Nd:YAG laser operating at 1064 nm. Laser light was focused on the sample from below the bottom quartz plate of the rheometer using a fiber-optic cable, which also collected the scattered light. A power level of 400 mW was used, and 512 scans were collected and averaged at each temperature to obtain the Raman spectra with a resolution of4 cm^{-1}.

III. Results and Discussion

It has been shown in previous studies in the literature that, while pure S is a molecular liquid at $T< T_\lambda$, progressive addition of As to S breaks up an increasing fraction of the S_8 rings and forms S_n chain segments in the network that are cross-linked by $AsS_{3/2}$ pyramids.[31] However, a significant fraction of the S_8 rings still survive in binary As-S liquids with As contents ranging between 5 and 15 at%, such that the ring-to-chain (RTC) transformation can be clearly detected in a DSC scan, albeit the corresponding $T_\lambda \sim 413$K is now located in the supercooled regime for liquids with >5 at% As.[32,33] Additionally, the RTC conversion in these binary liquids has been shown to be preceded by an exothermic event near ~ 393K (see Supplementary Materials), whose atomistic origin remains unknown.[32,33] The DSC heating scan of the $As_{2.5}S_{97.5}$ glass/liquid investigated in this study (*Figure 1*) displays a low-temperature endotherm corresponding to the glass transition with $T_g \sim 261$K, and a high-temperature endothermic peak located near 423K, which can be assigned to the RTC transformation based on the above discussion (see Supplementary Materials). It may be noted that, consistent with the role of arsenic as a cross-linker in chalcogenide networks, the T_g of this glass is somewhat higher than that reported for fast-quenched molten sulfur, which displays a glass transition between 233K and 253K, depending on the thermal history.[34] It is also clear from *Figure 1* that the RTC transformation endotherm is preceded by a strong exothermic peak with an onset just above 378K. Typically, the appearance of an exothermic peak above T_g in a DSC upscan of a glass signifies crystallization. However, the peak of the exotherm in Figure 1 is located at ~ 395K, which is significantly higher than the liquidus temperature (388K) and comparable to the melting points of crystalline α-S (383K) and β-S (393K).[35] Besides, powder x-ray diffraction measurements on glass samples quenched after holding at the onset temperature for the duration of the DSC scans indicate the absence of any crystallization and confirms the amorphous nature of the sample. Moreover, as discussed below, *in situ* Raman spectroscopic measurements do not show any evidence of crystallization of the $As_{2.5}S_{97.5}$ liquid at this temperature upon heating, even at a slower rate than the DSC scans.

The Raman spectra of this liquid (*Figure 2*), collected *in situ*, shed light on the nature of these structural transitions. These Raman spectra are characterized by three strong bands centered at ~ 150, 218 and 472 cm^{-1} and a shoulder near ~ 460 cm^{-1} (Figure 2). Previous Raman spectroscopic studies of crystalline and amorphous S assigned the 150 and 218 cm^{-1} band to S-S-S bending modes and the 472 cm^{-1} band to S-S stretching mode of the S_8 ring molecules.[17] On the other hand, the shoulder near 460 cm^{-1} has been shown to correspond to the S-S stretching modes of $[S]_n$ chains.[15–17] The absence of any other bands in the Raman spectra indicate that the concentration of other molecular allotropes of S is negligible in the liquid.[35] Increasing the temperature above 348K results in a decrease in the relative intensity of this shoulder band with respect to the 472 cm^{-1} band, a trend that continues up to ~ 383K (*Figure 3*). This trend is a clear indication of a chain-to-ring (CTR) transformation in the liquid in this temperature range where the DSC exotherm is observed. Further increase in temperature above 393K results in a remarkable reversal in this trend and the intensity of the 460 cm^{-1} shoulder band continues to increase with respect to that of the 472 cm^{-1} band, up to the highest temperature of 453K reached in these experiments (*Figure 3*). Therefore, the endothermic peak in the DSC upscan indeed corresponds to the RTC transformation in the liquid, consistent with previous studies on S-rich As-S binary liquids. It may be noted here that these temperature dependent changes in the Raman spectra were found to be completely reversible upon cooling. Moreover, no evidence for the crystallization of α and β polymorphs of S was observed in the form of narrowing and splitting of the S-S-S bending modes at 150 and 218 cm^{-1} into multiplets.[17]

Additional insight regarding the temperature dependence of the thermal volume expansivity of the $As_{2.5}S_{97.5}$ liquid can be gained from the temperature-induced mode frequency shifts for the S-S-S bending modes at 150 and 218 cm^{-1} (*Figure 4*). These mode frequencies in the supercooled $As_{2.5}S_{97.5}$ liquid soften at a rate of –0.005 cm^{-1}/K at temperatures below ~ 383K. An increase in temperature results in a slight hardening of these modes, followed by a rapid softening at a rate of – 0.016 and – 0.013 cm^{-1}/K, respectively, at temperatures above ~ 393K. These changes in the temperature dependence of the mode frequencies coincide well with the CTR and RTC transformations, as observed in the high-frequency region of the Raman spectra (*Figure 3*). The temperature dependence of the vibrational mode frequencies $\left(\frac{\partial \nu}{\partial T}\right)_P$ of a material has an explicit phonon contribution $\left(\frac{\partial \nu}{\partial T}\right)_v$, and a contribution from the implicit quasiharmonic effect $\frac{\alpha}{\beta}\left(\frac{\partial \nu}{\partial P}\right)_T$ related to the thermal volume expansion such that: $\left(\frac{\partial \nu}{\partial T}\right)_P = \left(\frac{\partial \nu}{\partial T}\right)_v - \frac{\alpha}{\beta}\left(\frac{\partial \nu}{\partial P}\right)_T$. Here α and β are the volume thermal expansion coefficient and compressibility, respectively. Previous studies on sulfur have shown that the frequency softening for the 150 and 218 cm^{-1} band corresponding to the S-S-S bending modes in S_8 molecules is controlled entirely by the volume expansion term.[36] Therefore, the sharp changes in the $\left(\frac{\partial \nu}{\partial T}\right)_P$ of these modes in *Figure 4* indicate a corresponding change in the equation of state of the $As_{2.5}S_{97.5}$ liquid that accompany the CTR and RTC transformations.

The temperature dependence of the shear viscosity of the $As_{2.5}S_{97.5}$ liquid, measured simultaneously during the Raman spectroscopic measurements, shows a highly unusual and rather curious behavior (*Figure 5*). The viscosity of a glass-forming liquid (GFL) and its activation energy are normally expected to decrease monotonically with increasing temperature, resulting in a negative curvature. In contrast, the viscosity of the $As_{2.5}S_{97.5}$ liquid displays a sharp kink near the onset of the exotherm at ~ 383K, followed by a region of positive curvature at higher temperatures. The activation energy drops sharply at this point and then rises again near the inflexion point of the endotherm (~ 423K). These changes in the activation energy of viscous flow are remarkable telltale signs of relatively sharp structural transitions in the liquid, which are consistent with the appearance of the exotherm and the endotherm in the DSC upscan (*Figure 1*).

When taken together, the DSC, viscosity and Raman spectroscopic results indicate that with increasing temperature above T_g the $As_{2.5}S_{97.5}$ liquid first undergoes a CTR transformation that involves a shortening of the -S-S-S- chain segments cross-linked by the AsS_3 pyramids via scission of As-S bonds, and the condensation of these segments into S_8 rings (*Figure 6*). Consequently, this results in a shortening of the length of the intervening -S-S-S- chain segments and brings the AsS_3 pyramids closer to one another, which effectively gives rise to a spatial clustering of As atoms in the structural network. Such a transformation involving ring-condensation and atomic clustering can be expressed in the form of a reaction: $AsS_{n+8} \rightleftharpoons AsS_n + S_8$, which is consistent with a lowering of enthalpy and a corresponding exothermic signature observed in the DSC upscan. On the other hand, the RTC transformation at a higher temperature is essentially a reversal of this reaction, which involves opening of the S_8 rings into -S-S-S- chain segments. This transformation increases conformational entropy as well as redistributes the As atoms by increasing the spatial separation between the AsS_3 pyramids (*Figure 6*). In comparison with the case for liquid elemental S, the entropy change for the RTC transformation was speculated by Ward and Myers[37] to be larger in As-S liquids with 2-15% As, and consequently to be responsible for the composition-independent lowering of the temperature of this transformation in these binary liquids. This sequence of transformations implies the existence of a reentrant LLT in the $As_{2.5}S_{97.5}$ liquid that involves temperature induced chain ↔ ring conversion and clustering and re-homogenization of cross-linkers. This temperature-dependent clustering and homogenization is somewhat reminiscent of the reentrant coil ↔ globule transition displayed by certain polymer and protein solutions, which leads to liquid-liquid separation with the coexistence of lower and upper critical solution temperatures (LCST and UCST). In the case of a closed loop spinodal with LCST and UCST, the existence of the latter can be explained by an increase in mixing entropy and thus can have positive mixing enthalpy. On the other hand, the LCST is not favored by entropy and is expected to have negative enthalpy of mixing.[38] Interestingly, these enthalpic signatures are indeed consistent with the observation of the low-temperature exothermic and high-temperature endothermic signatures in the DSC upscan of the $As_{2.5}S_{97.5}$ liquid (*Figure 1*).

IV. Conclusions

The structural and thermodynamic nature of LLT in $As_{2.5}S_{97.5}$ liquid and its effect on viscosity are investigated. The LLT displays a unique reentrant behavior where the constituent $[S]_n$ chains first undergo an exothermic conversion to S_8 rings near ~383K, which is likely driven by the enthalpy of mixing. Further heating results in an endothermic, entropy-driven ring-to-chain conversion in the liquid above 393K. These structural changes are reflected in an unusual temperature dependence of the viscosity of this liquid. The existence of such reentrant liquid-liquid transitions in glass-forming liquids may have far reaching implications as it may be utilized in future in switching, sensing and other technological applications. Moreover, the application of simultaneous *in situ* rheological and spectroscopic measurements as presented in this study offers exciting opportunities in developing direct atomistic understanding of viscoelastic phenomena and liquid-liquid transitions in glass-forming liquids.

Supplementary Material

1. DSC scans of As_xS_{100-x} glasses with $2.5 \leq x \leq 40$
2. Schematic of the combined rheometry-Raman spectroscopy set up used in this study

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Figure captions:

Figure 1. DSC scan of $As_{2.5}S_{97.5}$ glass obtained at a heating rate of 10 K/min. Arrows show location of glass transition and location of maxima for the exothermic chain-to-ring and endothermic ring-to-chain transformation.

Figure 2. Temperature dependent evolution of unpolarized Raman spectra of $As_{2.5}S_{97.5}$ liquid. All spectra are normalized to the band at 472 cm^{-1} and temperatures are denoted alongside the spectra. Arrows and dashed vertical lines denote location of the individual bending and stretching modes.

Figure 3. Temperature dependent evolution of the high-frequency region in the Raman spectra (see Figure 2) of $As_{2.5}S_{97.5}$ liquid normalized to the 472 cm^{-1} band corresponding to the S-S stretching mode of the S_8 ring molecules. Arrows denote the change in the relative intensity of the 460 cm^{-1} band corresponding to the S-S stretching modes of $[S]_n$ chains, which decreases with increasing temperature up to 383 K (bottom) followed by a monotonic increase on heating up to 453 K (top) and serves as a marker of the chain : ring ratio in the liquid.

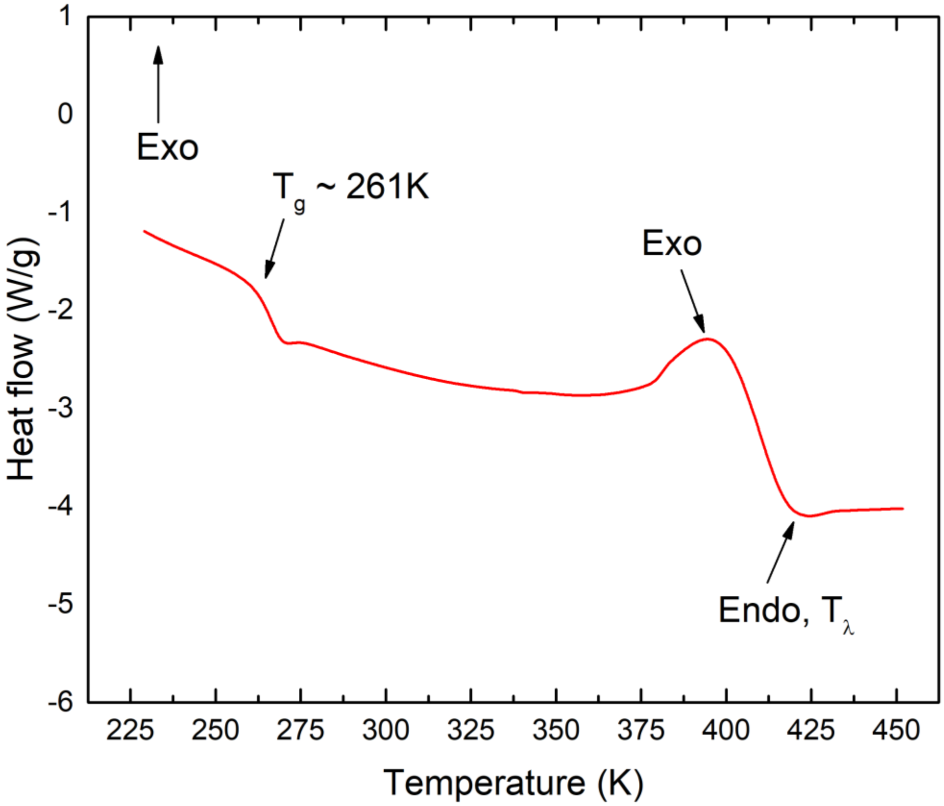
Figure 4. Temperature dependent frequency shift of the S-S-S bending modes at (a) 150 cm^{-1} and at (b) 218 cm^{-1} in the Raman spectra in Figure 2. Straight line segments through the data points are linear least squares fits in the low and high temperature regions.

Figure 5. Temperature dependence of viscosity (filled squares) of $As_{2.5}S_{97.5}$ liquid. Blue and red shaded regions correspond to temperature ranges over which chain-to-ring and ring-to-chain

transformations occur in the liquid. These transformations are shown schematically in the inset where yellow spheres represent S atoms and As atoms are not shown for clarity.

Figure 6. Schematic representation of reentrant chain-to-ring and ring-to-chain transition in $As_{2.5}S_{97.5}$ liquid at elevated temperatures. The red and yellow spheres denote arsenic and sulfur atoms, respectively.

Figure 1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T_g ~ 261K
Exo
Endo, T_λ
Heat flow (W/g)
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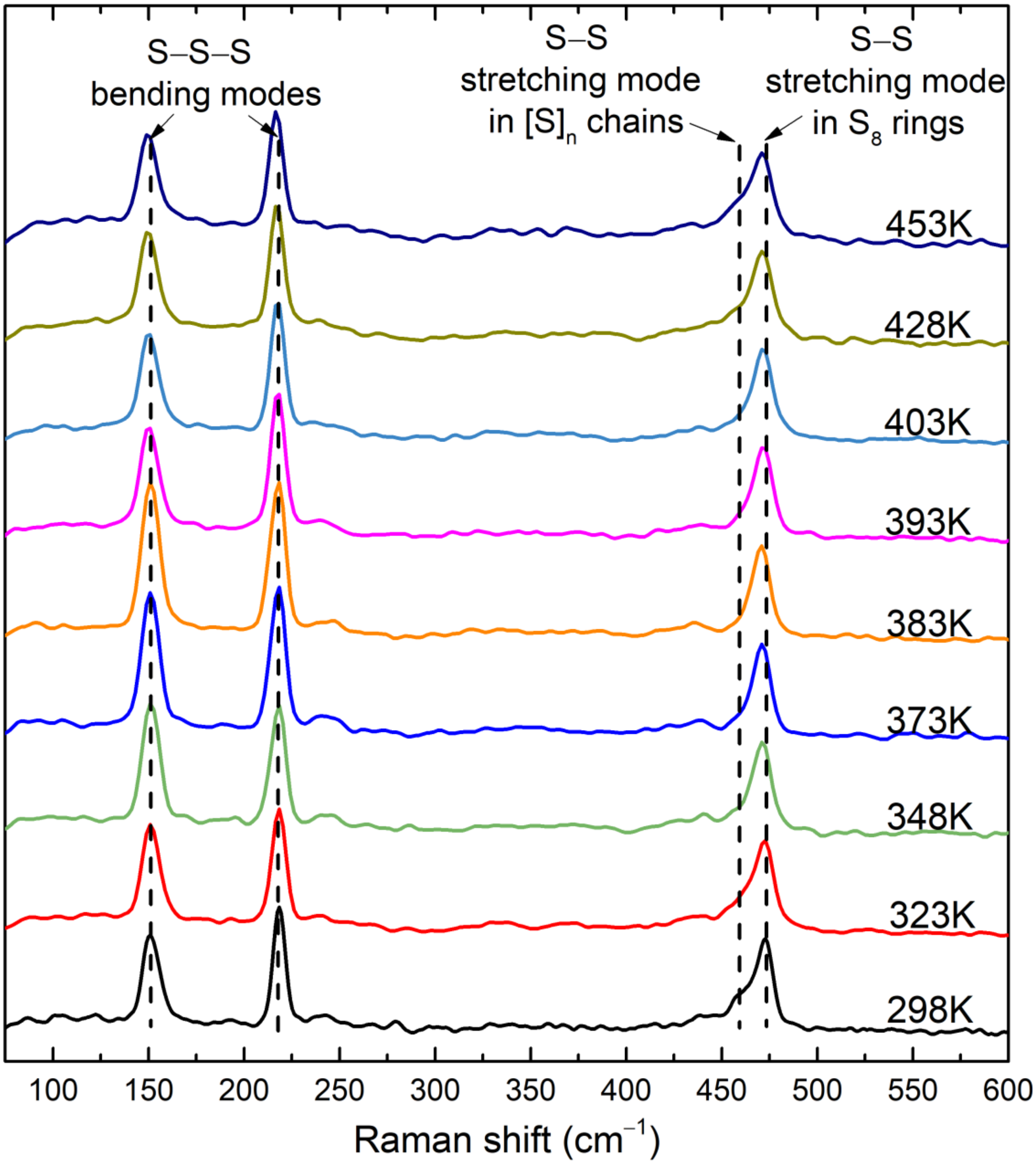
0
-1
-2
-3
-4
-5
-6
225
250
275
300
325
350
375
400
425
450
Temperature (K)

Figure 2


S–S–S
bending modes
S–S
stretching mode
in $[S]_n$ chains
S–S
stretching mode
in S_8 rings
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403K
393K
383K
373K
348K
323K
298K
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150
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250
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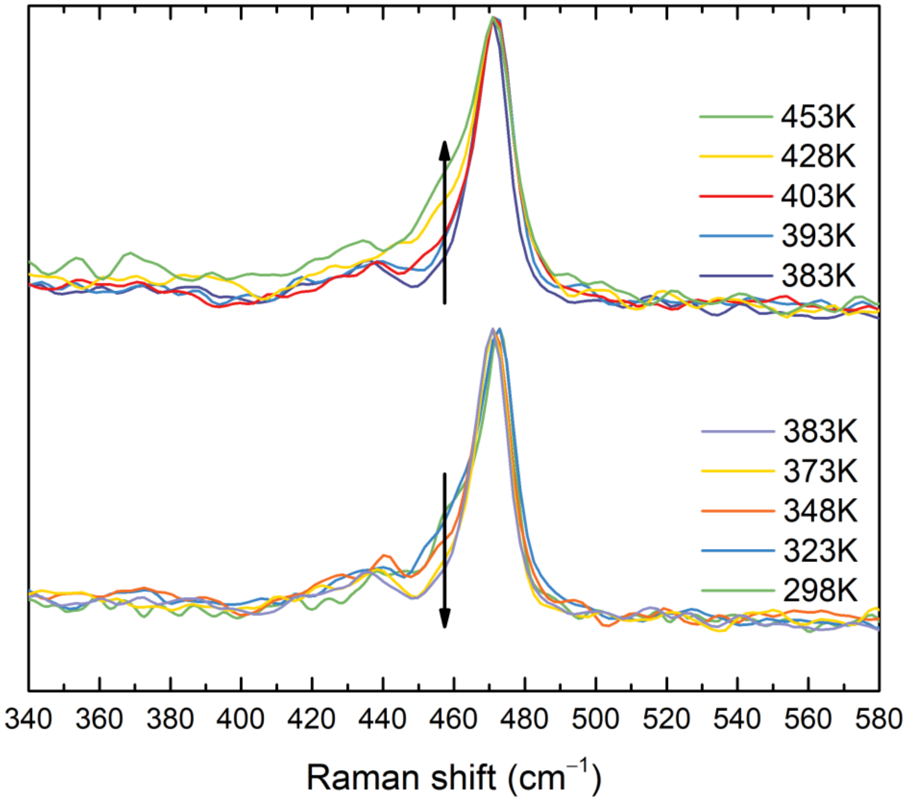
350
400
450
500
550
600
Raman shift (cm^{-1})

Figure 3



453K
428K
403K
393K
383K
383K
373K
348K
323K
298K
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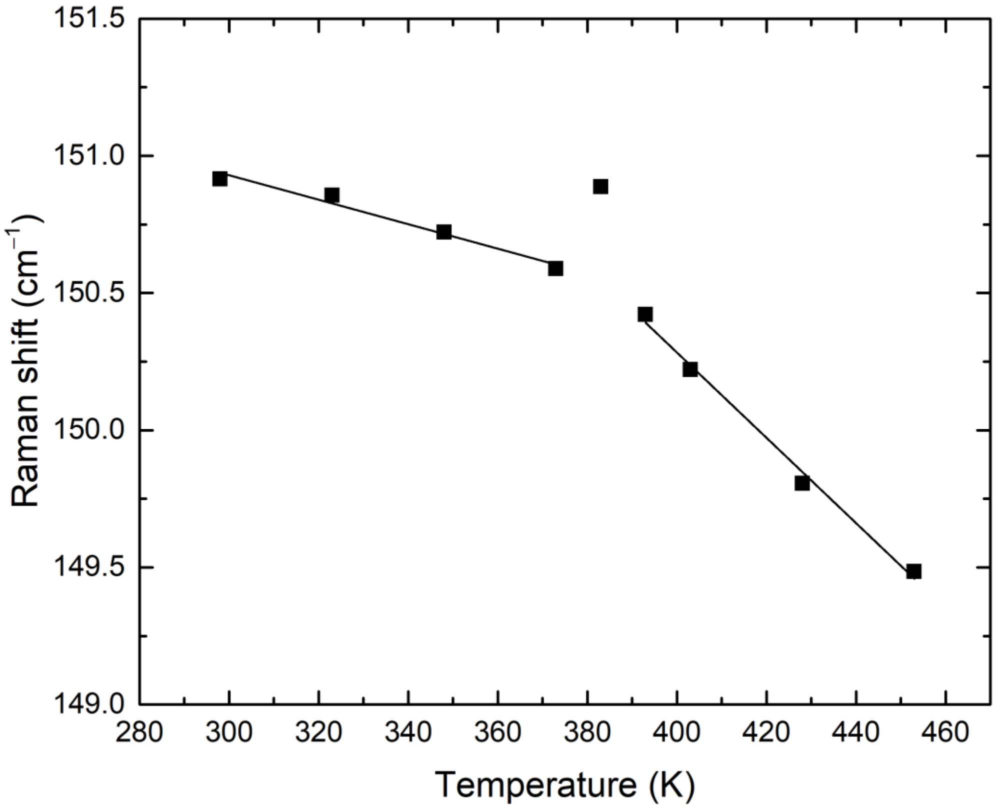
480
500
520
540
560
580
Raman shift (cm^{-1})

Figure 4a


151.5
151.0
150.5
150.0
149.5
149.0
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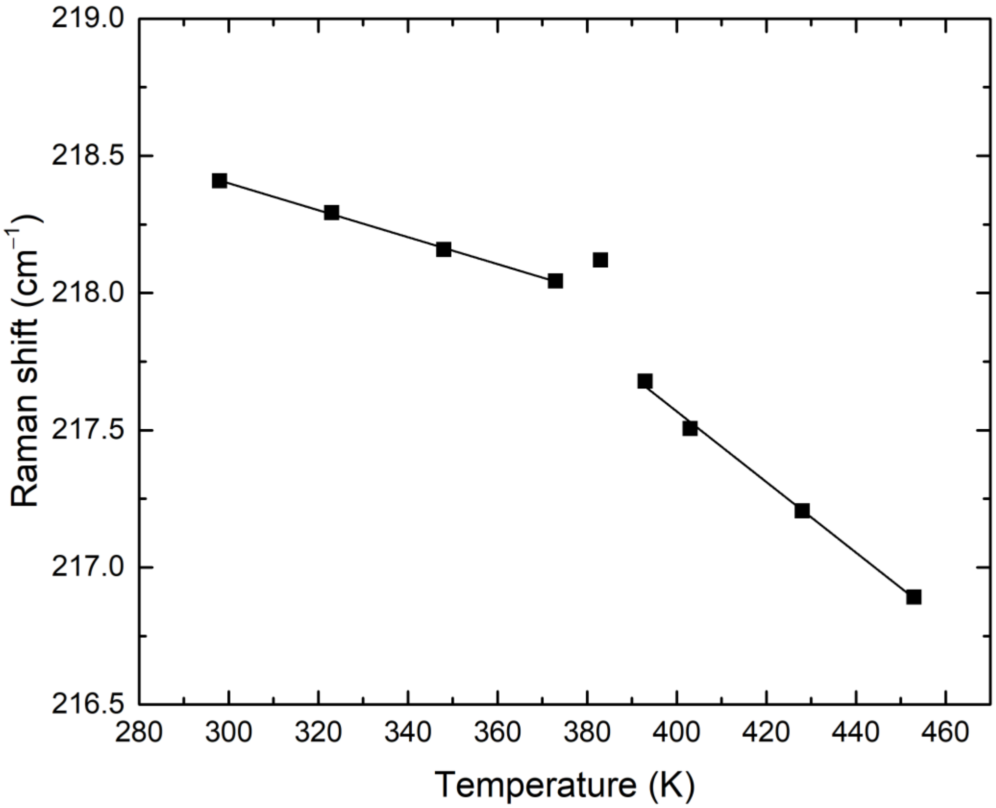
300
320
340
360
380
400
420
440
460
Temperature (K)

Figure 4b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218.5
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217.5
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440
460
Temperature (K)

Figure 5

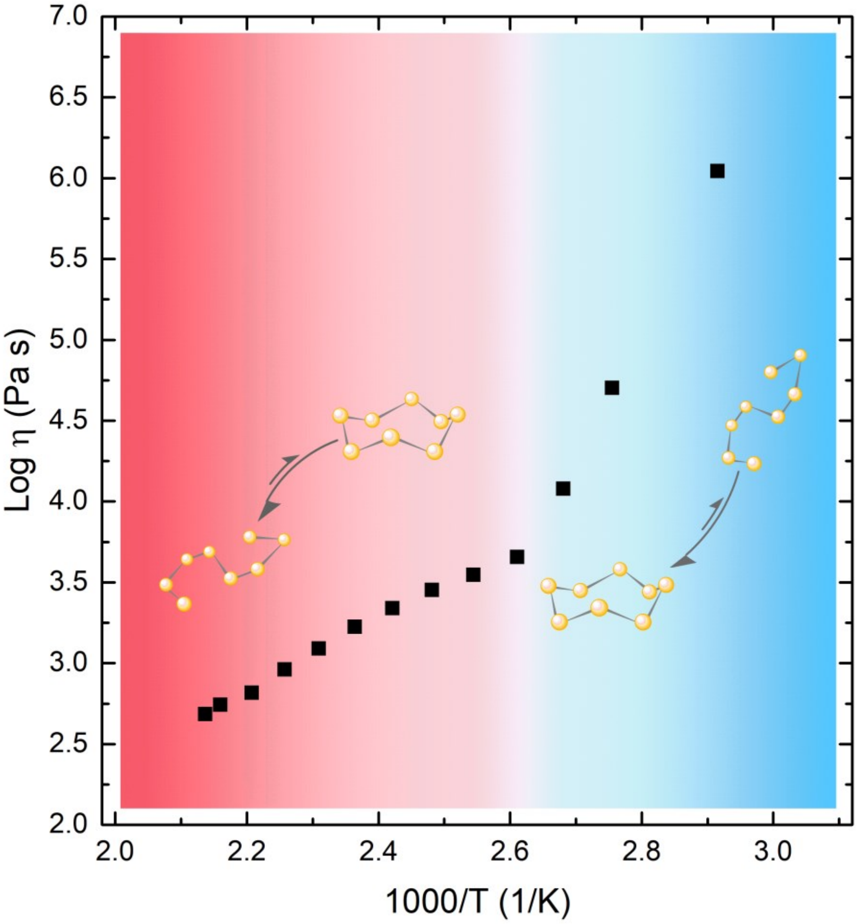

Figure 6