Structural Studies of Phosphorus–Sulfur–Tellurium Glasses by ^{31}P MAS NMR and Vibrational Spectroscopies

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The region of glass formation in the new glass-forming system phosphorus–sulfur–tellurium has been established, and the local structure investigated using ^{31}P wide-line and magic-angle spinning (MAS) NMR as well as vibrational spectroscopies. The results are consistent with the absence of phosphorus–tellurium bonds, and a structure dominated by $S{=}PS_{3/2}$ units. Characteristic chemical shift effects and changes in the vibrational frequencies of the P=S bond suggest that these units associate with tellurium in the glasses. In addition, the presence of tellurium tends to suppress the formation of molecular P_4S_n species, which form at higher phosphorus concentrations in the binary system. All of these results indicate active participation of tellurium in the network consistent with compositional trends of the glass transition temperatures.

Introduction

Non-oxide chalcogenide glasses have attracted widespread attention in the past two decades for their infrared transparency and resultant potential applications in optical fiber technology.[1] Their broad glass-forming regions are a favorable attribute offering compositional tailoring of physical and chemical properties over wide ranges. Among the multitude of glass-forming systems known, glasses based on the heaviest chalcogen, tellurium, enable the furthest possible excursions into far-infrared transmission. However, significant drawbacks of pure telluride systems are their generally low glass-forming abilities, their limited glass-forming regions, and their generally high tendency of crystallization.[2] These difficulties can be avoided by stabilizing the glassy state in ternary mixed-chalcogen systems. In particular, incorporation of tellurium into Ge–Se and As–Se glasses and their sulfur analogs has been studied extensively,[3–7] and wide glass-forming regions have been identified. Further, the structural and solid-state chemistry of crystalline and glassy germanium and arsenic tellurides is well-known, and the role of tellurium in As and Ge mixed chalcogenide glasses is generally understood in terms of mixed assemblies of $AsX_{3/2}$ or $GeX_{4/2}$ environments, respectively (X = S, Se, Te).

This situation is strikingly different for the analogous phosphorus-based systems, which have remained virtually unexplored, because of their relative air and moisture sensitivity. However, the structural aspects of tellurium incorporation into phosphorus chalcogenide glasses are of particular fundamental interest, because neither crystalline nor glassy phases exist in the P–Te binary, and only a few, rather unstable, organometallic compounds with phosphorus–tellurium bonds have been characterized.[8] Therefore, the structural role of tellurium in phosphorus chalcogenide glasses might be expected to differ from that in the analogous arsenic- and germanium-based systems. Indeed, previous ^{31}P magic angle spinning NMR studies of phosphorus–selenium–tellurium glasses suggest the absence of phosphorus–tellurium bonds and indicate further that strong intermolecular interactions between $Se_{3/2}P{=}Se$ sites and tellurium atoms are present.[9] This interaction has been modeled quantitatively by postulating the formation of an association pair $Se_{3/2}P{=}Se{\cdots}Te{<}$ in an equilibrium reaction. The effect appears to be stronger than analogous interactions between structural fragments in the binary tellurium-free glasses, resulting in a significant shift in the equilibrium $PSe_{3/2} + Se \leftrightarrow Se_{3/2}P{=}Se$ units to the right side, along with an increase in the glass transition temperature.

The present contribution deals with the structural effects of tellurium in the previously unknown glass-forming system phosphorus–sulfur–tellurium. We report here, for the first time, the glass-forming region and the glass transition temperatures measured for such glasses.[10] For binary P–S glasses ^{31}P wide-line and MAS-NMR[11] and vibrational spectroscopies[12] suggest that $S{=}PS_{3/2}$ groups are dominant structural features. If, in the ternary P–S–Te system, association of tellurium with such units were to occur as suggested

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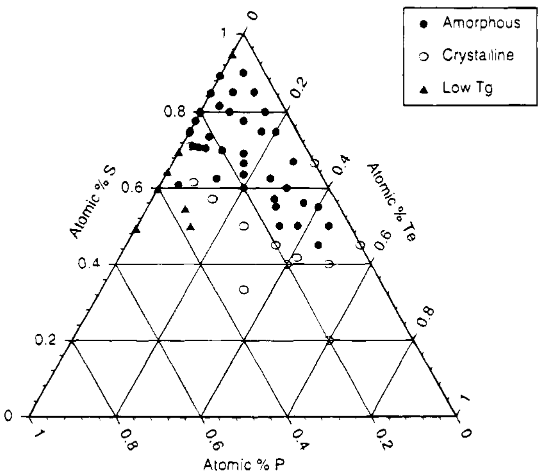

Figure 1. Compositions studied and region of glass formation established in the phosphorus–sulfur–tellurium system.

for the analogous P–Se–Te system, the NMR chemical shifts and vibrational frequencies assigned to the phosphorus–chalcogen double bonds would be affected. This question will be addressed using ^{31}P solid-state NMR and FTIR spectroscopies.

Experimental Section

Sample Preparation and Characterization. Orange to black P–S–Te 2.5 g glass samples were prepared from stoichiometric quantities of the elements (phosphorus, pieces, 99.99%; sulfur, powder, 99.99%; tellurium, powder, 99.99% (Aldrich)). These mixtures were sealed into silica glass ampules under vacuum (10^{-3} Torr) and heated at 700 °C for 2 days. Glasses were formed by plunging these ampules from 700 °C into water at 0 °C. All sample manipulations were carried out under argon in a drybox (Vacuum Atmospheres HE493). The glass-forming region of this system, as determined during the course of this study, is shown in Figure 1.[10] Amorphicity was established using X-ray powder diffraction under an inert atmosphere, using a Scintag diffractometer. Glass transition temperatures and recrystallization exotherms (Table 1) were measured on a DuPont 912 dual-sample differential scanning calorimeter, using 5–10 °C/min heating rates. Figure 2 illustrates that for glasses with fixed phosphorus contents, T_g increases markedly when part of the S atoms are substituted by Te.

Spectroscopy. Solid-state ^{31}P MAS-NMR spectra were recorded at 81.008 MHz using a Nicolet NT spectrometer interfaced with a 4.65 T Oxford magnet. A multinuclear MAS-NMR probe from Doty Scientific was operated under the following conditions: 90° pulses of 6.5 μs length, recycle delay 30 min (resulting in spectra free from saturation effects), spinning speeds 6–9 kHz. In certain cases, liquid-state ^{31}P NMR spectra of CS_2 extracts were examined at 121.65 MHz, using a General Electric GN-300 spectrometer. Complementary midrange infrared spectra were obtained on KBr pellets using a Biorad FT/IR spectrometer.

Table 1. Elemental Compositions x, y Glass Transition Temperatures (($T_g \pm 2$)/°C), and Recrystallization Temperatures (($T_r \pm 2$)/°C) in the Glass System $P_{1.0-x}(S_{1.0-y}Te_y)_x$

sample	% P	% S	% Te	x	y	T_g (°)	T_r (°C)
$S_2Te_{1.0}$	0.00	75.0	25.0	1.00	0.250	*c*	
$S_{9.0}Te_{11.0}$	0.00	47.6	52.4	1.00	0.524	*c*	
$PS_{0.97}$	50.6	49.4	0.00	0.494	0.00	*a* (8)	
$PS_{1.0}Te_{1.0}$	33.3	33.4	33.3	0.667	0.500	*a* (4, 37)	
$PS_{1.0}Te_{3.0}$	20.0	20.0	60.0	0.800	0.750		
$PS_{1.3}Te_{0.33}$	37.5	50.0	12.5	0.625	0.200	*a*	
$PS_{1.5}$	40.3	59.7	0.00	0.598	0.00	*a* (6)	
$PS_{1.5}Te_{0.25}$	36.4	54.5	9.09	0.636	0.143	*a*	
$PS_{1.8}Te_{0.13}$	34.8	60.9	4.35	0.652	0.0667	*a*	
$PS_{1.8}$	35.6	64.4	0.00	0.644	0.00	*a* (23)	
$PS_{2.0}Te_{0.25}$	30.8	61.5	7.69	0.692	0.111		
$PS_{2.0}Te_{0.50}$	28.6	57.1	14.3	0.714	0.200		
$PS_{2.0}Te_{1.0}$	25.0	50.0	25.0	0.750	0.333		
$PS_{2.0}Te_{2.0}$	20.0	40.0	40.0	0.800	0.500		
$PS_{2.3}Te_{1.8}$	20.0	45.0	35.0	0.800	0.437		
$PS_{2.3}$	30.4	69.6	0.00	0.696	0.00	*a* (25)	
$PS_{2.5}Te_{0.50}$	25.0	62.5	12.5	0.750	0.167	130, *b*	217
$PS_{2.5}Te_{2.5}$	16.7	41.7	41.7	0.833	0.500		
$PS_{2.7}Te_{0.083}$	26.7	71.1	2.22	0.733	0.0303		
$PS_{2.7}Te_{0.10}$	26.3	71.1	2.63	0.737	0.0357	115, *b*	143
$PS_{2.8}Te_{0.17}$	25.0	70.8	4.17	0.750	0.0556	136, *b*	251
$PS_{3.0}$	25.3	74.7	0.00	0.747	0.00	145	
$PS_{3.0}$	25.0	75.0	0.00	0.747	0.00	143	175
$PS_{3.0}Te_{0.25}$	23.5	70.6	5.88	0.765	0.0769	123, *b*	176
$PS_{3.0}Te_{1.0}$	20.0	60.0	20.0	0.800	0.250	132, *b*	200
$PS_{3.0}Te_{2.0}$	16.7	50.0	33.3	0.833	0.400	114	
$PS_{3.5}$	22.2	77.8	0.00	0.778	0.00	127, *b*	168
$PS_{3.5}Te_{0.25}$	21.1	73.7	5.26	0.789	0.0667	143	
$PS_{3.5}Te_{0.50}$	20.0	70.0	10.0	0.800	0.125	145	
$PS_{3.5}Te_{1.0}$	18.2	63.6	18.2	0.818	0.222	148, *b*	
$PS_{3.7}Te_{2.0}$	15.0	55.0	30.0	0.850	0.353	124, *b*	196
$PS_{4.0}$	20.2	79.8	0.00	0.798	0.00	130	
$PS_{4.0}$	20.2	79.8	0.00	0.798	0.00	131	
$PS_{4.0}Te_{1.0}$	16.7	66.7	16.7	0.833	0.200	142, *b*	224
$PS_{4.0}Te_{2.0}$	14.3	57.1	28.6	0.857	0.333	132	
$PS_{4.0}Te_{3.0}$	12.5	50.0	37.5	0.875	0.429	113	177
$PS_{4.0}Te_{5.0}$	10.0	40.0	50.0	0.900	0.556		
$PS_{4.5}Te_{1.0}$	15.4	69.2	15.4	0.846	0.182	135	
$PS_{4.5}Te_{4.5}$	10.0	45.0	45.0	0.900	0.500	111	166
$PS_{5.0}Te_{2.0}$	12.5	62.5	25.0	0.875	0.286	116	
$PS_{5.5}Te_{0.25}$	14.8	81.5	3.70	0.852	0.0435	106	
$PS_{5.6}$	15.2	84.8	0.00	0.848	0.00	104	
$PS_{6.0}Te_{0.50}$	13.3	80.0	6.67	0.867	0.0769	109	
$PS_{6.0}Te_{3.0}$	10.0	60.0	30.0	0.900	0.333	106, *b*	
$PS_{7.0}Te_{1.0}$	11.1	77.8	11.1	0.889	0.125	109	
$PS_{7.0}Te_{4.5}$	8.00	56.0	36.0	0.920	0.391	88, *b*	170
$PS_{8.2}$	10.8	89.2	0.00	0.892	0.00	67, *b*	
$PS_{8.5}Te_{0.50}$	10.0	85.0	5.00	0.900	0.0556	102	
$PS_{9.0}Te_{2.0}$	8.33	75.0	16.7	0.917	0.182	115	
$PS_{10.0}Te_{9.0}$	5.00	50.0	45.0	0.950	0.474	108, 82, *b*	129
$PS_{11.0}Te_{8.0}$	5.00	55.0	40.0	0.950	0.421	107, 68, *b*	133
$PS_{15.0}Te_{4.0}$	5.00	75.0	20.0	0.950	0.211	121, 97, *b*	201
$PS_{16.0}Te_{3.0}$	5.00	80.0	15.0	0.950	0.158	111, 103, *b*	
$PS_{17.0}Te_{2.0}$	5.00	85.0	10.0	0.950	0.105	115, 98, *b*	
$PS_{18.0}$	5.25	94.8	0.00	0.947	0.00	*a* (9)	
$PS_{18.0}Te_{1.0}$	5.00	90.0	5.00	0.950	0.0526	106, *b*	
$PS_{13.0}Te_{6.0}$	5.00	67.0	28.0	0.950	0.295	111, *b*	192

[a] Samples were viscous liquids. [b] Differential scanning calorimetry plot indicated more than two thermal transitions. [c] Sample was X-ray crystalline.

Results, Assignments, and Interpretation

Figure 3 shows representative ^{31}P MAS-NMR spectra of binary P–S glasses. The results are identical with those reported previously[11] for a more limited composition range. At the lowest phosphorus concentrations (≤15 at. %), the spectra are characterized by a broad asymmetric MAS central peak in the spectral region 100–115 ppm. On the basis of the anisotropic chemical shift parameters, this resonance has previously been assigned to $S{=}PS_{3/2}$ units within a polymerized matrix. There are at least three partially resolved spectral contributions to this line, their centers being located near −113, −106, and −95 ppm, respectively. The population ratio of these three components is approximately constant and independent of the S/P ratio. Their specific structural assignments are uncertain at the present time. Glasses with phosphorus contents exceeding 15 at. % show in addition several sharp resonances in the 50–65 ppm range (see Table 2), which have been assigned previously to molecular P_4S_9 andP_4S_{10} species.[11] The fraction of phosphorus present in the

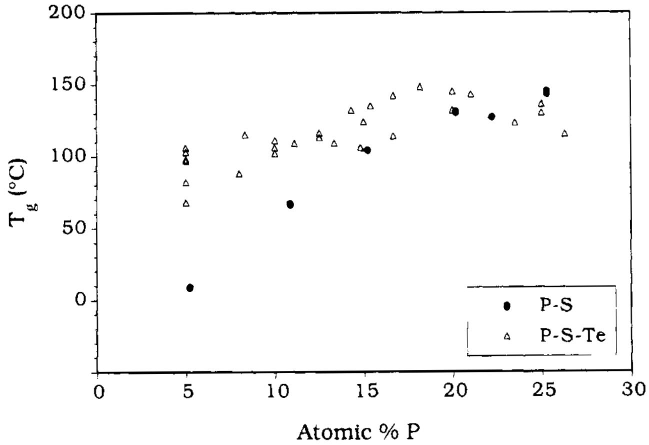

Figure 2. Glass transition temperatures in the systems P−S (circles) and P−S−Te (triangles). Note the significant enhancement of T_g for the ternary glasses containing tellurium.

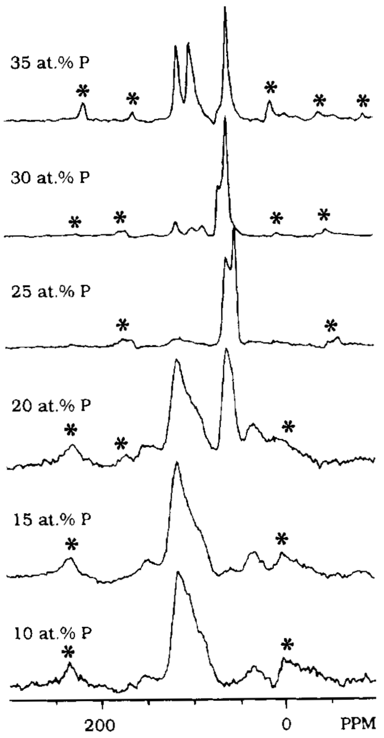

Figure 3. The 81.008 MHz ^{31}P MAS-NMR spectra of binary P−S glasses. Spinning sidebands are indicated by asterisks.

form of these molecules increases with increasing phosphorus content. Glasses with P contents exceeding 30 at. % are essentially entirely composed of P_4S_n molecules. The lack of two-dimensional connectivity of these glasses manifests itself here in a dramatic decrease of the T_g values, which lie below ambient temperature in this concentration region. Solid-state NMR spectra (obtained where possible) and liquid-state NMR spectra of CS_2 extracts reveal large contributions from molecular P_4S_{10}, P_4S_9, P_4S_7, P_4S_5, P_4S_3 in these glasses, their respective ratios reflecting the S/P ratio of the samples. Overall, our results are consistent with previous high-temperature studies of P−S melts.[13]

Figure 4 shows representative results in the ternary P−S−Te system. There are no new resonances that might be attributable to Te-bonded phosphorus atoms,and thus there is no positive evidence for the existence of such species. Compounds with phosphorus−tellurium bonds are generally scarce. Kuhn and coworkers have characterized a series of phosphane tellurides with the general formula $R_3P{=}Te$.[8] For all of these compounds, the ^{31}P resonances are systematically displaced by more than 50 ppm to lower frequency compared to those measured for the analogous sulfur compounds $R_3P{=}S$.[14] Thus, if phosphorus−tellurium bonding would occur to considerable extent in P−S−Te glasses, significant chemical shift effects would be expected in comparison to the binary phosphorus−sulfur glasses, at variance with the experimental results. Inspection of the NMR spectra on an expanded scale (Figure 4b) does reveal, however, subtle low-frequency displacement effects for the polymeric $S{=}PS_{3/2}$ site as the tellurium content is increased. As shown in Figure 5, the magnitude of this effect increases with increasing tellurium content. Figure 6 illustrates an even greater effect when the whole chemical shift tensor is considered. Shown are the wideline spectra, obtained upon Fourier transformation of the free induction decay following a 90°−τ−180°−τ spin echo pulse sequence ($\tau = 50\ \mu s$). In glasses, such line shapes generally arise from the combined effects of (1) the chemical shift anisotropy reflecting nonspherical bonding symmetry and (2) from a distribution of chemical shift tensor values due to variations in local environments. The spectra shown in Figure 6 can be simulated either by

Table 2. ^{31}P **MAS-NMR Data Analysis for P−S−Te Glasses**

sample	S/P	Te/P	%P_4S_n (±1%)	δ (ppm)
$PS_{1.5}Te_{0.2}35$	1.50	0.25	100	236.1,^{a} 141.3,^{a} 122.2,^{a} 111.6,^{a} 98.7,^{a} 83.8,^{a} 100.0,^{a} 65.5^a
$PS_{1.8}Te_{0.13}$	1.75	0.13	100	235,^{a} 140,^{a} 113,^{a} 96,^{a} 83^a
$PS_{1.8}$	1.81	0.00	100	112.3,^{a} 99.0,^{a} 87.1,^{a} 59.1^a
$PS_{2.0}Te_{0.50}$	2.00	0.50	100	113.7,^{a} 97.4,^{a} 84.6,^{a} 60.0^a
$PS_{2.3}$	2.29	0.00	100	113.6,^{a} 96.2,^{a} 85.3,^{a} 67.8,^{a} 60.0^a
$PS_{2.5}Te_{0.50}$	2.50	0.50	100	112.1,^{a} 99.5,^{a} 87.6,^{a} 59.8^a
$PS_{2.7}Te_{0.08}$	2.67	0.08	92	101, 59.4,^{a} 50.7^a
$PS_{2.7}Te_{0.10}$	2.70	0.10	100	58.4,^{a} 51.5^a
$PS_{2.8}Te_{0.17}$	2.83	0.17	74	108, 58.7,^{a} 53.5^a
$PS_{3.0}$	3.00	0.00	84	112, 60.1,^{a} 57.1^a
$PS_{3.0}$	2.95	0	74	112, 60.0,^{a} 51.2^a
$PS_{3.0}Te_{0.25}$	3.00	0.25	58	106, 58.4,^{a}, 32
$PS_{3.0}Te_{1.0}$	3.00	1.00	18	93, 60.5^a
$PS_{3.0}Te_{2.0}$	3.00	2.00	10	95, 62.1^a
$PS_{3.5}$	3.50	0.00	44	114, 60.4^a
$PS_{3.5}Te_{0.25}$	3.50	0.25	9	113, 61.7^a
$PS_{3.5}Te_{0.50}$	3.50	0.50	6	108, 60.7^a
$PS_{3.5}Te_{1.0}$	3.50	1.00	3	102, 64.3^a
$PS_{4.0}$	3.95	0.00	17	113, 61.2^a
$PS_{4.0}$	3.95	0.00	16	112, 101, 93.0, 60.3,^{a} 31
$PS_{4.0}Te_{1.0}$	4.00	1.00	0	106
$PS_{4.0}Te_{2.0}$	4.00	2.00	0	104
$PS_{4.0}Te_{3.0}$	4.00	3.00	5	98, 61^a
$PS_{4.5}Te_{1.0}$	4.50	1.00	0	107
$PS_{5.0}Te_{2.0}$	5.00	2.00	0	106
$PS_{5.5}Te_{0.25}$	5.50	0.25	0	112
$PS_{5.7}$	5.57	0.00	0	113.7, 93.3, 34
$PS_{6.0}Te_{0.50}$	6.00	0.50	0	110
$PS_{6.0}Te_{3.0}$	6.00	3.00	0	108
$PS_{7.0}Te_{1.0}$	7.00	1.00	0	108
$PS_{7.0}Te_{4.5}$	7.00	4.50	0	105
$PS_{8.5}Te_{0.5}$	8.50	0.50	0	110
$PS_{9.0}$	9.00	0.00	0	111.1, 101.9, 89.8, 78.8, 34

^{a} Indicates resonances attributed to molecular P_4S_n clusters.

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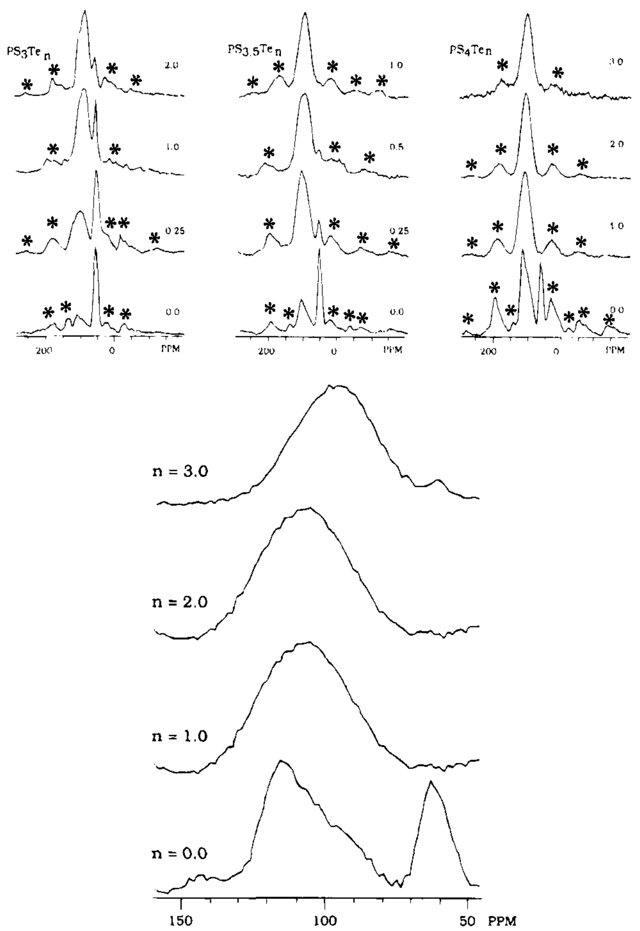

Figure 4. (a, top) 81.008 MHz ^{31}P MAS-NMR spectra of ternary P–S–Te glasses along the series PS_mTe_n (m = 4.0, 3.5, 3.0). Values of n are indicated in the figure. (b, bottom) Expansion of the 81.008 MHz NMR spectra of glasses along the series PS_4Te_n, illustrating the effect of n on the MAS centerband position. Spinning sidebands are indicated by asterisks.

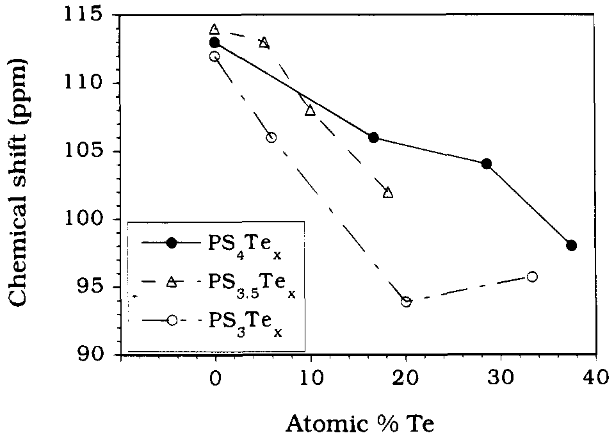

Figure 5. Plot of the ^{31}P chemical shift at peak maximum for the $S{=}PS_{3/2}$ site in P–S and P–S–Te glasses as a function of the Te content at different S/P ratios.

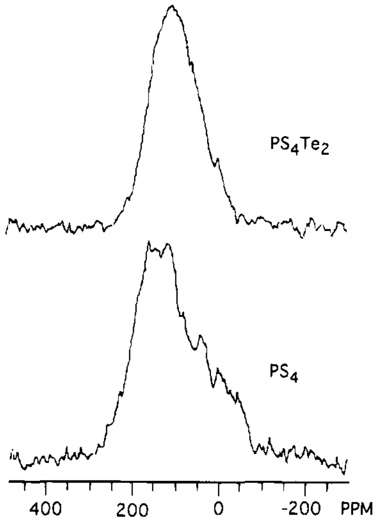

Figure 6. The 121.66 MHz ^{31}P spin echo Fourier transforms of glasses with compositions PS_4 and PS_4Te_2, respectively. Note the dramatic effect of tellurium on the ^{31}P chemical shift tensor.

Table 3. Wavenumbers of Infrared Absorbance Attributed to P=S Stretching Mode in P–S–Te Glasses

sample	$\bar{\nu}$ (cm^{-1})	sample	$\bar{\nu}$ (cm^{-1})
PS_3	690	PS_4	683
$PS_3Te_{0.25}$	667	PS_4Te_1	635
PS_3Te_1	637	PS_4Te_2	613
PS_3Te_2	638	PS_4Te_3	610

assuming a distribution function of axially symmetric shift tensors or by invoking deviations from local axial symmetry. Since it is principally impossible to distinguish between these two alternatives, reliable average chemical shift tensor values cannot be extracted. Despite these difficulties, it is clear from Figure 6 that there is a substantial difference in the overall span $\delta_{33}-\delta_{11}$ for both glasses. For a $S{=}PS_{3/2}$ unit with C_{3v} symmetry an axially symmetric chemical shift tensor is expected, with maximum shielding along the S=P double bond. This has been verified previously for various binary phosphorus sulfide compounds.[15,16] The spectrum of glassy PS_4 is fairly consistent with this expectation, suggesting at least approximately axial symmetry, with a chemical shift component near −70 ppm parallel to the principal axis. In contrast, the chemical shift anisotropy in glassy PS_4Te_2 is substantially reduced, indicating that the Te atoms have a profound influence upon the geometry of the $S{=}PS_{3/2}$ groups. The same conclusion is suggested by the infrared spectroscopic data, summarized in Table 3 and illustrated in Figure 7. While the multiline spectra of these P–S glasses are difficult to interpret in detail, the absorbances in the 600–700 cm^{-1} region can be assigned unambiguously to the P=S stretching mode.[17–19] Table 3 illustrates that this line is successively red-shifted as increasing amounts of Te are added. As discussed in refs 20 and 21 for a variety of tris(alkylthio)phosphine sulfides, the frequency at which the P=S stretching mode is observed in the IR spectrum can be dramatically affected by the coupling of this mode to the PS_3 mode. Similar effects may be operative in crystalline phosphorus sulfides and the binary or ternary glasses based on them. Alternatively, the red shift might simply reflect

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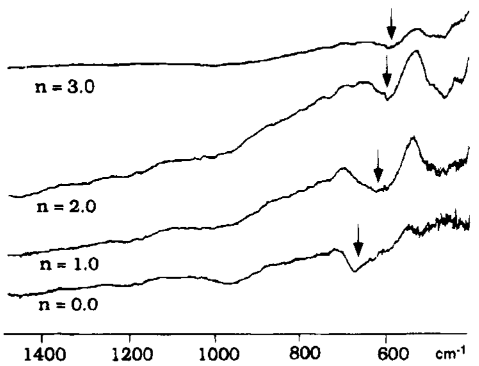

Figure 7. FT-IR spectra obtained in transmission geometry on KBr pellets of glasses with the compositions PS_4Te_n. Arrows indicate absorbances in the S=P valence region.

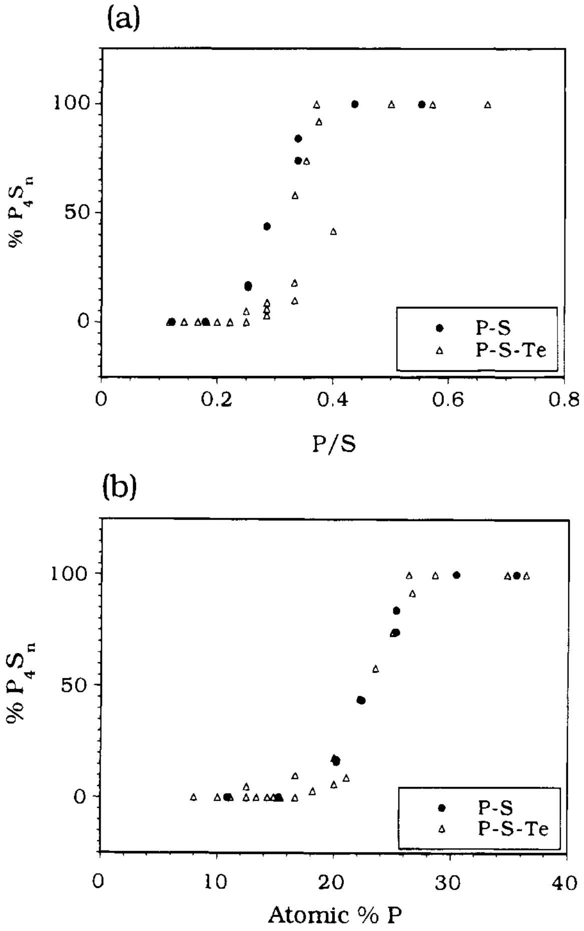

Figure 8. Effect of tellurium on the fraction of P atoms occurring in the form of molecular P_4S_n units: (a) shown as a function of P/S ratio; (b) shown as a function of overall phosphorus content. Circles denote binary P–S glasses; triangles denote ternary P–S–Te glasses. Note the uniform dependence on the atomic percentage of P.

a reduction in P=S bond order in the P–S–Te glasses. In view of the NMR results we favor the latter interpretation.

Inspection of Figure 3 reveals further that the addition of tellurium to a melt with a constant P/S ratio results in a distinct attenuation of the sharp resonances in the 50–65 ppm range due to isolated P_4S_n molecules in the glasses. This result indicates that when introduced into a glass with fixed P/S ratio, the tellurium atoms tend to suppress the formation of P_4S_n units. This effect is documented quantitatively in Figure 8a, on the basis of peak integrations. Figure 8b suggests that the fraction of P atoms present in the form of molecular P_4S_n simply depends on the total phosphorus content only. This uniform behavior suggests that the tellurium atoms are well dispersed within the glass structure and that their effect is equivalent to that of those non-P-bonded sulfur atoms in excess of the $PS_{2.5}$ stoichiometry (corresponding to the $S{=}P_{3/2}$ group) that are present in rains linking the P-containing fragments.

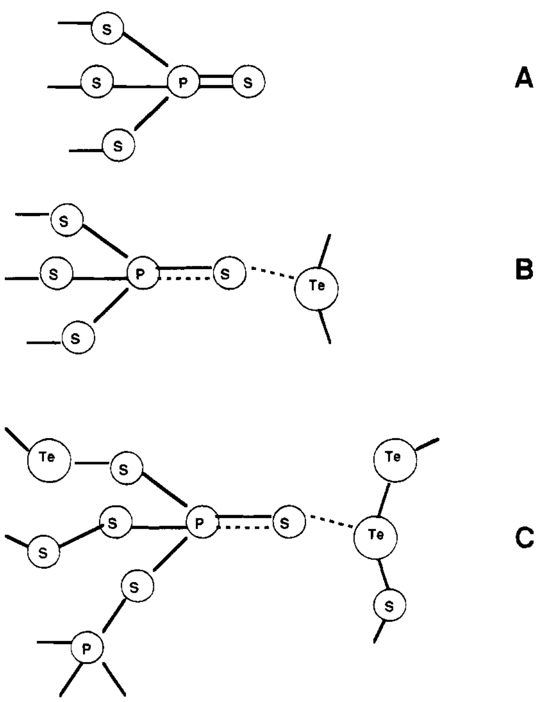

Figure 9. Structural proposal for P–S–Te glasses. (A) isolated $S{=}PS_{3/2}$ unit in P–S glasses; (B) proposed interaction between Te and $S{=}PS_{3/2}$ units in P–S–Te glasses; (C) representative part of the glass structure showing typical connectivities present.

Discussion and Conclusions

The results discussed above shed significant light on the structural role of tellurium in these glasses. While they indicate the absence of P–Te bonds, the equivalence of sulfur and tellurium with respect to their effect on the concentration of isolated P_4S_n molecules in the structure suggests that S–Te bonds are being formed in these glasses. Thus, Te can function equivalently to excess S in forming bridges between isolated $S{=}PS_{3/2}$ groups in the polymeric glass matrix. The dramatic effect of tellurium both on the P=S stretching frequency and on the ^{31}P chemical shift tensor suggest a direct interaction between tellurium and the P=S bond, as sketched in Figure 9. This specific model has been proposed previously for the P–Se–Te system,[9] where it was demonstrated that the experimentally observed enhancement of the fraction of four-coordinate P atoms can be explained quantitatively in terms of this association model. As previously discussed, this hypothesis also explains the experimental observation (see Figure 2) that the glass transition temperatures for the P–S–Te and P–Se–Te glasses are significantly increased over those measured for the binary P–S and P–Se glasses with the same phosphorus concentrations. As discussed in the literature, there is an intimate link between trends in T_g values and the overall connectivity of the network as reflected in the average coordination number $\langle r \rangle = \sum_n r_n f_n$, where r_n is the coordination number and f_n is the atomic fraction of the specific element n involved.[22] The interaction complex proposed in Figure 9 implies an effective Te coordination number higher than two, and thus an increased average coordination number for ternary P−S−Te (P−Se−Te) glasses compared to the binary P−S and P−Se glasses with the same phosphorus contents. As such, the conclusions of the present study represent another interesting example of intermediate range order in chalcogenide glasses.

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