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Novel organic-inorganic glasses

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The preparation and properties of novel organic-inorganic glasses with phenyl groups covalently bonded to phosphorus in an inorganic glass are presented. Phenyl phosphonic acid (PPA) can be incorporated into tin and zinc fluorophosphate glasses ($MO/MF_2/PO_{2.5}/PPA$) at levels up to 72 mol%. The T_g's of these glasses range from below room temperature to near 200°C depending on glass composition. For low melt glasses, these glasses have low moisture absorption and may solubilize dyes, organic photoconductors, NLO molecules, and pharmaceuticals. Several applications have been considered. © *2001 Kluwer Academic Publishers*

1. Introduction

Specialty glasses have been prepared and studied intensively in the past 10 years because there are a myriad of applications in optoelectronics and as substitutes for conventional glasses [1–8]. Low melt glasses have also received attention for certain applications and phosphate glasses are members of this class. In this report we will describe low melt phosphate glasses that have organic substituents, phenyl groups covalently bonded to phosphorus in the glass structure. Organic substituents serve to lower T_g, reduce moisture sensitivity, and confer special properties to the glass, such as optical absorption or nonlinear optical susceptibility. These glasses are prepared by melting metal oxides and salts at temperatures between 300 to 400°C and quenching the glass melt to ambient temperature. Some of the glasses are optically clear and many resist crystallization without rapid quenching. At this time, we know of no other glass compositions described in the patent or scientific literature where an organic group is covalently bonded into the glass structure. Recent research at Corning Glass [9–11] has demonstrated the utility of low melt inorganic glasses in modifying the mechanical properties of polymers. The glasses described herein provide similar properties. Moreover, if the glass and the polymer were miscible, then the T_g would change and the yield stress and toughness may increase. Corning's glasses are more expensive than most engineering polymers. The cost of our glasses is uncertain, but for some, the raw material cost would be less than $1.50/lb. These glasses may serve as useful matrices for dyes, organic photoconductors, NLO molecules, or for pharmaceuticals [l2, 13]. These applications have not been investigated but should be considered.

2. Experimental

Stable glasses in the tin fluorophosphate system (Sn-O-P-F) [1–3] exist, which possess the attribute of combining unusually low T_g with good durability towards water. We have shown that it is possible to introduce a considerable portion of an organic modifier into such glasses. Molten PhH_2PO_3, phenyl phosphonic acid (PPA) can dissolve unexpectedly high levels of metal oxide or fluorides; in particular, binary melts have been made which contain up to 40 mol% of SnO or 60% of SnF_2. We have prepared Sn-O-P-F glasses with considerable phenyl content in 5–100 g quantities by the following procedure. The appropriate quantities of SnO, SnF_2, $NH_4H_2PO_4$, and PPA were weighed into a plastic screw-top container. All large lumps were broken up and the mixture was shaken, tumbled for a few minutes and transferred to a porcelain crucible.

In most cases, melting was done at 300°C for 1 hr in a small box furnace; however, for some mixtures, higher temperatures were necessary, to a maximum of 450°C. Beyond this temperature, degradation of the organic material was considerable, as shown by discoloration of the melt. At the end of the melting the contents of the crucible were either poured onto a graphite block, or allowed to cool in the crucible if too viscous to pour. Some mixtures produced melts that were covered with a dome of solid material. In such cases, the crust was broken and stirred back into the melt, in which it redissolved: the more viscous melts were allowed to cool with the crust undisturbed. Samples that were not poured were extracted from the crucible by breaking it after cooling. The formation reaction of these glasses can be written as:

$$x\mathrm{SnO} + y\mathrm{SnF_2} + z\mathrm{NH_4H_2PO_4} \rightarrow (\mathrm{SnO})_x(\mathrm{SnF_2})_y(\mathrm{P_2O_5})_{z/2} + \frac{3}{2}z\mathrm{H_2O} + z\mathrm{NH_3}$$

Addition of phenyl phosphonic acid, PPA, instead of $NH_4H_2PO_4$ incorporates phenyl groups into the organic glass.

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3. Results

3.1. Chemical analysis

Chemical analyses of glasses were made for Sn and P by ICP-AES, inductively coupled atomic emission spectroscopy. Phosphorus, oxygen, and fluorine levels were determined by neutron activation analysis. Typical results are listed in Table I. The wt% Sn, O, F, P retained is 88–112%, 104–127, 37–68, 99–106%, respectively. More fluoride is lost than any other element during the preparation as has been reported for other fluoride glasses [14]. Most of the phosphorus and tin are retained within experimental uncertainties. The oxygen levels are slightly higher probably due to a few percent water and the replacement of fluorine bonded to Sn by oxygen.

3.2. DSC analysis

The glasses prepared varied from 30 to 80% P_2O_5 and in the organic-inorganic glasses, PPA replaces up to 100% of the P_2O_5. The ratio of $SnO:SnF_2$ affects T_g and ranges from 4 : 1 to 1 : 6. The compositions studied are listed in Tables II and III with T_g's measured at 20 deg/min using a Perkin-Elmer DSC-II. T_g was the primary screening technique for these glasses. In addition to T_g, the ΔCp at T_g provides information on the amount of amorphous phase (or the % crystallinity). ΔCp for inorganic glasses is smaller on a per gram basis than for organic glasses and, therefore, ΔCp increases with PPA content. The changes in T_g and ΔCp are shown in Fig. 1 for H-0, 50, 100. The H series, ranging in composition of $SnO/SnF_2/PO_{2.5}$/PPA from 7/38/55/0 to 8/46/0/44, are listed in Table II. To study the effect of processing time and temperature on properties, this series was treated for 45 and 90 min at 300°C (H0-1, 2), and for 45 and 90 min 400°C (H0-3, 4). The increase in T_g with temperature, and time is shown in Fig. 2 and the increase can be attributed to the loss of H_2O and fluoride. To increase T_g the amount of P_2O_5 was increased from 50 to 80%. At a fixed $SnF_2/(SnF_2 + SnO)$ ratio, T_g increases with P_2O_5 mole fraction. Increasing the mole fraction of PPA reduces T_g and increases the tendency to crystallize. Crystallization was observed in some glasses as an exotherm above T_g. This is illustrated in Fig. 3 for 116-2 where the exothermic crystallization at 180 to 200°C is followed by the endothermic melting at 220 to 230°C. T_g decreases with increasing SnF_2 content because P-O-P bonds are broken and replaced by P-F bonds that reduce the chain length. The change in T_g with $SnO/(SnF_2 + SnO)$ ratio is shown in Fig. 4 for several $PO_{2.5}$ levels. These results show that

TABLE II Organic-inorganic glasses

	SnO	SnF_2	$PO_{2.5}$	$PhPO_3$	T_g °C
H-0	8.6	47.0	44.4	0	58
H-50	8.6	47.0	22.2	44.2	43
H-100	8.6	47.0	0	44.4	35
L-0	10.8	56.6	33.0	0	*
L-50	11.0	60.2	17.6	11.2	43
L-100	11.8	64.3	0	24	*
112-1	22	33	0	44	80
112-2	33	22	0	44	80
114-1	22	33	22	22	105
114-2	33	22	22	22	115
114-3	37.8	17.7	22	22	109
114-4	44	11	22	22	115
116-1	8.5	46.5	22	22	91
116-2	8.5	46.	50	4	67
117-1	55.6	44.4	0	0	73
117-2	40	0	60	0	173
117-3	60	0	40	0	44
118-1	7.7	42.3	25	25	69
118-2	7.7	42.3	25	25	101
118-3	7.0	38.0	27.5	27.5	71
118-4	7.0	38.0	27.5	27.5	109
122-1	6.2	33.8	30	30	124
122-2	16	24	30	30	135
122-3	6.2	33.8	36	24	142

*No T_g observed.

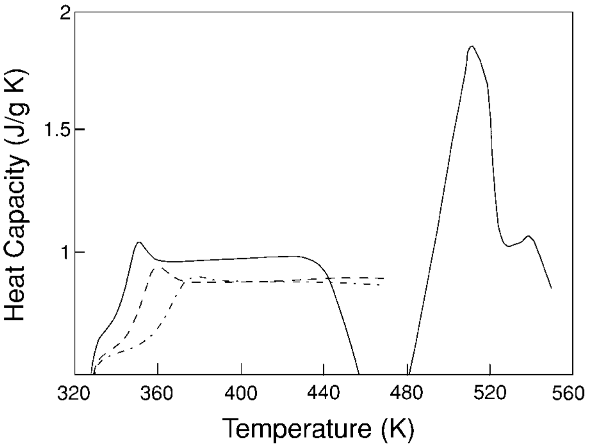

Figure 1 Specific heat and T_g of H0 (- - - -), H50 (- - -), H100 (-.-).

TABLE I Chemical analysis of tin fluorophosphate glasses

	Chemical analysis				Theoretical			
	Sn	O	F	P	Sn	O	F	P
SnOFP1	50	22.7	2.6	15	51.4	22.7	7.1	16.8
SnOFP2	53	25.9	2.2	18	51.4	22.7	7.1	16.8
114-1	48	19.5	4.8	11	51.1	15.2	9.8	10.7
114-2	46	19.4	4.4	11	52.1	16.8	6.7	10.9
114-3	51	19.4	3.6	11	52.5	17.6	5.3	11.0
114-4	48	19.4	2.2	11	53.1	18.6	3.4	11.1
129-1	44	20.2	4.7	12.2	45.6	16.0	8.8	11.9
129-2	50	20.8	4.3	12.9	46.8	16.7	9.0	12.2
129.3	47	21.5	3.6	14.2	41.6	17.3	8.0	13.3
129-4	47	23.2	3.0	13.5	42.9	18.2	8.2	13.7
133A	50	23.5	3.2	14.0	42.9	18.2	8.2	13.7
133B	49	23.6	3.3	14.9	42.9	18.2	8.2	13.7

TABLE III Composition and T_g of organic-inorganic glasses

	SnO	SnF_2	$PO_{2.5}$	PhH_2PO_3	T_g °C
122-4	16	24	36	24 mol%	168
122-5	4.6	25.	35	35	180
122-6	12	18	35	35	151
122-7	4.6	25.4	42	28	157
122-8	12	18	42	28	157
129-1	20	30	20	30	101
129-2	20	30	25	25	122
129-3	18	27	22	33	125
129-4	18	27	27.5	27.5	144
133-1	18	27	27.5	27.5	101
133-2, 3, 4					110, 138, 141
133-5, 6					135, 148
163-1	18	27	55		77
163-2	18	27	55		98
178-1	0	50	5	45	46
178-2	16.7	33.3	5	45	57
178-3	33.3	16.7	5	45	67
178-4	50	0	5	45	*
178-5	0	35	6.5	58.5	54
178-6	11.7	23.3	6.5	58.5	54
178-7	23.3	11.7	5	58.5	54
178-8	35.0	0	5	58.5	*
178-9	0	20	8	72	−6
178-10	6.7	13.3	8	72	25
178-11	13.3	6.7	8	72	37
178-12	20	0	8	72	52

*No T_g observed.

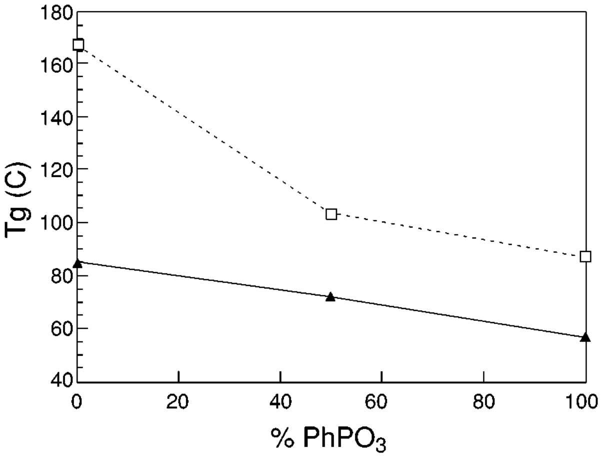

Figure 2 T_g vs PPA level for different preparation times and temperatures. (△ 90 min @ 300C) □ 90 min @ 400C).

the T_g can be effectively controlled by processing conditions and composition. For example, to obtain a glass with a T_g above 100°C processed at 350°C for 90 min the P_2O_5 level must be greater than 40% and SnF_2 less than 30%. A few Zn glasses were made and are listed in Table IV. A limited number of experiments suggested that the glass forming region in the Zn system may be narrower than the Sn system.

3.3. TGA analysis

A typical TGA run in N_2 for these glasses is shown in Fig. 5. The initial weight loss at 30 to 200°C is probably due to the loss of water. Most glasses show a weight loss of 15–20% between 400 to 600°C, which could be due to the loss of fluoride or PPA. This is an encouraging result since glasses prepared at 300–400°C only lose 15–20% weight up to 700°C. Using air ambient does not change the results significantly. This indicates that oxidation of the phenyl group does not lead to additional weight loss. TGA of H0-1 to H0-4 shows that the weight loss at 700°C decreases as the time and temperature of preparation increases. The same effect is observed in H50-2 to H50-4. In all the H100 samples, which are 44% PPA, the weight loss increases with increasing preparation time, suggesting that PPA is one of the more volatile components. In going from H0 to Hl00, PPA increases from 0 to 44 mol%, the weight loss at 700°C increases from 3% to 27%. The binary glass, $(SnF_2)_{0.66}(PO_{2.5})_{0.44}$, 117-1, loses more weight (12%) than $(SnO)_{0.4}(PO_{2.5})_{0.6}$, 117-2, (2%).

TABLE IV T_g and change in specific heat at T_g

Composition	T_g °C	ΔCp J/g K
ZnF_2/PPA 20/80	25	0.25
25/75	37	0.25
ZnO/ZnF_2/PPA 5/20/75	25	0.25

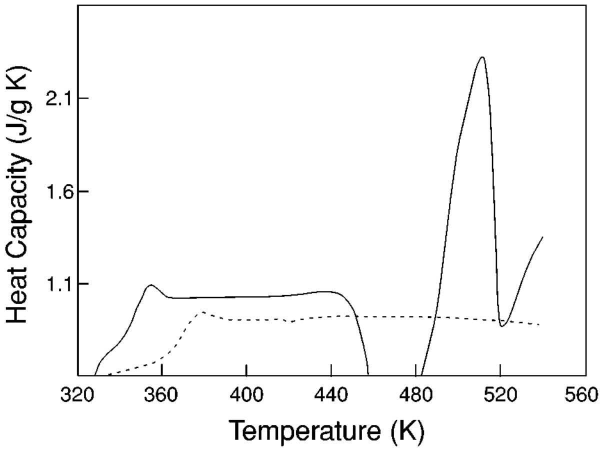

Figure 3 Specific heat and crystallization behavior of 166-1 (---) and 166-2 (---).

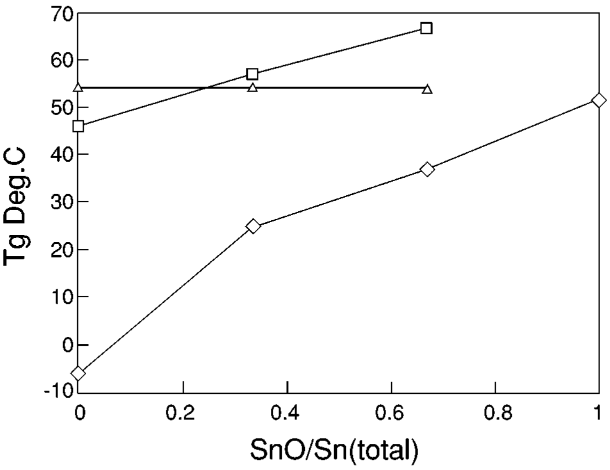

Figure 4 T_g as a function of SnO/Total Sn ratio, (P = 50 ♦, P = 65 □, P = 85 △).

TABLE V Phenyl content by IR

	mol% (measured)	mol% (theoretical)
122-2	21	30
122-4	18	24
122-6	18	35
129-1	28	30
129-2	25	25
129-3	23	33
129-4	21	27.5
133A	21	27.5
133B	21	27.19

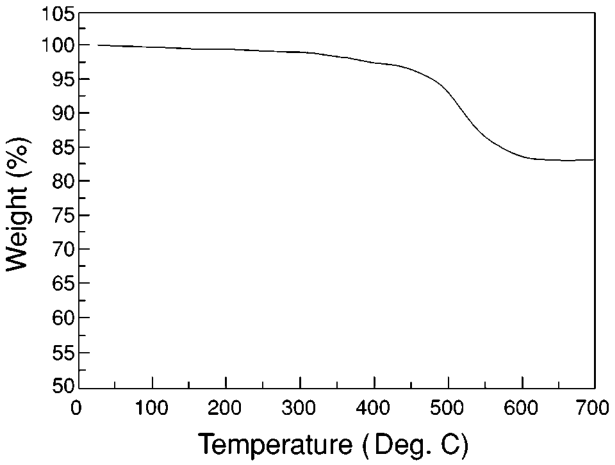

Figure 5 TGA curve for H50-4 in nitrogen.

3.4. IR analysis

The organic (phenyl) content was measured by IR spectroscopy using a phenyl ring vibration. There is interference on the baseline due to other absorptions in the glass and these limit the precision of the phenyl content measurement. A series of different measurements are listed in Table V. Although the uncertainty is about ±5%, it appears that 5–10% PPA is lost in the preparation. IR can also provide evidence of P-F bonds through the absorption at 785 cm^{-1}, but at this time, the amount has not been quantified [15].

3.5. NMR analysis

Some information about the microstructure and bonding of these glasses has been obtained from solution ^{19}F and ^{31}P NMR in polyphosphoric acid. ^{31}P resonances reported for end groups and middle groups have been observed and the number of phosphate groups in the chain is 8–10. ^{19}F resonance shows that all the fluorine is connected to phosphorus. High PPA content glasses had some solubility in NMP. Glass 178-1 gave a single fluorine resonance and 178-5 gave multiple fluorine resonances, but the assignments of these resonances have not been made.

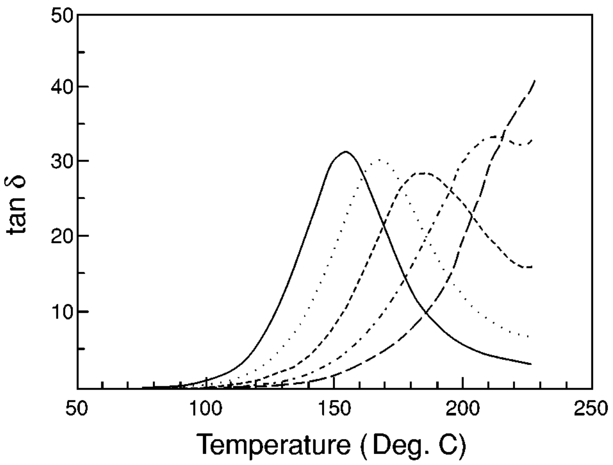

Figure 6 Dielectric loss for H0-2 versus temperature (1 KHz ----- 3 KHz ..... 10 KHz ----- 30 KHz -.-.- 100 KHz ----.

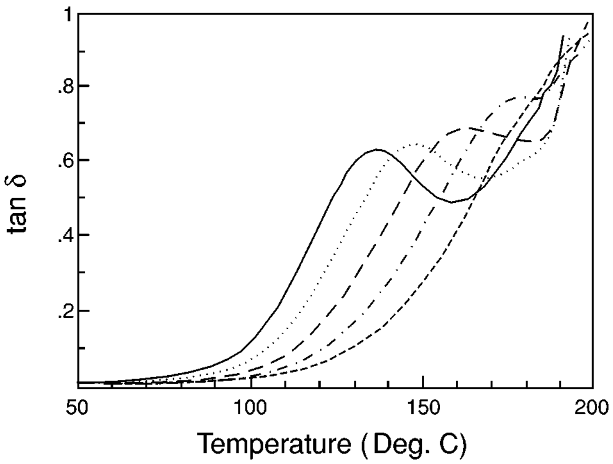

Figure 7 Dielectric loss for 121-1 versus temperature (1 KHz ----- 3 KHz ..... 10 KHz ----- 30 KHz -.-.- 100 KHz ----.

3.6. Dielectric thermal analysis

(DETA) Dielectric data were obtained on several of these glasses as shown in Figs 6 and 7, for HO-2 and 121-1, respectively. Although the loss maximum resembles dipole losses observed in polymers, it is more likely due to separated ion pairs as reported for other ion containing glasses rather than dipole motion. The activation energies are 110 kJ/mol and 128 kJ/mol for HO-2 and 121-1, respectively. These activation energies are lower than for polymers with comparable T_g's and this has been previously observed [13]. The distribution of dielectric relaxation times is similar to that observed for polymers and is characterized by a Williams-Watts parameter $\beta = 0.55$. At high-temperature dc, conductivity is observed and the conductivity is higher than for polymers because of the motion of ions.

3.7. Viscoelastic analysis

The viscoelastic behavior of HO-3 and 114-2 was investigated to compare with conventional glasses and polymers. The Newtonian viscosity data for HO-3 ($T_g = 140$°C) are shown in Fig. 8 at 180 to 220°C. The activation energy for viscous flow is 240 kJ/mol, which is higher than the activation energy for dielectric relaxation, but in agreement with Shelby's results [14] on tin fluorophosphate glasses. There is no evidence of rubbery plateau and the high frequency shear compliance, $J'(\omega)$, approaches 10^{-9} m^2/N. or a glassy

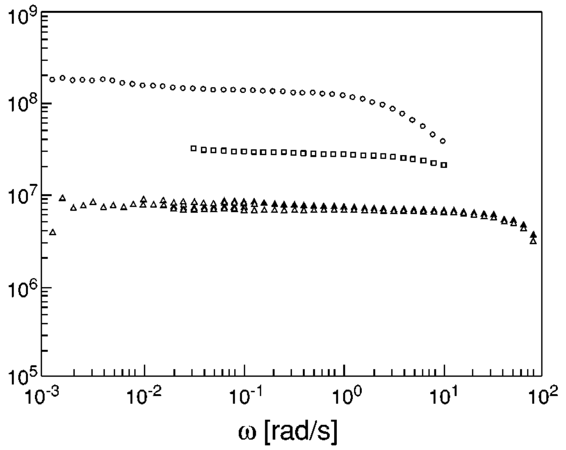

Figure 8 Complex viscosity for H0-3 at several temperatures. (180C O, 190C □, 200C △).

type response. Eisenberg and King [16] have reported a rubbery plateau in some different phosphate glasses in support of the idea of a long chain network structure of those glasses. It would appear that the chain lengths in these glasses are not long enough to show viscoelastic behavior. Glass 114-2 was also examined, but crystallization of the glass interfered with proper measurements. A more detailed investigation of these glasses may be warranted in the future.

4. Discussion

4.1. Structure

The structure of these fluorophosphate glasses has not been definitively established. A proposed structure [15] is depicted in Fig. 9a. The main features are that there are phosphate chains with SnF or PF end groups. When PPA is substituted for $PO_{2.5}$, a phenyl group will reside on the phosphorus atom as indicated in Fig. 9b. The phenyl groups could aggregate to form hydrophobic regions or phase separate. We see no evidence of phase separation in the T_g and ΔCp data. At high levels of PPA, crystallization is observed. Xu and Day [17, 18] have proposed more detailed structures of tin fluorophosphate glasses consisting of tin and phosphorus polyhedra based on x-ray photoelectron spectroscopy, XPS. Phenyl or other organic substituents could be incorporated into these structures at the phosphorus atom, just as in Fig. 9b. The organic groups would modify the structure and ultimately the properties of these glasses. XPS studies of organic inorganic glasses would provide important structural information. This is a subject for future investigation.

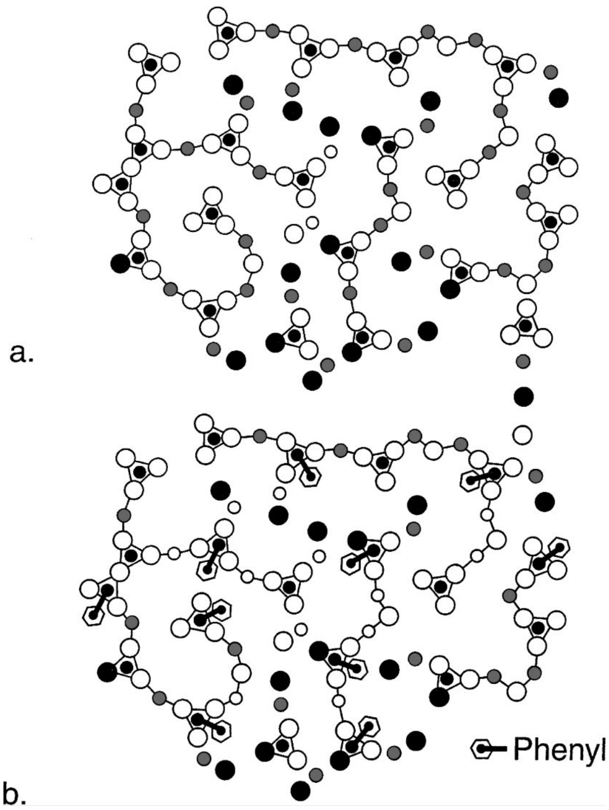

Figure 9 (a) Structure of tin fluorophosphate glasses. (b) Proposed structure of tin fluorophosphate/phenyl phosphonate glasses.

4.2. Properties

These glasses are unusual in that organic phenyl groups are incorporated into glass structure and contribute to the low T_g. Our preparations indicate that organic groups are stable in these glasses at temperatures up to 400°C. A few runs at 450°C gave brown, inferior glasses. TGA analysis shows that these glasses lose only 15–20% of their weight up to 700°C. There is some loss of phenyl content and fluorine during the preparation, which affects the final composition and the resultant properties. Although we did not obtain durability measurements on these glasses, the moisture content and general handleability and processabilty of these glasses confirms that the organic phenyl group reduces moisture absorption and increases durability. Other organic groups should be tried, such as, vinyl, methyl, propyl, phosphinic acid, and aminophenyl phosphonic acid. Other metals can be substituted for Sn and Zn, such as, Al, Pb, Na, K, Li, Ca, Ba, Sr, Si, Ge, In, Cu, Ni, Fe, and Mn. Chlorine could be substituted for fluorine, but the glasses may be less stable and more corrosive because of the more labile P-Cl bond. Crystallization of high PPA content glasses may be a problem for certain optical applications. Mechanical measurements of moduli and strength of these glasses were planned but samples had not been prepared. Future research on this topic is uncertain but many opportunities exist.

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