



A MOLECULAR DYNAMICS SIMULATION OF TERNARY GLASSES $\text{Li}_2\text{S}-\text{P}_2\text{S}_5-\text{LiI}$

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ABSTRACT

The structure of superionic glasses in the ternary systems $x(0.4\text{Li}_2\text{S}-0.6\text{P}_2\text{S}_5)-(1-x)\text{LiI}$ and $x(0.5\text{Li}_2\text{S}-0.5\text{P}_2\text{S}_5)-(1-x)\text{LiI}$ (with $x = 0.9$ and 0.75) has been studied by molecular dynamics (MD) simulations. The configurations obtained by MD were analyzed by graph theory. The average coordination number of sulfur around phosphorus ($n_{\text{P-S}}$) is 4.28 and the average P-S distance ($r_{\text{P-S}}$) is 2.10 Å. For lithium, the corresponding parameters are $n_{\text{Li-S}} = 3.53$ and $r_{\text{Li-S}} = 2.47$ Å respectively. In addition, P-I bonds appear at 2.60 Å. LiI type of clusters are not seen as speculated by earlier reports. The glass transition temperature (T_g) decreases and ionic conductivity (σ) increases with LiI addition as reported for other ternary glasses.

Key words: A. Sulfide glasses; C. Molecular dynamics; D. Glass transition temperature and ionic conductivity.

1. INTRODUCTION

It is well known from earlier studies that replacement of oxygen with sulfur and addition of halide dopants to oxide glasses increase the ionic conductivity (σ) by two to three orders of magnitude [1]. Decrease in glass transition temperature (T_g) is also observed with increase in dopant content [2]. But no systematic study has been done so far that connects structural changes with observed variations in σ and T_g . To understand structural changes due to the addition of both modifier (Li_2S) and dopant (LiI) to the parent glass P_2S_5 , MD simulation of $45\text{Li}_2\text{S}-45\text{P}_2\text{S}_5-10\text{LiI}$ (glass A), $37.5\text{Li}_2\text{S}-37.5\text{P}_2\text{S}_5-25\text{LiI}$ (glass B), $36\text{Li}_2\text{S}-54\text{P}_2\text{S}_5-10\text{LiI}$ (glass C) and $30\text{Li}_2\text{S}-45\text{P}_2\text{S}_5-25\text{LiI}$ (glass D) was undertaken.

2. MOLECULAR DYNAMICS (MD) SIMULATION

Constant volume MD was performed on cubic cells calculated with measured densities (Table 5) of glasses prepared using high energy planetary ball mill. Starting at a temperature of 3000 K, the system was cooled by scaling velocities to 2000 K, 1500K, 1000K, 750 K, 400 K and finally to 300K with time step size of 10^{-15} s. At each temperature, the system was equilibrated for 20 ps and various parameters such as pair correlation function (PCF) and running coordination number (RCN) for various atomic pairs were averaged for another 10 ps. At 750 K, 400 K and 300 K, the equilibration and averaging times were increased to 40 ps each. The interatomic potential used was of the form

$$\phi_{ij} = \frac{Z_i Z_j e^2}{r_{ij}} + A_{ij} \exp\left(\frac{-r_{ij}}{\rho_{ijo}}\right) + \frac{k_{ij}}{8(\theta_{jik} - \pi)^2} \left\{ \left[(\theta_0 - \pi)^2 - (\theta_{jik} - \pi)^2 \right]^2 \right\} \exp\left[-\frac{(r_{ij} + r_{ik})}{\rho_{ij}} \right]$$

Where Z_i is the atomic number of atom i and θ_0 is the equilibrium angle subtended by r_{ij} and r_{ik} . A_{ij} , ρ_{ijo} , k_{ij} , ρ_{ij} are constants of simulation. The third term in the potential is the three body vessal term introduced to account for the covalent nature of interactions. Z_i for Li, P, O and Cl

are 0.4e, 2e, -0.8e and -0.4e respectively. Tables 1 and 2 contain the relevant potential parameters used. The structure of the simulated glass was analysed from connectivity matrices and graph theory techniques as reported by us earlier [3] and averaged over 50 different equilibrated configurations at 300K. The bonding distance for connectivity matrices calculations between atoms *i* and *j* were chosen from peaks in the pair correlation function (PCF) and the coordination numbers were calculated at the minimum distance after the first peak for each pair of atoms. Running coordination number (RCN) shown along with PCF in fig.1. gives the coordination number in the plateau region.

To calculate the mean square displacement [MSD] for all atoms, the averaging time was increased to 20 ps at all temperatures. The diffusion constant *D* for Li^+ was obtained from the slope of the linear part of the mean square displacement (MSD) Vs time interval (τ) curve (fig.2.).

T_g , the glass transition temperature was obtained from the change in slope in the *D* (for Li^+) Vs temperature plot.

3. RESULTS AND DISCUSSIONS

The bonding distances obtained are compared with reported values [4,5] in similar crystalline compounds in Table.3. The coordination around P is made up of sulfur and iodine atoms. The units found are PS_4 , PS_4I , PS_4I_2 , PS_5 , PS_5I and PS_6 . But Li is coordinated only to sulfur. Though Li is predominantly coordinated to four sulfurs, equal number of 3 and 5 coordinated Li atoms are also found. But six coordinated Li atoms are considerably smaller in number. Such variations in coordination are not found in crystalline compounds wherein only 4 and 6 coordinated Li atoms are present. The surprising thing observed here is the absence of Li-I bonding contacts as the shortest Li-I observed here is close to 6 Å. The Li atom thus is surrounded by sulfurs alone. The coordination around I gives an average $n_{\text{I,P}}$ of 2.6. The I-I distance observed here is much larger than 3.54 Å, the closest non-bonded approach in crystalline iodine [6] and 3.7 Å, the intermolecular distance in crystalline $\text{P}_2\text{S}_3\text{I}_2$ [5]. These results lead us to conclude that LiI aggregates are absent in these glasses. Unlike in binary lithium phosphate glasses, lithium is found near bridging sulfurs.

The above quoted results are common to glasses A, B, C and D. Now we discuss the structural variations among these glasses from the parameters shown in Table.4. Since LiI aggregates are absent in the network, we can presume that all the Li in the glass act in the capacity of a modifier and take part in breaking P-S-P bonds and forming Li-S-Li and Li-S-P linkages. The

ratio, $y = \frac{\# \text{Li}}{\# \text{P}}$ increases in the order for glasses C,D, (A,B) where A and B have the same *y*.

Then the ratio of bridging sulfurs (BS) to non-bridging sulfurs (NBS) ($R = \frac{\# \text{BS}}{\# \text{NBS}}$) should

decrease in the same order since they are inversely related as shown in Table.4. The number of P-Li-Li-P should also increase with *y* which is observed here. These results confirm the role played by the modifier in which all the Li atoms take part. In crystalline Li, P, S compounds, edge connected LiS_n units are present [4]. In binary $\text{Li}_2\text{S-P}_2\text{S}_5$ glasses, edge connected Li atoms increase in number with increase in Li_2S content [7]. Edge sharing decreases the average Li-Li distance ($r_{\text{Li-Li}}$) compared to corner sharing and is more likely to be found with increasing Li/S ratio. The fraction of edge sharing Li atoms should change in the same order as these two parameters which is found in Table 5. But the ratio of #edge sharing/#corner sharing remains constant at 0.36 for all the glasses, which indicates that corner sharing is preferred for all compositions studied. The rate of change of the number of Li-Li neighbours in shells 1 to 6 should depend on the number of Li atoms and the Li-S-Li linkages it forms. This parameter

increases in the order of C, (A, D), B which agrees with the Li content variation. Unlike in oxide glasses, Li has bridging sulfurs in its immediate environment. The fraction of Li atoms near bridging sulfurs increases with the increase in R . The iodine atoms are randomly distributed around P, since the ratio $\#P/\#I$ and the observed n_{P-I} are inversely related. Since I is bonded only to P, we expect the ratio $\#P/\#I$ to be directly related to n_{I-P} and this is observed for the four glasses.

The MD simulated conductivity values and the corresponding T_g values are given in Table 3. σ increases with increasing Li content (% Li in Table 4.). This indicates that σ is controlled by the Li ion population in the glass and other structural variations do not seem to influence σ significantly. In AgI containing oxide glasses [8], the lower activation energy [higher σ] for Ag^+ diffusion is attributed to aggregates of AgI in the network. Since similar LiI aggregates are not found in this glass, the reasons for higher σ in the ternary glass should be found elsewhere. The presence of bonding and non-bonding sulfurs around Li may facilitate the motion of Li atoms in the glass. As in other glasses, T_g decreases with increasing halide content. Structurally this weakening of glass is mainly attributed to a softening of the network when I atoms occupy spaces between structural units. In addition, a decrease in P-P bridges characterized by shorter P-S-P chain lengths also contribute to the weakening of the network. Among the larger LiI content glasses, the one with smaller chain lengths would be the weaker of the two. This reasoning leads to the structural order in increasing T_g as D, B, C, A which is observed in Table.5. From graph theory spectra [9], it is known that higher the maximum eigenvalue (evp) of the connectivity matrix, larger is the number of bonds in the matrix and stronger is the glass. The maximum eigenvalue of the P-P matrix and the T_g increase in the order for glasses B, D, C, A. This shows the role played by the P-S-P bridges in enhancing T_g .

4. CONCLUSIONS

The glass matrix is made up of PSI and LiS polyhedra connected by P-S-P, Li-S-Li and Li-S-P linkages. No LiI aggregates are found as in other AgI based oxide glasses. The high ionic conductivity at room temperature is attributed to the presence of bridging and non-bridging sulfurs around diffusing Li atoms.

5. REFERENCES

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TABLES

Table1. Potential parameters used in two body Buckingham term.

Interaction(i-j)	$A_{ij}(\text{ev})$	$\rho_{ij}(\text{\AA})$
P-P	3.91	0.001
P-S	13000.57	0.28
S-S	4000.43	0.30
Li-S	800.42	0.21
I-I	40.5	0.60
Li-I	900	3.2
P-I	700.1	5.2

Table 2. Potential parameters used in the three body Vessel term.

Interaction (i-j-k)	$k_{ij}(\text{ev})$	θ_0^0	$\rho_{ij}(\text{\AA})$	$r_c^*(\text{\AA})$
S-P-S	0.01	109	0.22	3.6
S-Li-S	0.01	90.5	0.68	3.8

*cut off in r_{ij} and r_{ik}

Table 3. Structural parameters for glass C.

Parameter	Reported[ref.]	Our MD values
$r_{P-S}(\text{\AA})$	2.05[4]	2.10 *
$r_{Li-S}(\text{\AA})$	2.41-2.47[4]	2.47 *
$r_{P-I}(\text{\AA})$	2.47[5]	2.53*
$r_{I-I}(\text{\AA})$ (non-bonded)	3.7[5]	4.12 *
PS-P-S	110 ⁰ [4]	89 ⁰ (1) **
PS-Li-S	85 ⁰ -120 ⁰ [4]	92 ⁰ (17)**
PP-S-P	135,141 [9]	155 ⁰ (4)**

*peak values in PCF and ** values obtained from graph theory.

Table 4. Structural parameters obtained from graph theory.

Parameter	Glass A	Glass B	Glass C	Glass D	Increasing order of parameter in glasses
n_{Li-S}	3.39(3)	3.92(2)	3.51(4)	3.30(3)	D,A,C,B
n_{P-S}	4.28(1)	4.25(2)	4.49(1)	4.10(1)	D,B,C,A
n_{P-I}	0.303(4)	0.84(1)	0.248(5)	0.68(1)	C,A,D,B
r_{Li-Li} (Å)	3.97(2)	4.04(1)	3.97(2)	3.92(2)	(D,A,C),B
n_{I-P}	2.72(4)	2.53(3)	2.68(5)	2.47(3)	D,B,C,A
Y	1.11	1.11	0.759	0.944	C,D,(A,B)
R	1.00(1)	1.00(2)	1.73(2)	1.05(1)	(A,B),D,C
P-Li-Li-P/Li+P	9.6(3)	17.4(5)	8.1(3)	7.7(3)	(D,C),A,B
#P/#I	9	3	10.8	3.6	B,D,A,C
Li-Li neighbours (1 st -6 th)	3.95(8)-21(1)	6.95(8)-45(1)	3.43(7)-10(1)	3.96(8)-20(2)	C,(A,D),B
Average P-S-P Chain length	12.0(2)	13.2(4)	11.6(2)	12.9(4)	C,A,D,B
Fraction of Li near BS	0.173(6)	0.199(6)	0.285(8)	0.112(7)	D,A,B,C
evp	4.0(1)	2.52(9)	3.5(1)	2.71(5)	B,D,C,A
% Li	0.212	0.235	0.162	0.186	C,D,A,B
#Li/#S	0.37	0.44	0.26	0.33	C,D,A,B
Fraction of edge connected Li atoms	1.05	1.77	0.84	0.97	C,D,A,B

Table 5. Physical parameters of glasses A, B, C and D.

Parameter	Glass A	Glass B	Glass C	Glass D
Density (gm/c.c.)	1.80(2)	2.10(3)	1.85(2)	2.06(3)
Σ (MD) (s/cm)	3.233×10^{-2}	3.425×10^{-2}	1.312×10^{-2}	2.645×10^{-2}
T_g (MD)(K)	658.09	549.92	648.31	529.05
T_g (exp) (K)	433.6	421.3	434	411.8

FIGURES

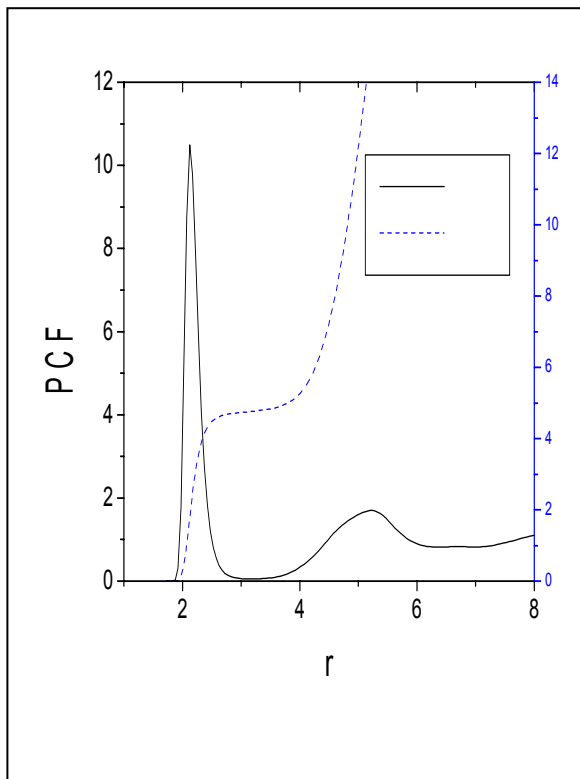


Fig.1. PCF and RCN for P-S interaction for glass C.

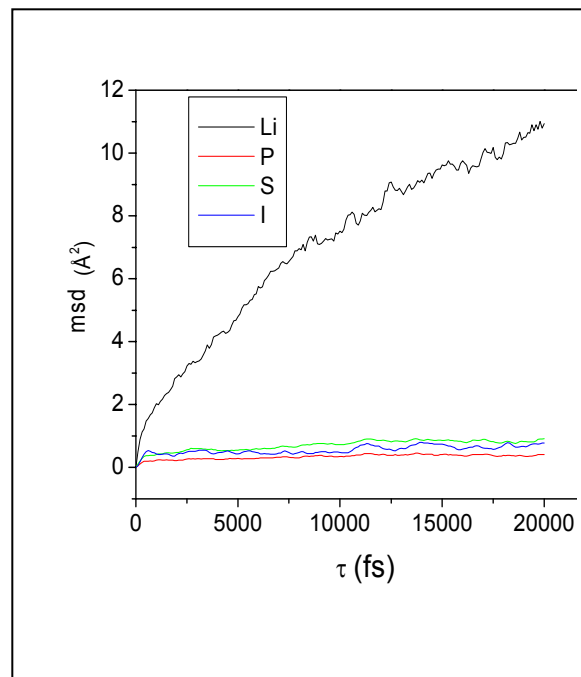


Fig.2. MSD plot for glass B at 300K