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MOLECULAR DYNAMICS STUDY OF THE STRUCTURE AND
DYNAMICS OF NETWORK GLASSES*

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Molecular Dynamics Study of the Structure and Dynamics of Network Glasses

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Structure and dynamics of binary SiO_2 , GeSe_2 and SiSe_2 , and ternary Ag/Ge/Se chalcogenide glasses are studied using the molecular dynamics (MD) method. Effective potentials consisting of two-body (steric repulsion, Coulomb interactions due to charge transfer, and charge-dipole interaction due to large electronic polarizability of anions) and three-body covalent interactions are proposed for chalcogenide glasses. Using these, MD simulations are performed to study short range order, intermediate range order manifested as the first sharp diffraction peak (FSDP), the vibrational density of states, and the participation ratios. MD results are compared with x-ray and neutron experiments.

Key Words: Chalcogenide Glasses, Network Glasses, Ion Conducting Glasses, Molecular Dynamics Simulation, Structure, Vibrational Spectra.

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1. Introduction

The structure of binary chalcogenide glasses has been widely studied by neutron and x-ray scattering measurements.[1-7] These measurements reveal many similarities in the static structure factor, $S(q)$, when expressed in terms of the dimensionless quantity $Q_0 = qr_0$, where r_0 is bond length.[4] The most celebrated structural feature in these glasses is the first sharp diffraction peak (FSDP) observed between 1.0 and 1.5 Å⁻¹, which is believed to be a signature of intermediate range correlations. Although the chemical constituents and topologies of these glasses are widely different, the dimensionless quantity Q_0 for the FSDP is nearly the same. So the key issues in chalcogenide glasses are: i) What is the nature of correlations that give rise to the FSDP? ii) Why are these intermediate-range correlations so strong in the molten state? Related to these structural issues is the question of the connectivity of the glassy network: In other words, what is the population of edge and corner-sharing tetrahedra, and what is the statistics of rings? Questions related to the phonons density-of-states and the nature of spatial localization of phonons are also discussed. Molecular dynamics method in conjunction with recently developed two-body and three-body covalent interactions is used to address these issues.[8-11]

2. Interaction Potentials

Recently, we have developed effective potentials for MD simulations of chalcogenide glasses.[8-11] These potentials include two-body and three-body interactions:

$$V = \sum_{i < j} V_2(r_{ij}) + \sum_{i < j < k} V_3(r_{ij}, r_{jk}, r_{ik}).$$

The two-body part of the potential, V_2 , consists of three terms: 1) Steric repulsion due to ionic sizes, 2) Coulomb interactions to take into account charge transfer, and 3) charge-dipole interaction to include the effect of electronic polarizabilities. The three-body potential, V_3 , includes the effects of bond stretching and variation of bond angles.

3. Molecular Dynamics

Using these potentials, molecular dynamics simulations are performed on 648 and 5,184 particle systems to study structural and dynamical correlations in glassy and molten states. Cooling, quenching and thermalizing schedules used in the preparation of vitreous states are schematically described in Fig. 1.

Structural and dynamical correlations were obtained by calculating appropriate correlation functions.[10] Vibrational density-of-states was calculated using three methods: 1) Fourier transform of velocity auto-correlation functions, 2) Displacement auto-correlation functions using the equation of motion method, and 3) Direct diagonalization of the dynamical matrix.

4. Results

To provide a broad overview, we shall discuss a few results for the structural and dynamical correlations for vitreous and molten states. For a detailed discussion the reader should look into the appropriate references.[8-11]

a) Short Range Order

From partial distribution functions and bond angle distribution functions we can determine the bond lengths and the nature of the structural unit. For vitreous SiO_2 ,[10] GeSe_2 ,[8] and SiSe_2 [9] the unit is a tetrahedron which remains intact in the molten phase. MD results are in good agreement with diffraction experiments.[5-7]

b) Connectivity of two tetrahedra

There are two possible connectivities for the tetrahedra in these chalcogenide systems. In the vitreous state SiO_2 has only the corner sharing configuration whereas GeSe_2 and SiSe_2 have both corner sharing and edge sharing configurations. These configurations are shown schematically in Fig. 2.

Connectivity of many tetrahedra is best described in terms of n-fold rings. Results for ring statistics for a-GeSe₂ and a-SiO₂ are given elsewhere.

c) Static Structure Factor

The neutron static structure factors from MD[8-10] and experiments [5-7] are shown in Fig. 3. The agreement between theory and experiment is very good for the vitreous states as well as for the molten GeSe₂.

d) Intermediate Range Order (IRO) and The Origin of FSDP

MD results for the partial static structure factors, $S_{\alpha\beta}(q)$, obtained by Fourier transformation of the partial pair distribution functions, $g_{\alpha\beta}(r)$, for GeSe₂ are shown in Fig. 4. Also shown are the experimental anomalous x-ray scattering results for vitreous GeSe₂.[3] From the MD results one can infer that the first sharp diffraction peak arises from Ge-Ge and Ge-Se correlations. This is in agreement with experimental result shown in the figure.

By analyzing the structural correlations in real space and q-space we conclude that the intermediate range order in binary chalcogenide glasses arises from the coherent packing of the elementary unit in the range of 4-8Å.[8,10]

e) Destruction of the Intermediate Range Order

The IRO in vitreous GeSe₂ can be destroyed by alloying it with Ag. This leads to broken Ge-Se bonds and distortion of the Ge(Se_{1/2})₄ tetrahedra resulting in the destruction of the coherent packing of the elementary units. In Fig. 5 the MD results [11] for the neutron static structure factor, $S_N(q)$, for Ag₄Ge₃Se₉ are shown along with the experimental results.[12] The FSDP in GeSe₂ at 1Å⁻¹ (see Fig. 2), the signature of the IRO, is almost totally destroyed in Ag₄Ge₃Se₉.

f) Vibrational Density-of-States (DOS)

The dynamical matrix for a 648 particle a-GeSe₂ system was diagonalized

from all the three methods mentioned above are essentially the same. The results for the vibrational DOS and the participation ratio calculated using the eigenvectors are shown in Fig. 6. The vibrational DOS is in good agreement with the experiments. The arrows marked A_1 and A_{1c} indicate the symmetric breathing mode ($26.4 \text{ meV} = 213 \text{ cm}^{-1}$) and its companion line ($27.8 = 224 \text{ cm}^{-1}$), respectively, which are also in good agreement with the corresponding experimental values of 24.5 and 26.3 meV.[13] The participation ratio determines the number of particles participating in a particular mode. For a fully extended mode it is unity and for a localized mode it tends to zero. From the figure it is clear that modes beyond 20 meV including the A_1 and A_{1c} modes are spatially localized, whereas for energies less than 20 meV the vibrational modes are extended.

5. Conclusions

Proposed interaction potentials in conjunction with molecular dynamics method provide a satisfactory description of structure and dynamics of binary and ternary chalcogenide glasses. We have carried out MD simulations for permanently densified a-SiO₂ under a hydrostatic pressure of 16 GPa resulting in 20% higher density of a-SiO₂.[14] Our results are in very good agreement with experiments. Calculations for GeO₂, B₂O₃, and ZnCl₂ are in progress.

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Figure Captions

Figure 1 Preparation of amorphous states from the molten phase. Cooling, quenching, and thermalization schedules used in the preparation of a-SiO₂.

Figure 2 Connectivity of two tetrahedra: Corner sharing and edge sharing configurations.

Figure 3 Neutron Static structure factor, S_N(q). MD results, continuous line and experiment, solid circles.

Figure 4 Experimental results from anomalous x-ray scattering and MD results for partial static structure factors, S_{αβ}(q), for a-GeSe₂.

Figure 5 Neutron static structure factor for a-Ag₄Ge₃Se₉. MD results, continuous line and experiment, solid circles.

Figure 6 Vibrational density of states and participation ratio for a-GeSe₂. A₁ and A_{1c} denote the symmetric breathing mode and its companion line.

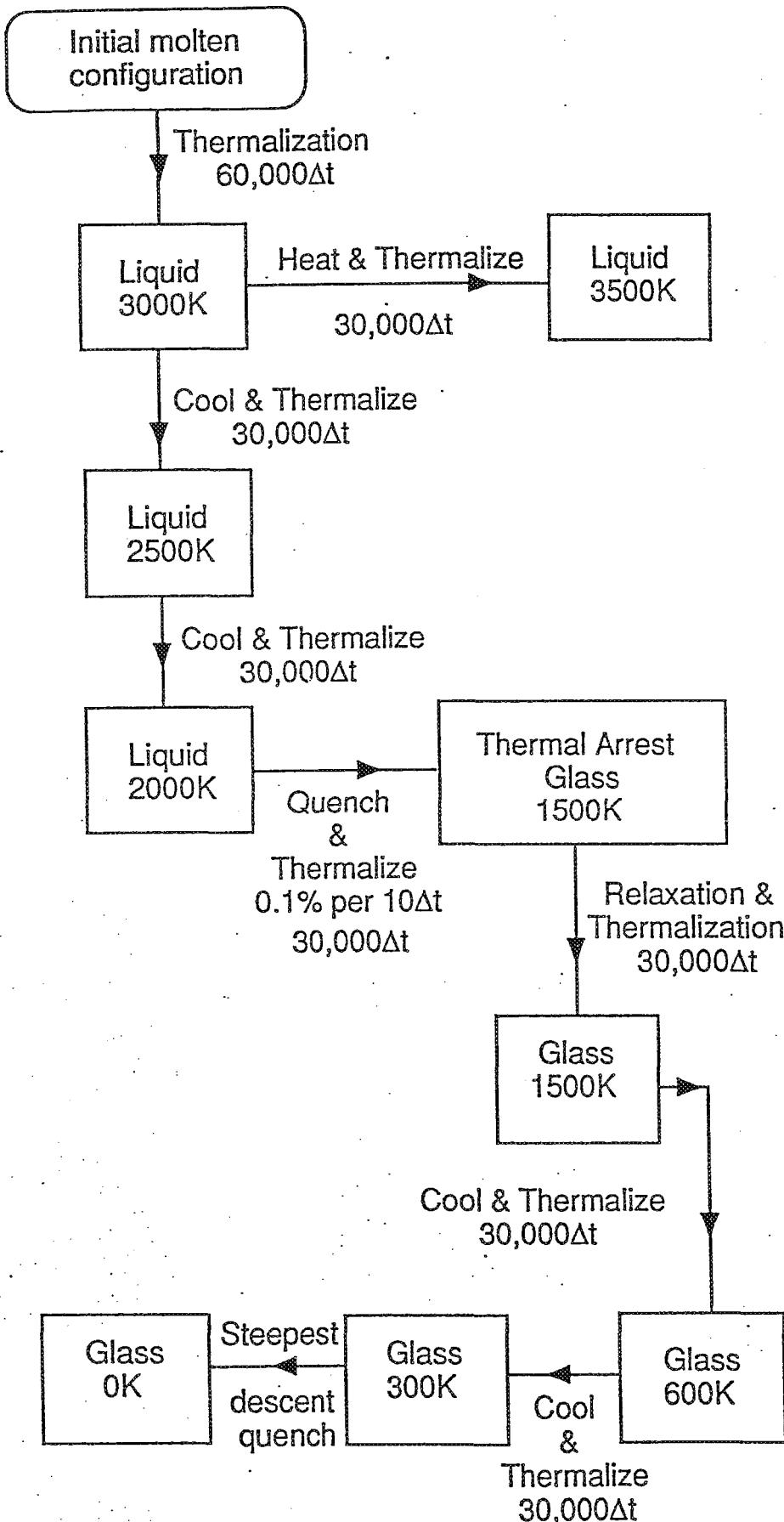
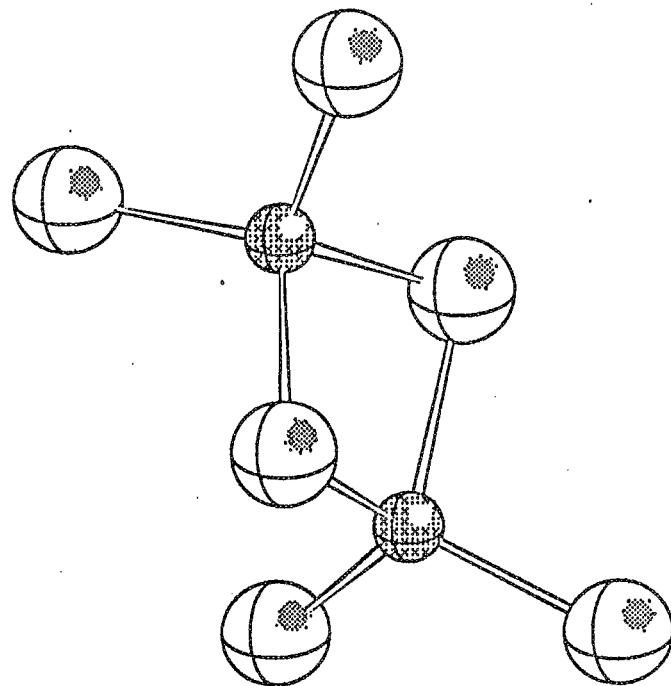
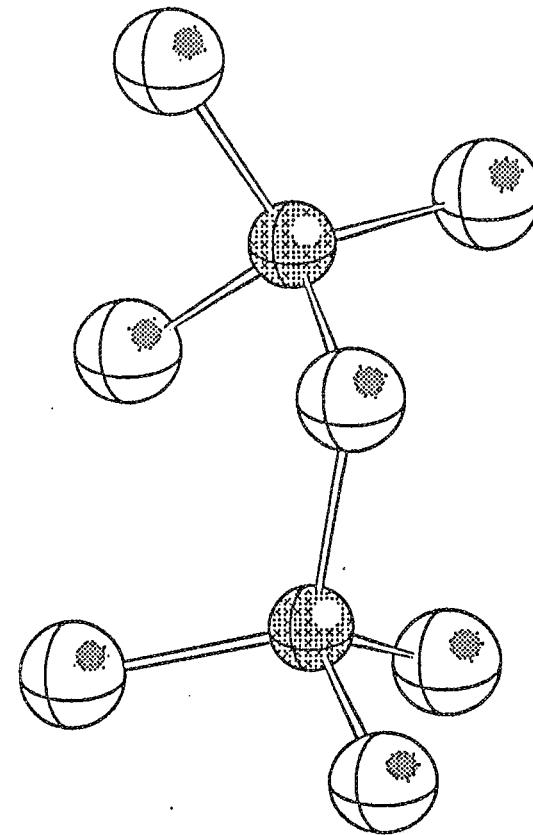


Fig 1



Edge-sharing



Corner-sharing

