

An Atomic-Scale View of Network-Forming Disordered Materials via First-Principles Molecular Dynamics

Carlo Massobrio

Institut de Physique et de Chimie des Matériaux (IPCMS), 23 Rue du Loess, BP 43,
F 67034 Strasbourg Cedex 2, France

In network-forming liquid and glasses structural order extends well beyond nearest-neighbor distances, leading to the appearance of a first sharp diffraction peak (FSDP) in the total neutron structure factor. Whenever available, partial structure factors convey an even more detailed set of information on the structure of these systems. In particular, the existence of concentration fluctuations at short and intermediate range distances is revealed by the behavior of the concentration-concentration structure factor.

Computer modeling at the atomic scale is ideally suited to link the presence of this signature to specific features in real space. We work within a first-principles framework combining the appropriate account of space and time scales with an accurate description of bonding. We were able to follow the self-consistent temporal evolution of a sufficiently large collection of atoms during intervals ranging in between 10 and 50 ps.

This talk will focus on the description of short and intermediate range order in prototypical disordered AX_2 networks: $SiSe_2$, $GeSe_2$ and $GeSe_4$. Very recently, we have obtained a picture of amorphous $SiSe_2$ fully consistent with diffraction data, the number of Si atoms in corner- and edge-sharing configurations following closely the experimental estimate [1]. By focusing on all the possible sequences of three Si atoms, we show that the series made of both corner- and edge-sharing connections are more numerous than those formed exclusively by edge-shared atoms. This result clearly demonstrates that the amorphous phase does not feature the extended edge-sharing Si atoms chains which characterize crystalline $SiSe_2$.

A comparative study of the charge-charge $S_{zz}(k)$ and the concentration-concentration $S_{cc}(k)$ structure factors has been carried out for disordered $GeSe_4$, $GeSe_2$ and $SiSe_2$. We found that the FSDP is present in $S_{cc}(k)$ while it is absent in $S_{zz}(k)$, i.e. fluctuations of charge do not occur over intermediate range distances [2,3]. This shows the inadequacy of the point-like charge model in the treatment of highly ionic disordered materials, the two structure factors being simply proportional within this approach. We show that a FSDP in $S_{cc}(k)$ is generally associated to a small departure from chemical order. The constraint of charge neutrality is at the very origin of the appearance of fluctuations of concentration. These are observed when the atoms occur in configurations with different coordinations.

This work has been done in collaboration with A. Pasquarello (IRRMA, Lausanne). Calculations on $SiSe_2$ have also involved M. Celino (ENEA, Rome).

References

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- [3] *Charge fluctuations and concentration fluctuations at intermediate-range distances in the disordered network-forming materials SiO_2 , $SiSe_2$ and $GeSe_2$* , C. Massobrio, M. Celino, A. Pasquarello, to be published.