X 線異常散乱測定による赤外線光ファイバーガラス材料の原子配列の研究

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As-Se 系ガラスは赤外線光ファイバーの原料として知られている。多元系機能性ガラスの原子配列について、元素ごとの部分構造を求めるために、九州シンクロトロン光研究センターで X 線異常散乱実験の新しい手法を開発した。ほぼ同じエネルギー分解能を持つ 2 つのシリコン・ドリフト検出器を準備し、一方は角度を変化させて散乱 X 線強度を測定し、そのシグナルに含まれる蛍光 X 線やコンプトン散乱成分を除去するために、もう一方の検出器を後方散乱位置に固定した。この方法により、入射 X 線エネルギーを組成元素の吸収端付近で変化させたときの散乱 X 線強度のコントラスト（差構造因子）について、大幅な解析時間の短縮と測定精度の改善を行うことができた。本稿では、As-Se 系赤外線ガラスファイバー材料の、九州シンクロトロン光研究センターで行った As *K* 吸収端付近の測定結果、ESRF で行った Se *K* 吸収端付近の結果、および J-PARC で行った相補的な中性子回折実験の結果を全て取り入れた逆モンテ・カルロ計算による As-Se ガラスの部分原子配列の結果を報告する。

Local- and intermediate-range local structures of As-Se glasses in a wide concentration region including the stiffness transition

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Abstract

The stiffness transition [1,2] is an attractive and simple idea for describing physical properties of network glasses. This idea was substantially developed by Boolchand and coworkers [3] as the so-called intermediate phase (IP) using thermodynamic and Raman scattering experiments. Bauchy et al. [4] carried out ab initio molecular dynamics simulation on As-Se glassy system, and found the specific structural signatures for the IP in the first sharp diffraction peak of the As-Se partial structure factor, $S_{AsSe}(Q)$, in the reciprocal space, and the fraction of the As-As wrong bonds in the real space. They requested experimentalists in their paper to find the partial structural signatures for the IP.

We carried out an anomalous x-ray scattering (AXS) experiment on As-Se [5,6] glasses at BL15/Saga-LS and BM02/ESRF, and analyzed the results using reverse Monte Carlo (RMC) modeling to obtain its partial information, such as partial structure factors, $S_{ij}(Q)$, and partial pair-distribution functions, $g_{ij}(r)$, and three-dimensional (3D) atomic configuration. However, results from RMC modeling highly depend on the constraints in the RMC fit procedure, such as shortest interatomic distances and bond angles. For the further structural investigations, we carried out neutron diffraction (ND) measurements using the NOVA diffractometer installed at the J-PARC, and real-space $g_N(r)$ functions could be included in the RMC modeling, which supports the determination of the above constraints.

In this presentation, we will exhibit a better quality of $S_{ij}(Q)$, $g_{ij}(r)$, and 3D atomic configuration, and the obtained results will be carefully discussed in relation to the stiffness transition by comparing with the above theoretical results by Bauchy et al. [4]. AXS experiments were carried out at BL15 of the Saga-LS (Proposal No. 1802007A). ND experiments were performed at BL21 of MLF/J-PARC (Proposal No. 2017B0047). This work was supported by JST CREST (No. JPMJCR1861).

[1] J. C. Phillips, J. Non-Cryst. Solids 34, 153 (1979).
[2] M. F. Thorpe, J. Non-Cryst. Solids 57, 355 (1983).
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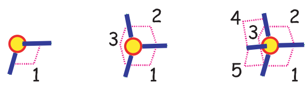
Stiffness transition theory

J. C. Phillips 1979
M. F. Thorpe 1983



Constraints per atoms	twofold	threefold	fourfold
bond	2/2	3/2	4/2
angle	1	3	5

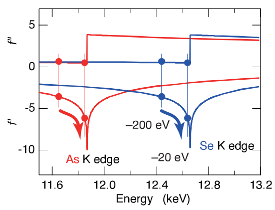
Number of constraints ↕ Degree of freedom: 3 — $\langle r \rangle = 2.4$

floppy: $\langle r \rangle < 2.4$ — rigid: $\langle r \rangle > 2.4$

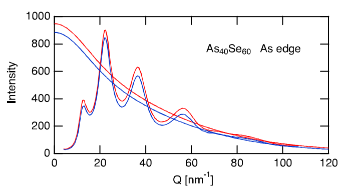
Principle of AXS

$f(Q,E) = f_0(Q) + f'(E) + if''(E)$

Usual terms — Anomalous terms

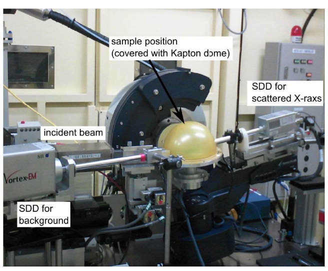


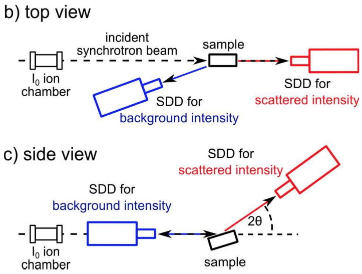
Normalized scattering data



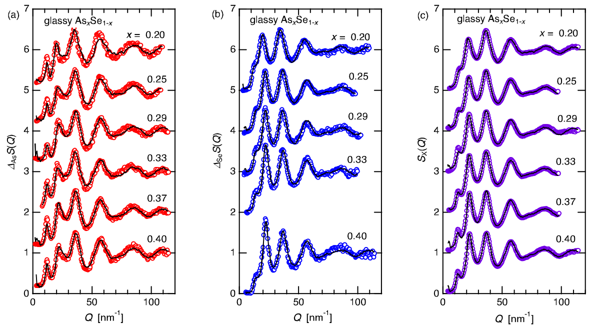
AXS experiment at BL15/Saga-LS

a)

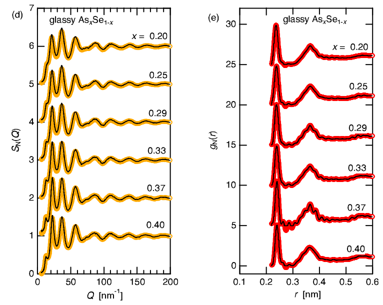




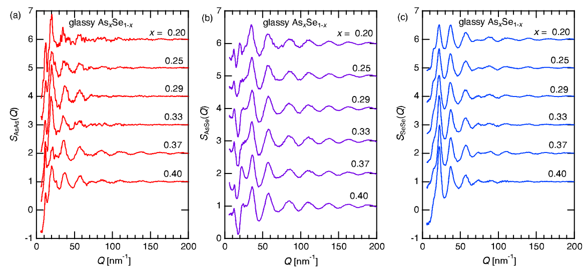
Experimental results: Anomalous x-ray scattering



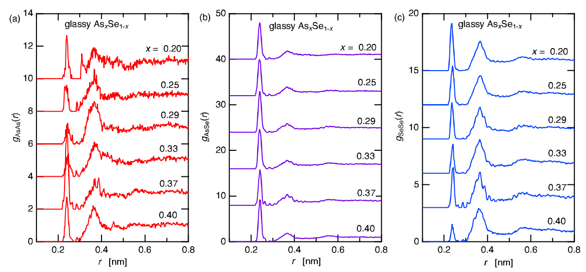
Experimental results: Neutron diffraction



$S_{ij}(Q)$



$g_{ij}(r)$



3D atomic configurations