Quantitative Measurements of Phase Transitions in Nano- and Glassy Materials

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Abstract. Novel approaches to the collection and treatment of total x-ray scattering using high energy (> 65 keV) x-ray beams and area detectors allow in situ studies of unprecedented precision to be performed on nano-crystalline (n) and glassy materials at extremes of pressure (p) and temperature (T). Gradual structural transitions in glasses, liquids and nano-materials occurring via continuous changes in density, or involving phases related by pseudo symmetry are inherently difficult to identify due to their disordered nature. In such cases supplementary physical measurements along with modeling of the pair distribution function (PDF) provide powerful constraints on the possible models for the transition. Examples include transitions from n-FeS with a mackinawite-like structure to high p forms with structures related to NiAs structure-type. The distinction between the various high p models - MnP-type, trolite, FeS-III related or mixtures of these phases – is subtle; great care needs to be exercised in refining structure models to fit the observed data. Acoustic techniques are particularly valuable in identifying high p phase transitions in glasses, since measured changes in compressional velocities relate to density changes in the glass while shear waves provide an insight into network rigidity.

1. Introduction

The nature of the atomic arrangements and their changes with high-pressure (p) in nano-crystalline (n) and glassy materials impacts our understanding of size-dependent compression mechanisms [1,2], amorphization and polymorphism [3]. Defining the arrangement of atoms in poorly crystalline materials is challenging because Bragg diffraction data obtained from these materials is often limited in range and quality. The data are also often compromised by parasitic scattering arising from high pressure (HP) cells. Data collected from nano-crystalline and glassy materials often consist of a few broadened peaks and the information loss implied by this makes use of traditional crystallographic techniques, such as Rietveld methods, inappropriate. Further, gradual structural transitions in glasses, or transitions involving order-disorder or magnetic transitions in crystalline solids, that occur via continuous and not abrupt changes, are sometimes difficult to identify in diffraction studies alone. Measurements of elastic properties, and especially shear wave propagation, can identify changes in network rigidity, magnetism and order as a function of p [4-6]. While measurements of physical properties offer useful complementary information, modelling of diffraction data provides compelling information on the nature of the transitions. Two recent studies provide excellent examples and...
cautionary lessons in the collection, reduction and analysis of in situ total x-ray scattering data collected from glasses and nano-materials at high $p$.

2. Experimental set-up for total scattering measurements

Focused x-rays with $E > 65$ keV ($\lambda < 0.2$ Å) allow measurement of total elastic scattering to $Q (=4\pi\sin(\theta)/\lambda) > 25$ Å$^{-1}$ minimizing artifacts in the pair distribution function (PDF) derived from such scattering data. These quantitative [7] data can be analyzed using model refinement analysis common in studies at low $p$ [8-12]. Investigations of poorly crystalline materials at high $p$ [13-16] especially benefit from scattering of high energy x-rays because of the increased penetrating power and the increased coverage of $Q$-space in a single exposure of area detectors [17]. The latter point is especially important for poorly scattering materials where small sample size severely limits the efficiency of point counters.

2.1. Total scattering and the pair distribution function (PDF)

The pair distribution function PDF or $G(r)$, gives the probability of finding an atom at a given distance $r$ from another atom and can be considered as a bond length distribution [10].

$$G(r) = 4\pi\rho(\rho(r) - \rho_0) = \frac{2}{\pi\rho_0^2} Q[S(Q) - 1] \sin(Qr)dQ$$

where $\rho(r)$ is the microscopic pair density, $\rho_0$ is the average number density, and $Q$ is the magnitude of the scattering vector. Experimentally it is not possible to measure data up to infinite $Q$, and the cutoff at finite values of $Q_{\text{max}}$ decreases the real space resolution of the PDF. This causes some aberrations in the form of “Fourier or termination ripples” which propagate through $G(r)$ as high frequency noise. For both x-ray and neutron scattering experiments, high energies are required in order to access high values of $Q_{\text{max}}$ to obtain the most accurate Fourier transform of the reduced structure function $F(Q)$.

The PDF is obtained from the powder diffraction (x-ray or neutron) via a Fourier transform of the normalized total scattering intensity, $S(Q)$:

$$S(Q) = 1 + \left[ I^{\text{coh}}(Q) - \sum c_i f_i(Q) \right] / \sum c_i f_i(Q)^2$$

Where $I^{\text{coh}}(Q)$ is the coherent scattering intensity per atom, $c_i$ is the atomic concentration and $f_i$ is the x-ray scattering factor for species $i$.

2.2. Quantitative high pressure PDF

In order to obtain reliable data from a sample surrounded in a pressure vessel several data collection strategies are employed to maximize sample volume and $Q$-range and/or minimize parasitic scattering from the pressure vessel. For data from diamond anvil cells the sample volume is small and focused high-energy ($E > 60$ keV) beams of around 20 µm diameter introduced, as shown in figure 1 [1,18-20], minimize absorption, as well as the Bragg and diffuse scattering from diamond. A heavy metal gasket serves to eliminate scattering from the upstream diamond; the diffraction cone being considerably compressed in cases of scattering using 100 keV beams, for example [19]. Sample volume can be increased using composite gaskets as was demonstrated in experiments by Martin et al. [20]. The use of area detectors [9,17] and especially detectors with repetition rates greater than 20 Hz [17] allows rapid data collection and over sampling. With little overhead due to readout time, many short exposures are collected to maximize the signal from the sample and minimize blooming on the detector from Bragg spots arising from the small amount of diamond in the perforated downstream anvil (figure 1).

Large volume apparatus [21,22] such as the Paris-Edinburgh (PE) pressure cells [23,24] generate pressure through compression of the sample, confined within a gasket, between a pair of tungsten carbide (or sintered diamond) anvils. For a given anvil/gasket size, the physical properties of the gasket material largely limit the range of pressures accessible. For samples greater than about 1 mm diameter a set of slits [25,26] can be used to exclude scattering from the high pressure apparatus. This
works especially well for studies utilizing the Bragg scattering alone [5,27] and has been used for studies of total scattering as well [25,28]. Provided the data for suitable blanks, i.e., gasket material without sample, can be scaled to the total data collected without slits, reliable PDFs have been obtained using subtraction methods [21,29].

![Figure 1. (a) Schematic drawing of a DAC with downstream PPA: Partial Perforated Anvil made of 0.25-carat diamond with a conical hole. The heavy metal (Re) gasket masks most Compton scattering from the upstream diamond. (b) Raw diffraction data from nanocrystalline SrTiO$_3$ collected at 100 keV on an amorphous Si detector showing spots from the downstream diamond. $Q[S(Q)-1]$ for nanocrystalline CeO$_2$ in (c) a diamond anvil cell fitted with un-perforated diamonds and (d) fitted with perforated diamonds. The decrease in contributions to the overall scattering from diamonds in the perforated cell leads to much better signal to noise discrimination at high $Q$, an important factor in deriving better resolved real space correlation functions containing fewer “ripples” due to Fourier termination errors.

3. Case studies

We have investigated a variety of disordered and poorly crystalline materials at high pressure using x-ray and neutron total scattering coupled with pair distribution function methodologies [1,4,15,18,29-32]. These studies include the differences in HP behaviour of bulk and nano-sized FeS and the use of ultrasonic data to confirm the mechanism for structural collapse in GeSe$_2$ glass up to 9 GPa.

3.1. Nanocrystalline FeS

The pair distribution function, PDF or $G(r)$, gives the probability of finding an atom at a given distance $r$ from another atom and can be considered as a bond length distribution [10]. This distribution is in principle unique and dependent on the atomic arrangement in the bulk crystalline or nano-material. Variation due to surface reconstruction, particle shape and size distribution can also affect the PDF. While, single crystal or high resolution powder diffraction easily distinguishes members of a closely related structural family based on superlattice and other weak diffraction features, the limits of the PDF technique were not systematically investigated in this regard.

Nanocrystalline FeS, which can be synthesized in nano-crystalline form without stabilizing capping agents [33], is an excellent candidate material to observe high pressure phase transitions for comparison with bulk materials [1]. Previous studies showed that FeS synthesized by high temperature routes crystallizes in the NiAs-related troilite structure with iron octahedrally coordinated to sulphur. Troilite undergoes transitions to MnP-type FeS-II [34,35] and FeS-III [36] structures, also NiAs-related, at pressures of approximately 4.5 and 7.6 GPa, respectively.
Nano-crystalline FeS crystallizes in the mackinawite structure with Fe 4-coordinated to sulphur and this material clearly undergoes transitions at high pressure (figure 2). Analysis of the total X-ray scattering and evaluation of the PDF (figure 3) confirms the transition is to a NiAs-related structure. Although testing using least squares of the competing models (FeS-II and –III) for the high-pressure phase (figure 3) favours the FeS-II model, the exercise also highlights the limitations of applying periodic structure models to atomic arrangements in nanomaterials. When closely related structure models need to be distinguished the data need to be of the highest quality and resolution - challenging criteria for scattering data collected from samples in a high-pressure cell. Energy discriminating low-noise area detectors would allow us to push beyond current limitations.

3.2. Tracking transitions in GeSe\textsubscript{2} glass

While observations in \(Q\)-space readily identify structural phase transitions in crystalline and nano-crystalline materials (figure 2) gradual structural transitions in glasses and liquids as a result of increasing pressure are inherently difficult to identify due to their disordered nature. Binary Ge-Se glass, long the basis for network rigidity theories, reaches a fully polymerized network for composition GeSe\textsubscript{2} [37] where a rigid glass structure comprises of GeSe\textsubscript{4} tetrahedra, of which 34\% are in edge sharing configurations and the rest are corner shared. These tetrahedra are arranged in a distribution of ring sizes containing predominantly 3-, 6-, 7- and 8-Ge atoms.

While x-ray scattering measurements at high pressure provide tantalizing evidence in the disappearance of the first sharp diffraction feature of possible phase transitions [15], the measurement of S-waves in glasses provides insight into network rigidity. A minimum observed in the shear velocity, \(v_s\), and associated anomalous behaviour in Poisson’s ratio below 4 GPa (figure 4) are indicative of a second order-type transition in GeSe\textsubscript{2} glass [4]. This is attributed to a competition between two densification mechanisms. At pressures up to 3 GPa, a conversion from edge-to-corner sharing tetrahedra results in a more flexible, floppy network followed by a gradual increase in coordination number with pressure, which leads to an overall stiffening of the glass above 4 GPa.
A conversion from edge-to-corner sharing at low P results in larger and more flexible rings, which may be compressed more readily, while an increase in coordination reduces the average ring size as the density increases. The innovative use of transfer function ultrasonics [38] in the case of this glass highlights the power of supplementing total scattering approach with measurements of physical properties that are sensitive to particular structural features, such as network rigidity.

Figure 4. Variations with pressure of (a) Shear velocity $V_S$ and (b) Poisson's ratio. Solid and open symbols are data on pressurization and depressurization. Lines in (a) are guides to the eye.

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