Solving the Low Temperature Structure of a New Solid Superionic Conductor $Ag_7P_3S_{11}$ Using the RA-PDF Technique

Ahmad Masadeh, Emil S. Božin, Simon J.L. Billinge

Department of Physics and Astronomy and Center for Fundamental Materials Research
Michigan State University, East Lansing, MI 48824-1116, USA

Introduction

Superionic conductors are a class of solids which exhibit exceptionally high ionic conductivity, comparable with that of molten salts while still in solid-state phase. These materials have potentially important technological applications in, for example, solid state batteries. An understanding of the structural properties of superionic conductors and determination of the features required for high ion mobility may lead to identification of candidate materials for further investigation.

The transition from non-conducting to conducting phase in these materials may either take place gradually as is the case in fluorine ion conductor (e.g. lead fluoride), or at a specific temperature as it is found in the case of silver iodide (147 ^{0}C). In both the cases, as in many others, it involves the *disordering* of the sublattice of the material. At low temperatures, the same lattice is ordered and conductivity is low. The crystal lattice consists of two sublattices—one of mobile ions and that of immobile ones. It is the immobile ion lattice through which the mobile ions move. The properties are dependent on its crystal structure [1].

An IP detector coupled with high-energy synchrotron radiation has been recently successfully used for atomic pair distribution function (PDF) analysis [2], with high probed momentum transfer Q_{max}, from several crystalline materials [3]. Medium-high real-space resolution PDF data analysis from crystalline materials has been performed using image-plate data and shows promising results. Comparable or even better statistics than from conventional X-ray measurements can be achieved with significantly shorter counting times. This new combination of a real-space probe and fast counting time, named RA-PDF, opens up a broad field for future applications to a wide variety of materials of both scientifc and technological interest [4].

Measurements were carried out using the RA-PDF method on a powdered $Ag_7P_3S_{11}$ sample to slolve the low temperature structure for this system.

Methods and Materials

High energy X-ray diffraction experiment was performed at the 6-ID-D MU-CAT beam line at the Advanced Photon Source (APS) at Argonne National Laboratory. A powdered $Ag_7P_3S_{11}$ sample was loaded into a hollow flat metal plate with thickness of 1.0 mm, and then sealed between thin Kapton films. Data acquisition at various temperatures between 10 K and 300 K employed the recently developed rapid acquisition PDF (RA-PDF) technique [3] with an X-ray energy of 98.0 keV (λ=0.126530 Å). A single exposure of the image plate detector was limited to 40 seconds to avoid detector saturation, and was repeated 10 times to achieve better counting statistics in the high-Q region.

Measurements were carried out in flat-plate transmission geometry. A Mar345 image-plate camera, a round disk with a usable diameter of 345 mm, was mounted orthogonal to the beam centered on the IP. Silicon standard sample was used to calibrate the sample-to-detector distance and the tilt of the IP relative to the beam path, using the software Fit2D [5, 6]. The sample to detector distance was 178.4 mm. All raw 2D data were integrated and converted to intensity versus 2θ format using the Fit2D program package [5, 6], where 2θ is the angle between the incident and scattered X-rays. Standard corrections for multiple scattering, polarization, absorption, Compton scattering and Laue diffuse scattering were applied to the integrated data to obtain the reduced total structure function F(Q). Direct Fourier transformation gives the pair distribution function G(r). Data correction and processing utilized the PDFgetX program package [7]. The structure models were refined using the profile-fitting least-squares regression program PDFFIT [8].

Data for powder superionic conductor $Ag_7P_3S_{11}$ sample were collected at series of temperatures as follows: 10 K, 20 K, 40 K, 60 K, 90 K, 100 K, 120 K, 140 K, 160 K, 180 K, 185 K, 190 K, 195 K, 200 K, 205 K, 210 K, 220 K, 225 K, 230 K, 240 K, 245 K, 250 K, 270 K, 280 K, 290 K, and 298 K. Low temperature measurements were carried out by utilizing a displex closed cycle refrigerator, which has a beryllium window. Upon reaching the target temperature, the system was allowed to equilibrate for 10 minutes prior collecting the data. To reduce the background, lead shielding was placed before the sample with a small opening for the incident beam.

Results

Structural properties of new superionic conductor $Ag_7P_3S_{11}$ were addressed using the RA-PDF method, well suited for detailed structural studies in materials [3]. The PDF gives the number of atoms in a spherical shell of unit thickness at a distance r from a reference atom [2]. This gives peaks at characteristic distances separating pairs of atoms. Fourier transform from reciprocal to real space was carried out up to Q_{max}=20Å^{-1}. Beyond that value of Q the signal to noise ratio was unfavorable.

Experimental reduced total structure function, F(Q)=Q(S(Q)-1), and corresponding atomic G(r)'s for $Ag_7P_3S_{11}$ at room temperature are shown in Fig. 1. Reduced total structure function, F(Q)=Q(S(Q)-1), and corresponding atomic G(r)'s for

the entire temperature series investigated in this experiment are shown in Fig. 2 and Fig. 3 respectively.

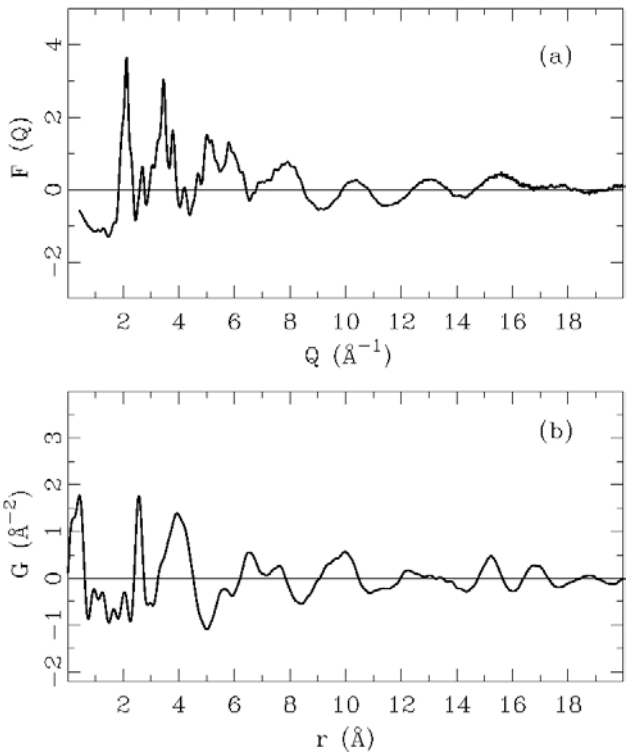

Fig.1. Room temperature experimental reduced total structure function F(Q)=Q(S(Q)-1) of the new superionic conductor $Ag_7P_3S_{11}$ sample, (top), and corresponding G(r) (bottom). Data were collected using the RA-PDF experimental setup. F(Q) was Fourier-transformed using Q_{max}=20Å^{-1}.

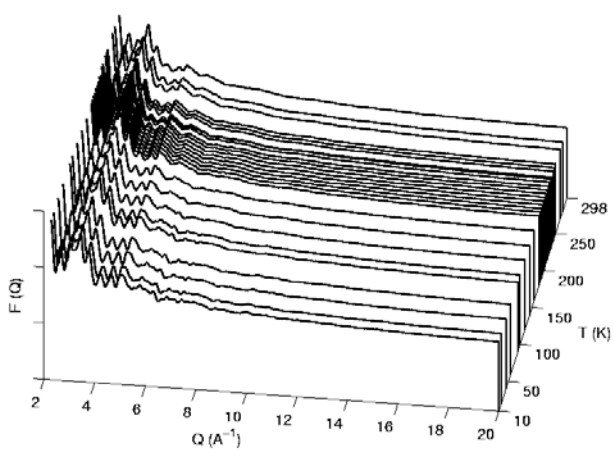

Fig.2. Evolution of the experimental reduced structure function F(Q)=Q(S(Q)-1) of the new superionic conductor $Ag_7P_3S_{11}$ with temperature with temperatures in 10 K – 300 K range. Data were collected using the RA-PDF experimental setup.

Discussion

The room temperature data was modeled (not shown) using the PDFFIT modeling program, the results agree well with the literature [9]. The low temperature data were analyzed and PDFs, *G(r)'s*, were obtained (Fig. 3). We modeled the low temperature data starting with the room temperature model and refining the lattice parameters, Ag-ion positions, thermal factors and occupancies of partially occupied sites. The disagreement is found between the room temperature model and the low temperature data, due to the structural changes expected to be happening in the material. Further modeling is in progress in effort to solve the structure at low temperature.

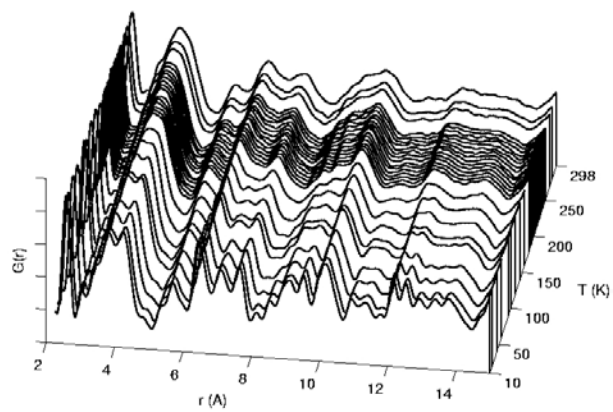

Fig.3. Evolution of the experimantal reduced pair distribution function, G(r), for new superionic conductor $Ag_7P_3S_{11}$ with temperature with temperature in 10 K – 300 K range. PDFs shown here were obtained from Q-space data through a Fourier transform up to Q_{max}=20Å^{-1}.

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