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# Study of short range structure of amorphous Silica from PDF using Ag radiation in laboratory XRD system, RAMAN and NEXAFS

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ABSTRACT

At present synchrotron and neutron sources are the preferred choices for the Pair Distribution Function (PDF) analysis, but there is a need to explore PDF in a laboratory XRD system for quick feedback about the short range structure of the amorphous materials. Present work considered both crystalline (quartz) and amorphous silica to study the structural differences in silica by PDF analysis using Ag radiations in laboratory XRD. The structural information about short range ordering of the oxygen (O) atoms around silicon (Si) atoms as obtained by the PDF were compared with the results as obtained by Near Edge X-ray Absorption Fine Structure (NEXAFS) and RAMAN experiments. The PDF studies showed that the amorphous silica possessed short range periodicity within the basic unit of $(SiO4)^{4-}$ tetrahedra with a Si—O & O—O distance are of about 1.622 Å and 2.713 Å while the short range as well as long range ordered structure present in quartz with Si—O & O—O distance are 1.562 Å and 2.661 Å respectively. Raman spectra showed some asymmetry in amorphous silica which corresponds to the defects present in the lattice and thus forming the n-fold ring structure with Si and O resulting in the wide variation of bridging bond angle Si—O—Si in amorphous silica. NEXAFS studies revealed the structure of amorphous silica and quartz in the intermediate range (3–5 Å) at the Si L and O K edges. The structural information about short range ordering of the O around Si atoms as obtained by these methods were found to be in good match with the results as obtained by PDF, suggesting this technique may be used as a screening tool for routine PDF studies of amorphous materials.

## 1. Introduction

Glass is considered to be a thermodynamically metastable state between liquid and crystalline state. The amorphous silica has two dimensional structures with local short range ordering with respect to the tetrahedral arrangement of O atoms around the Si atoms. This structural environment basically controls the structure as well as the properties of the glass. In the recent years, glass is one of the technologically important materials due to wide applications in the field of optical communications, photovoltaic cells and electronic devices and building materials [1–3]. X-ray diffraction (XRD) technique is one of the most powerful techniques [4,5] for structural characterization of material at micro and even at nano levels. But the crystallographic structure solution based on XRD by Rietveld technique [6] reveals only the average structure of the long range periodic materials. In fact, even for crystalline nano particles, Bragg peaks become so much broadened due to the small size of the particles which leads many approximations, commonly accepted for micrometer size domains, fail almost drastically. Sometimes the classical crystallographic formalism becomes quite useless for the structural solution for nano and disordered materials. Then the Debye scattering function [7] followed by the PDF [8,9] is the only possible choice where the direct evaluation of the nano-particle structure factor from the interatomic distances is necessary. Synchrotron radiation and neutron radiation are the preferred choices for PDF analysis due to the tuning of wavelength with inter atomic distances of the experimental samples. But there is a need for routine analysis of such type of samples in a laboratory XRD system to get the quick feedback about the short range structure. In the present work, PDF experiments were carried out in a laboratory XRD system using Ag radiation to obtain high Q value ($Q = 4\pi \sin\theta / \lambda$) for shorter wavelength ($\lambda = 0.5608$ Å) of X-ray beam. The same experiments were performed using synchrotron radiations as well to corroborate the usefulness of the former technique. NEXAFS spectroscopy experiments were carried out to get an approximate estimate of the nearest

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neighbour Si—O and O—O bonds along with understanding the arrangement of bridging (BO) and non-bridging oxygen (NBO) around the Si atoms. Finally the structural information about the short range and long range distribution of Si and O atoms in both form of silica as obtained by PDF and NEXAFS were correlated with the results as obtained by Raman study. These structural information about the short range ordering of the glass help one to better understand the properties of glass for various applications.

## 2. Experimental procedure and methods

Commercially available quartz and amorphous silica were taken for the study of the long range and short range structure in silica. Crystal structure and microstructure of silica were investigated by XRD, high resolution transmission electron microscope (HRTEM), PDF, RAMAN and NEXAFS studies. The XRD patterns of quartz and amorphous silica were recorded in X″Pert Pro MPD diffractometer (PANalytical) using X′Celerator operating at 40 kV and 30 mA using Cu $K_\alpha$ radiation. Selected area diffraction pattern (SADP) were recorded through Tecnai transmission electron microscope (FEI, USA, Model: $G^2$ 30ST). NEXAFS measurements [10,11] at O K-edge (~530 eV) and Si $L_{2,3}$ - edge (~100 eV) were carried out in reflection mode at an incident angle of 45°, using synchrotron radiation at BEAR beamline, ELETTRA synchrotron, Italy. The spectra were recorded by total electron yield (TEY) and normalized [12] with respect to the same recorded for clean gold to account for oxygen and silicon in mesh ($I_0$). Monochromator slits (70 μm) were set to provide an energy resolution of 0.1 eV. Raman spectra for bulk glass samples were recorded using HORIBA Jobin Yvon Lab Ram HR 800 Evolution confocal Raman spectroscope with 488 nm (2.54 eV) Ar ion laser as excitation wavelength and a 100× objective lens (NA = 0.9). The incident laser power projected on the bulk samples was 20 mW with spot size of ~3.14 μm$^2$. In order to remove the Rayleigh scattering part the excitation wavelength specific notch filter was used during the Raman study. Raman spectrum was recorder for the range from 50 to 1700 cm$^{-1}$ for both the silica samples with an integration time of 5 s and 20 accumulations per spectrum. A Peltier-cooled charge coupled device (CCD) detector with spectral resolution of 2 cm$^{-1}$was used for the detection of Raman signal. Raman data were collected using Labspec6 software and then converted to ASCII file which were plotted using Origin scientific plotting program.

In the present work, the shape-convolution method [4,9] was used to calculate the diffraction pattern of the samples based on Debye scattering function followed by the PDF analysis. This includes a real space refinement of crystal structure and the development of the capability to fit a theoretical three dimensional structure to atomic pair distribution function data from total scattering data which include both Bragg peaks and diffuse peaks. XRD experiments were carried out in Bruker D8 Advance Davinci multipurpose diffractometer with Lynxeye detector using Ag radiation to obtain maximum Q value i.e. 22 Å$^{-1}$ in a Laboratory X-ray diffractometer. PDF experiments were performed at room temperature up to angle 60° for the silica samples corresponds to a scattering vector ~ 20 Å$^{-1}$for Ag radiation using Ag radiations operating at 40 kV and 30 mA with step size 0.01° (2θ) and step time 8 s from 0.2° to 60°. Then the experimental data of both the silica were subtracted from the experimental data of an empty capillary to get the actual total scattering from the sample. Then the raw data was corrected for experimental artifacts (Compton scattering, detector dead time etc.) and then scaled into electron units.

RAD [13] software was used to interpret the experimental data based on atomic pair distribution function in laboratory XRD system for the two samples. Total scattering experiments based on PDF using synchrotron radiation were carried out at the beamline P02.1 (DESY Synchrotron, Germany) using high energy (~60 keV) X-rays at room temperature. Two dimensional total scattering raw data were collected using PerkinElmer XRD1621 fast area detector with exposure time 10 s and 60 s for quartz and amorphous silica respectively. The corresponding images were combined, integrated and reduced to one dimensional XRD pattern using FIT2D [14] and the corresponding PDF curves were generated using PDFgetX2 [15] software.

### 2.1. Pair distribution function analysis

The PDF function G (r) gives the probability of finding any two atoms separated by a distance r, which is to be obtained by Fourier transformation of the total scattering function from Braggs peaks as well as from diffuse peaks by

$$G(r) = 4\pi r\,[\rho(r) - \rho_o] \tag{1}$$

where, ρ (r) = local atom number density and $\rho_0$ = average atom number density. Since, the PDF technique takes both Bragg and diffuse scattering into account; it provides information, not only about the long range atomic ordering but also about the short-range ordering in materials. The total scattering data which include both Bragg peaks and diffuse peaks were recorded using transmission geometry employing a rotating capillary (Hilgenberg GmbH, Germany) configuration having capillary diameter 0.5 mm and wall thickness of 0.01 mm, specially made for PDF experiments. Actual total scattering data were obtained by background correction i.e. subtracting the scattering data of the empty capillary from the scattering data of the sample [9,16]. The measured intensity was corrected for background, Compton and multiple scattering, absorption, detector dead time, diffraction geometry and polarization [9,16]. Then the experimental PDF G(r) of the radial distribution function $4\pi r^2 G(r)$ were directly obtained [8,9] from the diffraction data by sine Fourier transformation of the total scattering function, S (Q). The pair distribution function, G(r) is related to the total scattering structure function, S(Q) with the following equation

$$G(r) = \frac{2}{\pi}\int_{Qmin}^{Qmax} Q\,[S(Q) - 1]\sin(Qr)dQ \tag{2}$$

And the inverse transformation of the Eq. (2) i.e. the total structure factor S(Q) can be expressed in terms of the atomic pair distribution function as,

$$S(Q) = 1 + \frac{1}{Q}\int_{0}^{\infty} G(r)\sin(Qr)dr. \tag{3}$$

## 3. Results and discussion

Present work considered commercially available quartz and amorphous silica to study the structural difference in both form of silica. XRD, PDF, RAMAN and NEXAFS analyses had been performed on both samples to explore the structural environment in glass matrix to better understand how the bridging oxygen (BO) and non-bridging oxygen (NBO) [17] were arranged around the silicon atoms. In quartz, each silicon ion is tetrahedrally surrounded by four oxygen ions. The $(SiO4)^{4-}$ tetrahedral units are indeed connected with other tetrahedra to make long range periodicity in quartz. While in amorphous silica, these individual tetrahedral units are joined together in a random manner. There is a short range periodicity within this basic unit of $(SiO4)^{4-}$ but beyond this basic tetrahedral unit, there is no periodicity in their arrangements. Hence, these closely resemble short range atomic arrangements determine the structure of quartz and amorphous silica. Therefore, determination of these short range atomic arrangements is very important for better understanding the structure of glass for various applications. XRD pattern of amorphous silica (Fig. 1a) showed the diffuse peak over the angular range 10° to 35° whereas the quartz contained hexagonal silica phase having space group P3121 (Space Group No: 152) and XRD pattern was indexed accordingly. Values of cell parameters, unit cell volume and reliability parameters were determined for this quartz sample from XRD line profile analysis using Rietveld analysis by X'pert High Score Plus software (PANalytical). The quality of the fitting of observed diffraction pattern with the simulated

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