

Synchrotron WAXS and XANES studies of silica (SiO₂) powders synthesized from Indonesian natural sands

Khairanissa Muchlis¹, Nur Aini Fauziyah¹, Siriwat Soontaranon², Wanwisa Limpirat² and Suminar Pratapa¹

¹Department of Physics, Faculty of Mathematics and Natural Sciences, Institute of Technology Sepuluh Nopember (ITS), Surabaya 60111, INDONESIA

²Synchrotron Light Research Institute (Public Organization), Nakhon Ratchasima, THAILAND

E-mail: suminar_pratapa@physics.its.ac.id

Abstract. In this study, we have investigated polymorphic silica (SiO₂) powders using, Wide Angle X-ray Scattering (WAXS) and X-Ray Absorption Near Edge Spectroscopy (XANES), laboratory X-Ray Diffraction (XRD) instruments. The WAXS and XANES spectra were collected using synchrotron radiation at Synchrotron Light Research Institute (SLRI), Nakhon Ratchasima, Thailand. The silica powders were obtained by processing silica sand from Tanah Laut, South Kalimantan, Indonesia. Purification process of silica sand was done by magnetic separation and immersion with HCl. The purification step was needed to reduce impurity or undesirable non Si elements. Three polymorphs of silica were produced, i.e. amorphous phase (A), quartz (B), and cristobalite (C). WAXS profile for each phase was presented in terms of intensity vs. 2θ prior to analyses. Both XRD ($\lambda_{\text{CuK}\alpha}=1.54056 \text{ \AA}$) and WAXS ($\lambda=1.09 \text{ \AA}$) pattern show that (1) A sample contains no crystallites, (2) B sample is monophasic, contains only quartz, and (3) C sample contains cristobalite and tridymite. XRD quantitative analysis using *Rietica* gave 98,8 wt% cristobalite, while the associated WAXS data provided 98.7 wt% cristobalite. Si K-edge XANES spectra were measured at energy range 1840 to 1920 eV. Qualitatively, the pre-edge and edge features for all phases are similar, but their main peaks in the post-edge region are different.

1. Introduction

Silica is a fundamental building block of many rock-forming minerals and naturally occurs substances that comprise the vast majority of the earth's crust. Its structure which is obtained through patterns of Si-O linking and physicochemical properties have been the subject of numerous investigations for decades. Because of their prevalence and commercial applications, SiO₂ are widely used in the ceramic and glass industries and has an enormous application potential in optical fibres, in microelectronics [1-5]. Even if it is a very simple system, its properties and structures can be very complex as a function of temperature and pressure. Silica exists in many different phases at ambient pressure and temperature, e.g. α -quartz, tridymite, α -cristobalite, glass. Most of these structures are composed of corner-sharing tetrahedral SiO₄ units with a fourfold-coordinated silicon at the centre and twofold-coordinated oxygen atoms at the corners [1-4].

Synchrotron facility such as that at Synchrotron Light Research Institute (SLRI), Nakhon Ratchasima, Thailand provides Small/Wide Angle X-Ray Scattering (SAXS/WAXS) and X-Ray



Absorption Near Edge Spectroscopy (XANES) at region between 0-50 eV above the edge of X-Ray Absorption Spectroscopy (XAS) instruments. These instruments can be utilized for phase analysis of crystalline samples and “local structure” studies of samples, respectively.

Phase analyses of silica has been extensively done particularly on their structures, including “local” structure [1]. They used XANES data in their study. Meanwhile, phase composition examination is usually done using XRD data, not WAXS data. The latter data was used mainly for determining degree of crystallinity. Combination of XRD, WAXS and XANES data analysis, therefore, is a subject of phase analysis which will enrich one’s knowledge on phase structure and composition as well as local structure.

In this paper, we present polymorphic silica, SiO₂ (amorphous, quartz, and cristobalite) powders using CuK α radiation XRD and synchrotron radiation WAXS and XANES. Phase identification and composition determination of the polymorphs from XRD and XANES data are compared, while the local structure of each phase in the samples is reported

2. Experimental Method

In the experimental procedures of this research. SiO₂ polymorph samples are natural samples provided by processing natural silica sands. The silica sand was taken from Tanah Laut, Pelaihari, Kalimantan Selatan. The purification step is needed to reduce impurity or undesirable non Si element. The steps were cleaning and sieving, extracting by using permanent magnet repeatedly, milling and soaking with hydrochloric acid. Meanwhile, solvent extraction results Na₂SiO₃ titrated with HCL 2 M. The process produces SiO₂ gel. SiO₂ gel was neutralized to pH 7, dried to obtain an amorphous silica powder. Furthermore the amorphous SiO₂ sample was sampled and calcined at 950°C to produce cristobalite powder.

The XRD pattern were recorded by X-Ray Diffractometer Philips X’Pert MPD (Multi Purpose Diffractometer) ($\lambda_{\text{CuK}\alpha}$ =1.54056 Å) for all samples. The XRD patterns were collected with step size of 0.0170°. The XRD patterns were analysed using *Match!2* for phase identification and using *Rietica* based on Rietveld method to provide accurate phase compositions of the samples. The WAXS profile is measured using WAXS instrument at Beam Line 2.2 (BL 2.2) SLRI. A Double Multilayer Monochromator was adopted to monochromatize synchrotron x-rays within the energy 9 keV. The WAXS measurement was conducted using a CCD detector, 89 cm distance of sample to detector (SDD), and the standard material of 4-Bromobenzoic Acid. The WAXS profile was presented with scattering intensity (I) curves over a range of scattering vector magnitude (q) (I vs q) or two dimensional (2D) scattering intensity maps. Conversion of curves (I vs q) to (I vs 2 θ) is needed before analysis.

Si K-edge XANES Spectra were recorded with 0.2 eV step size in fluorescence mode with fixed-exit double crystals X-ray monochromator and Silicon drift detector using X-Ray Absorption Spectroscopy (XAS) instrument at Beam Line 8 (BL8) SLRI. The beam size was 14 mm (width) x 1 mm (height) [12]. XANES spectra were normalized using the Athena software [13]

3. Results and Discussion

Figure 1 shows the XRD and WAXS patterns of all samples, respectively. Phase identification reveals that sample A contains no crystalline phase, sample B comprises only quartz (NO PDF 16-2490) and sample C consist of cristobalite (NO.PDF 76-1390) and tridymite (NO. PDF 21-0442). The difference in Bragg peak positions of each phase in the XRD and WAXS patterns is due to the difference in radiation wavelength. The overall results demonstrate that phase identification using WAXS confirms that of XRD.

Further analyses using *Rietica* [9] gives goodness-of-fit 3.12% and 1.06% with the typical difference plots as given in Figure 2. These parameters indicate that the Rietveld refinements were succesfull and acceptable. Following the succesfull refinement, the phase composition in each sample is presented in Table 1. Phase composition results for A sample is not given since it is amorphous. Difference plot for sample B on XRD and WAXS is similar. This proves that the XRD and WAXS

difference plots (shown by green lines) for sample B are similar in terms of number of Bragg peaks for the associated wavelengths, i.e. 8 peaks up to $2\theta = 55$ for XRD and up to 38 for WAXS. It means only quartz presents in sample B. [Since quartz is the sole phase in sample B, its content is 100%]. Sample C, the Rietveld refinements of XRD and WAXS give goodness-of-fit using *Rietica* are 3.35% and 3.92%. The XRD quantitative analysis gave 98.8 ± 1.9 wt% cristobalite, while the associated WAXS data provided 98.7 ± 2.8 wt% cristobalite. These results confirm that XRD and WAXS are similar.

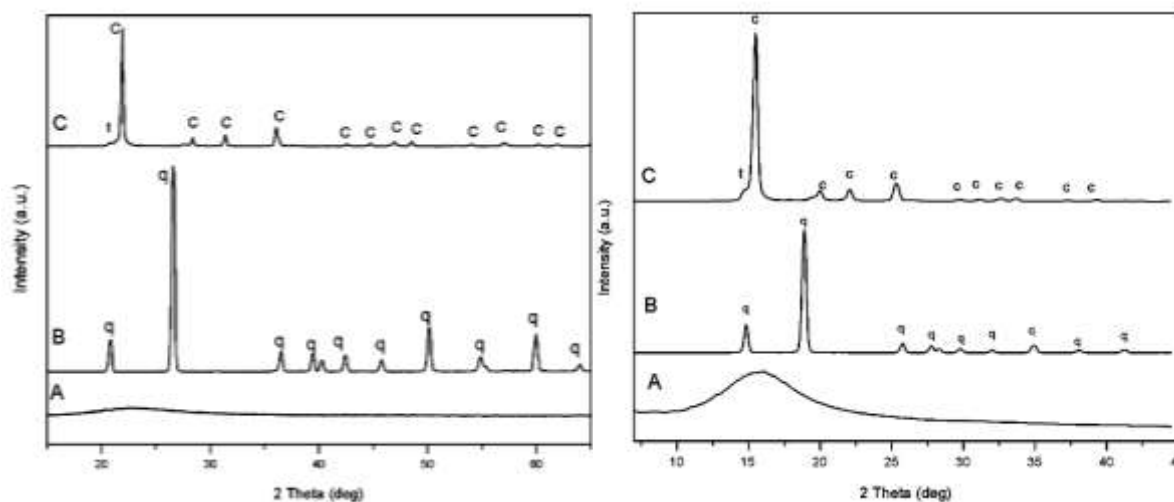


Figure 1 (XRD) Pattern of (A) amorphous, (B) quartz, (C) Cristobalite. XRD & WAXS. Note the difference in Bragg peak positions.

Table 1. Quantitative phase analyses of samples using *Rietica* by Rietveld method

	% weight	
	XRD	WAXS
Sample A	Amorphous	Amorphous
Sample B	100 Quartz	100 Quartz
Sample C	98 ± 1.9 Cristobalite	98.7 ± 2.8 Cristobalite
	1.2 ± 0.6 Tridymite	1.3 ± 0.5 Tridymite

Figure 3 shows the Si K-edge XANES spectra of amorphous (A), quartz (B) dan cristoballite (C) at energy range 1840 to 1920 eV.

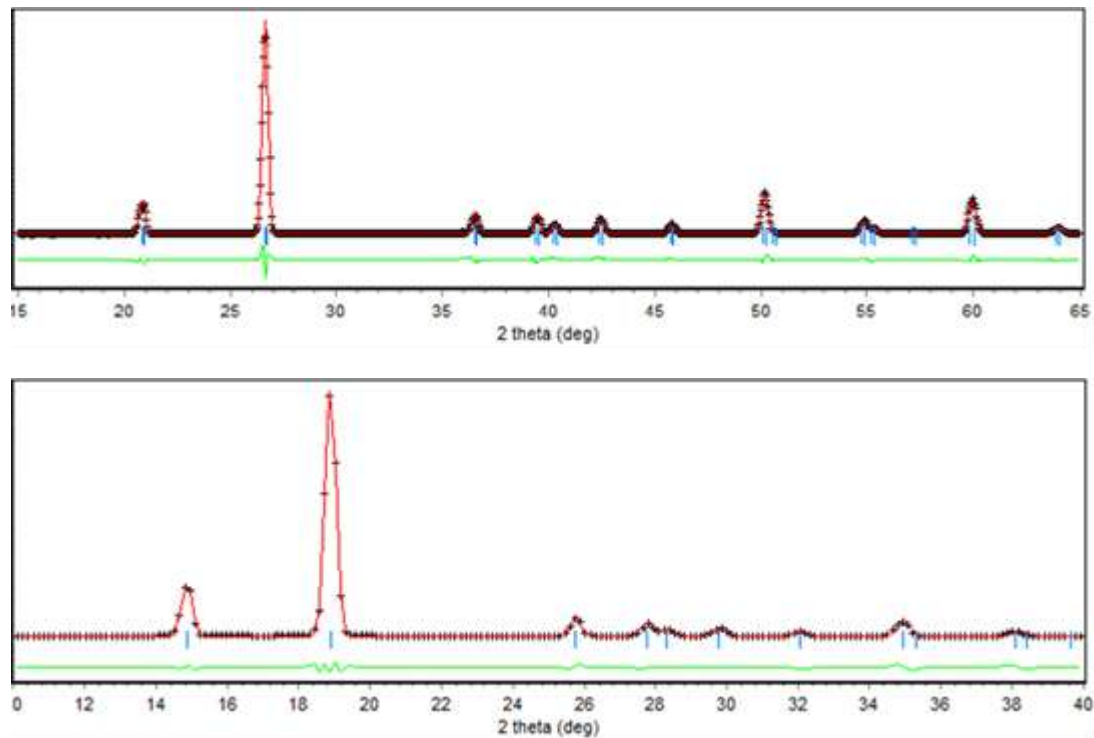


Figure 2. Typical (a) XRD and (b) WAXS Rietveld refinement plots using *Rietica* for quartz sample. The GoF values are 3.12% (XRD) and 1.06% (WAXS). The raw data, calculated pattern and difference between them were marked by black cross, red line and green line, respectively. The blue tick marks underneath the pattern indicates the calculated peak position

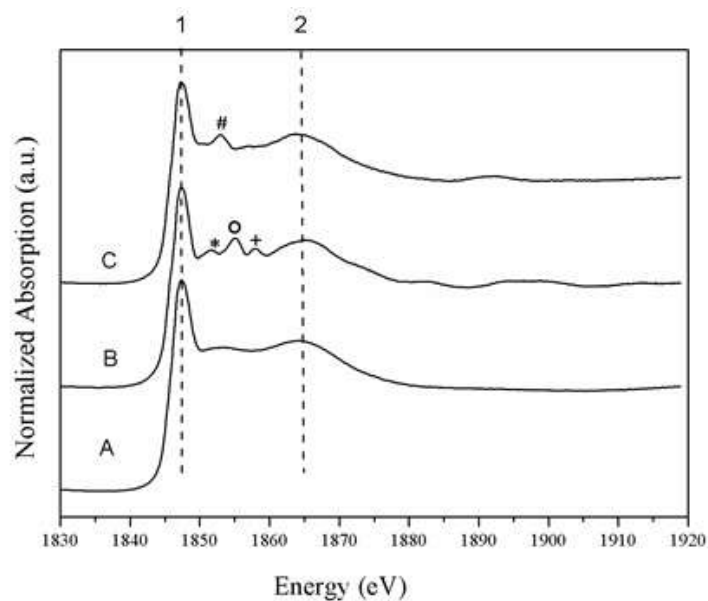


Figure 3 Si K-edge Spectra (A) amorphous, (B) quartz, (C) cristobalite
Noted peak position # = 1853.2 eV, * = 1853.2 eV, O = 1855.2 eV and + = 1853.2 eV

Many change are served between energy about 1847 and 1865 eV (it is noticed between 1 and 2 region). The strongest peak, line 1, on the absorption edge about 1847.4 eV are similar for all samples. Meanwhile, Ligny et al in their study obtain the absorption edge at 1847.1 eV. At the region, the peak position for amorphous (A) is totally different, because there is no absorber crystalline atom arrangement. For the sample the peak of quartz (B) exist at 1853.2, 1855.2 eV, and 1853.2 eV and Cristobalite (C) at 1853.2 eV. Line 2 are present for all samples, they can be assigned to Si electronic structure on which is superimposed some multiple scattering [1].

4. Conclusion

The phase identification and phasecomposition was successfully investigated by Rietveld analysis of X-Ray Diffraction (XRD) data using Match2! and *Rietica* software respectively. i.e. amorphous phase (A), quartz (B), and cristobalite (C). Both XRD ($\lambda_{\text{CuK}\alpha}=1.54056 \text{ \AA}$) and WAXS ($\lambda=1.09 \text{ \AA}$) pattern show that (1) A sample contains no crystallites, (2) B sample is monophasic, contains only quartz (100% quartz), and (3) C sample contains cristobalite and trydimite. XRD quantitative analysis using *Rietica* gave 98,8 wt% cristobalite, while the associated WAXS data provided 98.7 wt% cristobalite. Si K-edge XANES spectra were measured at energy range 1840 to 1920 eV. Qualitatively, the pre-edge and edge features for all phases are similar, but their main peaks in the post-edge region are different.

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