X-Ray Peak Profile Analysis of Silica by Williamson–Hall and Size-Strain Plot Methods

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Abstract. Annealed silica has been prepared by various annealing temperatures at 800 °C and 1000 °C. The crystallite size and lattice strain of silica were estimated by x-ray diffraction spectra analysis using various calculation methods; Modified Scherrer, Williamson-Hall (W-H), and Size-Strain Plot. Qualitative analysis confirms that the XRD patterns were hexagonal quartz. Annealing temperature cause a change in crystal size and lattice strain and all methods showed a decrease in the value of the crystal size with increasing annealing temperature from 800 °C to 1000 °C.

1. Introduction
Silica (SiO₂) has occupied the prime position for nano-sized materials and devices due to their facile synthesis, high surface area, suitable dielectric and thermal properties, low toxicity, and controllable properties such as optoelectronic, mechanical, and chemical stability [1, 2]. Silica is one of the most abundant families of materials, naturally having major crystalline phases such as quartz, cristobalite, and tridymite as well as several other polymorphs. In addition, amorphous silica can be transformed into the crystalline phase by thermal treatment [1].

Thermal treatment influences the structure and gives impacts for the intensity and 2θ peak position. Because X-ray diffraction peak profile analysis provides information about the crystalline size and lattice strain, it would change the crystallite size and the lattice strain value [2–4]. The crystallite size is a single crystal inside the particles or grains, and it is not generally the same as the particle size due to the formation of polycrystalline aggregates [5,6]. Lattice strain is a measure of the distribution of lattice constants arising from crystal imperfections. The most common sources of the lattice strain are dislocation density, point defects, grain boundary junction, contact or sinter stress, and stacking faults [7]. Crystallite size and lattice strain affect the Bragg peak in different ways. Both these effects increase the peak width and intensity and shift the 2θ peak position accordingly.

X-ray profile analysis is a simple tool for estimating crystal size and lattice strain. There are several methods for this analysis, including modified Scherrer [8], Williamson-Hall method [9], and Size-Strain Plot [5–7]. Previous studies [7,10] reported that the crystal sizes determined from XRD data using these methods were in good agreement with those obtained by Transmission Electron
Microscopy. So, this study focuses on the x-ray peak profile of annealed silica to obtain crystallite size, lattice strain, and its annealing effect.

2. Materials and Method
The material in this study was SiO$_2$ powder (Sigma-Aldrich 99%, USA). Furthermore, the SiO$_2$ powder was annealed at 800 °C and 1000 °C for 1 hour. We annealed at that temperature according to previous research [11,12]. Annealed SiO$_2$ was characterized using a Rigaku Miniflex II x-ray diffractometer with Cu-Kα ($\lambda = 1.54056$ angstrom). XRD patterns were collected with a step size of 0.02° and a range of 2θ from 15 to 60°. The XRD data analysis provides information such as the phase of the sample, purity, crystallite size, and lattice strain [13,7]. Crystallite size and lattice strain were analyzed using several methods: modified Scherrer, Williamson-Hall, and Size-Strain Plot.

3. Results and Discussion

3.1. XRD analysis
Fig. 1 shows XRD spectra of SiO$_2$ annealed at 800 °C and 1000 °C for 1 hour (denoted S800 and S1000). Qualitative analysis using Match! software confirms that the XRD patterns were hexagonal quartz (ICDD#00-046-1045). Furthermore, the inset presents selected Bragg reflections (102) and (111), where it is clear that there is a slight shift in peak position due to the increase in annealing temperature. The shift in peak position indicates that there is a change in the structure, in this case, the crystal size and lattice strain [2,4].

![Figure 1. XRD pattern of SiO$_2$. Inset: zoom of the peak corresponding to the plane (102) and (111)](image)

3.2. Crystallite size and strain estimation
3.2.1. Modified Scherrer method
Derived from the Scherrer equation (Eq. (1)), the modified Scherrer formula aims to reduce errors and obtain the average value of crystallite size through the least-squares method diffraction peaks [8]. After that, by making logarithms on both sides, the modified Scherrer equation can be written as Eq. (2).

\[ D = \frac{k \lambda}{\beta \cos \theta} \]  
\[ \ln \beta = \ln \left( \frac{k \lambda}{D} \right) + \ln \left( \frac{1}{\cos \theta} \right) \]
Where $D$ is the average crystal size, $\lambda$ is the X-ray wavelength used in nanometers (nm), $\beta$ is the integral breadth of the full width at half maximum (FWHM) resulting from the small crystal size in radians, $\theta$ is the Bragg angle, and $k$ is a constant associated with the crystalline form. By plotting $\ln(1/\cos \theta)$ on the $x$-axis and $\ln \beta$ along the $y$-axis, the crystallite size can be determined from the intercept of the $y$-axis, see Fig. 2.

3.2.2. Williamson-Hall (W-H) method

Crystal imperfections and distortions induce strain resulting in the broadening of the peak, given by the relation [6, 7]:

$$\beta_{\text{strain}} = 4\varepsilon \tan \theta$$

But

$$\beta_{\text{hkl}} = \beta_{\text{crystallite size}} + \beta_{\text{strain}}$$

Therefore

$$\beta_{\text{hkl}} = \frac{k\lambda}{D \cos \theta} + 4\varepsilon \tan \theta$$

Rearranging this equation,

$$\beta_{\text{hkl}} \cos \theta = \frac{k\lambda}{D} + 4\varepsilon \sin \theta$$

The above equations are W-H equations [9]. A plot is drawn with $4\sin \theta$ along the $x$-axis and $\beta_{\text{hkl}} \cos \theta$ along the $y$-axis (Fig.3). The crystallite size was estimated from the $y$-intercept and the lattice strain ($\varepsilon$) of the slope via a linear fit of the data.
3.2.3. Size-strain plot (SSP) method

W-H method shows that peak profile broadening was essentially isotropic, so that the diffraction domains were isotropic, and there was also a microstrain contribution. SSP method was expanding the isotropic basis for evaluating the calculation of the W–H method. In this approach, the “crystallite size” profile was assumed to be described by a Lorentz function and the “strain profile” of a Gaussian function as follows [5–7]:

\[(d_{hkl}\beta_{hkl} \cos \theta)^2 = \frac{K}{D} (d_{hkl}^2 \beta_{hkl} \cos \theta) + \left(\frac{\varepsilon}{D}\right)^2\]  

(7)

Where K is a constant that depends on the shape of the particles; for spherical particles, it is given as 3/4, and \(d_{hkl}\) is the lattice distance between the (hkl) planes [10]. The term \((d_{hkl}^2 \beta_{hkl} \cos \theta)^2\) was plotted with respect to \(d_{hkl}^2 \beta_{hkl} \cos \theta\), shown in Fig.4. The crystallite size was determined from the slope, and the y-intercept gives the strain.

![Figure 4. Size-Strain Plot of SiO₂.](image)

The results obtained from the modified Scherrer, Williamson-Hall method, and SSP are summarized in Table 1. Increasing annealing temperature causes a change in crystal size and lattice strain [2–4], although all methods show different results. In addition, the results of all methods showed a decrease in the value of the crystal size with increasing annealing temperature. These results confirm the previous XRD pattern analysis regarding the shift in diffraction peak position.

| Sample  | Modified Scherrer | Williamson-Hall method | Size-Strain Method |
|---------|-------------------|------------------------|-------------------|
|         | D (nm)            | D (nm)                 | \(\varepsilon\) (10⁻⁴) | D (nm) | \(\varepsilon\) (10⁻⁴) |
| SiO₂ 800 | 46,79             | 54,64                  | 3,60              | 42,01  | 5,58         |
| SiO₂ 1000| 43,67             | 54,03                  | 6,05              | 35,33  | 5,11         |

4. Conclusion

The XRD analysis was successfully carried out on SiO₂ annealed at 800 °C and 1000 °C. The qualitative analysis confirmed that SiO₂ was in the quartz phase. Furthermore, increasing annealing temperature caused crystal size and lattice strain changes, although the modified Scherrer method, Williamson-Hall method, and SSP showed different results. The crystal size decreases as the annealing temperature increases from 800 °C to 1000 °C.

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References

[1] Prabha S, Durgalakshmi D, Rajendran S and Lichtfouse E 2021 Environ Chem Lett 19 1667–91
[2] Oufakir A, Khouchaf L, Afqir M, Elaatmani M, Zegzouti A and El H DIRECT DEPENDENCE BETWEEN TEMPERATURE, MICRO STRAINS AND STRUCTURAL DISTORTIONS IN NATURAL SiO2 QUARTZ 12
[3] Haq S, Rehman W, Waseem M, Javed R, Mahfooz-ur-Rehman and Shahid M 2018 Appl Nanosci 8 11–8
[4] Kumar D, Singh M and Singh A K 2018 2ND INTERNATIONAL CONFERENCE ON CONDENSED MATTER AND APPLIED PHYSICS (ICC 2017) (Bikaner, India) p 030185
[5] Irfan H, Racik K. M and Anand S 2018 Journal of Asian Ceramic Societies 6 54–62
[6] Augustin M and Balu T 2017 Int. J. Nanosci. 16 1650035
[7] Khorsand Zak A, Abd. Majid W H, Abrishami M E and Yousefi R 2011 Solid State Sciences 13 251–6
[8] Monshi A, Foroughi M R and Monshi M R 2012 WJNSE 02 154–60
[9] Williamson G K and Hall W H 1953 Acta Metallurgica 1 22–31
[10] Nath D, Singh F and Das R 2020 Materials Chemistry and Physics 239 122021
[11] M. H. Shahrokh Abadi 2015 J. Ceram. Sci. Tech.
[12] Hapsari I L, Irzaman and Indro M N 2020 IOP Conf. Ser.: Earth Environ. Sci. 460 012024
[13] Holder C F and Schaak R E 2019 ACS Nano 13 7359–65