Assessing Rietveld refinement results on silicon carbide nanoparticles produced by magnesiothermal treatment

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Abstract. Collection and evaluation of X-ray diffraction (XRD) data are essential not purely for phase and structural investigation, but more importantly for all intends and purposes of comprehensive materials characterizations. Incorrect XRD analysis result will lead to misinterpretation of the phase and structural characteristics. The worst part is that instigates inappropriate interpretation of other phase-dependent or structural-dependent properties, e.g. electric, magnetic, or thermodynamic properties. Consequently, accurate phase identification and crystal structure quantification from XRD data is inevitable prior to further materials characterizations, most significantly for nanomaterials. In this present study, we reported the complete XRD qualitative and quantitative analyses of silicon carbide (SiC) nanoparticles. The phase identification was run using X’Pert High Score Plus (HSP) software. Furthermore, the crystal structure computation was executed by means of different Rietveld-based computer programs, i.e. HSP, MAUD (Material Analysis using Diffraction), GSAS (General Structure Analysis System) and Rietica. Our research revealed that the synthesized silicon carbide preserved a cubic crystal structure. MAUD and GSAS could predict the equivalent particle size which was close to that of captured by transmission electron microscopy (TEM). In addition, MAUD produced the most accurate value of the particle size. In this case, Rietica and MAUD extracted similar lattice parameter of the silicon carbide. At last but not least, the electron density mapping also presented to confirm the cubic crystal structure formation of the silicon carbide nanoparticles.

1. Introduction

Until today, powder X-ray diffraction (XRD) have become the primary experimental approach with huge range of applications, from the very fundamental to the miscellaneous ones [1–3]. The use of XRD is not only for crystallographers, but it is also for other scientists in various fields who are dealing with materials characterizations [4–6]. The XRD data can be used to identify complex phases in natural minerals, find crystallinity, determine crystal structure, calculate temperature vibrations, and analysis the strain-size properties [7]. Analyzing crystals from XRD profile is crucial due to the scientific reality that atomic-level structure of materials dictates their characteristics, and in turns, their performances [8,9]. The way to obtain the detailed information from powder XRD data is to use Rietveld refinement method. This is one of the most powerful technique to quantitatively analyze XRD data to perceive accurate crystallographic properties [10]. We can safely say that without any knowledge of Rietveld method, the powder XRD is not possibly prevalent.

What makes the Rietveld method so powerful is that it came up with a very brilliant and simple idea, i.e. implementing least-squares technique to fit the XRD measured data with adjustable calculated XRD
profile [11]. In other words, the main goal of Rietveld method, especially for structural analysis, is to refine the model and to solve the true crystal structure. For this purpose, many computer programs were designed for Rietveld refinement that some of them can be implemented for specific structures only, but some others can be executed for any materials. Intended for the second implementation, HSP, GSAS [12], MAUD [13], and Rietica [14] are good programs that can be used. Even though the softwares were set up with the same refinement principles, but the order of refinement set by different software can vary. For instance, in HSP, the refinement can be done by means of manual, semi-automatic, and automatic manners; in GSAS, the background function could be a bit different than that in Rietica. Therefore, investigating the Rietveld fitting using different softwares will provide essential information to choose the most appropriate program for crystal structure analysis, particularly with more specific purposes.

Instead of using complex structure with multiple phases, a single-phase crystalline structure with nanometer sized particle could be used to evaluate the Rietveld refinement output by those softwares. Therefore, we picked up silicon carbide nanoparticles to be tested. Silicon carbide, in particular the 3C-SiC, has become a prospective superconducting spintronic due to its crystal structure specification [15]. Besides that, other structural-dependent properties of 3C-SiC have been widely explored, for example the chemical bonding and optical characteristics [16], the heat flux and thermal stability [17], and the magnetic properties [18]. Among other expensive and highly technological approaches for synthesizing 3C-SiC, e.g. pico-second pulsed laser ablation [19], dense plasma focus [20], and laser-hybrid chemical vapor deposition [21], the magnesiothermic reduction approach is preferable in many studies [22–25].

2. Methods

The silicon carbide was produced by employing magnesiothermal treatment, which was exclusively described in the previous reports [23,25]. However, in this study, the magnesiothermic reduction of silica was done by setting 50-wt% magnesium in the silica/carbon/magnesium system. The composite was heated at a relatively low temperature, i.e. 700 °C for 20 h. Further leaching process, using strong acids, could yield the formation of fine structure of silicon carbide. The sample was characterized by means of XRD. Fix divergence slit was chosen for the Cu radiation with Kα1 and Kα2 wavelengths of respectively 1.54060 Å and 1.54443 Å. The ratio of the two wavelengths was 0.5. The XRD machine was XPert MPD using Bragg-Brentano optical geometry and a solid-state detector. The XRD scan was run at step size of 0.02° and step of 0.7 s with continuous scanning mode. In addition, the generator was set at 40 kV and 35 mA. The phase quantification was carried out by HSP software. Meanwhile, the silicon carbide XRD profile was refined using HSP, MAUD, GSAS, and Rietica computer programs to obtain the detailed crystal structure analyses, including the estimated crystallite size in which equivalent to the particle size. In addition, the “real” nanometric dimension of the silicon carbide was captured by TEM.

3. Results and Discussion

Figure 1 represents the XRD profile, as well as the refined patterns, of silicon carbide produced by magnesiothermic reduction route. As can be seen from the inset of Figure 1, all the detected crystalline peaks of the sample were well matched with the standard SiC having moissanite 3C phase with PDF code 01-075-0254. This phase was the cubic structure of SiC, the most favoured polytype of SiC crystals. The Bragg angles of around 35.6°, 41.4°, 59.9°, 71.8°, and 75.5° corresponded to respectively diffraction planes of (111), (200), (220), (311), and (222) with the intensities as depicted in Figure 1. The relative-intensity-ratio from the HSP program can be used for phase quantification in semiquantitative manner when the XRD profile consists of more than one phase [26]. Since in our study there only existed a single crystalline phase, then the phase quantification based on the relative-intensity-ratio method showed 100 % moissanite 3C-SiC. Put another way, because there were no extra peaks detected other than the 3C-SiC, the as produced silicon carbide crystallized in a purely single phase. In terms of phase formation, this result provided better purity than that of SiC produced by carbothermic reduction route [27].
Figure 1. Rietveld Refinement Fitting in the Cubic 3C-SiC Nanoparticles. The Inset Represents Matched Profile Between SiC with Moissanite 3C-SiC (PDF Code: 01-075-0254).

Figure 2. 3-Dimensional (Left) and 2-Dimensional (Center) Fourier Maps of Electron Density for the corresponding cubic structure of the 3C-SiC Produced by Magnesiothermal Treatment (Right).
Table 1. Rietveld Refinement Output Using Different Softwares

| Output Parameter          | HSP   | Rietica | MAUD  | GSAS  |
|---------------------------|-------|---------|-------|-------|
| Weighted $R$ profile (%)  | 17.82 | 17.02   | 17.13 | 16.83 |
| $R$ expected (%)          | 15.65 | 15.66   | 15.67 | 16.27 |
| Goodness of Fit (%)       | 1.29  | 1.18    | 1.09  | 1.07  |
| Unit Cell (Å)             | 4.370087 | 4.365762 | 4.365181 | 4.37558 |
| Equivalent Particle Size (nm) | 2.79   | 4.41    | 9.47  | 8.93  |

Crystal System: Cubic
Bravais Type: Cubic F
Point Group: -43m
Symbols: $F -4 3 m$ (Hermann-Mauguin); Td2 (Schoenflies)

Figure 3. TEM Image (Left) and Particle Size Distribution Plot (Right) of the 3C-SiC Nanoparticles.

The Rietveld-refinement plots from several computer programs are displayed by green-, navy-, blue-, and red-coloured lines in that order for Rietica, MAUD, HSP, and GSAS. All software were employed to run the refinement under the same general procedure introduced by Hugo Rietveld [10,11]. The fundamental idea of the Rietveld fitting approach is straightforward, it uses least-squares technique to refine the crystal parameters of the calculated pattern until it fits the measured XRD data. Successful Rietveld refinement is obviously required for extracting accurate crystal properties of materials [28]. Generally, the XRD profile elements, i.e. intensity, shape, and position, dictate not only the crystal structure properties, but also the instrument and specimen parameters [10]. Therefore, it is crucial, during the refinement process, to take into account those parameters. In terms of crystal structure properties, the peak position is strongly related to the lattice parameters and their relationship obeys the Bragg’s law utilizing the interplanar $d$-spacing and X-ray radiation wavelength [11]. On the other hand, the peak width tells us the crystallite size and the peak intensity determines the phase weight fraction. Since, in our case, the diffraction peaks were very close to the accepted model (01-075-0254), then it could be predicted that the lattice parameter of the synthesized silicon carbide should be near that of the model, i.e. $\approx 4.3580$ Å. The crystallite size would be in the range of nanometric scale due to the broad peaks.

The results of the Rietveld fitting are tabulated in Table 1. As far as the structural refinement was concerned, the refined parameters were set as similar as possible amongst the softwares. However, we used Voight function for HSP and Rietica, the pseudo-Voight was set in MAUD and GSAS. As depicted in Table 1, the weighted $R$ profile, $R$ expected, and goodness of fit for all softwares were in a very good agreement and in the accepted values in such a way that those refinement results could be used for
further data analyses [28]. The unit cell extracted from HSP and GSAS, $\approx 4.37 \, \text{Å}$, were relatively different from those obtained by Rietica and MAUD, i.e. $\approx 4.36 \, \text{Å}$. The silicon carbide was formed in cubic structure having space group of Td2. Since there are 3 Si-C double-layers that exhibit periodicity in this cubic crystal structure, this polytype is referred as 3C-$\text{SiC}$.

In addition to show how well the calculated pattern fitted the measured data, the Fourier maps of the electron density are given in Figure 2. The maps are displayed in isosurfaces, representing points with a constant value within a space, that used the information of structure factor. It was calculated from Fourier transform as the function of coordinates or position. From Figure 2, we can clearly see the average unit cells within the SiC cubic crystal. Furthermore, spherical symmetry was visible near carbon atoms indicating strong Si-C bonding character [29]. Based on these data, the cubic crystal of SiC could be then generated and it is given in Figure 2 (Right). This cubic polytype is one amongst hundreds of SiC polymorphs [30]. As can be seen from the crystal model in Figure 2 (Right), the composition of silicon and carbon atoms bounded in that cubic structure is 50:50.

Furthermore, the other three programs, but MAUD, could not display the size distribution. Therefore, in terms of micro(nano) structure and size distribution analysis, the most powerful program went to MAUD. In the equivalent particle size context, both MAUD and GSAS, unlike HSP and Rietica, could produce similar crystallite size, i.e. around 9 nm. The particle size distribution obtained from MAUD is given in Figure 3 (Right), which implied that the most frequent particle size was in between 9-11 nm. Compared to Figure 3 (Left), the TEM image of the 3C-SiC, it was revealed that the “real” particle size was around 10 nm. Therefore, MAUD provided the estimated particle size which was very close to the data from TEM image. This is in line with other report—working on ferrite, magnesia, yttria, and spinel nanomaterials—that for nanometric samples, the crystallite size is equivalent to the particle size captured by electron microscopy [28].

4. Conclusion
As the conclusion, we have performed Rietveld structural analyses using different computer programs, namely GSAS, HSP, Rietica, and MAUD. All refinements have attained acceptable Rietveld parameters in such a way that the crystallographic properties represented the sample (3C-$\text{SiC}$) crystal structure characteristic. The electron density mapping provided visual representation of the characteristic of the cubic structure of SiC, in particular the Si-C bonding behavior. The unit cell parameter obtained by GSAS and HSP were relatively similar and higher than those of obtained by Rietica and MAUD. The last software could produce not only accurate estimated particle size, as compared to TEM image, but also the size distribution that cannot be extracted from the other programs. The study, therefore, suggests that using more than one computer program for Rietveld refinement is at some point needed to accurately extract the lattice parameter and equivalent particle size. Most importantly, that approach is essential in order to have a comprehensive crystal structure analysis from powder X-ray diffraction.

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