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Quantitative polytype-composition analyses of SiC using X-ray diffraction: a critical comparison between the polymorphic and the Rietveld methods

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Abstract

X-ray powder diffraction (XRD), in conjunction with an analysis routine, is the method of choice for performing quantitative phase-composition measurements in multi-phase mixtures. However, accurate determination of phase compositions in SiC-based ceramics, which can contain a multitude of SiC polytypes with overlapping Bragg reflections, is a difficult task. In order to determine the best analysis method for the quantitative phase-composition measurement in SiC-based ceramics, a critical comparison between two commonly used analysis methods — polymorphic method (Ruska) and whole pattern method (Rietveld) — was performed. Owing to the difficulty in obtaining high-purity standard mixtures of SiC polytypes experimentally, we have simulated a set of XRD patterns corresponding to different SiC polytype mixtures of wide ranging compositions as standards. Within the polymorpic method, the following three different approaches were used: (i) raw XRD peak heights were obtained and corrected for mean background level; (ii) a non-linear Levenberg-Marquardt least-squares fit was used to obtain peak heights; and (iii) using the same fitting procedure as in (ii) integrated intensities were obtained. We demonstrate that the Rietveld method yields the most accurate phase-composition measurements, with mean and maximum errors of 0.5 wt.% and 0.9 wt.%, respectively. In the polymorphic method, we show that a fitting procedure is essential for the improvement in the accuracy of the analysis. Furthermore, we find that the use of integrated intensities, obtained from the fit, for quantitative XRD analyses gives results that are less accurate compared with when corrected raw peak heights are used. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Polytypes; Rietveld method; SiC; X-ray methods

1. Introduction

Accurate measurement of the relative abundance of the various polytypes[†] present in silicon carbide (SiC) is essential for understanding various phenomena in SiC-based materials, including processing, microstructure development, and mechanical, electrical, electronics, and optical properties.[4–8] Quantitative X-ray powder diffraction (XRD) is the most suitable method for performing such measurement,[9,10] where experimental XRD patterns are analyzed and the phase-composition information extracted. The methods used to analyze XRD SiC patterns[11–20] can be classified into two categories: (i) polymorphic methods; and (ii) whole pattern methods. The so-called polymorphic methods[11–14] are based on the analysis of only a given set of Bragg reflections (or lines), where the sum of intensities over an angular region (peak heights or integrated peak areas) is expressed as a linear combination of the intensities calculated from the crystal structure of the phases present. Here, the coefficients of the combination

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[†] Pure SiC exists in several different polytypic forms[1,2] which can be described by the Ramsdell notation *nS*.[3] In this notation, *n* is the number of Si–C layers along the *c*-axis of an equivalent hexagonal unit cell, and *S* refers to the cell symmetry, i.e. either cubic (C), hexagonal (H) or rhombohedral (R). The cubic form of SiC is referred to as β-SiC, and all the others are collectively referred to as α-SiC.

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represent the weight fractions of the various crystalline phases present.[8] The Rietveld method is based on the analysis of the whole pattern,[15,16] which is fitted using a non-linear least-squares regression. This results in a set of fitted parameters, including the important Rietveld scale factors. The relative weight fractions of the various crystalline phases present in the sample are directly related to the overall Rietveld scale factors.[21–24] Note that the Rietveld method was originally applied for crystal-structure refinement using X-ray and neutron diffraction data,[21] and has been applied to quantitative phase-composition analysis in last decade.[22–24]

The polymorphic methods are significantly easier to employ compared to the Rietveld method, however, the Rietveld method is presumed to be more accurate. For simple mixtures of crystalline phases, whose Bragg reflections do not overlap significantly, a polymorphic method may be the appropriate choice for XRD data analysis. However, for more complicated cases, the choice between the above methods is not clear. XRD quantitative phase-composition analysis of SiC-based ceramics presents a particularly difficult challenge, primarily because of the significant overlap of the Bragg reflections from the different polytypes.

Thus, the objective of the present work was to compare critically the accuracy and precision of a polymorphic (Ruska et al.)[11] and the Rietveld[15] methods in the quantitative polytype-composition analysis of standard mixtures of SiC polytypes. Since it is difficult to obtain high-purity, standard mixtures of SiC polytypes experimentally, we have simulated a set of XRD patterns corresponding to different SiC polytype mixtures of wide ranging compositions. This approach eliminates any unknown contaminants or other effects that may be present in experimental standard mixtures. Thus, by studying simulated standard mixtures we are able to compare the analyses obtained from the polymorphic and the Rietveld methods without introducing any “external agents” that can affect the interpretation of the results.

2. Fitting procedures

2.1. The polymorphic method

XRD quantitative phase-composition analysis has been traditionally performed using individual peak intensities.[8,25–27] Thus, it is well known that the intensity of the gth reflection of the jth phase can be obtained (neglecting texture and extinction effects) using the following equation:

$$I_{jg} = \frac{K M_{jg} LP_{jg} F_{jg}^2 \rho X_j}{V_j^2 e^{2m_{jg}} \mu \rho_j} \tag{1}$$

where M_{jg}, LP_{jg}, F_{jg}, $e^{2m_{jg}}$ are (for the gth reflection of the jth phase) the multiplicity, the Lorentz-polarization factor, the structure factor and the Debye–Waller temperature factor, respectively. The terms V_j, ρ_j and X_j in Eq. (1) represent the volume of the unit cell, the density, and the weight fraction of the jth phase, respectively. Finally, μ, ρ, and K are the linear absorption coefficient of the mixture, the density of the sample and an instrumental constant, respectively. Note that Eq. (1), which constitutes the core of what is nowadays known as the polymorphic method, assumes a flat-plate geometry with an infinitely thick polycrystalline sample. If the crystallographic structure of jth phase is known, we can then define the factor R_{jg}, which only depends on the crystallographic structure, as follows:

$$R_{jg} = \frac{M_{jg} LP_{jg} F_{jg}^2}{V_j^2 e^{2m_{jg}} \rho_j} \tag{2}$$

Thus, by including the factors ρ and μ in the constant K and using Eq. (2), the intensity of the gth reflection of the jth phase can be expressed as follows:

$$I_{jg} = K' R_{jg} X_j \tag{3}$$

Note that the use of a set of Eq. (3) in conjunction with the normalization condition $\sum_j X_j = 1$ (where the index j in the summation runs over all the phases) lead to the weight fractions of the crystalline phases in a multicomponent mixture of n different phases. So far, it has been assumed that there is no significant overlap of the Bragg reflections from the different phases in the sample. If there is a significant overlap, then Eq. (3) needs to be modified to use sums of intensities over groups of reflections instead of intensities of individual reflections. In this regard, the total intensity of a group of overlapping peaks, I, can be expressed using the following equation:

$$I = \sum_j \sum_g I_{jg} = K' \sum_j \sum_g R_{jg} X_j = \sum_j \sum_g R_{jg} X'_j, \tag{4}$$

where the indices j and g in the summation covers all phases and individual intensities contributing to that group, respectively. Thus, in a sample with n different phases and m groups of reflections (with $m \geqslant n$), a linear multiple regression method provides the weight fractions of the different crystalline phases as follows:

$$X_j = \frac{X'_j}{\sum_j X'_j} \tag{5}$$

In the case of SiC-based ceramics, several procedures based on Eq. (4) have been developed to perform the

quantitative phase-composition analysis, the best known being the one developed by Ruska et al.[11] In the Ruska method, the R_{jg} factors in Eq. (2) are calculated neglecting the temperature factor and the density of the different SiC polytypes, and choosing $R_{jg} = 100$ for the 111 Bragg reflection of the 3C-SiC polytype as the normalization condition.[11] Subsequently, Ruska corrected the calculated R_{jg} factors using measured XRD data (experimental calibration) where the intensity of groups of peaks at the 2θ Bragg angles 33.6°, 34.0°, 34.8°, 35.6°, 38.2° and 41.4° (CuK_α incident radiation) was considered for obtaining the amounts of the 3C, 4H, 6H and 15R SiC polytypes.[11] Thus, a system with six equations and four unknowns is used to perform the quantitative phase-composition analysis. Because the density of the different SiC polytypes is quite similar ($\rho \approx 3.21$–3.22 g cm^{-3}),[28] the Ruska procedure makes no distinction between volume and weight fractions.[11]

In this study, we have used different approaches to obtain the intensities of groups of peaks as input to the polymorphic method:

1. The intensities of the groups of peaks were directly obtained from the XRD data by subtracting the mean background level. Thus, although the Ruska method can be applied using both height-peaks and integrated intensities, in this first approach only height-peaks were used to perform the quantitative phase-composition analysis.
2. A non-linear Levenberg–Marquardt least-squares fit[29] was used to obtain the intensities of the different groups of peaks. Here, we have assumed pseudo-Voigt functions to describe the shape of the groups of peaks, which included $CuK_{\alpha1}$ and $CuK_{\alpha2}$ incident radiation components. In addition, the non-linear Levenberg–Marquardt least-squares fits included parameters describing a linear background, peak height, positions of the maximum peak intensities, peak half-widths at half-maxima (HWHM) and mixing parameters (η) of the pseudo-Voigt functions. It is important to note that the use of the non-linear Levenberg–Marquardt least-squares fit allows us to apply the Ruska method using both peak heights and integrated intensities.

As example, Fig. 1 shows two overlapped groups of peaks and the three different approaches used here to obtain the intensities as input to the polymorphic method. Note from Fig. 1 the differences among raw peak-heights, fitted peak-heights and fitted integrated-intensities.

2.2. The Rietveld method

It is known that many Bragg reflections can contribute to the observed intensity, y_i^{OBS}, at the ith step (in the step-scanning mode) in the XRD pattern. Thus, in the Rietveld method, the calculated intensity, y_i^{CAL}, at that point is determined from the structural and the profile models plus the background contribution. A non-linear least-squares refinement is carried out until the best fit is obtained between the entire observed XRD pattern taken as a whole and the entire calculated XRD pattern based on the following equation:[21]

$$y_i^{\mathrm{CAL}} = b_i + \sum_j S_j \sum_g M_{jg} LP_{jg} F_{jg}^2 A_{jg} \Omega_{jg} (2\theta_i - 2\theta_{jg}), \qquad (6)$$

where b_i represents the background intensity at the ith step, and the double summation represents the structural and the profile models. Here, the subscript j refers to the different crystalline phases, while the subscript g refers to the Miller indices (which are h, k, and l) for the Bragg reflections. The term S_j in Eq. (6) represents the Rietveld scale factor for the jth phase, while the terms M_{jg}, LP_{jg}, F_{jg} and A_{jg} are (for the gth reflection of the jth phase) the multiplicity, the Lorentz-polarization factor, the structure factor and a function that takes into account absorption and/or texture effects, respectively. Finally, Ω_{jg} is the reflection profile function (normalized to unit area and with maximum at $2\theta_{jg}$) which approximates the effects of both instrumental and sample features (such as diffraction domain sizes and lattice microstrains). Therefore, it can be seen that the model parameters that may be refined include not only atomic positions, thermal and site-occupancy factors, but also parameters for the background, lattice, instrumental geometrical-optical features, and specimen reflection-profile-broadening agents. Multiple phases may be refined simultaneously and comparative analysis of the separate overall Rietveld scale factor for the phases offers what is probably the most reliable method for performing quantitative phase-composition analysis.[21] In this regard, the weight fraction of the jth phase (X_j) can be obtained using the following equation:[22–24]

$$X_j = \frac{S_j Z_j M_j V_j}{\sum_j S_j Z_j M_j V_j}, \qquad (7)$$

where S_j, Z_j, M_j and V_j are the Rietveld scale factor, the number of formula units per unit cell, the formula unit molecular weight, and the unit cell volume of the jth phase, respectively, and the index j in the summation is over all phases included in the model.

In this study the Rietveld refinements were performed using the version 3.1 of the Rietveld analysis program FULLPROF,[30] where the peak shape was assumed to be a pseudo-Voigt function. Among the many different analytical functions that can be found in the literature, the pseudo-Voigt function best describes (usually) XRD profiles.[21,31] In addition, the conventional refinement

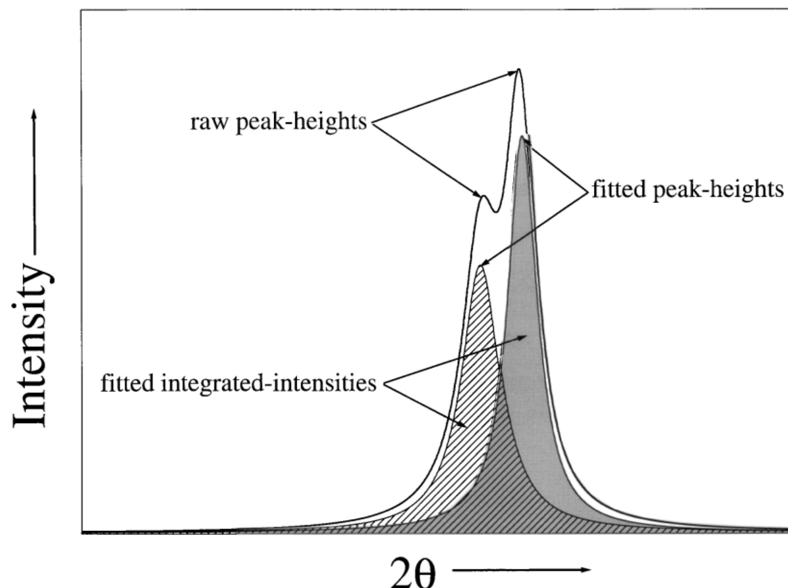

Fig. 1. Schematic representation showing the differences among raw peak-heights, fitted peak-heights and fitted integrated-intensities in the case of two overlapped groups of peaks.

protocol, which takes into account structural, profile and global parameters, included:

- the background, which was modeled as a third-order polynomial function,
- the Rietveld scale factors,
- the global instrumental parameters (zero-point $2\theta_o$ shift and systematic shifts, depending on the transparency and off-centering of the sample),
- the lattice parameters for all phases,
- the profile parameters for all phases [Caglioti[32] half-width parameters U, V and W and the mixing parameter (η) of the pseudo-Voigt function].

3. Simulated XRD data

Simulated XRD data were used as raw data to test the accuracy of both the polymorphic and the Rietveld methods. The final compositions of the standard mixtures were designed to be a combination of at least three of the four most-commonly found SiC polytypes, viz. 3C, 4H, 6H, and 15R. These simulated compositions and the sample designation are shown in Table 1. The computation of the XRD data can be summarized as follows:

1. The individual XRD patterns of the different SiC polytypes were obtained from their crystallographic structures[28] considering CuK_α incident radiation ($\lambda_{\alpha1}$ = 1.54056 Å, $\lambda_{\alpha2}$ = 1.54439 Å and $I_{\alpha2}/I_{\alpha1}$ = 0.48).[33] In these simulations, the diffraction domain size was chosen to be 20 nm, and all the samples were considered to be free of lattice micro-strains. Subsequently, these XRD data were used to obtain the XRD patterns of the different standard mixtures (pure profiles) in the compositions shown in Table 1.
2. A convolution program was used to introduce the instrumental contribution in these XRD patterns.[34,35] To obtain the instrumental broadening, a Monte Carlo simulation was carried out using the geometrical condition for a Philips PW-1800 powder diffractometer (goniometer radius, receiving slit, etc.).[19,20] These instrumental peaks were then compared with those obtained from a α-Al_2O_3 standard specimen; no differences in the peak widths were observed.[19,20]
3. The background intensities and the statistical noise were introduced in the XRD data. The background level accounting for incoherent scattering, air scattering, and thermal diffuse scattering was described by a polynomial function. The statistical variation of the counting of random events was assumed to follow the Poisson distribution.

Finally, the XRD data were obtained over a 2θ range of 20 to 130° with a step width of 0.01°, conditions used to obtain experimental diffraction patterns.

4. Results and discussion

Fig. 2(a)–(g) show the simulated compositions of the standard mixtures and the concentrations of the SiC polytypes as estimated using the polymorphic and Rietveld methods. As alluded to in Section 2, in the case of the polymorphic method we have included results from

Table 1
Simulated compositions and sample designation for the standard mixtures

Phase proportions (wt.%)	Sample designation						
	SiC1	SiC2	SiC3	SiC4	SiC5	SiC6	SiC7
3C	16.4	58.6	36.5	00.0	16.5	29.3	06.0
4H	47.6	28.0	00.0	33.1	36.7	25.8	05.6
6H	36.0	00.0	10.4	32.8	28.6	19.7	06.9
15R	00.0	13.4	53.1	34.1	18.2	25.2	81.5

both the raw data (using directly measured peak-heights) and fitted data (using peak-heights and integrated intensities calculated from the fit). Note that most studies in the past[11,36–39] have used directly-measured peak-heights for the quantitative phase-composition analysis of SiC, thereby avoiding the more complicated use of fitting procedures. For some compositions, the polymorphic method fails to give a physically meaningful result (the method leads to negative compositions), as indicated by i.c. (intractable case) in Fig. 2(a)–(g). The results shown in Fig. 2(a)–(g) can be summarized as follows:

(a) As alluded to in Section 1, the Rietveld method gives the most accurate result in the quantitative polytype-composition analysis of SiC, with a mean error of 0.5 wt.%.
(b) The accuracy of the polymorphic method using the fitted peak-height intensities is next best, with a mean error of 2.8 wt.%.
(c) The peak-height intensities measured directly from the raw data yields the third best accuracy, with a mean error of 5.4 wt.%.
(d) The poorest agreement is obtained when integrated intensities (areas under fitted peaks) are used. In this case, the mean error is 7.6 wt.%.
(e) The Rietveld method could be applied to all seven compositions studied. The number of intractable cases using the fitted peak-height intensities was found to be fewer than those using fitted integrated intensities.

With regards to (b)–(d) above, it should be noted that the significant overlap of the Bragg reflections from the different SiC polytypes makes it difficult to separate accurately the different groups of XRD peaks. Under these conditions, the non-linear Levenberg-Marquardt least-squares fit yields well-defined peak-maxima; see e.g. Fig. 3 showing the fit for the sample SiC1. In contrast, integrated intensities for those fitted peaks can be ambiguous. Thus, the use of integrated intensities (fitted) in the polymorphic method results in the poorest accuracy and precision in the quantitative phase-composition analysis, even when compared with the least-involved method of using raw peak heights (not fitted). However, the accuracy of this analysis is expected to improve if the integrated intensities are unambiguously obtained, as is done using the Rietveld method. Also note that, although the number of parameters used in the Rietveld method is greater than what is used in the non-linear least-squares fit, the precision of the Rietveld method was found to be relatively better.

Fig. 2(a)–(g) also show that, in those cases where the peak-height intensities were directly obtained from the XRD data, systematic differences appear between the simulated and calculated compositions. There are four different sources of systematic errors in the measurement of XRD intensities and are as follows:[40–43] (i) the incorrect determination of the background level; (ii) the overestimation of intensities of weak peaks that overlap with the tails of strong peaks; (iii) the texture effects (not considered in this study); and (iv) the line broadening of reflections from the different polytypes. The accuracy of the polymorphic method cannot take into account some of these important factors influencing the X-ray intensities. When the non-linear Levenberg–Marquardt least-squares fit was used to resolve the peak-height intensities of the groups of peaks, a significant improvement in the accuracy was obtained (from a mean error of 5.4 to 2.8 wt.%). Thus, a fitting procedure is essential for the improvement of the accuracy of the quantitative phase-composition analysis. However, because all the factor affecting the XRD intensities are not considered in the polymorphic method, these results are still less accurate compared with those of the Rietveld method (mean error of 0.5 wt.%).

In Fig. 2(a)–(g) note that, in some cases, the polymorphic method leads to finite concentrations of some polytypes which were not included in the standard mixtures. Also, in some other cases, physically meaningless negative compositions were obtained [denoted by "intractable case" or i.c. in Fig. 2(a)–(g)]. This is due to the considerable overlap of several peaks and the inherent limitation of the polymorphic procedures.

This situation is avoided when the whole-pattern Rietveld method is employed, and remains the most important advantage of the Rietveld method over the more "classical" polymorphic techniques. Since all lines for each polytype are explicitly included in the Rietveld refinement, the difficulties associated with overlapping peaks are minimized.[21] In addition, the Rietveld method

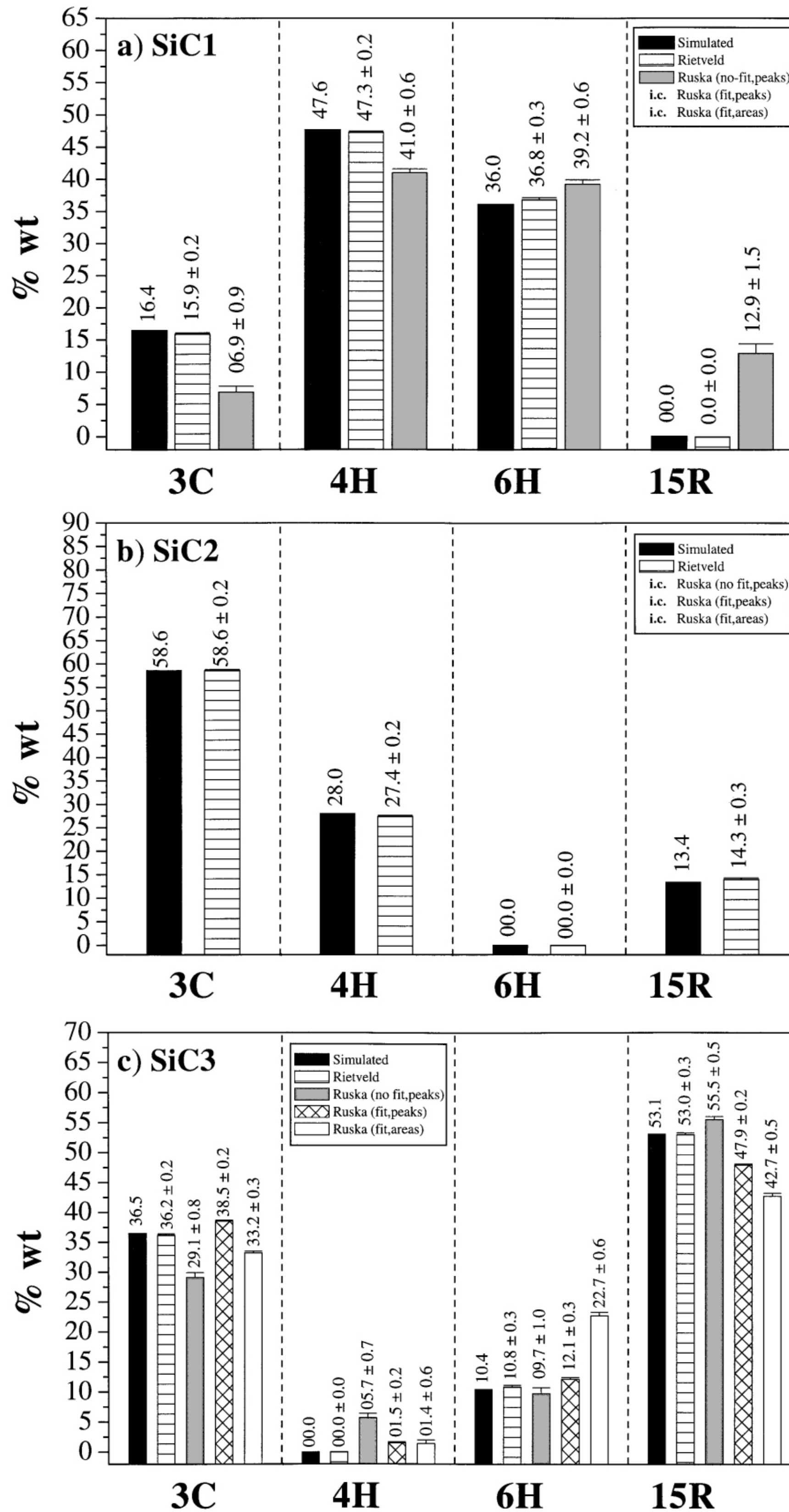

Fig. 2. Simulated compositions of the standard mixtures and the concentrations of the SiC polytypes as estimated using the polymorphic and Rietveld methods: (a) SiC1; (b) SiC2; (c) SiC3; (d) SiC4; (e) SiC5; (f) SiC6; (g) SiC7. The intractable cases are denoted by i.c.

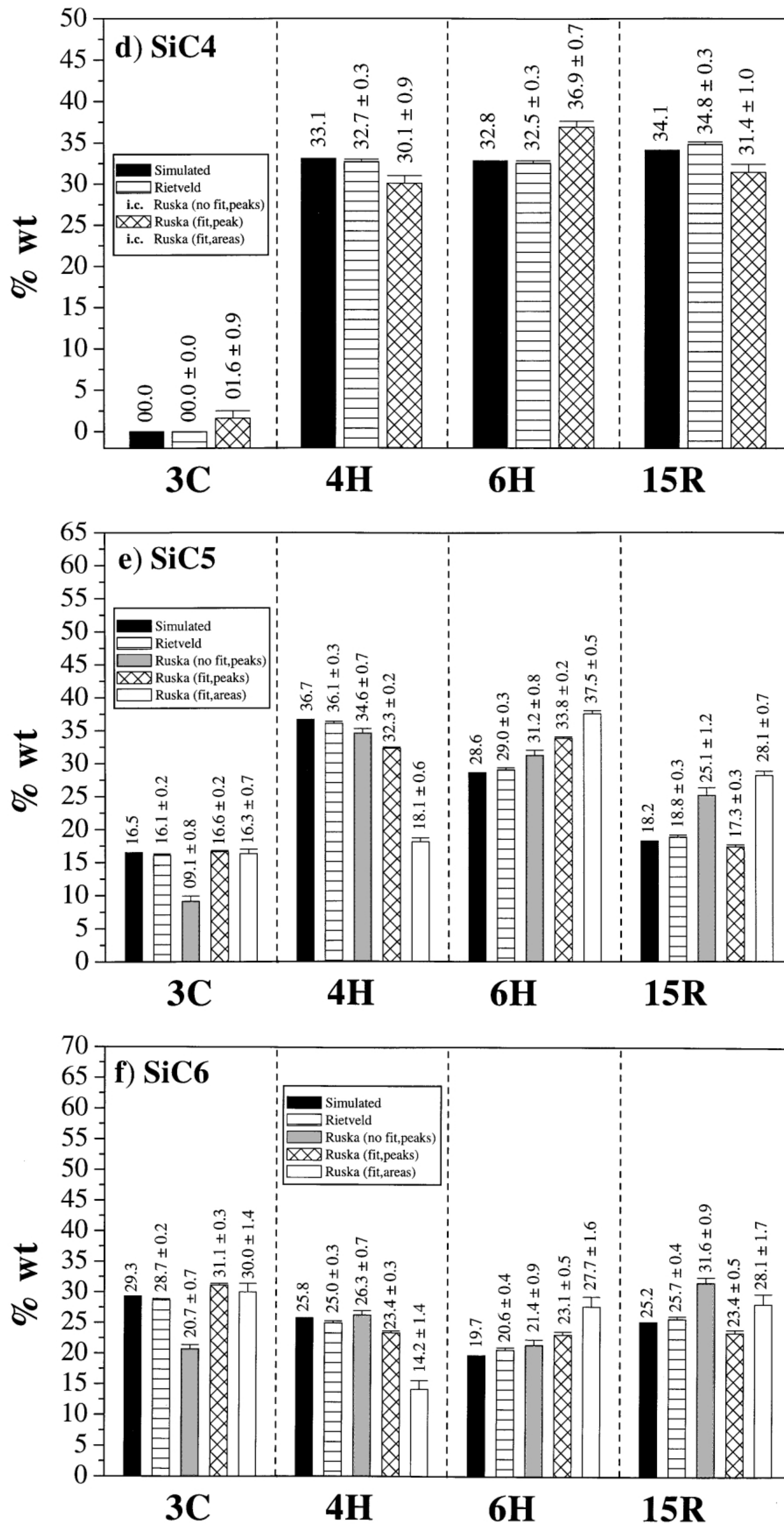

Fig. 2. (*continued*)

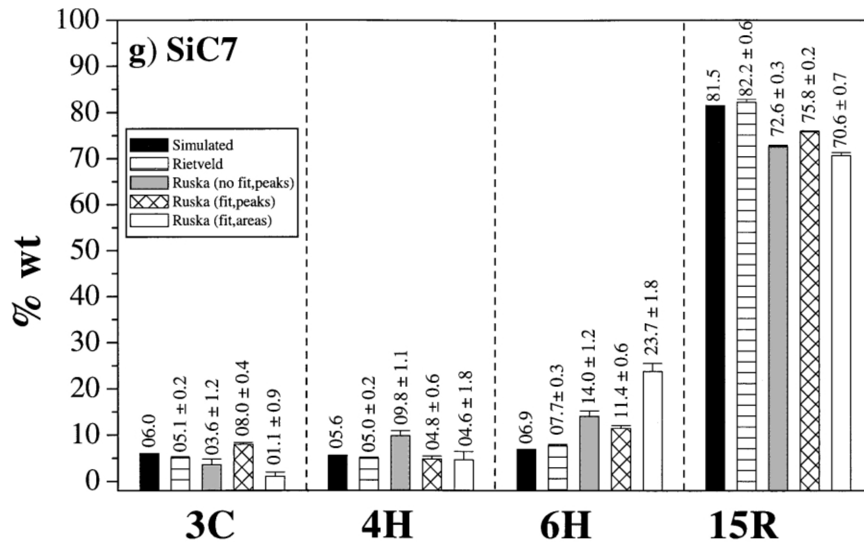

Fig. 2. (*continued*)

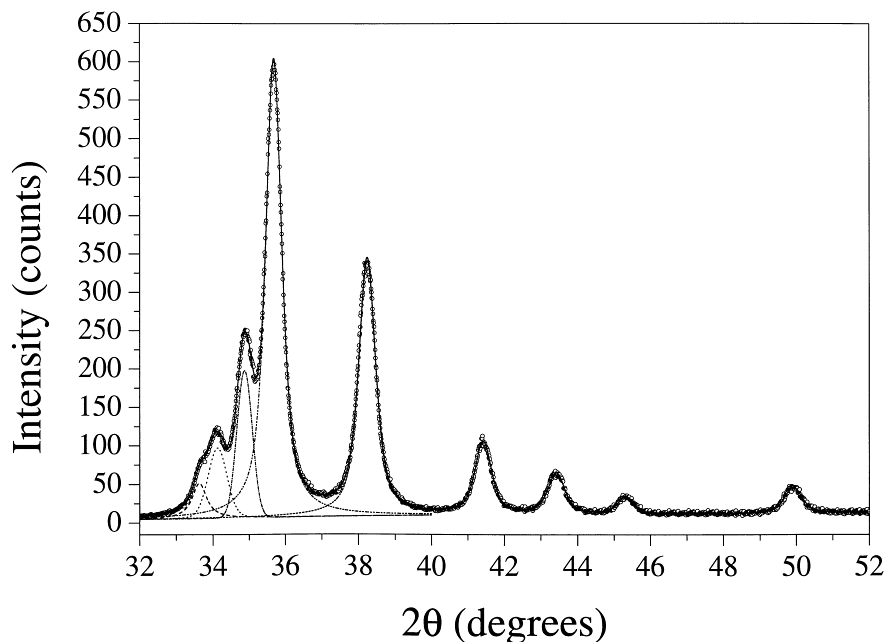

Fig. 3. Plot output from the non-linear Levenberg–Marquardt least-squares fit for the sample SiC1. Points represent the XRD data and the solid line represents the calculated pattern (both corrected by the Lorentz-polarization factor). The contribution of the different groups of peaks is shown by the dash, dot, dash-dot and dash-dot-dot lines.

uses integrated intensities that are normalized to the unit area of the profile functions[21] [Eq. (6)] which is not the case in the polymorphic method. Furthermore, the undesirable effects of the background and the texture can be minimized with the use of reliable corrections,[21,43–47] and the structural and chemical details of the different phases can be adjusted dynamically during the refinement.[21] Since all factor affecting the Bragg reflections are considered in the Rietveld method, this method not only results in the accurate quantitative phase-composition analysis of SiC polytypes mixtures, but also can be used for the analysis of cases which are intractable using the polymorphic method. Thus, results in Fig. 2(a)–(g) show excellent agreement among the simulated weight fractions of the different SiC polytypes and the weight fraction obtained using the Rietveld method. Most significantly, results in Fig. 2(a)–(g) show differences of less than 1 wt.% in all the cases between the nominal and the Rietveld values for the standard mixtures.

In addition to the improved accuracy of the quantitative phase-composition analysis, the Rietveld method can be applied in conjunction with line-broadening methods for carrying out accurate microstructural analysis, such as diffraction domain size measurement. Note that, in the case of materials with significantly overlapping XRD peaks, the use of line-broadening methods by themselves or in conjunction with the polymorphic method, is likely to lead to erroneous diffraction domain size results (note that, in the polymorphic methods, individual overlapping Bragg reflections are not resolved).

With regards to accurate estimation of the errors[21,48] during the quantitative phase-composition analysis using the Rietveld method, certain statistical indicators are evaluated at the end of each iteration. Based on these indicators, one can judge if the refinement is proceeding satisfactorily and one can then evaluate the goodness of the quantitative analysis. A description of these agreement indices and the graphical criteria of fit is beyond the scope of this study; see more specific references for a discussion.[21,49,50] Note that graphical criteria are probably the best way of following and guiding a Rietveld refinement process. Fig. 4(a) and (b)

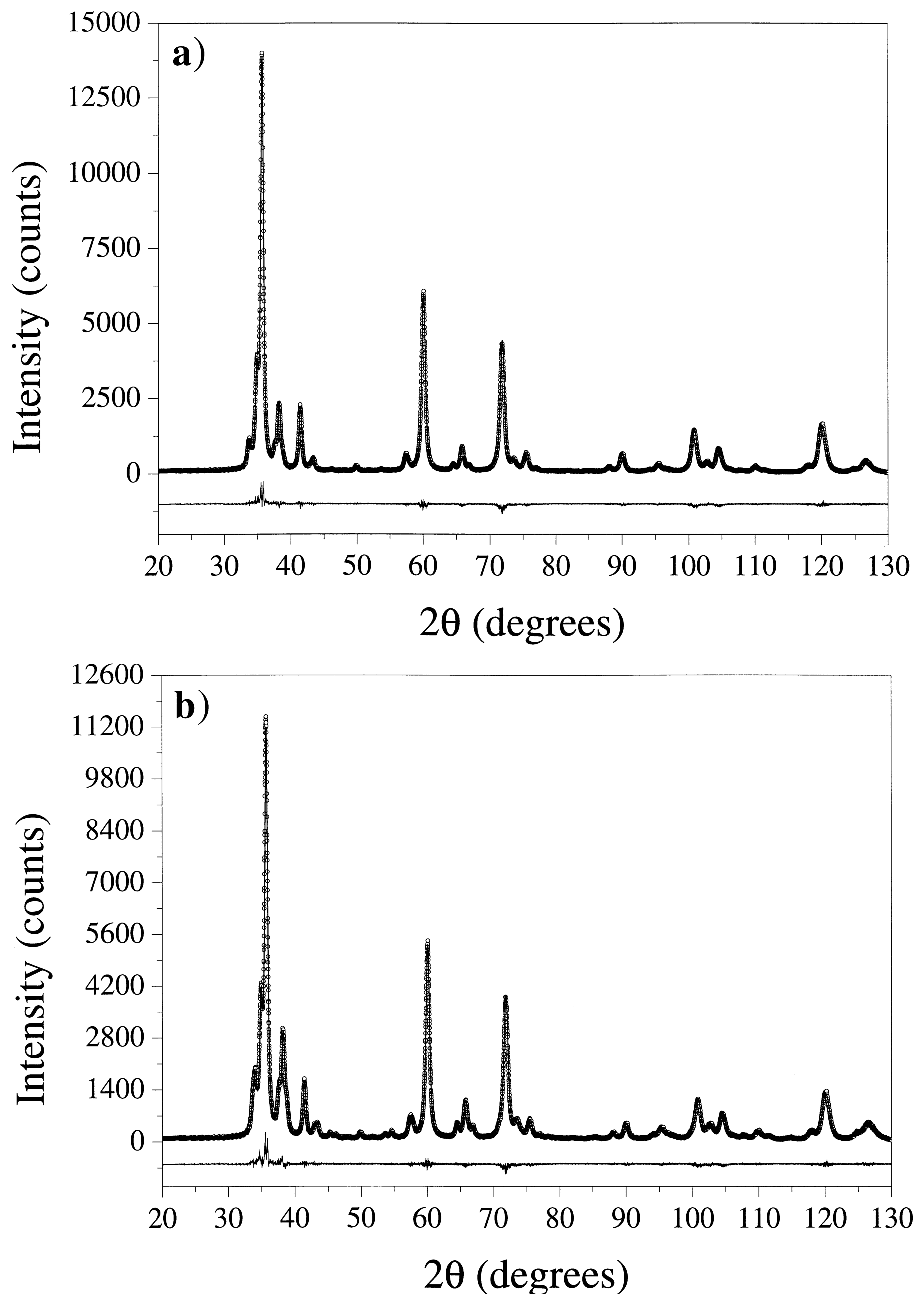

Fig. 4. Plot output from the Rietveld refinements of the samples: (a) SiC2 and (b) SiC6. Points represent the XRD data and the solid line represents the calculated pattern. The difference plot is shown at the bottom.

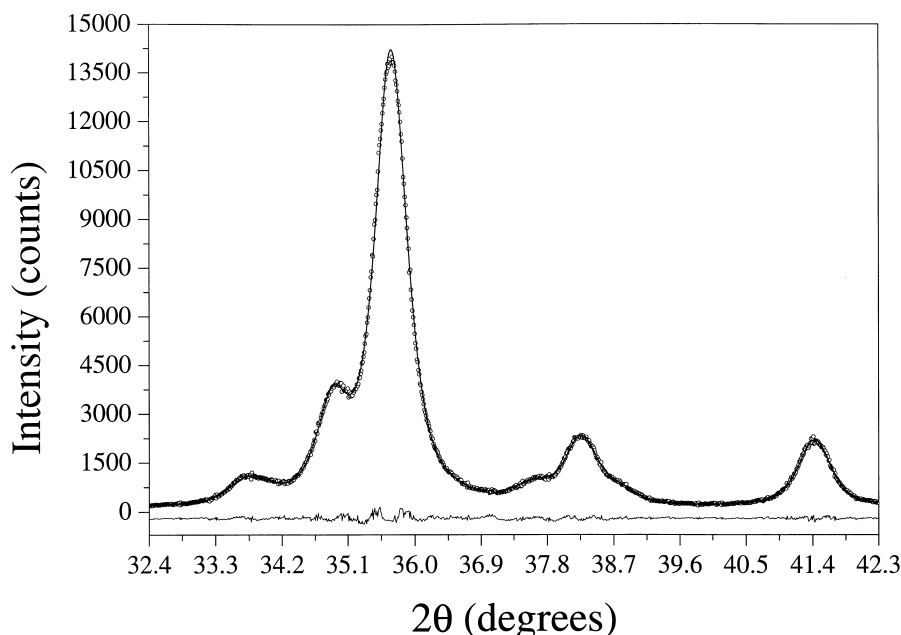

Fig. 5. Plot output from the non-linear Levenberg–Marquardt least-squares fit for the sample SiC2. Points represent the XRD data and the solid line represents the calculated pattern. The difference plot is shown at the bottom.

show refinement results for two representative examples SiC2 and SiC6, respectively; note the excellent agreement between the simulated XRD data and the calculated XRD patterns using the Rietveld method. In the case of the polymorphic method, where no fitting procedure is used, there are no statistical indicators to guide the analysis. When fitting procedures are used to obtain the intensities of the groups of peaks, the fit, unlike the Rietveld method, is carried out without reference to the quantitative phase-composition analysis. Therefore, the qualitative and quantitative assessments of the results are not reliable. For example, Fig. 5 shows that the non-linear Levenberg–Marquardt least-squares fit leads to an excellent agreement between the simulated and calculated XRD data for the sample SiC2. However, this fit resulted in a physically meaningless negative composition (i.c.).

5. Conclusions

A critical comparison between polymorphic methods (using raw peak heights, fitted-peak heights, and fitted-peak integrated intensities) and the Rietveld method for XRD quantitative phase-composition analysis of SiC-based ceramics was performed. The following conclusions can be drawn from this study:

(a) The Rietveld method gives the most accurate result in the quantitative polytype-composition analysis of SiC, with a mean error of 0.5 wt.%.
(b) The accuracy of the polymorphic method using the fitted peak-height intensities is next best, with a mean error of 2.8 wt.%.
(c) The peak-height intensities measured directly from the raw data yields the third best accuracy, with a mean error of 5.4 wt.%.
(d) The poorest agreement is obtained when integrated intensities (areas under fitted peaks) are used. In this case, the mean error is 7.6 wt.%.
(e) The Rietveld method could be applied to all seven compositions studied. The number of intractable cases using the fitted peak-height intensities was found to be fewer than those using fitted integrated intensities.

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