

# A simple, accurate and effective polymorphic method to determine phase compositions of SiC-based ceramics

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## Abstract

A new polymorphic method to determine phase compositions of SiC-based ceramics from their X-ray diffraction profiles has been proposed. Basically, this polymorphic method differs from others already proposed in the literature as follows: (1) a set of parameters is introduced to take into account the possible overlap between different groups of peaks and, (2) a square system is used instead of an overdetermined system to determine the phase composition. The accuracy of the method has subsequently been evaluated using a set of standard X-ray diffraction patterns as a benchmark and the corresponding absolute mean and maximum errors were found to be as low as 2.7 and 6.4%, respectively. In addition, it was also found that the method is much more effective than its polymorphic counterparts, as no physically meaningless negative compositions were found in this study. Moreover, the practical application of the method is quite simple and the phase composition can be determined quickly even using a conventional scientific pocket calculator. We have then demonstrated that the use of the proposed method to determine phase compositions of SiC-based ceramics has several important advantages over other polymorphic methods in terms of enhanced simplicity, accuracy and effectiveness. Parallel analyses of a commercially available  $\alpha$ -SiC powder and of a liquid-phase-sintered SiC ceramic further reinforced these arguments.

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## 1. Introduction

Accurate quantitative phase-composition analysis is a critical aspect to understand the microstructure and properties of many engineering materials, especially of those exhibiting polytypism or polymorphism. This is especially relevant in the case of SiC-based ceramics because pure SiC exists in a huge number of different polytypic forms;<sup>a</sup> in addition, due to the small differences in the free energies of the different polytypes,

many of them can occur simultaneously as a mixture of metastable phases. In this way, quantitative polytype-composition analysis of SiC-based ceramics presents a particularly difficult challenge that requires special attention.

The typical procedure to determine the relative abundance of polytypes in SiC-based ceramics consists of collecting their corresponding X-ray diffraction (XRD) patterns and then analyzing them using either the Ruska,<sup>2,3</sup> Tanaka,<sup>4,5</sup> or Rietveld methods.<sup>6,7</sup> Both the Ruska and Tanaka methods are polymorphic procedures explicitly developed for quantitative-polytype-composition analysis of SiC-based ceramics, while the Rietveld method is a structural refinement procedure appropriately adapted for quantitative phase-composition analysis of all kind of multiphase materials. Also importantly, the polymorphic methods use only a part of the XRD pattern to extract the phase composition ( $2\theta$  in the range 33–42° for the Ruska method, and

<sup>a</sup> Already, more than 250 different polytypic forms have been identified, although the number of polytypes with known crystallographic structures is only about 60. The most commonly occurring polytypic forms are 3C, 4H, 6H and 15R (in the Ramsdell notation  $nS$ ).<sup>1</sup>

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33–50° for the Tanaka method), whereas the Rietveld method uses the whole XRD pattern. Although the Rietveld method is undoubtedly the best choice to determine the phase composition in materials, application of this procedure to SiC-based ceramics has been surprisingly sparse and limited to researchers acquainted with structural resolution. In this way, the major advantage of the Rietveld method, that is, the refinement of a structural and profile model to extract phase-composition information from the whole XRD pattern, constitutes itself its own stumbling block for a widespread use in material science and engineering. For that reason, XRD quantitative polytype-composition analysis of SiC-based ceramics has been traditionally performed using either the Ruska or Tanaka methods.<sup>b</sup> These polymorphic methods are significantly easier to employ compared to the Rietveld method, although as we already showed in preceding works there is a price to pay: their accuracy is substantially lower than that of the Rietveld method.<sup>8,9</sup> Nevertheless, we also found that the accuracy of the Ruska and Tanaka methods improves significantly if the refinement of a profile model is previously used to resolve the maximum of the overlapped XRD peaks.<sup>8,9</sup> Unfortunately, this approach is time-consuming and far apart from being trivial, which again seriously hampers its use as a procedure for quantitative polytype-composition analysis of SiC-based ceramics.

So far, it seems that simplicity and accuracy could never be achieved simultaneously in an XRD analysis routine of SiC-based ceramics, which in turn provides great motivation to develop an alternate polymorphic method with enhanced efficiency. Thus, the main objective of the present work is to demonstrate that simplicity and accuracy are not necessarily two confronted concepts when determining the phase composition in these ceramics. To this end, we have developed a new polymorphic method that is not only easier to use but also more accurate than the existing ones. Firstly, the simplicity is clear in terms of the significant reduction in the computational time as well as in the mathematical and crystallographical expertise needed. Secondly, the accuracy has been evaluated using a set of standard XRD patterns as a benchmark and was shown to improve as compared with those of the Ruska and Tanaka methods. Finally, the procedure has also been applied to determine the phase composition of a commercially available  $\alpha$ -SiC powder and of a liquid-phase-sintered (LPS) SiC material.

The present study is a contribution towards the broad goal of developing simple procedures with both

enhanced accuracy and effectiveness to determine phase compositions of multiphase ceramic systems, which will benefit both ceramic manufacturers and researchers concerning these advanced materials.

## 2. Core mathematics

Consider the case of a uniform-mixture of  $n$  different crystalline phases. The ability to extract the phase composition from its XRD pattern using polymorphic methods relies on finding explicit relations between the experimentally observed peak-height intensities ( $I_{2\theta}$ ) and the weight fractions of the different phases in the mixture ( $X$ ). In this regard, the kinematical XRD theory states that the intensity of the  $g$ th Bragg-reflection of the  $j$ th phase ( $I_{jg}$ ) is directly proportional to the weight fraction of the  $j$ th phase in the mixture ( $X_j$ ). More specifically,  $I_{jg}$  is related (neglecting texture and extinction effects) to  $X_j$  through:<sup>10</sup>

$$I_{jg} = \frac{K M_{jg} L P_{jg} F_{jg}^2 \rho}{V_j^2 e^{2m_{jg}} \mu \rho_j} X_j \quad (1)$$

where  $M_{jg}$ ,  $L P_{jg}$ ,  $F_{jg}$  and  $e^{2m_{jg}}$  are (for the  $g$ th Bragg-reflection of the  $j$ th phase) the multiplicity, the Lorentz-polarization factor, the structure factor and the Debye–Waller temperature factor, respectively. The terms  $V_j$  and  $\rho_j$  in Eq. (1) represent the volume of the unit cell and the density of the  $j$ th phase, respectively. Finally,  $\mu$ ,  $\rho$ , and  $K$  are the linear absorption coefficient of the mixture, the density of the sample and an instrumental constant, respectively.

Ideally, the experimental intensity ( $I_{2\theta}$ ) in the absence of any overlap between different Bragg-reflections is given by:

$$I_{2\theta} = B_{2\theta} + I_{jg} \quad (2)$$

where  $B_{2\theta}$  represents the background contribution. Strictly, this latter equation has to be slightly modified to incorporate a new term ( $\psi_{2\theta}$ ) if there exists a partial overlap between different Bragg-reflections. Specifically,  $\psi_{2\theta}$  represents the contribution to the experimentally observed peak intensity arising from the tails of neighboring Bragg-reflections. Under this condition,  $I_{2\theta}$  now becomes:

$$I_{2\theta} = B_{2\theta} + I_{jg} + \psi_{2\theta} \quad (3)$$

In contrast, Eq. (2) does not further hold if there exists a significant overlap between different Bragg-reflections; in this particular case, Eq. (2) has to be generalized to use sums of intensities over groups of reflections instead of the intensity of an individual Bragg-reflection [see Fig. 1(a) for a schematic representation of severe overlap between Bragg reflections to form a group of peaks]. Thus, the total intensity of a

<sup>b</sup> Note that the Ruska and Tanaka polymorphic methods are cited in more than 90% of the papers concerning quantitative phase composition analysis in SiC-based ceramics.

group of overlapping peaks ( $I_{\text{group}}$ ) can be expressed as follows:

$$I_{\text{group}} = B_{2\theta} + \sum_j \sum_g I_{jg} \quad (4)$$

where the indices  $j$  and  $g$  in the summation cover all phases and individual intensities constituting the group of peaks, respectively. Ruska and Tanaka have pro-

posed the use of Eq. (4) as the physical basis to determine phase compositions of SiC-based ceramics. Note then that, implicitly, both Ruska and Tanaka have assumed that the intensity  $I_{2\theta}$  may be reasonably approximated by the intensity  $I_{\text{group}}$ , this is:

$$I_{2\theta} \cong I_{\text{group}} = B_{2\theta} + \sum_j \sum_g I_{jg} \quad (5)$$

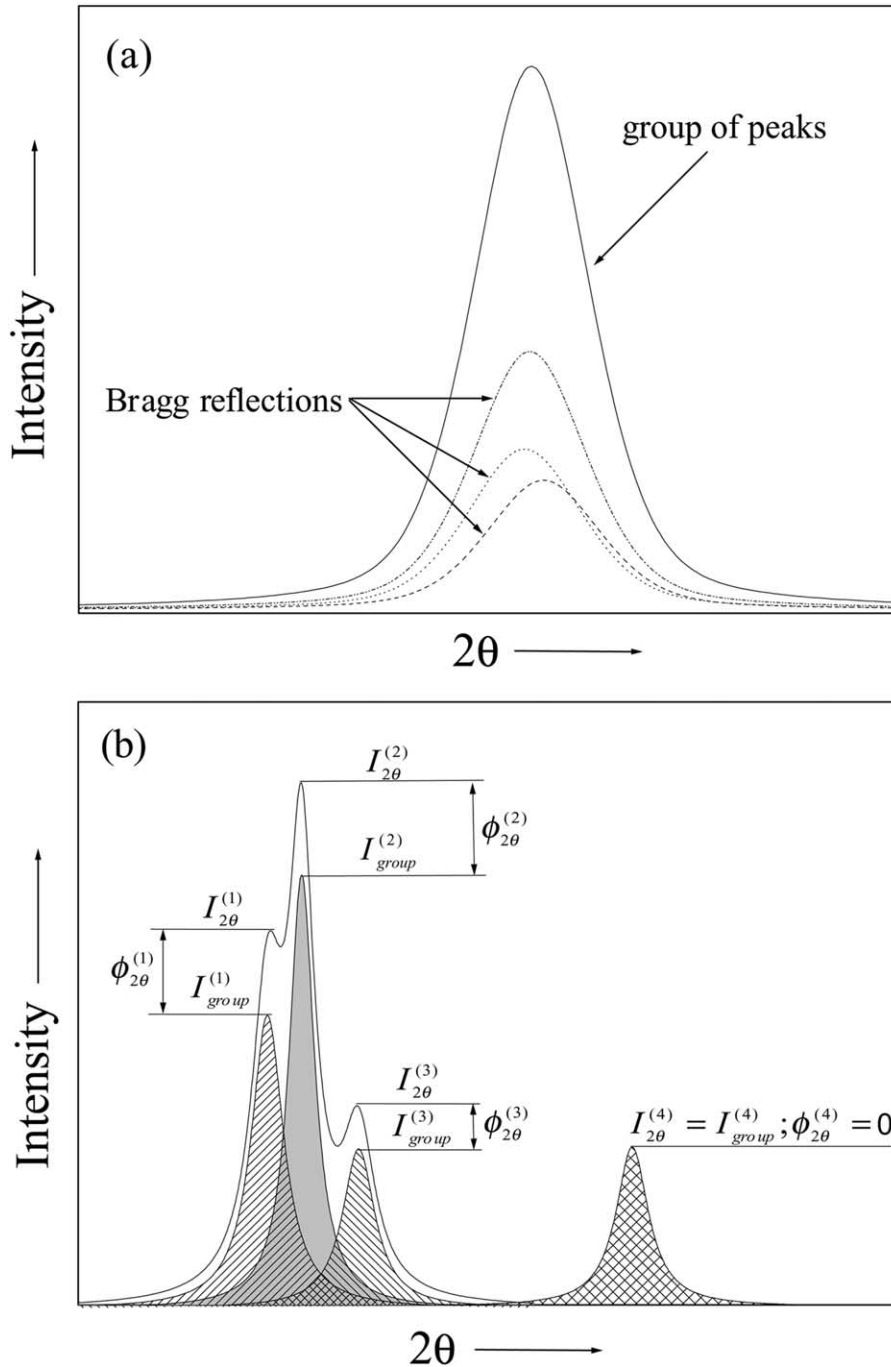


Fig. 1. Schematic representation showing: (a) severe overlap between three Bragg reflections (shown by the dash, dot, and dash-dot-dot lines) to form a group of peaks (shown by the solid line), and (b) overlap between groups of peaks (shown by the fill areas) to form the diffracted profile (shown by the solid line). The terms  $I_{2\theta}$ ,  $I_{\text{group}}$  and  $\phi_{2\theta}$  in (b) represent the intensity at the  $2\theta$  angular position, the intensity of the group of peaks and the contribution to  $I_{2\theta}$  do not associated to its corresponding  $I_{\text{group}}$  (that is,  $I_{2\theta} - I_{\text{group}}$ ), respectively.

Basically, the Ruska and Tanaka methods determine the phase composition by solving linear overdetermined systems<sup>c</sup> constituted by sets of Eq. (5) and subsequently imposing the normalization condition  $\sum_{j=1}^n X_j = 1$ . Strictly, the premise  $I_{2\theta} \cong I_{\text{group}}$  can only be realized in the absence of any overlap between different groups of peaks, which rarely occurs in the XRD patterns of SiC-based ceramics [see Fig. 1(b) for a schematic representation of overlap between groups of peaks]. Consequently, we propose here that Eq. (5) must be modified in order to incorporate the contributions from neighboring groups of peaks ( $\phi_{2\theta}$ ):

$$I_{2\theta} = I_{\text{group}} + \phi_{2\theta} = B_{2\theta} + \sum_j \sum_g I_{jg} + \phi_{2\theta} \quad (6)$$

Also, note that the introduction of  $\phi_{2\theta}$  parameters in Eq. (6) opens up a unique opportunity to use a system with a higher number of equations than phases in the mixture and, at the same time, to establish a linear square system instead of an overdetermined system. This is because the number of  $\phi_{2\theta}$  parameters can be deliberately chosen in such a way that the total number of unknowns<sup>d</sup> matches the total number of equations. Note here that the  $\phi_{2\theta}$  parameters are only needed in the case of overlap between different groups of peaks and that Eq. (6) reduces to Eq. (5) at  $\phi_{2\theta} = 0$ . Unfortunately, Eq. (6) is quite general and has to be particularized to each case; nevertheless, the only information needed is knowledge of the crystallographic structure of the phases that could be present in the mixture. As an example, we have deferred detailed consideration of one of the systems used in this study to an Appendix.

### 3. Experimental procedure

#### 3.1. Simulation and characterization of standard XRD patterns

In order to evaluate the accuracy and effectiveness of our polymorphic method in determining polytype compositions of multiphase SiC-based ceramics, a set of

<sup>c</sup> Overdetermined systems are algebraic systems that have more equations than unknowns. In general, these will not have a solution in the sense that one gets exact equality for each equation. Thus, the unknowns are evaluated using multiple linear regression procedures so that all the equations are as close to being satisfied as possible. The Ruska method uses a system with six equations and four unknowns, whereas the Tanaka method considers a system with 15 equations and four unknowns.

<sup>d</sup> Number of phases in the mixture + number of  $\phi_{2\theta}$  parameters + 1 additional parameter to estimate the mean background level. Note that nowadays the modern diffractometers provide an almost flat background for full-crystalline specimens. Nevertheless, in the case of specimens with significant amounts of grassy phases we suggest to previously subtract the background from the raw data and then to incorporate a B parameter to describe a flat background.

standard XRD patterns were generated in the computer by simulation.<sup>e,11</sup> The crystallographic data reported in the literature for the most commonly-found polytypes (3C, 4H, 6H, and 15R) were used for the simulations.<sup>3,11–13</sup> The patterns of these four single-SiC polytypes were then simulated considering CuK $\alpha$  incident radiation ( $\lambda_{\alpha 1} = 1.54056 \text{ \AA}$ ,  $\lambda_{\alpha 2} = 1.54439 \text{ \AA}$  and  $I_{\alpha 2}/I_{\alpha 1} = 0.48$ ) in a Bragg–Brentano diffractometer. In all cases, the diffraction domain size was chosen to be 20 nm and the patterns were obtained by simulating a step-scan mode over a  $2\theta$  range of 20–130° with a step width of 0.01°. Subsequently, different multiphase patterns<sup>f</sup> of wide ranging compositions were prepared by combining these four single patterns in various proportions.

To obtain the instrumental broadening, a Monte Carlo simulation was carried out using the geometrical conditions (goniometer radius, receiving slit, etc.) for a Philips PW-1800 powder diffractometer.<sup>g</sup> A convolution program was then used to incorporate the instrumental broadening into the pure patterns. Finally, the background contribution and the statistical noise were also introduced into these patterns to obtain XRD patterns similar to the experimental ones. 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 have a Poisson distribution.

The standard XRD patterns were then analyzed using the new polymorphic method to determine the phase composition. Polytype compositions determined previously using the Rietveld,<sup>8,9</sup> Ruska<sup>8</sup> and Tanaka<sup>9</sup> methods were used as baseline references to compare accuracy.

#### 3.2. Processing and XRD characterization of experimental samples

Application of our polymorphic method to experimental samples was performed on an  $\alpha$ -SiC powder and on an LPS SiC material. We describe next the processing and XRD characterization of these two specimens.

The  $\alpha$ -SiC powder was prepared from commercially available submicrometer  $\alpha$ -SiC powders (UF-15, H.C. Starck, Berlin, Goslar, Germany). To promote grain coarsening, this powder was isothermally heat-treated in a graphite furnace (Astro Industry, Santa Rosa, CA) at

<sup>e</sup> The use of the simulation procedure is justified due to the inherent difficulty in preparing such standards experimentally.

<sup>f</sup> These multiphase patterns are referred to as pure patterns since they do not present any instrumental contribution.

<sup>g</sup> The instrumental peaks were compared with those obtained from an  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> standard specimen and no difference in the peak widths were observed.<sup>11,14</sup>

Table 1

Simulated compositions of the seven standard mixtures (SiC1–SiC7) and the concentrations of the SiC polytypes as calculated using the polymorphic method proposed in this study

Polytype	Simulated compositions/calculated compositions						
	SiC1	SiC2	SiC3	SiC4	SiC5	SiC6	SiC7
3C	16.4/17.4	58.6/53.8	36.5/35.9	0.0/1.0	16.5/12.7	29.3/26.9	6.0/4.3
4H	47.6/42.2	28.0/24.8	0.0/0.2	33.1/29.0	36.7/32.9	25.8/23.0	5.6/5.8
6H	36.0/37.7	0.0/2.8	10.4/12.5	32.8/33.9	28.6/29.8	19.7/20.8	6.9/11.4
15R	0.0/2.7	13.4/18.6	53.1/51.4	34.1/36.1	18.2/24.6	25.2/29.3	81.5/78.5

a temperature of 1800 °C for 5 h in a flowing argon atmosphere.

The LPS SiC material was processed from commercially available submicrometer powders of  $\beta$ -SiC (BF-12, H.C. Starck, Goslar, Germany),  $Y_2O_3$  (fine grade, H.C. Starck, Goslar, Germany) and  $Al_2O_3$  (AKP-30, Sumitomo Chemical, Tokyo, Japan). These powders were combined in the following proportion: 86.41 wt.%  $\beta$ -SiC, 7.75 wt.%  $Y_2O_3$  and 5.84 wt.%  $Al_2O_3$ . The  $Y_2O_3:Al_2O_3$  molar ratio was 3:5, to result in  $Y_3Al_5O_{12}$  (YAG) after sintering. The final composition of the sintered product was designed to be 90 vol.% SiC and 10 vol.% YAG. The powder batch was blended intimately by wet-ball-milling in methanol for 24 h in a polyethylene bottle using  $ZrO_2$  balls. Then, the slurry was carefully dried in a Teflon beaker on a hot-plate while being continuously stirred. This dried powder was placed into a plastic bag that was thermally sealed. The powder was then deagglomerated by crushing with a roller. Subsequently, approximately 10 g of the mixed powder was pressed uniaxially (manual model, Carver Inc., Wabash, IN) into a pellet (25 mm diameter  $\times$  7 mm thick) at a pressure of 50 MPa in a graphite die. The pellet was sealed in a latex bag and cold-isostatically pressed at 350 MPa (CP360, AIP, Columbus, OH). Then, the green body was embedded in a loose powder bed (15 g) inside a graphite crucible with screw lid. The powder bed composition consisted of 90 wt.% SiC (600 grit; Crystolon, Norton Co., Worcester, MA) and 10 wt.%  $Al_2O_3$  (15  $\mu$ m, Buehler Ltd., Lake Bluff, IL). The arrangement of the coarse SiC and  $Al_2O_3$  powders inside the crucible cavity is described in detail elsewhere.<sup>11</sup> The pellet was sintered isothermally in a graphite furnace (Astro Industry, Santa Rosa, CA) at a temperature of 1950 °C for 0.5 h in a flowing argon atmosphere with heating and cooling rates of 600 and 1200 °C h<sup>-1</sup>, respectively. The sintered pellet was then removed from the furnace and its surface was cleaned and ground ( $\sim$ 1 mm surface layer) to remove extraneous powder that was sticking to the sample. Finally, the ground-surface was polished with diamond pastes to a 1  $\mu$ m finish using ceramographic techniques.

The XRD patterns of the heat-treated  $\alpha$ -SiC powder and the LPS SiC specimen were obtained via conventional powder diffractometry (model PW-1800, Philips

Research Laboratory, Eindhoven, The Netherlands) using  $CuK_{\alpha}$  radiation (at a wavelength of  $\lambda = 1.54183$  Å), a take-off angle of 6°, and a graphite secondary monochromator. The generator settings were 40 kV and 35 mA. The diffraction data were collected over a  $2\theta$  range of 20–95°, with a step width of 0.05° and a counting time of 5 s per step. The XRD patterns were then analyzed using the new polymorphic and Rietveld methods to determine the phase composition. The Full-Prof Rietveld software package was used; application of this Rietveld program for quantitative phase-composition analysis of SiC-based ceramics has been described in earlier publications.<sup>8,15,16</sup>

#### 4. Results and discussion

Table 1 gives the simulated compositions of the standard mixtures and the concentrations of the SiC polytypes as calculated using our polymorphic procedure. Note the absence of any systematic difference between the simulated and calculated compositions, as well as the lack of physically meaningless negative compositions. It should be borne in mind that no intent was made in this study to previously identify the polytypes present in each standard mixture by qualitative phase-composition analysis. Values of absolute mean and maximum errors<sup>h</sup> for our polymorphic method, as well as for the Rietveld, Ruska and Tanaka methods are appropriately listed in Table 2. Note that the absolute mean and maximum errors of our polymorphic procedure were measured to be 2.7 and 6.4%, respectively, which favourably compares with 5.4 and 12.9% for the Ruska method<sup>8</sup>) as well as with 7.4 and 22.4% for the Tanaka method.<sup>9</sup> In other words, the errors of our procedure are at least  $\sim$ 50% lower than those of the Ruska and Tanaka procedures (classical approaches), under identical standard compositions. Also note from Table 2 that our polymorphic method could be applied to the seven compositions studied here; in contrast,

<sup>h</sup> The absolute mean and maximum errors have been defined here as the mean and maximum differences between the simulated and calculated compositions, respectively.

Table 2  
Comparative study of accuracy and effectiveness for the methods considered in this study

Magnitude	Method							
	This work	Ruska (classical approach)	Tanaka (classical approach)	Ruska (with profile fit)	Tanaka (with profile fit)	Ruska (areas)	Tanaka (areas)	Rietveld
Mean error	2.7	5.4	7.4	2.8	2.6	7.6	8.0	0.5
Maximum error	6.4	12.9	22.4	5.7	7.5	18.6	22.5	0.9
Negative compositions	0	2	3	2	1	3	4	0

The absolute mean and maximum errors, as well as the number of physically meaningless negative compositions were determined by comparing the simulated and calculated compositions for the seven standard mixtures listed in Table 1.

application of the Ruska and Tanaka methods to the same standard compositions yielded to two and three physically meaningless negative compositions of a total of seven, respectively. This clear evidence of a significant improvement in the accuracy and applicability can be unequivocally attributed to the introduction of the  $\phi_{2\theta}$  parameters in Eq. (6).

Recently, we have reported<sup>8,9</sup> that the reasons by which the Ruska and Tanaka methods fail could be varied, but the most important is undoubtedly the overestimation of some intensities as a consequence of the overlap between different groups of peaks. This undesirable effect, which is inevitable in SiC-based ceramics, can be minimized if a set of parameters is explicitly used to estimate the contribution to the experimentally observed peak intensities arising from the tails of neighbouring groups of peaks. The introduction of the  $\phi_{2\theta}$  parameters in Eq. (6) provides a simple and effective way to estimate these parasitic contributions, thereby improving the accuracy and effectiveness of the quantitative polytype-composition analysis. We mark here that the values of the  $\phi_{2\theta}$  parameters experimentally determined with our polymorphic method ( $\phi_{2\theta,e}$ ) were always positives and close to those theoretically calculated from the simulations ( $\phi_{2\theta,i}$ )—see Fig. 2 for an example. Clearly, certain differences between  $\phi_{2\theta,i}$  and  $\phi_{2\theta,e}$  are always expected considering the errors in the determination of the phase composition.<sup>i</sup> It is also worth mentioning that in previous works<sup>8,9</sup> we proposed the use of a profile refinement (carried out using a non-linear Levenberg–Marquardt least-squares fit) as another way to overcome the prob-

lem of the overlap between different groups of peaks (as given in Table 2). Nevertheless, this latter approach has two important drawbacks. First, it is time-consuming and much more complex to employ, thereby limiting its use in those potential applications where a fast analysis is required. Second, the fit can conclude in a local-minimum instead of in the global-minimum, thereby providing ambiguous peak-height intensities that will be later used to determine the phase composition. Thus, although both approaches help to improve the accuracy and effectiveness of the quantitative phase-composition analysis, the use of  $\phi_{2\theta}$  parameters is a more appropriate choice. It is also interesting to note that the use of the profile refinement allows one to apply the Ruska and Tanaka methods using the integrated intensities (areas) of the groups of peaks. Nevertheless, we reported elsewhere<sup>8,9</sup> that approach yields to the poorest accuracy and to the highest incidence of negative compositions (see Table 2) because the non-linear Levenberg–Marquardt least-squares fit provides well-defined peak-maxima but ambiguous integrated intensities.

In addition to high accuracy, our polymorphic method also satisfies another important requirement: simplicity. In fact, we have determined the phase composition of the standard mixtures using a conventional scientific pocket calculator in less than 5 min per mixture, which is remarkably quick. Note that the method is just based on using the raw height-peaks to solve a linear square system, thereby precluding the use of multiple linear regression procedures to determine the phase composition. In contrast, these procedures are essential in the Ruska and Tanaka methods since over-determined systems without solutions are considered there.<sup>j</sup> Thus, a multiple linear regression procedure is then needed to determine the values of the unknowns that minimize the difference between the observed and calculated intensities. Again, an additional drawback is

<sup>i</sup> In the case of the diffractogram shown in Fig. 2 the nominal polytype composition introduced into the simulation was 25 wt.% 3C, 50 wt.% 4H and 25 wt.% 6H, whereas that determined with our polymorphic method was 26.0 wt.% 3C, 48.8 wt.% 4H, 24.8 wt.% 6H and 0.4 wt.% 15R. Thus, the differences between the simulated and calculated compositions could explain the differences between the sets of  $\phi_{2\theta,i}$  and  $\phi_{2\theta,e}$ . Also, the fact that the method determines a slight concentration of 15R would account for the differences between  $\phi_{2\theta,i}$  and  $\phi_{2\theta,e}$  at 38.2 and 43.3°.

<sup>j</sup> Note that, in a general case, all the equations are linearly independent as they are affected by overlapping, statistical noise and background.

that the regression can conclude in a local-minimum instead of in the global-minimum, thereby providing an incorrect quantitative phase-composition analysis.

It is worth mentioning here that the accuracy of our polymorphic method is lower than that of the Rietveld method (as given in Table 2). This fact is not unex-

pected, considering that the Rietveld method introduces complex analytical equations to model all the factors affecting the diffracted intensities and that we have only used a simple set of  $\phi_{2\theta}$  parameters to correct just for overlap between different groups of peaks. Note then that the phase composition determined with this and

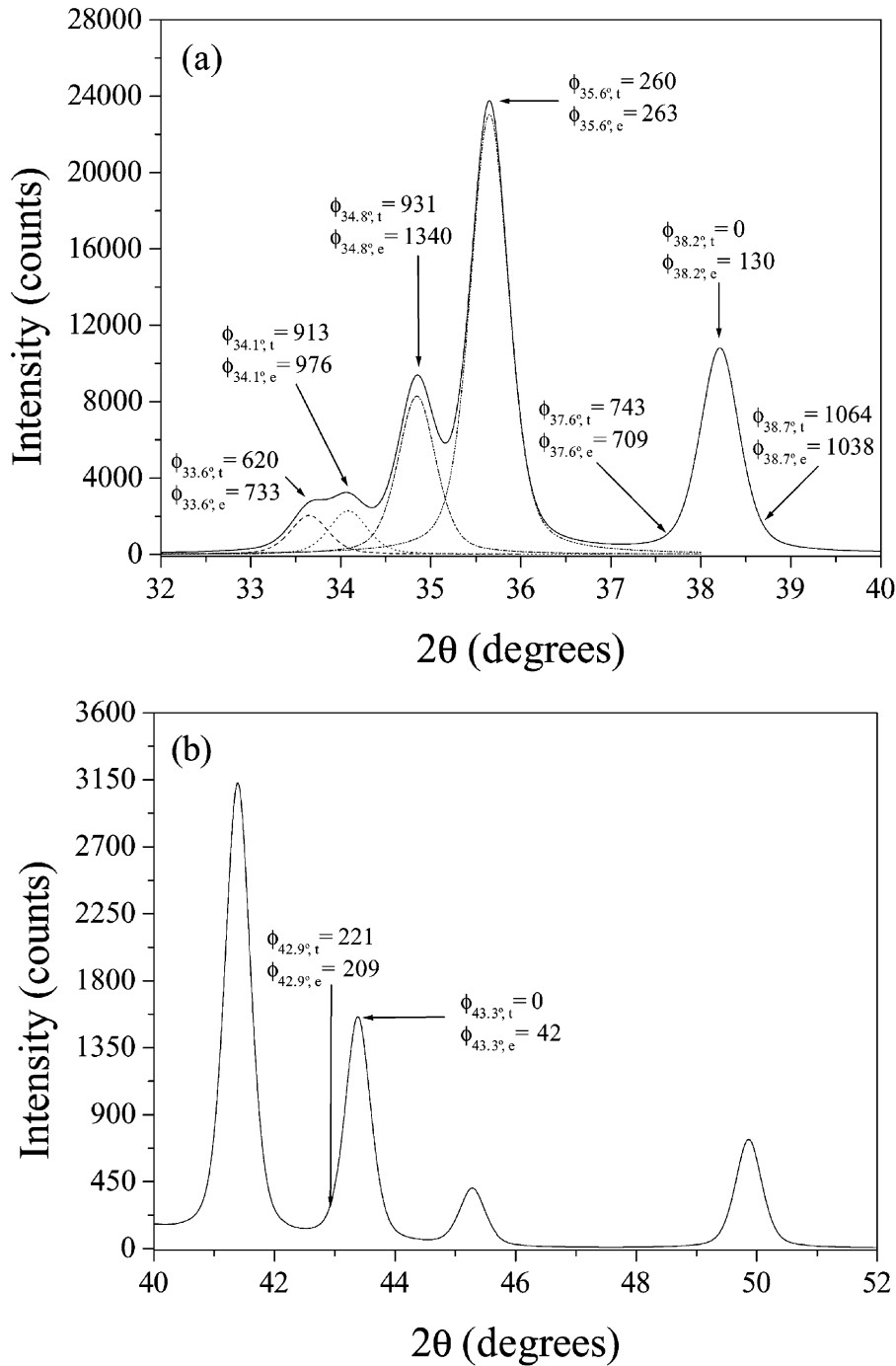


Fig. 2. Comparison between the  $\phi_{2\theta}$  parameters experimentally determined with our polymorphic method ( $\phi_{2\theta,e}$ ) and those theoretically calculated from the simulation ( $\phi_{2\theta,t}$ ) for the  $2\theta$  range between: (a) 32–40° and (b) 40–52°. The simulated pattern is shown by solid line, whereas the theoretical contribution from the different overlapping groups of peaks is shown by the dash, dot, dash-dot, and dash-dot-dot lines. The nominal phase composition introduced into the simulation was 25 wt.% 3C, 50 wt.% 4H and 25 wt.% 6H, whereas that determined with our polymorphic method was 26.0 wt.% 3C, 48.8 wt.% 4H, 24.8 wt.% 6H and 0.4 wt.% 15R.

other polymorphic methods for textured specimens must be handled carefully.

So far, we have shown that despite its simplicity, our polymorphic method is remarkably accurate. Clearly, the next step consists of applying the polymorphic procedure to quantitative phase-composition analysis of experimentally processed SiC samples. We have

Table 3

Weight fractions of the different phases in the commercially available  $\alpha$ -SiC powder and in the liquid-phase-sintered SiC ceramic determined using the polymorphic method proposed here and the Rietveld method

Phase	Polymorphic compositions/Rietveld compositions	
	Commercial $\alpha$ -SiC powder	Liquid-phase-sintered SiC sample
3C	4.1/2.9 $\pm$ 0.1	65.0/66.7 $\pm$ 0.1
4H	5.5/6.1 $\pm$ 0.2	13.7/13.5 $\pm$ 0.1
6H	85.6/83.2 $\pm$ 0.5	7.5/5.5 $\pm$ 0.1
15R	4.8/7.8 $\pm$ 0.2	–
Y <sub>3</sub> Al <sub>5</sub> O <sub>12</sub>	–	13.8/14.3 $\pm$ 0.2

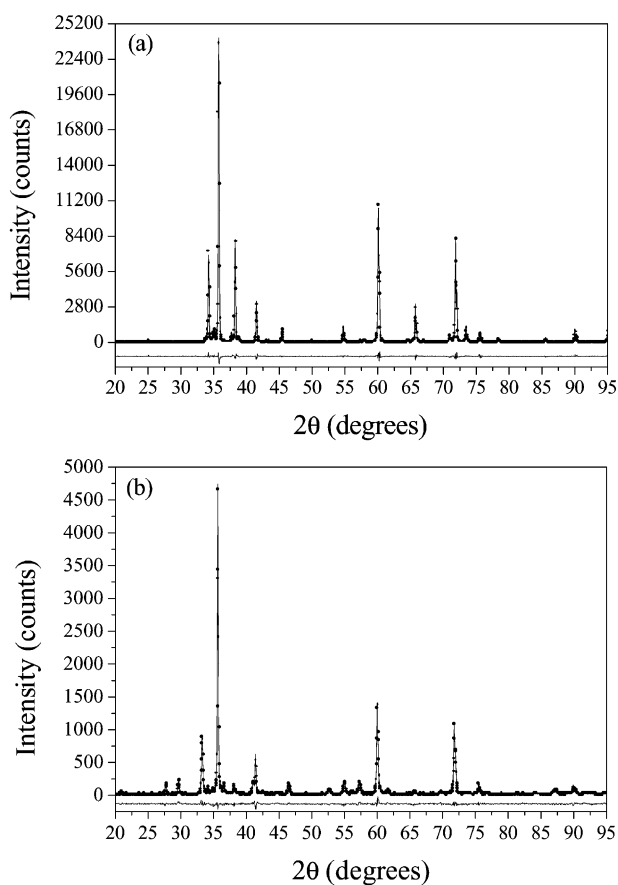


Fig. 3. Plot output from the Rietveld analyses of the X-ray diffraction patterns corresponding: (a) to the  $\alpha$ -SiC powder, and (b) to the liquid-phase-sintered SiC ceramic. Points represent the experimental X-ray diffraction data and the solid lines represent the calculated patterns. The difference plots are shown at the bottom of each graph.

considered here two different systems: (i) an  $\alpha$ -SiC powder and, (ii) an LPS SiC sample. The choice of these two particular SiC-based systems was not arbitrary, but related to the following interests. First, most industrial SiC powders are currently manufactured as a mixture of metastable polytypes; in addition, although manufacturers have dramatically increased the chemical and microstructural characterizations of their SiC powders, the quantitative polytype-composition analysis is still an overriding concern. Second, conclusions obtained from the  $\alpha$ -SiC powder case can be extendable to solid-state-sintered SiC samples; this is a valid assumption considering the negligible amount (less than 5 wt.%) of sintering additives (B and C, or even Al) commonly used and that these do not form additional phases during sintering. Third, nowadays there is a growing interest in pressureless LPS SiC ceramics, one of the most widely used structural ceramics. Thus, we cover potentially a broad range of SiC-based materials of interest to both ceramic manufacturers and researchers.

Table 3 gives the composition determined using our polymorphic method for the  $\alpha$ -SiC powder and for the LPS SiC sample.<sup>k</sup> Unfortunately, the accuracy of these analyses can not be independently evaluated since we have not used standard compositions. However, at least in the case of the LPS SiC specimen, the amount of Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub> could be used as an internal standard to test accuracy. Note here that the calculated Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub> content is in good agreement with that expected from the starting powders (Y<sub>2</sub>O<sub>3</sub> + Al<sub>2</sub>O<sub>3</sub>). This seems to indicate that the polymorphic method has successfully determined the phase composition. Also note that comparison of compositions determined using the polymorphic and Rietveld methods could be used as an alternative and indirect way to assess accuracy. In this regard, Table 3 shows the marked similarity between the compositions determined using both procedures, proving in some way the remarkable accuracy of our polymorphic method. The excellent agreement between the experimental XRD data and the calculated profiles using the Rietveld method (see Fig. 3) ensures that the implicit correspondence made here between goodness of fit and accuracy of quantitative-phase-composition analysis is a valid assumption.

To conclude, we mark that the procedure presented here to determine phase-compositions is also readily extendable to other SiC-based ceramics and even to other advanced ceramics such as Si<sub>3</sub>N<sub>4</sub>, ZrO<sub>2</sub>, and Al<sub>2</sub>O<sub>3</sub>, to name but a few. We believe that this versatility renders the method highly attractive to a broad part of the ceramic community.

<sup>k</sup> Note here that the phases present both in the  $\alpha$ -SiC powder and in the LPS SiC sample were previously identified by qualitative phase-composition analysis.



## 5. Summary

In this work, we have proposed a new polymorphic method to determine the phase composition of SiC-based ceramics. A critical comparison between results obtained with this method and with other methods previously used in the literature was also performed. Results from this work clearly showed that the accuracy of the procedure proposed here is significantly higher than those of the Ruska and Tanaka methods, nearly identical or comparable to those of more complex variants of the same polymorphic methods and lower than that of the Rietveld method. In addition, it has been shown that the procedure is much simpler than all the others, as well as remarkably effective (no physically meaningless negative compositions were obtained in our study). It is then concluded that the use of this new method to determine the phase composition of SiC-based ceramics offers several advantages over the conventional polymorphic methods in terms of accuracy, simplicity and effectiveness. The enhanced accuracy, simplicity and effectiveness is solely attributed to the

introduction of a simple set of parameters which are used to estimate the contribution to the experimentally observed peak intensity arising from the tails of neighboring groups of peaks.

The method is generic in nature and could potentially be used to determine the phase composition of a wide variety of ceramic systems. We believe that this versatility renders the method highly attractive to a broad part of the ceramic community.

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## Appendix. More detailed quantitative phase-composition analysis

As mentioned in Section 2, the experimentally observed peak-height intensities ( $I_{2\theta}$ ) in the presence of overlap is given by:

$$I_{2\theta} = I_{group} + \phi_{2\theta} = B_{2\theta} + \sum_j \sum_g I_{jg} + \phi_{2\theta} = B_{2\theta} + \sum_j \sum_g \frac{K M_{jg} L P_{jg} F_{jg}^2 \rho}{V_j^2 e^{2m_{jg}} \mu \rho_j} X_j + \phi_{2\theta} \quad (A1)$$

If the crystalline structure of the  $j$ th phase is known, we can then define the crystallographic factor  $R_{jg}$  as follows:

$$R_{jg} = \frac{M_{jg} L P_{jg} F_{jg}^2}{V_j^2 e^{2m_{jg}} \rho_j} \quad (A2)$$

Also note that the factors  $K$ ,  $\mu$ , and  $\rho$  in Eq. (A1) do not depend on the  $j$ th phase and therefore can be included in a new constant  $C$  (being  $C = K \cdot \mu \cdot \rho$ ). Using the above-mentioned expressions for  $R_{jg}$  and  $C$ , Eq. (A1) takes the form:

$$I_{2\theta} = B_{2\theta} + \sum_j \sum_g C R_{jg} X_j + \phi_{2\theta} = B_{2\theta} + \sum_j \sum_g R_{jg} X'_j + \phi_{2\theta} \quad (A3)$$

where  $X'_j = C X_j$ . These unknowns  $X'_j$  are subsequently evaluated by solving a system constituted by a set of Eq. (A3). Note here that in the case of square systems conventional linear-matrix algebra procedures are used to determine the solution of the system, whereas multiple linear regression procedures are used in the case of overdetermined systems only to find the best solution. Finally, by imposing the normalization condition  $\sum_{j=1}^n X_j = 1$ , the relative amounts of the  $n$  different phases are evaluated as follows:

$$X_j = \frac{X'_j}{\sum_{j=1}^n X'_j} \quad (A4)$$

Unfortunately, Eq. (A3) is quite general and has to be particularised to each case, although that does not constitute any limitation of the procedure. As an example, we describe next the square system used in this study for the quantitative polytype-composition analysis of standard mixtures of 3C, 4H, 6H and 15R polytypes, which is also applicable to commercially available SiC powders and to solid-state sintered SiC ceramics. In the particular case of room-temperature

XRD analysis of such mixtures, the  $R_{jg}$  factors in Eq. (A3) can be calculated neglecting the Debye–Waller temperature factor and the density of the different SiC polytypes.<sup>1</sup> Here we have considered the raw intensity at the  $2\theta$  Bragg-angles 33.6, 34.1, 34.8, 35.6, 37.6, 38.2, 38.7, 41.4, 42.9, 43.3, 45.3, 46.2, 47.9 and 49.8° to determine the relative amounts of the 3C, 4H, 6H and 15R polytypes. Also,  $\phi_{2\theta}$  parameters have been introduced to correct for overlap between groups of peaks with maximum-positions separated in less than 0.9°. Thus, the following linear square system with 14 equations and 14 unknowns (four  $X_j$  or  $X'_j$  parameters, nine  $\phi_{2\theta}$  parameters and the  $B$  parameter) was used to perform the quantitative polytype-composition analysis:

$$\begin{pmatrix} I_{2\theta=33.6^\circ} \\ I_{2\theta=34.1^\circ} \\ I_{2\theta=34.8^\circ} \\ I_{2\theta=35.6^\circ} \\ I_{2\theta=37.6^\circ} \\ I_{2\theta=38.2^\circ} \\ I_{2\theta=38.7^\circ} \\ I_{2\theta=41.4^\circ} \\ I_{2\theta=42.9^\circ} \\ I_{2\theta=43.3^\circ} \\ I_{2\theta=45.3^\circ} \\ I_{2\theta=46.2^\circ} \\ I_{2\theta=47.9^\circ} \\ I_{2\theta=49.8^\circ} \end{pmatrix} = \begin{pmatrix} 0 & 3.293 & 0 & 1.073 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 7.412 & 3.7239 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 13.5046 & 0 & 9.1437 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \\ 35.844 & 8.9846 & 22.4014 & 13.3068 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 6.8711 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 1 \\ 0 & 13.7488 & 8.0931 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 4.9568 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 1 \\ 6.713 & 0 & 3.3578 & 1.0779 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 1.7577 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 1 \\ 0 & 2.5225 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 1 \\ 0 & 0 & 1.2745 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0.6457 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0.1895 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 1.2352 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix} \cdot \begin{pmatrix} X'_{3C} \\ X'_{4H} \\ X'_{6H} \\ X'_{15R} \\ \phi_{2\theta=33.6^\circ} \\ \phi_{2\theta=34.1^\circ} \\ \phi_{2\theta=34.8^\circ} \\ \phi_{2\theta=35.6^\circ} \\ \phi_{2\theta=37.6^\circ} \\ \phi_{2\theta=38.2^\circ} \\ \phi_{2\theta=38.7^\circ} \\ \phi_{2\theta=42.9^\circ} \\ \phi_{2\theta=43.3^\circ} \\ B \end{pmatrix}$$

Formulation of square systems for other SiC-based ceramics is straightforward after choosing the appropriate groups of peaks and recalculating the  $R_{jg}$  factors in Eq. (A3) to take into account the differences in densities of the phases in the material.

<sup>1</sup> The density  $\rho_j$  ranges between 3.21 and 3.22 g cm<sup>-3</sup> for all the polytypes and, therefore, it can be considered as a constant.

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