RESEARCH PAPERS

A standardless method of quantitative ceramic analysis using X-ray powder diffraction

SUJATA MAZUMDAR

*Central Glass and Ceramic Research Institute, 196 Raja S. C. Mallik Road, Calcutta 700032, India.
E-mail: model@cscgcri.ren.nic.in*

Abstract

A new procedure using X-ray powder diffraction data for quantitative estimation of the crystalline as well as the amorphous phase in ceramics is described. Classification of the crystalline and amorphous X-ray scattering was achieved by comparison of the slopes at two successive points of the powder pattern at scattering angles at which the crystalline and amorphous phases superimpose. If the second slope exceeds the first by a stipulated value, the intensity is taken as crystalline; otherwise the scattering is considered as amorphous. Crystalline phase analysis is obtained by linear programming techniques using the concept that each observed X-ray diffraction peak has contributions from n component phases, the proportionate analysis of which is required. The method does not require the measurement of calibration data for use as an internal standard, but knowledge of the approximate crystal structure of each phase of interest in the mixture is necessary. The technique is also helpful in qualitative analysis because each suspected phase is characterized by the probability that it will be present when a reflection zone is considered in which the suspected crystalline phase could contribute. The amorphous phases are determined prior to the crystalline ones. The method is applied to ceramic materials and some results are presented.

1. Introduction

Quantitative determination of the crystalline and amorphous contents of a mixture is certainly important for many practical applications. X-ray diffraction analysis appears to be the perfect technique for this purpose based on the following facts: (i) each crystalline component has a unique set of X-ray diffraction peak profiles in the intensity pattern; (ii) the X-ray diffraction patterns of the components overlap without interference; (iii) the intensity pattern of each component is a function of the amount of the component present. With the advent of automated X-ray powder diffractometers, the data can be computationally analysed by a variety of numerical techniques. Various methods for this purpose have been developed which can be classified into two categories depending on whether independent peaks of the contributing phase are present or no independent peaks occur. Methods for solving the problem related to the presence of independent peaks are the external and internal standard method (Klug & Alexander, 1974), the matrix-flushing method (Chung, 1974*a,b*, 1975), the doping method (Popovic & Grzeta-Plenkovic, 1979; Popovic *et al.*, 1983), the dilution method (Lennox, 1957; Clark & Preston, 1974; Grzeta & Popovic, 1985), the standardless method (Zevin, 1977; Rius, 1987; Wang, 1988; Zangalis, 1991), *etc.* Methods in the other category are based on whole-powder-pattern fitting, using the Rietveld refinement approach (Werner *et al.*, 1979; Toraya *et al.*, 1984; Hill & Howard, 1987) or digitized whole-pattern traces (Smith *et al.*, 1989). Various software packages are available for this purpose. These methods require an internal standard for absolute quantification as they do not deal directly with amorphous phases present.

In the present paper, a method is described in which the quantitative determination of amorphous phases is done prior to crystalline-phase analysis. Since the X-ray diffraction technique is highly suitable for the characterization of crystalline material, an extension of this method was sought to estimate the glass/amorphous contents in a mixture as well. In the case of composites containing glass/amorphous material, X-ray or neutron scattering will have contributions from air, incoherent and amorphous scattering, as well as crystalline contributions. Various techniques have been developed (Snyder, 1979, 1983; Mallory & Synder, 1980) for determining the background level in diffraction patterns. The estimation of the background by a polynomial fit of degree n will be possible if each of the components contributing the background are independent of one another. In that case, each polynomial describing the contribution of a component remains independent of all others throughout the scattering zone. If the background is considered as having a contribution from air, incoherent and amorphous scattering, the independent character of each component no longer remains valid, as amorphous scattering also

includes incoherent and air scattering. Therefore, the background dependent on all three effects is estimated by pattern analysis. The pattern analysis method for calculating and eliminating background has been reported earlier (Mallory & Synder, 1980). In the present study, the pattern analysis method has been extended in order to separate the crystalline scattering from the background containing air, incoherent and amorphous scattering in the first stage, and then to separate amorphous scattering from the background. The basis of the separation of crystalline scattering from the background lies in the comparison of slopes at two successive points on the intensity pattern. If the difference exceeds a stipulated value, the scattering is deemed crystalline. The choice of stipulated value depends on the level of noise in the scattering zone. Once the crystalline intensities are eliminated, the background comprising air and incoherent scattering is estimated according to the method of Steenstrup (1981), who presented a numerical procedure involving an orthogonal polynomial for extracting the background from measured spectra when the independent character of component scattering remains valid. For a weak reflection this correction is essential, since the contribution of incoherent scattering may become comparable to the reflection intensity. After the crystalline-phase intensity is separated, the method uses integrated intensities over several reflection zones having contributions from component phases; hence overlapping lines are not problematic. The observed integrated intensity when converted to electron unit scale will represent the cumulated intensity due to different volume concentrations of the phases multiplied by their intensities for the total number of unit cells per unit volume. The observed integrated intensity over a reflection zone can then be expressed as a linear combination of simulated intensities arising from the crystal structure of the contributing phases, the coefficient of the combination being the volume fraction of the crystalline components. Although theoretically a solution of this type of equation can be obtained in a straightforward manner, leading to the concentrations of individual crystalline phases, uncertainty arises when the contribution of a distinct reflection to the observed intensity is very low and lies within the error limit of estimation. In the present paper, a method is described by which such difficulty can be overcome.

2. Theory

2.1. *Amorphous-phase analysis*

The pattern analysis technique has been developed for obtaining the consistent concentration factor of the crystalline matter as a ratio of crystalline integrated intensity to the total intensity in different diffraction zones of measurements. Mathematically, the concentration C of the crystalline part is given by

$$C = \int_0^\infty s^2 I_c(s)\, \mathrm{d}s \bigg/ \int_0^\infty s^2 I_s(s)\, \mathrm{d}s \tag{1}$$

where I_s is the intensity of coherent X-ray scattering at a point $s = 2\sin\theta/\lambda$ in the spectrum, and $I_c(s)$ is the contribution of the crystalline intensity at the same point. The integral of these intensities over the entire reciprocal zone is given by

$$\int_0^\infty I(s)\, \mathrm{d}v_s = 4\pi \int_0^\infty s^2 I(s)\, \mathrm{d}s \tag{2}$$

and

$$\int_0^\infty I_c(s)\, \mathrm{d}v = 4\pi \int_0^\infty s^2 I_c(s)\, \mathrm{d}s. \tag{3}$$

The procedure determines the lowest data points in each quarter degree of span of a five degree section. Each point is compared with the previous accepted minimum data point according to the condition

$$Y_A + \mathrm{YSIG}\sigma(Y_A) \geq Y_B - \mathrm{YSIG}\sigma(Y_B) \tag{4}$$

where Y_A and Y_B are two successive minimum point counts (counts s^{-1}) at locations A and B, respectively. YSIG, a constant value, is the standard deviation of the minimum data points obtained at the tail of peaks where the intensity is supposed to remain constant. The stipulated value chosen for YSIG varies between 1.5 and 1.7. $\sigma(Y_x)$ is the standard deviation of the point, given by

$$\sigma(Y_x) = [(Y_x)/(\text{counting time})]^{1/2}.$$

If condition (4) is not satisfied, the accepted minimum at A remains as the current acceptable minimum at B for the next quarter-degree segment.

The elimination of the estimated background intensity leaves only the crystalline intensity. The remaining intensities have contributions due only to glass/amorphous/air/incoherent scattering and thermal diffuse scattering (TDS). The incoherent TDS and air scattering are of separate origin. Thus, it is possible to make the polynomial fit of the background. The background at any 2θ is given by

$$Y(i) = \sum_{j=1}^n C_j P_j(i) \tag{5}$$

where n is the number of independant polynomials. The orthogonality condition of the set of polynomials imposes certain boundary conditions. With their help, a linearized fit of the background is possible. A numerical procedure using orthogonal polynomials has been used by Steenstrup (1981) for extracting the backgrounds in measured spectra. Elimination of background leaves only the amorphous/glassy scattering.

2.2. *Crystalline-phase analysis*

Let there be m crystalline phases present in the material and n phase reflection intensities under consideration. Then

$$\sum_{i=1}^{n}\sum_{j=1}^{m} C_{ij}X_j = \sum_{i=1}^{n} I_i \qquad (6)$$

where C_{ij} corresponds to the simulated intensity pattern with reflection index i and phase index j. X_j is the composition concentration column matrix and I_i is the observed intensity column matrix. This can be expressed for n atoms as

$$C_{ij} = [(\text{scale})^2/V^2]\{\sum f_n^j \exp[2\pi i(h_i^j x_n + k_i^j y_n + l_i^j z_n)]$$
$$\times \exp(-2B\sin^2\theta/\lambda^2)\}$$

where V is the volume of the unit cell, 2θ is the diffraction angle, f is the scattering factor for atom n, x, y, z are positional parameters of atom n, h, k, l are the reflection indices of reflection i and phase j, and B is the isotropic temperature factor for atom n. C_{ij} elements can be prepared theoretically, as in the present case. Alternatively, they can be prepared experimentally when a sample of 100% purity is available, as in the internal-standard method. There may be n sets of linear equations. If in any of the n sets of equations, a situation arises that for component k the phase reflection intensity is very low and falls within the limit of error of estimation of I_i, then equation i can be written as

$$\sum_{j=i\neq k} C_{ij}X_j < I_j.$$

Thus a set of inequalities can be set up and a solution can be sought to maximize the concentration of phases under consideration. Linear programming is a technique that yields an optimum solution for independent variables when they are subjected to a number of constraints. The function to be optimized is $Z = \sum_j A_j X_j$ and the applied constraints are

$$\sum_{j} C_{ij}X_j < I_i \qquad (7)$$

where C_{ij}, A_j and I_i are known quantities and X_j will optimize the function. A solution of these various sets of inequalities is obtained by applying the revised simplex method. The inequalities are transformed to equalities by introducing the slack variables. There may arise a number of solutions to the problem, but by using the optimizing criteria, *i.e.* improving the Z function in an iterative manner, the optimum solution is obtained.

In the present problem, a set of inequalities are set up and a solution is sought to maximize the concentration of phases under consideration. While seeking the solution we set some bound values for X as per our choice of estimation but within the limits $0 < X < 1$. From inspection of the X-ray diffraction pattern, if it is apparent that some of the phase intensities have feeble contributions to the total scattering intensities, then those intensity contributions need not be taken into account in the first instance. Then the inequalities can be solved by the above method. The weak phase intensities are taken into consideration after the contribution of the strong phase intensities to the total intensity has been ascertained. The consistency in the agreement between observed and calculated intensities is sought in this fashion from several combinations of intensities collected over several reflection zones. The optimum solution of independent variables obtained through linear programming can then quantify the low-concentration phases. Moreover, this method is helpful in qualitative analysis because each suspected phase is characterized by its presence probability ($X \neq 0$) when a reflection zone is considered in which the suspected crystalline phase contributes. Computer programs for estimation of glass as well as crystalline scattering have been written to be compatible with any computer systems supporting Fortran IV. The computer program used for the determination of phase concentrations, employing linear programming and revised simplex methods, follows the flowchart of the algorithm given by Kanti, Gupta & Manmohan (1982).

2.3. *Experimental testing of the method*

Before practical application of the model, the method was tested for some standard mixtures. The pure (>99.9%) powders used for preparing sample mixtures were TiO_2 (rutile), α-Al_2O_3, $CaCo_3$, ZnO and amorphous silica. All the raw materials had a grain size of about 1 μm. The compositions were chosen in order to test the method for mixtures containing or not containing the amorphous phase, with or without overlapping lines, and with or without large differences between the contents within a mixture. The results were obtained using the integrated intensities over several reflection zones and no deconvolution was needed to carry out the quantitative analysis.

2.4. *Practical application of the model*

Thermal endurance of ceramics as refractory support materials is closely related to the crystalline phases present. In the aluminosilicate refractory family, cordierite–α-alumina-based refractories are proposed to give a better performance when used as kiln furniture (Singer & Singer, 1963) up to a temperature of 1353 K. A cordierite body formed *in situ* with high-expansion grog as additive is likely to contain the following crystalline phases: (i) cordierite; (ii) mullite; (iii) α-Al_2O_3; (iv) cristobalite and quartz. Of these, the first three phases are relevant in enhancing the life cycle of kiln furniture, *vis-a-vis* their thermal endurance. So the prime importance of the estimation of phases (both qualitative and quantitative) lies in offering a technically attractive and cost-effective product. Glassy phase may

also be present. For quality control of the product, the present method for quantitative phase estimation is applied. The more crystalline phases are present, the better is the material.

X-ray powder diffraction data of the experimental ceramic powder were collected on a Siemens D500 X-ray diffractometer with a copper target, a curved graphite monochromator and a scintillation counter. The X-ray generator was operated at 35 kV and 25 mA. Each sample was packed into the hollow of a glass speciman holder with 0.5 mm depth, and a 10.0 × 8.0 mm surface was pressed flat using a glass slide. The intensity
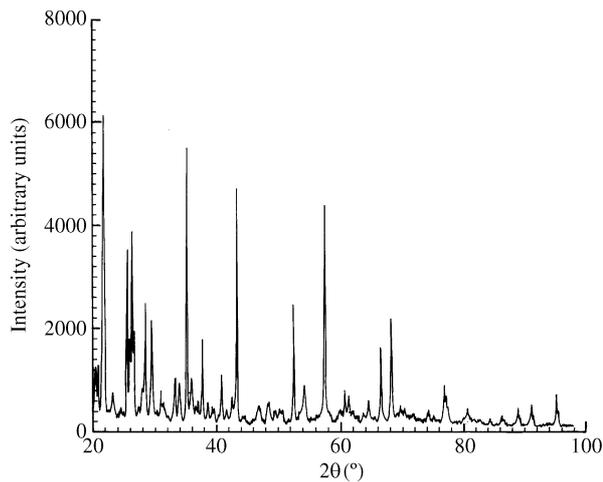

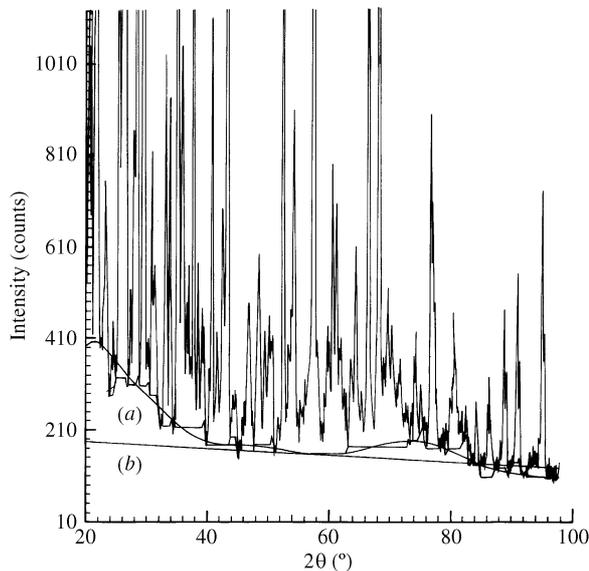Fig. 1. X-ray diffraction pattern of cordierite–mullite-based kiln furniture material.

Fig. 2. X-ray diffraction pattern of the experimental material showing (a) background intensity counts composed of air scattering, TDS and glass/amorphous scattering, and (b) background intensity counts composed only of air scattering and TDS.

Table 1. *Content (%) of crystalline/amorphous phases in the cordierite–mullite-based kiln furniture*

2θ (°)	Phase	Integrated intensity	Content (%)
54.5–97.75	Crystalline	1937	80.14
	Amorphous	480	19.86

profile was scanned using the step-scanning technique in a 2θ range from 20 to 100° with a step interval of 0.02° and a fixed counting time of 5 s for each step.

3. Results and discussion

Fig. 1 shows the XRD pattern of a sample as obtained from the diffractometer. The pattern shows the domination of crystalline phases in the material, although amorphous scattering seems to appear in a few diffraction zones. Elimination of background together with the glass/amorphous scattering has been done through comparison of slopes at two successive points of the intensity pattern over scattering angles at which both the crystalline and amorphous phases superimpose (Fig. 2). The stipulated value chosen for comparison of slopes at two successive points of the intensity pattern was 1.5 for the present calculation. Such a pattern analysis separates the crystalline part (Fig. 3) from the observed pattern. The residual scattering now comprises air and incoherent scattering together with the amorphous scattering. The contribution of air scattering and TDS to the background intensity is eliminated following the procedure of Steenstrup (1981); this leaves only the glass/amorphous scattering (Fig. 4). The estimated glass/amorphous scattering fitted with a polynominal of degree n ($n < 15$) gives the amorphous phase present in the material.

Table 1 shows the integrated intensities measured for crystalline and amorphous/glass contents present in the
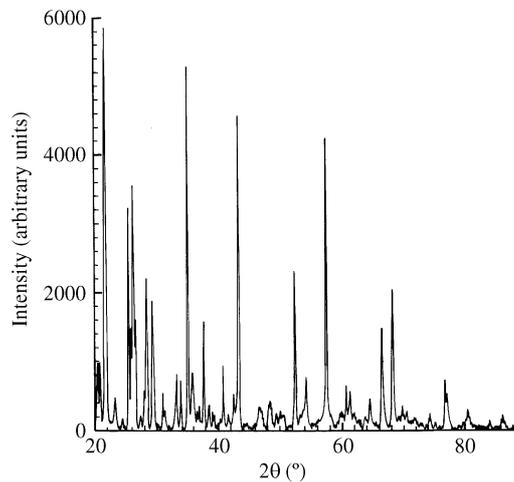

Fig. 3. X-ray diffraction pattern of the crystalline phase in the cordierite–mullite-based kiln furniture after subtraction of the amorphous part.

Table 2. *Volume fraction and weight fraction of crystalline phase present in the ceramic material under study*

Crystalline phases	Volume fraction (X_j)	Crystal density (g ml^{-1})	wt% of phases
Cordierite	9.0196	2.49	36.4659
Mullite	4.6955	3.13	23.8631
α-Al$_2$O$_3$	6.1082	4.0	39.6711
Cristobalite	–	2.33	–
α-Quartz	–	2.66	–
Total			100

Table 3. *Estimation of crystalline phase and amorphous phase in the ceramic material under study*

Oxide	wt% by chemical analysis	wt% per phase
α-Al$_2$O$_3$	50.03	50.102 (crystalline)
SiO$_2$	37.90	27.325 (crystalline)
		10.575 (amorphous)
MgO	3.63	3.63 (crystalline)
TiO$_2$	2.09	2.09 (amorphous)
CaO	2.30	2.30 (amorphous)
Fe$_2$O$_3$	2.19	2.19 (amorphous)
K$_2$O	0.38	0.38 (amorphous)
Na$_2$O	0.22	0.22 (amorphous)
LOI†	1.25	
Total		81.057 (crystalline)
		18.943 (amorphous)

† Loss on ignition.

Table 4. *Agreement between observed and total estimated intensity*

2θ range (°)	Estimated intensity, I_{calc}	Observed intensity, I_{obs}
25.05–26.95	129.543	131.00
32.20–34.40	34.60	30.00
34.4–39.90	147.00	143.00
40.05–43.85	91.282	92.00
47.85–51.10	31.30	31.30

material over a reflection zone as mentioned above. Once the intensity profile due to crystalline components is established, different angular zones are chosen for which the quantitative phase analysis for the crystalline components is performed. The observed intensity pattern is compared to the calculated intensity pattern obtained from the crystallographic data (Wyckoff, 1948) and is amended in accord with more recent unpublished work for better agreement. Isotropic temperature factors were determined for the system. The set of equations satisfying relation (7) for different 2θ ranges is constructed with the simulated intensity values for
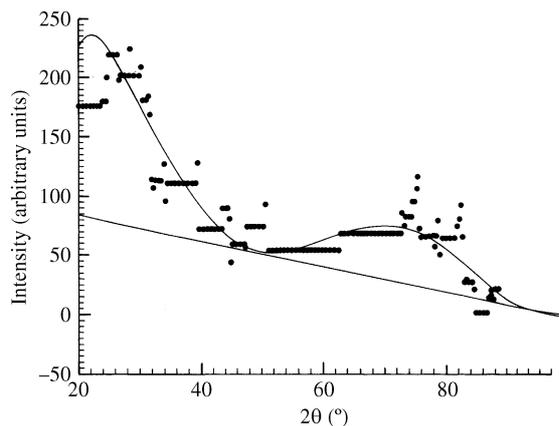

Fig. 4. Amorphous scattering in the 54.5–97.75° (2θ) diffraction zone with polynomial fit of degree n ($n = 10$).

different phases in that zone. The volume concentrations of different phases as calculated are listed in Table 2. The wt% of each different phase was calculated considering the crystal density. Table 2 shows the wt% of each different phase when the quantitative analysis is based on 100% crystalline components. The wt% of each of the different oxides in the above crystalline phases were calculated assuming that α-alumina does not contribute to glass formation. The assumption seems to be reasonable as Al$_2$O$_3$ does not show any phase transformation. Al$_2$O$_3$ may form a noncrystalline phase but the heat treatment was done exactly at 1533 K, at which Al$_2$O$_3$ does not readily form the glassy phase. Based on the crystalline composition, the total chemical composition and the glass component present, the wt% of each crystalline/amorphous phase was calculated; results are listed in Table 3. Since MgO and Al$_2$O$_3$ do not form amorphous phases, we can assume that their oxides are totally consumed in the crystalline phases and subsequently they will not contribute to the total amorphous scattering. The wt% of these oxides in the crystalline phases will be the same as found by chemical analysis. The situation differs for SiO$_2$; a part of it is incorporated in the amorphous phase, which amounts to 10.575 wt%, and the rest is used to form crystalline phases, like mullite and cordierite. As evident from Fig. 4, the amorphous-silica pattern consists of a main hump at $2\theta = 21.5°$ and a broad minor hump at $2\theta = 75°$ (Cu $K\alpha$ radiation). The amorphous-silica pattern is unlikely to be changed by the addition of small amounts of other amorphous oxides, such as TiO$_2$, Fe$_2$O$_3$, CaO, K$_2$O and Na$_2$O, as found by chemical analysis. These other oxides mainly contribute to amorphous scattering and contribute to 8.3 wt% of the total oxides. Table 4 shows the agreement between the estimated and observed intensity for different 2θ zones as obtained by the linear programming technique.

4. Conclusions

Quantitative estimation of phases of a complex ceramic system is possible by using several numerical techniques provided that the crystal structures of the individual phases are known. In my opinion, the perfection of the method depends on the quality of the measurements and on computational techniques. If the primary data do not have large systematic errors, the method becomes acceptable (relative error ±5%). The accuracy of the present procedure will primarily depend on the accuracy of the determination of integrated intensity data and hence preferred orientation will become an additional problem. If intensity data of reflections of moderate intensity are used by choosing the optimum 2θ range, the weight fraction can be measured accurately by the present procedure, even when the sample has preferred orientation. The major advantage of this method over other methods lies in the fact that due to the consideration of intensity profiles over a limited angular zone covering a peak area, errors introduced in intensity measurements due to variation of particle size, thermal motion of ions, etc., are eliminated. This method, however, has limitations. If the sample contains two or more phases having widely different linear absorption coefficients, the situation will become very much more complicated in the sense that the diffraction spectra will result from the penetration of the incident beam throughout the sample in the case of a phase having a low absorption coefficient, whereas the diffraction is due to the surface only in the case of a phase having a high linear absorption coefficient. A compromise may be possible by making a proper choice of X-ray radiation. The proposed inequality model based on linear programming can be applied in qualitative X-ray analysis; a step by step procedure allows the selection of the more probable components present in the mixture by the appearance and disappearance of the value of X in the solution. For the present study, the error in the intensity measurement is minimized by taking the different diffraction zones and applying the inequality model for the solution of the phase concentration through the linear programming technique.

In the present investigation, results of quantitative estimation of phases corroborated the chemical analysis data as well as the X-ray diffraction pattern. Inspite of having 19 wt% of the amorphous phase, which is found in commercially available raw materials, it is possible to develop cordierite–mullite-based kiln furniture suitable for use up to 1553 K.

References

Chung, F. H. (1974a). J. Appl. Cryst. **7**, 519–525.
Chung, F. H. (1974b). J. Appl. Cryst. **7**, 526–531.
Chung, F. H. (1975). J. Appl. Cryst. **8**, 17–19.
Clark, N. H. & Preston, R. J. (1974). X-ray Spectrom. **3**, 21–25.
Grzeta, B. & Popovic, S. (1985). J. Appl. Cryst. **18**, 80–84.
Hill, R. J. & Howard, C. J. (1987). J. Appl. Cryst. **20**, 467–474.
Karti, S., Gupta, P. K. & Manmohan (1982). Operational Research, ch. V, pp. 226–230. New Delhi: Schand.
Klug, H. P. & Alexander, L. E. (1974). X-ray Diffraction Procedure for Polycrystalline and Amorphous Materials. New York: John Wiley.
Lennox, D. H. (1957). Anal. Chem. **29**, 767–770.
Mallory, C. L. & Snyder, R. L. (1980). Accuracy in Powder Diffraction. NBS Special Publication 567, pp. 95–110. Gaithersburg: National Bureau of Standards.
Popovic, S. & Grzeta-Plenkovic, B. (1979). J. Appl. Cryst. **12**, 205–208.
Popovic, S., Grzeta-Plenkovic, B. & Balic-Zunic, T. (1983). J. Appl. Cryst. **16**, 505–507.
Rius, J. (1987). J. Appl. Cryst. **20**, 457–460.
Singer, F. & Singer, S. S. (1963). Industrial Ceramics, ch. 11, pp. 954–956. London: Chapman & Hall.
Smith, D. K., Johnson, G. G. Jr, Kelton, M. J. & Anderson, C. A. (1989). Adv. X-ray Anal. **32**, 489–406.
Snyder, R. L. (1979). Adv. X-ray Anal. **22**, 121–132.
Snyder, R. L. (1983). Adv. X-ray Anal. **26**, 1–11.
Steenstrup, S. (1981). J. Appl. Cryst. **14**, 226–229.
Toraya, H., Yoshimura, M. & Somiya, S. (1984). J. Am. Ceram. Soc. **67**, C191–C121.
Wang, H. (1988). Powder Diffr. **3**, 165–167.
Werner, P. E., Salom, S. & Malmros, G. (1979). J. Appl. Cryst. **12**, 107–109.
Zangalis, K. (1991). J. Appl. Cryst. **24**, 197–202.
Zevin, L. S. (1977). J. Appl. Cryst. **10**, 147–150.