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Rietveld refinement of $ZrSiO_4$: Application of a phenomenological model of anisotropic peak width

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Abstract. The anisotropic broadening of $ZrSiO_4$ sample is modelled using the Stephens's phenomenological model for anisotropic line broadening and the three dimensional strain distribution in the sample is plotted. The microstructural parameters like domain size and dislocation density are estimated using the variance method.

Introduction

Line broadening is a well known feature of the diffraction profiles from polycrystalline samples. The phenomenological line-broadening theory of plastically deformed metals and alloys was developed more than 50 years ago [1]. It identifies that besides the instrumental contribution there are two main types of broadening: the size and the strain components. The former one depends on the finite size of the coherent diffraction domains and the latter is caused by any lattice imperfection (point, line or plane defects). There are many approaches of line profile analysis to extract the size and strain information from the line broadening.

The Full Width at Half Maxima (FWHM) and the integral breadth (area of the peak divided by the maximum intensity) are often considered as a measure of the broadening of the diffraction peaks. If the FWHM of the reflections of a line profile increases more or less monotonically with the diffraction angle in a θ/2θ scan the broadening is called isotropic otherwise it is termed as anisotropic peak broadening.

This anisotropic line shape broadening is frequently observed in powder diffraction pattern and creates a serious difficulty for the Rietveld analysis.

The anisotropic peak broadening may arise due to variety of reasons like anisotropic size broadening, stacking fault or anisotropic strain broadening. In simple case the strain broadening is isotropic and the FWHM is proportional to *tan*θ i.e.

$$\Gamma_{2\theta} = X \tan\theta \qquad (1)$$

This relation does not hold well for anisotropic strain broadening. Anisotropic strain distribution has been introduced by several authors [2] to model the anisotropic peak broadening.

Stephens model

Recently P. W. Stephens [3] proposed a phenomenological model of anisotropic broadening in powder diffraction considering the distribution of lattice metric parameters within the sample. In this model each crystallite is regarded as having its own lattice parameters, with multidimensional distribution throughout the powder sample. The width of each reflection can be expressed in terms of moments of this distribution, which leads naturally to parameters that can be varied to achieve optimal fits. Further description of the model can be found in the Stephens paper [3].

Let d^*_{hkl} be the inverse of the *d* spacing of the (*hkl*) reflection. Then d^{*2} is bilinear in the Miller indices and so can be expanded in terms related to the covariances of the distribution of the lattice metrics. In the general case this leads to an expression in which the variance of d^{*2} is a sum of 15 different combinations of Miller indices in the fourth order. Imposing the symmetry of the tetragonal lattice reduces the number of independent terms to the following four:

$$S^2 = S_{400}(h^4 + k^4) + S_{004}l^4 + 3.S_{202}(h^2l^2 + k^2l^2) + 3S_{220}h^2k^2 \qquad (2)$$

The anisotropic strain contribution to the angular width in 2θ of the reflection is given by

$$\delta 2\theta = (360/\pi)(\delta d/d)\tan\theta\,, \qquad (3)$$

where

$$\delta d/d = \pi(S^2)^{1/2}/18000d^*_{hkl} \qquad (4)$$

The Rietveld refinement package GSAS [4] has implemented Stephens's model to account for strong anisotropy in the half widths of reflections. Using this package the three dimensional strain field within the material can be reconstructed.

Experiment and data analysis

Zircon ($ZrSiO_4$) is one of the technologically important oxide ceramic materials known for its high refractoriness and chemical stability. It shows excellent thermal shock resistance as a result of its very low thermal expansion coefficient (5.3×10^{-6} K^{-1} from 25 to 1500 °C) and low heat conductivity coefficient of 6.1 W m^{-1} K^{-1} at 100 °C and 4.0 W m^{-1} K^{-1} at 1500 °C. It possesses a tetragonal crystal structure. Zircon powders were prepared from tetraethoxysilane and zirconyl nitrate hydrate mixed in water in a stoichiometric ratio. X-ray diffraction pattern of zircon powder sample was recorded using a Philips PW3710 diffractometer with CuKα radiation (40kV, 40mA). Sample was scanned in a step-scan mode (0.02°/step) over the angular range (2θ) of 5° to 150°. X-ray diffraction data were collected for 3 sec at each step.

Figure 1 shows the variation of the observed FWHM of the peaks with the peak angles. The anisotropy of the width of the peaks is clear from this figure. We have used GSAS to carry out Rietveld refinement of the line profiles of the Zircon. The profiles have been fitted without and with using the Stephens model. It is found that the incorporation of Ste phens's model improved the quality of the fit. A typical result of the Rietveld refinement (with Stephens's model) is shown in the Figure 2. The fitting parameter in this case was R_{wp}=4.65%.

Without Stephen's model the fitting parameter was R_{wp}=8.63%. This suggests that the Stephens model fit the data very well.

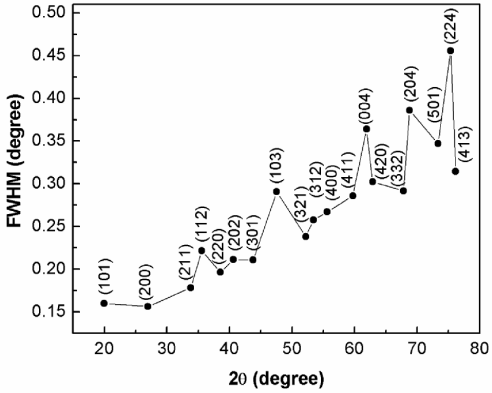

Figure 1. Variation of FWHM with 2θ

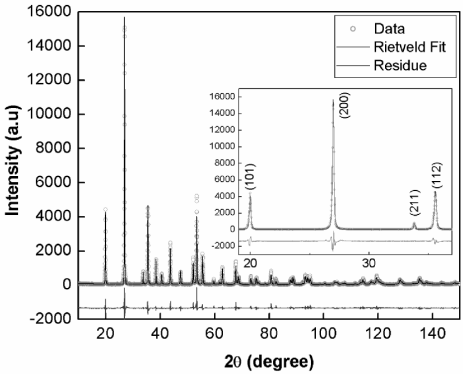

Figure 2. Result of the Rietveld refinement

We have used S_{hkl} as the free parameters to obtain the best fit between the model and the experiment. The anisotropic broadening has both Gaussian and Lorentzian components. Therefore we have included both to get an acceptable fit of the diffraction data.
The graphical representation of the three-dimensional strain distribution can be obtained using the refined values of the S_{hkl}. The three-dimensional strain distribution plot of the studied Zircon sample is shown in Figure 3.

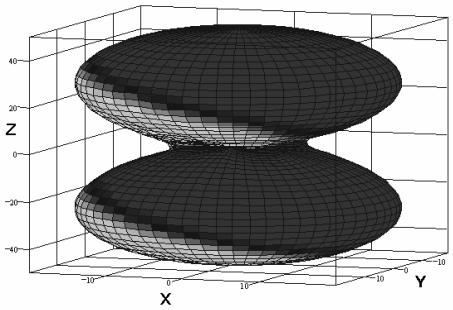

Figure 3. Three-dimensional strain distribution of $ZrSiO_4$. The x axis is horizontal, the z axis is vertical and the y axis out of the plane of the paper. The scale is in δd/d 10^{-6} strain.

Microstructural analysis

X-ray diffraction (XRD) is a powerful tool to characterize the microstructure of the polycrystalline samples. XRD gives the microstructure of the sample in a statistical sense. There are various methods to determine the microstructural parameters like domain size, microstrain, dislocation density from the broadened XRD peaks. We have used the *variance method* developed by Groma [5] and further modified by Borbely and Groma [6] to characterize the microstructure of the zircon sample. In the variance method one computes the k-th order restricted moment

$$M_k(q') = \frac{\int_{-q'}^{q'} q^k I(q)dq}{\int_{-\infty}^{\infty} I(q)dq} \tag{5}$$

Here *I(q)* is the intensity distribution as a function of $q = 2/\lambda[sin\theta - sin\theta_0]$, where λ is the wavelength of the X-radiation, θ is half of the diffraction angle and θ_0 is the Bragg angle. The second and the fourth order moments have the forms:

$$M_2(q) = \frac{1}{\pi^2 \varepsilon_F} q - \frac{L}{4\pi^2 K^2 \varepsilon_F^2} + \frac{\Lambda \langle \rho \rangle \ln(q/q_0)}{2\pi^2} \tag{6}$$

and

$$\frac{M_4(q)}{q^2} = \frac{1}{3\pi^2 \varepsilon_F} q + \frac{\Lambda \langle \rho \rangle}{4\pi^2} + \frac{3\Lambda^2 \langle \rho^2 \rangle}{4\pi^2 q^2} \ln^2(q/q_1) \tag{7}$$

respectively, where K is the Scherrer constant, L is the so called taper parameter depending on the rate of decrease of the cross sectional area of the crystallites. ε_F is the area weighted domain size measured in the direction of the diffraction vector. <ρ> is the average disloca-

tion density and $<\rho^2>$ is the average of the square of the dislocation density. q_0 and q_1 are fitting parameters not interpreted physically. Λ is a geometrical constant describing the strength of dislocation contrast and its value is of the order of one.
We have used the (200) peak (this is the main peak of $ZrSiO_4$) and the variance method to estimate the microstructural parameters of the sample. Figure 4 (a) shows the (200) peak. Figure 4 (b) and (c) respectively show the variation of the second order and forth order moment of the peak. The large q regions of the curves are fitted with equation (6) and (7). The values of the domain size and the dislocation density obtained from the fitting are: from $M_2(q)$, domain size=131Å and dislocation density= 5.3×10^{15} m^{-2}, from $M_4(q)$, domain size=135Å and dislocation density=4.8×10^{15} m^{-2}.

Conclusion

We have used Stephens's phenomenological model of anisotropic strain broadening to model the anisotropic broadening of the zircon sample. The Stephens model is found to very well fit the data. The microstructural parameters (domain size and dislocation density) are obtained using the variance method. The dislocation density in the sample is very high.

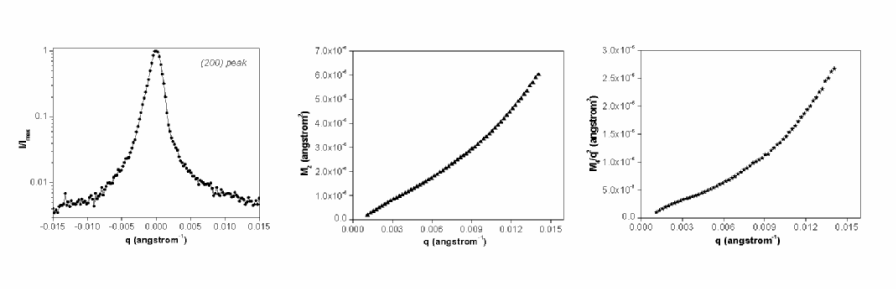

Figure 4. (a) (200) peak (b) variation of the second moment (c) variation of the fourth moment

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