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A new method for measuring the degree of preferred orientation in bulk textured $YBa_2Cu_3O_x$

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Abstract

A new technique for estimating the preferred orientation in bulk textured $YBa_2Cu_3O_x$ and related structures is developed. Conventional X-ray diffraction patterns, as measured from the bulk samples, and the March function in a program for refinement of the structure are used in order to generate a calibration curve for measuring the degree of preferred orientation in such samples without getting into the complication of pole-figure analysis. It is found that the values of the March coefficient G for a series of purposefully textured bulk samples range from 0.62 to 0.17.

Keywords: grain alignment (texturing); bulk textured superconductors

Powder diffractometry (X-ray or neutron) combined with a Rietveld code [1] is routinely used for structure analysis studies of polycrystalline high temperature superconductors (HTSC). As part of the refinement procedure, all codes include a function to correct the measured intensities for the lack of randomness of the orientation of the crystallites, or preferred orientation (PO). PO can be a major problem in the structural studies of HTSC, because of their layered structures, but it is highly desirable for applications purposes, since it increases the critical current J_c that a specimen can carry while in the superconducting state; therefore an evaluation of the degree of PO is a quite useful part of the characterization of textured samples. The classic way to measure the degree of PO is by pole figure analysis [2], which is a complicated method and requires special equipment, while the majority of the papers in the literature obtain rather a rough estimate of the amount of the PO from visual comparisons of the X-ray diffractograms of the textured specimen with a powdered one or by analyzing scanning electron microscopy (SEM) photographs. In this work we propose a method of characterization that provides a quantitative measure of PO for the case of single-pole oriented, bulk textured samples of HTSC without getting into the complication of the pole figure analysis.

The programs for structure refinement normally include the March–Dollase function [3,4] as a correction of the measured intensities for any remaining PO in carefully powdered samples. It is written as

$$I_{\text{corr}} = I_{\text{obs}}\left(G^2\cos^2 a_k + \frac{1}{G}\sin^2 a_k\right)^{-3/2}, \qquad (1)$$

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where I_{corr} is the intensity as corrected for PO, I_{obs} is the measured intensity, a_k is the acute angle between the scattering vector of reflection k and the orientation direction, and G is the March coefficient that ranges from 0 to 1, where zero refers to a 100% preferentially oriented crystallites in a specimen, and 1 refers to a completely random orientation of its crystallites. In the standard use of this correction function, the refinable coefficient G is set equal to 1, assuming a completely random orientation of the crystallites in the powdered sample, and then it is refined to correct for any remaining PO. Judson et al. [5] used the above function in a Rietveld program to study the PO in films of $YBa_2Cu_3O_{7-x}$ deposited by CVD on single crystal and polycrystalline substrates. They analyzed the PO of their films with pole figures, and then they compared experimental θ–2θ X-ray powder diffraction patterns with those calculated for the material using the March–Dollase function in a Rietveld code. They concluded that the March function serves as excellent indicator of PO in the case of strong single-pole oriented films of $YBa_2Cu_3O_{7-x}$.

Recently, von Dreele [6] has introduced a full implementation of the generalized spherical harmonics description of texture into the Rietveld refinement program GSAS [7], and has tested it in neutron time-of-flight (TOF) data of a standard calcite sample against pole figures measurements. Although it is clear that more complete representations of PO can be included in a Rietveld analysis, the one-parameter March-Dollase function seems to work well for the materials in which we are interested [5].

In the present work, we will use the coefficient G of the March-Dollase function in a Rietveld code in order to generate a calibration curve for estimating the degree of PO in bulk textured $YBa_2Cu_3O_x$ from conventional X-ray diffractograms. First we calculate a series of canonical X-ray diffraction patterns using the Win-Rietveld program [8] with the input structural parameters, other than the PO, taken from the combined refinement of X-ray and neutron powder diffraction data on $YBa_2Cu_3O_{7-x}$ by Williams et al. [9]. The PO is introduced into these patterns by varying the coefficient G from 0.05 to 1 in steps of 0.05. Figs. 1a and 1b show the calculated diffraction patterns for $G = 0.3$, and 0.2 in the angle range 20° to 60°, where the strongest (00l) Bragg reflections

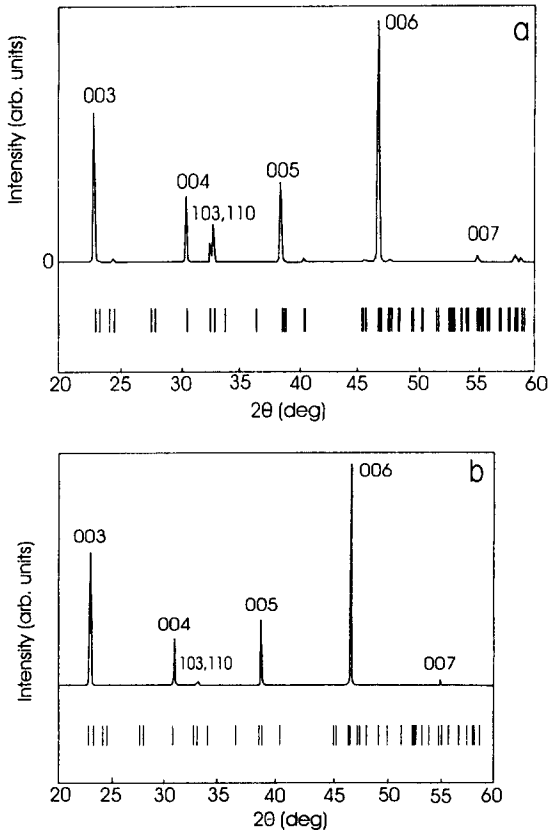

Fig. 1. Calculated diffraction patterns for $YBa_2Cu_3O_{7-x}$ using the Win-Rietveld program (Ref. [8]) for: (a) $G = 0.30$, and (b) $G = 0.20$. Tick marks represent the calculated positions of the allowed Bragg reflections.

appear. The (006) peak is the strongest among the (00l) reflections in textured samples of this material, and so the ratios of the intensities I_{006} to the intensities I_{110} of the characteristic Bragg peak (110) were calculated, and plotted in Fig. 2 versus the March coefficient G. A least squares fit to the data yields the equation

$$I_{006}/I_{110} = 0.10953G^{(-4.701)}, \quad (2)$$

which can be considered as a relation between the relative intensity of the (006) Bragg peak and the degree of PO. We will use this relation to estimate the PO in a series of bulk, c-axis, highly textured samples, and demonstrate that the results are reasonable.

The required textured samples with various degrees of PO were prepared either by the solid state

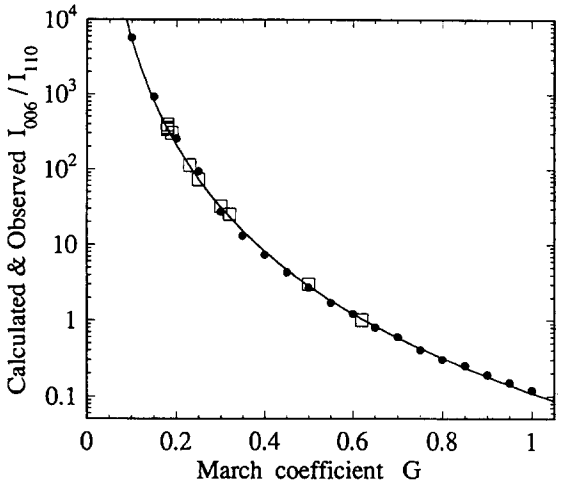

Fig. 2. The calculated intensity ratios $(I_{006}/I_{110})_{calc}$ as a function of the March coefficient G for $YBa_2Cu_3O_{7-x}$. The measured intensity ratios $(I_{006}/I_{110})_{obs,norm}$, marked as open squares, are scaled to the standard, and fitted to the curve for the calculated ones. The observed values of the March coefficient, G_{obs}, are deduced from this curve.

reaction method, or by a variation of the melt texture technique that we had developed [10]. The samples S1 to S5, listed in Table 1, were prepared from high purity powders of Y_2O_3, $BaCO_3$, and CuO. They are pellets ~ 12 mm in diameter and ~ 1.5 mm thick, and were produced by repeating the processing cycles [11] of the solid state reaction method; one processing cycle is comprised of one grinding, pressing, overnight sintering at 950°C in oxygen, and annealing at 480°C for 6 h. The samples M1 to M5 of the Table 1 were either pellets ~ 12 mm in diameter and ~ 2 mm thick, or bars ~ 15 mm long, and were synthesized by a variation of the melt-textured technique; in this method, named PAMP (Partially Aligned Melt Processing) [10], the sintered, already partially bulk textured pellets of $YBa_2Cu_3O_x$ are used as precursors, instead of randomly oriented powders. They are placed in an alumina boat next to a thermocouple to monitor the temperature, and are given the melt-textured growth processing in a computer controlled tube furnace with a preset temperature profile. A programmable step motor is connected to the boat for pulling it through the furnace. The processing time and the cooling rate dT/dt are varied, resulting in specimens with various degrees of PO. The transition temperatures were determined from AC magnetic susceptibility measurements, and are ~ 90 K for the samples S1 to S5, and ~ 88 K for the melt-textured samples M1 to M5. Scanning Electron Microscopy (SEM) studies showed that the sintered samples had an average crystallite size of ~ 30 μm in length and ~ 6 μm in width, whereas the crystallites in the melt textured samples become about 300 μm long on the average.

Table 1
Bulk textured samples of $YBa_2Cu_3O_x$: M5 to M1 are the melt textured samples, S5 to S1 are the sintered ones. $(I_{006}/I_{110})_{obs}$ are the observed intensity ratios of the (006) and (110) Bragg peaks. They are scaled to the standard of Ref. [12], and listed as $(I_{006}/I_{110})_{obs,norm}$. G_{obs} are the observed values for the March coefficient

Sample	$(I_{006}/I_{110})_{obs}$	$(I_{006}/I_{110})_{obs,norm}$	G_{obs}
M5	70	391	0.17
M4	65	359	0.18
M3	61	340	0.18
M2	54	300	0.19
M1	20	113	0.23
S5	13	73	0.25
S4	5.7	32	0.30
S3	4.5	25	0.32
S2	0.54	3	0.50
S1	0.20	1	0.62

Conventional diffraction patterns from the samples, as bulk textured pellets or bars, were measured with an X-ray powder diffractometer (Siemens D5000) with a monochromator and CuKα radiation. The observed relative intensities of the (006) Bragg peak, measured as peak heights, are listed in Table 1 as $(I_{006}/I_{110})_{obs}$. Figs. 3a and 3b show the diffractograms for the samples S4 and M4 in the same angle range as the calculated patterns of Fig. 1. In order to compare intensities from textured and powdered samples, and evaluate the degree of PO, the $(I_{006}/I_{110})_{obs}$ were normalized to the relative intensity of the standard powdered sample [12] and are listed in Table 1 as $(I_{006}/I_{110})_{obs,norm}$. Then they were fitted in the curve of the Fig. 2, where they are marked as open squares, and the observed values of the coefficient G were deduced; they are listed in Table 1 as G_{obs}.

To confirm that these G_{obs} measure the degree of PO in the specimens, we refined the X-ray pattern of each sample, entering the corresponding G_{obs} as

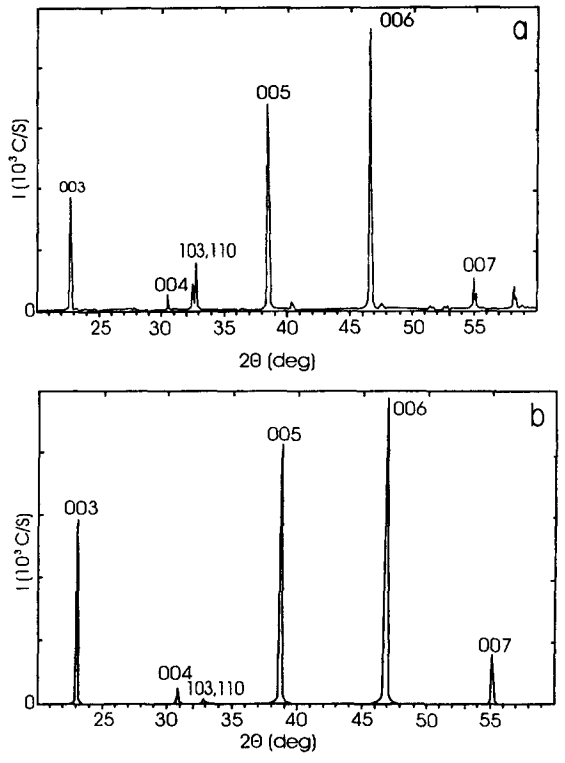

Fig. 3. The observed X-ray diffraction patterns for two of the bulk textured samples: (a) the sintered S4 with $G_{obs} = 0.30$, and (b) the melt textured M4 with $G_{obs} = 0.18$. Miller indices are marked for the characteristic and the 00l peaks.

input for the March coefficient (instead of 1). Initially, G_{obs} was kept fixed and all the other adjustable parameters were refined. At various stages of converged refinements G_{obs} was made the only refinable parameter. The quality of the refinement would not change, and the refined values of the March coefficient, $G_{obs,ref}$ were approximately the same as the observed values G_{obs}. For example, for the case of the sample S4 with $G_{obs} = 0.30$, at the refining stage where the goodness of fit S (defined as the ratio of the residual weighted pattern R_{wp} to the expected residual R_{exp}) was equal to 2.73, all the refinable parameters were turned off, and G_{obs} was turned on as the only refinable parameter. The program was then converged with $S = 2.49$, essentially meaning same quality of refinement, and $G_{obs,ref} = 0.321$ ($\sigma = 0.0022$), which is in good agreement with the measured value G_{obs}, especially for practical applications.

In conclusion, we have shown that the degree of PO in single-pole, c-axis oriented bulk textured YBa_2Cu_3O can be measured by using conventional X-ray diffractograms, and the calibration curve of Fig. 2, generated from a Rietveld analysis program with the March coefficient G as the indicator of PO. The observed G's for sintered bulk textured samples do not go below 0.25, whereas melt textured specimens are highly oriented with G_{obs} ranging from 0.23 to 0.17. Similar calibration curves can be generated for all types of materials that show single-pole oriented preferred orientation. Studies of the correlation between the degree of PO, as measured by G, and other physical properties of bulk highly textured samples are in progress.

Although the March–Dollase function includes only one coefficient to describe a three dimensional problem, this practice provides a reasonable good estimate of the degree of PO for the case of the strong single-pole oriented HTSC studied in this paper. See however Ref. [6] for a more complete description of PO.

Acknowledgements

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