

# Determination of grain size and lattice distortions in ground $\text{YBa}_2\text{Cu}_3\text{O}_7$

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Grain size and lattice distortions as a function of milling time have been determined using X-ray peak broadening analysis and Brunauer–Emmett–Teller (BET) measurements. The grain size decreases from 0.22  $\mu\text{m}$  in unmilled samples to 0.06  $\mu\text{m}$  at 25 h milling time. Prolonged milling produced no further decrease of the grain size. The unmilled powder contained lattice distortions of 0.06%. During the first 25 h of milling only small changes of the lattice distortions occurred; longer milling times resulted in a rapid increase of the lattice distortions. At 47 h of milling, the lattice distortions had increased to about 0.11%. The results obtained by BET measurements agreed well with those obtained by X-ray analysis. No anisotropic grain size decrease was indicated during milling.

## 1. Introduction

High-temperature superconductors were mostly prepared by conventional sintering techniques during the first years following their discovery. The need for low processing temperatures, for compatibility with semiconductors and easily reduced metals, and for relatively low melting temperatures has more recently led to the use of a variety of novel metallurgical and ceramic processing techniques. To circumvent the problem of brittleness and thereby make them more useful for practical applications, the superconductors have been manufactured as composites consisting of fibres, tapes or wires [1, 2]. Growth of thin films on substrates has proved successful to increase the transport critical currents of the superconductors.

Regardless of the preparation method used, process control is an essential feature. It is very important that the starting materials possess a high reaction ability, leading to lower processing temperatures and times which reduces the possibility of unwanted chemical reactions that can occur at high temperatures. The milling of the powder is an important step to enhance the reaction ability of superconductors. The milling leads to several changes of the powder properties, such as smaller grain sizes, lattice distortions and stacking faults. Reduction of the grain size increases the surface energy, while introduction of lattice distortions mechanically activates the powder. It can be assumed that to achieve a fully dense body after sintering, the particle size should be small and the grains should contain a large amount of stored energy [3–6]. The increase in internal energy is often larger than the increase in surface energy. It is thus important to obtain knowledge of grain size and of lattice distortions. According to the literature, [7] stacking faults play only a minor role in ceramic materials.

The most common way to study the sintering ability has been by practical sintering experiments, which are

quite tedious and rather expensive. These drawbacks can be evaded by using X-ray powder peak broadening analysis [3]. X-ray analysis is one of the few methods available for the separation of the grain size and lattice distortions.

Both crystallite size and lattice distortions in the crystals cause broadening of the X-ray peaks [8]. The basis for a separation of the contributions of crystallite size and lattice distortions is the different angle dependence of the two broadening effects. Several (at least two) diffraction lines must therefore be measured. The X-ray method has its optimum sensitivity with mean grain sizes less than about 0.3  $\mu\text{m}$ . Larger grain sizes are measured by other methods such as sieving, sedimentation, centrifugal techniques etc. [9]. Another convenient method available is the Brunauer–Emmett–Teller (BET) technique. The BET apparatus determines the total specific area of the powder by calculating the amount of nitrogen adsorbed on the surface. This method thus gives the powder grain size, while the X-ray method gives the crystallite size. Depending on whether agglomeration of the powder occurs and/or formation of domains within the grain takes place, different values of the grain size are obtained by BET and by X-ray diffraction (XRD). The assumptions that have to be made when converting the specific area to grain size are also sources of error. The BET values are usually larger than those obtained by X-ray analysis, and the two analyses should be used as complementary methods. Supplementary morphological studies can further broaden understanding of the spatial arrangement of the materials [3].

The aim of the present investigation was to study the crystallite size and lattice distortions by  $\text{YBa}_2\text{Cu}_3\text{O}_7$  powder as a function of milling time, using XRD and BET measurements, to gain knowledge of the sintering properties of the superconductor.

## 2. Experimental procedure

### 2.1. Materials preparation

The superconductor was prepared from  $Y_2O_3$  (99.9%, CERAC Inc., Milwaukee, Wisconsin, USA),  $BaCO_3$  (99.999%, CERAC) and  $CuO$  (99.9%, CERAC). The powder was reaction sintered in air at 930 °C for 15 h. After crushing and grinding, the powder was re-sintered at 930 °C for about 15 h. The final heat treatment was performed at 475 °C for 7 h under 1 atm oxygen pressure. A batch of 200 g was prepared, and 20 g were taken from the batch for the milling experiment. An XRD analysis showed that the sample contained single-phase  $YBa_2Cu_3O_7$  with the lattice parameters  $a = 0.38300$   $b = 0.38858$ ,  $c = 1.1674$  nm. Resistivity measurements revealed a transition temperature of 93 K.

The milling was performed using a planetary ball mill (Retsch PM4) equipped with a 50 ml zirconia grinding jar. Ten zirconia balls (diameter 10 mm) were used. The rotation speeds of the sun disc and the jar were 175 and 310 r.p.m. respectively. The powder was ground in 5 ml of alcohol (purity 99.5%) up to 47 h. Small amounts of powder were taken at various milling times for analysis. The lattice parameters and phase composition were determined by a Guinier–Hägg focusing XRD camera using  $CuK_{\alpha 1}$  radiation and silicon ( $a = 0.5431065$  nm [10]) as internal calibration standard. The positions and intensities of the diffraction peaks were measured using an automatic film scanner. The unit cell dimensions were refined by the least-squares method using the local program UNITCELL (B. Noläng, Institute of Chemistry, University of Uppsala). No contaminations from the grinding jar could be seen on the X-ray films.

### 2.2. Measurement of grain size and lattice distortions

The crystallite size and lattice distortions were investigated using an automatic X-ray powder diffractometer (STOE & CIE GmbH, Darmstadt) equipped with a linear position-sensitive detector covering an angular range of 4–7° depending on the distance from sample to detector. Compared with the scintillation counter, the position-sensitive detector supplies the same order of magnitude of the peak half width but has symmetrical profiles and much improved peak-to-background ratios, whereby the time gain is about a factor of 10. The apparatus was used in the transmission mode.

The data were collected by focused  $CuK_{\alpha 1}$  radiation using a step-scan mode with 0.01° in  $2\Theta$  per step. Three peaks were measured to allow the effects of crystallite size and lattice distortions to be separated.

The data of the peaks and measurement parameters are shown in Table I.

Squared Lorentz functions (Equation 1) were used to describe the peaks

$$y = y_0(1 - c_L(x - x_0/h)^2)^{-2} \quad (1)$$

where  $y_0$  = maximum intensity,  $x_0$  = peak position,  $h$  = half width, and  $c_L$  = constant. The full width at half maximum was measured. The data were corrected for instrumental broadening using a certified sample of  $LaB_6$  as standard reference material (SRM 660). The sample was purchased from the National Institute of Standards and Technology (NIST), Gaithersburg, USA. The instrumental broadening was 0.100° in  $2\Theta$  over the whole angular range investigated. The specific area was simultaneously determined using a BET apparatus.

## 3. Results and discussion

The relation between half width ( $B_D$ ), grain size ( $D$ ) and Bragg angle ( $\Theta$ ) is given by the Scherrer equation [11] (see Equation 2). It can be seen that a decrease in the grain size will increase the peak half width. The half width is also dependent on the Bragg angle according to the following expression

$$B_D = K\lambda/(D \cos \Theta) \quad (2)$$

where  $B_D$  = peak half width,  $K$  = shape factor,  $\lambda$  = X-ray wave length and  $\Theta$  = Bragg angle. An expression for the lattice distortion ( $\Delta d/d$ ) is obtained by differentiating the Bragg equation giving

$$B_d = 4\Delta d/d \tan \Theta \quad (3)$$

Several expressions exist to describe how the half widths of the two components,  $B_D$  and  $B_d$ , respectively, are combined to the total  $B$  values. The use of different expressions does not alter the relationship of individual values to one another. A relative comparison is therefore possible. In the present investigation, the Cauchy expression was used, i.e. the total broadening is the sum of  $B_D$  and  $B_d$ . Equations 2 and 3 give

$$\begin{aligned} B_{\text{tot}} &= B_D + B_d \\ &= K\lambda/(D \cos \Theta) + 4\Delta d/d \tan \Theta \end{aligned} \quad (4)$$

leading to

$$B_{\text{tot}} \cos \Theta = K\lambda/D + 4\Delta d/d \sin \Theta \quad (5)$$

Before using the half widths to calculate the grain size and the lattice distortions, the peaks must be corrected for the instrumental broadening,  $b$ . It has been found that lattice distortions are best approximated by a Gauss distribution ( $\beta^2 = B^2 - b^2$ ) while crystallite

TABLE I Diffraction peaks and measurement parameters used

$hkl$	$2\Theta^\circ$	Angle interval ( $2\Theta^\circ$ )	Step length ( $2\Theta^\circ$ )	Time (h interval <sup>-1</sup> )
100	23.10	22.10–23.50	0.01	2
013	32.40	31.50–33.50	0.01	2
213	58.54	57.50–59.20	0.01	2

size is best approximated by a Cauchy distribution ( $\beta = B - b$ ). When the peak broadening is caused by crystallite size and lattice distortions simultaneously an empirical formula, as discussed by Ziegler [4], has proved to be a very good approximation for the separation of the instrumental broadening (see Equation 6).

$$\beta = B - b^2/B \quad (6)$$

where  $\beta$  = corrected half width,  $B$  = uncorrected half width, and  $b$  = instrumental broadening. This approximation has been used in the present investigation.

An intricate problem in deconvoluting the X-ray peaks of  $\text{YBa}_2\text{Cu}_3\text{O}_7$  is the severe overlap between adjacent peaks. These overlaps are of course due to the fact that two of the axes are nearly the same. In the present investigation, peaks with smallest possible overlaps were selected to facilitate the deconvolution.

The uncorrected half width of the three peaks investigated as a function of milling time is shown in Fig. 1. It is easily seen that a substantial broadening of the peaks occurs. The broadening of the peaks was approximated as a linear function of milling time. The crystallite sizes and lattice distortions were achieved using the method described by Williamson & Hall [12]. In this method,  $\beta \cos \Theta$  against  $\sin \Theta$  is plotted. A straight line should be obtained where the intercept on the  $\beta \cos \Theta$  axis gives the mean crystallite size and the slope of the line gives the lattice distortions (see Equation 5). It should be possible to detect easily any systematic deviation from the linear relation caused by strong anisotropy effects.

Fig. 2 shows the  $\beta \cos \Theta$  against  $\sin \Theta$  plot for the data in the present investigation. It is clearly seen that the grain size decreases with increasing grinding time. A positive slope for the unground sample indicates lattice distortions, even in the unground sample.  $\text{YBa}_2\text{Cu}_3\text{O}_7$  has an asymmetrical structure which is easily cleaved normal to the  $c$  axis. It would therefore be expected that the grains should decrease aniso-

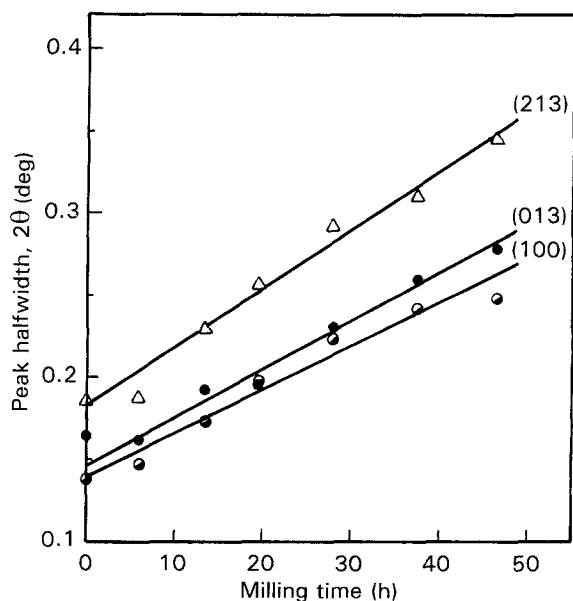


Figure 1 Uncorrected peak widths against milling time.  $2\theta = (100), 23.10^\circ$ ;  $(013), 32.56^\circ$ ;  $(213), 58.52^\circ$ .

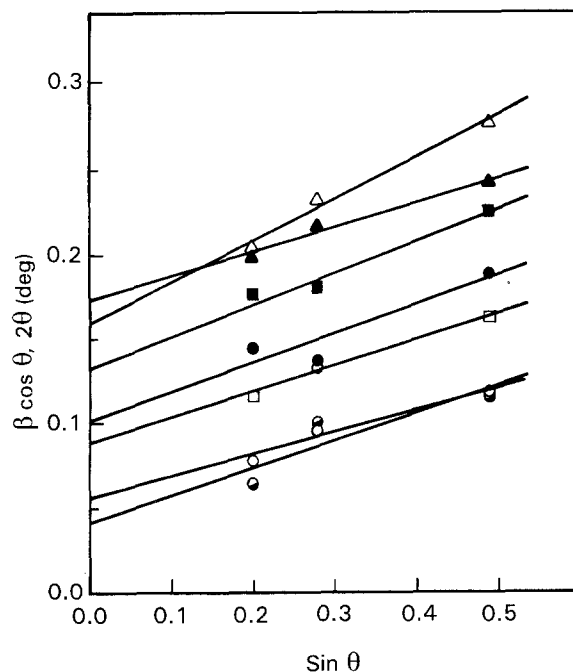


Figure 2  $\beta \cos \Theta$  against  $\sin \Theta$  at various milling times: ●, 0; ○, 6; □, 13.5; ●, 19.5; ■, 28; ▲, 37.5; △, 46.5 h.

tropically during milling. This would give a more rapid broadening of peaks corresponding to planes perpendicular to the  $c$  axis than of peaks corresponding to planes parallel to the  $c$  axis. Calculations show that the angle between the  $(013)$  plane and the  $c$  axis is  $45^\circ$  and that the angle between the  $(213)$  plane and the  $c$  axis is  $24^\circ$ . A more rapid decrease of the grains perpendicular to the  $c$  axis would therefore produce a larger increase of the half width of the  $(013)$  and  $(213)$  peaks than the broadening of the  $(100)$  peak. However, no systematic deviations from the straight line could be observed, i.e. no signs of anisotropic decrease in grain size were observed. The grains were therefore assumed to be spherical, giving the shape factor  $K = 1.0747$  [11].

Figs 3 and 4 show the crystallite size and lattice distortions against milling time. It is seen that during the first 15 h a rapid decrease in crystallite size occurs. During the same time, no or little change in the lattice distortions occurs. This understandable, as during the first milling time the grains are easily crushed. There is also a possibility that voids are present in the unground sample, making it easier for the grains to crack. As the milling time increases it becomes more difficult to reduce the grain size. The minimum grain size achieved is  $0.06 \mu\text{m}$ . This size is obtained after about 30 h of milling. Increasing the milling time gives no further reduction in grain size. The lattice distortions, however, increase rapidly from about 0.07% at 15 h of milling to about 0.11% at 47 h of milling. It is seen that the value of the lattice distortions obtained at 37.5 h milling is much lower than the expected value. Fig. 2 shows that this is most probably due to the small peak half width of the  $(213)$  peak. This peak becomes very broad as the milling time increases, making it difficult to determine the correct half width.

Fig. 5 shows the result of the BET measurements. It is seen that powder surface area increases with increasing milling time, indicating a decrease in grain

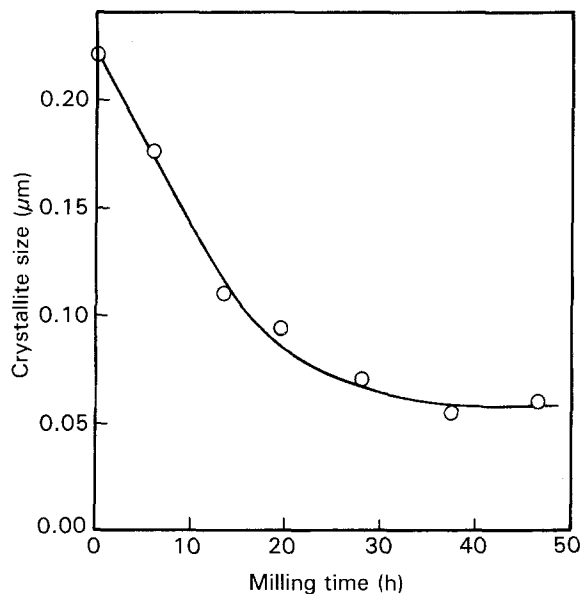


Figure 3 Crystallite size against milling time.

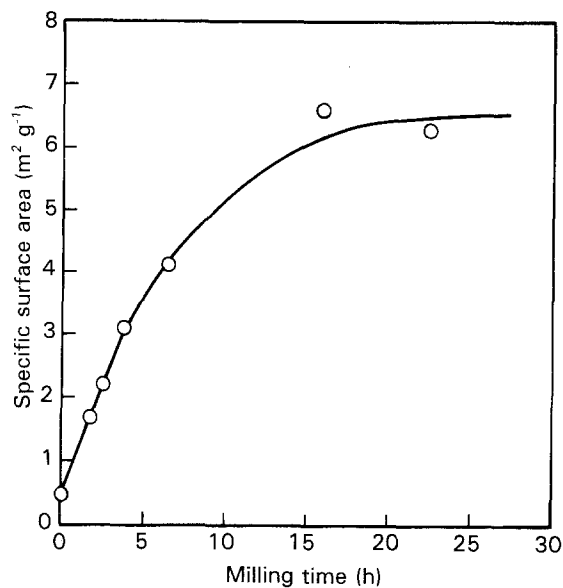


Figure 5 Specific surface area against milling time.

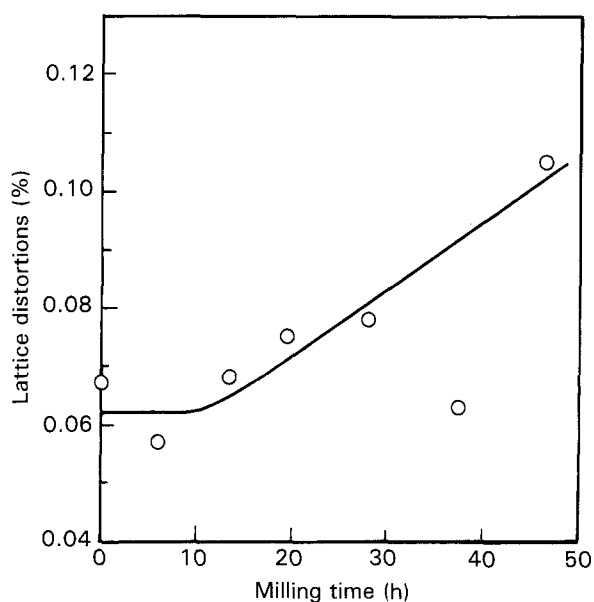


Figure 4 Lattice distortions against milling time.

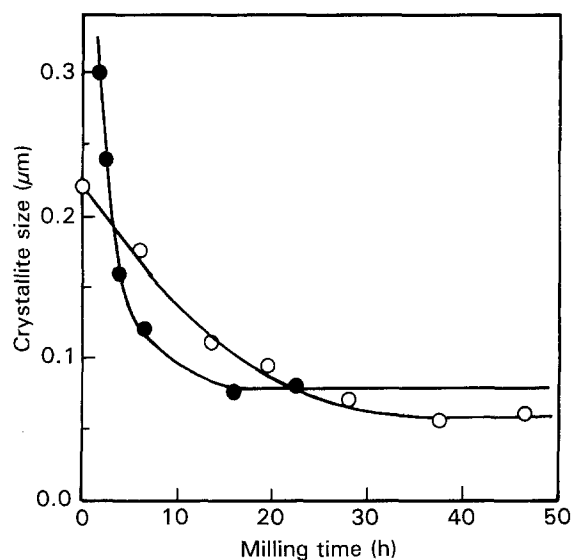


Figure 6 Crystallite size against milling time. Comparison between data obtained by BET analysis (●) and X-ray diffraction (○).

size. Under certain assumptions, the area can be converted into an equivalent particle size. Fig. 6 shows a comparison between the grain size obtained by X-ray analysis and the grain size calculated from BET measurements. It is seen that the grain sizes obtained by the two methods agree well. The grain size of the unmilled powder was 1.1  $\mu\text{m}$  as determined by BET. The corresponding grain size obtained by X-rays was 0.22  $\mu\text{m}$ . As mentioned earlier, the X-ray method has very low sensitivity with grain sizes larger than about 0.3  $\mu\text{m}$ . It is therefore expected that the values determined by X-rays and by BET should deviate at large grain sizes. At milling times longer than 25 h, the values determined by BET are about 30% higher than those determined by X-ray analysis.

Finally, it should be mentioned that ball milling produces a broad particle size distribution rather than a single particle size. This is fortunately beneficial for

the powder properties. In most cases, the objective of the consolidation step is to achieve maximum packing and uniformity, so that minimum shrinkage and retained porosity will result during densification. A single particle size does not produce good packing. Optimum packing for particles all of the same size results in over 30% void space. Adding particles of a size equivalent to the largest voids reduces the void content to 26%. Adding a third, still smaller particle size can reduce the pore volume to 23%. Therefore to achieve maximum particle packing, a range of particle sizes is required [13].

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