2.10. SPECIMEN PREPARATION
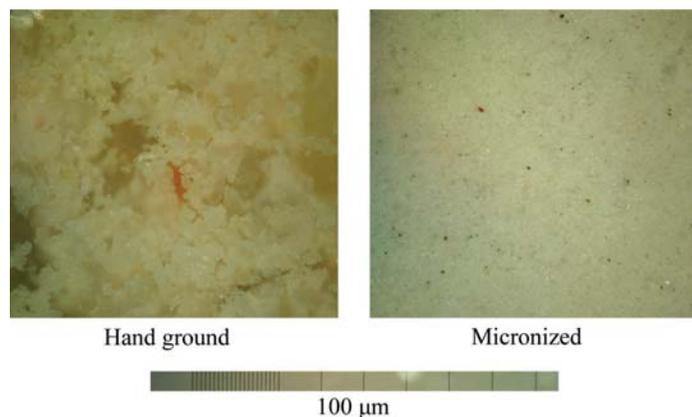


**Figure 2.10.7**
Optical microscope images of the surfaces of the hand-ground and micronized specimens of Scott's Moss Control Granules. The full length of the bar at the bottom is 100 μm. The hand-ground specimen contains grains much too large to yield a random powder pattern. Courtesy of B. J. Huggins, BP Analytical.



**Figure 2.10.9**
A rocking curve ($\varphi$ scan) of $(Ba_{0.7}Sr_{1.3})TiO_4$, with the detector fixed at 9.647° $2\theta$, the top of a strong peak in the synchrotron pattern. The jagged plot is from a static specimen, and shows individual grains moving in and out of diffracting position. The flat curve is from a rotating specimen, and indicates that a powder average was obtained.

Smith (Smith, 2001; Buhrke *et al.*, 1998) is considered, which followed principles first described by de Wolff (1958). By considering the effects of crystallite size, illuminated volume and beam divergence, for a monodisperse 40 μm specimen Smith calculated that only 12 crystallites would be in the diffracting condition (assuming a point detector). Obviously this is nowhere near enough to create the desired smooth Debye rings. To obtain a standard error of less than 1% the number of diffracting crystallites should be over 52 900, which even the 1 μm sample fails to meet.

Why then does a powder diffraction experiment work? A number of factors may affect the effective number of crystallites, many of which will be mentioned in the following paragraphs. One that isn't is the multiplicity due to the crystal symmetry, meaning that there are always at least two equivalent orientations of each crystallite that would meet the diffraction condition, up to 48 for some cubic reflections. It is worth remembering that these figures relate to a single phase, so the impact on the errors in quantitative phase analysis can be considerable. For low-concentration phases, the n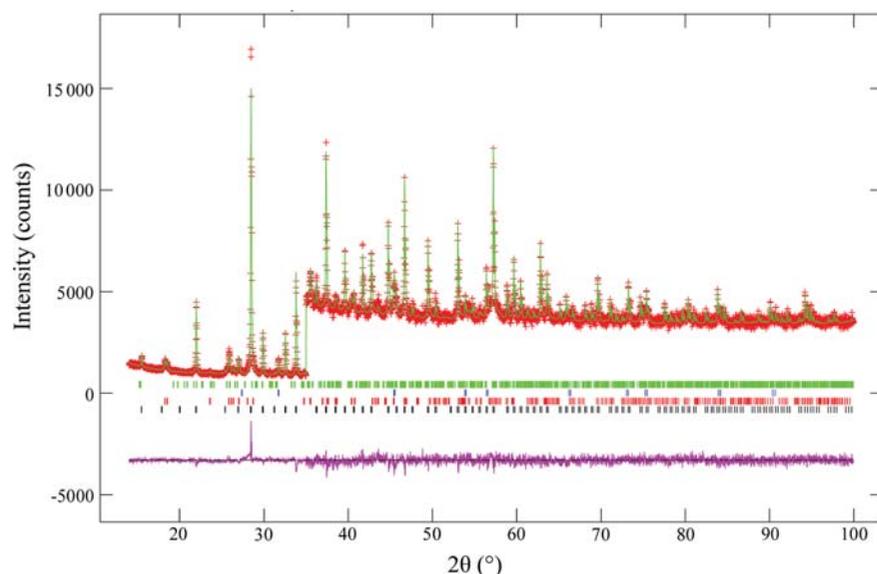umber of crystallites is automatically smaller than those of the major phases, so the effects of granularity might be more pronounced.

When considering the granularity of a particular specimen there are a few things to consider. The number of diffracting crystallites depends on the illuminated volume ($V$), the size of the crystallites ($s$), the packing density ($\rho$) and the probability that a crystallite is in the correct orientation ($P$).

The illuminated volume $V$ depends on a combination of instrument geometry, specimen geometry and the X-ray absorption of the sample. The footprint of the X-rays on a specimen in reflection depends on the beam width, beam length, the beam divergence (if any) and the diffraction angle. The effective beam width at the tube window with a typical long-fine-focus X-ray tube is 0.04 mm, with a length of 12 mm. The beam width may be increased up to 0.2 mm by using a broad-focus tube (Jenkins & Snyder, 1996), but these are rarely used in modern powder diffractometers. With Bragg–Brentano geometry the beam divergence may be increased to cover the available specimen, but large divergence angles degrade the peak resolution. A parallel-beam primary optic produces negligible beam divergence. The beam width may be reduced using an exit slit, but the largest beam width attainable is dependent on the characteristics of the mirror.

Additionally, $V$ also depends on how deeply the X-rays can penetrate into the sample. This depends on the linear absorption coefficient of the specimen for the particular radiation being used, and is given (Klug & Alexander, 1954) by $t = (3.2\rho \sin \theta)/(\mu\rho')$, in which $\mu$ is the linear absorption coefficient, $\rho$ is the crystal density and $\rho'$ is the packing density. In the absence of other information, a reasonable assumption for the value of $\rho'/\rho$ is 0.5. The penetration with Cu $K\alpha$ radiation can range from >1 mm for an organic material to a few μm for heavily absorbing specimens. With Bragg–Brentano geometry this leads to a potential trade-off between improving particle statistics and the peak shifts resulting from sample transparency. As a rule, doubling the diffracting volume will reduce the errors in intensity by about 1.5 times (Zevin &



**Figure 2.10.8**
Rietveld refinement plot for micronized Scott's Moss Control Granules. No preferred orientation correction was necessary, and the specimen scattered as a random powder. For angles > 35° the vert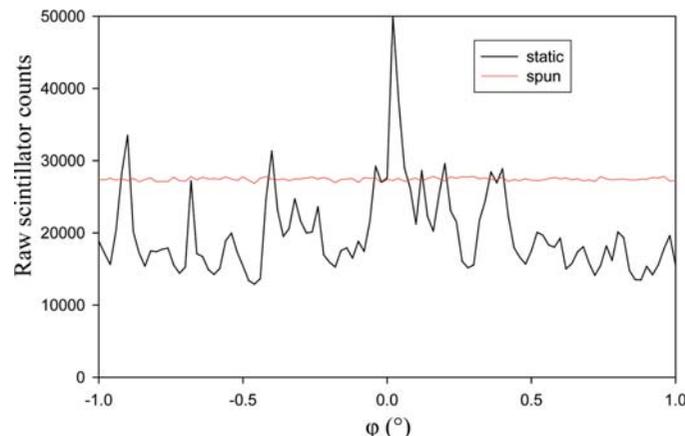ical scale has been multiplied by a factor of 5.