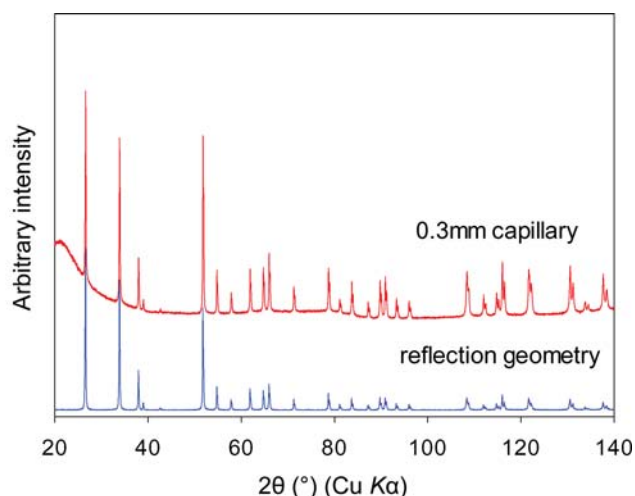


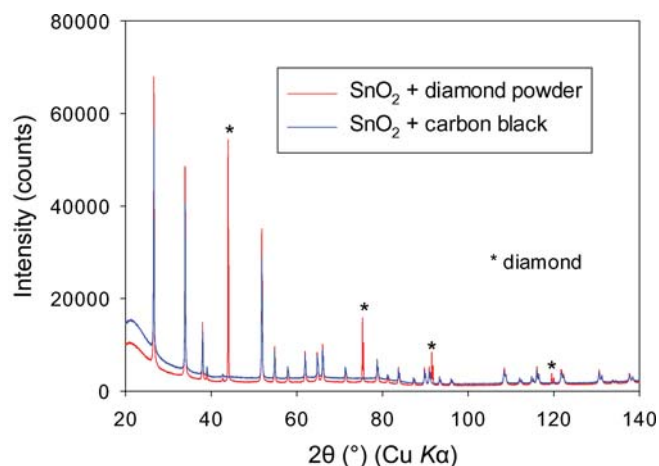
## 2. INSTRUMENTATION AND SAMPLE PREPARATION

**Figure 2.10.42**

Comparison of the diffraction patterns of pure  $\text{SnO}_2$  from a 0.3 mm quartz capillary in transmission and reflection geometries with  $\text{Cu K}\alpha$  radiation. The very high absorption of  $\text{SnO}_2$  leads to severe attenuation of the lower-angle reflections in the transmission data.

Where contaminating the sample is acceptable, another option is to dilute the sample with a material with very low absorption to reduce the overall sample absorption. There are two options here: either an amorphous material or a crystalline one. The addition of an amorphous material such as fumed silica (others could include amorphous boron, carbon black *etc.*) does not add any additional reflections to the pattern but will increase the background. Given that the backgrounds of capillaries using  $\text{Cu K}\alpha$  radiation are often quite high already, this may not be desirable. Alternatively, a material such as diamond powder can be used, which will add a small number of lines at high angles but does not add to the background. The closely defined crystallite sizes of diamond polishing powder can also improve the flow characteristics of materials that tend to agglomerate. The phase purity of polishing media is not relevant to their intended use, and some diamond polishing powders can contain some  $\text{SiC}$ , corundum or quartz. Check the phase purity of any diluting phase before use.

Fig. 2.10.42 shows the pattern from a 0.3 mm capillary of pure  $\text{SnO}_2$  (cassiterite) taken with  $\text{Cu K}\alpha$  radiation compared with that from reflection geometry. The linear absorption coefficient of  $\text{SnO}_2$  with  $\text{Cu K}\alpha$  radiation is  $\sim 1400 \text{ cm}^{-1}$ . Assuming a 50%

**Figure 2.10.43**

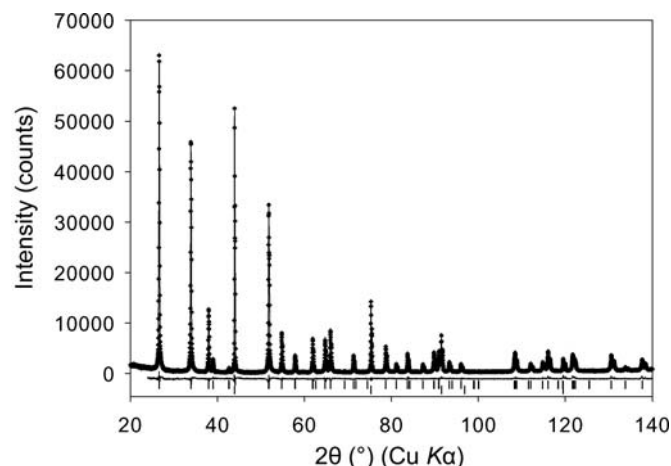
Raw diffraction data from 0.3 mm capillaries of  $\text{SnO}_2$  diluted with 8000 grit diamond powder and carbon black. In each case the capillaries had approximately the same packing density of  $\text{SnO}_2$ , so yielded almost identical intensities.

packing density,  $\mu R$  with a 0.3 mm diameter capillary is 10.5, which is much higher than can be tolerated in any structural analysis. Absorption attenuates the lower-angle reflections as the X-rays cannot penetrate properly compared to the high angles. However, in addressing capillary absorption, less really can be more. Fig. 2.10.43 shows data sets from  $\text{SnO}_2$  diluted with 8000 grit diamond powder and with amorphous carbon black. As expected, the background is higher with the amorphous carbon but without the additional reflections from the diamond powder. Despite there being only approximately 10 vol%  $\text{SnO}_2$  in each of the sample mixtures, the raw low-angle intensities are much higher, and the relative intensities are comparable with those from the reflection data in Fig. 2.10.42. Assuming a 50% packing density for the mixture, the value of  $\mu R$  with a 0.3 mm capillary would be approximately 2.3, which is in the acceptable range for structural analysis.

The relative intensities are such that a good-quality Rietveld refinement of a heavily absorbing compound such as  $\text{SnO}_2$  with  $\text{Cu K}\alpha$  laboratory data can be easily carried out. Fig. 2.10.44 shows the fit of the diamond-diluted sample to the literature cassiterite  $\text{SnO}_2$  structure. With very high dilution factors one should be careful not to compromise the particle statistics too much. Utilizing the full width of the detector with a full capillary will maximize the available statistics.

An alternative approach to dilution of heavily absorbing samples inside a capillary is to coat the outside (or inside) of a capillary. An appropriate absorption correction for annular samples does exist (Bowden & Ryan, 2010), so this is not an impediment. However, it is not available in common software packages so may have to be applied to the raw data prior to a structural analysis. One requirement is that a known thickness of sample needs to be applied to the surface of the capillary as uniformly as possible. This can be difficult to achieve and may require the use of an adhesive to bond the sample sufficiently to the capillary while spinning. The additional effect of an adhesive on the background should be considered in the same way as for a smear mount. Similar results to dilution may be achieved if done with care, as shown in Fig. 2.10.45.

Depending on the instrument geometry, a large diameter capillary can have an additional effect. Where an instrument does not have a focusing geometry (either primary or secondary), the peak resolution is degraded with increasing capillary diameter. With organic samples this can lead the analyst to use a smaller

**Figure 2.10.44**

Rietveld refinement of the diamond-diluted data with the  $\text{SnO}_2$  cassiterite structure. The capillary background was subtracted prior to the fitting whilst maintaining the correct counting statistics. The  $R_w$  value for this fit was 8.4%.