

## 2.10. Specimen preparation

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Powder X-ray diffraction is a popular technique, as it is quick and easy to obtain a data set in a non-destructive manner. However, the old adage ‘garbage in, garbage out’ is as applicable to powder diffraction as to any other technique. Obtaining a high-quality data set is often not straightforward, and it can be impossible to distinguish visually a poor data set from a good one prior to attempting an analysis. This can be problematic if someone collects poor data and then spends days in a fruitless attempt to analyse it – or even worse unknowingly produces erroneous results. Specimen preparation is a key element in the quest to produce good data.

One of the tasks of the analyst is to determine what is required for a ‘fit-for-purpose’ data set. Practically, in the interests of time and instrument efficiency one might not need to aim for perfection in the preparation of every specimen. The majority of analyses carried out in most laboratories are for phase identification, whose minimum requirements for sample preparation are less stringent than for quantitative phase analysis or structure refinement. However, the need for more detailed analysis is never clear at the outset, and if the specimen has been altered or destroyed by other analyses, any economy in specimen preparation will turn out to have been false.

Although the laboratory instrument appears to be very different from synchrotron or neutron diffractometers at large central facilities, many of the concepts in the collection of powder diffraction data are common. Whether in the home institution with a basic laboratory system or in a huge instrument hall at a central facility, the basic concepts of specimen preparation are very similar (although neutrons have some unique issues). The imposing surroundings at large facilities may make specimen preparation seem like an unimportant distraction, but it is worth bearing in mind that repeating experiments if the data are poor may be impossible with limited beam time available. At the risk of overusing everyday sayings, ‘if it’s worth doing, it’s worth doing right’. One common scenario is a user trying to replicate what has been seen in a literature paper without assessing critically whether the authors took the necessary care to collect accurate data.

Many of the problems that occur with powder diffraction specimens are related to size in some form – most often crystallite size, but sometimes particle size as well. Although the problems relating to size are described separately for the sake of clarity, where one of the issues exists the others are likely to follow. The first size-related problem to be described is particle statistics (granularity). Although theoretical models of varying success exist for the other issues of preferential orientation, micro-absorption and extinction, no

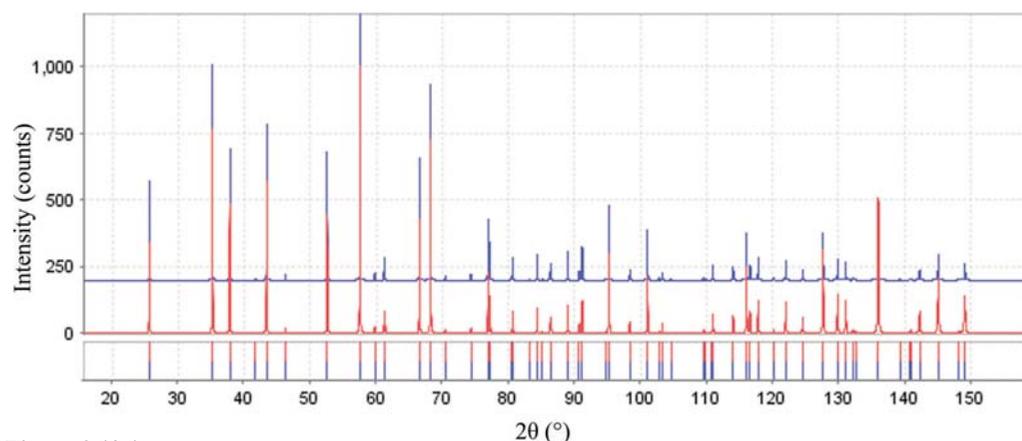
such model is possible when the data suffer from poor particle statistics. Consequently the message here is ‘prevention through proper specimen preparation’; taking steps in specimen preparation to improve particle statistics will automatically reduce the effects of other potential problems.

The classic work on preparation of X-ray diffraction specimens is Buhke *et al.* (1998). This book should be on the shelf of every powder diffractionist. It provides an excellent discussion on sampling, a discussion which is not necessary to repeat here. This chapter attempts to update and expand the advice given there on specimen preparation.

### 2.10.1. X-ray powder diffraction

Most people first encounter X-ray powder diffraction with laboratory instrumentation, but concepts applying to laboratory systems are also applicable to synchrotron and neutron beamlines. The scattering mechanisms of X-rays in the laboratory and at a synchrotron are the same, and apparent differences are usually due to specifics of the wavelength used or beamline/instrument geometry. Differences and similarities between synchrotron and laboratory experiments will be highlighted where they are significant. For example, differences in the polarization factor result in different intensities from the same specimen on laboratory and synchrotron instruments (Fig. 2.10.1). Issues specific to neutron powder diffraction will be covered in Section 2.10.2.

A typical laboratory instrument has the Bragg–Brentano reflection geometry, either with  $\theta$ – $\theta$  (fixed specimen) or  $\theta$ – $2\theta$  (fixed tube) setup. Other laboratory configurations are possible, such as transmission (capillary or flat plate) and spot focus with area detectors. Some of the concepts described affect both reflection and transmission, but some will be more important for one geometry over the other. Synchrotron beamlines can also be operated in reflection or transmission geometry, but capillary transmission geometry is much more common than in the laboratory. Some of the apparent differences are due to the



**Figure 2.10.1**

Calculated corundum powder patterns using the structure of Lewis *et al.* (1982; PDF entry 04-004-2852) for laboratory and synchrotron instruments, using the default profile settings from the Powder Diffraction File. The synchrotron pattern is displaced by 200 intensity units for clarity.