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# Use of double Göbel mirrors with high-temperature stages for powder diffraction – a strategy to avoid severe intensity fade

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This paper describes an approach for countering an issue that can occur when using a high-temperature stage with a diffractometer equipped with double Göbel mirrors. The optical characteristics of the dual-mirror configuration make it more susceptible to intensity loss with sample displacement than conventional parallel-beam secondary optics. This issue has been apparent in the use of a high-temperature stage on a diffractometer equipped with dual mirrors, where data could not be obtained from the full room temperature to 1273 K range without resetting the sample height manually part way through the experiment. A simple technique involving controlled contouring of the sample surface has been demonstrated to allow data to be collected uninterrupted over the full temperature range, while retaining satisfactory intensities. The extent to which this technique extends the tolerable sample displacement range has been quantified using a computer-controlled *XYZ* stage.
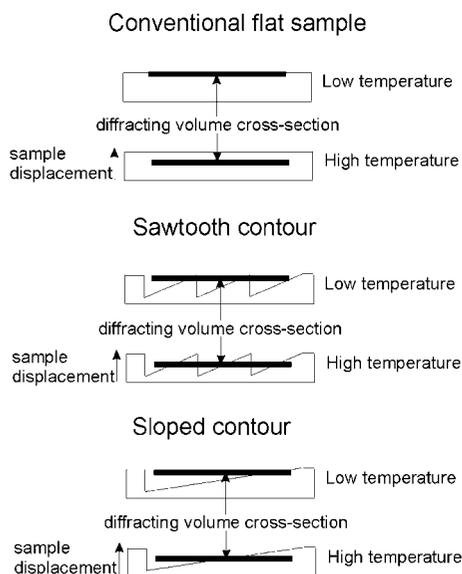
## 1. Introduction

Graded parallel-beam multilayer optics are a relatively recent development in the field of powder diffraction (Schuster & Göbel, 1995). The use of a parallel non-divergent X-ray beam makes an instrument insensitive to many of the sample-induced peak distortions that plague the Bragg–Brentano geometry, *i.e.* sample displacement, sample roughness and transparency. Sample displacement is an issue in variable-temperature studies using the Bragg–Brentano geometry, due to the inherent thermal expansion experienced by both the sample and the sample holder. To separate the effect of sample displacement from unit-cell expansion, an internal standard is often used to provide a correction. This is often not a satisfactory solution (Mantler & Hammerschmid, 2000), so the use of parallel-beam optics is an attractive alternative. Primary Göbel mirrors are usually coupled with long Soller slits and possibly a flat monochromator, *e.g.* LiF, on the diffracted-beam side. A flat monochromator strips out fluorescence and $K\beta$ radiation, but at a severe cost with respect to intensity. With or without the monochromator, the angular resolution obtained is significantly worse than that of the corresponding Bragg–Brentano instrument. Consequently, the significant advantages that parallel-beam geometry offer can be offset by a reduction in data quality.

More recently, Göbel mirrors in the primary beam have been partnered with matching optics in the secondary beam. Such an arrangement is very effective at removing fluorescence and $K\beta$ radiation, as well as increasing angular resolution, intensity and signal-to-noise ratio with respect to the single-mirror approach. For routine powder data collection, they produce excellent data and are the standard configuration for our machine. The secondary mirror does have a tight acceptance angle for incoming radiation, which means that the detector 'sees' a more limited volume in the centre of the goniometer circle than would be the case with conventional parallel-beam secondary optics, *e.g.* long Soller slits. Consequently, excessive sample displacements lead to much more rapid intensity loss at the detector compared with conventional parallel-beam optics. The most common example where such a displacement can occur is when heating a sample from ambient to high temperature. High-temperature experiments suffer from thermal expansion of both the sample holder and the sample itself. Where resources permit, the use of other secondary optics or a position-sensitive detector could ameliorate this problem. However, there are instances where this is not possible, whether for financial, logistical or sample-related reasons, so this is an issue that needs to be addressed.

It is possible to halt a high-temperature experiment part way through and readjust the sample height manually. However, it is inconvenient and produces a severe discontinuity in the data. A technological solution could be envisaged, *e.g.* automatic motorized sample-height adjustment to optimize intensities. This could work well, but would require high-temperature stages with precisely controlled motorized sample holders, together with dedicated software for the task. Furthermore, it would not be straightforward, cheap, or in many cases possible to retrofit many of the current high-temperature stages with such an arrangement. The development and use of special high-temperature stages mounted on

Conventional flat sample
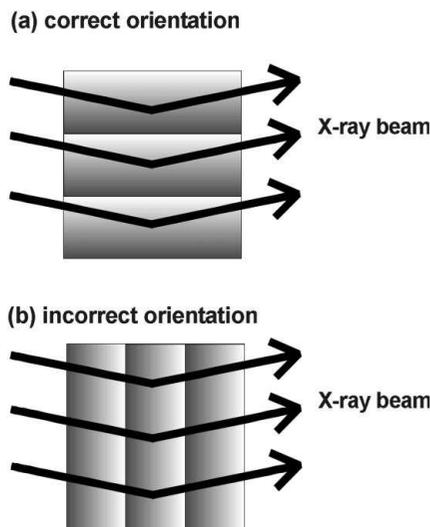


Sawtooth contour

Sloped contour

**Figure 1**
Diagrams showing the effect of vertical sample displacement on the diffracting volume visible to the detector, relative to the sample surfaces for a conventional flat sample and the geometrically most promising surface profiles used in this study. The view is from the detector at 0° $2\theta$, *i.e.* beam out of the page. Consequently the cross section illustrated will remain constant with changing $2\theta$.

Eulerian cradles provides the option of tilting the whole furnace from the horizontal, but such systems are currently very rare.
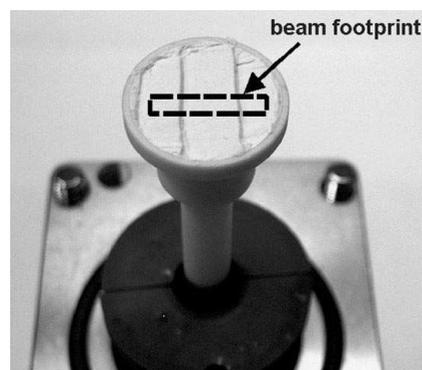
An alternative approach is to make use of the inherent characteristics of the double-mirror optics to provide a solution. By deliberately introducing an uneven sample height, the Bragg condition could be satisfied by a similar volume of 'visible' sample throughout the range of displacements occurring during data collection at varied temperatures. Different parts of the sample would be visible to the detector at different displacement/temperatures, which will minimize the variation in intensity across the range of data sets. The range of sample displacement that could be tolerated is then a function of the sample depth and the contouring of the sample surface. The parallel-beam geometry means that displacement errors would not be introduced, although the intensity would be reduced from optimal, due to the inevitable reduction in diffracting volume. Despite the trade-off, such an arrangement has the advantage that it could be applied to existing high-temperature stages with no modifications.

## 2. Experimental

The instrument used in this work was a Cu $K\alpha$ Bruker $\theta$–$\theta$ D8 equipped with 40 mm Göbel mirrors in both the primary and the secondary beam, using a 600 mm circle with a scintillator detector. The slits used were 4° axial Soller slits for the primary and secondary mirrors, a 1 mm exit slit for the primary mirror, a 2 mm entrance slit for the secondary mirror, and a 0.2 mm detector slit. The instrument was mated with an Anton Parr HTK1200 high-temperature stage. Samples
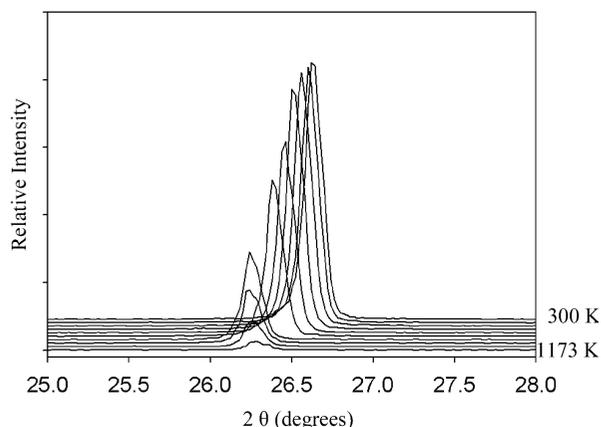


**Figure 2**
Schematic diagram of (*a*) the correct orientation of the contour ridges with respect to the beam, and (*b*) the incorrect orientation
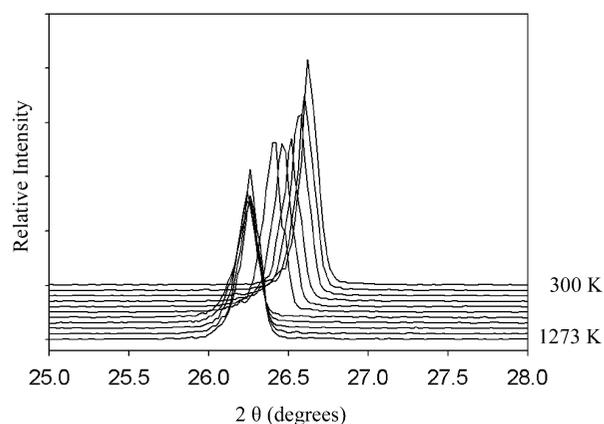


**Figure 3**
Photograph showing a quartz sample that has been contoured by hand into a sawtooth profile with a spatula. In the sample chamber, the holder is orientated such that the X-ray beam direction is parallel to the ridges. The rectangle superimposed on the photograph represents the beam 'footprint' on the sample surface for a long fine-focus source. The alumina HTK1200 holder shown here has a diameter of 18 mm.

examined were −325 mesh (<45 µm) crushed single-crystal natural quartz and 0.3 µm polishing corundum. The polishing corundum was found by X-ray analysis to be predominantly $\alpha$-$Al_2O_3$ with a minor contribution from $\gamma$-$Al_2O_3$. Quartz undergoes the $\alpha$- to $\beta$-quartz transition at 846 K, and since $\beta$-quartz is essentially a zero-expansion material, sample-holder expansion should predominate at temperatures above this transition. High-temperature data were collected from the quartz at room temperature from 15 to 70° $2\theta$ with a 0.02° step, and between temperatures of 373 and 1173 or 1273 K in 100 K steps. The Anton Parr HTK1200 uses radiative heating rather than a strip heater, and uses an alumina ceramic sample holder with a diameter of 18 mm and a recess approximately 1 mm deep. The samples were not rotated during data collection.

A number of approaches were used to introduce sample surface contours in order to determine which gave the best results with regard to maintaining intensity with increasing
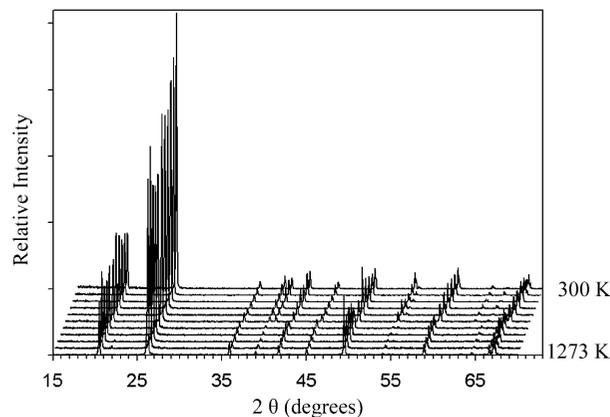
**Figure 4**
Plot showing the evolution of the quartz 011 reflection intensity with temperature for a conventional flat sample. The data were incremented in the *y* direction only, in order to increase clarity.
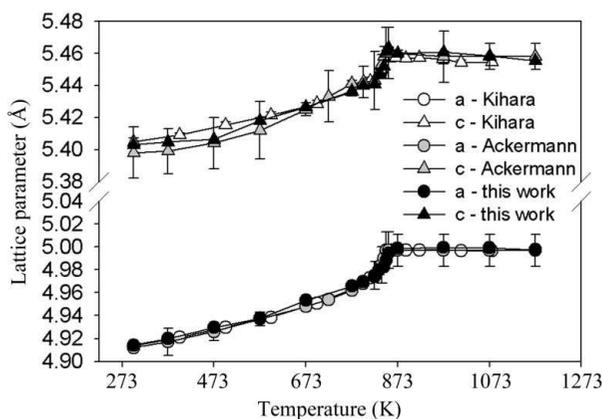


**Figure 5**
Plot showing the evolution of the quartz 011 peak intensity with temperature for a sample with a 'sawtooth' contoured surface sloped perpendicular to the beam direction. The data were incremented in the *y* direction only, in order to increase clarity.
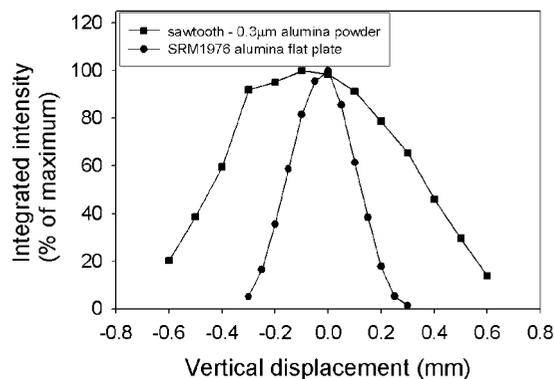
temperature. A number of possibilities present themselves as likely candidates from a simple geometric point of view. Fig. 1 shows the geometric relationship between a number of profiles and the beam position with increasing sample displacement. The orientation of the sample ridges to the beam is very important; the X-ray beam must be parallel to the ridges as indicated by the schematic diagram in Fig. 2(*a*). In this orientation, with a straight and smooth sample contour, the fraction of beam diffracted by the sample will remain constant over the complete 2θ range, the diffracting sample visible to the detector simply moving along the fixed beam width. Geometrically, this will yield correct relative intensities for the sample through the full 2θ range as the percentage of the beam footprint visible to the detector will remain constant if the contour surfaces are straight and aligned properly. Additionally, the ridges do not obstruct the beam at low angles, as would be the case as illustrated in Fig. 2(*b*). This orientation is tolerant of slight imperfections in the configuration and production of the contours, which is important when sample



**Figure 6**
Plot showing the full quartz pattern collected between room temperature and 1273 K using a sawtooth contour. Perspective has been added to this plot for increased clarity. All scans were taken between 15 and 70° 2θ.



**Figure 7**
Plot showing the quartz cell parameters refined by full-pattern fitting using the Pawley method. The unfilled symbols correspond to parameters calculated using literature cell parameter data for quartz (Kihara, 1990; Ackermann & Sorrell, 1974). Errors are plotted at the 2σ level.



**Figure 8**
Comparison of intensity of the corundum 104 reflection with vertical displacement for flat-plate SRM1976 and 0.3 μm alumina powder prepared in a parallel sawtooth profile.

preparation is performed by hand. Should the holder be orientated as in Fig. 2(*b*), problems with relative intensities would occur over large angular ranges where the contour was

**Figure 9**
Plot showing the position of the corundum 104 reflection with vertical displacement for the 0.3 μm alumina powder with a parallel sawtooth profile.

not produced perfectly in relation to the centre of the goniometer circle. Fig. 3 shows a photograph of a powdered quartz sample prepared by hand using a spatula with the parallel sawtooth geometry, with a representation of the beam footprint on the sample surface for a long fine-focus tube.

Lattice parameters and cell volume were obtained by Pawley (Pawley, 1981) and Le Bail (Le Bail *et al.*, 1988) full-pattern fitting using the Bruker *TOPAS* 2.1 beta software (Bruker AXS, 2000). Fundamental parameters (Cheary & Coelho, 1992) were used to calculate peak profiles, which were derived using the SRM660a profile standard.

The actual displacements that occurred at a particular temperature in the high-temperature stage are unknown and it was deemed desirable to quantify the effect of displacement on intensities. Consequently, the sensitivity of the double-mirror configuration to intensity degradation with precise vertical sample displacement was tested using an *XYZ* stage. The *XYZ* stage was computer controlled with a vertical position control to within 5 μm. A NIST SRM1976 flat alumina plate was used as a flat-material standard. The corundum 104 reflection was scanned, with the plate height adjusted a total of 0.6 mm in 0.05 mm steps. For comparison, a sawtooth-profile sample was prepared from 0.3 μm corundum powder in the HTK1200 alumina sample holder. Data were taken from the corundum powder sample in the HTK1200 holder in the range 20–80° 2θ using a step of 0.03° and a counting time of 3 s. The total vertical displacement during the powder experiment was 1.2 mm in 0.1 mm increments.

## 3. Results and discussion

The intensities and fade of the quartz 011 reflection shown by a conventionally prepared sample heated from room temperature to 1173 K are shown in Fig. 4. It can be seen that the conventionally mounted flat sample showed significant fade by 673 K, and continued worsening through the α- to β-quartz transition, becoming effectively unusable at 1073–1173 K. This indicates that the displacement included a significant contribution from the sample holder and not just sample expansion. Fig. 5 shows the data from a repeat

experiment where the sample was prepared with a 'sawtooth' contoured surface sloped perpendicular to the beam direction. The intensities were lower overall as a result of the smaller diffracting volume of material, but the intensities varied over the temperature range by only 30%. In this particular case, the intensities of the 011 reflection actually increased between 973 and 1273 K, so there is no reason to expect that data could not be collected to significantly higher temperatures. There is scope to improve this stability by optimizing the properties of the profile and the sample. As expected from parallel-beam geometry, the change in sample configuration had no effect on the peak positions. The effect of the sawtooth profile on relative intensities is shown in Fig. 6. The cell parameters refined by the Pawley method from the sawtooth profile are shown in Fig. 7. Overlaid on this graph are literature cell parameter values for quartz with increasing temperature, determined from X-ray data (Kihara, 1990; Ackermann & Sorrell, 1974). The data obtained here compare fairly well with the literature values. Ackermann & Sorrell (1974) did not use their full patterns for cell parameter determination; therefore their errors are significantly higher than those obtained in this study and by Kihara (1990). It can be seen that the data from this study are comparable with that found in the literature.

The reduction in the volume of diffracting material at a particular temperature has an obvious impact on powder average. The variation in relative intensities in Fig. 6 illustrates this clearly for this quartz, although it does not affect results from full-pattern lattice parameter refinements. Results from a study of data quality with crystallite size for the sawtooth profile have confirmed that it is possible to obtain data good enough for Rietveld refinements using this technique if the crystallites are sufficiently small (Whitfield, 2002). Therefore, it is recommended that powder samples consist of sub-micrometre particles to improve the powder average in the restricted diffracting volumes.

The response of the double Göbel mirror optics to progressive sample displacement of SRM1976 corundum plate is shown in Fig. 8. This demonstrated that a displacement of a flat sample by 0.25 mm from optimal results in a minimum of 80% loss of intensity. Fig. 8 also shows the results for a 0.3 μm corundum powder sample prepared in the parallel sawtooth configuration. It can be seen that the intensities are much more stable for the sawtooth sample with sample displacement than for a flat sample. Fig. 9 shows the peak position for the corundum 104 reflection of the sawtooth-profile 0.3 μm powder. This demonstrates that even sample displacement of ±0.6 mm does not affect the peak position. Such sample displacements would cause significant problems for the Bragg–Brentano geometry. The peak shift in degrees induced by such a displacement in a Bragg–Brentano instrument can be calculated using the equation

$$\Delta 2\theta_{\mathrm{deg}} = -2(180/\pi)\cos(\theta_{\mathrm{rad}})d/R, \quad (1)$$

where $d$ is the sample displacement in mm and $R$ is the circle radius in mm (Klug & Alexander, 1974). Using equation (1), a 0.25 mm sample displacement with a 300 mm radius would produce a peak shift of 0.091° 2θ for the corundum 104

reflection. A circle radius of 300 mm is unusually large, and the same 0.25 mm displacement would induce an even larger shift on most instruments, *e.g.* 0.109° 2θ for a radius of 250 mm.

Strip-heater-equipped stages are more common and have different characteristics. However, they still present problems with sample displacement, compounded by thermal-gradient issues (Brown *et al.*, 1993). Our institution does not possess a strip-heater high-temperature stage, so cannot test sample contouring in those configurations with double Göbel mirrors. However, geometrically it makes no difference what the sample is mounted on. Potentially, contoured samples on strip heaters may be more prone to thermal-gradient issues due to the requirement for relatively thick samples, but the extent of this would have to be tested experimentally.

Another profile is a sample sloped in a direction perpendicular to the X-ray beam as shown in Fig. 1. Experiments have shown that this arrangement tends to have a lower tolerance for sample displacement than the sawtooth profile. Theoretically, this need not be the case, but difficulties arise in optimizing the angle of the sample to maintain good intensities and good stability. However, it does produce useful data over a larger temperature range than a conventionally mounted level sample. The same effect could be achieved by manually lowering the level of the sample stage, but this adjustment is coarse and often difficult to reproduce. Although not as effective as a contoured sample, the simple sloped profile is of interest as it would be applicable to the study of thin films.

## 4. Conclusions

It has been demonstrated that sample displacement of flat level samples by 0.25 mm, when used in an instrument equipped with double Göbel mirrors, leads to at least 80% loss of intensity. Consequently, when double Göbel mirrors are used with a high-temperature stage, a large intensity fade can occur with increasing temperature, causing severe degradation of collected data. However, it has been shown that the properties of this particular geometry can be harnessed with judicious sample preparation to circumvent the issue to a considerable degree. Using this approach, it is therefore possible to benefit from the increased intensity and resolution of the double-mirror configuration, while still maintaining the advantages inherent in parallel-beam geometry. This approach is applicable to existing high-temperature stages at no additional cost.

As a result of the reduction in diffracting volume, there is a compromise between stability of intensity with increasing temperature and the absolute intensity in counts per second. The reduction in diffracting volume also has an adverse effect on powder average. Consequently, the particles/crystallites in a sample must be very fine to counteract this effect.

Of the contours examined in this study, the sawtooth profile, with grooves parallel to the beam direction, gave the most stable intensity profile where the powder average was sufficient. It should be possible to optimize the shape of the sample surface with regard to stability of intensity with displacement. The samples examined here were prepared by hand, but a simple mould/form could be made to contour the sample for optimal and reproducible performance. The contouring approach is not universally applicable to all samples, but it can yield excellent data when circumstances permit.

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