CALIBRATION OF A HIGH TEMPERATURE X-RAY DIFFRACTION STAGE BY DIFFERENTIAL THERMAL EXPANSION

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ABSTRACT
A new method for determining the temperature calibration function for a high-temperature X-ray diffraction stage is described. This method utilizes the relative thermal expansion of two diffraction peaks, either for peaks from a mixture of phases, or from a single phase that has anisotropic thermal expansion. A calibration function is derived from data at many temperatures and collected over a narrow angular range. Because only the relative separations of closely spaced peaks are used, this method is fast and insensitive to geometric aberrations. Materials used for calibration can include phase transition standards for an independent check on the calibration function. A new type of single-point temperature calibration standard can also be constructed that relies only on the observation of peak-crossing events at specific temperatures that are caused by relative thermal expansion.

INTRODUCTION
The thermocouple calibration in high-temperature X-ray diffraction (HTXRD) stages is accurate only for situations where the specimen is in direct thermal contact with the thermocouple. Any thermal impedance between the specimen and the thermocouple in the presence of a temperature gradient will lead to a discrepancy between the specimen temperature and the thermocouple temperature. In strip-heater HTXRD furnaces where the thermocouple is welded to the underside of the primary heating strip, there is reasonably good thermal contact between the thermocouple and small, thin specimens that can be placed directly on the heating strip above the thermocouple. For reactive specimens that may damage the heating strip, protective barriers between the specimen and the heating strip are necessary, but at the expense of invalidating the thermocouple calibration. The preferred method of calibration in HTXRD is to use the temperature dependence of the X-ray diffraction from a standard material. These reference materials are generally either single point calibrants, (phase transition standards), or multipoint calibrants, where direct measurement of the thermal expansion of the reference provides a calibration curve.

The most frequently used materials for single-point temperature calibration are melting point standards. There are numerous examples of common materials with very well established melting temperatures that are adequate for this technique, such as NaCl, Ag or Au. These materials can be used for a very rapid calibration by monitoring a prominent peak (narrow angular range) at a small number of temperatures that span the melting transition. The melting
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transition is judged by the disappearance of the diffraction peak as crystalline order is lost. Although this technique is very convenient, it suffers from several shortcomings. First, as stated above, it provides only one calibration point. For temperatures other than the reference materials melting point, the measured temperature is assumed to fall on a line between the melting temperature and room temperature. Second, the reference material may undergo rapid changes in crystallographic texture below the melting temperature that may lead to a misinterpretation of the true melting transition. Third, it may be difficult to find materials that have an appropriate melting temperature. Lastly, judging a freezing transition (cooling) may be confounded by under-cooling, or completely impossible if the molten material rolled off of the stage (vertical specimens are particularly susceptible to the problem).

Materials that undergo solid-solid (SS) crystallographic phase transitions are used in a similar fashion to that of melting transition standard. An important difference between the use of SS phase transition materials and melting transition materials is that SS transitions give data that bracket the transition. This is not the case in the melting transition standards, since there is no crystal phase above the transition. In addition, SS transition materials don't roll off the substrate and hence, are better suited for vertical sample holders. Unfortunately, the available choices of SS reference materials is limited.

Direct measurement of the thermal expansion of a reference material may be used to produce a complete calibration curve (at many temperatures) if the thermal expansion is known very accurately and if the confounding effects of temperature dependent aberrations (such as changes in sample displacement) can be eliminated. To correctly account for these aberrations, a complete diffraction pattern must be refined at each temperature using parameter(s) to account for each confounding effect(s). The requirement of full pattern analysis greatly increases the time required for data collection and analysis.

In this report an X-ray temperature-calibration method is described that uses differential thermal expansion of two diffraction peaks to determine a complete calibration curve (at many temperatures) from data collected over narrow angular ranges (fast). The two peaks in the reference material must be close together and characterized by a difference in their thermal expansion. This differential thermal expansion can be because each peak is from a different phase in a two phase mixture, or from anisotropy in the thermal expansion of a single phase. By analyzing the differential thermal expansion of narrowly separated peaks, the geometrical aberrations (e.g., sample displacement peak shift) cancel, eliminating the need for full pattern refinement. An independent check on the calibration can be determined if one or both of the
phases in the reference mixture is also a phase transition standard. Reference mixtures can also be devised that have peaks that pass through a common position at a particular temperature, providing a single-point temperature reference. The use of peak crossing events represents a fundamentally new method for temperature calibration in HTXRD.

EXPERIMENTAL METHOD
A calibration mixture of $\alpha$-Al$_2$O$_3$ (SRM 674a) [1] and fine filings of Ag (>99.99%) was prepared by mixing in a mortar and pestle. The ratio of the two components was adjusted to give approximately equal heights for the $\alpha$-Al$_2$O$_3$ (110) and Ag (111) peaks. This mixture was dispersed onto a 0.5 mm thick sapphire single crystal (10 mm × 8 mm). The crystal substrate was mounted onto the center of the primary heating strip of a Bühler HDK 2.4 furnace equipped with a secondary surround heater and attached to a Scintag X1 $\theta–\theta$ diffractometer (horizontal specimen) using Cu radiation and an energy dispersive Si(Li) detector. Temperature control (±1º) during each scan was maintained by a MicriStar controller with input from a calibrated Pt-Rh thermocouple welded to the underside of the primary heating strip. The thermocouple temperature $T_{T.C}$ was collected and stored with each diffraction scan. To avoid diffraction peaks from the single crystal substrate, data were collected using 2$\theta$ scans (36.8°-38.3°, 0.03° steps, 5 second dwell time) with $\omega$ fixed at 18°. Scans were collected at 20C, and every 25C from 50C-1050C.

DATA ANALYSIS
Each diffraction scan was background subtracted and profile fitted (Pearson 7) to determine the peak positions. The parameter(s) of a trial calibration function $\Gamma(T_{T.C})$, were determined by fitting the absolute difference in the $d$-spacings of the peaks:

$$\left| \Delta d(T_{T.C}) \right| = \left| d_{1,0} \left[ 1 + 0.01 \frac{\Delta L}{L_0} \left( \Gamma(T_{T.C}) \right) \right] - d_{2,0} \left[ 1 + 0.01 \frac{\Delta L}{L_0} \left( \Gamma(T_{T.C}) \right) \right] \right|$$

where the subscripts 1,0 and 2,0 refer to the two materials used in the calibration mixture, measured at 273K. The thermal expansion [2] for the materials in this study are

$$\frac{\Delta L_{\alpha-Al_2O_3}}{L_0} (T) = -0.176 + 5.431 \times 10^{-4} T + 2.150 \times 10^{-7} T^2 - 2.810 \times 10^{11} T^3$$

$$\frac{\Delta L_{Ag}}{L_0} (T) = -0.515 + 1.647 \times 10^{-3} T + 3.739 \times 10^{-7} T^2 + 6.283 \times 10^{-11} T^3$$
where these express percent expansion relative to 273K. In the present case, the thermocouple output \( T_{T.C.} \) at 20C was accurate and since there can be no temperature offsets at room temperature, the temperature calibration function must be of the general form \( \Gamma(T_{T.C.}) = \beta(T_{T.C.} - 20) + 293K \). Because the values of \( d_{1,0} \) and \( d_{2,0} \) are not easily measured in a HTXRD furnace, they can be fitted as free parameters or calculated from the measure room temperature (20C) values.

**RESULTS AND DISCUSSION**

Raw data from the Ag-Al\(_2\)O\(_3\) calibration mixture are shown in Fig. 1. The two peaks cross near a thermocouple temperature of 700C and the Ag peak is noticeably reduced in the final scan shown (1025C) and completely absent at 1050C (not shown), so the melting point of Ag was judged to be very nearly 1025C. Near the crossing temperature, peak positions had larger uncertainties in position, so it was not possible to assign peaks in this region to their respective phases. Analyzing the absolute difference in peak positions eliminates the problem of ambiguity.

![Fig. 1 Raw 2θ scans (ω=18°) over the Al\(_2\)O\(_3\) (110) and Ag (111) peaks at 20C and every 25C for 50C-1025C. The maximum of the intensity envelope is in the 700C scan, corresponding to the peak crossing. The scan at 1025C shows partial melting of the Ag component. The weak peak near 37.2° is a Renninger reflection associated with the sapphire crystal substrate.](image-url)
of assignment, without any loss of validity. The fitted values of $|\Delta d(T_{T.C.})|$ vs. $T_{T.C.}$ are shown in Fig. 2, with the fitting curve based on the refined linear calibration function

$$\Gamma(T_{T.C.})=0.9377(\pm0.0087)\times(T_{T.C.}-20)+293K.$$  From the closeness of the fit, it is apparent that higher order terms in the calibration function are not needed to accurately describe the peak position differences.

Fig. 2  Relative separation of the $\text{Al}_2\text{O}_3$ (110) and Ag (111) peaks fitted using the tabulated thermal expansion data and a linear temperature calibration function: $\Gamma(T_{T.C.})=0.9377\times(T_{T.C.}-20C)+20C$. Near the peak crossing temperature (700°C) the peak positions suffer from greater uncertainty and ambiguity in assignment.

The melting temperature of the Ag component can be used as an independent check of the calibration function: $0.9377\times(1025C-20C)+20C=962.4C (\pm8.5C)$. This compares quite well with the established melting temperature of Ag of 961C [3]. In a similar fashion, the calibrated temperature at which the Ag and $\text{Al}_2\text{O}_3$ peaks cross (658C) compares fairly well to the crossing temperature calculated from the room temperature $d$-spacing’s and the thermal expansion formulae (667C).

A rough multipoint calibration function can also be constructed from peak crossing events that occur at different temperatures within a single calibration standard. In addition to the crossing event described above, the Ag (311) and $\text{Al}_2\text{O}_3$ (119) peaks should cross at 165C and the Ag (200) and $\text{Al}_2\text{O}_3$ (113) peaks would cross at 1295C, were it not for the fact that Ag melts before
this temperature is reached. A mixture of two low-symmetry materials could provide many more crossings events. This is a technique that is unique to diffraction.

CONCLUSIONS
Temperature calibration of HTXRD stages by analysis of differential thermal expansion combines the advantages of the more commonly used calibration techniques (fast and complete characterization of the temperature range). The essential requirements for this method are that two peaks can be found within a narrow angular range that are characterized by different thermal expansion behavior. By examining the difference in position for peaks within a narrow range, the geometric errors which can contribute to the peak positions cancel. The two peaks do not necessarily need to be from different phases, but could be peaks from a common phase that has anisotropic thermal expansion (e.g., the (020) and (002) peaks of ZrO$_2$ are separated by less than 1° and have ~1.3% relative expansion between 273K and 1400K [4]). In the present case, Al$_2$O$_3$ and Ag were chosen to demonstrate the method because: (1) they have markedly different thermal expansion (1.2% relative at 1200K); (2) they have prominent peaks very near to one another (Al$_2$O$_3$ (110) and Ag (111)); (3) they are un-reactive (with each other, with the sapphire substrate or with the air in the furnace chamber); (4) the two peaks cross within the temperature window; and (5) the melting point of Ag provides an independent check on the calibration function. A simple linear function of the thermocouple temperature was adequate to fit the data, and accurately predicted the observed melting point of the Ag component. Other furnace environments, or other temperature ranges may yield calibration functions that are not well described as linear, and in these cases a multipoint calibration method is the only way to accurately characterize the specimen temperature. The present method provides such a calibration with the benefit of fast data collection and analysis.

REFERENCES