

# XRD Temperature Calibration with Phase Transitions

## Sources of error, advantages and limitations



### Introduction

XRD measurements at non ambient temperatures often require calibration of the temperature readout of the sample chamber.

Two methods of relating the XRD signal from the sample to sample temperature are generally used for calibration:

1. observation of **crystalline phase transitions or sample melting**
2. determination of **thermal expansion** from lattice parameters

Both methods can be used for external calibration and for internal calibration, where the reference substance is added to the actual sample.

### Using phase transitions for calibration

A number of compilations with applicable substances and their transition temperatures exist (e.g. [1],[2]). Some of the listed substances, however, show hysteresis of their transition temperatures, which can lead to calibration errors.

Two examples are shown for which the transition temperature changes when the phase transition is repeated.

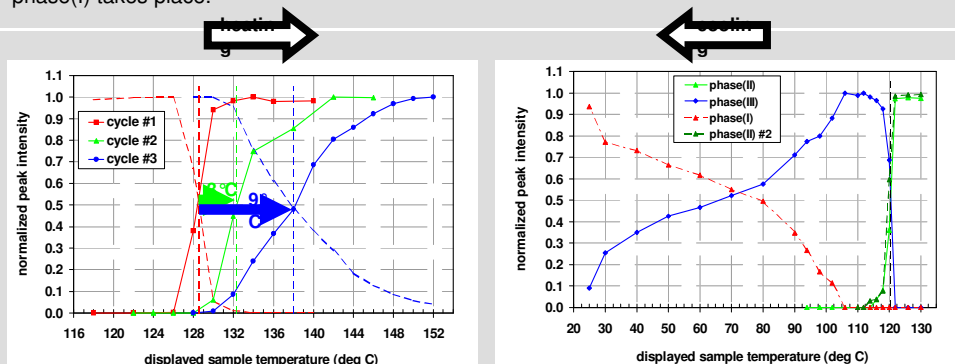
### Experimental set-up

The data presented were measured with a PANalytical X'Pert Pro diffractometer and Anton Paar high temperature attachments HTK1200N and XRK.

Sample height variations due to thermal expansion of the sample holder were compensated using a motorized alignment stage.

### Potassium nitrate $\text{KNO}_3$

$\text{KNO}_3$  undergoes a phase transition from orthorhombic(I) to trigonal(II) phase at  $T(\text{Lit})=129\pm1^\circ\text{C}$  (e.g. [3],[4]). Upon cooling down a metastable phase(III) forms at  $120^\circ\text{C}$  before conversion back to phase(I) takes place.



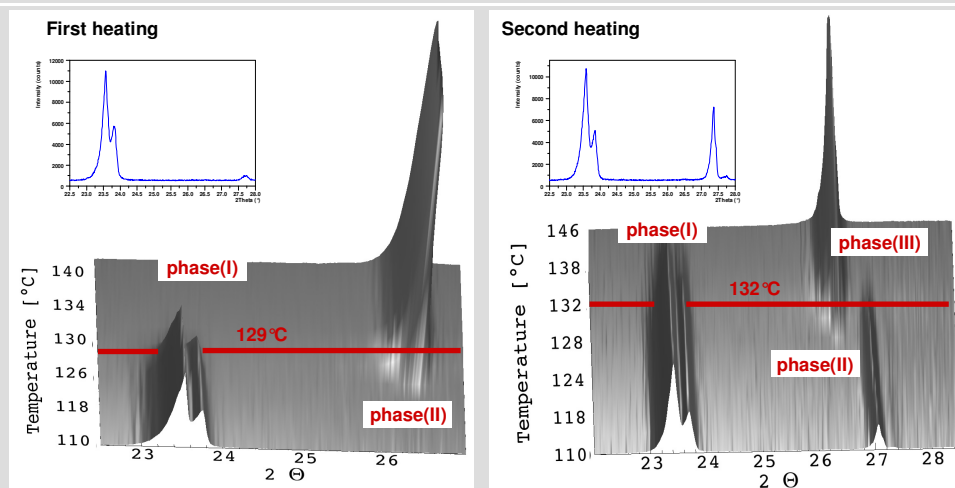
**Fig. 1**  
Formation of  $\text{KNO}_3$  phase(II) during three consecutive heating cycles.

The dashed lines show the decrease of phase(I) peak intensity.

**Fig. 2**  
 $\text{KNO}_3$  phase formation during cooling, starting with purely phase(II).

The dark green curve shows the transition of phase(II)  $\rightarrow$  (III) for a second cooling cycle.

Fig.1 shows that the transition temperature for the **first heating cycle** is  $T(\text{meas})=128^\circ\text{C}$ , which is in very good agreement with the literature value. When cooling down the sample (Fig.2), a sharp transition from phase(II) to the metastable phase(III) occurs at  $120^\circ\text{C}$ . This transition is very reproducible. The conversion from phase(III) back to phase(I) proceeds slowly and is not complete. A **fraction of phase(III) remains, changing the temperature at which the transition (I) $\rightarrow$ (II) takes place during the next heating cycles** (see Fig.3b).



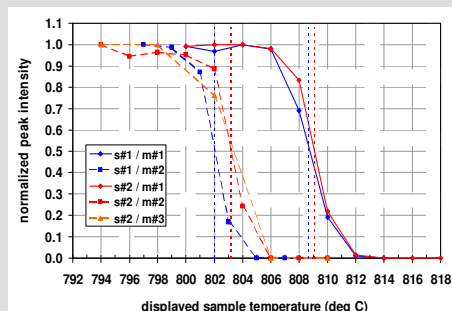
**Fig. 3**  
a) Peak pattern during first heating  
b) Peak pattern during second heating  
The inserts show scans at  $25^\circ\text{C}$  before the first and second heating cycle

(Graphics Powder3D)

When heating up the sample for the second time, phase(III) is present. The transition from phase(I)  $\rightarrow$  phase(II) starts later, not before the residual amount of phase(III) has disappeared. Additionally, the transition proceeds slower than during the first heating cycle when no phase(III) was present.

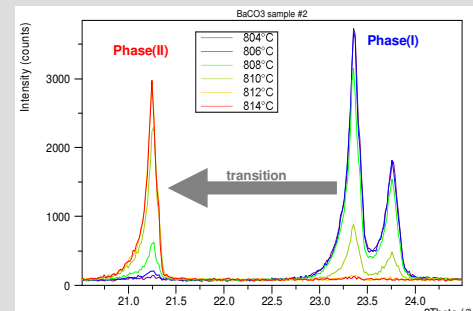
### Barium carbonate $\text{BaCO}_3$

$\text{BaCO}_3$  has two listed phase transitions, one changing from ortho(I) $\rightarrow$ hex(II) at  $T(\text{Lit})=810\pm1^\circ\text{C}$  ([2],[4]) and another one at  $982^\circ\text{C}$ [4]. The effect of a systematic change in transition temperature from the first to subsequent heating cycles was only observed for the first phase transition.



**Fig. 4**  
Transition of  $\text{BaCO}_3$  from phase(I) $\rightarrow$ phase(II) of 2 samples (s#1,s#2) for repeated heating cycles (m#1-3).

The Graph shows the decrease of the phase(I) peak intensity at  $\approx 23.4^\circ 2\theta$



**Fig. 5**  
Change in diffraction pattern at the ortho $\rightarrow$ hex phase transition.

Scans every  $2^\circ\text{C}$  at constant T  
Scan duration 80sec

The transition temperature of  $T(\text{meas})=809^\circ\text{C}$  for the **first heating cycle** is very close to the tabulated value.

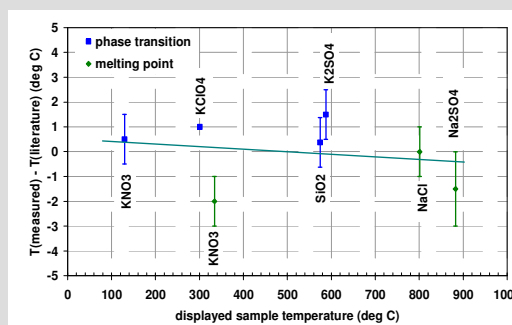
For **subsequent heating cycles** the **transition temperature** is **6-7°C lower**.

The reason for the observed shift in transition temperature is probably the strong sintering of the  $\text{BaCO}_3$  powder during the first heating cycle, which changes the thermal properties of the sample.

Because of the shown change in transition temperature and other disadvantages like its toxicity and its destructive effect on platinum heating strips,  **$\text{BaCO}_3$  is not a very suitable substance for XRD temperature calibration.**

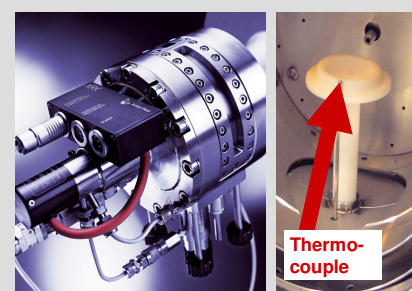
### Temperature calibration with phase transitions – An example

As an example for a calibration with phase transitions and melting points, the following graph shows the calibration curve obtained for an **Anton Paar XRK900** chamber (furnace type).



**Fig. 6**  
Calibration curve with phase transitions / melting points for an XRK900 heating attachment.

Atmosphere in the chamber: air, 1 bar



**Fig. 7**  
XRK900 heating attachment (left) and sample holder with thermocouple (right).

Calibration of the temperature measurement in air shows very good agreement between displayed and „real“ sample temperature. The spread of the calibration points is larger than the deviation between displayed and „real“ temperature, so no temperature correction needs to be applied in this case.

### Advantages and limitations

- Monitoring phase transitions and melting points is **not sensitive to sample position and data quality** and requires only very **simple data evaluation**.
- The method is **most feasible for calibration over a small temperature range**. To obtain a calibration curve for the complete temperature range, measurement of thermal expansion is preferable.
- When doing a straight forward calibration measurement, the estimated **remaining absolute error after calibration** for the Anton Paar furnace chambers HTK1200N and XRK is  $\pm 3^\circ\text{C}$ .
- Many tables with calibration standards are for calorimetry. It is wise to **use substances for which XRD data exist** in the literature.
- The **thermal properties of the actual sample can have a large impact on the temperature error**, especially for strip heaters. Calibration with internal standards added to the sample is needed to account for that error.

### References

- [1] Table of Calibration Standards by Dr. M. Emrich. [http://www.mpi-stuttgart.mpg.de/xray/html/temperature\\_calibration.html](http://www.mpi-stuttgart.mpg.de/xray/html/temperature_calibration.html)
- [2] Misure, S., (2004). Poster presented at 2004 Denver X-ray conference, Temperature Calibration For High-Temperature X-Ray Diffraction.
- [3] Table of Calibration Standards by Prof. Gallagher. [http://www.chemistry.ohio-state.edu/~gallagher/ta/calib\\_stand.htm](http://www.chemistry.ohio-state.edu/~gallagher/ta/calib_stand.htm)
- [4] Handbook of Chemistry and Physics, 64th Ed. (1984). CRC Press.