Temperature Validation for In-Situ X-ray Diffraction Below Ambient Temperatures

Relevant for: pharmaceuticals, quality control, non-ambient XRD

Validation of the temperature readout is an essential requirement for high quality non-ambient X-ray diffraction (XRD) experiments. This is typically done by comparing phase transition temperatures of well-known reference materials to the literature values. While many different reference materials for validation at temperatures above room temperature are known, finding suitable materials for validation below ambient temperatures is challenging.

1   Introduction

The relevance of in-situ XRD at varying temperatures is steadily increasing in academia and industry. Today, a large variety of different non-ambient attachments covering a wide range of temperatures is commercially available. This catalogue is extended even further by customized and self-made solutions that are specially designed for certain facilities or experiments.

One major challenge in the design of any non-ambient XRD attachment is the temperature measurement. The temperature reported by the thermosensor inside the attachment always deviates slightly from the actual temperature of the sample surface where the X-rays are diffracted from. The magnitude of the deviation depends on the heater design, the sample properties, the contact surface between sample and heater, and even the gas atmosphere surrounding the sample. In addition, depending on the thermal properties, size and shape of the sample, and on the type of heater employed, there might be a significant temperature gradient within the sample. While certain heater designs, such as environmental (oven) heaters, can improve temperature accuracy and homogeneity in comparison to other designs, such as direct heaters, a slight deviation in temperature is inevitable.

2   Temperature Validation

Temperature validation is essential to determine the magnitude of the deviation between the temperature of the sample surface and the temperature measured by the thermosensor. The validation is performed by measuring a sample with well-known thermal properties and comparing the experimentally determined temperature dependent material properties to literature values. There are two methods to perform a temperature validation:

1. A material with a suitable crystallographic solid-solid phase transition or melting point can be measured by XRD. Suitable phase transitions should be fast, clearly visible in diffraction data, and the transition temperature should be well-established. By comparing the temperature at which a phase transition is observed in the diffractogram to the expected value from the literature, it is possible to determine the temperature deviation. While this method is fast, does not require complex analysis of the diffraction data, and can be done at any temperature as long as a suitable reference material is available, it only provides information in a narrow temperature range and requires many XRD measurements with small temperature steps to precisely determine the transition temperature.

2. In the second method, a material with a well-established thermal lattice expansion can be measured over a wide temperature range. Several XRD measurements with large temperature steps (50 °C – 100 °C) between ambient temperature and the desired target temperature have to be performed. With this data the temperature dependent lattice expansion can be calculated. This can then be compared to known thermal expansion curves from literature to determine the actual sample surface temperature. With this method, the temperature deviation over a wide temperature range can be determined. While the measurement effort is lower compared to the phase transition method, and validation over a wide continuous temperature

range is possible, this method requires high quality diffraction data and careful analysis to determine the correct lattice parameter values. It is also less suitable for temperatures below 400 °C, where the lattice expansion is typically too small to be determined precisely.

Substance	Transition Temp. (°C)	Type[1]
NH_4NO_3	54	p.t.
NH_4NO_3	127	p.t.
KNO_3	128.7	p.t.
In	156.6	m.p.
$RbNO_3$	166	p.t.
$RbNO_3$	222.7	p.t.
Sn	231.9	m.p.
Bi	271.4	m.p.
$RbNO_3$	285	p.t.
$KClO_4$	299.4	p.t.
Cd	321	m.p.
Pb	327.5	m.p.
KNO_3	334	m.p.
Zn	419.5	m.p.
$AgSO_4$	426.4	p.t.
CuCl	430	m.p.
CsCl	476	p.t.
SiO_2	573	p.t.
Li_2SO_4	577.9	p.t.
K_2SO_4	584	p.t.
Sb	630.5	m.p.
Rb_2SO_4	653	p.t.
Al	660.3	m.p.
KCl	776	m.p.
NaCl	804	m.p.
Bi_2O_3	820	m.p.
Ag	961.8	m.p.
NaF	988	m.p.
Au	1064.2	m.p.
K_2SO_4	1069	m.p.
Cu	1083	m.p.
CaF_2	1360	m.p.
Ca_2SiO_4	1425	p.t.
Fe	1535	m.p.

Table 1: Reference materials with suitable transitions for temperature validation.[1] p.t.: solid-solid phase transition, m.p.: melting point.

The reference materials for both methods differ in their requirements, though certain materials (e.g. SiO_2) can be reliably used for both methods. A selection of possible materials for temperature validation measurements is given in Table 1 and Table 2.

One thing that all of the reference materials given in Table 1 have in common is that they only have transitions above room temperature. Validation of temperatures below ambient conditions, and particularly below 0 °C, is challenging as materials that fulfill the requirements for suitable phase transitions in this temperature region are harder to find.

In this report two candidates for low temperature validation, ammonium dihydrogen phosphate (ADP, $NH_4H_2PO_4$) and potassium dihydrogen phosphate (KDP, KH_2PO_4) are tested for their suitability as reference materials. ADP transitions from a tetragonal structure with the space group $I\bar{4}2d$ to an orthorhombic structure with the space group $P2_12_12_1$ at -125 °C,[2] while KDP transitions from the tetragonal space group $I\bar{4}2d$ to the orthorhombic space group $Fdd2$ at a temperature of -150 °C.[3]

Substance	T interval[1]	
	T_{min} (°C)	T_{max} (°C)
Si	20	1327
Pt	20	1627
MgO	20	1427
$MgAl_2O_4$	20	1927
Al_2O_3	20	1627
SiO_2	-223	527

Table 2: Reference materials for temperature validation by the thermal expansion method.[1] T_{min} and T_{max} indicate the temperature interval over which the reference material can be used.

3 Experimental Setup

3.1 Sample Preparation

ADP and KDP were obtained as fine powders and used without further treatment or purification.

3.2 X-ray Diffraction Measurements

XRD measurements were performed on the Automated Multipurpose Powder X-Ray Diffractometer XRDynamic 500 by Anton Paar with a Primux 3000 sealed-tube Cu X-ray source. Anton Paar's TTK 600 Low-Temperature Chamber was used for the low temperature XRD measurements with liquid nitrogen as the cooling medium. All measurements were performed under vacuum, in addition to the standard sample holder of TTK 600, the optional heating

environment available for TTK 600 (Figure 1) was used to evaluate its performance at low temperatures.
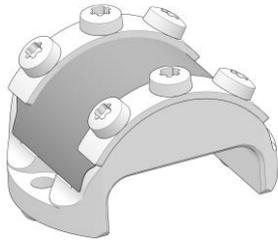

Figure 1: The optional TTK 600 heating environment

At each temperature step, measurements were started after a waiting time of one minute to allow for sample equilibration.

3.3 Temperature Profile

Measurements were performed at 30 °C and at -180 °C to identify the changes to the diffractogram that occur during the phase transition. Additionally, preliminary measurements with 10 °C temperature steps over the full temperature range and more accurate measurements with 1 °C temperature steps around the expected transition temperature were performed to determine the temperature of the phase transition.

3.4 Identification of Phase Transitions in Heatmaps

Visualizing the XRD data as heatmaps allows quick analysis and comfortable visualization of the results. On the x-axis, the scattering angle 2θ is plotted, and the y-axis gives the displayed temperature of the thermosensor. The intensity is color-coded, from black (zero intensity), over red, orange and finally white for high intensity. As phase transitions are sometimes indicated by the appearance of reflections with low intensity, and sometimes by changes to reflections with high intensity, the correct contrast of the plots is important. Lowering the contrast to a point where low intensity reflections are clearly visible can lead to the impression of broadening of the reflections with higher intensity (similar to overexposure on film), making the precise observation of peak positions or splitting difficult. It is not always possible to observe all changes of the diffractogram in the same plot, but focusing on one or two reflections is usually sufficient to determine the transition temperature. The intensity difference between the high intensity and low intensity reflections can be reduced by plotting the square root or decadic logarithm of the intensity instead of the absolute value. For all heat map plots of ADP and KDP, the square root of the intensity was plotted.

4 Results

4.1 ADP

4.1.1 Standard TTK 600 Set Up

Comparing the 30 °C and -180 °C patterns gives an overview of the visible changes. The intensity of the reflection at 29.0° 2θ increases, while the intensity of the reflection at 23.75° 2θ decreases, making the reflection at 29.0° 2θ the stronger of the two reflections in the low temperature form (Figure 2a). At the same time, the position of both peaks shifts slightly towards lower angles. Additionally, the appearance of reflections with very low intensity at 26.6°, 36.0°, 40.0° and 43.5° 2θ (Figure 2b) can be observed.
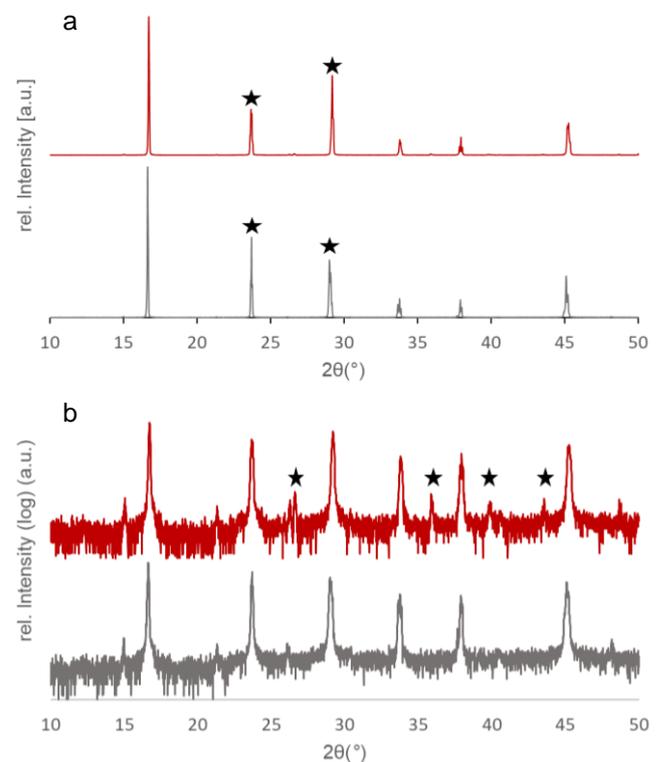

Figure 2: Diffractograms of ADP at 30 °C (grey) and -180 °C (red) plotted on a linear (a) and on a logarithmic scale (b). Reflections that visibly change intensity and newly appearing reflections are marked with stars.

In a preliminary measurement of ADP between -50 °C and -180 °C, the transition temperature could be identified to be between -140 °C and -150 °C. While the observed structural changes are fast, reversible and reproducible, they are not very significant and might be missed in measurements with low resolution or short exposure times.

The results of the measurements with smaller temperature steps are depicted in Figure 3. From these data, it can be deduced that the phase transition occurs at -142 °C.
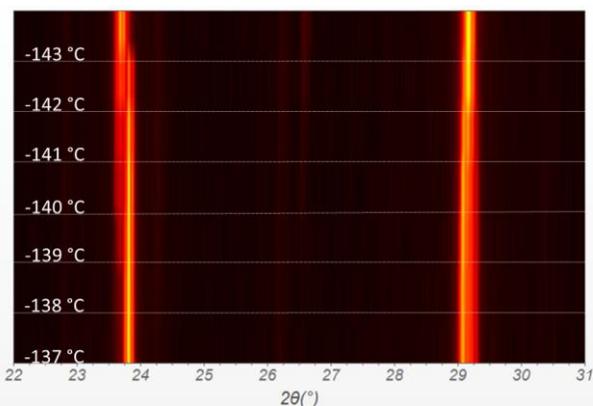
Figure 3: Heatmap of the low temperature measurements with small temperature steps of ADP zoomed in to the region between 22° and 31° 2θ. A lower contrast was chosen to show the peak shifts and intensity changes in the stronger reflections. Due to this, the expected additional peak at 26.6° 2θ is barely visible.

The literature value for the phase transition of ADP is -125 °C, 17 °C above the measured temperature of -142 °C, i.e. the phase transition occurs with a delay of 17 °C. The observed deviation corresponds to roughly 14 %, which is to be expected for a direct heater/cooler as the sample is only heated or cooled from below so temperature gradients are unavoidable.

4.1.2   TTK 600 Heating Environment

Experiments were repeated with the optional heating environment available as an accessory for TTK 600. The heating environment transforms the direct heater inside TTK 600 into a miniature environmental heater, increasing the temperature homogeneity around the sample. The transition temperature with the heating environment was determined to be at -128 °C, only 3 °C (2 %) below the literature value (see Figure 4). This deviation is very small, making it clear that the use of the optional heating environment is highly beneficial even for low temperature experiments despite its name.
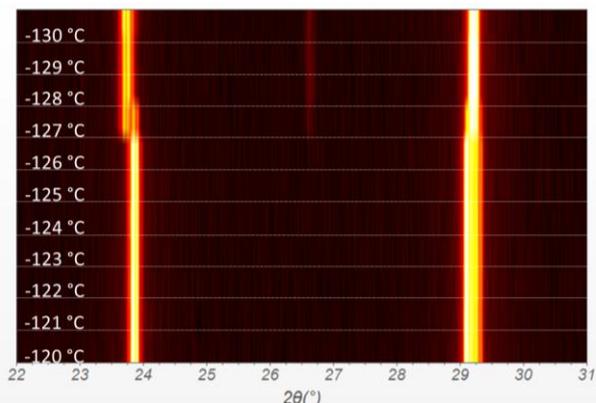

Figure 4: Heatmap of the low temperature measurement with small temperature steps of ADP with the heating environment for TTK 600.

4.2   KDP

4.2.1   Standard TTK 600 Set Up

The phase transition in KDP does not lead to the appearance of new reflections, but several existing reflections, both of low and high intensity, change. Most notably, the double peak making up the second strongest reflection in the pattern at 30.8° 2θ splits into multiple reflections. Similar splitting, usually accompanied by a loss of intensity and a slight positional shift, can be observed for the reflections at 29.7°, 34.1°, 45.8° and 46.5° 2θ (Figure 5).
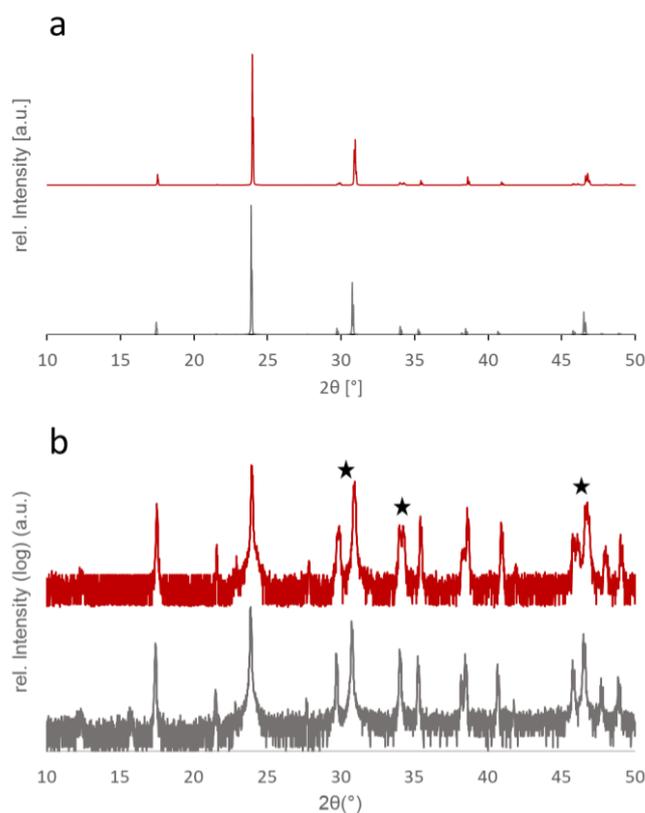

Figure 5: Diffractograms of KDP at 30 °C (grey) and -180 °C (red) plotted on a linear (a) and on a logarithmic scale (b). Reflections that show significant changes during cooling are marked with stars.

The preliminary temperature-dependent measurements show that the changes occur between -160 °C and -170 °C. Subsequent measurements with smaller temperature steps showed the transition temperature to be at -162 °C (see Figure 6). This is 12 °C below the literature value for KDP of -150 °C, a deviation of 8 %, again indicating a delayed phase transition as is to be expected with the direct heater/cooler set up.
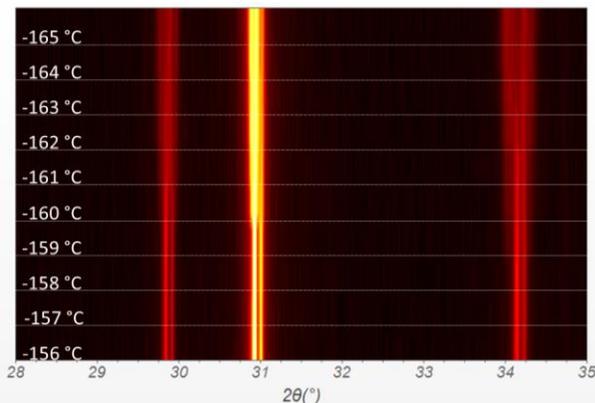
Figure 6: Heatmap of the low temperature measurements with small temperature steps of KDP zoomed in to the region between 28° and 35° 2θ.

4.2.2 TTK 600 Heating environment

The influence of the optional TTK 600 heating environment was also studied for the measurements of KDP.
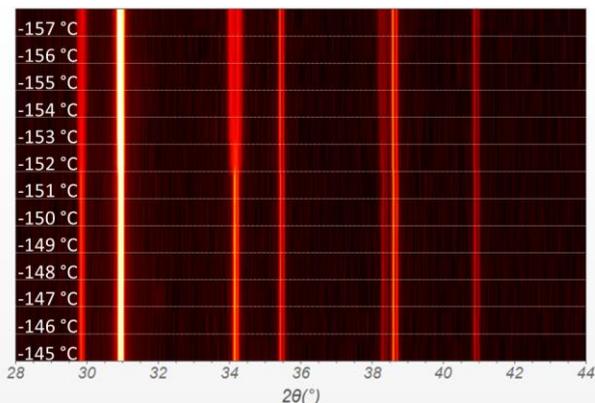

Figure 7: Heatmap of the low temperature measurements with small temperature steps of KDP with the optional heating environment for TTK 600.

Figure 7 shows that the observed transition temperature of KDP with the optional heating environment is -152 °C, which is only 2 °C below the literature value. This corresponds to a deviation of only 1.3 % again showing the benefits of using the heating environment to reduce the size of the deviation between the measured and actual sample temperature.

5 Conclusion

ADP and KDP work well as temperature validation materials in the temperature range from -125 °C to -150 °C. As the phase transitions in both materials only lead to slight changes in the diffraction patterns, the resolution and signal-to-noise ratio of the validation measurements play an important role.

Only a few reflections in both materials show clear signs of the phase transitions, so validation measurements only need to be performed over a small angular range (e.g. 22° to 31° 2θ for ADP and 28° to 34° 2θ for KDP).

Both materials can be used with the standard sample holder or with the optional heating environment of TTK 600. It was shown that the heating environment significantly reduces the temperature deviation between the measured and sample temperature, and should therefore be used whenever possible at temperatures below ambient conditions.

6 References

1. Pein, A, Puhr, B, Jones, A: *The Non-ambient Guide: Principles of Non-ambient X-ray Diffraction.* https://www.anton-paar.com/corp-en/the-non-ambient-guide/ (accessed 04.02.2022)
2. Fukami, T, Akahoshi, S, Hukuda, K and Yagi, T: *Refinement of the Crystal Structure of $NH_4H_2PO_4$ above and below Antiferroelectric Phase Transition Temperature.* J. Phys. Soc. Jpn. *56*, 2223-2224 **1987** https://doi.org/10.1143/JPSJ.56.2223
3. Melo, F.E.A. *et al.*: *New Phase transition in KDP.* Brazillian Journal of Physics, *22*, 2, **1992**.