In situ powder X-ray diffraction for the investigation of phase transitions and structural changes by the use of novel X-ray diffraction equipment

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While most X-ray diffraction (XRD) measurements are performed under ambient conditions (i.e. room temperature, ambient pressure), many geological, catalytical or industrial processes occur under non-ambient conditions. Non-ambient parameters, such as temperature, pressure, humidity or different gas atmospheres can change a material's structure, property or reactivity significantly. Since many of these changes are reversible, or occur stepwise with multiple intermediates, *in situ* and operando investigation of materials under non-ambient conditions is an essential tool in establishing a detailed understanding of a materials properties. With this, non-ambient X-ray diffraction (NA-XRD) is one of the most powerful characterization methods to investigate the structure-property relationship of crystalline materials. It can be used to follow the activation and degradation processes of heterogeneous catalysts, the phase transitions occurring in the sintering processes of cement materials, or the freezing processes in biological materials, just to name a few examples.

The most prominent non-ambient parameter in XRD is temperature. There is an increasing demand for higher temperatures without losing accuracy in temperature control and measurement. Highest temperature accuracy is required, e.g. for lattice parameter determination and structure analysis, identification of thermal expansion coefficients, measurement of temperature induced phase changes and investigation of chemical reactions and processes *in situ* (e.g. annealing, sintering, calcination, ...). The HTK 1500 High-Temperature Chamber (Fig. 1) is an environmental heater for high-temperature XRD studies that allows users to homogeneously heat crystalline powders and bulk samples up to 1500 °C. The temperature sensor in the HTK 1500 is located directly under the sample in a protective ceramic sample holder. This arrangement provides highly reproducible and reliable temperature measurement and stable temperature control. The possibility to switch between different measurement geometries - reflection geometry and transmission geometry using a capillary extension - allows a wide variety of sample types to be investigated.

XRD and Raman spectroscopy (Raman) are complementary analysis methods in that XRD provides abundant information on the atomic arrangement of the sample revealed through the diffraction pattern and Raman spectroscopy can measure the characteristic vibration frequencies determined by the chemical composition and chemical bond. The combination of XRD and Raman provides a deeper insight into material properties and is therefore gaining increasing interest. Even more information can be obtained by adding the possibility of varying non-ambient parameters to the experiment. A customized XRD-Raman-Humidity Sampler includes a sample changer for conditioning up to 8 samples in one run to the desired temperature (between 10 °C and 60 °C) and relative humidity (between 0% and 95% rH). The XRD measurements are done in transmission geometry, making the XRD-Raman-Humidity Sampler an optimal choice for, e.g., pharmaceutical or food samples, just to mention the most prominent ones. The given non-ambient parameter ranges allow to mimic the effect of storage conditions on the structural characteristics of such samples *in situ*. Raman measurements can be performed at any time during the condensation-free sample conditioning and at a specific temperature and relative humidity setpoint.

In this presentation, we will give an overview of the technical specifications of the non-ambient XRD equipment as well as a summary of its benefits and application data, like the investigation of crystallographic changes in pharmaceutics and piezoceramics.

Figure 1. HTK 1500 High-Temperature Chamber