APPLICATION NOTE

Dynamic studies with ARL EQUINOX 100 and BTS500 chamber

Introduction

X-ray diffraction is one of the commonly used structural analysis techniques to characterize materials as a function of temperature, environment and other external conditions. Phase transitions take place when materials undergo thermal cycles (at high temperatures or low temperatures) and their crystal structures can vary significantly leading to different properties of materials.

Thanks to the real-time detector technology of the Thermo Scientific™ ARL™ EQUINOX 100, one can perform rapid XRD measurements to study structural phase transitions of materials at high temperature. With the recent availability of a compact high-temperature chamber, designed for integrating inside a bench-top XRD instrument and coupled with a simultaneous full pattern XRD capability, it is now possible to do dynamic studies at high temperature much faster and more conveniently.

This application note presents an example of such a study with ARL EQUINOX 100 coupled with Anton-Parr BTS500 chamber to illustrate this new cost-effective solution for material scientists.

When combining the ARL EQUINOX 100 with Anton Paar BTS500 high temperature chamber we obtain probably the fastest benchtop XRD for dynamic studies. In a very small form factor and very low power requirements (less than 250 Watts) we have the possibility to study phase transitions, or chemical reactions, extremely easily and with full computer control of the ARL EQUINOX 100 itself but also on the high temperature chamber.

To demonstrate the performance of this system, we did a quick experiment, less than 3 hours from start to 3D result plot.

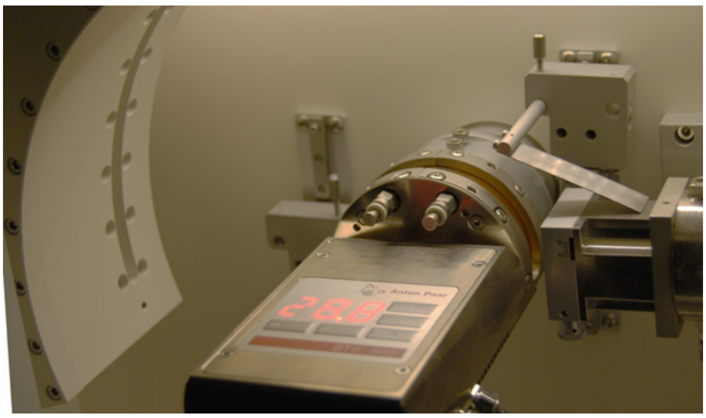
Instrument

The Thermo Scientific™ ARL™ EQUINOX Series represent a portfolio of XRD instruments from simple, easy to use bench-top systems for routine analysis to more advanced floor-standing, high performance, research grade systems for investigative laboratories.

The ARL EQUINOX 100 employs a custom-designed micro-focus tube (50 W for Cu or 15W for Co) which does not require an external water chiller. The same unit can be transported between laboratories or into the field and does not require any special infrastructure.

The ARL EQUINOX 100 provides very fast data collection times compared to other diffractometers due to its unique curved position sensitive detector (CPS) that measures all diffraction peaks simultaneously and in real time.

Figure 1: BTS500 chamber into the ARL EQUINOX 100



Experimental conditions

We used $RbNO_3$ powder, as received from supplier (alfa aesar, 13496, 99% purity) in a BTS500 nickel sample cup for these studies.

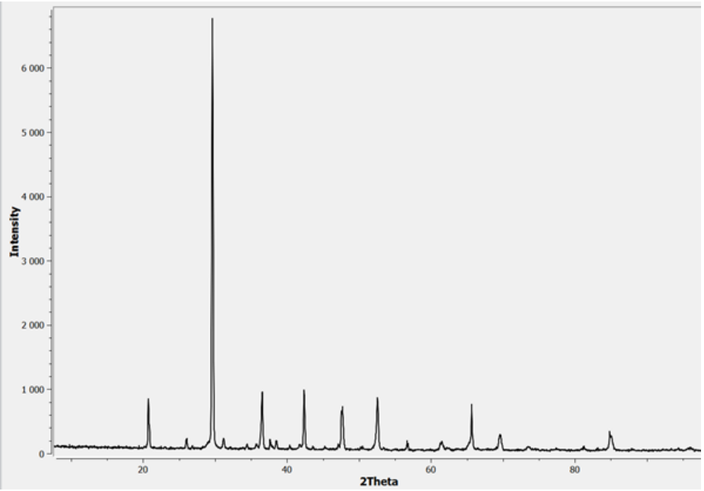
Using Symphonix software we prepared a batch run, as follows:

- We used 2°C/min heating ramp on the furnace to reach 350°C.
- We then started a cycle of 2-minute acquisitions.

This means that thanks to the curved detector, that permits to get a full XRD pattern over 110° all the time, every 2 minutes we will get a new pattern that covers the total angular range. Without doing any dwell we get like this a new pattern every 4°C.

On the ARL EQUINOX 100, we used a copper minisource coupled with SmartOptics, running at 36 W power (40 kV, 0.9 mA). During the whole experiment, we have a live display of the on-going full XRD pattern.

Figure 2: Typical $RbNO_3$ pattern obtained in 2 minutes at room temperature

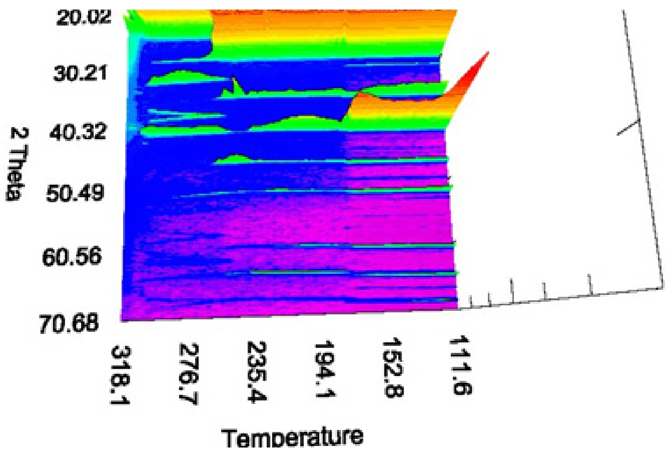


Results

Rubidium nitrate exhibits a number of phase transitions between room temperature and 310 °C, the melting temperature.

If all the patterns obtained are plotted from room temperature up to 350 °C, the following picture is obtained (the 20 to 70° 2θ region was zoomed in on, which is more interesting, but the full angular range is always available with a curved detector).

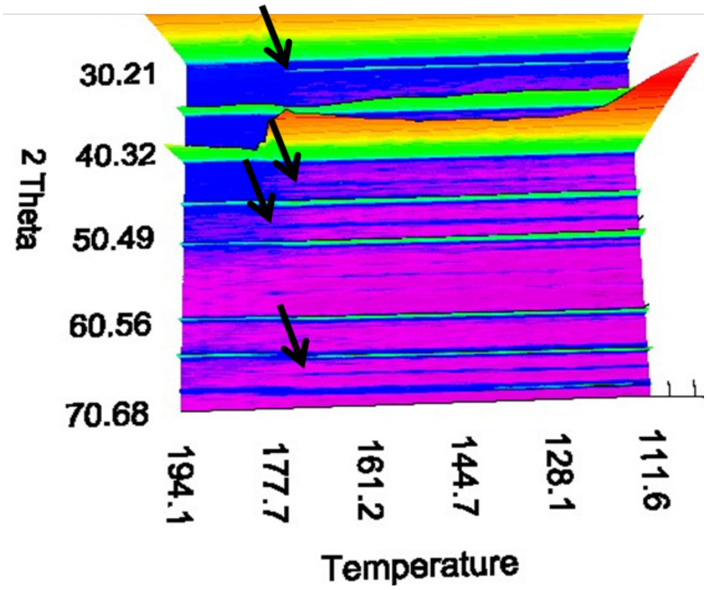
Figure 3: Rubidium nitrate patterns obtained from temperature up to 350°C



It is obvious that the pattern changes several times during the experiment.

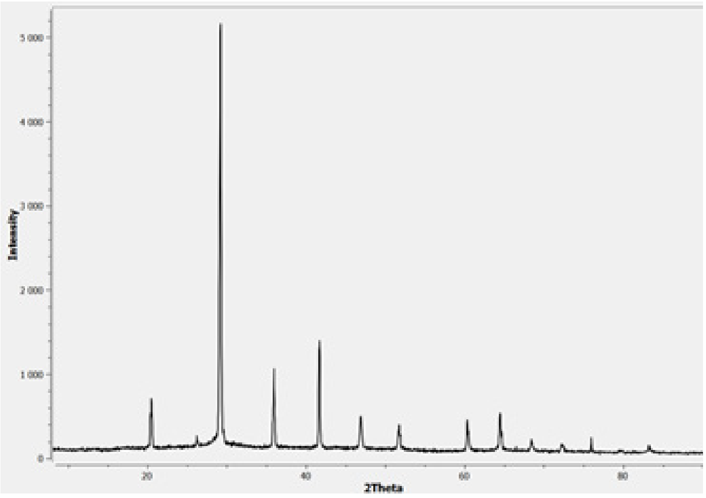
At room temperature rubidium nitrate has a trigonal structure up to around 160°C, then it changes suddenly to another structure, which is reported as being cubic.

Figure 4: Trigonal structure of rubidium nitrate at temperature around 160°C



A closer look at around 165°C where we see that the small peaks between the higher ones disappear around 170°C.

Figure 5: Rubidium nitrate pattern saved at 181°C



Phase transitions shown here happen at higher temperature as reported in the literature, but since we are not doing any dwells around phase transition temperature, and the fact that the sample is heated from the bottom, and with the X-rays we see the top of the surface it takes time before we effectively see it in the diffraction pattern. The experiment done here should be considered as a fast screening before repeating the measurements with much slower speed around phase transition temperature.

At higher temperature, around 250°C in our experiment (while reported at 219°C in the literature) a second phase transition is seen. It is very clear since we switch from cubic to rhombohedral.

Figure 6: Rubidium nitrate patterns at around 250°C

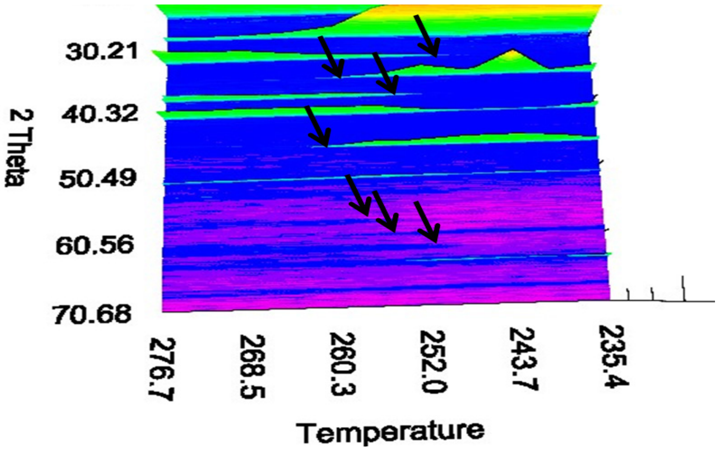
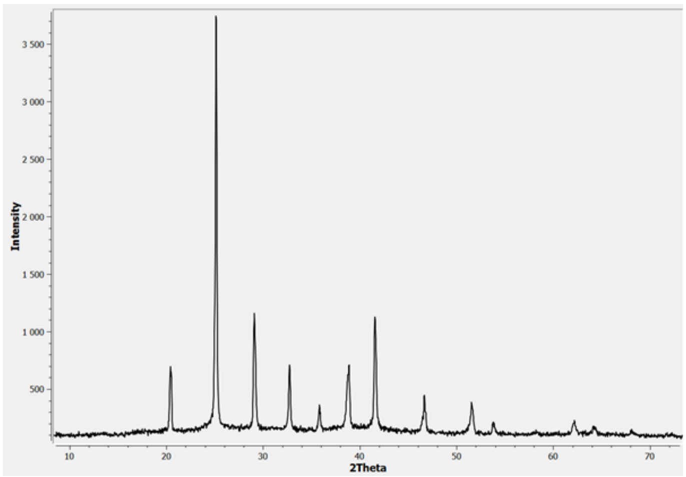


Figure 7: Rubidium nitrate pattern saved at 260°C

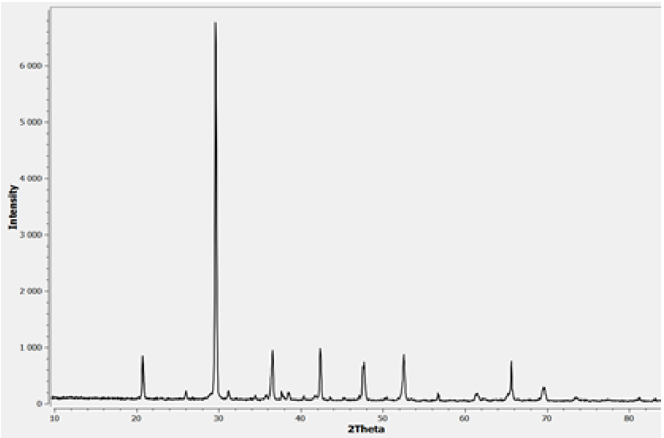


Conclusion

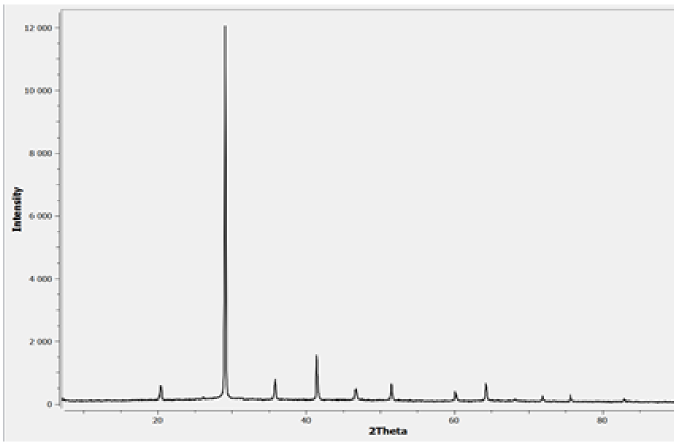
With ARL EQUINOX 100 equipped with a BTS500 high temperature chamber, we could evidence in less than 3 hours and 10 clicks the 4 known structures of $RbNO_3$.

The next step would be to ramp quickly around approximately known phase transition temperatures and then record the sample slowly every degree or so, to have a very nice view at exact temperatures of phase transitions.

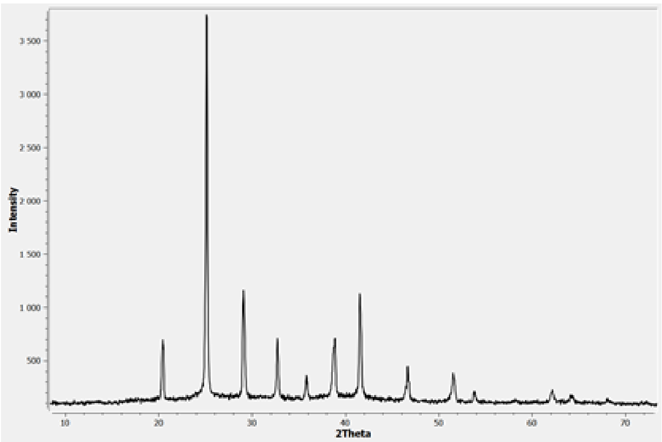
Figure 8: Rubidium nitrate pattern saved at various temperatures



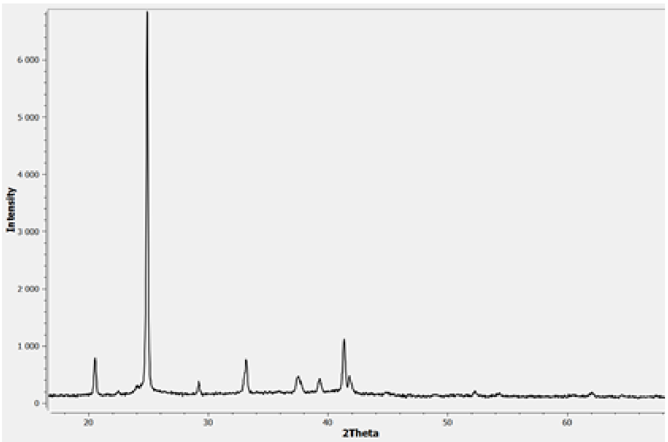
Room temperature



180°C



260°C



292°C

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