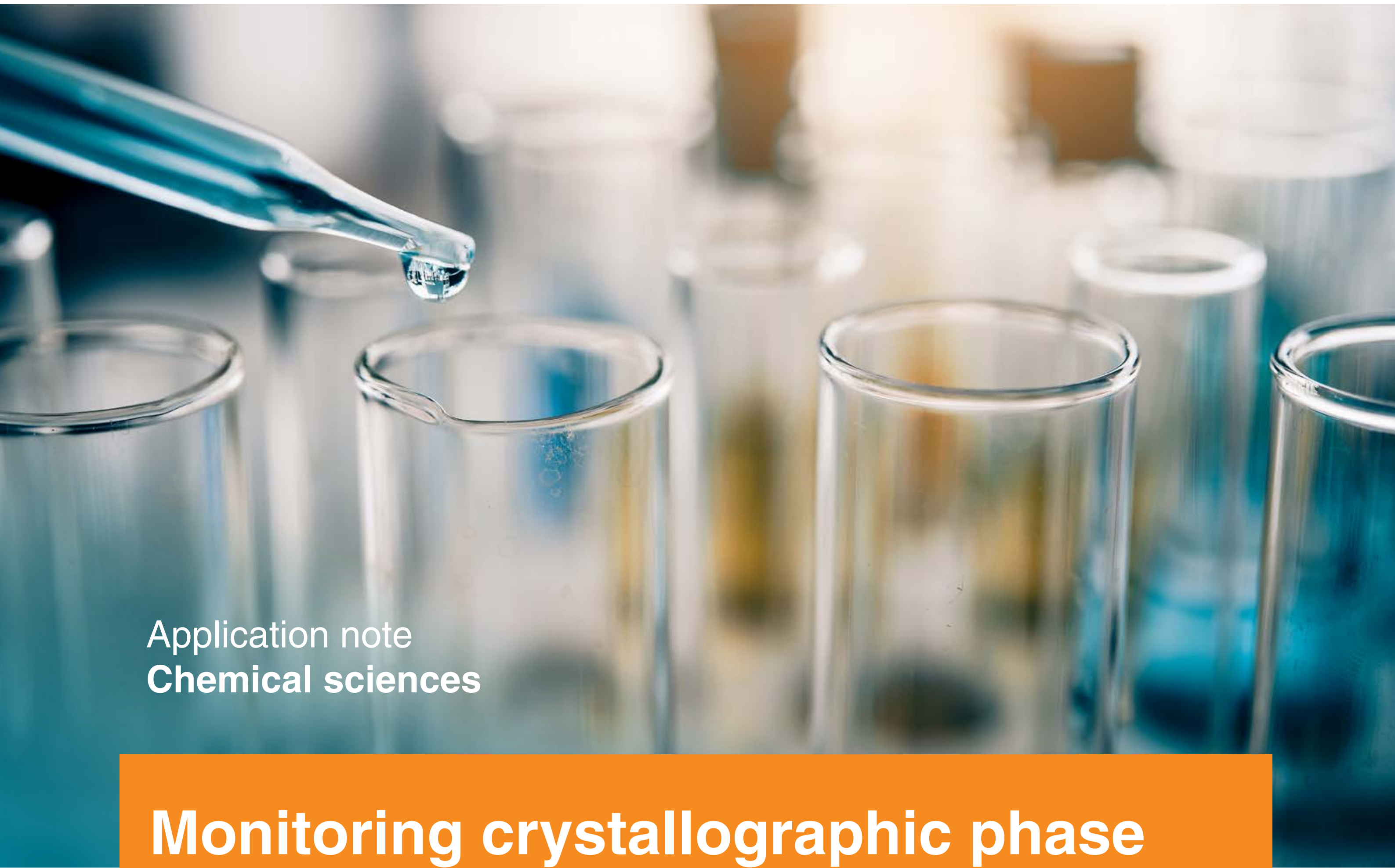


Application note
Chemical sciences

Monitoring crystallographic phase changes with Raman spectroscopy

Many materials exhibit polymorphism, existing in multiple crystalline phases. These range from the well-known example of carbon—existing in forms that include graphite, graphene, and diamond—to more complex polymorphs of many chemicals used in pharmaceuticals.

These phases undergo transitions at certain temperatures or pressures, can often be unstable, or can exist in yet undiscovered forms. Researchers therefore need a convenient non-destructive method to study these materials during their transitions, to help them understand and improve syntheses of these different crystalline forms.

Monitoring active experiments during a phase transition

Raman spectroscopy can be used to identify crystalline forms. It offers sampling flexibility and can monitor changes in chemistry and crystallography during phase transitions.

The Renishaw inVia™ Raman microscope is ideal for such studies as it can be equipped with a range of variable temperature sample stages. These can be directly controlled by the inVia microscope so that Raman measurements may be automated during experiments where temperatures or pressures are changed systematically.

In this example we monitored the phase changes of potassium nitrate (KNO_3), a chemical widely used in fertilizers, solid rocket propellants, and fireworks. The salt exhibits three crystallographic phases. The stable form depends on temperature, pressure, and thermal history.

We studied the heating and cooling of KNO_3 in situ using an inVia Qontor® confocal Raman microscope with 532 nm excitation. Renishaw's Monitor™ software module enabled observation of the Raman spectra live, revealing the transition process, transition temperatures, and the transformation steps.

Temperature control

A Linkam THMS600 stage was used to heat and cool the sample (Figures 1 and 2). The stage was controlled directly from the inVia microscope's software (Renishaw WiRE™ software), using the advanced temperature control (ATC) option.

Figure 1. The Linkam THMS600 stage used for the study.

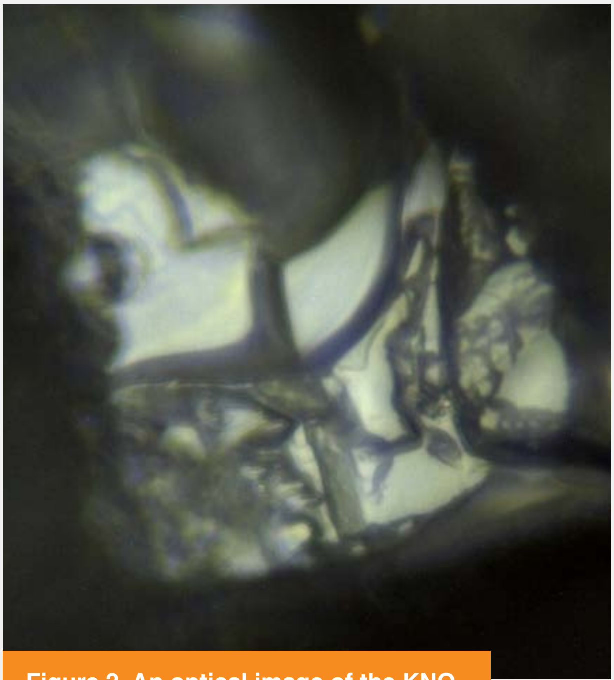


Figure 2. An optical image of the KNO_3 crystallite within the Linkam stage.

Determining the phases present

We ran a heating-cooling cycle, acquired the Raman spectra, and confirmed the phase assignments by comparing them with those in the literature[1,2]. The three phases of potassium nitrate can be distinguished by differences in their spectra in the 1200 cm^{-1} to 1600 cm^{-1} range (Figure 3).

Specifically:

- Phase I (β-phase, paraelectric): two broad and convolved Raman bands (1355 cm^{-1} and 1420 cm^{-1})
- Phase II (α-phase, paraelectric): two sharp bands (1344 cm^{-1} and 1359 cm^{-1})
- Phase III (γ-phase, ferroelectric): three bands (1349 cm^{-1}, 1424 cm^{-1}, and 1436 cm^{-1})

Phase II is stable under ambient conditions. Upon heating above 133 °C it changes to phase I (a disordered calcite-like structure). The cooling process is more complex[3], as it also involves phase III, and the phase changes have very different kinetic rates. When cooling the sample we saw the beginning of the phase I to phase II transition when the temperature dropped below 126 °C. Phase III was unstable below 96 °C, and we observed Raman band shifting. Below 96 °C we detected mainly phase III. Phase III fully transformed to phase II when the temperature dropped below 33 °C.

We used the Raman spectra of all the confirmed phases as reference spectra in our subsequent analysis using the WiRE software. Analysis was based on the comparison of the chemical components with reference spectra (non-normalised component analysis). We then created an 'analysis chain' file for the WiRE software that enabled us to perform the same processing during a subsequent experiment so that the phase transitions could be monitored live.

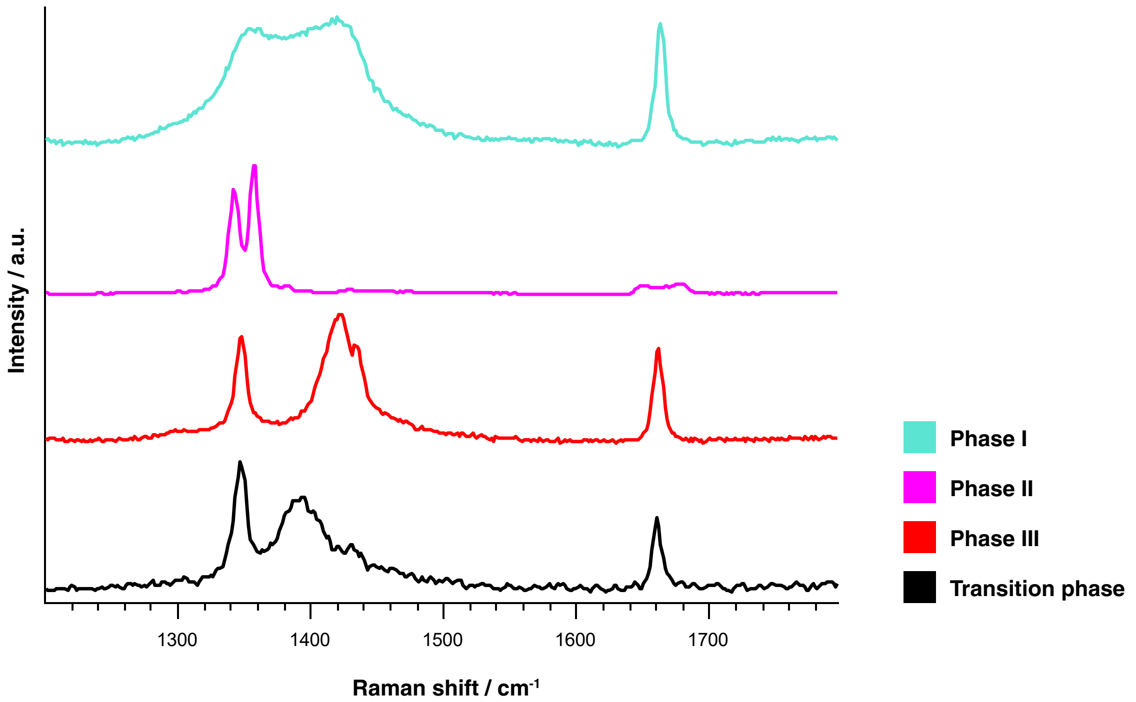


Figure 3. Raman spectra of the potassium nitrate phases that were detected during the thermal process. We saw an intermediate transition stage in addition to the standard three phases.

Monitoring phase changes live as they occur

We used Renishaw's Monitor software module to track the changes in the material, live as they occurred. This can analyse and monitor changes at up to 20 spectra per second.

Figure 4 illustrates the phase changes that were induced by the heating and cooling process. You can also view and analyse the files generated by the Monitor software module within the main WiRE software if you need to extract additional analytical information.

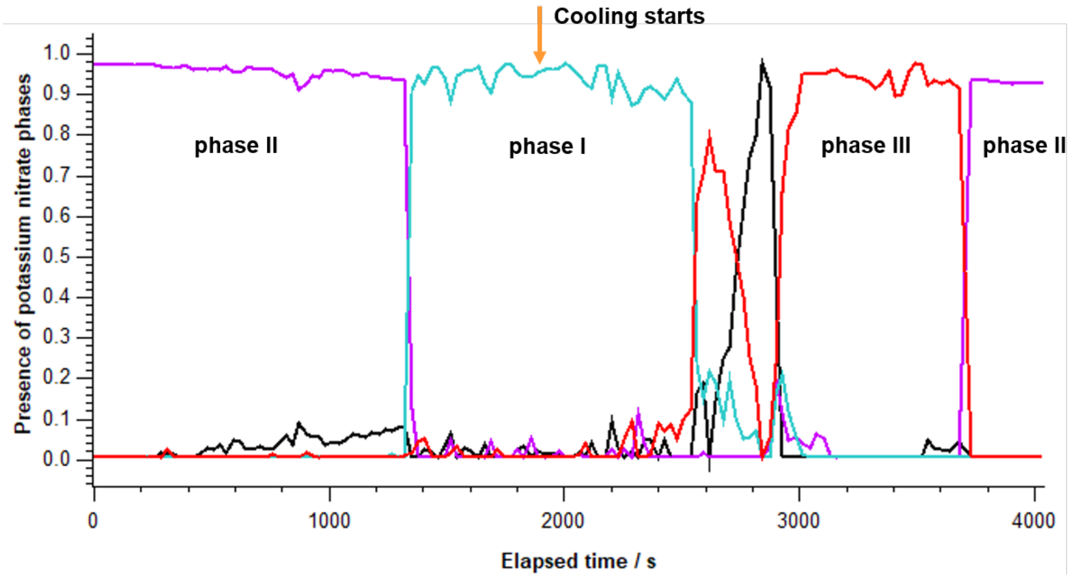


Figure 4. Phase transitions seen during Raman monitoring: phase II (magenta); phase I (cyan); phase III (red); and the transition phase (black).

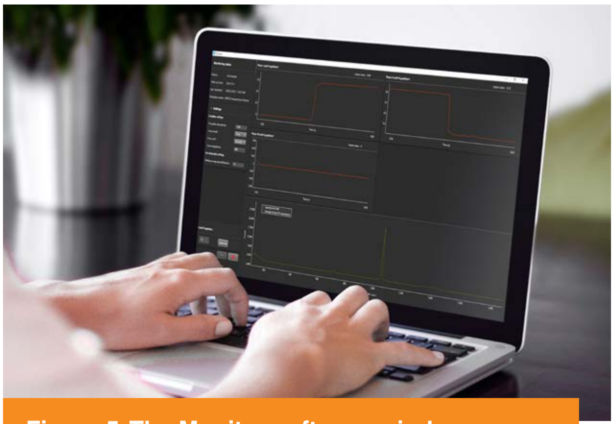


Figure 5. The Monitor software window showing a potassium nitrate transition from phase II to phase I during the heating process.

Renishaw's WiRE Monitor software module enables you to quickly and easily track changes occurring in real time (Figure 5). It has measurement templates that make it easy to repeatedly acquire data, and automated spectral analysis that processes data as it is live streamed. In this case we could observe the phase changes when they were occurring, using a separate analytical window for each KNO_3 phase.

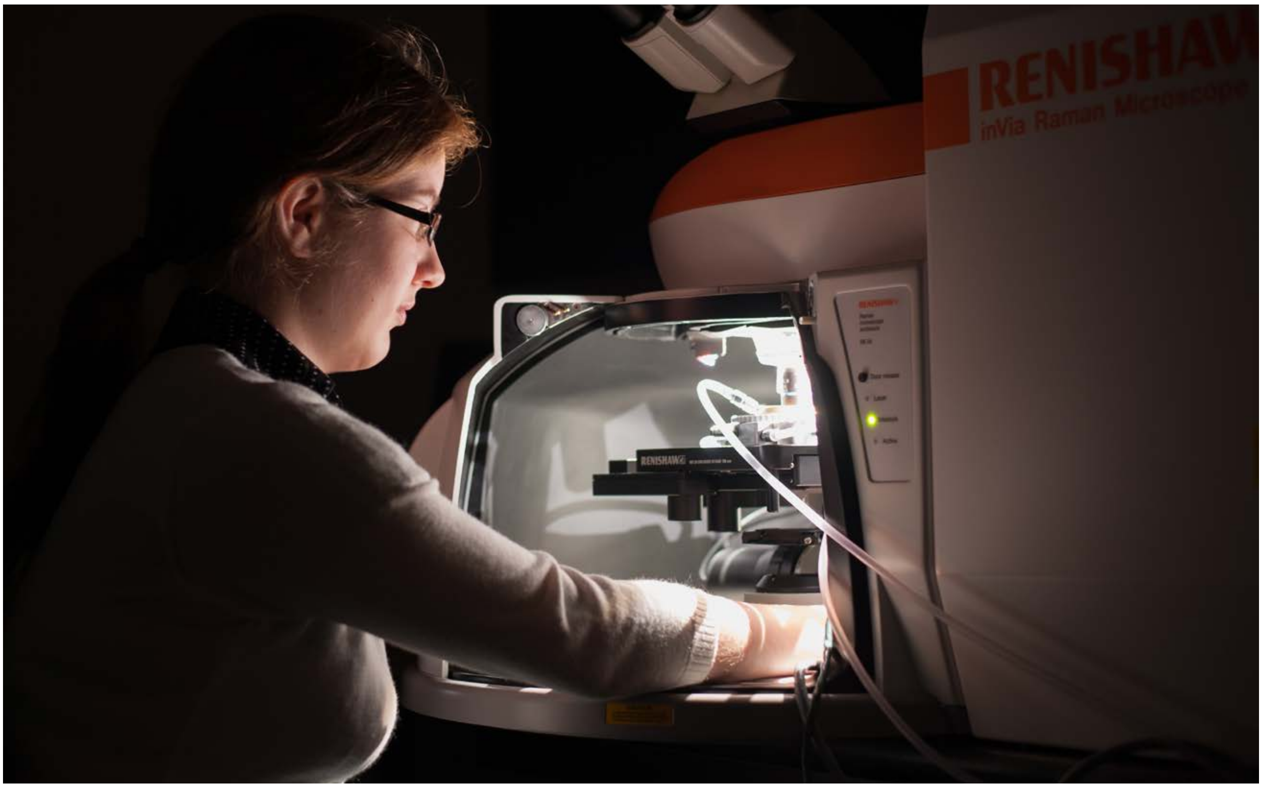
The software provides information on the last recorded spectrum and displays it together with the average of the last 10 spectra. The data can be saved and re-analysed using the Renishaw WiRE software for more detailed analysis.

An ideal tool for live process screening

In this example we have used an inVia Raman microscope and temperature controlled stage to analyse phase changes. Renishaw's advanced software enabled us to control the stage, data acquisition, and monitoring of the phase changes as they occurred.

The high specificity of Raman spectroscopy allowed us to unambiguously differentiate between the potassium nitrate phases during the heating and cooling.

When monitoring a chemical process that occurs in a remote location, reactor or pilot plant, Renishaw's Virsa™ fibre-optic-coupled Raman analyser offers an ideal solution. Raman spectroscopic monitoring is applicable to a very wide range of physical and chemical processes, where it can be used for research, quality screening, and synthesis control.



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References

(1) M.H. Brooker, Can. J. Chem., 55 (1977) 1242

(2) M.H. Brooker, J. Phys. Chem. Solids, 39 (1978) 657

(3) Deshpande V. V., Karkhanavala M. D., Rao U. R. K., Journal of thermal analysis, vol. 6, pp. 613–621 (1974). https://doi.org/10.1007/BF01911781

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