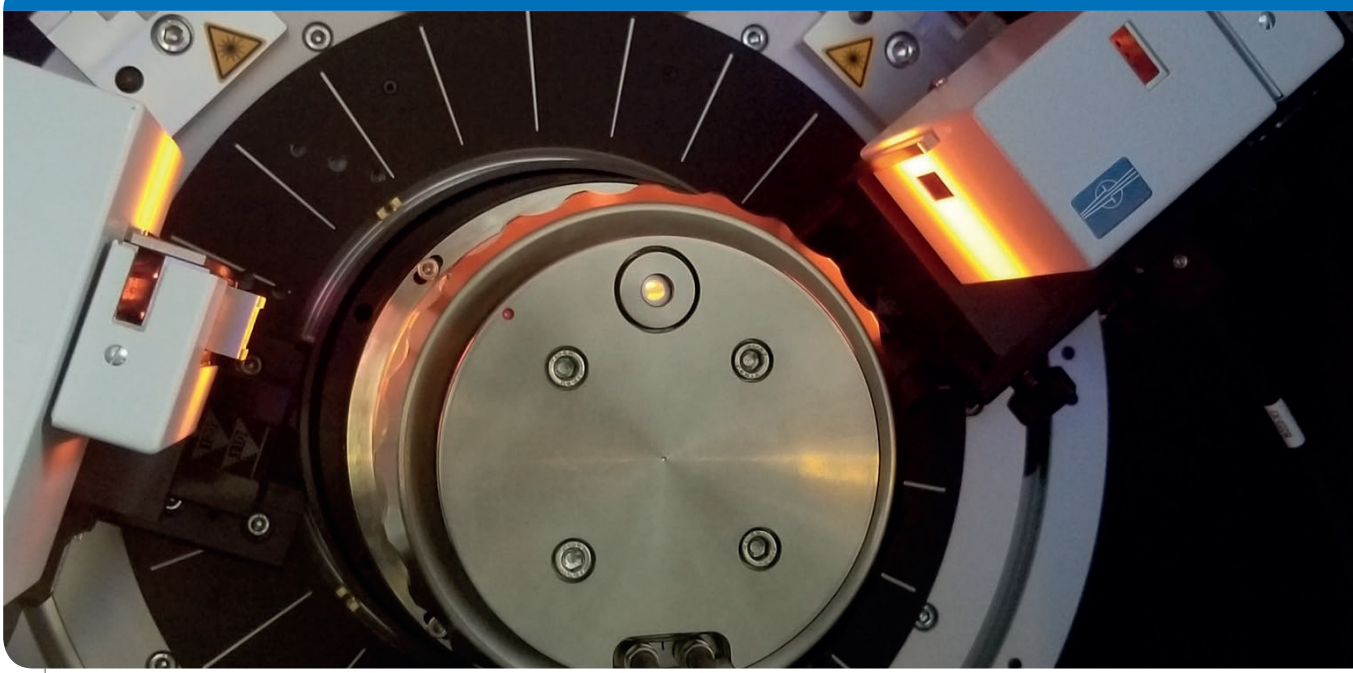


Application Note XRD 611

Non-Ambient Diffraction with D8 ADVANCE ECO and MTC-HIGHTEMP

In-situ diffraction studies provide insight into structural changes and reactivity under non-ambient conditions. For example, barium titanate ($BaTiO_3$) undergoes a reversible phase change from tetragonal to cubic above 130 °C.[1]

Access to higher temperatures, however, is often required. Anatase (TiO_2) converts irreversibly to the rutile polymorph at elevated temperatures. Reported transition temperatures vary from 400 °C - 1200 °C due to differences in particle size/shape, surface area, impurities, and various other parameters.[2-3]

Direct measurement of this conversion is possible with non-ambient diffraction.

Summary

- Ceramic materials were characterized by XRD at high temperatures
- D8 ADVANCE ECO (1 kW) provides fast scan speeds with exceptional signal-to-noise
- MTC-HIGHTEMP capable of accessing temperatures up to 1600 °C

Data were collected using a D8 ADVANCE ECO diffractometer configured with copper (Cu) radiation (40 kV, 25 mA), fixed divergence slits (0.6 mm), MTC-HIGHTEMP stage, 4.0 degree axial Soller slits, and SSD160 silicon strip detector.

Two titanate systems, (1) $BaTiO_3$ and (2) $CaTiO_3$ (perovskite), were characterized in this study. Reversible structural transitions were observed in phase pure $BaTiO_3$ on both heating and cooling. For the perovskite system, $CaCO_3$ and TiO_2 precursors were mixed together and characterized while heating to investigate formation of the final $CaTiO_3$ phase.

Case Study: $BaTiO_3$

$BaTiO_3$ was characterized as received without any additional processing. Diffraction data were collected in 5 degree increments from 100 °C to 150 °C and again on cooling to 100 °C. Each scan was collected over 5 min with rapid heating steps (< 1 min) between each scan.

Diffractograms are shown in Figure 1 as a 2D intensity map, showing a clear, reversible transition between tetragonal and cubic symmetries at 130 °C on both heating and cooling. Temperatures are indicated with the side-view. Figure 2 shows a closer look at the high angle region. Individual scans taken at 100 °C and 140 °C are shown in Figure 3 along with reference patterns for the two $BaTiO_3$ polymorphs.

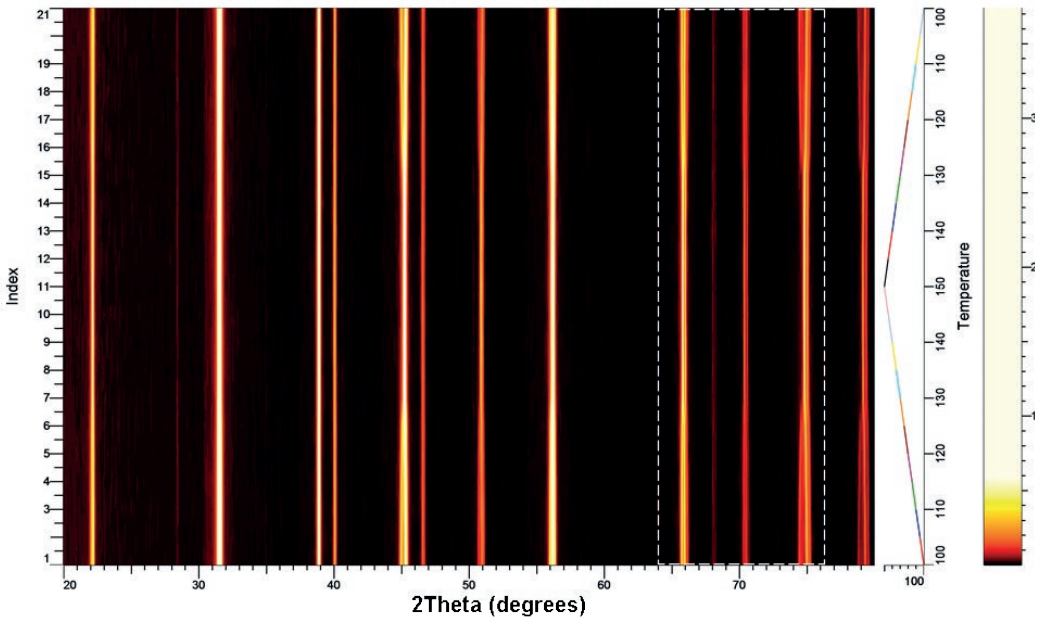


Figure 1 2D intensity map for $BaTiO_3$ scans taken from 100 °C to 150 °C and back to 100 °C. A clear phase transition is observed at 130 °C on both heating and cooling. The region indicated by the dashed white line is highlighted in figure 2 for clarity.

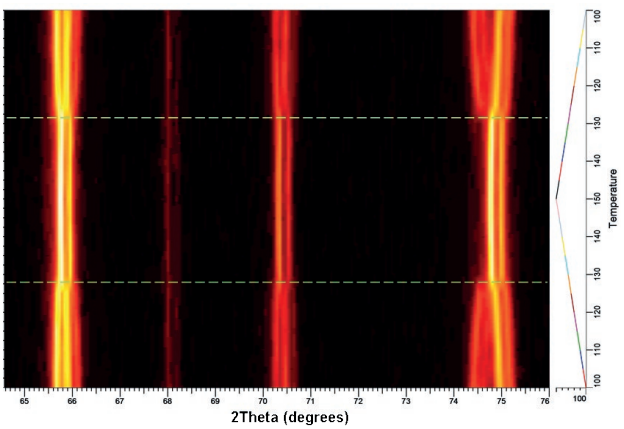


Figure 2 Zoomed in region of 2D intensity map for $BaTiO_3$. The dashed line is drawn at 130 °C as a visual guide.

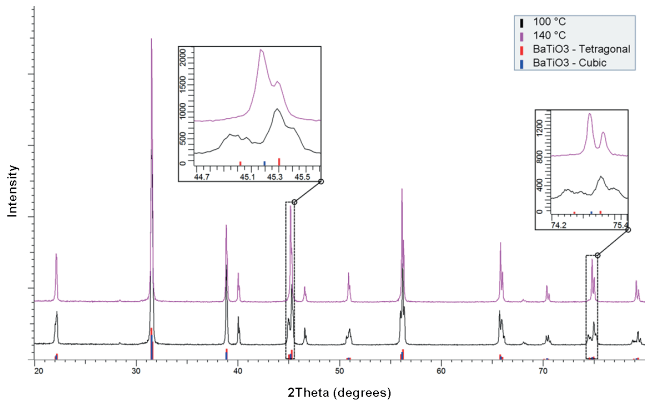


Figure 3 Identification of $BaTiO_3$ polymorphs at 100 °C and 140 °C.

Case Study: $CaTiO_3$

Calcite ($CaCO_3$) and anatase (TiO_2) were ground together and then mounted onto the heating filament. Diffractograms were collected every 100 °C from 30 °C - 1000 °C and then every 50 °C from 1000 °C - 1500 °C.

Data visualization by 2D intensity map (Figure 4) helps to identify regions of interest. For example, $CaCO_3$ decomposition is observed at ~ 700 °C with full conversion to lime (CaO) at 800 °C. The perovskite structure begins to form in conjunction with the formation of lime and continues until the Ca precursor is fully consumed at 1200 °C – this is evidenced by the appearance of new, strong diffraction peaks at ~33 °2θ, 47 °2θ, and 58 °2θ. Excess anatase is converted to rutile at 900 °C before finally melting above 1400 °C. Selected scans (30 °C, 800 °C, 1000 °C, 1400 °C) are shown in Figure 5 along with reference patterns for identified phases. In addition to the phase transformations linked to the appearance and disappearance of peaks, increases in lattice parameter due to thermal expansion are clearly shown as shifts in the peaks to lower angles.

Conclusions

Measurements of several oxide materials were successfully performed with the D8 ADVANCE ECO equipped with MTC-HIGHTEMP stage. The reversible phase transition of barium titanate at 130 ˚C was clearly observed. Additionally, the complex reaction between calcite and anatase was characterized at temperatures ranging from 30˚C to 1500˚C. The data described here highlight the importance of diffraction studies at high temperatures, providing insights into structural changes and reactivity.

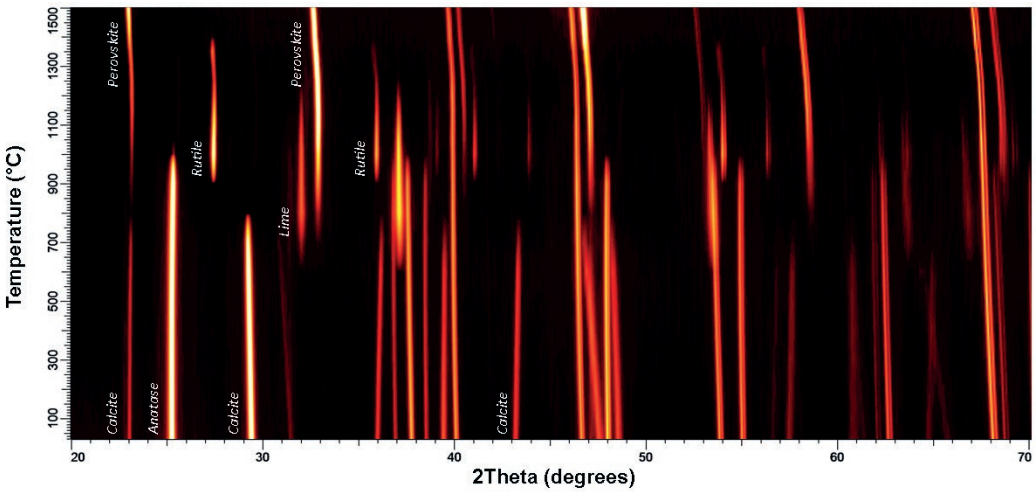


Figure 4 2D intensity map for reaction of calcite ($CaCO_3$) and anatase (TiO_2) on heating from room temperature to 1500 °C. Calcite decomposes to lime (CaO) and reacts with anatase to form the perovskite ($CaTiO_3$) phase between 700 °C and 800 °C. At higher temperatures, the formation of perovskite continues while excess anatase is converted to the rutile polymorph. At 1400 °C, the excess rutile melts to a glassy phase.

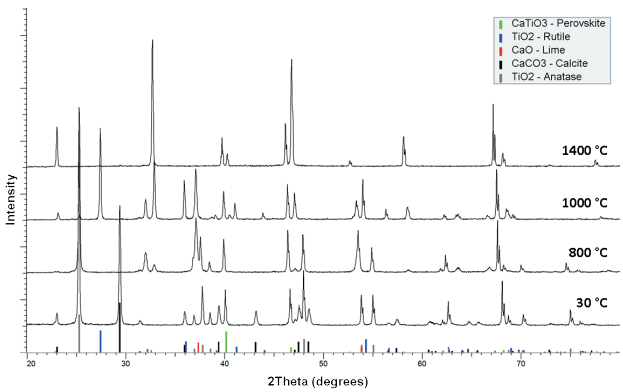


Figure 5 Identification of crystalline phases present at various temperatures.

References

[1] M.B. Smith; K. Page; T. Siegrist; P.L. Redmond; E.C. Walter; R. Seshadri; L.E. Brus; M.L. Steigerwald J. Am. Chem. Soc. 2008, 130, 6955-6963.

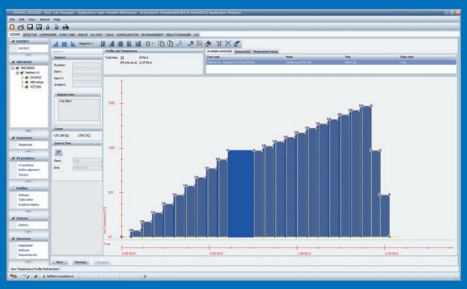
[2] A.W. Czanderna; C.N. Ramachandra Rao; J.M. Honig Trans. Faraday Soc. 1958, 54, 1069-1073.

[3] D.A.H. Hanaor and C.C. Sorrell J. Mater. Sci. 2011, 46, 855-874.

DIFFRAC.SUITE Workflow for Non-Ambient Diffraction

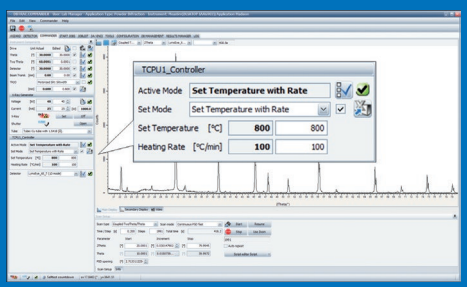
PLAN in DIFFRAC.WIZARD

- Configure physical and computer controlled instrument settings
- Setup snapshot and advanced scanning 0D, 1D or 2D measurements
- Create detailed temperature profiles including soak times and temperature ramp rates



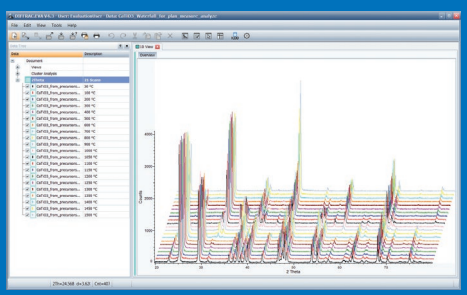
MEASURE in DIFFRAC.COMMANDER

- Launch complex experiments
- Directly control the non-ambient condition
- View data in real time



ANALYZE in DIFFRAC.EVA

- Begin analysis while the data is collecting
- Identify phases with search/match
- Visualize phase changes in waterfall and 2D plots



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