Experimental report

07/05/2024

Proposal: **5-24-665** **Council:** 10/2020

Title: In situ observation of the hydrothermal crystallisation of ruthenates

Research area: Chemistry

This proposal is a new proposal

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Samples: NaOD in D2O
Sr(NO3)2
KRuO4

Instrument	Requested days	Allocated days	From	To
D20	4	3	09/06/2023	12/06/2023

Abstract:

The formation mechanisms of solids with extended structures largely remain poorly understood but are of increasing importance for the design of new materials in many areas of technology and industry. More than 20 years ago, a cell was designed and built to measure neutron diffraction data during solvothermal crystallisations. This was used to monitor the formation of the prototypical ferroelectric perovskite BaTiO3, and porous zeolites using ISIS and the ILL (D20) providing novel kinetic data. In the intervening years, solvothermal synthesis of a huge range of materials has been developed to the point of manufacture at industrial scale (e.g., materials for rechargeable battery cathodes and metal-organic framework adsorbents). The need to understand crystallisation is greater than ever: to guide the preparation of optimised materials tuned for application, and in the discovery of new materials. Here we propose to study phase evolution during synthesis of some ruthenium oxides with exotic magnetic properties, including the rare case of a material that is synthesised below its magnetic ordering temperature (SrRu2O6), using a new design of reactor that will minimise background scatter.

In situ observation of the hydrothermal crystallisation of ruthenates

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The formation mechanisms of solids with extended structures largely remain poorly understood but are of increasing importance for the design of new materials in many areas of technology and industry. The aim of this experiment was to study phase evolution during synthesis of some ruthenium oxides with exotic magnetic properties, including the rare case of a material that is synthesised below its magnetic ordering temperature, $SrRu_2O_6$, using a new design of hydrothermal reactor that minimises background scatter to allow neutron scattering to be recorded during crystallisation.

Figure 1 shows the design of the reaction cell that had been commissioned on Polaris at ISIS but was constructed to be used on various instruments at different sources. The cell is designed to be heated by an external furnace to ~ 250 °C and is attached to a pressure relief system, since it is designed to heat liquids in a sealed environment.

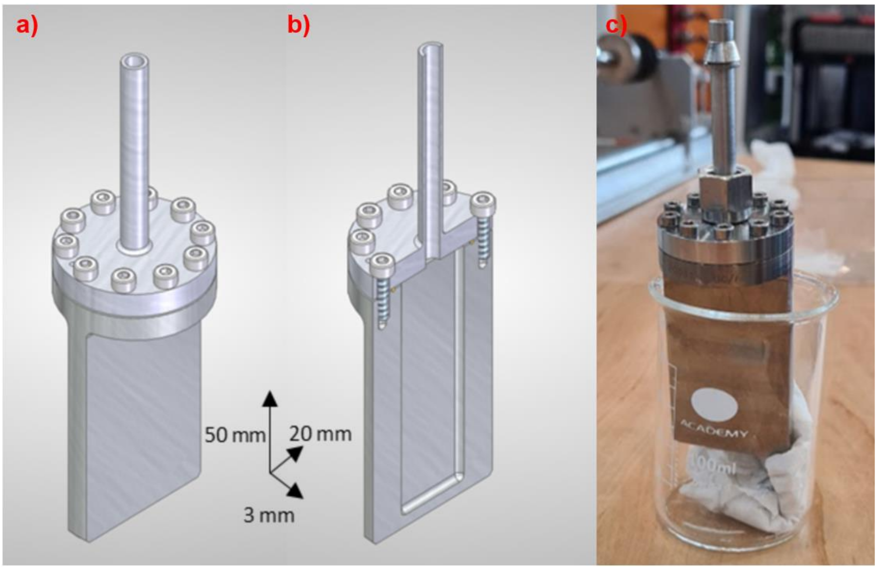

Figure 1: a) 3D rendering of fully assembled* in situ *solvothermal cell b) 3d rendering of half the cell showing the internal reaction cavity, c) photo of the cell.

The material $SrRu_2O_6$ was chosen as a model system to study in the new reactor. It crystallises from $KRuO_4$ and Sr salts in water around 200 °C, and, unusually, is antiferromagnetically ordered at its synthesis temperature, with a Néel temperature of 565 K (~ 292 °C).[1,2] Hence we would expect to see magnetic Bragg peaks as well as atomic structure Bragg peaks forming upon crystallisation.

Figure 2a shows an example of diffraction data recorded from the cell at 180 ° where diffraction peaks associated with $SrRu_2O_6$ can be seen growing in intensity as the reaction progresses. Figure 2b shows a Rietveld fit of the final diffraction pattern using the atomic scale structure. Weak diffraction peaks due to the magnetic structure are evident, with the strongest indicated.

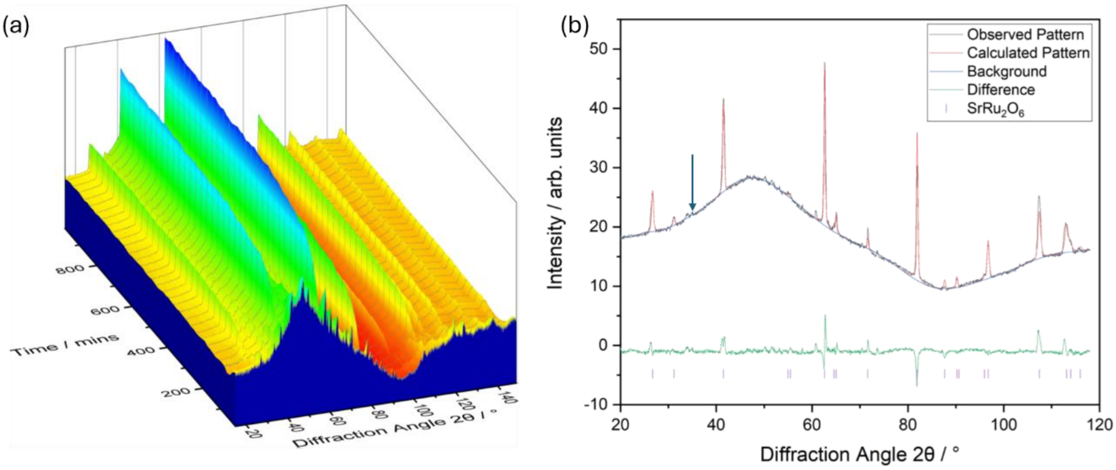

Figure 2: Neutron diffraction data collected in situ on D20, λ = 2.14 Å of $SrRu_2O_6$ crystallisation at 180 °C: (a) 3D map of data of hydrothermal synthesis and (b) Rietveld fitted final diffraction pattern: a = 5.1826(7) Å, c = 5.2254(7) Å, V = 121.55(2) Å^3 ($P\overline{3}1m$). The arrow indicates the strongest magnetic Bragg peak.

Sequential fitting of the diffraction was used to produce crystallisation curves, such as shown in Figure 3a. Fitting using an Avrami-type kinetic model allowed normalised growth curves for various Bragg peaks to be produced. This reveals that the growth of magnetic order lags behind the growth of atomic structure. Study of crystallisation as a function of temperature provides further kinetic data, Figure 3b and we are currently quantifying the kinetics of crystallisation.

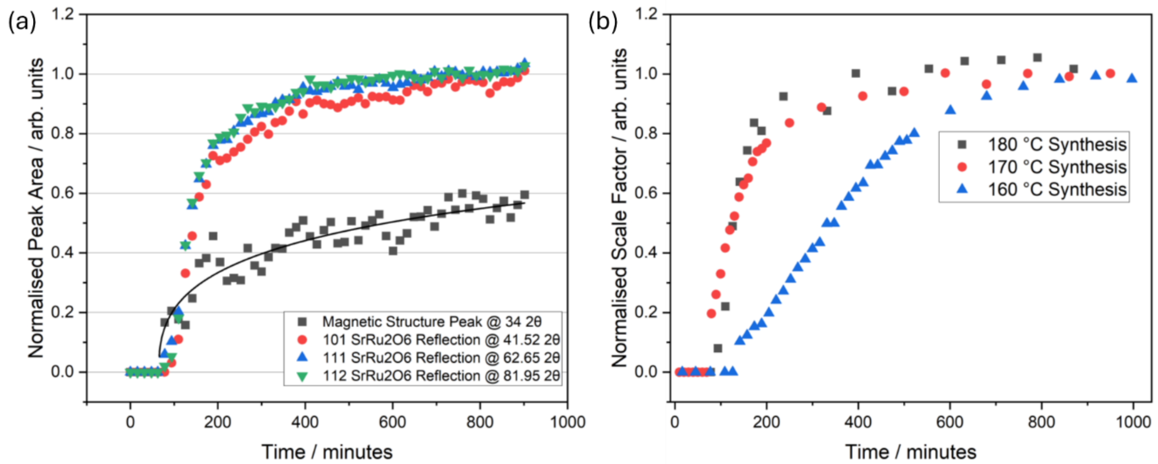

Figure 3: (a) Crystallisation curves of $SrRu_2O_6$ at 180 °C for three atomic-structure peaks and the strongest magnetic Bragg peak and (b) crystallisation curves at three temperatures.

The high neutron flux on D20 and the large position-sensitive detector has provided high-quality data to follow crystallisation. The results form part of Mark Crossman's PhD thesis which was submitted in April 2024 and we are currently preparing a paper that will include the data from this experiment.

1. C.I. Hiley, M.R. Lees, J.M. Fisher, D. Thompsett, S. Agrestini, R.I. Smith and R.I. Walton, *Angew. Chem. Int. Ed.*, 2014, 53, 4423–4427.

2. C. I. Hiley, D. O. Scanlon, A. A. Sokol, S. M. Woodley, A. M. Ganose, S. Sangiao, J. M. De Teresa, P. Manuel, D. D. Khalyavin, M. Walker, M. R. Lees and R. I. Walton, *Phys. Rev. B*, 2015, 92,104413.