

An *in situ* time-resolved neutron diffraction study of the hydrothermal crystallisation of barium titanate

Richard I. Walton,^a Ronald I. Smith,^b Franck Millange,^a Iain J. Clark,^c Derek C. Sinclair^c and Dermot O'Hare^{*a}

^a *Inorganic Chemistry Laboratory, University of Oxford, South Parks Road, Oxford, UK OX1 3QR.*

E-mail: dermot.ohare@chem.ox.ac.uk

^b *ISIS Facility, Rutherford Appleton Laboratory, Chilton, Didcot, Oxon, UK OX11 0QX*

^c *Department of Engineering Materials, University of Sheffield, Mappin Street, Sheffield, UK S1 3JD*

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The hydrothermal crystallisation of barium titanate, BaTiO₃, has been studied for the first time by *in situ* time-resolved neutron powder diffraction; we deduce that BaTiO₃ is formed from solution by reaction between [Ti(OH)_x]^{(4-x)+}_(aq) and [Ba(OH)_x]^{(2-x)+}_(aq) species, rather than by a heterogeneous reaction between solid TiO₂ and Ba²⁺_(aq) ions.

Tetragonal barium titanate, t-BaTiO₃, finds widespread application in the electroceramics industry. The ferroelectric properties and high permittivity of t-BaTiO₃ are exploited in, for example, thermistors, capacitors, and electro-optic devices. Traditional routes to the synthesis of the material employ direct solid-state reaction between barium carbonate and titanium dioxide at elevated temperature (> 900 °C). Hydrothermal routes to BaTiO₃ have been the focus of much recent research as an efficient low temperature method for its manufacture (see, for example, refs. 1–3). The reaction of a number of barium and titanium sources in water at temperatures as low as 80 °C has enabled the production of t-BaTiO₃ and by varying reaction conditions and choice of starting materials it has proved possible to change the particle size and morphology of the material produced. Particular attention has been paid to the production of ultrafine (submicron) powders^{1–4} and to the production of thin films^{5–7} by the hydrothermal method. Such control of morphology is extremely desirable and has huge potential value, both in the manufacture of miniaturised devices^{8,9} and in the production of dense fine-grained ceramics by sintering of the fine powders initially prepared.¹⁰

An understanding of the formation mechanism will be vital if controlled growth of t-BaTiO₃ is to be performed and the potential applications described above are to be exploited. Although the kinetics and mechanism of hydrothermal barium titanate production have been discussed by several authors,^{11–14} no agreed description of its formation mechanism has been reached. Two extreme models have been postulated: one involving a homogenous solution phase reaction between titanium and barium hydroxy anions (the dissolution–precipitation mechanism) and another involving the reaction between solid TiO₂ and soluble barium species (the *in situ* heterogeneous transformation mechanism).¹² The data previously used to probe the kinetics of barium titanate crystallisation were derived entirely from quenching experiments, whereby material was removed from the reaction cell after given period of time and examined.

Because of the absorbing nature of the sample, we were unfortunately unable to probe the barium titanate crystallisation using *in situ* time-resolved synchrotron X-ray diffraction experiments, which are now well established.^{15,16} Powder neutron diffraction, however, offers an alternative means of following the crystallisation. In recent months we have developed a gold coated, null-scattering (67.7 atom% Ti, 32.3 atom% Zr) environmental cell that enables us to record *in situ* high-resolution powder neutron diffraction patterns of highly

reactive and/or corrosive materials reacting under hydrothermal conditions.¹⁷ Only one previous report of the use of neutron diffraction to follow reactions under hydrothermal conditions appears in the literature, and this did not overcome the problem of significant scattering from the reaction vessel appearing in the diffraction patterns, which seriously limited the amount of quantitative and structural information that could potentially be extracted.¹⁸ Here, we describe the first use of the Oxford-ISIS hydrothermal cell to study a hydrothermal synthesis using *in situ* neutron diffraction.

Fig. 1(a) shows the time-of-flight powder neutron diffraction patterns of the crystalline starting materials [TiO₂ (2.12 g) Ba(OD)₂·8D₂O (9.81 g), Ba:Ti ratio of 1.1:1] as a suspension in 10 ml D₂O in the hydrothermal cell before heating.† The cell was then heated to 125 °C and neutron diffraction patterns

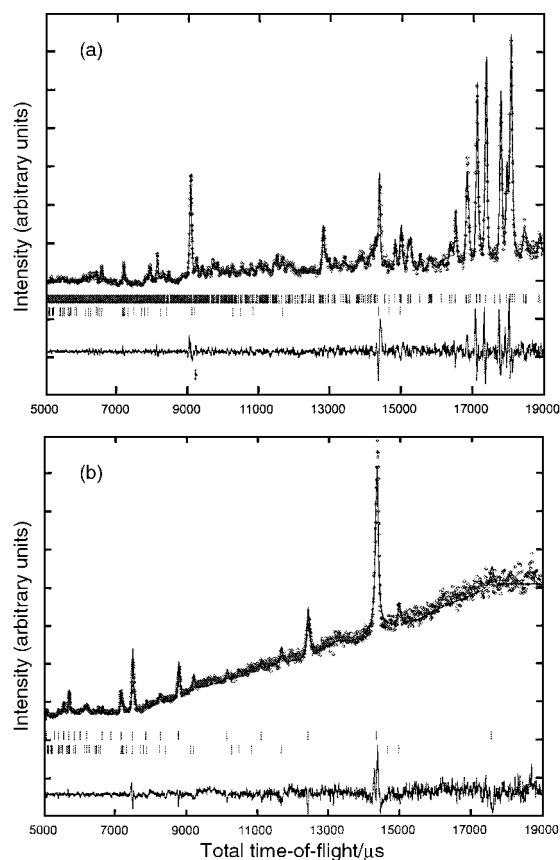


Fig. 1 Powder neutron diffraction data obtained from within the hydrothermal cell. for (a) Ba(OD)₂·8D₂O (upper tick marks) and TiO₂ (lower tick marks) in D₂O and (b) for the barium titanate produced by heating the mixture at 125 °C for 12 h (lower tick marks are unreacted TiO₂). The points are the experimental data, the full line the result of the whole pattern fitting, and the lower line the difference curve.

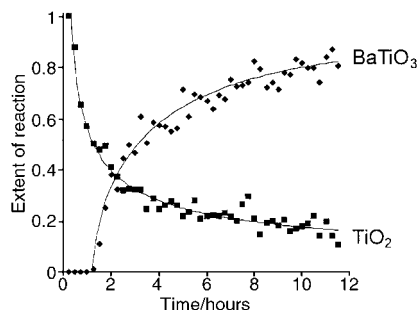


Fig. 2 Changes in integrated Bragg peak intensities for TiO_2 and BaTiO_3 during reaction at 125°C . Line are guides to the eye and have no physical significance.

recorded every 15 min for a period of 12 h. Fig. 1(b) shows the sum of the four final diffraction patterns obtained, *i.e.* 1 h of data in total. These data can be successfully modelled as arising from cubic BaTiO_3 . At 125°C we would have expected *t*- BaTiO_3 to have formed since at temperatures below 130°C the lower symmetry form is thermodynamically more stable. These synthesis conditions, however, produce submicron-sized particles of BaTiO_3 and as has previously been pointed out, it is very difficult to identify the BaTiO_3 polymorph using diffraction methods when the Bragg reflections are considerably broadened by the small particle size.^{2,19}

Integrated intensities of the well resolved Bragg reflections were determined by Gaussian-fitting and this enabled decay and growth curves of both the starting materials and products to be quantitatively determined. Fig. 2 shows the extent of reaction ($\alpha = I/I_\infty$) curves *vs.* time derived from integrated intensities of TiO_2 and BaTiO_3 as a typical reaction mixture was heated at 125°C . The growth curves for all the resolved Bragg reflections of BaTiO_3 were identical suggesting that crystal growth is isotropic, which is not unexpected given the spherical morphology of particles typically produced by this hydrothermal synthesis. We also have investigated the use of amorphous $\text{TiO}_2\cdot\text{H}_2\text{O}$ as a titanium source, which has recently been used to prepare submicron BaTiO_3 particles,² and confirmed that the rate of reaction is considerably more rapid compared to the crystalline source.

The neutron diffraction data clearly show that the crystalline barium source, barium deuteroxide octahydrate dissolves rapidly before any other changes in crystallinity are apparent in the reaction mixture; in all cases the Bragg reflections of $\text{Ba}(\text{OD})_2\cdot 8\text{D}_2\text{O}$ disappear in less than 1 h and always before the appearance of any BaTiO_3 . All previously discussed mechanisms for the hydrothermal crystallisation of barium titanate suggest that the barium source is in solution and our *in situ* results provide clear evidence for this assumption. Most significantly, when crystalline TiO_2 is used as the titanium source its initial decay is rapid and more than 50% of the TiO_2 dissolves before the appearance of any of the BaTiO_3 product. This strongly suggests that a dissolution–precipitation mechanism is taking place, *i.e.* that barium titanate is formed by reaction between dissolved $\text{Ba}^{2+}_{(\text{aq})}$ and $[\text{Ti}(\text{OH})_x]^{(4-x)+}_{(\text{aq})}$ species. If reaction between Ba^{2+} ions in solutions and solid TiO_2 particles was taking place, then we would expect the rate of formation of BaTiO_3 to mirror the decay of TiO_2 . Some previous studies have assumed the latter *in situ* heterogeneous transformation mechanism,¹¹ but more recent studies using electron microscopy techniques find no evidence for this model; for example Pinceloup *et al.* examined the quenched material from barium titanate crystallisations after various periods of time and always observed distinct titania or barium titanate particles, and that there was no relationship between particle size distribution in the titanium oxide starting material and the barium titanate product.¹⁴ Our study thus provides independent evidence for the dissolution–precipitation mechanism by a novel technique.

The kinetic crystallisation curves can be analysed quantitatively using the Avrami–Erofe'ev expression for a nucleation-

growth mechanism.^{20–23} We find that the power dependence (n) of the rate expression is 1.1 ± 0.5 . A value of $n = 1$ suggests that the rate determining step of reaction is the reaction at the phase boundary, *i.e.* the chemical reaction taking place at the nucleation sites between solution Ba^{2+} and $[\text{Ti}(\text{OH})_x]^{(4-x)+}$ anions. This study has thus provided a firm foundation on which to base a mechanism for the hydrothermal crystallisation of barium titanate.

In summary, we have demonstrated in this paper that neutron diffraction has the potential to be a powerful technique for the study of chemical processes under non-ambient conditions. It offers the potential for collecting new data not available using other sources and also data complementary to that available from analogous *in situ* synchrotron X-ray diffraction experiments. We believe with the ongoing improvements in available neutron flux and in detector technology it will be possible to collect data of higher quality in shorter time intervals from reaction vessels such as we have described.

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Notes and references

† Neutron diffraction patterns presented were recorded in the high resolution backscattering detector bank [$2\theta(\text{av.}) = 45^\circ$] of the POLARIS diffractometer at the UK pulsed spallation neutron source ISIS, Rutherford Appleton Laboratory. The hydrothermal autoclave was loaded with TiO_2 (2.12 g), $\text{Ba}(\text{OD})_2\cdot 8\text{D}_2\text{O}$ (9.81 g) and D_2O (10 g) under a dry nitrogen atmosphere and rapidly heated under autogeneous pressure at 125°C . The TiO_2 was purely in the anatase polymorph, and this was confirmed by the good fit achieved to the neutron diffraction data. The structure of barium hydroxide octahydrate has been determined using single crystal X-ray diffraction methods²⁴ and using the cell parameters previously found as a starting point for refinement against the neutron data allowed confirmation of the identity of the barium source [X-ray values: $a = 9.274 \text{ \AA}$, $b = 9.260 \text{ \AA}$, $c = 11.817 \text{ \AA}$, $\beta = 98.95^\circ$,²⁴ neutron refined values: $a = 9.3137(3) \text{ \AA}$, $b = 9.3043(3) \text{ \AA}$, $c = 11.860(8) \text{ \AA}$, $\beta = 98.995(3)^\circ$].

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