



## Bench- and pilot-scale continuous-flow hydrothermal production of barium strontium titanate nanopowders



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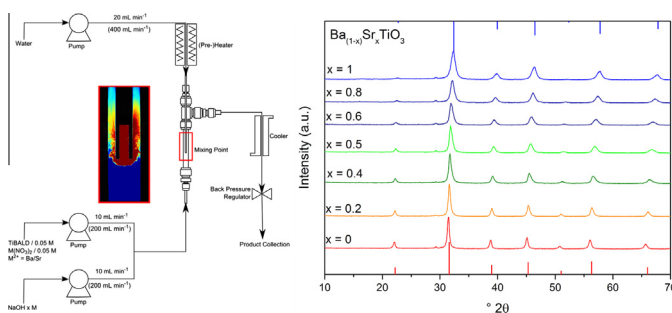
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### HIGHLIGHTS

- Continuous-flow hydrothermal synthesis of barium titanate nanopowders.
- Base is necessary for the generation of the crystalline perovskite.
- Barium strontium titanate nanoparticles produced across the targeted full stoichiometric range.
- Products are substoichiometric single phase crystalline nanoparticles.
- Pilot-scale production of perovskite nanoparticles.

### GRAPHICAL ABSTRACT



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### ABSTRACT

Barium strontium titanate ( $\text{Ba}_{(1-x)}\text{Sr}_x\text{TiO}_3$ ) nanopowders have been prepared at both bench- and pilot-scales using a fully hydrothermal continuous-flow system. A mixed solution of barium nitrate (and/or strontium nitrate) with titanium bis (ammonium lactato) dihydroxide was mixed in-flow with a sodium hydroxide stream before meeting a pre-heated flow of supercritical water at a counter-current mixing point which resulted in the crystallisation of  $\text{Ba}_{(1-x)}\text{Sr}_x\text{TiO}_3$ . The obtained nanopowders were characterised by ICP-MS, powder X-ray diffraction, transmission electron microscopy and Raman spectroscopy. All products were found to be sub-stoichiometric with the total  $\text{M}^{2+}:\text{Ti}$  ratio varying between 0.8:1 and 0.96:1, attributed to the formation of divalent metal carbonates preventing full incorporation of the  $\text{M}^{2+}$  ions into the perovskite structure in the extremely short reaction times employed. The obtained products were found to adopt the expected perovskite structure, while increasing strontium content led to a decrease in both particle size and lattice parameter. Products with target compositions of  $\text{Ba}_{(1-x)}\text{Sr}_x\text{TiO}_3$  ( $0 \leq x \leq 1$ ) were produced for the first time by a fully hydrothermal route at both the bench-scale of  $\sim 5 \text{ g h}^{-1}$  and pilot-scale at  $\sim 80 \text{ g h}^{-1}$ .

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### 1. Introduction

Barium titanate ( $\text{BaTiO}_3$ ) was discovered in the early 1940s as a capacitor material to replace mica, the supplies of which were under threat from German U-boats, and has since been the subject

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of intense and sustained research. Initially it posed an interesting conundrum to the scientific community – a simple ceramic material exhibiting ferroelectric properties previously unheard of in anything but hydrogen-bonded systems. BaTiO<sub>3</sub> adopts the perovskite ABO<sub>3</sub> structure: a network of corner-sharing [BO<sub>6</sub>] octahedral with the 12-coordinate interstitial site occupied by the larger A metal cations [1,2]. The ideal archetypal structure, adopted by the closely related SrTiO<sub>3</sub>, is that of a centrosymmetric primitive cubic system. Pure cubic symmetry prohibits ferroelectric behaviour, however below the Curie temperature of 120 °C the titanium atoms of BaTiO<sub>3</sub> are offset from the centre of the [BO<sub>6</sub>] octahedral elongating the *c*-axis creating a tetragonal phase with a permanent dipole [3]. This dipole gives rise to the important ferroelectric properties of BaTiO<sub>3</sub>. Its high dielectric constant, low dielectric loss and general ferroelectric properties make BaTiO<sub>3</sub> ideally suited to a vast array of applications [4], including capacitors, RF devices, microwave dielectrics, infrared sensors, and more recently memory devices [5]. Historic applications make use of the commensurate piezoelectric properties arising from the non-centrosymmetric structure – microactuators, microphones and sonar devices.

The flexibility of the perovskite structure is such that a wide range of metal cations may be accommodated, particularly in the A position. With respect to barium titanate this allows significant variation in composition, with barium easily replaced by alternative M<sup>2+</sup> ions. One of the most common substituents is strontium – a smaller member of group 2. The full phase diagram of Ba<sub>(1-x)</sub>Sr<sub>x</sub>TiO<sub>3</sub> from *x* = 0 to *x* = 1 is known. It has been shown that increasing strontium content stabilises the cubic phase (as mentioned above SrTiO<sub>3</sub> itself adopts the cubic perovskite structure at room temperature). This substitution has the effect of altering the ferroelectric properties of the base BaTiO<sub>3</sub>, allowing fine tuning to suit the desired application.

Conventionally BaTiO<sub>3</sub> and related ceramics have been prepared by traditional ceramic methods: the high temperature (>1000 °C) sintering of BaCO<sub>3</sub> or BaO and TiO<sub>2</sub> [6]; however due to the high temperatures this yields large particles with poor monodispersity, unsuitable for the increasing miniaturisation required of components and devices using the material. Vapour deposition techniques are widely used in the production of thin films for various applications [7,8]. These offer the advantage of producing high purity and high quality thin films, suitable for miniaturisation, but are limited to deposition of the materials on substrates and are generally restricted to small surfaces due to the nature of the deposition equipment. Wet-chemical methods have developed greatly over the last several years. Sol-gel techniques have been widely explored and allow the preparation of powders or films at the expense of costly and air-sensitive precursors and the need for post-synthetic calcination steps [9]. Hydrothermal and solvothermal techniques (whereby precursors are heated in water/solvent at temperatures above the boiling point of the solvent) can use simple and cheap precursors to produce high quality nanocrystals with tuneable compositions and sizes [10–12]. As such hydrothermal and solvothermal methods are increasingly finding favour; although the use of conventional batch processes (in sealed vessels under autogenous pressure) can hinder scale-up potential.

Continuous-flow hydrothermal and solvothermal synthesis was originally described by Adschiri et al., in the early 1990s as a method for the production of fine metal oxide nanopowders [13]. The process has emerged over the past 20 years as a viable, scalable, alternative to the traditional batch methods. The properties of supercritical water (and the high temperatures required to achieve this state) promote both the rapid hydrolysis of metal salts and the fast nucleation of metal oxides when a supercritical water stream is brought into contact with a stream containing metal salts [14–17]. The general technique has since been expanded to pro-

duce many metal oxides [14], as well as sulphides [18] and phosphates [19–22], with Hanwha Chemicals Ltd., producing lithium iron phosphate at an industrial scale using a continuous-flow reactor [23]. Barium titanate has also been produced in continuous-flow systems under both hydrothermal and solvothermal conditions [24–29]. Hydrothermally this has been achieved from dispersions of TiO<sub>2</sub> or titanium tetrachloride and a variety of barium sources [25,26,29]. Barium strontium titanate has also been produced under continuous solvothermal conditions (in an approximation of existing sol-gel routes) rather than hydrothermal conditions though precautions were needed as a result of the instability of the alkoxide based precursors in the presence of water [24,27,28].

Here we report the continuous flow hydrothermal production of Ba<sub>(1-x)</sub>Sr<sub>x</sub>TiO<sub>3</sub> nanopowders at both bench- and pilot-scale. The reactions are performed using the counter-current nozzle reactor designed at the University of Nottingham [30,31], and make use of water soluble precursors without the need for special treatment or precautions.

## 2. Experimental

The counter-current reactor used in this work is comprised of a preheater section which feeds supercritical water downwards through an inner tube into a vertically aligned outer tube through which room temperature reagent streams flow. The supercritical water and reagent streams mix thoroughly at the outlet of the inner tube before immediately passing through a heat exchanger to cool down. The product stream exits through a back pressure regulator which maintains pressure within the system. Both the bench- and pilot-scale reactors are constructed from stainless steel 316 Swagelok<sup>®</sup> components. The mixing point of the bench-scale system employs an outer tube of 3/8" diameter, and an inner tube 1/8" diameter at the mixing point. The heater consists of 6 m of 1/8" tubing coiled around an aluminium cylinder heated by Watlow<sup>®</sup> cartridge heaters. The water and reagent streams are delivered into the high pressure system via Gilson<sup>®</sup> 305 HPLC pumps. Pressure is maintained using a Pressuretech<sup>®</sup> manual back pressure regulator. The pilot-scale system is owned by Promethean Particles and operates on the same principle with a 20–30× scale up.

The synthesis of the barium titanate and barium strontium titanate nanocrystals was performed as shown in Fig. 1. A 0.05 M solution of titanium bis(ammonium lactato) dihydroxide with appropriate amounts of the divalent metal nitrate salts Ba(NO<sub>3</sub>)<sub>2</sub> and/or Sr(NO<sub>3</sub>)<sub>2</sub>, to a total M<sup>2+</sup> concentration of 0.05 M, was used as the metal precursor stream. A solution of NaOH at various concentrations was mixed with this in flow at a T-piece mixer, to act as a precipitating agent to ensure the intimate mixing of the metals by gelation prior to crystallisation on further mixing with the preheated stream of supercritical water. The temperature of the preheater was set to 430 °C giving a post-mixing temperature of ~390 °C. The system pressure was maintained at 25 MPa with the back pressure regulator. Products were collected and washed with water by centrifugation before drying under air at 70 °C. It was found that all products as prepared contained barium/strontium carbonate impurities which can be easily and cheaply removed by an additional washing step with 1 M acetic acid prior to the final drying stage, as discussed below.

Compositional analysis was performed by Inductively Coupled Plasma Mass Spectrometry (ICP-MS; ELAN DRC-e, Perkin Elmer, Waltham, USA) in a class 1000 (ISO class 6) clean room. Samples were digested by heating in closed PTFE vessels using concentrated HCl (ROMIL-SpA<sup>™</sup> Super Purity Acid, 32–25%, ROMIL, USA). Powder X-ray diffraction patterns of the products were collected on a Bru-

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