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# Self-propagating high-temperature synthesis of $SrTiO_3$ and $Sr_xBa_yTiO_3$ ($x + y = 1$)

A. V. KOMAROV, I. P. PARKIN*
*Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ, UK*
M. ODLYHA
*Department of Chemistry, Birkbeck College, 20 Gordon Street, London WC1H 0AJ, UK*

Thermal initiation of mixed powders of $SrO_2$ and titanium and/or TiE ($E = O_2, Cl_3$) induces a self-propagating reaction. Trituration of the product with water yielded fine crystalline particles of cubic $SrTiO_3$. Stepwise replacement of $SrO_2$ with $BaO_2$ in the reaction mixture generates a solid solution $Sr_xBa_yTiO_3$ ($x + y = 1$). Products were characterized by X-ray powder diffraction, scanning electron microscopy, energy-dispersive analysis of X-rays and Fourier transform–infrared spectroscopy. Thermal studies were monitored by thermogravimetric analysis and differential scanning calorimetry measurements.

## 1. Introduction

Strontium titanium oxides ($SrTiO_3$, $Sr_2TiO_4$) have high charge-storage density, are good insulators and their dielectric performance is not temperature dependent under normal operating conditions [1–4]. Applications include optical shutters and modulators, infrared sensors and, recently, in dynamic random access memory (DRAM) circuits and capacitors [1–4]. Strontium titanates have a range of structures from perovskite in $SrTiO_3$ to the $K_2NiF_4$ structure for $Sr_2TiO_4$ [5].

A number of pathways have been developed for producing strontium titanates including traditional ceramic synthesis from the co-firing of oxides and carbonates [6]; sol–gel synthesis [7]; CVD [8]; r.f. sputtering and co-evaporation methods [9]. These techniques often involve high temperature and long timescale reactions. Bulk preparations of $BaTiO_3$ have been investigated by self-propagating high-temperature synthesis (SHS) using titanium metal and barium peroxide as the oxidizing agent [10–12] and by reactions using strontium sulphate and $TiO_2$ in molten NaCl [13]. These SHS reactions have difficulties associated with the high reaction exothermicity and short timescale, which can mean that it is difficult to isolate thermally sensitive phases. We have helped to develop a modification of the SHS process by employing metal halides as one of the reagents [14–17]. This approach gives an in-built "heat brake" in the reaction corresponding to the vaporization temperature of the co-produced salt, thereby enabling "thermally sensitive" phases to be isolated which are not always able to form under conventional SHS reactions because of high reaction exothermicities and temperatures. The sub-branch of the SHS reaction that includes metal halides and alkali/alkali earth chalcogenides as starting materials, has been termed the solid state metathesis (SSM) reaction. In this paper, we report the simple straight-forward rapid SSM preparation of $SrTiO_3$ and $Sr_xBa_yTiO_3$ and investigate the initiation temperature and reaction duration by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) studies.

## 2. Experimental procedure

All preparations were conducted in a nitrogen-filled glove box. Reactions were carried out in air on a supporting ceramic tile and initiated by the application of a heated filament (700 °C). Reagents ($SrO_2$, $BaO_2$, $TiCl_3$, Ti and $TiO_2$) were purchased from Aldrich Chemical Co. and used as-supplied. Powder X-ray diffraction (XRD) patterns were obtained with a Siemens D5000 diffractometer using germanium monochromated $CuK_{\alpha 1}$ radiation ($\lambda = 0.15406$ nm); scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDXA) were conducted on a Hitachi S-4000 scanning electron microscope; Fourier transform–infrared (FT–IR) as-pressed KBr discs were examined in a Nicolet 205 spectrometer. Sintering was carried out at 1300 °C for 2 h in a Lenton Thermal Designs tube furnace (heating and cooling rates were $\sim 10\,°C\,min^{-1}$). Combustion rate and temperature measurements were taken by optical pyrometer and platinum–rhodium (Pt/PtRh (13% Rh)) thermocouples. Thermogravimetric and

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* Author to whom all correspondence should be addressed.

DSC measurements were performed on Shimadzu TGA-50 and DSC-50 thermoanalysers using both closed (pin-hole opening) and open aluminium crucibles under an oxygen atmosphere. Thermal scans were measured from 20–500 °C at heating rates of 20 or 40 °C $\text{min}^{-1}$. The dielectric measurements were obtained at room temperature at a frequency of 1 kHz on a Wayne Kerr automatic precision bridge.

### 2.1. Preparation of $SrTiO_3$

Various ratios of $SrO_2$ (0.40 g, 2.4 mmol) and a titanium source ($TiO_2$, Ti, $TiCl_3$, typically, 1.2–2.4 mmol) were ground together and a reaction initiated in air by a heated filament (Table I). This produced a self-propagating reaction of 2–3 s duration and, in some instances, a partly fused product. The product was washed with water (3 × 15 ml), air dried and analysed by X-ray powder diffraction (Table I), scanning electron microscopy/energy dispersive analysis of X-rays (EDAX) and FT–IR.

The material was compressed into a thin disc (16 mm diameter, ~2 mm thick) and sintered at 1300 °C for 2 h. The dielectric constant and density of the sintered material were determined.

### 2.2. Preparation of $Sr_xBa_yTiO_3$

The same reaction scale and conditions were followed for the preparation of $SrTiO_3$ except that a mixture of $SrO_2$ and $BaO_2$ was pre-ground prior to the reaction (Table II).

### 2.3. Thermal studies

The maximum temperature in the reactions was determined by optical pyrometry and ranged between 750 and 2000 °C. Direct thermal readings of selected reactions were obtained by thermocouple measurements by placing the thermocouple at the centre of a pile of reacting powders, initiating the reaction, and recording the EMF produced [18].

## 3. Results and discussion

### 3.1. Synthesis and characterization

Various ratios of $SrO_2$ and a titanium fuel source ($TiO_2$, Ti, $TiCl_3$) were ground together and a reaction initiated in air by a heated filament. On a scale of 1 g, the entire reaction was over in 2–3 s as assessed by the thermal flash which accompanied the propagation wave, and a seemingly homogeneous product of white/cream colour was produced. The product was triturated with water, air-dried and analysed by X-ray powder diffraction, SEM/EDAX, and FT–IR.

$$SrO_2 + 0.5Ti + 0.5TiO_2 \rightarrow SrTiO_3 \qquad (1)$$

$$6SrO_2 + 2TiO_2 + 2TiCl_3 \rightarrow 3SrTiO_3 + 3SrCl_2 + 7/2O_2 \qquad (2)$$

$$2SrO_2 + TiCl_3 \rightarrow SrTiO_3 + SrCl_2 + 1/2Cl_2 + 1/2O_2 \qquad (3)$$

X-ray powder diffraction patterns [19, 21] of the triturated powders revealed a single phase of material corresponding to cubic $SrTiO_3$ in all of the reactions (Equations 1–3, Fig. 1). EDAX showed only strontium, titanium and oxygen in the triturated material (no chlorine 0.5% detection level). The scanning electron micrographs of the prewashed powders revealed a smooth morphology (Fig. 2a) consistent with a surface coating of $SrCl_2$. Washing the particles with water removes $SrCl_2$ and leaves agglomerates of cubic crystallites with typical size 1–2 μm (Fig. 2b). The crystallite size of $SrTiO_3$ obtained from reaction of $SrO_2$ and $TiCl_3$ as determined by the Scherrer equation [21] (based on the XRD line widths) gave a value of

TABLE I Powder XRD data from the reactions of strontium peroxide with titanium metal, chloride and oxide

| Reaction | Colour | Crystal structure ($SrTiO_3$) | Cell parameters (observed) | | | Cell parameters [19, 20] | | |
|---|---|---|---|---|---|---|---|---|
| | | | *a*(nm) | *b*(nm) | *c*(nm) | *a*(nm) | *b*(nm) | *c*(nm) |
| $SrO_2 + 0.5Ti + 0.5TiO_2$ | White cream | Cubic | 0.3904 | 0.3904 | 0.3904 | 0.3905 | 0.3905 | 0.3905 |
| $SrO_2 + TiCl_3$ | White cream | Cubic | 0.3912 | 0.3912 | 0.3912 | 0.3917 | 0.3917 | 0.3917 |
| $SrO_2 + 0.1TiO_2 + 0.9TiCl_3$ | White cream | Cubic | 0.3904 | 0.3904 | 0.3904 | 0.3905 | 0.3905 | 0.3905 |
| $SrO_2 + 0.2TiO_2 + 0.8TiCl_3$ | White cream | Cubic | 0.3904 | 0.3904 | 0.3904 | 0.3905 | 0.3905 | 0.3905 |
| $SrO_2 + 0.3TiO_2 + 0.7TiCl_3$ | White cream | Cubic | 0.3904 | 0.3904 | 0.3904 | 0.3905 | 0.3905 | 0.3905 |

TABLE II Powder XRD data from the reaction of $SrO_2$ and $BaO_2$ with titanium chloride

| Reaction | Colour | Crystal structure | Cell parameters (observed) | | |
|---|---|---|---|---|---|
| | | | *a*(nm) | *b*(nm) | *c*(nm) |
| $BaO_2 + 0.5TiO_2 + 0.5TiCl_3$ | White cream | $BaTiO_3$ tetragonal | 0.3994 | 0.3994 | 0.4038 |
| $0.75BaO_2 + 0.25SrO_2 + TiCl_3$ | Light grey | $Ba_xSr_yTiO_3$ | 0.3968 | 0.3968 | 0.3968 |
| $0.25BaO_2 + 0.75SrO_2 + TiCl_3$ | Light grey | $Ba_xSr_yTiO_3$ | 0.3913 | 0.3913 | 0.3913 |
| $SrO_2 + 0.5TiO_2 + 0.5TiCl_3$ | White cream | $SrTiO_3$ cubic | 0.3904 | 0.3904 | 0.3904 |

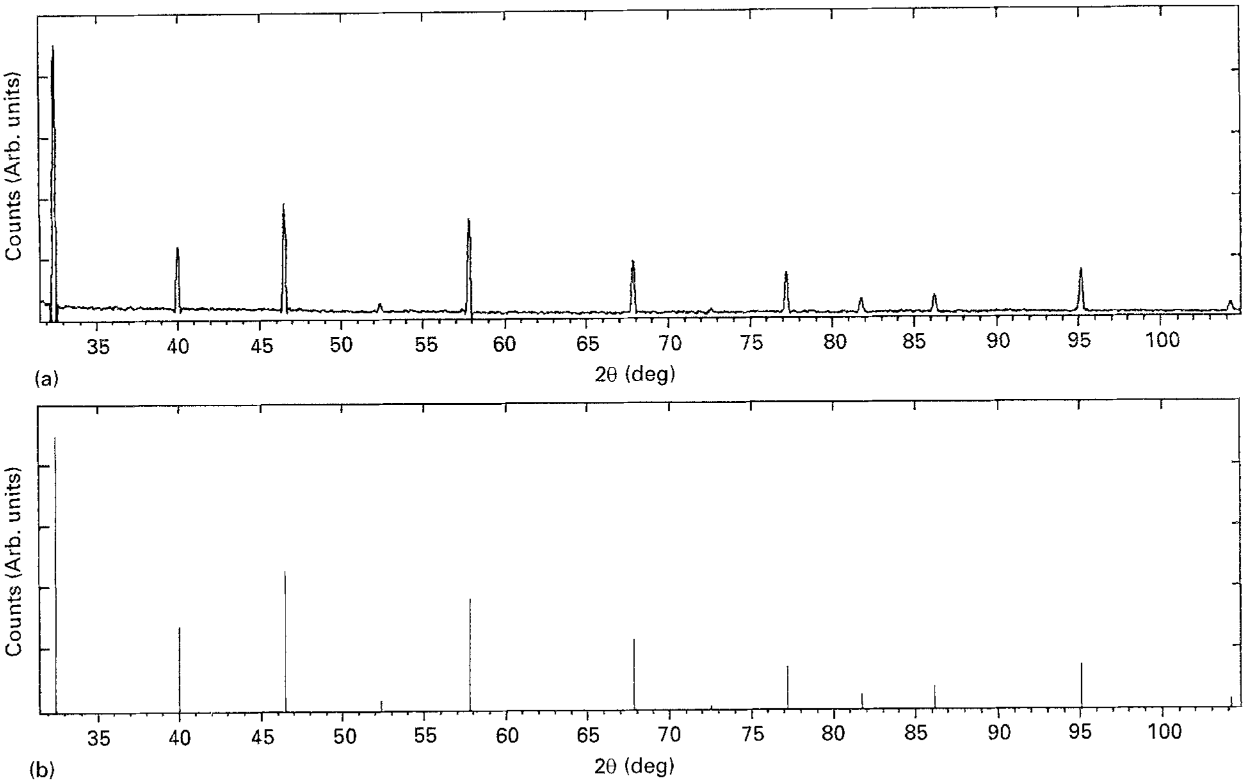

*Figure 1* (a) Powder XRD pattern obtained from the reaction of $SrO_2$ and $TiCl_3$. (b) Stick diagram for $SrTiO_3$ [18].

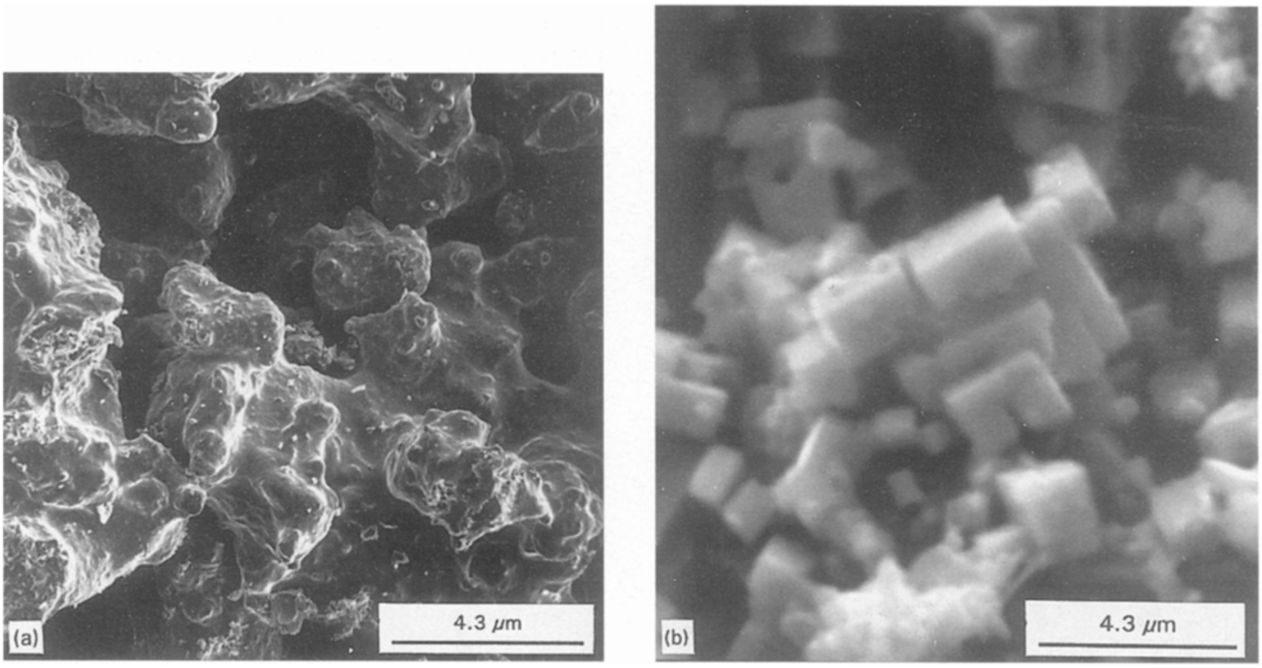

*Figure 2* Scanning electron micrographs of $SrTiO_3$ obtained from the reaction of $SrO_2$, $TiO_2$ and $TiCl_3$ (a) before trituration with water, (b) after trituration with water.

~100 nm. Infrared analysis showed only a broad band at ~600 $cm^{-1}$, corresponding to a Ti–O stretch [22].

This new SSM method allows the isolation in good yield and purity of $SrTiO_3$ and is faster than conventional methods and does not require the use of a furnace, using the in-built reaction exothermicity as the driving force for a crystalline product. The use of $TiCl_3$ is crucial in the reaction in controlling the maximum reaction temperature to the boiling point of the co-produced $SrCl_2$. Without the use of this "heat brake" it would be difficult to control the reaction and obtain a single phase of product. A case in point is the reaction of $SrO_2$ and titanium which is extremely violent, exothermic, and produces reaction temperatures in excess of 2000 °C (as assessed by optical pyrometry). The product from the reaction includes $SrTiO_3$ as well as some unreacted starting material that is ejected from the reaction site during the course of the reaction. Addition of $TiO_2$ to the $SrO_2$/Ti

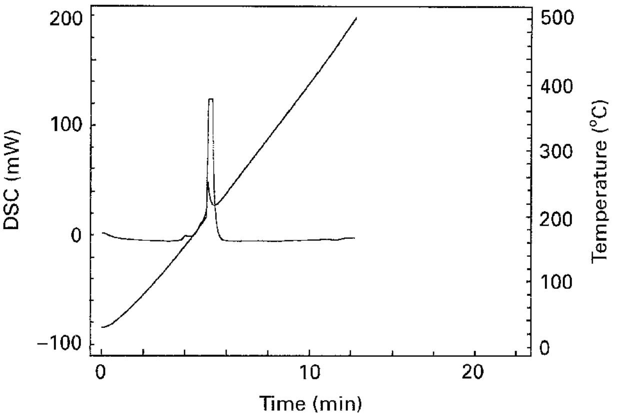

*Figure 3* DSC curve for the reaction of $SrO_2$ and $TiCl_3$ at a heating rate of 40 °C min$^{-1}$.

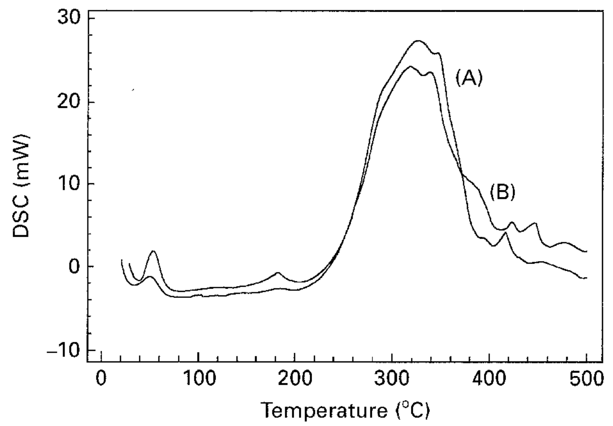

*Figure 4* DSC curve for the reaction of $SrO_2$ and $TiCl_3$ diluted (1 : 1) with $TiO_2$ at a heating rate of 20 °C min$^{-1}$ (curve A is for a sample of 16.9 mg and curve B is for a sample of 13.5 mg).

reaction mixture is required to reduce [8] the reaction voracity and obtain a single-phase product, $SrTiO_3$.

## 3.2. Thermal studies

The DSC curve (Fig. 3) for reaction of $SrO_2$ and $TiCl_3$ in oxygen at a heating rate of 40 °C min$^{-1}$ showed a single sharp exotherm initiated at 200 °C. The TGA also shows a small mass loss that occurs at ~200 °C and could be due to the partial sublimation of $SrCl_2$ or the explusion of material accompanying the reaction. The DSC experiments were very scale dependent. With ~2 mg material (heated in an open aluminium crucible under oxygen 20 ml min$^{-1}$) the reaction showed a number of broad exotherms, if the reaction scale was above ~10 mg then a thermal explosion of 12 s duration occurred over the temperature range (203–222 °C) as illustrated in Fig. 3. In the cases where a thermal explosion occurred, the initiation temperature was constant at 200 °C. Thermal explosions are common features of SHS reactions [10,11].

Reaction of $TiCl_3$ and $SrO_2$ produces a temperature of 1000 °C as determined by thermocouple measurements. The maximum temperature obtained in the reaction is successively reduced by the addition of $TiO_2$ to the reaction mixture (to ~800 °C). The DSC trace of the diluted reaction (1 : 1 $TiCl_3$ to $TiCl_4$; 14 and 17 mg scales) under oxygen showed a single broad but reproducible exotherm, Fig. 4, indicating that on the scale of the DSC experiment, unlike the bulk reaction, a thermal explosion did not occur. The crystallite sizes of the product from the bulk reaction (Scherrer equation [21] ) are reduced with successive addition of $TiO_2$ also correlating with a reduction in reaction temperature. Uncombined $TiO_2$ was not de-

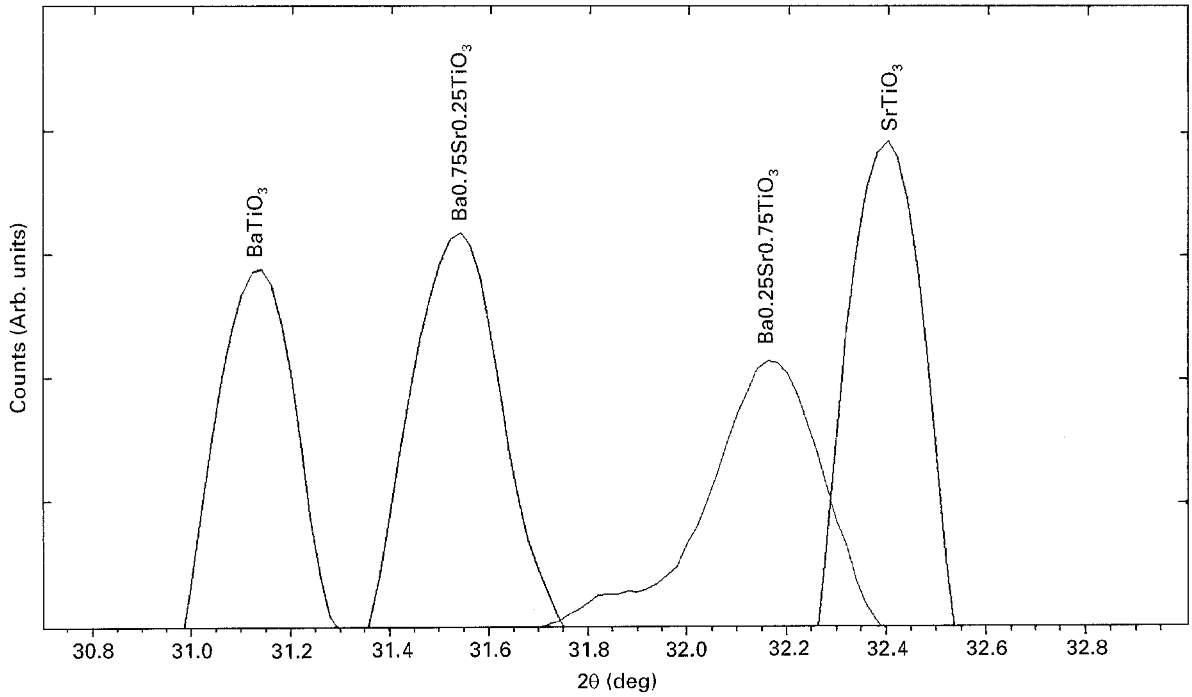

*Figure 5* Powder XRD patterns for the (2 0 0) reflection obtained from reactions of $SrO_2$ and $BaO_2$ with titanium chloride.

tected in the products by X-ray powder diffraction. Hess's law [23] calculations reveal lower exothermicities with successive dilution with $TiO_2$. All of the reactions had calculated enthalpies in excess of 400 kJ $mol^{-1}$ the minimum energy required for a self propagation in SHS reactions [10, 11].

### 3.3. $Sr_xBa_yTiO_3$

Reaction of mixtures of $SrO_2$ and $BaO_2$ with $TiCl_3$ and $TiO_2$ produces $Sr_xBa_yTiO_3$, Equation 4, Table II. The co-produced barium and strontium halides are removed on trituration with water. Successive substitution of barium into the $SrTiO_3$ lattice increases the size of the *a* lattice parameter from 0.3904 nm ($SrTiO_3$) to 0.3991 nm ($BaTiO_3$), consistent with the formation of a solid solution. Fig. 5 shows the shift of the 2 0 0 reflection with changes in the strontium to barium ratio. EDAX analysis of the mixed materials show constant ratios for strontium and barium across the surfaces.

$$2x\ SrO_2 + 2y\ BaO_2 + 0.5\ TiCl_3 + 0.5\ TiO_2 \rightarrow Sr_xBa_yTiO_3 + xSrCl_2 + yBaCl_2 \qquad (4)$$

### 3.4. Dielectric measurements

Cubic $SrTiO_3$ made from reaction of $TiCl_3$, $SrO_2$ and $TiO_2$ was pressed into a disc (16 mm diameter) and heated to 1300 °C for 2 h. This produced a material with a density of 3.4 g $cm^{-3}$ and a room-temperature dielectric constant (1 kHz) of 250 (typical dielectric constants for cubic $SrTiO_3$ prepared by hydrothermal synthesis vary from 250–300 [7]. The density of the $SrTiO_3$ prepared by this new route also agrees with the measurements for hydrothermally processed and sintered powders (2.70–4.02 g $cm^{-3}$).

## 4. Conclusion

The thermal initiation of a preground mixture of strontium oxide and a titanium source (titanium and $TiCl_3$) produces cubic $SrTiO_3$ in a rapid exothermic reaction. Addition of $TiO_2$ to the green mixture reduces the combustion temperature and the crystallite size of the product. The reaction of $SrO_2$ and titanium chloride initates at 200 °C and has a combustion temperature of 1000 °C. The $SrTiO_3$ produced from these methods after sintering shows good density and dielectric measurements. Mixed solid solutions of $Sr_xBa_yTiO_3$ can be synthesized by the reaction of $SrO_2$ and $BaO_2$ with $TiCl_3$ and $TiO_2$. The new processing routes developed in this work are easy to reproduce and can be scaled up at least to the kilogram scale. The product shows comparable properties to commercial materials; however, the new route shows dramatic reductions in reaction duration and external energy input compared to conventional processes.

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