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Low temperature crystallization of $La_{0.15}Sr_{0.775}TiO_3$ using ionic liquids

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Abstract

The n-type thermoelectric oxide $La_{0.15}Sr_{0.775}TiO_3$ (LST) has been synthesized at 600 °C using an ionic

liquid method. The method uses the ionic liquid 1-ethyl 3-methylimidazolium acetate as the sole

complexing agent: the lack of a second, carbon-rich template decreases the quantity of reduced

intermediate phases which form during heating. By suppressing these phases, greatly reduced

temperatures can be used to crystallize the perovskite LST phase, enabling the formation of

nanoscale crystallites of the LST phase. These nanoparticles have the potential to be used to increase

the figure of merit in n-type thermoelectric oxide devices.

Introduction

Control of crystallisation in oxide systems is becoming increasingly important for the functionality of

technological materials. One such type, thermoelectric oxides, could benefit significantly from the

control of nanostructure as a means to reduce thermal conductivity.[1] Most current schemes for nanoscaling of thermoelectric oxides in bulk rely on costly nanoscale starting reagents, still leaving little opportunity for the bespoke control of morphology, so schemes are sought to synthesize these oxides using bottom-up approaches which can control morphology or particle size. With the advent of cold sintering[2], if such nanostructures can be formed, new morphology-function relationships can be accessed as the technology now exists to retain nanostructuring during post-processing and sintering. Additionally, the ability to synthesize highly complex oxides at reduced temperatures is of great importance for a sustainable future, and novel methods which reduce reliance on high temperatures are urgently needed.

Thermoelectric materials enable the capture and recycling of waste heat energy; however further optimisation of materials is required to enable commercialisation of oxide-based technology.[3] One of the primary reasons for this is the lack of n-type thermoelectric oxides with high figure of merit.[4] One of the highest values for ZT achieved thus far in an n-type oxide has been found in $La_{0.15}Sr_{0.775}TiO_3$ (LST, 0.41 at 973 K),[5] however this material has only been synthesized using solid state synthesis. Nanoscaling is likely to improve the figure of merit[1,6] as has been observed in other materials, but due to the sensitivity of the La-Sr-Ti system to processing conditions,[5] a reliable, low temperature nanoscale synthesis for the A-site deficient material has not yet been found. Additionally, LST in its various stoichiometries has a number of other applications including as an anode[7] or anode backbone[8] in solid oxide fuel cells.

There are numerous schemes for the direction of crystal morphology in oxides. One such method is the use of ionic liquids[9] or deep eutectic solvents[10] to form transient intermediates which lower the reaction temperature required, either through a high degree of intermediate-composition nanoparticle mixing, low temperature decomposition, or through complex eutectic mixtures of the reagents themselves. These types of synthesis lend themselves to technologically useful titanate materials as they enable easy incorporation of Ti ions from alkoxide precursors. Choline

chloride/malonic acid deep eutectic solvents, for example, has been used to form barium titanate at reduced temperatures through the formation of titanium dioxide nanoparticles and barium chloride, which reacted at lower temperatures than typically encountered in solid state reactions.[10] The nanoscale nature of the intermediates formed enabled easy egress of the chloride ions during heating, however some concerns remain regarding the retention of small (often undetectable) quantities of the chloride ions which can have an effect on functionality.[10]

The ionic liquid 1-ethyl 3-methylimidazolium acetate has also been used as a solvent medium to synthesize complex oxide materials,[9,11] however this has always been with the inclusion of a secondary, carbon-rich biotemplate (e.g. cellulose), which will create a greater degree of reduction in the early stages of synthesis, leading to well-formed albeit nanoscale oxide or carbonate intermediate phases.[9] Whilst this can be effective at reducing reaction temperature in many syntheses, wide-scale formation of highly-reduced titanate phases (e.g. TiO_2) can be difficult to react with other oxides or carbonates, often reverting to similar temperatures as required by solid state.[9]

Herein we describe the use of 1-ethyl 3-methylimidazolium acetate without an added biotemplate to crystallize nanoscale LST between 350 °C and 420 °C, forming phase-pure LST phase by 600 °C, 500 °C lower than solid state through suppression of an intermediate titania phase.

Experimental

All chemicals were obtained from Sigma Aldrich UK, and used without further purification.

Stoichiometric quantities of lanthanum and strontium acetates were dissolved in water, and added to the ionic liquid (1-ethyl-3-methylimidazloium acetate). Samples was heated at 90 °C with continuous stirring until all of the water evaporated. Once dry, a stoichiometric volume of titanium isopropoxide was added under vigorous stirring to form a gel. Samples were then heated in a muffle furnace in air with a heating rate of 5 °C/min to a variety of temperatures, each held at temperature for 2 h.

X-ray diffraction (XRD) was performed using a PANalytical X'pert[3] Powder diffractometer. Lattice parameters were calculated using Bragg's law from the peak positions. Single crystalline domain sizes were estimated using the Scherrer equation (k=0.9).

Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) were performed on an as-prepared sample from the gel state using a Perkin Elmer SDT Q600.

Samples for scanning electron microscopy (SEM) were affixed to carbon tape and sputtered with 15 nm of gold before examination using a Phillips Inspect F SEM. Particle size was estimated by manually measuring a statistically significant (>500) particles on SEM images.

Results and discussion

Phase pure LST phase is produced at 600 °C (Figure 1), significantly lower than the temperature required for solid state synthesis (1100 °C).[5] Examination of the phases formed at intermediate temperatures indicate that nanoscale anatase TiO_2 emerges first, with the peak width indicating that the particles are of the order 15 ± 2 nm (at 300 °C) calculated using the Scherrer relationship. This initial crystallisation of TiO_2 is rapidly followed by strontium carbonate (or more likely a mixed strontium/lanthanum carbonate phase), and interestingly, by 400 °C the amount of anatase phase has been reduced to an undetectable level. This is key to the successful low temperature phase formation, as large quantities of TiO_2 (as observed in similar titanate syntheses[10]) require elevated temperatures to react. The absence of TiO_2 is concurrent with the emergence of the LST phase (visible as a minor phase in the 400 °C sample) indicating that the newly formed carbonate and anatase nanoparticles are acting as reaction sites, with the high surface area promoting rapid formation of the LST phase.

The lattice parameter of the phase pure (600 °C) sample was calculated and found to be 3.9076 ± 0.0009 Å, higher than previously reported for solid state LST phase.[5] This is commensurate with previous work using combustion-type syntheses, where lattice parameters for on-stoichiometry LST were found to be higher when using the Pechini or combustion methods than when using solid state.[12-15] This has been attributed to a higher oxygen content in the combustion method syntheses, creating a slight lattice expansion or due to the formation of a difficult-to-detect Ruddlesden Popper phase, although there is still ongoing debate about this.[16]

DTA and TGA were conducted to more closely examine the thermal processes during the reaction (Figure 2). Evaporation of the ionic liquid is detected in the TGA with an onset temperature of 200 °C (A) commensurate with the endothermic feature in the DTA (X). This is rapidly followed by crystallisation of the anatase phase evident as an exothermic event (Y), as the ions are released from complexation with the ionic liquid. Initial formation of the carbonate phase (shoulder at Z, 400 °C) and LST phase can be identified (Z) at 420 °C, in agreement with the emergence of the LST phase on XRD (between the 400 °C and 500 °C patterns). The continued slight mass loss between 350 °C and 430 °C (B) can be attributed to egress of CO_2 from the carbonate phase as this is reacted to form LST, after which the TGA remains stable. The DTA indicates that at the temperature range covered by the feature at Z (peaking at 420 °C), all of the ions in the system react to form LST. Above this temperature, the reaction is complete, and the system exhibits normal thermally driven grain growth. SEM (Figure 3) demonstrates the typical particle sizes obtained, of the order 26 ± 10 nm at 300 °C, increasing to 36 ± 12 after heating to 600 °C (Figure 3c) at which point the sample is phase pure. This represents a significant decrease in particle size as compared to powders produced using standard solid state processes, which are more usually of the order of 0.5-2 μm.[4,17]

Evaporation, rather than combustion prevents reduction of the intermediate materials, which is known to promote wide-scale oxide/carbonate intermediate phase formation. Eliminating any combustible template, as has been used with the ionic liquid systems previously,[9,11] decreases the likelihood of reduced phases forming, promoting the almost immediate crystallisation of the LST phase in this case. This leads to a reduced reaction temperature, and enables the formation of significantly smaller LST crystallites than solid state, or indeed many combustion-type syntheses.

In conclusion we have demonstrated that by omitting a carbon-rich, reducing template in ionic liquid syntheses, it is possible to promote perovskite crystallisation by reducing the quantities of reduced intermediate phases produced, synthesizing nanoscale A-site deficient LST as an example. The temperatures required to produce phase pure LST have been significantly reduced over solid state and these reduced temperatures enable synthesis of nanoscale crystallites. In the case of LST this may have significant benefits to functional properties, in particular improvements in the thermoelectric figure of merit, providing the nanostructuring can be retained during post-processing using, for example, cold sintering[2]. Given the previously demonstrated flexibility of ionic liquid/biotemplate composite syntheses, it is likely that this "biotemplate-free" method can be applied across a wide range of oxide materials, perhaps enabling access to otherwise unavailable reaction mechanisms.

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Figure 1. XRD patterns for LST samples heated to different temperatures to show phase evolution during heating. Symbols correspond to the following phases: □ anatase, O SrCO$_3$ (or mixed La/Sr carbonate) and ● LST.

Figure 2. DTA (left axis, red) and TGA (right axis, black) plots showing the progress of thermal events throughout heating. The ionic liquid evaporates at A, commensurate with an endothermic event in the DTA, X. Crystallization events of the carbonate phase and LST phase are shown as Y and Z respectively.

Figure 3. SEM micrographs of LST samples heated to a) 300 °C and b) 600 °C, showing an increase in particle size c) a histogram of particle size.