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Synthesis of Nb-doped $SrTiO_3$ by a modified glycine-nitrate process

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Abstract

The objective of the present investigation was to develop a technique to synthesize submicronic particles of Nb-doped strontium titanate with a homogeneous composition. This was achieved by a modified glycine-nitrate process, using Ti-lactate, Nb-oxalate, and $Sr(NO_3)_2$ as starting materials. A combination of both citric acid and glycine was needed in order to integrate the useful features of both complexation and combustion natures of citric acid and glycine, respectively. The amount of citric acid, glycine, and nitrates in the starting solution, as well as the source for extra nitrates, and the uniformity of heating during the thermal dehydration step were found to have significant influence on the final phase purity of the material. Calcination at 1100 °C in 7% H_2 in N_2 produced single phase Nb-doped strontium titanate with grain sizes of about 100 nm in diameter on average.

Keywords: Nb-doped $SrTiO_3$; Powders-chemical preparation; Electron microscopy; Microstructure-final

1. Introduction

Recently composites with doped strontium titanates have been reported to show promising electrocatalytic and conductivity results appropriate for solid oxide fuel cell (SOFC) applications.[1] The doped strontium titanate composite anodes were tolerant to oxygen-, carbon, and sulphur-containing atmospheres. Other research groups have reported that titanate-based anodes were remarkably active for the oxidation of CH_4 at high temperatures in the absence of excess steam.[2] Some n-doped titanates have also been found to be dimensionally phase stable during redox cyclings[3] and highly tolerant to extremely high sulfur-containing (up to 1% H_2S) fuel atmospheres.[4] By introducing deficiency on the A-site in n-doped strontium titanates it has been suggested that titanate based materials are potential candidates as part of an SOFC anode.[5–8] However, it seems that the performance of the $SrTiO_3$-based anodes depends on the thermal history and calcination (sintering) atmosphere during the synthesis of the materials.[3,5,7,8] The most common synthesis route employed when synthesizing and testing Nb-doped strontium titanate for SOFC applications has been the solid state synthesis route. However, the solid state synthesis is known to result in ceramics with compositional inhomogeneity and/or excessive grain growth.[9] In this study, a novel synthesis route based on the glycine nitrate combustion process (GNP),[10] is reported for fabricating submicronic particles of Nb-doped strontium titanate. The phase purity has been investigated as a function of various synthesis parameters, such as the amount of different additives in the precursor solution. The positive effect of the synthesis route on the powder microstructure and the compositional homogeneity is discussed.

2. Experimental

Vacancy-compensated Nb-doped strontium titanate with some extra A-site deficiency ($Sr_{0.94}Ti_{0.9}Nb_{0.1}O_{3-\delta}$) has been synthesized by a new synthesis route (from here on referred to as CitrGNP). The synthesis was developed and improved at various stages by combining the complexing ability of citric acid with the advantages of the GNP combustion technique.

The syntheses started with mixing stoichiometric amounts of $Sr(NO_3)_2$ (dissolved in water) and Ti-lactate solution (water-based solution produced according to Shacklett).[11] Citric acid and Nb-oxalate (provided from H.C. Starck, Germany) were then added to the solution under some heating (~50 °C) to increase the solubility of the Nb-complex. Extra nitrates were then added in the form of either NH_4NO_3 or HNO_3. Glycine was added as the last component. The molar ratios

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Table 1
Summary of the various syntheses displaying the precursor molar ratios (Gl = glycine, CA = citric acid, NO_3^- = nitrate, ΣM^{n+} = cations), the source for extra NO_3^-, the characteristics of the auto-ignition step, and finally general observations during and after the synthesis

Sample	Gl:CA:NO_3^-:ΣM^{n+}	Extra NO_3^- source	Auto-ignition	Observations
1	1.7 : 0 : 3.1 : 1	HNO_3	Partial	Precipitation,[a] impurity phases[b]
2	1.7 : 0.75 : 3.1 : 1	HNO_3	No[c]	Precipitation[a]
3	1.7 : 0.75 : 3.1 : 1	NH_4NO_3	Moderate	Clear solution,[a] impurity phases[b]
4	0 : 0.75 : 3.1 : 1	NH_4NO_3	Partial	Precipitation,[a] impurity phases[b]
5	2.3 : 0.75 : 5.1 : 1	NH_4NO_3	Moderate	Clear solution,[a] impurity phases[b]
6	1.5 : 0.75 : 8.4 : 1	NH_4NO_3	Moderate	Clear solution,[a] traces of impurities[b]
7	2.0 : 0.5 : 10.2 : 1	NH_4NO_3	Good	Clear solution,[a] traces of impurities[b]
8	2.0 : 0 : 7.7 : 1	NH_4NO_3	Excellent[d]	Some precipitation,[a] traces of impurities[b]
9	2.0 : 0.5 : 9.8 : 1	NH_4NO_3	Excellent[d]	Clear solution,[a] single phase[b]

[a] During the thermal evaporation.
[b] After calcination of powder.
[c] No auto-ignition probably due to irreversible reaction between acid and hydrocarbons.
[d] Heating mantle used during the thermal evaporation.

between glycine/cations, citric acid/cations, and nitrate/cations were varied according to Table 1. The concentrations of the various cations were determined by thermogravimetric analysis on the starting solutions/compounds ([Ti] ≈ 6.7 mg Ti/g lactate-solution, [Sr] ≈ 131 mg Sr/g $Sr(NO_3)_2$-solution, [Nb] ≈ 198 mg/g Nb-oxalate).

The precursor solution was heated on a hot-plate or in a heating mantle at about 100 °C to evaporate excess water. The precursor solution had a turbid appearance during the initial stage of the thermal evaporation. As more water evaporated and the temperature in the solution increased, the solution became transparent with a slight yellowish tint. When almost all water had evaporated, further heating to about 200–250 °C resulted in a brown/black foam that eventually auto-ignited into a self-sustained combustion reaction, which produced a voluminous powder ash of submicronic particles.

The powder ash was exposed to 350 °C in air for 3 h to fully combust all hydrocarbons and then calcined in 7% H_2 in N_2 at 1100 °C for 2 h. The partial pressure of oxygen ($P(O_2)$) during calcination was monitored with an external oxygen sensor ($P(O_2) \approx 10^{-18}$ atm).

The phase identification of the powders was carried out using an X-ray diffractometer (STOE Theta–Theta diffractometer). X-ray diffractograms were collected at $20° \le 2\theta \le 90°$ using Cu Kα radiation (40 kV and 30 mA). The average grain size d_{avg} was calculated from the XRD diffractograms using Scherrer's Eq. (1):

$$d_{avg} \approx \frac{\kappa\lambda}{\beta\pi\cos(\theta)} \qquad (1)$$

where κ, λ, β, and θ are the shape factor (taken as 0.9), the wave length of the Cu Kα radiation (1.54056 Å), the full width at half maximum (FWHM) of the (1 1 0) reflection, and the Bragg angle of the (1 1 0) reflection, respectively.

The powder microstructure was investigated by scanning electron microscopy (JEOL JSM-6700F). The phase homogeneity was examined with a transmission electron microscope (JEOL 3000F) equipped with an X-ray energy dispersive spectrometer (XEDS). For the TEM investigations, the powder was suspended in ethanol and transferred to a copper–carbon grid by dipping into the solution.

3. Results

Table 1 summarizes the characteristics of the auto-ignition step and the general observations during and after the synthesis of $Sr_{0.94}Ti_{0.9}Nb_{0.1}O_3$. Impurities were clearly present in the as-synthesized and calcined powders when precipitates formed during the thermal evaporation and/or no auto-ignited combustion reaction occurred. $Sr(NO_3)_2$ and $SrCO_3$ were found in these as-synthesized powders, while carbonitrides, various Ruddlesden–Popper impurity phases ($Sr_{n+1}Ti_nO_{3n+1}$, n = 1–3), and reduced titanium oxides were present after calcination. The XRD diffractograms from two different syntheses are shown in Fig. 1. A single phase material was only achieved in the synthesis of sample 9 (see Table 1 and Fig. 1).

The uncertainty in the stoichiometry of the synthesized powder was estimated to maximum ±0.01 of the nominal content for each element. This value is based on the uncertainty in the determination of the concentrations of the cations in the various precursors and in the weighing procedure of the precursors.

The total amount of nitrate ions in sample 9 was lower than the stoichiometrically calculated amount. This was due to safety issues during the development of the synthesis. Increasing the amount of nitrate ions more than shown in Table 1 will increase the combustion temperature, which in turn will increase the average grain size.

After calcination the average grain size was approximately 80 nm (from Eq. (1)). Fig. 2 clearly shows that the grain sizes on average were about 100 nm, which was in good agreement with calculations from XRD (Eq. (1)). The TEM investigation (Fig. 3) showed that the particles visible in Fig. 2 were single grains, agglomerated in a particle network.

XEDS analysis on two randomly selected particle agglomerates (similar to Fig. 3) showed that the Sr/(Ti + Nb)- and Ti/Nb-ratios were: 0.96 ± 0.03 and 9.07 ± 0.5 for one agglomerate, and 0.95 ± 0.05 and 9.16 ± 1.1 for another agglomerate, respectively.

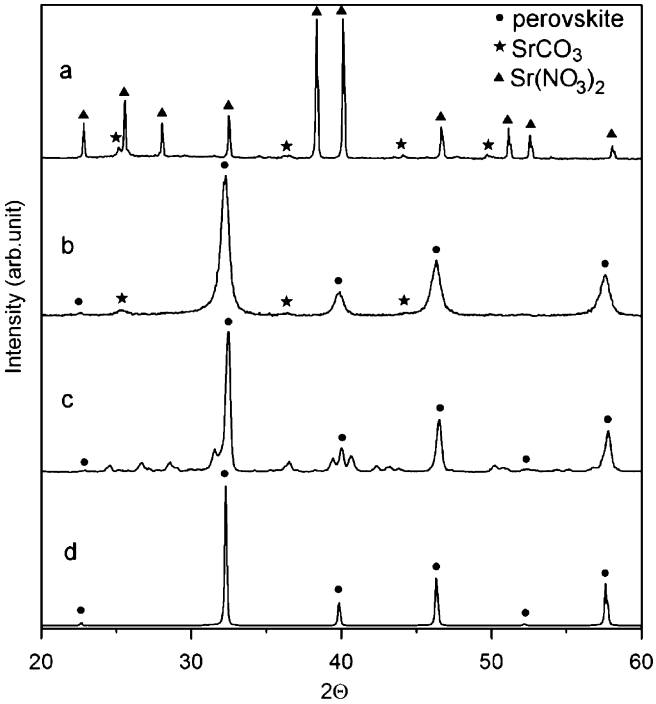

Fig. 1. XRD diffractograms showing (a) as-synthesized powder of sample 4. Note that the crystalline phases only consist of a mixture of $SrCO_3$ and $Sr(NO_3)_2$. (b) As-synthesized powder of sample 9. Note the drastic decrease of impurity phases and the virtually single perovskite phase compared to sample 4. (c) Sample 4 after calcination. Large amount of impurity phases ($Sr_{n+1}Ti_nO_{3n+1}$ with $n = 1–3$ and various reduced titanium oxides, not indexed in figure). (d) Sample 9 after calcination. Single phase material.

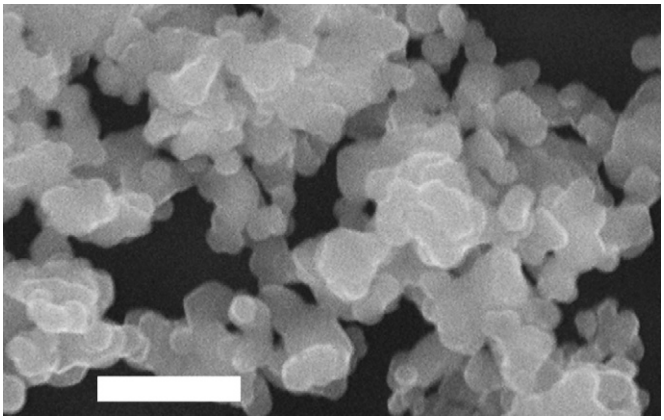

Fig. 2. SEM micrograph of $Sr_{0.94}Ti_{0.9}Nb_{0.1}O_{3-\delta}$ powder. Scale bar = 500 nm.

4. Discussion

Previous studies with $BaTiO_3$ have shown that a glycine/cation molar ratio of 1.2–1.5 resulted in an active auto-combustion reaction.[12] In the original paper about GNP a glycine/cation ratio around 2 was reported to give the best results.[10]

Similarly, a citric acid/cation molar ratio between 0.5 and 1 has been reported to give a good microstructure when $BaTi_4O_9$ was synthesized using the citrate route.[13] Based on this, $Sr_{0.94}Ti_{0.9}Nb_{0.1}O_{3-\delta}$ was prepared with various precursor ratios to investigate their effect on the amount of impurities in the calcined powder. A problem with using Ti- and Nb ions in GNP is that they do not exist as water soluble nitrates. Organic complexing agents must therefore be used to avoid precipitation in aqueous solutions.

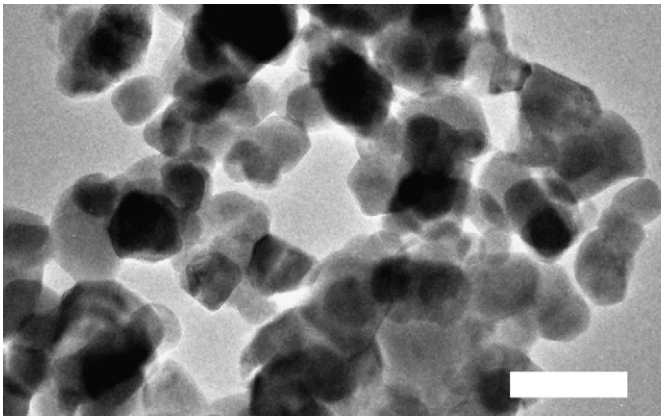

Fig. 3. TEM micrograph of $Sr_{0.94}Ti_{0.9}Nb_{0.1}O_{3-\delta}$ powder. Single grains in an agglomerate. Scale bar = 200 nm.

The first goal, set to avoid precipitation during the thermal evaporation step, was achieved when a mixture of both citric acid and glycine was used in combination with NH_4NO_3 as the extra nitrate source. Irreversible precipitation occurred when only one of either glycine or citric acid was present in the precursor solution or when HNO_3 was used as the extra nitrate source.

The next goal was to get a reactive, auto-ignited combustion reaction in order to minimize the amount of carbonaceous residues. These residues will cause impurities in the as-synthesized powders which in turn will increase the risk of getting impurities in the final calcined powder. This assumption is corroborated in Table 1 and Fig. 1.

Both goals were fulfilled when three criteria were satisfied: (1) the total amount of nitrate ions in the precursor solution was close to the stoichiometric ratio for complete combustion of the organic material in the precursor solution (i.e. only N_2, CO_2, and H_2O as combustion reaction products). (2) NH_4NO_3 was used as the extra NO_3^- source. (3) Both citric acid and glycine were present in the solution.

The Nb-oxalate complex has been reported by the manufacturer (H.C. Starck, Germany) to only be stable up to 70 °C in water. The precipitation that occurred at elevated temperatures, when no citric acid was used (see Table 1), was therefore believed to be due to decomposition of the Nb-complex, possibly forming hydrated niobium oxide. When citric acid was used no precipitation occurred, which could indicate a stronger complexing ability of citric acid, stabilizing both Ti- and Nb-ions during the thermal evaporation. Glycine was also needed in combination with citric acid to prevent precipitation during the thermal evaporation. A possible explanation could be that glycine forms a complex with the strontium ions, as reported in the original GNP paper.[10] The Sr-glycine complex could probably prevent precipitation of Sr-oxalate and/or $Sr(NO_3)_2$, which are well known precipitation reactions (oxalate from destabilization of Nb-oxalate above 70 °C, and NO_3^- from saturation during evaporation).

The formation of a foam during the evaporation caused a problem with non-uniform heating when a hot plate was used. The auto-ignition started at the bottom and the middle of the beaker and the flame then progresses outwards throughout the foam. At the beaker walls where there was no supply of heat the auto-combustion reaction ceased. This resulted in more carbonaceous residues in the as-synthesized powder which resulted in impurities in the calcined powder in the next step. Using a heating mantle (Isopad U2HB) solved the problem. Better uniform heating of the whole glass beaker resulted in a more homogeneous combustion reaction and resulted in a single phase material after calcination (sample 9).

The XEDS results from the TEM investigation were in good agreement with the desired target composition, 0.94 and 9.0, respectively, for $Sr_{0.94}Ti_{0.9}Nb_{0.1}O_{3-\delta}$. No statistically detectable grain-to-grain variation was observed when the composition between different grains was investigated. The slight differences from the target composition were within the range of the achievable accuracy of the XEDS measurements and the compositional uncertainty during the synthesis work.

The small grain sizes obtained with the CitrGNP synthesis method, proven to be about 100 nm diameter on average after calcination, is a promising feature for improved electrocatalytic activity of this fuel cell anode candidate.[6–8] Decreasing the particle sizes have been known for many years to generally improve the catalytic activity of catalysts. Recently it was reported for novel fuel cell anodes that smaller particle sizes (achieved with attrition milling) had a strong positive effect on the electrocatalytic performance.[1]

5. Conclusion

By using a combination of both citric acid and glycine in a modified GNP synthesis, a successful technique to synthesize submicronic particles of Nb-doped strontium titanate, with homogeneous composition, has been developed. The synthesis integrates the useful features of both complexation and combustion natures of citric acid and glycine, respectively. Process parameters such as the amount of citric acid, glycine, and nitrates in the starting solution as well as the source of extra nitrates, and the uniformity of heating during the thermal dehydration step were found to have significant influence on the final phase purity of the material. The precursor and additive ratios were adjusted in such a way that an auto-ignited combustion reaction occurred, which was needed in order to prevent the formation of impurity phases.

The structural characterization and microstructure analysis of the powder showed that the sample was single phase after calcination and consisted of submicronic grains (about 100 nm diameter on average).

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