Auto-combustion synthesis of perovskite-type oxides $\text{SrTi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$

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Abstract

A versatile one-pot auto-combustion method for the synthesis of powders of iron-doped strontium titanate, $\text{SrTi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$, has been developed. The synthesis is optimised by the combined use of EDTA and citric acid as chelating agents, and an appropriate balance between fuel and oxidising elements in the reaction mixture. The method produces immediately an almost phase-pure perovskite oxide powder, with an ultra-fine crystallite size of 20-40 nm, and with a low level of organic residues. Highly sinter-active powders are obtained after calcination and ball-milling of the powders.

Keywords

Combustion synthesis, $\text{SrTi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$, chelating agent

Highlights

- Simple and fast synthesis route for $\text{SrTi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ powders
- EDTA and citric acid are used as combined chelating agents
- Combustion leads to formation of almost phase-pure powders

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1. Introduction

The non-stoichiometric perovskite oxides $\text{SrTi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ (STF) are presently extensively investigated. The STF materials are good mixed ionic-electronic conductors [1-3], while other functional properties such as stability in reducing atmospheres, creep, and stability in CO_2 -containing atmospheres can be tuned by the Ti/Fe ratio. Especially the compositions with high Fe concentrations exhibit fast oxygen surface exchange and transport kinetics, which render them as viable candidates for use as cathode for solid oxide fuel cells (SOFCs) [4], and as dense ceramic membrane for oxygen separation [2].

STF is known to form a continuous solid solution between the two end members $\text{SrFeO}_{3-\delta}$ and SrTiO_3 over the whole composition range $0 < x < 1$ [5]. At high temperatures, all compositions in the series $\text{SrTi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ adopt the cubic perovskite structure (space group $\text{Pm}\bar{3}\text{m}$). While the end-member $\text{SrFeO}_{3-\delta}$ undergoes a structural phase transition to the ordered orthorhombic brownmillerite $\text{SrFeO}_{2.5}$ phase below $\sim 800\text{-}900^\circ\text{C}$ [6], substitution of Ti as low as $x = 0.01$, is sufficient to prevent this transition [5].

STF powders are typically synthesized by solid-state reaction, in which a stoichiometric mixture of solid reactants, e.g. carbonates, hydrates, oxalates or nitrates, is calcined at elevated temperature [1,7-9]. Multiple grinding and calcination steps are necessary to improve chemical homogeneity of the powder. The wide particle size distribution of the powder obtained via solid-state reaction often leads to poor sintering characteristics [1,8]. Intimate mixing of reactants on a molecular level on the other hand is a key benefit of wet synthesis methods. Examples of wet synthesis methods include co-precipitation [10,11], hydrothermal synthesis [12,13], solvent vaporization (spray drying, spray pyrolysis, and freeze drying), and combustion synthesis methods [14-16]. In general, these methods yield powders with higher compositional uniformity, smaller particle size and larger surface area than those prepared by solid-state reaction.

Combustion synthesis routes are inspired by the work of Pechini [15], in which citric acid and ethylene glycol are added to an aqueous solution of suitable metal salts or oxides, taken in appropriate proportions. Gelation occurs upon solvent evaporation due to poly-condensation of the citric acid and ethylene glycol. Immobilisation of the metal citrate complexes in the gel prevents precipitation of the cations, ensuring that the chemical homogeneity is retained in the precursor solution during drying [17]. After drying, the gel is fired at elevated temperature to obtain a finely dispersed powder of metal oxides and/or metal carbonates [18]. A phase-pure ceramic powder is obtained after calcination at a suitable temperature.

Alternatively, in modified Pechini synthesis routes, different chelating or combined chelating agents are employed [19]. The synthesis typically consists of four steps: (i) formation of organometallic complexes in solution, (ii) solvent evaporation and gel formation, (iii) auto-combustion (pyrolysis) followed by (iv) a heat treatment of the obtained powder [20,21]. Among several chelating agents, ethylene-diamine-tetraacetic acid (EDTA) and citric acid (CA) are used most frequently [11, 20]. Due to its higher chelating power, a far more extensive range of cations can be chelated with EDTA compared to CA [22]. Possessing three carboxyl groups and one hydroxyl group, however, CA is the chelating agent with the stronger gelation ability [23]. The sole use of CA as chelating agent, however, may result in a highly exothermic, non-uniform combustion reaction, adversely affecting the morphology of the powder [24]. For these reasons CA and EDTA are often employed as combined chelating agents [20,23,25,26].

In this work, we have developed a versatile one-pot auto-combustion route for the preparation of $\text{SrTi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ (STF) powders, using EDTA and citric acid as combined chelating agents. The synthesis is exemplified by the preparation of $\text{SrTi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ with $x = 0.3$, $x = 0.5$ and $x = 0.7$ (abbreviated as STF30, STF50, and STF70,

respectively). Water-soluble nitrates are used as precursors for strontium and iron, while titanium (IV) n-propoxide dissolved in ethanol is used as precursor for titanium.

2. Experimental

Synthesis of STF powders was carried out following the scheme as depicted in Fig. 1. High purity (> 99%) $\text{Sr}(\text{NO}_3)_2$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, citric acid (CA, $\text{C}_6\text{H}_8\text{O}_7$), ethylene-diamine-tetra-acetic acid (EDTA, $\text{C}_{10}\text{H}_{16}\text{N}_2\text{O}_8$), and titanium (IV) n-propoxide, $(\text{Ti}(\text{OC}_3\text{H}_7)_4)$ were purchased from Sigma-Aldrich, Inc. In beaker 1, $\text{Ti}(\text{OC}_3\text{H}_7)_4$ was dissolved in dry ethanol in a glove box under dry N_2 conditions. Beaker 2 contained a solution of EDTA in Q_2 -distilled water brought to a pH of 5.5 by the addition of concentrated NH_4OH (30 vol%, Sigma-Aldrich, Inc.). In beaker 3, stoichiometric proportions of strontium and iron nitrates were dissolved in Q_2 -distilled water. The EDTA solution (beaker 2) was added to the titanium (IV) n-propoxide solution (beaker 1) under vigorously stirring followed by the addition of the metal nitrate solution (beaker 3). Next, CA powder was added to beaker 1 up to a CA /total metal molar ratio of 1.5. In selected experiments only EDTA or CA was used as chelating agent. In all cases the total chelating agent : total metal molar ratio was maintained at 2.5 : 1. The pH of the precursor solution was re-adjusted to a value of 7 with NH_4OH (30 vol%, Sigma-Aldrich, Inc.) before splitting of the solution into smaller batches. Each batch comprised an amount equivalent to produce approximately 3.5 gram of powder, and was transferred to a tall glass beaker (2 L borosilicate 3.3). The amount of oxidizer NH_4NO_3 (Sigma-Aldrich) added to the precursor solution was varied in different experiments to study its influence on combustion characteristics. After addition of NH_4NO_3 , the precursor solution was heated on a ceramic hot plate, set to 350 °C, until a vigorously boiling gel was obtained. Upon further heating, a foam-like structure developed which eventually self-ignited. The temperature of the gel and that of the gas phase just above the gel during combustion were monitored using K-type thermocouples. These were

positioned just below and ~10 cm above the (initial) surface of the precursor solution, respectively, and were connected to a data logging device with a measuring frequency of 1 Hz. The beaker containing the precursor solution was covered with a stainless steel wire screen (100-mesh) to prevent undesired powder loss during combustion. The obtained flakes were crushed with a single zirconia ball ($\varnothing$ 52 mm) to obtain a raw powder with a high pouring density.

The powders were heat treated in air for 12 h either at 300, 500, 700, 900, or 1100 °C, using heating and cooling rates of 5 °C·min⁻¹. Powder X-ray diffraction patterns were obtained using a Bruker D2 Phaser with Cu-K α radiation (λ = 1.54184 Å). The XRD patterns were fitted by a Monte Carlo and grid search using the X'Pert Highscore Plus software package (PANalytical, version 3.0e). Powder samples were imaged using a JEOL JSM-6010LA analytical scanning electron microscope (SEM), operated at an acceleration voltage of 5 kV.

Raw powders obtained from synthesis were studied by thermogravimetric analysis (TGA) using a Netzsch STA 449 F3 Jupiter. The measurements were performed on 10 mg of the sample enclosed in an α -Al₂O₃ crucible under a flow of synthetic air (70 ml·min⁻¹ (STP)), using heating and cooling rates of 10 °C·min⁻¹.

To investigate the sintering activity of the powder, dilatometric measurements (Netzsch dilatometer 402 C) were performed on green rectangular bars in the temperature range 25 - 1400 °C, using heating and cooling rates of 2 °C·min⁻¹. Prior to these measurements, the powders were calcined at 950 °C for 12 h in stagnant air and ball-milled in ethanol for 48 h. Green rectangular bars (15 × 4 × 4 mm³) were obtained by uniaxial pressing at 50 MPa followed by isostatic pressing at 400 MPa.

3. Results and discussion

3.1 Precursor solution

Metal nitrates are widely used as precursors in aqueous synthesis routes [27]. Due to its high volatility at room temperature, however, titanium nitrate is less suitable as precursor [28]. For this reason, titanium (IV) n-propoxide dissolved in dry ethanol (beaker 1) was used in this study as precursor for titanium. After addition of the content of beaker 2, containing the aqueous solution of the EDTA with a pH of 5.5, a white turbidity (due to precipitation of $\text{Ti}(\text{OH})_2$) appeared in the solution, disappearing within less than about 10 s, upon which the solution became colourless and transparent again.

Condensation of metal alkoxides following hydrolysis by water can occur via two basic processes: (i) *via* the formation of hydroxy-bridges between the metal centres (ololation) or (ii) *via* the formation of more stable oxo-bridges (oxolation) [29]. Whether ololation or oxolation occurs will depend strongly on the pH of the solution. In a test experiment, first Q₂-distilled water with a pH of 11.8 was added to the solution of titanium (IV) propoxide in dry ethanol (beaker 1). Immediately, a white precipitate was formed. Next, EDTA in the form of powder was added to the solution, but the precipitation persisted even after stirring at 65°C for 24 h. This simple experiment demonstrates that it is important to control the pH of the solution in which hydrolysis and condensation of the titanium (IV) n-propoxide precursor occurs.

Some precipitation was observed after the addition of the aqueous solution of iron and strontium nitrates (beaker 3). Addition caused a drop in the pH of the solution, lowering the EDTA solubility. Readjusting the pH to ~7 by adding NH_4OH dissolved EDTA again, upon which a dark brownish solution was obtained. Unless specified otherwise, the CA : EDTA molar ratio during synthesis was 1.5 : 1, while the total chelating agent : total metal molar ratio was 2.5. After addition of CA, NH_4OH was

again used to readjust the pH to ~7 (Fig. 1). Subsequently, the precursor solution was divided into smaller batches for further processing.

3.2 Combustion characteristics

Traditionally, the constitution of a combustion reaction mixture is expressed in terms of the oxidizer-to-fuel ratio, ϕ , which quantity is referred to as the equivalence ratio [30]. This concept is however less useful when the fuel molecules contain oxidizer elements and/or the oxidizer molecules contain fuel elements. Combustion reactions are redox reactions and, hence, oxidation numbers can be used to determine which elements in the reactant mixture act as an oxidizer, and which act as a fuel (i.e., reductor). In this study, the method proposed by Jain *et al.* [30] was pursued by calculation of the so-called elemental stoichiometric coefficient for a given combustion reaction mixture:

$$\phi_e = - \frac{\sum_{i \text{ reaction mixture}} z_i n_{O,i}}{\sum_{j \text{ reaction mixture}} z_j n_{R,j}} \quad (1.1)$$

where $n_{O,i}$ and $n_{R,j}$ are the number of moles of oxidizing and reducing (fuel) elements in the reaction mixture, respectively, whilst z_i and z_j are their corresponding valences. Under stoichiometric conditions, the total number of oxidizing elements, i.e., oxygen, and reducing elements, such as carbon, hydrogen, and iron, in the reaction mixture are balanced, i.e., $\phi_e = 1$. In calculation, the following valences were taken: $z(\text{O}) = -2$, $z(\text{H}) = 1$; $z(\text{C}) = 4$, $z(\text{Sr}) = +2$; $z(\text{Ti}) = +4$; $z(\text{Fe}) = +3$; $z(\text{N}) = 0$. These correspond to the valences in the products of the combustion reaction. It was further assumed that ethanol

in the precursor solution was evaporated before the actual combustion reaction took place.

Assuming complete combustion to CO₂, H₂O and N₂, the overall stoichiometric reaction for the formation of, for example, SrTi_{0.5}Fe_{0.5}O_{3-δ} (STF50) at a CA : EDTA ratio of 1.5 can be written as

Hence, in this case 76.5 moles of oxidizer NH₄NO₃ per mole of product are required to achieve a stoichiometric balance of fuel and oxidizer. For a fuel-rich composition of the reaction mixture, O₂ from the gas phase will be required to achieve complete combustion.

To ensure complete combustion during synthesis of the different STF compositions an overstoichiometric amount of oxidizer NH₄NO₃ was added to the reaction mixture corresponding to a value for ϕ_e of 1.25. Gelation occurred after evaporation of the water, and in all cases the dried nitrate-citrate gels exhibited self-propagating combustion. Fig. 2 shows the typical evolution of the temperature in the gel core and just above the gel with time during combustion synthesis of STF50. The results show that under the conditions of the experiment the onset of ignition occurs at a gel temperature of ~220 °C, while the combustion is completed within about 50 s. The temperature in the core and above the gel reaches as high as ~800 °C and ~1100 °C, respectively. The data will depend on the exact positioning of the thermocouples in the glass beaker and the extent of swelling of the gel, and therefore should be taken with some care. The combustion was found to propagate like a wave through the gel. A video

recording showing the auto-combustion reaction is available on-line [31]. High local temperatures are maintained only for a short time and may lead to incomplete combustion. Some non-combusted gel was indeed observed at the wall of the glass beaker after the combustion reaction when only EDTA was used as chelating agent, while the combustion was considered too violent when only CA was used as chelating agent.

Fig. 3a shows TGA patterns of the as-synthesized STF50 powder or ash obtained from synthesis using either EDTA or CA as chelating agent or using them as combined chelating agents (in a ratio of CA : EDTA of 1.5). Data of mass spectroscopic analysis of the evolved gases in the effluent of the TGA indicates that up to ~ 150 °C (region A) mainly desorption of water and some organic species takes place, whilst the burn out of remaining organics occurs between 150 °C and 650 °C (region B). The temperature regions C, D and E are dominated by reversible oxygen non-stoichiometry changes of STF50 [32]. It is clear from Fig. 3a that the smallest fraction of organics in the as-synthesized powder remains when during its synthesis CA is used as chelating agent, which is followed by the powder obtained from synthesis using EDTA and CA as combined chelating agents, and that using solely EDTA as chelating agent.

In additional synthesis experiments, the amount NH_4NO_3 added to the reaction mixture was lowered to values for ϕ_e of 1 and 0.4, maintaining the CA : EDTA molar ratio at 1.5. The lower amount of oxidizer expectedly decreased the intensity of the combustion process, and led to a more incomplete combustion as quantified by subsequent TGA analysis of the powders obtained. As can be judged from the corresponding weight losses in Fig. 3b, the combustion efficiency is found to decrease with lowering ϕ_e .

Based upon above observations, it was decided to prepare powders of the other STF compositions using combustion reaction mixtures having a ϕ_e of 1.25, while using

CA and EDTA as combined chelating agents (in a ratio of CA : EDTA of 1.5). Although the lowest organic residue in this work was found in the ash produced using solely CA as chelating agent, the combustion reaction with CA was considered too violent. TGA registered a weight loss of 8-9 % for the powder obtained from the synthesis using CA and EDTA as combined chelating agents (Fig. 3a). This value is favourably low when compared with weight losses between 22 and 50 % as reported for powders from combustion syntheses of related perovskites oxides [14,26,33-35].

3.3 Powder characteristics and sintering behaviour

XRD patterns were recorded for as-synthesized STF powders before, and after calcination in air at different temperatures, as shown for STF50 in Fig. 4. A small peak at $2\theta = 25^\circ$ is assigned to an unknown impurity phase. It is no longer found to be present in the XRD pattern of the powder obtained after calcination at 700 °C. Similarly low calcination temperatures were required to obtain phase pure powders of STF30 and STF70. Indexing of the XRD patterns confirms that all STF compositions adopt the cubic perovskite structure with cell parameters 3.8936(8) Å, 3.8910(2) Å and 3.8831(2) Å for STF30, STF50 and STF70, respectively, in good agreement with literature data [2,36].

Typical SEM micrographs of the ceramic powders obtained after calcination at different temperatures are given in Fig. 5. These show porous, agglomerated structures with an estimated particle size between 10 and 100 µm. The pictures clearly evidence densification of the grains in the temperature range between 700 and 900 °C along with pore coarsening. The crystallite size, d_c , of the STF powders after calcination at different temperatures was estimated from the (110) reflection at 2θ of about 32.3°, using the Scherrer equation

$$d_c = \frac{k\lambda}{\beta \cos \theta} \quad (1.3)$$

where k ($= 0.94$) is the Scherrer constant, λ ($= 1.54184 \text{ \AA}$) is the wavelength of Cu-K α radiation, θ is the Bragg angle, and β is the full width at half maximum of the (110) reflection. Corresponding results are displayed in Fig. 6. The results confirm that nano-sized crystallites (20-40 nm) are obtained from synthesis, and that densification and grain growth is initiated around 800 °C. The sintering behaviour of STF was further examined by dilatometric measurements. Fig. 7 shows the densification behaviour for the three STF compositions. The results confirm that sintering starts around 800 °C, which is consistent with the SEM observations and the results obtained from the Scherrer equation. As shown in Fig. 7b, maximum sintering rates are between 1120 °C (STF70) and 1180 °C (STF30). These temperatures are 120-150 °C lower than those observed for STF powders prepared by the method of solid-state reaction [37]. For STF70 some swelling is observed in the final stage of the sintering process. The swelling is related with oxygen nonstoichiometry changes with increase of temperature, and is due to the building up of high pressures in sub-micron pores [38]. As this is beyond the scope of this research, the observation was not further investigated.

4. Conclusions

In this work, combustion synthesis has been successfully employed for the preparation of powders of the perovskite oxide $\text{SrTi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ (STF). This synthesis method represents an alternative to the solid-state reaction method conventionally used for the preparation of STF powders. The synthesis is optimised by the combined use of EDTA and citric acid as chelating agents, and an appropriate balance between fuel and oxidising elements in the reaction mixture. Combustion is found to produce an almost

phase-pure perovskite oxide powder with an ultra-fine crystallite size (20-40 nm), and with a low level of organic residues. Highly sinter-active powders are obtained after calcination and ball-milling of the powders.

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