

Synthesis of BaCeO_3 and $\text{BaCe}_{0.9}\text{Y}_{0.1}\text{O}_{3-\delta}$ from mixed oxalate precursors

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Abstract

An oxalate precipitation route is proposed for the synthesis of $\text{BaCe}_{1-x}\text{Y}_x\text{O}_3$ ($x = 0$ and 0.1) after calcination at 1100°C . The precipitation temperature (70°C) was a determinant parameter for producing a pure perovskite phase after calcination at 1100°C for 1 h. TG/DTA measurements showed that the co-precipitated (Ba, Ce and Y) oxalate had a different thermal behaviour from single oxalates. Despite a simple grinding procedure, sintered $\text{BaCe}_{0.9}\text{Y}_{0.1}\text{O}_{3-\delta}$ pellets (1400°C , 48 h) presented 90.7% of relative density and preliminary impedance measurements showed an overall conductivity of around $2 \times 10^{-4} \text{ S cm}^{-1}$ at 320°C .

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1. Introduction

Perovskites based on BaCeO_3 have proved proton conduction properties which reveal their potential use as solid membranes and electrode materials at proton ceramic fuel cells (PCFC). The partial substitution of Ce^{4+} ions by Y^{3+} ions at the perovskite structure creates oxygen vacancies ($\text{V}_\text{O}^{\bullet\bullet}$) in the bulk material which favours water adsorption and, consequently, the formation of proton defects.

Solid state reaction has been widely used as the preparation method for producing BaCeO_3 based materials^{1,2} by diffusion mechanisms. This process involves the mechanical mixing of precursor powders (metal oxides and/or carbonates) and subsequently thermal treatment at elevated temperature ($>1200^\circ\text{C}$).

Actually, improvements on the proton conduction of these materials and more economical synthesis routes are investigated. The proton conduction occurs in the bulk material at an atomic scale (KREUER³); therefore a more accurate control of their microstructure and chemical homogeneity may enhance their conduction performance which may be achieved by chemical synthesis routes.

Few works on chemical synthesis specifically applied to BaCeO_3 -based materials^{4,5} have been developed. As a consequence, in this work, an oxalate precipitation method is used to prepare pure and Y-doped- BaCeO_3 . The influence of some precipitation parameters on the characteristics of oxalate precursors and calcined/sintered powders was investigated.

2. Experimental

2.1. Oxalate precipitation

The stoichiometric ratio of $\text{Ba}(\text{NO}_3)_2$ (ACS, 99+% grade), $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Reacton[®], 99.5% grade), $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (99.9% grade), all furnished by Alfa Aesar, to yield the composition $\text{BaCe}_{1-x}\text{Y}_x\text{O}_3$ ($x = 0$ or 0.1) was used in precipitation tests. According to the experiment, solutions of 0.03 mol $\text{Ba}(\text{NO}_3)_2$, 0.027–0.03 mol $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, 0–0.003 mol $\text{Y}(\text{NO}_3)_3$ were prepared separately in 400 ml, 300 ml, 100 ml distilled water, respectively. These solutions were further mixed under magnetic agitation for 30 min and placed in the reactor. The 0.09 mol or 0.18 mol ammonium oxalate ($(\text{NH}_4)_2\text{C}_2\text{O}_4$, ACS, 99.0–101.0% grade, Aldrich) solution prepared in 200 ml distilled water was placed in a separate reservoir. All the apparatus was double-walled, water-jacketed, thermostated interconnected to control

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precipitation temperature. The pH and the temperature were recorded by a pH-controller radiometer PHM290 coupled with a computer.

When the system achieved the selected temperature ($T=25\text{ }^{\circ}\text{C}$ or $70\text{ }^{\circ}\text{C}$), the ammonium oxalate solution was injected ($6.0\text{ dm}^{-3}\text{ min}^{-1}$) in the reactor. Then, this mixture was stirred for a defined time, called here precipitation time ($t=30\text{ min}$ or 2 h) after which the thermostatic bath was switched off. The precipitate was recuperated when the room temperature was reached. Typically, at the beginning of ammonium oxalate addition, pH was reduced to 2.8, but it rapidly increased and remained stable at around 4.4.

The following steps consisted of several cycles of distilled water washing-centrifugation that was completed when the conductivity of the liquid phase remained stable (CDM210-Radiometer Analytical). The solid product was dried in an oven at $60\text{ }^{\circ}\text{C}$ for 24 h. Afterwards, the dried powder was ground and calcined in static air at $1100\text{ }^{\circ}\text{C}$ for 1 h.

2.2. Sintering

Calcined $\text{BaCe}_{0.9}\text{Y}_{0.1}\text{O}_{3-\delta}$ samples were reground and then uniaxially pressed into pellets at 9 MPa for 5 min with an intermediate step at 4.5 MPa also for 5 min, without binder. Their final dimensions were 18 mm-diameter and 1.5 mm-thickness. These pellets were sintered in air at $1400\text{ }^{\circ}\text{C}$ during 48 h.

2.3. Grinding

All grinding steps were performed in an agate mortar during 10 min.

2.4. Characterization

Several techniques were employed for the characterization of the as-precipitated, calcined, and sintered samples.

Dried-powder X-ray patterns were recorded on a Bruker D8 diffractometer in θ - θ configuration, with $\text{Co K}\alpha$ radiation ($\lambda=1.789\text{ \AA}$), and equipped with a position-sensitive detector. The X-ray powder diffraction (XRD) was used to identify the precipitated powder crystalline phases.

Scanning (SEM-Zeiss Leo 982) electron microscopy was used in the analysis of particle morphology and size.

Simultaneous differential thermal analysis and thermogravimetry (DTA-TG) were carried out on the precipitated powders using a SETARAM thermal analyser. Samples were heated from $25\text{ }^{\circ}\text{C}$ to $1500\text{ }^{\circ}\text{C}$ at a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$ under static air and cooled down to $25\text{ }^{\circ}\text{C}$ at a rate of $10\text{ }^{\circ}\text{C min}^{-1}$.

Electrical measurements used the sintered sample (18 mm-diameter and 1.5 mm-thickness) which was placed between two painted Pt-electrodes in a furnace with a flow of pure H_2 gas. This furnace was not completely air-tighten, so platinum catalysed the exothermic reaction between oxygen and hydrogen which produced water. The impedance spectroscopy measurements were done after the stabilisation of the furnace temperature. A Hewlett Packard 4192A LF impedance analyser programmed via an IBS-

Table 1

Summary of experimental conditions of undoped precipitation tests

Test	$T\text{ (}^{\circ}\text{C)}$	$t\text{ (min)}$	Molar ratio, $(\text{NH}_4\text{ oxalate})/(\text{total cation})$
BC1	25	30	3 (stoichiometric)
BC2	70	30	3 (stoichiometric)
BC3	70	120	3 (stoichiometric)
BC4	70	30	6

Informatics-compatible computer was used for data collection and analysis. Impedance spectra were recorded in a frequency range from 1 kHz to 13 MHz with an oscillating voltage of 100 mV.

3. Results and discussion

Experiments on undoped material were performed to establish the influence of some precipitation parameters (precipitation temperature, precipitation time, oxalate concentration) on the crystalline phase and the morphology of calcined powders. A summary of their experimental conditions are presented in Table 1.

DRX patterns (Fig. 1) show that the precipitation temperature was an important parameter to achieve a pure perovskite phase. At $25\text{ }^{\circ}\text{C}$ (BC1), the presence of CeO_2 could be depicted. The absence of any phase containing barium, except BaCeO_3 , suggests that these barium ions remained in solution and were discharged during washing steps. An increase in the precipitation temperature from $25\text{ }^{\circ}\text{C}$ to $70\text{ }^{\circ}\text{C}$ reduced considerably the presence of CeO_2 in the precipitate and a quite pure perovskite phase was produced. As a result, the precipitation temperature for our further tests was fixed at $70\text{ }^{\circ}\text{C}$. No influence of the precipitation time and of the ammonium oxalate/total cation molar ratio (o/c) on the nature, the morphology and the size of precipitated phase was detected.

Comparing the XRD patterns of co-precipitated oxalates (Fig. 1) to those of single oxalates (Fig. 2), it can be depicted that the co-precipitated product was not a simple mixing of single oxalates, but rather a weakly crystallised barium–cerium or barium–cerium–yttrium oxalate solid solution.

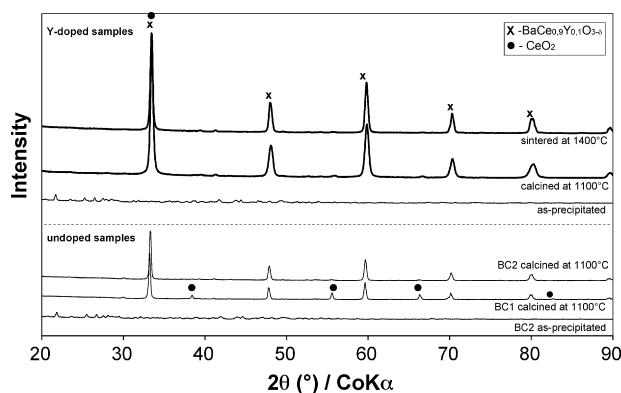


Fig. 1. XRD patterns of as-precipitated (BC2) and calcined undoped powders (BC1 and BC2 calcined at $1100\text{ }^{\circ}\text{C}$ for 1 h) and of as-precipitated, calcined ($1100\text{ }^{\circ}\text{C}$, 1 h) and sintered ($1400\text{ }^{\circ}\text{C}$, 48 h) Y-doped powders.

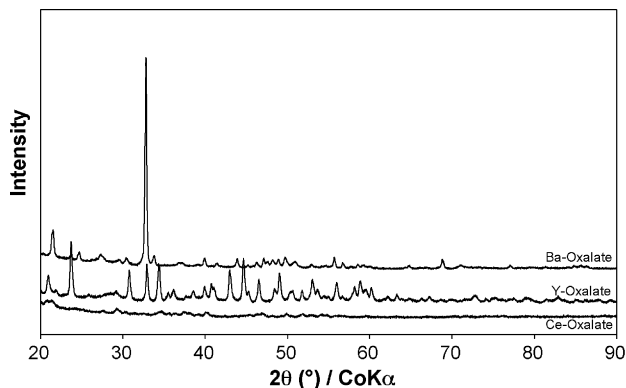


Fig. 2. XRD patterns of as-precipitated single (Ba, Ce and Y) oxalate powders.

Fig. 3 shows that the co-precipitated oxalate precursors were constituted of agglomerated thick plates with a faceted base, typically hexagonal, measuring around $15\ \mu\text{m}$ and are $1.5\ \mu\text{m}$ thick as presented. As a result of the thermal treatment at $1100\ ^\circ\text{C}$, calcined particles started sintering leading to three size scales: single particle ($\sim 300\ \text{nm}$), initially sintered particle ($\sim 900\ \text{nm}$) and heterogeneously sized agglomerates.

For the synthesis of $\text{BaCe}_{0.9}\text{Y}_{0.1}\text{O}_{3-\delta}$, precipitation temperature and time were fixed at $70\ ^\circ\text{C}$ and 30 min, respectively, and the o/c ratio was 3.

DTA measurements of co-precipitated oxalate precursor (BCY-ox) and individual oxalates (Ba-oxalate, Ce-oxalate and Y-oxalate) are presented in Fig. 4.

The thermal behaviour of Ba-oxalate indicated that after the of H_2O loss at $135\text{--}202\ ^\circ\text{C}$, the decomposition of Ba-oxalate into BaO occurred in three steps: (a) at $365\text{--}573\ ^\circ\text{C}$, the decomposition of Ba-oxalate to BaCO_3 , (b) further decomposition of BaCO_3 to BaO_2 took place; (c) the last transformation at $814\ ^\circ\text{C}$ corresponded to the decomposition of BaO_2 into BaO.⁶ For Ce-oxalate, the H_2O loss occurred at $100\text{--}190\ ^\circ\text{C}$ and further decomposition into CeO_2 was presented by the exothermic peak at $295\ ^\circ\text{C}$.⁷ Y-oxalate sample presented H_2O loss at $130\text{--}246\ ^\circ\text{C}$ and decomposition into Y_2O_3 at $400\text{--}687\ ^\circ\text{C}$.

It can be depicted from BCY-ox curve in Fig. 4 that the exothermic peak associated to Ce-oxalate decomposition reaction shifted from $295\ ^\circ\text{C}$ to $321\ ^\circ\text{C}$, the decomposition of

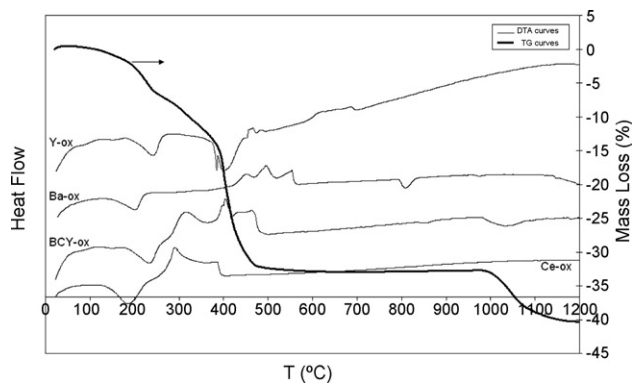


Fig. 4. DTA analysis of co-precipitated oxalate precursor (BCY-ox) and individual oxalates (Ba-oxalate, Ce-oxalate and Y-oxalate) and TG analysis of BCY-ox.

Ba-oxalate occurred at lower temperatures $363\text{--}467\ ^\circ\text{C}$ and perovskite formation took place at $1050\ ^\circ\text{C}$. No peak related to Ba_2O decomposition into BaO was observed. The TG curve shows that, during perovskite formation ($1050\ ^\circ\text{C}$), a mass loss of 7% was measured probably as a result of BaCO_3 decomposition. This value is inferior to the stoichiometric CO_2 weight loss of 12% predicted by the reaction between BaCO_3 , CeO_2 and Y_2O_3 to produce $\text{BaCe}_{0.9}\text{Y}_{0.1}\text{O}_{3-\delta}$. On the other hand, the overall weight loss is compatible with the theoretical value of 42%, once water removal is excluded. This result pointed out the thermal behaviour differences between co-precipitated oxalates and single oxalates; hence a further detailed study should be considered.

XRD patterns of calcined ($1100\ ^\circ\text{C}$, 1 h) and sintered powders ($1400\ ^\circ\text{C}$, 48 h) presented in Fig. 1 show that perovskite phase was maintained stable during thermal treatment steps.

Fig. 5 shows that yttrium doping reduced the size ($\sim 8\ \mu\text{m}$) and the thickness (200 nm) of the as-precipitated sample. After calcination, the initial sintering of doped particles was less important than for undoped product.

After being submitted to sintering, the pellet achieved a relative density of 90.7%. The relative density is the ratio of the density of the samples and the theoretical density of the material.

It is important to notice that the grinding procedure was not optimized at this work, so this result must be considered carefully. Nevertheless, it indicated that the oxalate precipitation

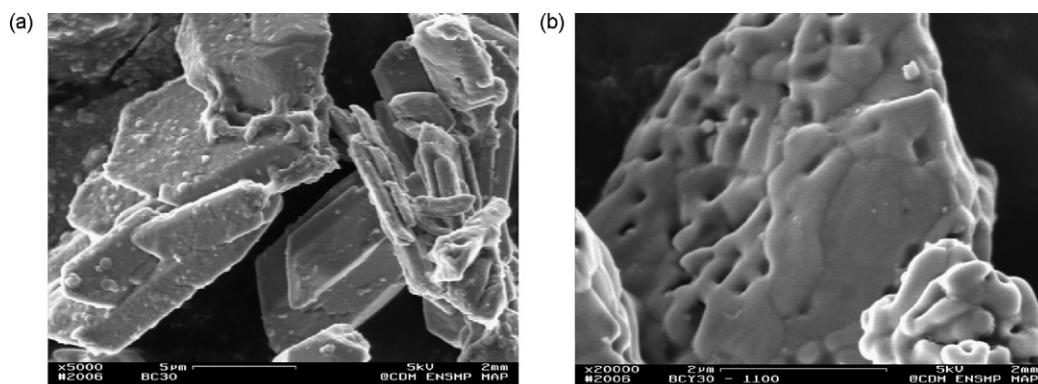


Fig. 3. Scanning electron micrographs of (a) as-precipitated oxalate particles and (b) calcined particles ($1100\ ^\circ\text{C}$, 1 h). Precipitation conditions: $t = 30\ \text{min}$; o/c = 3.

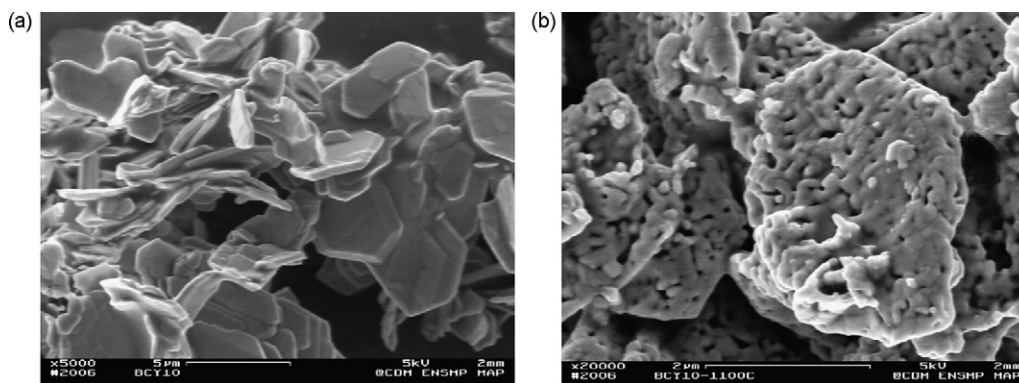


Fig. 5. Scanning electron micrographs of $\text{BaCe}_{0.9}\text{Y}_{0.1}\text{O}_{3-\delta}$ samples originated from different synthesis routes (a) as-precipitated sample and (b) sample issued from oxalate precipitation after calcination at 1100°C for 1 h (c) sample issued from solid state synthesis after calcination at 1100°C for 1 h.

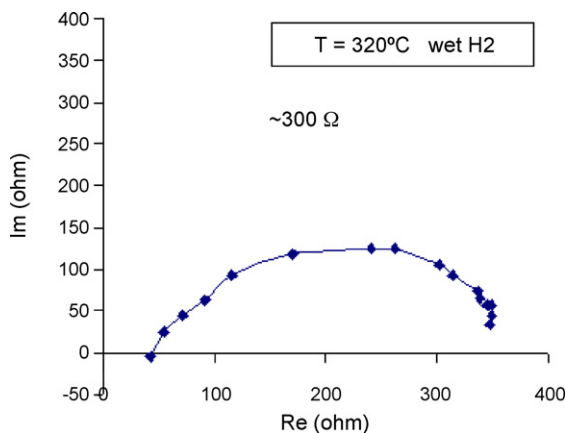


Fig. 6. Impedance spectrum of $\text{BaCe}_{0.9}\text{Y}_{0.1}\text{O}_{3-\delta}$ obtained by oxalate precipitation route at 320°C .

route produced a rather dense material using unsophisticated equipment suggesting that the compaction level can still be improved.

The preliminary impedance measurement under wet H_2 at 320°C (Fig. 6) for $\text{BaCe}_{0.9}\text{Y}_{0.1}\text{O}_{3-\delta}$ sample (oxalate precipitation route) showed that the material's resistance was about $300\ \Omega$. The overall conductivity was then calculated from the relation, $\sigma = e/RA$ (where e is the thickness of sample, A the surface of sample and R is the resistance of sample) and its value, $2 \times 10^{-4}\ \text{S cm}^{-1}$, corresponded to a better result than those given at the literature data^{5,8} for solid state reaction products at the same test conditions. Further impedance measurements should be done to establish the proton conductivity.

4. Conclusions

The oxalate precipitation showed to be a simple method to produce dense BaCeO_3 -perovskite type materials. Reducing the initial sintering during calcination step is an important challenge to increase the relative density. The improvement on overall conductivity due to a more homogeneous product during precipitation process was observed. These preliminary results indicated that soft chemical routes should be considered as an alternative to solid state reaction to produce dense BaCeO_3 based perovskites.

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