SYNTHESIS OF Nd-DOPED BARIUM CERATE PROTON CONDUCTOR FROM OXALATE COPRECIPITATE PRECURSOR

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Abstract

The decomposition process of barium, cerium and neodymium oxalates in air was investigated by DTA-TG. Decomposition of an oxalate coprecipitate precursor and formation of barium cerate were examined in air, N_2 and CO_2 atmospheres, respectively, by employing DTA-TG and XRD. The results showed that, in air, cerium oxalate could easily be decomposed to CeO_2 below 350°C and Nd_2O_3 could be obtained at 670°C, while a high temperature of >1400°C was needed to obtain BaO. Although some amount of $BaCeO_3$ was formed at 500°C in air, at 650°C in N_2 and at 800°C in CO_2, single perovskite phase of $BaCeO_3$ could only be obtained at a much higher temperature.

Keywords: barium cerate, oxalate coprecipitation, proton conductor, synthesis

Introduction

$BaCeO_3$ doped with rare earth oxides such as Nd_2O_3 is known to exhibit significant protonic conduction in hydrogen or water vapour containing atmospheres at elevated temperatures [1–3]. Their ability to conduct protons makes these systems potential candidates for applications in many novel electrochemical devices such as solid oxide fuel cells, hydrogen or steam sensors, electrolyzers for hydrogen production and high temperature membrane reactors [4].

These materials are conventionally produced by solid-state reaction from the mixture of CeO_2, Nd_2O_3 and $BaCO_3$ which involves high calcination (>1100°C) and sintering (1500°C) temperatures [6]. In the present work, Nd doped $BaCeO_3$ is prepared *via* a homogeneous oxalate coprecipitation route. The reaction process from the oxalates was studied by employing DTA-TG and XRD.

Experimental

Stoichiometric ratio of $Ba(NO_3)_2$ (Merck), $Ce(NO_3)_3 \cdot 6H_2O$ (Alfa) and $Nd(NO_3)_3 \cdot 6H_2O$ (Alfa) to yield the composition of $BaCe_{0.9}Nd_{0.1}O_{3-\alpha}$ were weighed and dissolved in de-ionized water and heated to boiling. Excess hot aqueous ammonium oxalate was added to the nitrate solution with vigorous stirring to produce an
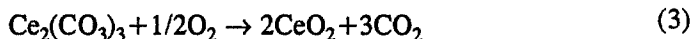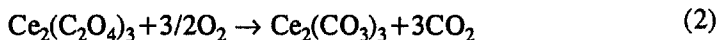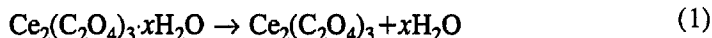
instantaneous oxalate coprecipitation. Individual barium, cerium and neodymium oxalates were precipitated using the same procedure. The precipitate was kept at room temperature for 10 h to crystallize. It was then filtered, washed with de-ionized water and dried in an oven at 50°C for 24 h.

Differential thermal analysis (DTA) and thermogravimetry (TG) were carried out on a NETZSCH STA 429 thermal analyzer. Samples were heated from 25 to 1400°C (or 1000°C) at a heating rate of 2°C min^{-1} and a cooling rate of 5°C min^{-1} to 100°C, in a dynamic atmosphere of air, N_2 or CO_2. Phase compositions were determined by X-ray powder diffraction (Philips PW 1078/ 10) using CuK$_\alpha$ radiation.
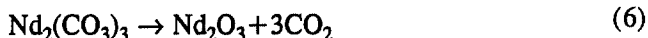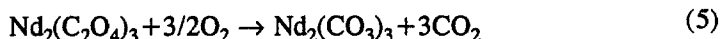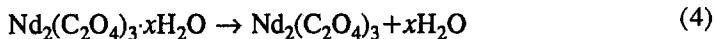
Results and discussion

DTA-TG results of cerium, neodymium and barium oxalates

Figure 1a shows the DTA-TG diagrams of cerium oxalate in air. The TG curve shows three mass loss steps, which correspond to the following reactions:

$$Ce_2(C_2O_4)_3 \cdot xH_2O \rightarrow Ce_2(C_2O_4)_3 + xH_2O \qquad (1)$$

$$Ce_2(C_2O_4)_3 + 3/2O_2 \rightarrow Ce_2(CO_3)_3 + 3CO_2 \qquad (2)$$

$$Ce_2(CO_3)_3 + 1/2O_2 \rightarrow 2CeO_2 + 3CO_2 \qquad (3)$$

The first mass loss is due to the hydrate water evolution, which is accompanied by a strong endothermic effect. Cerium oxalate normally has 9 molecules of hydrated water [7], but in our experiment, x was found to be about 7, probably because some of the hydrate water was released during drying. The second mass loss, closely following the first one, corresponds to exothermic Reaction (2). Finally, the strongly exothermic mass loss is the result of the decomposition of cerium carbonate and simultaneous oxidation of Ce(III), as expressed in Reaction (3). The overall mass loss from anhydrous cerium(III) oxalate to cerium(IV) oxide is 35.3%, which is close to the theoretical value (36.7%).

Figure 1b illustrates the DTA-TG results of neodymium oxalate. Three successive TG curves correspond to the following reactions:

$$Nd_2(C_2O_4)_3 \cdot xH_2O \rightarrow Nd_2(C_2O_4)_3 + xH_2O \qquad (4)$$

$$Nd_2(C_2O_4)_3 + 3/2O_2 \rightarrow Nd_2(CO_3)_3 + 3CO_2 \qquad (5)$$

$$Nd_2(CO_3)_3 \rightarrow Nd_2O_3 + 3CO_2 \qquad (6)$$

The pronounced endothermic peak near 160°C in the DTA curve can be attributed to the evolution of the hydrate water. The corresponding mass loss is 25%, and x is calculated to be 10, which corresponds to the chemical formula of $Nd_2(C_2O_4)_3 \cdot 10H_2O$ [7]. The second exothermic mass loss step results from Reac-

tions (5). The third endothermic mass loss is due to Reaction (6). The observed mass loss from anhydrous neodymium oxalate to neodymium oxide is 30%, which is close to the calculated value 29.5%.
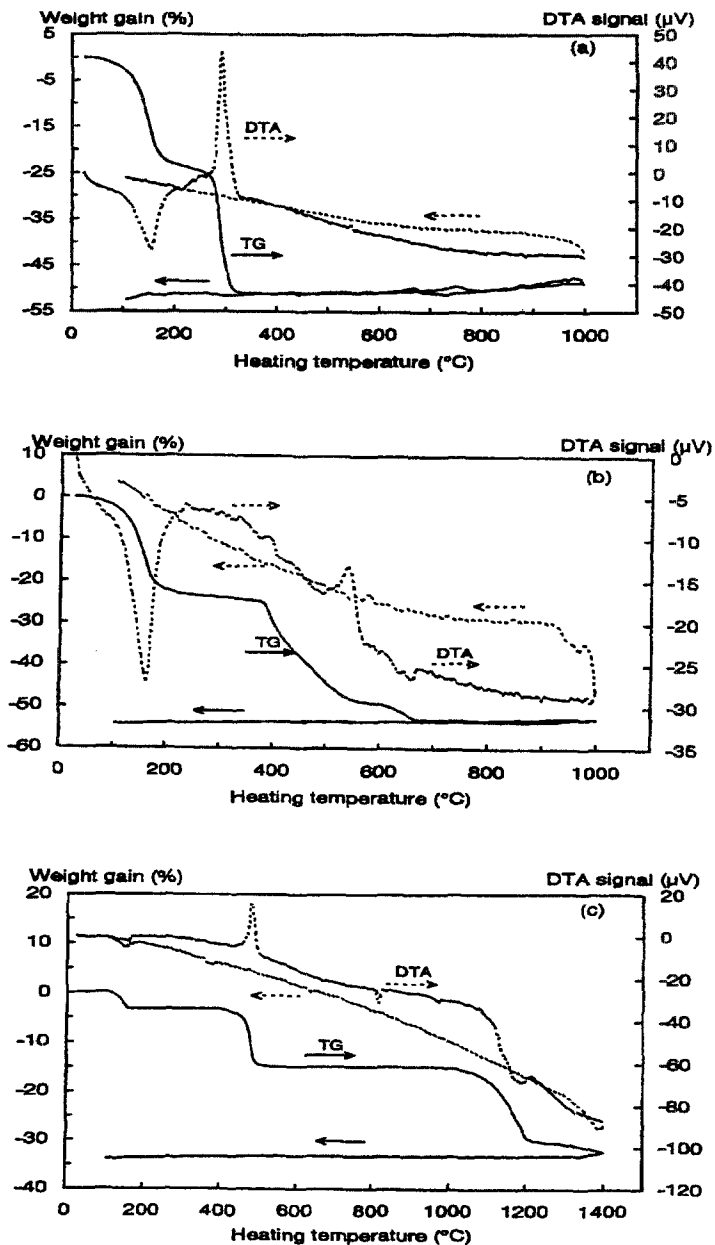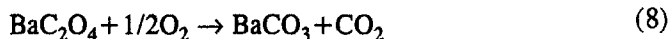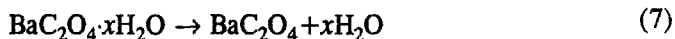

Fig. 1 DTA-TG results of the individual oxalates in air. a) cerium oxalate; b) neodymium oxalate; c) barium oxalate

Figure 1c shows the DTA-TG results of barium oxalate. Four consecutive mass loss peaks appeared in the TG curve which may be assigned to the following reactions:

$$BaC_2O_4 \cdot xH_2O \rightarrow BaC_2O_4 + xH_2O \tag{7}$$

$$BaC_2O_4 + 1/2O_2 \rightarrow BaCO_3 + CO_2 \tag{8}$$

$$BaCO_3 + 1/2O_2 \leftrightarrow BaO + CO_2 \tag{9}$$

The first endothermic mass loss is the result of the evolution of the hydrate water and x is found to be 0.5. The second mass loss peak is due to the decomposition of barium oxalate to barium carbonate, as expressed in Reaction (8). A strongly exothermic effect associated with the oxidation of CO was observed. The mass loss is 12.5%, which is in good agreement with the calculated value (12.4%). Two endothermic peaks due to the phase transition of $BaCO_3$ are observed in the DTA curve, i.e., at 814°C from the orthorhombic to the rhombohedral and at 970°C from the rhombohedral to the cubic. This is in good agreement with the onset temperatures for the phase transitions determined by Scholten [9]. The last two mass loss peaks in the TG curve are due to the decomposition of $BaCO_3$, as expressed in Reaction (9). The total 19% mass loss is much smaller than the theoretical mass loss of 23.6%, indicating that incomplete removal of CO_2 from the reversible equilibrium takes place and the decomposition of $BaCO_3$ does not go to completion in air even at 1400°C. This is probably caused by the accumulation of CO_2 at the surface of the powder which suppressed $BaCO_3$ decomposition.

Based on the above observations, it can be seen that: (1) cerium oxalate can easily be decomposed to CeO_2 below 350°C; (2) the temperature needed for the complete decomposition of neodymium oxalate to Nd_2O_3 is about 670°C and (3) a high temperature of > 1400°C is needed for the complete decomposition of barium oxalate to BaO.

Formation of Nd-doped BaCeO_3 from the oxalate coprecipitate precursor

Figure 2 shows the DTA-TG curves of the oxalate coprecipitate precursor in different atmospheres of air, N_2 and CO_2, respectively. The TG curves are almost identical in air and N_2, the only difference is that the onset temperature of each mass loss step shifts slightly to a higher temperature in the case of N_2 atmosphere. With the increase in temperature, three distinctive mass loss steps can be observed in all TG curves. The first endothermic 12% mass loss is due to the evolution of the hydrate water, which is close to the calculated value of 12.7%. As shown in Fig. 2a, the second prolonged mass loss step in the temperature range of 170 to 400°C may be attributed to the decomposition of cerium and neodymium oxalates to their perspective oxides and the decomposition of barium oxalate to barium carbonate. A strongly exothermic effect was observed in the DTA curve, which is caused by the oxidation reaction to form CO_2. Figures 2b and 2c show that a slight endothermic effect was accompanied to the second mass loss step when the coprecipitate precur-
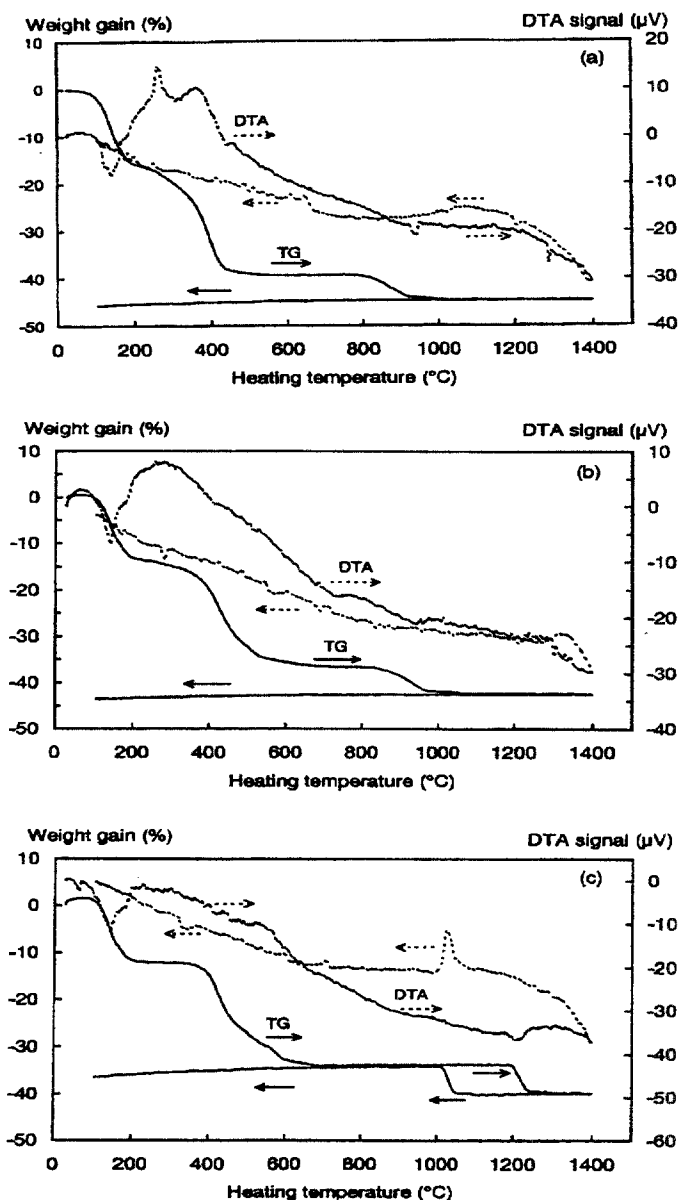
Fig. 2 DTA-TG results of the oxalate coprecipitate precursor in different atmospheres. a) in air; b) in N_2; c) in CO_2

sor decomposed in N_2 and CO_2. Flint [8] also found an endothermic effect of the decomposition of the oxalate in inert atmosphere environments. The third endothermic mass loss step in all three TG curves is supposed to be the decomposition of $BaCO_3$ to BaO and formation of $BaCeO_3$, which corresponds to a theoretical mass
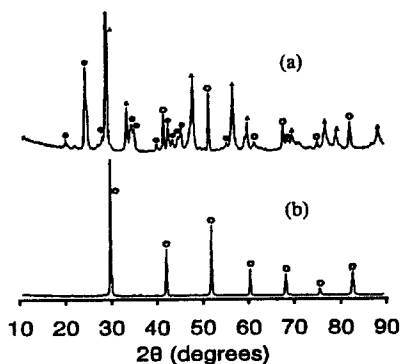
Fig. 3 XRD patterns of the powder after DTA-TG measurements of the oxalate coprecipitate precursor in different atmospheres. a) CO_2; b) air. •: $BaCO_3$; ▲: CeO_2; o: $BaCeO_3$

loss of 11.6%, but only about 9% mass loss was observed in the TG curves from all three atmospheres. XRD patterns of the powder after DTA-TG measurements in air and N_2, as shown in Fig. 3b, revealed a single $BaCeO_3$ perovskite phase, indicating that the decomposition of barium carbonate and formation of $BaCeO_3$ was already completed. The discrepancy of the calculated and observed mass loss value in the third step may be caused by two possible reasons. The first one is that some intermediate Ba/Ce compounds formed during the second mass loss step so that the third mass loss step does not correspond to the decomposition of $BaCO_3$ and the formation of $BaCeO_3$. The other possible explanation is that partial decomposition of $BaCO_3$ and the formation of $BaCeO_3$ took place in the second mass loss step. XRD patterns of the oxalate coprecipitate precursor calcined at 500°C in air and the powder after DTA-TG measurement of the oxalate coprecipitate precursor in CO_2 atmosphere are identical, as shown in Fig. 3a, which revealed a mixture of $BaCO_3$, CeO_2 and $BaCeO_3$. No intermediate Ba/Ce oxide phase was identified. Accordingly, it confirms that partial decomposition of $BaCO_3$ and the formation of $BaCeO_3$ took place in the second mass loss step. This implies that the decomposition of $BaCO_3$ is much easier for the coprecipitate precursor than for pure barium oxalate due to the reaction to form $BaCeO_3$.

The presence of some barium cerate at 500°C in air and below 1000°C in 1 atm CO_2 was not expected in light of the work of Gopalan et al. [10]. They found that $BaCeO_3$ was not stable with respect to $BaCO_3$ and CeO_2 below 560°C in air based on molten salt experiments and below 1090°C in 1 atm CO_2 using galvanic cell measurements. However, Schmutzler et al. [11] found that $BaCeO_3$ could be formed at 500°C by oxidation of solid metal-bearing precursors. Heat treatment of sintered $BaCeO_3$ powder in 1 atm CO_2 revealed the existence of some $BaCeO_3$ phase below 1000°C although most of it decomposed to $BaCO_3$ and CeO_2 [12]. Therefore, the thermodynamic data of $BaCeO_3$ obtained by Gopalan et al. [10] was not accurate as discussed by Scholten et al. [13]. It can also be noted that the decomposition process for the oxalate coprecipitate in air was accelerated compared with the individual oxalate due to the reaction to form $BaCeO_3$.

As shown in Fig. 2c, the DTA-TG diagrams of the oxalate coprecipitate precursor in CO_2 atmosphere is distinctive from those in air and N_2 in two aspects: the onset temperature for the decomposition of $BaCO_3$ and the formation of $BaCeO_3$ is much higher, and during cooling, barium cerate is not stable with respect to $BaCO_3$ and CeO_2 in CO_2 below $1000°C$. This caused partial decomposition of $BaCeO_3$. The formation of $BaCO_3$ by a decomposition of $BaCeO_3$ in CO_2 is a strongly exothermic reaction as revealed by DTA.

Conclusions

In air, cerium oxalate could be easily decomposed to CeO_2 below $350°C$ and Nd_2O_3 could be obtained at about $670°C$, while a high temperature of $> 1400°C$ is needed to obtain BaO possibly due to the CO_2 accumulation at the surface of the powder. The decomposition process of oxalate coprecipitate in air was accelerated compared with the individual oxalate due to the reaction to form $BaCeO_3$. Although some amount of $BaCeO_3$ was formed at $500°C$ in air, $650°C$ in N_2 and $800°C$ in CO_2, single perovskite phase of $BaCeO_3$ could only be obtained at a much higher temperature. No intermediate Ba/Ce oxide phase was identified.

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