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Letter

Synthesis of $\text{SmBaCo}_2\text{O}_{6-\delta}$ powder by the combustion process using Co_3O_4 as precursor

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ABSTRACT

A double perovskite phase $\text{SmBaCo}_2\text{O}_{6-\delta}$ powder was successfully synthesized by the citric acid–nitrate gel combustion process after calcining at 900°C for 4 h, using undissolved and relatively inexpensive Co_3O_4 as a starting material for the first time. TGA–DTA and XRD results revealed the formation mechanism of the double perovskite phase. The $\text{BaCoO}_{3-\delta}$ was generated firstly, then the formation of Ba-doped $\text{SmCoO}_{3-\delta}$ occurred, and finally Sm^{3+} and Ba^{2+} were distributed orderly, obtaining $\text{SmBaCo}_2\text{O}_{6-\delta}$ with a double perovskite phase. SEM analysis indicated that Co_3O_4 might play as a “template” in the synthesis process of $\text{SmBaCo}_2\text{O}_{6-\delta}$ via this special method. The conductivity of $\text{SmBaCo}_2\text{O}_{6-\delta}$ was still higher than 200 S cm^{-1} at 850°C , which is adequate as a cathode material for Solid Oxide Fuel Cells (SOFCs).

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1. Introduction

Recently double perovskite compounds $\text{LnBaCo}_2\text{O}_{6-\delta}$ ($\text{Ln} = \text{Pr}$, Nd , Sm , Eu , Gd , Tb , Dy , Ho , and Y) have attracted much attention because of their remarkable transport and magnetic properties [1–7]. These double perovskite compounds possess an ordered structure in which lanthanide (Ln^{3+}) and alkali-earth (Ba^{2+}) ions are distributed orderly in the A-site sub-lattice. Moreover, the oxygen atoms can be partially or even completely removed from the LnO layers, which generates lots of oxygen vacancies and results in the formation of chains of CoO_5 square pyramids and CoO_6 octahedra [2,3].

Due to their specific crystal structure we have discussed above, these double perovskite compounds exhibit high electronic and oxide ion conductivity and hence have been studied as alternative materials of cathodes for SOFCs [8–11] and oxygen permeation [12] recently. According to the literature reports, $\text{LnBaCo}_2\text{O}_{6-\delta}$ was usually synthesized via a solid state reaction [8–11] or a sol–gel combustion process [12]. However, the former method needs high synthesis temperature and long reaction time (usually at 1100°C for 24 h), and the latter one requires expensive soluble precursors, which limit the extensive application of $\text{LnBaCo}_2\text{O}_{6-\delta}$.

In this study, we introduced an improved combustion process combining a solid state reaction to synthesize $\text{SmBaCo}_2\text{O}_{6-\delta}$ (one typical example of $\text{LnBaCo}_2\text{O}_{6-\delta}$ compounds) powders at

a low temperature, using relatively inexpensive and undissolved Co_3O_4 as a precursor. Meanwhile, the formation mechanism of the double perovskite phase $\text{SmBaCo}_2\text{O}_{6-\delta}$ was also investigated in detail.

2. Experimental

2.1. Synthesis of powder

$\text{SmBaCo}_2\text{O}_{6-\delta}$ composite oxides were synthesized via a combustion process combined with a solid state reaction method, using undissolved Co_3O_4 as a starting material. The flowchart is given in Fig. 1. $\text{Ba}(\text{CH}_3\text{COO})_2$, Co_3O_4 and Sm_2O_3 (all A.R. grade) served as the raw materials for the necessary metal ions. First, Sm_2O_3 was dissolved in HNO_3 , then $\text{Ba}(\text{CH}_3\text{COO})_2$ and Co_3O_4 were added into the Sm^{3+} solution under stir. Subsequently, citric acid with molar ratios of soluble metal ions:citric acid of 1:1.5 was added and pH value was adjusted to about 7 with ammonia. The suspension was heated and stirred continuously at $80\text{--}90^\circ\text{C}$ till to ignition and combustion, getting as-prepared powders. And subsequently as-prepared powders were calcined at various temperatures for 4 h in air to yield the expected powders.

2.2. Characterization

Phase structures of the samples annealed at different temperatures were identified by X-ray diffraction (XRD) analysis on Philips PW 1730 diffractometer using $\text{CuK}\alpha$ radiation. Thermogravimetric and differential thermal analysis (TGA–DTA) of as-prepared powders were performed using a DTG-60H (Shimadzu) instrument with a heating rate of $10^\circ\text{C min}^{-1}$ to investigate the reaction process in flowing dry air. The microstructures of Co_3O_4 and $\text{SmBaCo}_2\text{O}_{6-\delta}$ powders were investigated by a scanning electron microscopy (SEM, JEOL JSM-6700F). Electrical conductivity of $\text{SmBaCo}_2\text{O}_{6-\delta}$ bar sintered at 1100°C for 5 h was studied using the standard dc four-probe technique on H.P. multimeter (Model 34401) in the temperature range of $50\text{--}850^\circ\text{C}$ in air, and Ag paste was used for the electrodes.

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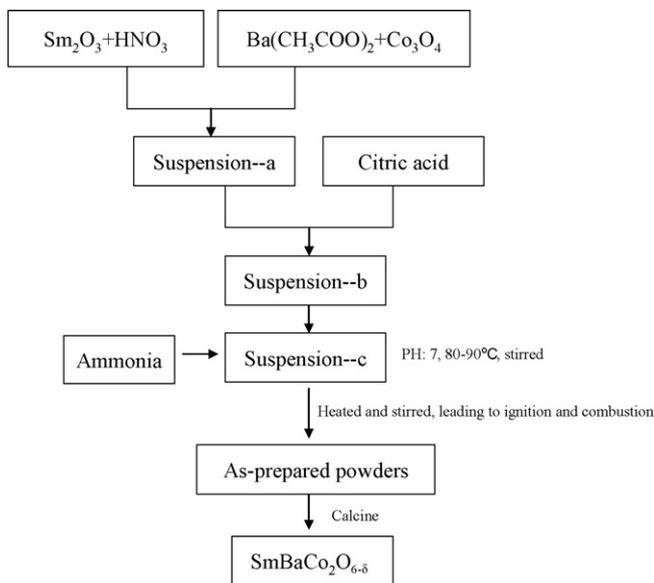


Fig. 1. Procedure for the preparation of SmBaCo₂O_{6-δ} powder.

3. Results and discussions

Fig. 2 is the TGA-DTA curves for the as-prepared powders, showing the reaction process behavior of the powders. At the first stage, the endothermic peak and exothermic peaks appeared in the DTA curve up to about 385 °C were corresponding to the evaporation of the absorbed moisture and combustion of the residual organic matter, respectively, with the weight loss about 3.10%. Then, from about 385 to 700 °C, the undecomposed samarium nitrate decomposed to samarium oxide. From 700 °C to 792 °C, a rapid mass decrease and a large endothermic peak can be observed, which is mainly associated with the formation of BaCoO_{3-δ} along with the evaporation of CO₂, according to reaction (1), and reaction (2) (in this case, 0.5 ≤ x ≤ 1) also occurred [13]. On increasing the temperature from 792 °C to 900 °C, reactions (2) and (3) occurred, dominating the loss of weight.

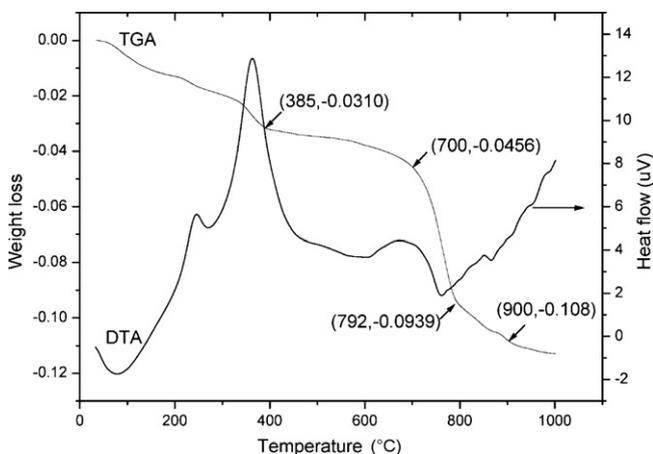
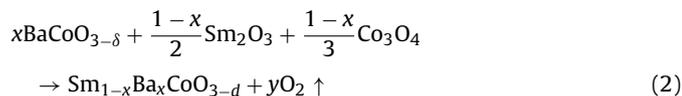
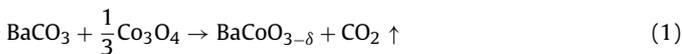


Fig. 2. TGA-DTA curves of as-prepared powders.

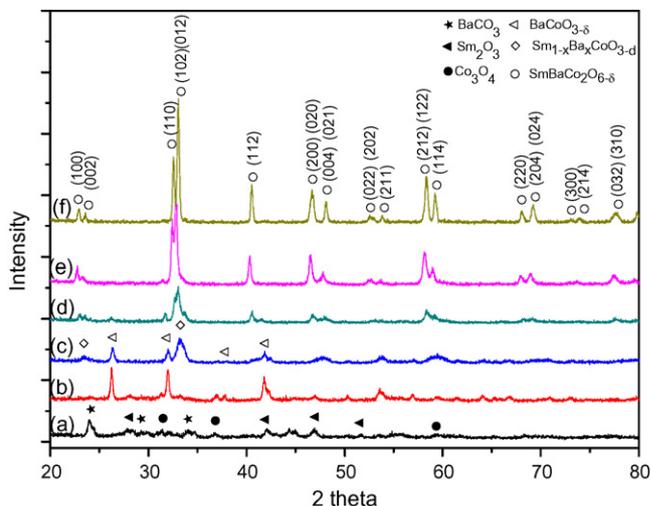
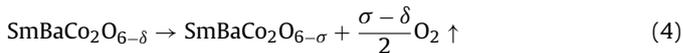
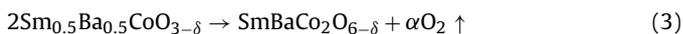


Fig. 3. XRD of as-prepared powders after being annealed at different temperatures for 4 h (a, as-prepared; b, 650 °C; c, 750 °C; d, 850 °C; e, 875 °C; f, 900 °C).



Finally, when the temperature was higher than 900 °C, a relatively smaller rate of weight loss suggests the evolution of oxygen from the double perovskite SmBaCo₂O_{6-δ}, just as reaction (4). All the reactions mentioned above will be confirmed later by the XRD patterns of powders annealed at different temperatures.

Fig. 3 gives XRD patterns of powders calcined at different temperatures for 4 h. Only BaCO₃, Co₃O₄ and Sm₂O₃ can be found in the as-prepared powders. CO₂ was produced during the combustion of the organic matter in the gel, and then reacted with barium, resulting in the formation of BaCO₃ which should be highly reactive. At 650 °C, BaCoO_{3-δ} appeared with intense peaks, and intensity of peaks for BaCO₃ was remarkably decreased; peaks of Co₃O₄ and Sm₂O₃ were also present now. On increasing the temperature from 750 °C to 875 °C, the SmCoO_{3-δ}-like peaks (here they were identified as Sm_{1-x}Ba_xCoO_{3-d}, or Ba-doped SmCoO_{3-δ}) appeared and intensity increased, whereas BaCoO_{3-δ} peak intensity decreased significantly, finally getting Sm_{0.5}Ba_{0.5}CoO_{3-δ}. At 875 °C, characteristic peaks of SmBaCo₂O_{6-δ} with double perovskite type structure could be detected as a result of gradually ordered distribution between Sm³⁺ and Ba²⁺ along the c axis. Finally, pure SmBaCo₂O_{6-δ} with double perovskite type structure was obtained after calcined at 900 °C for 4 h. Obviously, the synthesis temperature was remarkably decreased by 200 °C than the traditional solid state reaction method [10,11].

In the as-prepared powders after combustion of the gel, BaCO₃ and Sm₂O₃ adhered on the surface of Co₃O₄ grains homogeneously. Therefore, the decreased synthesis temperature was attributable to the more homogeneous mixing and more rapid diffusion of Sm³⁺ and Ba²⁺ to Co₃O₄. Furthermore, the in situ formed BaCO₃ and Sm₂O₃ are highly reactive, which could also highly promote their reaction with Co₃O₄.

The morphologies of the as-received Co₃O₄ and the synthesized SmBaCo₂O_{6-δ} powders calcined at 950 °C for 4 h are shown in Fig. 4. The SmBaCo₂O_{6-δ} powder grain was dense, not coral-like loose which is typical for powders via conventional sol-gel method. The grain size and distribution of the SmBaCo₂O_{6-δ} powders were similar to those of the Co₃O₄ powders, though the heat treatment at 950 °C for 4 h. However, there was a bit difference in the shape between Co₃O₄ and SmBaCo₂O_{6-δ} powders, which were

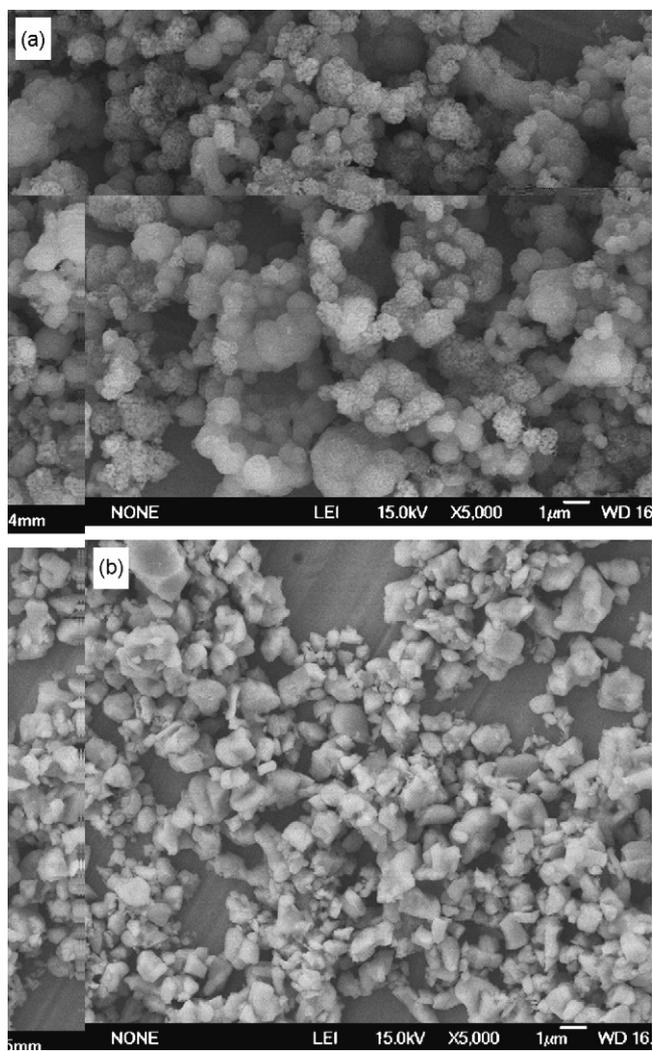


Fig. 4. SEM of as-received Co_3O_4 powders (a) and powders annealed at 950°C for 4 h (b).

sphere-like and quadrate-like, respectively; and the slight morphology change might be caused by the nucleation during the synthesis process. Based on the results shown above, we can assume that Co_3O_4 might play the role as a “template” in the process of synthesizing $\text{SmBaCo}_2\text{O}_{6-\delta}$, and the shape and size of $\text{SmBaCo}_2\text{O}_{6-\delta}$ grains almost inherit those of Co_3O_4 . Similar phenomenon was observed during the synthesis of CaZrO_3 via an improved molten salt synthesis process (MSS), in which process CaZrO_3 formed in situ with ZrO_2 as “template” [14]. Therefore, we might easily get $\text{SmBaCo}_2\text{O}_{6-\delta}$ owing various morphologies and grain sizes by adjusting those characters of Co_3O_4 .

Fig. 5 shows the temperature dependence of the electrical conductivity of $\text{SmBaCo}_2\text{O}_{6-\delta}$ in the temperature range of $50\text{--}850^\circ\text{C}$ measured in air. The conductivity is enhanced with the increase of the temperature from room temperature to 200°C . When the temperature is above 200°C , however, the conductivity begins to decrease with increasing temperature, showing a metallic behavior. Obviously, the conductivity is still higher than 200 S cm^{-1} up to 850°C , which is adequate as a cathode material for SOFCs.

Fig. 5. Temperature dependence of the electrical conductivity for $\text{SmBaCo}_2\text{O}_{6-\delta}$ in the temperature range of $50\text{--}850^\circ\text{C}$.

4. Conclusions

A combustion process combining with a solid state reaction method was successfully used to synthesize $\text{SmBaCo}_2\text{O}_{6-\delta}$ powders, and undissolved Co_3O_4 plays as a “template” in the synthesis process. The pure double perovskite phase could be obtained after calcined at 900°C for 4 h. It was demonstrated that $\text{BaCoO}_{3-\delta}$, Ba-doped $\text{SmCoO}_{3-\delta}$ and $\text{SmBaCo}_2\text{O}_{6-\delta}$ with double perovskite phase came into being in order. And the process developed can be extended to the synthesis of other LnCoO_3 -based perovskite materials in general.

Acknowledgments

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