1. Introduction

Recently double perovskite compounds LnBaCo$_2$O$_6$–$\delta$ (Ln = 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 Co$_5$ 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, LnBaCo$_2$O$_6$–$\delta$ was usually synthesized via a solid state reaction method [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 LnBaCo$_2$O$_6$–$\delta$.

In this study, we introduced an improved combustion process combining a solid state reaction to synthesize SmBaCo$_2$O$_6$–$\delta$ (one typical example of LnBaCo$_2$O$_6$–$\delta$ compounds) powders at a low temperature, using relatively inexpensive and undissolved Co$_3$O$_4$ as a precursor. Meanwhile, the formation mechanism of the double perovskite phase SmBaCo$_2$O$_6$–$\delta$ was also investigated in detail.

2. Experimental

2.1. Synthesis of powder

SmBaCo$_2$O$_6$–$\delta$ composite oxides were synthesized via a combustion process combined with a solid state reaction method, using undissolved Co$_3$O$_4$ as a starting material. The flowchart is given in Fig. 1. Ba(CH$_3$COO)$_2$, Co$_3$O$_4$ and Sm$_2$O$_3$ (all A.R. grade) served as the raw materials for the necessary metal ions. First, Sm$_2$O$_3$ was dissolved in HNO$_3$, then Ba(CH$_3$COO)$_2$ and Co$_3$O$_4$ 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 80–90 °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 CuK$_\alpha$ radiation. Thermogravimetric and differential thermal analysis (TGA–DTA) of as-prepared powders were performed using a DTA–60H (Shimadzu) instrument with a heating rate of 10 °C min$^{-1}$ to investigate the reaction process in flowing dry air. The microstructures of Co$_3$O$_4$ and SmBaCo$_2$O$_6$–$\delta$ powders were investigated by a scanning electron microscopy (SEM, JEOL JSM-6700F). Electrical conductivity of SmBaCo$_2$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 50–850 °C in air, and Ag paste was used for the electrodes.

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**Abstract**

A double perovskite phase SmBaCo$_2$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$_3$O$_4$ as a starting material for the first time. TGA–DTA and XRD results revealed the formation mechanism of the double perovskite phase. The BaCo$_3$O$_4$ was generated firstly, then the formation of Ba-doped SmCoO$_3$–$\delta$ occurred, and finally Sm$^{3+}$ and Ba$^{2+}$ were distributed orderly, obtaining SmBaCo$_2$O$_6$–$\delta$ with a double perovskite phase. SEM analysis indicated that Co$_3$O$_4$ might play as a “template” in the synthesis process of SmBaCo$_2$O$_6$–$\delta$ via this special method. The conductivity of SmBaCo$_2$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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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$_3$-$\delta$ along with the evaporation of CO$_2$, according to reaction (1), and reaction (2) (in this case, 0.5 $\leq x \leq$ 1) also occurred [13]. On increasing the temperature from 792 °C to 900 °C, reactions (2) and (3) occurred, dominating the loss of weight.

\[
\begin{align*}
\text{BaCO}_3 + \frac{1}{3} \text{Co}_3\text{O}_4 &\rightarrow \text{BaCoO}_3-\delta + \text{CO}_2 \\
x\text{BaCoO}_3-\delta + \frac{1-x}{2} \text{Sm}_2\text{O}_3 + \frac{1-x}{3} \text{Co}_3\text{O}_4 &\rightarrow \text{Sm}_{1-x}\text{Ba}_x\text{COO}_3-\delta + y\text{O}_2
\end{align*}
\]

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 SmBaCo$_2$O$_6$-$\delta$, 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 BaCo$_3$, Co$_3$O$_4$ and Sm$_2$O$_3$ can be found in the as-prepared powders. CO$_2$ was produced during the combustion of the organic matter in the gel, and then reacted with barium, resulting in the formation of BaCo$_3$ which should be highly reactive. At 650 °C, BaCo$_3$-$\delta$ appeared with intense peaks, and intensity of peaks for BaCo$_3$ was remarkably decreased; peaks of Co$_3$O$_4$ and Sm$_2$O$_3$ were also present now. On increasing the temperature from 750 °C to 875 °C, the SmCo$_3$-$\delta$-like peaks (here they were identified as Sm$_{1-x}$Ba$_x$Co$_3$-$\delta$) appeared and intensity increased, whereas BaCo$_3$-$\delta$ peak intensity decreased significantly, finally getting Sm$_{0.5}$Ba$_{0.5}$Co$_3$-$\delta$. At 875 °C, characteristic peaks of SmBaCo$_2$O$_6$-$\delta$ with double perovskite type structure could be detected as a result of gradually ordered distribution between Sm$^{3+}$ and Ba$^{2+}$ along the c axis. Finally, pure SmBaCo$_2$O$_6$-$\delta$ 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, BaCo$_3$ and Sm$_2$O$_3$ adhered on the surface of Co$_3$O$_4$ grains homogeneously. Therefore, the decreased synthesis temperature was attributable to the more homogeneous mixing and more rapid diffusion of Sm$^{3+}$ and Ba$^{2+}$ to Co$_3$O$_4$. Furthermore, the in situ formed BaCo$_3$ and Sm$_2$O$_3$ were highly reactive, which could also highly promote their reaction with Co$_3$O$_4$.

The morphologies of the as-received Co$_3$O$_4$ and the synthesized SmBaCo$_2$O$_6$-$\delta$ powders calcined at 950 °C for 4 h are shown in Fig. 4. The SmBaCo$_2$O$_6$-$\delta$ 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 SmBaCo$_2$O$_6$-$\delta$ powders were similar to those of the Co$_3$O$_4$ powders, though the heat treatment at 950 °C for 4 h. However, there was a bit difference in the shape between Co$_3$O$_4$ and SmBaCo$_2$O$_6$-$\delta$ powders, which were

\[
\begin{align*}
2\text{Sm}_{0.5}\text{Ba}_{0.5}\text{CoO}_3-\delta &\rightarrow \text{SmBaCo}_2\text{O}_6-\delta + \alpha\text{O}_2 \uparrow \\
\text{SmBaCo}_2\text{O}_6-\delta &\rightarrow \text{SmBaCo}_2\text{O}_6-\alpha + \frac{\sigma - \delta}{2}\text{O}_2 \uparrow
\end{align*}
\]
Fig. 4. SEM of as-received Co$_3$O$_4$ powders (a) and powders annealed at 950 °C for 4 h (b).

Fig. 5. Temperature dependence of the electrical conductivity for SmBaCo$_2$O$_6$-$\delta$ in the temperature range of 50–850 °C.

4. Conclusions

A combustion process combining with a solid state reaction method was successfully used to synthesize SmBaCo$_2$O$_6$-$\delta$ powders, and undissolved Co$_3$O$_4$ 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 BaCoO$_3$-$\delta$, Ba-doped SmCoO$_3$-$\delta$ and SmBaCo$_2$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.

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References


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$_3$O$_4$ might play the role as a “template” in the process of synthesizing SmBaCo$_2$O$_6$-$\delta$, and the shape and size of SmBaCo$_2$O$_6$-$\delta$ grains almost inherit those of Co$_3$O$_4$. 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 SmBaCo$_2$O$_6$-$\delta$ owing various morphologies and grain sizes by adjusting those characters of Co$_3$O$_4$.

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.