

Synthesis of mixed-conducting oxide $\text{SrFeCo}_{0.5}\text{O}_y$ powder by auto-combustion of citrate–nitrate gel

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Abstract Mixed-conducting oxide $\text{SrFeCo}_{0.5}\text{O}_y$ powders have been synthesized by auto-combustion of citrate–nitrate gel. The resulting powder is pure, homogeneous and possesses a reasonably fine particle size. Attempts have been made to understand the combustion process with the help of Differential Thermal Analysis (DTA) of the sample. The XRD, SEM and TEM studies on these powders confirmed that the method produces powder had greater composition uniformity, lower residual carbonate levels and smaller particle sizes.

Keywords Oxide materials · Chemical synthesis · Thermal analysis

1 Introduction

Mixed-conducting oxide $\text{SrFeCo}_{0.5}\text{O}_y$ (SFCO) exhibits high oxygen permeability and high oxide-ion conductivity as well as good structural stability [1, 2]. This material has been used to produce syngas [3] and oxygen separation membranes. Indeed, Balachandran et al. [4] demonstrated that extruded membrane tube of SFCO can be used for partial oxidation of produce syngas ($\text{CO}_2 + \text{H}_2$) in a methane conversion reactor operating at ~ 850 °C. The oxygen flux obtained from the separation of air in this reactor is commercially feasible, and the use of this technology could

significantly reduce the cost of oxygen separation [5]. Because of its properties and performances, SFCO was investigated by several other researchers [6, 7].

In addition, many methods have been employed to synthesize the SFCO oxides. SFCO oxides are usually prepared by grinding and calcinations of oxides and carbonates. However, this method has several disadvantages: inhomogeneity, nonuniformity of particle size and shape, high impurity content, lack of reproducibility and necessity of repeated processing. In our group [8, 9], we synthesized the SFCO oxides by using microwave heating and microwave mixed heating method, and found that the SFCO oxides exhibited different phase structures with the microwave field heating. The conventional heated sample is a three-phase mixture composed of a predominant orthorhombic phase, a cubic perovskite phase, and a CoO phase. In the microwave heating, the perovskite phase was the main phase in the multiphase structure. But the average particle size is 3–4 μm , and the particle size distribution is nonuniformity. These were disadvantage for sintering of SFCO ceramics.

In contrast, the auto-combustion of citrate–nitrate gel route applied in the present work is reported to lead to highly reactive, homogeneous powders, and it involves a low temperature initiated combustion process which makes use of the heat energy liberated by the exothermic anionic oxidation–reduction reaction between citrate and nitrate ions [10]. This simple technique has many advantages, such as homogeneous mixing good stoichiometric control, and the production of active submicron-size particles in a relatively short processing time.

In this paper, we report a successful preparation of SFCO oxide by the auto-combustion of citrate–nitrate gel route, in which citric acid was used not only as a chelating agent like in some chemical synthesis technology [11–14],

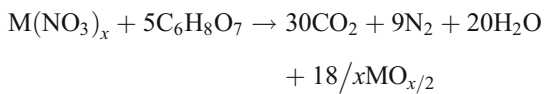
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but also as a combustion assistant agent [15]. The resulting powder is pure, homogeneous and possesses a reasonably fine particle size.

2 Experimental

2.1 Synthesis of SFCO powder

Reagent grade $\text{Sr}(\text{NO}_3)_2$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and citric acid were used as starting materials. The nitrates were weighed according to the nominal composition of SFCO, and then dissolved into deionized water in a beaker. Citric acid (fuel) required for complete reaction with nitrates was calculated by assuming complete oxidation of the fuel according to the following reaction [16–18].



In the above, M represents the metal and x the valency of the metal. When a mixture of metal nitrates with various valencies is taken, x is the weighted average of the valencies of the constituent metals. The citric acid were dissolved into deionized water in a beaker, and added to the above solution. During the synthesis process, it was found that the pH of precursor solution was contributing factors to the formation of the sol and gel. Our research results showed that the pH value close to 6 was the best condition to form the citrate–nitrate gel in this system. Therefore, after adding a designed amount of citric acid, ammonia was dropped to adjust the pH value of the mixed solution to 6. The precursor solution was dehydrated at 80 °C to form a

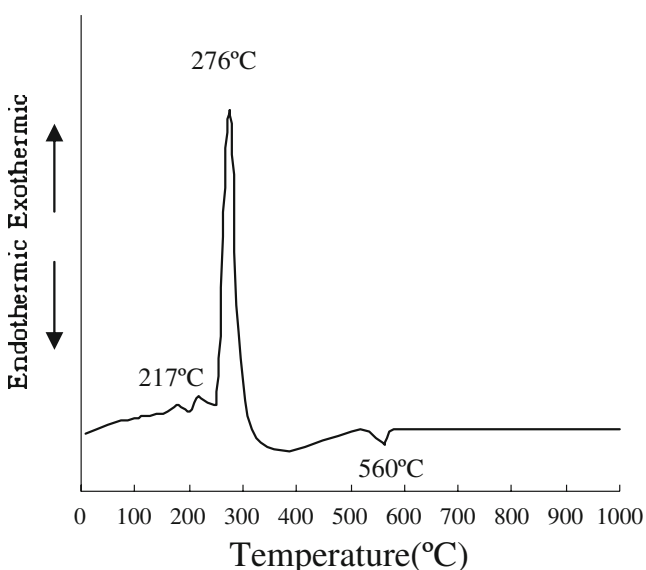


Fig. 1 DTA curves of the gel derived from the precursor solution with a pH=6

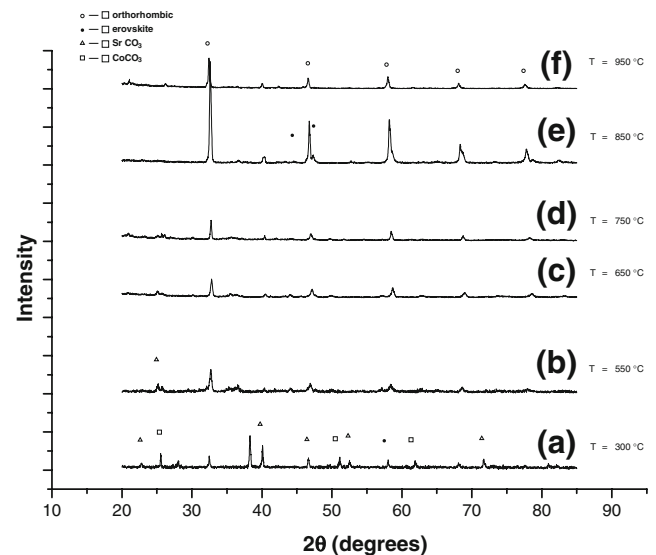


Fig. 2 XRD patterns of powders with different calcining temperature

sol, followed by a further heating at 120 °C to yield a citrate–nitrate gel. The resulting gel was pulverized and calcined at 550–950 °C for 2 h to obtain the powder.

2.2 Characterization techniques

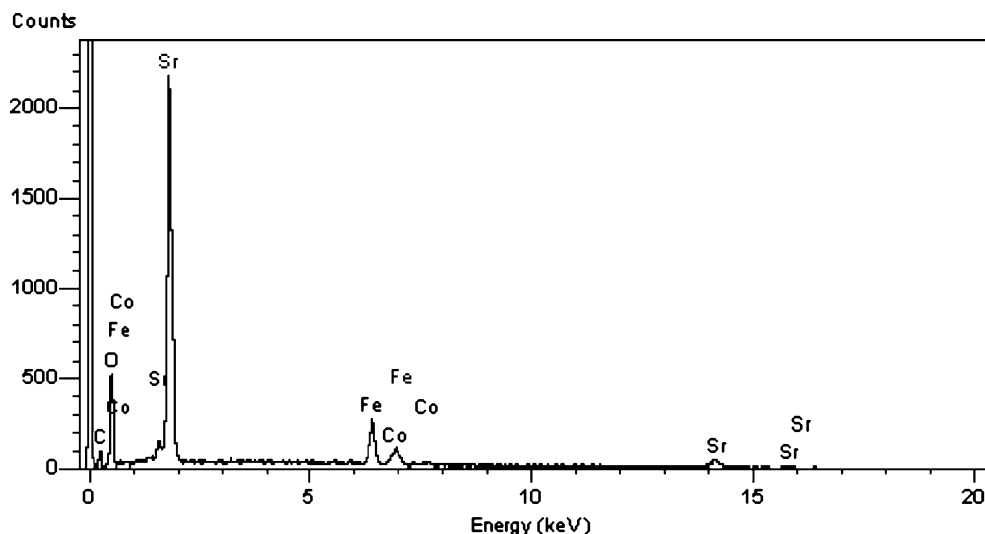
Differential thermal analysis (DTA) were carried out in LCT-2(Beijing Optical Instrument Factory) at a heating rate of 10 °C/min in static air. The crystalline structure of the calcined powder was examined by a D/MAX-RA X-ray diffractometer (Rigaku Corporation, Japan) using $\text{CuK}\alpha$ radiation. The SEM (Model JSM-6301F, JEOL, Tokyo, Japan) technique was used to determine particle size, morphology and nature of agglomerates in the calcined powders. The morphology and degree of agglomeration were also determined by TEM (Model EM-420, Philips, Eindhoven, The Netherlands) technique.

3 Results and discussion

3.1 Decomposition characteristics of dried gel

Figure 1 shows the DTA curve of the gel derived from the precursor solution with a pH=6. As expected the decomposition reaction is strongly exothermic which is evident from the DTA plot. This decomposition is a single step combustion reaction as observed in case of several other compounds prepared by this technique [19, 20]. This single step decomposition behavior associated with a very sharp and intense exotherm (Fig. 1) is a clear indication of an autoignited combustion process. This auto-combustion arises from a highly exothermic anionic oxidation–reduction reaction between citrate and nitrate ions. As also evident

Fig. 3 Composition analysis results of SFCO powders at 950 °C



from DTA the onset of this combustion process starts around 217 °C and as a result of this combustion process the temperature of the system as a whole increases to 276 °C as shown by DTA peak temperature.

The corresponding DTA curve also shows an endothermic peak around 560 °C. The endothermic peak around 560 °C might be due to carbonate decomposition together with the formation of the complex oxide phases.

3.2 Phase analysis of the powders

Figure 2 shows the XRD patterns of the powders calcined at different temperatures. The powder after the citrate–nitrate gel combustion is already a mixture of reactive oxides and carbonates (Fig. 2a). After calcining at 550 °C for 2 h, perovskite structure was detected together with a tiny amount of residual carbonate. Further increase of calcining temperature from 650 to 950 °C, respectively, the residual carbonate is less and less. Figure 3 is the composition analysis result for SFCO powder at 950 °C.

From Fig. 3, it can be known that the sample took nearly single perovskite phase, with a ratio of Sr, Fe and Co close to 2:1.5:1.5. Therefore, the SFCO oxide powders with nearly single perovskite phase were obtained.

3.3 Microstructure and particle size analysis

Figure 4 shows the SEM micrographs of the calcined powders at 950 °C for 2 h in air. It is shown that the ultrafine particles are agglomerated in a different fashion throughout the sample.

Figure 5 shows the TEM micrographs of the calcined powders at 950 °C for 2 h in air. It is shown that the powder calcined at 950 °C primarily consist of homogeneous, fine particles, possessing a major size distribution in 200–300 nm. There is a small amount of large particles agglomerated by the fine particles.

SEM and TEM observations show that all the samples have a regular particle shape, and have a narrow particle size distribution.

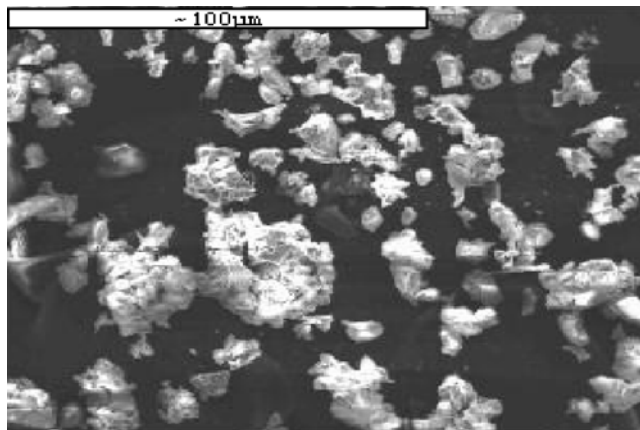


Fig. 4 SEM of SFCO powder heated at 950 °C/2 h in air

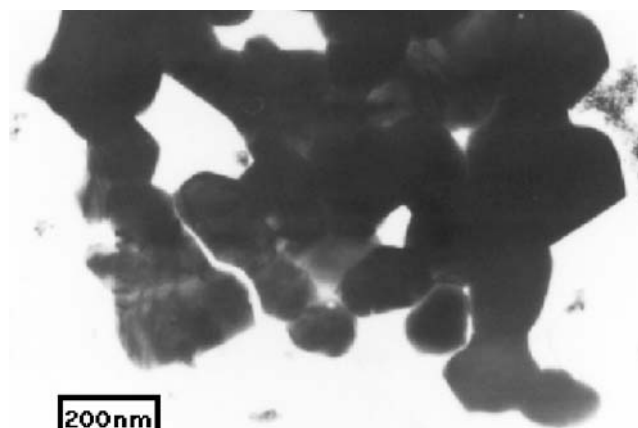


Fig. 5 TEM of SFCO powder heated at 950 °C/2 h in air

4 Conclusions

The auto-combustion of citrate–nitrate gel is a very simple, convenient and non-explosive route to obtain fine powder of SFCO. Nearly single perovskite phase SFCO powder were obtained by firing the citrate–nitrate gel to 950 °C in air for 2 h. Compared to the convention solid-state reaction technique, this method needs low-temperature treatment and produces active particles with excellent sinterability.

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