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Citrate–nitrate combustion route to the synthesis of (1–*x*)$LaCrO_3$–*x*$BiCrO_3$ solid solution

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Abstract Solid solution of (1–*x*)$LaCrO_3$–*x*$BiCrO_3$ (x = 0, 0.10, 0.15, 0.20 and 0.25) was prepared via the citrate–nitrate combustion synthesis. Pure perovskite phase was obtained at 800 °C, a much lower synthesis temperature than that needed in the solid-state reactions. The thermodynamics of phase formation and the ceramic sintering mechanism were investigated. The substitution of Bi^{3+} for La^{3+} was found to give a separate exothermic decomposition event in the gels and the precursor did not produce a transient liquid phase while heating to 1200 °C, as was found in ceramics prepared by solid state reaction. This finding shows that the role of Bi_2O_3 in the sintering of the $La_{1-x}Bi_xCrO_3$ ceramics depends on the processing method.

Introduction

Lanthanum chromite is one of the most promising candidates for use as the interconnect material in high-temperature solid oxide fuel cells. Its high electronic conductivity, low ionic conductivity and good chemical stability in both oxidizing and reducing environments at high temperatures have made it extremely attractive for this application [1]. However, the poor sinterability and low density of pure lanthanum chromite pose a significant challenge to the industry. Many methods have been exploited at overcoming this drawback, mostly with the substitution of alkaline earth or transition metal ions for La^{3+}, which was shown to be an effective solution [2, 3]. The Ca-doped $LaCrO_3$ can achieve very high density without requiring drastic sintering conditions due to the transient liquid phase $CaCrO_4$ [4]. Its electronic and conductivity properties, however, are not as superior as Sr-doped $LaCrO_3$ [5]. Another approach that is used to achieve high density at low sintering temperature is by producing highly reactive powder via autoignition, or commonly known as the combustion process. The citrate–nitrate combustion synthesis of Ca-doped $LaCrO_3$ has shown that >99% relative density can be achieved at 1250 °C [6] as compared to 1400 °C by the Pechini method [7] or solid state reactions [3]. Sintering of $La_{0.7}Sr_{0.3}CrO_3$ from combustion process, on the other hand, still required a temperature of 1600 °C to achieve a density of 96% [8].

Recently, we reported the synthesis of a new solid solution system between $LaCrO_3$ and "$BiCrO_3$" [$La_{1-x}Bi_xCrO_3$] by solid-state reactions [9]. The substitution of Bi^{3+} for La^{3+} seemed to introduce some degree of structure distortion, leading to the appearance of ferroelectric hysteresis loop at low temperature. In addition, the density of the solid solution ceramics was greatly enhanced compared with pure $LaCrO_3$, with the relative density reaching 90% after sintering at the temperature of 1200 °C. Such a significant improvement in the sinterability and densification of the $LaCrO_3$-type ceramics by the substitution of Bi_2O_3 has pointed to a new route to the sintering of highly densified interconnect materials for solid oxide fuel cells applications. During the investigation of the sintering mechanism, a transient liquid phase was detected by differential thermal analysis. This transient

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liquid phase arises from the eutectic-like melting in the La_2O_3–Bi_2O_3–Cr_2O_3 system and occurs at 950 °C, a temperature that is lower than the formation temperature of the solid solution (1200 °C). On the other hand, Bi_2O_3, when used as a sintering additive for La(Sr)MnO_3, favours sintering by increasing the overall diffusion rate of ions without forming transient liquid phase because Bi_2O_3 forms solid solution with La(Sr)MnO_3 at a much lower temperature (800 °C) [10]. Thus, if the formation temperature of $La_{1-x}Bi_xCrO_3$ solid solution can be lowered by means of producing finer and more reactive particles via combustion process, then the role of Bi_2O_3 in the sintering mechanism may be different. In this work, we report a new citrate–nitrate combustion route for the synthesis of the $(1–x)LaCrO_3–x$"$BiCrO_3$" solid solution and the subsequent sintering of the ceramics, and discuss the thermodynamics of phase formation and the sintering mechanism.

Experimental

Solid solution of $(1–x)LaCrO_3–xBiCrO_3$ (with $x = 0$, 0.10, 0.15, 0.20 and 0.25) was synthesized by a citrate–nitrate combustion process. The starting materials were $Cr(NO)_3·9H_2O$, La_2O_3, $Bi(NO_3)_3·5H_2O$, citric acid and reagent grade nitric acid. The nitrate solutions containing each metal ion of the stoichiometric amount were prepared separately. The solution containing La^{3+} was obtained by dissolving La_2O_3 in concentrated HNO_3, while the addition of a small amount of nitric acid to the Bi^{3+} nitrate solution and moderate warming were required to prevent the precipitation of bismuth hydroxide. The nitrate solutions of each metal were combined followed by the addition of aqueous citric acid solution. The citrate to nitrate molar ratio used was 0.19. Upon further heating, autoignition occurred and the self-propagating combustion reaction yielded ash-like precursor. Several heat treatments for the precursor were performed: (i) calcination of precursor powder at 500–650 °C for 1–5 h in air for monitoring phase transformation; (ii) calcination of pressed pellets at 800 °C for 5–7 h in air for obtaining pure phase, and (iii) calcination of powder at 600 °C for 2 h followed by pressing into pellet and ceramic sintering at 1200 °C for 5 h in a closed Bi_2O_3-rich environment. The setup for the closed Bi_2O_3-rich environment and its role in suppressing the volatilization of bismuth oxide have been discussed previously [9].

Phase analysis was performed at room temperature using a Phillips powder X-ray diffractometer with Cu K_α radiation in the range of $20 \le 2\theta \le 80°$, with an increment of 0.02° and an exposure time of 2 s/step. The phase transformation was also monitored using Siemens high-temperature X-ray diffractometer from room temperature to 775 °C. Thermogravimetric and differential thermal analyses (Seiko Instrument TG/DTA 6300) were carried out for both the gel and the combusted precursor in the temperature range of 30–1000 °C in air with a heating and cooling rate of 5 °C min^{-1}. The bulk density of the sintered samples was measured using the Archimedes method in water. The microstructure of the sintered ceramics was examined by a scanning electron microscope (FEI DualBeam Strata 235).

Results and discussion

The precursor obtained after combustion was amorphous. By heat treatment at 800 °C for 5 h, pure $LaCrO_3$-type perovskite phase was obtained for the $La_{1-x}Bi_xCrO_3$ solid solution with $0 \le x \le 0.25$. This significant decrease in the synthesis temperature, as compared to solid-state reaction which requires 1200 °C for the formation of the solid solutions, is attributed to the high reactivity of the fine precursor powders obtained by the combustion method. Previously we have shown that the $La_{1-x}Bi_xCrO_3$ solid solution with x up to 0.35 can be achieved by conventional solid-state reaction, and an increase in synthesis temperature is required as Bi^{3+} content increases [9]. This increase in temperature is also observed in the combustion synthesis, where a calcination temperature of 800 °C was not high enough to achieve complete dissolution of 25 mol% of Bi^{3+} into the perovskite $LaCrO_3$ phase. Upon increasing temperature to 850 °C, however, the volatilization of bismuth oxide became so severe that the attempts to suppress it by means of creating high Bi_2O_3 vapor pressure, which proved to be successful in solid state reaction, failed to produce a pure solid solution for $x > 0.25$. Incorporating excess Bi-precursor did not produce pure phase either. Therefore, it can be concluded that while the combustion method lowers the overall synthesis temperature as a result of the high surface area and reactivity of the particles produced, it also lowers the critical temperature at which the volatilization of bismuth oxide can no longer be suppressed, for the same reason. Thus only solid solution with Bi^{3+} content equal to or less than 25 mol% could be prepared by the combustion synthesis in pure perovskite phase.

The phase transformation from amorphous state of the precursor to the final perovskite structure was studied by performing X-ray diffraction on precursor powder that was heated to various temperatures (500–650 °C) and for different lengths of time (1–5 h). Figure 1 shows the X-ray diffraction patterns of the calcined powders at room temperature. After heat treatment at 500 °C for 1 h, the powders were still amorphous in nature. Increasing temperature from 500 to 600 °C gave rise to several peaks in the 2θ region of 27–28° that indicate the presence of crystalline Bi_2O_3 and La_2O_3. High temperature X-ray diffraction confirmed that the crystallization of Bi_2O_3 and La_2O_3 started at 550 °C, but did not detect any crystalline Cr_2O_3 during the transformation from the amorphous powder to the perovskite phase. Moreover, no evidence of $Cr(CO)_6$, CrO_2, Cr_5O_{11} or CrO_3 was found based on the X-ray diffraction patterns, and it is unlikely that Cr could form other complexes which have not been identified. These observations suggest that the Cr compounds may stay in amorphous phase and directly react with crystalline La_2O_3 and Bi_2O_3 to form the perovskite structure. The X-ray diffraction pattern has also excluded the formation of binary compounds between Bi_2O_3 and Cr_2O_3. On the other hand, it should be noted that the peaks at 24, 26 and 30° do not belong to La_2O_3 or Bi_2O_3 but coincide with those of $Bi_2O_2CO_3$ and $Bi_{0.775}La_{0.225}O_{1.5}$. To investigate the possibility of the formation of $Bi_2O_2CO_3$, the gel containing Bi^{3+} as the only metal ion was prepared. Upon calcination of this Bi_2O_3 precursor powder at 500 °C for 1 h, a clean α-Bi_2O_3 phase was established. Other calcination temperatures (650 and 750 °C) all yielded pure α-Bi_2O_3 phase. This shows that the precursor for Bi_2O_3 did not form $Bi_2O_2CO_3$ or any other secondary phases. As a result, the extra peaks in the calcined powder of the solid solutions most likely belonged to $Bi_{0.775}La_{0.225}O_{1.5}$. This secondary phase was not observed in the samples prepared by solid-state reaction. As calcination time was increased from 1 to 5 h at 600 °C, the perovskite phase grew at the expense of $Bi_{0.775}La_{0.225}O_{1.5}$, which eventually disappeared at 650 °C. All of Bi_2O_3 was finally incorporated into the lattice of the solid solutions after 5 h at 800 °C.

Figure 2 shows the DTA heating curves of the gels for different compositions of $La_{1-x}Bi_xCrO_3$ and Bi_2O_3. A single-step decomposition at 154 °C was observed for the gel of $LaCrO_3$, while a second exothermic decomposition at 280 °C became increasingly evident in the gels of the $La_{1-x}Bi_xCrO_3$ solid solution with increasing Bi^{3+} content. It has been suggested that in addition to the citrate–nitrate ratio, the nature of the cations also affect the combustion temperature. In particular, Chakraborty et al. [11] observed an increase in autoignition temperature as Ba^{2+} content in $La_{1-x}Ba_xMnO_3$ increased. In the present solid solution system, the addition of Bi^{3+} gave rise to a separate decomposition at a much higher temperature instead of shifting the temperature of the average exothermic event. In order to verify that the second decomposition was due to the Bi^{3+} ions, the gel for Bi_2O_3 was investigated. It can be seen that the gel for Bi_2O_3 combusted at a temperature close to the second decomposition of the gels for the solid solution. Although the role of cations in autoignition has not been well studied, the higher decomposition

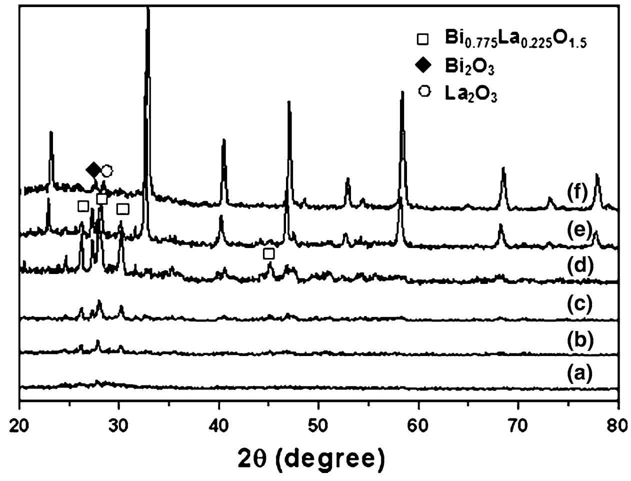

Fig. 1 XRD patterns of $La_{0.75}Bi_{0.25}CrO_3$ precursor heated at (**a**) 500 °C for 1 h; (**b**) 550 °C for 1 h; (**c**) 600 °C for 1 h; (**d**) 600 °C for 3 h; (**e**) 600 °C for 5 h and (**f**) 650 °C for 5 min and quenched

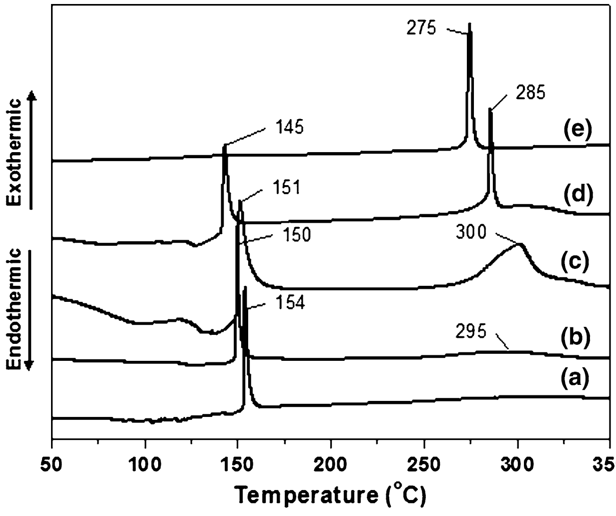

Fig. 2 Differential thermal analysis heating curves for the gels of $La_{1-x}Bi_xCrO_3$ with (**a**) $x = 0$; (**b**) $x = 0.1$; (**c**) $x = 0.20$; (**d**) $x = 0.25$ and (**e**) $x = 1$

temperature for gels containing heavier metal ions may be due to the mass effect. In general, polymers of higher mass melt or decompose at a higher temperature than low molecular weight polymers. As a result, the second exothermic event becomes more dominant in the gels of $La_{0.8}Bi_{0.2}CrO_3$ and $La_{0.75}Bi_{0.25}CrO_3$ than in that of $La_{0.9}Bi_{0.1}CrO_3$.

The decomposition behavior of the gels was also studied by heating them on hot plate while monitoring the temperature of the gels using a thermocouple. This allows the observation of the bulk activities of the gels as a function of temperature. For the gels containing 10–25 mol% of Bi^{3+}, the first exothermic event at about 150 °C was an autoignition process. At 150–155 °C, the gels burned with glowing flints and vigorous gas evolution was observed. The temperature of the gel soared to 330 °C within a few seconds and then gradually decreased as the autoignition process came to an end. At the end of the first exothermic event, ash-like precursor was produced, but it exhibited a light gray color. Upon further heating to 290 °C, the gel temperature increased by 20 °C in 2 s, a rate much lower than the first exothermic event. No gas evolution was observable by naked eye (however weight loss was detected in the TG measurements) and the ash material darkened to become greenish black in color. These observations combined with the vertical drop in weight loss in TG for the first exothermic event show that autoignition occurred at 150 °C for the $La_{1-x}Bi_xCrO_3$ gels with $0 \leq x \leq 0.25$.

DTA analyses of the combusted precursor were also performed and the heating curves for some representative compositions are shown in Fig. 3. The continuous weight loss up to 600 °C corresponds to the exothermic decomposition of organic residues in the precursor. An interesting feature observed is the endothermic event at 720 °C, which corresponds to the phase transition temperature of α-Bi_2O_3 to δ-Bi_2O_3 [12]. This endothermic event is not due to the decomposition of other Bi compounds as phase transformation study on the Bi_2O_3 precursor has ruled out this possibility, and furthermore, a decomposition activity should be exothermic. Since the formation of the $LaCrO_3$-type perovskite phase began at 600 °C, the endothermic event is also unlikely due to the crystallization activity. To elucidate the possibility of phase transition, high-temperature X-ray diffraction was performed to examine the phase transition of Bi_2O_3 obtained from the combustion synthesis. It was found that the transition from α- to δ-Bi_2O_3 indeed occurred at temperatures slightly above 720 °C, thus confirming the origin of the endothermic event as the phase transition of Bi_2O_3.

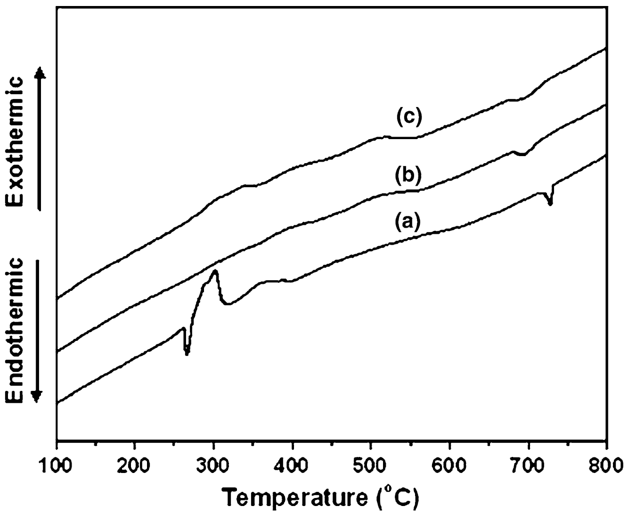

Fig. 3 Differential thermal analysis heating curves for combusted precursors of (**a**) Bi_2O_3; (**b**) $La_{0.75}Bi_{0.25}CrO_3$ and (**c**) $La_{0.85}Bi_{0.15}CrO_3$

Continued heating of the combusted precursor up to 1000 °C in DTA showed no other thermal events. This is in contrast to the previous study on the synthesis of the $La_{1-x}Bi_xCrO_3$ solid solutions by solid-state reactions, where an endothermic event was revealed at 950 °C due to partial melting of the mixture of metal oxides [9]. This melting behavior was not observed in the combusted precursors because the formation of the pure perovskite phase was achieved at 800 °C, and thereby, no residual metal oxides were present at 950 °C to form the transient liquid phase, as was the case in the process by solid-state reaction.

Pellets of $La_{1-x}Bi_xCrO_3$ solid solution ($0 \leq x \leq 0.25$) were sintered at 1200 °C for 5 h in a Bi_2O_3-rich environment. Scanning electron microscopy images of the microstructure of the polished surface of the ceramics are shown in Fig. 4. The grain size of the $La_{0.8}Bi_{0.2}CrO_3$ ceramic is much greater than that of pure $LaCrO_3$ and $La_{0.9}Bi_{0.1}CrO_3$. As suggested by Chakraborty and Maiti [10], Bi^{3+} may increase the overall diffusion rate of A-site ions, and therefore, ceramics containing a higher Bi^{3+} content would have larger grains and more well-defined grain morphology. The mechanism of grain growth in ceramics prepared by combustion process differs from those prepared by solid-state reaction. The mechanism of grain growth for the latter involves an increased rate of diffusion as well as the presence of a transient liquid phase, while the grain growth in the former is solely due to the diffusion effect of Bi^{3+} ions. The lack of transient liquid phase in the ceramics prepared by combustion synthesis resulted in a lower density than those prepared by solid-state reaction (Table 1), as a liquid phase generally promotes

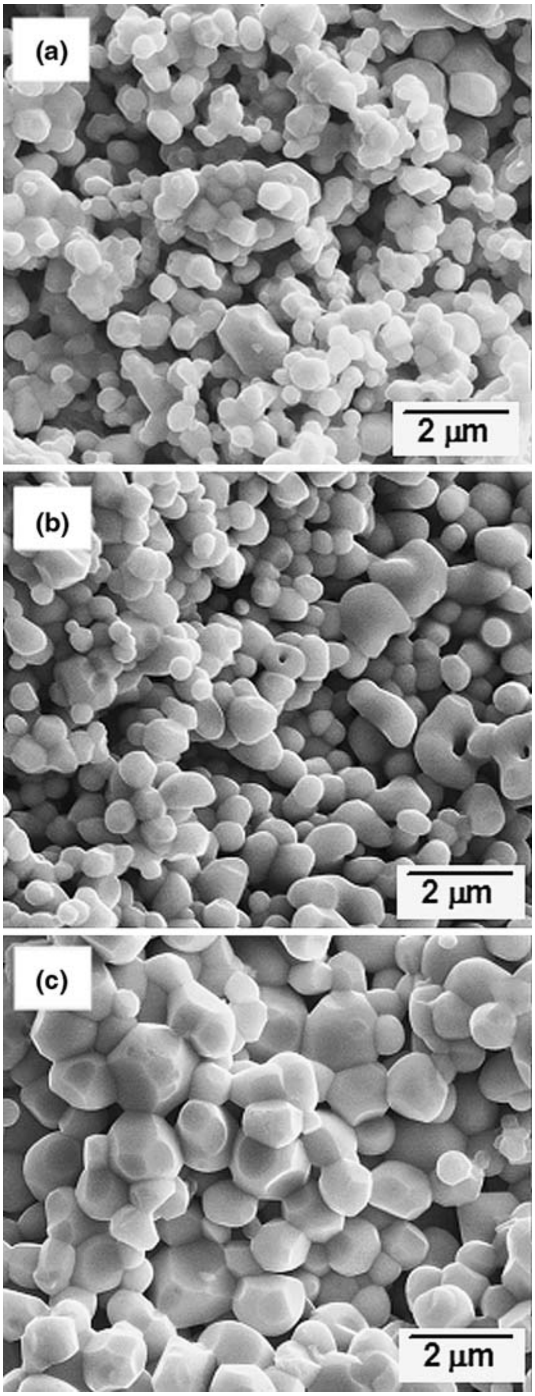

Fig. 4 SEM micrographs of the surface of $La_{1-x}Bi_xCrO_3$ ceramics sintered at 1200°C with (**a**) $x = 0$; (**b**) $x = 0.1$ and (**c**) $x = 0.2$

Table 1 Relative density of the $(1-x)LaCrO_3-xBiCrO_3$ ceramics prepared from combustion synthesis and sintered at 1200 °C for 5 h in closed Bi_2O_3-rich environment

x	0	0.1	0.2
Relative density (%)	45	47	67

densification. Although submicron precursor particles were initially obtained by combustion reaction, the grain growth during sintering lead to grain sizes that are comparable to the ceramics obtained by solid-state reaction. In the absence of a transient liquid phase, the density of the ceramics prepared by combustion process was not as high as those by the conventional solid-state reactions, even though the pure phase of $La_{1-x}Bi_xCrO_3$ solid solutions can be obtained at a very low synthesis temperature (800 °C).

Conclusions

The solid solution of $La_{1-x}Bi_xCrO_3$ ($0 \le x \le 0.25$) has been synthesis via the citrate–nitrate combustion process. The pure $LaCrO_3$-type perovskite phase was obtained at 800 °C, much lower than in solid-state reaction synthesis. During the transformation from initial amorphous precursor to final perovskite phase, crystalline La_2O_3, Bi_2O_3 and $Bi_{0.775}La_{0.225}O_{1.5}$ were detected by X-ray diffraction. The substitution of Bi^{3+} for La^{3+} gave rise to a separate exothermic decomposition in the gel. The transient liquid phase, previously revealed in the sintering process of the $La_{1-x}Bi_xCrO_3$ solid solution prepared by solid-state reactions, was absent in the materials prepared by combustion synthesis, showing that the sintering mechanism of a system depends primarily on the processing methods.

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