

Crystallization of LaCrO_3 powders and its solid solutions doped with Sr^{2+} and Al^{3+} under hydrothermal conditions.

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The crystallization of fine powders of LaCrO_3 and its solid solution doped with strontium and aluminum was investigated using different mineralizers under hydrothermal conditions. Compositions: LaCrO_3 , $\text{La}_{0.8}\text{Sr}_{0.2}\text{Cr}_{0.9}\text{Al}_{0.1}\text{O}_3$ were treated under hydrothermal conditions at 375 and 475 °C, respectively, for a reaction 1 h using water, aqueous NaOH, KOH and KF. The crystallization of both LaCrO_3 and $\text{La}_{0.8}\text{Sr}_{0.2}\text{Cr}_{0.9}\text{Al}_{0.1}\text{O}_3$ during the earlier stage of the reaction proceeded by the formation of $\text{La}(\text{OH})_3$, which was further dissolved with the increase of mineralizer concentration and reaction time. Furthermore, a preferential formation of submicron particles with pseudo-cubic shape (~ 550 nm) occurred when aqueous NaOH were used as mineralizers. In contrast, the powders crystallized in aqueous KOH and KF had different particle size, 400 nm and 1.5 μm ; respectively. Pseudo-hexagonal shaped particles were formed in both mineralizers. The difference in the size and shape of the particles is associated with the reactivity of precursor gel and mineralizer media.

1. Introduction

Lanthanum chromite (hereafter denoted as LC) powders substituted with alkaline metals (Ca or Sr) have been widely accepted as a candidate for the separator in Solid Oxide Fuel Cells (SOFCs) devices [1-3]. Recently, various chemical routes have been used to obtain powders of pure LC and its related solid solutions, such as glycine nitrate process [4] oxalic salt method [5], hydrazine [6], coprecipitation [7] and sol-gel [8]. These chemical processes, however, involve a subsequent calcination treatment at high temperatures beyond 700 °C, in order to obtain a stable crystalline phase.

The ordinary hydrothermal crystallization process, however, involves transformations of slurry solutions or gels into an anhydrous oxide in a single step process [9,10]. The reactions occurring in hydrothermal solutions lead the formation of fine particles with high purity and controlled morphology by rapid reaction kinetics [10-13].

The first evidence for the synthesis of the LaCrO_3 pure compound under hydrothermal conditions was reported by Yoshimura et al. [14]. The crystallization process of the stable perovskite phase was conducted from stoichiometric amount

of the La_2O_3 and Cr_2O_3 oxides in a platinum capsule using water as a solvent at low (400 °C) and high (700 °C) temperatures with a confining pressure of 100 MPa. Under these conditions, the crystallization of irregular shape monodispersed LC particles was achieved by a mechanism of dissolution-precipitation [14]. Moreover, the present authors in a recent study [15] reported that powders of pure LC and its solid solution, $\text{La}_{1-x}\text{Ca}_x\text{CrO}_3$ with 10 and 20 mol% Ca were prepared from a precursor gel under hydrothermal conditions at lower temperatures (350–475 °C). The crystallization of the gel proceeded simultaneously with the gel dehydration, and the nucleation of the oxide occurred on the surface of the gel, which underwent a continuous dehydration process. In the second stage of the reaction, particle growth was promoted by a continuous dissolution-precipitation mechanism resulting in the formation of agglomerated particles with irregular shape. In the present work, we aimed to investigate the experimental parameters that achieve a better control of the size and morphology of the particles of pure LC and its solid solution doped with Sr^{2+} and Al^{3+} ($\text{La}_{0.8}\text{Sr}_{0.2}\text{Cr}_{0.9}\text{Al}_{0.1}\text{O}_3$, hereafter denominated as LSCA). The experiments described

below differ from those proposed by the same authors in the previous work [15], because in order to avoid the dehydration process of the precursor gel during the hydrothermal treatment, a dried gel was used as a raw material. We investigated the effect of the hydrothermal mineralizer by using water and salt solutions (NaOH, KOH or KF), and concentration of the mineralizer.

2. Experimental

2.1 Gel coprecipitation Precursor lanthanum chromite gel was prepared by the alkaline coprecipitation method reported by Inagaki et al. [16], employing reagent grade chemicals of $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$ (99.999%), $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (99.9%), $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ (99%), $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (99.998%) and NaOH (99.998%) (Wako pure chemical industries, Ltd. Japan). The salts, LaCl_3 , $\text{Cr}(\text{NO}_3)_3$, SrCl_2 and $\text{Al}(\text{NO}_3)_3$, were separately dissolved in water to obtain aqueous solutions with a concentration of 0.05 M. A NaOH solution with a concentration of 0.5 M, was used as coprecipitation media. In general, a volume of 450 ml of the precipitating solution (NaOH) was poured in a beaker, and a mixture of the solutions of Cr^{3+} and Al^{3+} (500 ml) was then added, which resulted in the formation of an opaque whitish green precipitate. The vigorous stirring of the mixed solutions led to the dissolution of the preliminary precipitated gel of $\text{Cr}(\text{OH})_3$ and $\text{Al}(\text{OH})_3$. Finally, the coprecipitation of the complex gel was carried out by the addition of 500 ml of the solution containing the other elements, La or the mixture of La^{3+} and Sr^{2+} . The solutions were mixed in two different volume ratios, La: Sr: Cr: Al, 1.0:0.0:1.0:0.0 and 0.8:0.2:0.9:0.1 which matches the stoichiometry of the pure LaCrO_3 , and its solid solution of $\text{La}_{0.8}\text{Sr}_{0.2}\text{Cr}_{0.9}\text{Al}_{0.1}\text{O}_3$. The coprecipitated gel was washed using deionized water and centrifuged for 10 times, then the gel was dried at a temperature of 100 °C inside a glove box in inert atmosphere of nitrogen, which was used to prevent CO_2 absorption on the gel during the drying stage.

2.2 Hydrothermal treatments All hydrothermal treatments were carried out using 0.5 g of each dried gel, which was placed in the bottom of a Hastelloy C-lined microautoclave (40 ml capacity), together with 20 ml of the mineralizer solution. The mineralizers used for the gel crystallization were pure water, and salt solutions of NaOH, KOH and KF with a concentration between 0.1–1 M. The vessel was heated at a constant rate of 20 °C/min up

to a desired temperature, between 350–475 °C, and the vessel was held at each temperature for a reaction interval between 0.5 to 2 h. After the treatment, the reaction products were well washed with distilled water, decanted and then dried in an oven at 100 °C overnight.

2.3 Characterization Powder X-ray diffraction analyses were carried out to determine the crystalline phases. Measurements were made by an X-ray diffractometer (Rigaku Rotaflex) with graphite-monochromatized $\text{CuK}\alpha$ radiation at 40 kV and 100 mA. Diffraction patterns were taken from 10 to 70 ° at a scanning speed of 4°/min. Morphological aspects of the powders were examined by scanning electron microscopy (SEM, Philips XL30 ESEM) equipped with an energy dispersive X-ray (EDX) analyzer. Additional aspects such as particle size and shape were measured by transmission electron microscopy (TEM, Hitachi H-800).

3. Results and discussion

3.1. Crystallization of LaCrO_3 in different hydrothermal mineralizers The crystallization of pure LC powders using a dried gel was investigated in order to determine the differences in particle morphology, resulting from the use of different mineralizers such as, water and alkaline solutions of KOH (0.1 M), NaOH (0.5 M) and KF (0.1 M). Figure 1 shows typical X-ray diffraction patterns of the reaction products after hydrothermal treatments carried out at 375 °C for 1 h with different mineralizers. The diffraction pattern of the major crystalline phase obtained by the hydrothermal treatment was assigned to the orthorhombic pure LaCrO_3 (JCPDS Card 33-0701). In the case of treatments carried out with water as a mineralizer, the pure LC was formed, but the formation of a small amount of byproducts was only observed when the treatments were conducted in salt mineralizers of NaOH, KOH or KF (Fig. 1). The main byproducts obtained corresponded to the crystalline phases of $\text{La}(\text{OH})_3$ and $\text{La}(\text{CO}_3)\text{OH}$. The present results are in agreement with those previously reported by Yoshimura et al. [14], who found that $\text{La}(\text{CO}_3)\text{OH}$ is the stable phase under hydrothermal conditions over the range of temperature of 400–600 °C. The preferential formation of this phase might be attributed to CO_2 absorption in the alkaline media. In contrast, the presence of a small amount of $\text{La}(\text{OH})_3$ might be

due to an incongruent dissolution behavior of La^{3+} in alkaline solvents [17].

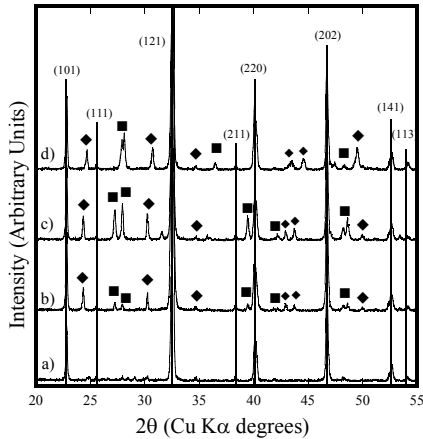


Fig.1. X-Ray diffraction patterns of products obtained at 375 °C for 1 h in different mineralizers (a) deionized water, (b) NaOH 0.5 M, (c) KOH 0.1 M or (d) KF 0.1 M. Solid line= orthorhombic LaCrO_3 diffraction pattern lines. (◆) $\text{La}(\text{CO}_3)\text{OH}$ and (■) $\text{La}(\text{OH})_3$.

The morphology of hydrothermally synthesized LC powders revealed by SEM observations (Fig. 2), showed some differences on shape and size of the particles when different mineralizers were used. In general, fine particles with a grain size less than 500 nm were preferentially grown in water, 0.1 M KOH and 0.5 M NaOH solutions, while very large particles (approximately 750 nm) were produced in a 0.1 M KF solution (Fig. 2d). Furthermore, the shape of the grown particles seems to be significantly affected by the type of the mineralizer. Irregular particles were obtained mainly in water and 0.5 M NaOH solution, and some shapes of the particles suggested that these particles had been further dissolved and subsequently joined together during the hydrothermal treatment. In contrast, when the LC crystals were produced in 0.1 M KOH and KF solutions, the particles had a different shape resembling hexagonal platelets (Figs. 2c and 2d).

We surmise that differences in the shape and size of the LC crystals hydrothermally prepared might be associated with the solubility of the precursor coprecipitated gel in different mineralizers. The

first evidence of the high solubility of the LC compound, even in water under hydrothermal conditions, was determined by Yoshimura et al. [14] who observed that LC particles were further dissolved by hydrothermal treatments conducted at high temperatures beyond 400 °C. Hence, we suggest that the irregular morphology must be the result of a subsequent dissolution of the particles crystallized during earlier stages of the hydrothermal reaction in water and NaOH mineralizers. Because in our case, the motion of species dissolved into the mineralizer did not take place by convection, due to the autoclave was kept at a uniform temperature without stirring.

3.2. Crystallization of $\text{La}_{0.8}\text{Sr}_{0.2}\text{Cr}_{0.9}\text{Al}_{0.1}\text{O}_3$ in alkaline mineralizers Based on preliminary experimental results reported elsewhere [15], the crystallization of the LSCA under hydrothermal conditions was determined to be carrying out at 475 °C for 1 h using different mineralizers.

Figure 3 shows typical X ray diffraction patterns of the reaction products obtained after treatments conducted for 1 h in different mineralizers. When the dried gel was treated in KF solution, a marked amount of byproducts was detected together with the LC phase. Strontium compounds, SrF_2 and SrCrO_4 , were simultaneously formed during the crystallization of the major LC solid solution (Fig. 3d). Energy dispersive analyses conducted on the particles of the LC solid solution, showed that they have a molar ratio $\text{La}:\text{Sr}:\text{Cr}:\text{Al} = 50.0(3):0.0:45.2(3):4.8(3)$, which corresponds to the chemical formula $\text{LaCr}_{0.9}\text{Al}_{0.1}\text{O}_3$ (hereafter referred as LCA). Hence, the results suggest that the crystallization of Sr^{2+} doped LC solid solution is limited by the formation of more stable strontium phases, fluoride or chromate, which are formed at very low temperatures, less than 250 °C [18]. In contrast, a small amount of $\text{La}(\text{OH})_3$ and $\text{La}(\text{CO}_3)\text{OH}$ was obtained when the gel was treated in water and NaOH and KOH solutions. X-ray diffraction patterns corresponding to the major crystalline phase obtained with these mineralizers, matched that of the orthorhombic LaCrO_3 (JCPDS Card 33-701) even though the peak shift due to the incorporation of Sr and Al was observed.

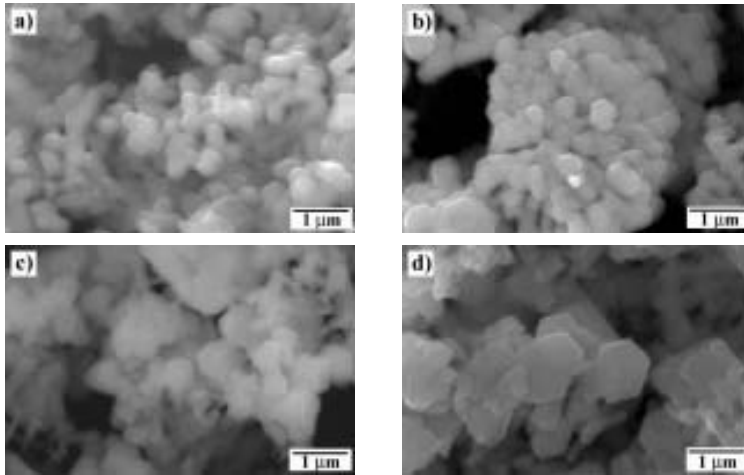


Fig. 2 SEM micrographs of lanthanum chromite powders obtained under hydrothermal conditions for 1 h at temperatures 375 °C in different mineralizers: (a) deionized water, and alkaline solutions of (b) NaOH 0.5 M, (c) KOH 0.1 M, and (d) KF 0.1 M.

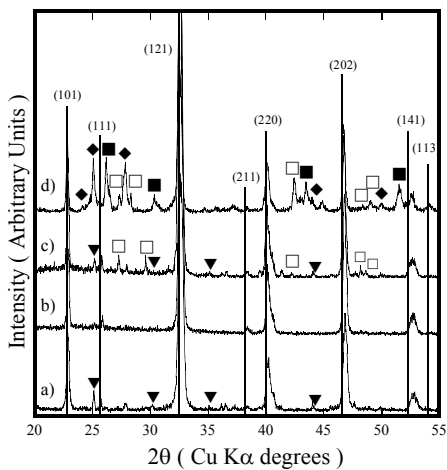


Fig. 3. X-Ray diffraction patterns of the LSCA powders obtained at 475 °C for 1 h in different mineralizers: (a) water, (b) NaOH 1 M, (c) KOH 1 M and (d) KF 1 M. Solid line= orthorhombic LaCrO_3 diffraction pattern lines. (◆) SrCrO_4 , (■) SrF_2 , (□) La(OH)_3 and (▼) $\text{La(CO}_3\text{)OH}$.

Figure 4 shows typical morphology of LSCA and LCA powders crystallized at 475 °C for 1 h in different mineralizers. These results showed that the type of mineralizer had a significant effect on the size of the obtained particles. When the hydrothermal treatments were conducted in water very fine LSCA particles with an average size of 100 nm were crystallized (Fig. 4a). In contrast, the hydrothermal treatments carried out in alkaline

NaOH and KOH solutions (Fig. 4b-c), resulted in the formation of larger particles with particles sizes of 600 nm and 475 nm, respectively. The treatments conducted in KF solution, however, led to the formation of LCA particles which have an average particle size of 1.5 μm (Fig. 4d), this particle size is larger than that of the powder obtained with the other mineralizers investigated in the present work. Another point that deserves emphasis is that related with the morphology of the LC doped powders grown in different mineralizers. The results determined by TEM micrographs depicted the formation of pseudo-hexagonal shaped particles of the LSCA and LCA powders, which were preferentially crystallized under hydrothermal conditions with mineralizers containing K^+ ions, KOH and KF (Figs. 4c-d). In addition, the LSCA powders obtained in water and NaOH solution had different particle morphology, consisting in nodular and regular pseudo-cubic shaped particles (Fig. 4a-b), respectively.

Typical TEM observations conducted on the LSCA powders hydrothermally obtained at 475 °C for 0.5 and 1.5 h in NaOH and KOH solutions, respectively, are showed in Figure 5. In general, the nearly monosize LSCA particles obtained in NaOH solution have larger particle size (~ 550 nm, Fig. 5c), in comparison with the particle size (~ 300 nm Fig. 5a) of LSCA powders crystallized in KOH solution. In addition, on both mineralizers a

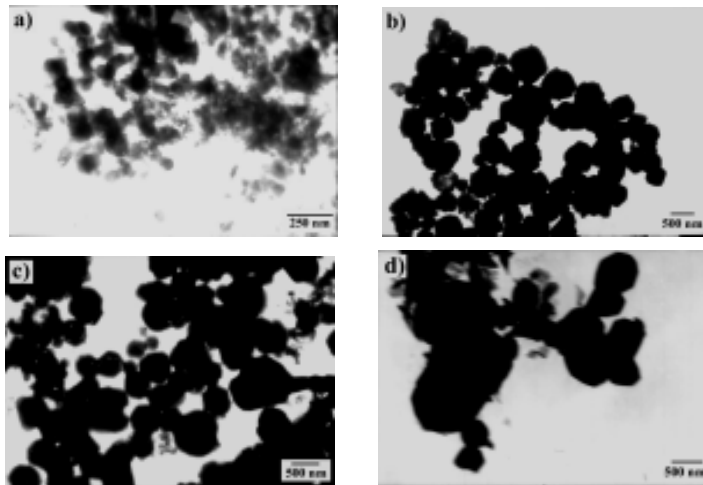


Fig. 4. TEM micrographs of $\text{La}_{0.8}\text{Sr}_{0.2}\text{Cr}_{0.9}\text{Al}_{0.1}\text{O}_3$ powders obtained under hydrothermal conditions for 1 h at a temperature of 475 °C in different mineralizers: (a) deionized water, and alkaline solutions of (b) NaOH, (c) KOH and (d) KF, with a concentration of 1 M, respectively.

coarsening of the LSCA particles formed at earlier stage of crystallization treatment proceeded by increasing the reaction interval up to 1.5 h. Thus, it is clear that a marked particle coarsening occurred for the LSCA particles formed in NaOH solution rather than those in KOH solution.

The differences found in the size, coarsening and morphology of the LSCA particles might be associated with the solubility of the precursor amorphous dried gel in alkaline mineralizers, NaOH or KOH [13]. We suggest based on our results that the solubility of the precursor gel is further increased preferentially in NaOH solutions, while in KOH is slightly decreased. In addition, the crystallization of the LSCA phase may proceed by a dissolution-crystallization mechanism [12]. This inference was supported by the fact that some fluorine compounds were crystallized with the LCA phase in KF solutions. Furthermore, the nucleation of the LSCA particles might occur when the solution becomes supersaturated, and it proceeds homogeneously in the solution [12,17]. However, once the precursor (gel) was completely converted to the LSCA crystalline particles, a second stage related with the particle coarsening must be achieved at the longest reaction interval of treatment (1.5 h, Figs. 5b and 5d). The powders obtained for 1.5 h showed the presence of a few amount of very tiny particles, therefore, these results suggest that the LSCA particle growth might

be explained by the coarsening mechanism known as Ostwald ripening [13].

The observed dependence on the particle morphology and size on the processing parameters, such as mineralizer and reaction time, suggests that hydrothermal derived lanthanum chromite and its Sr and Al doped solid solutions can be tailored to obtain a specific monosize powder with controlled morphology. Indeed, in a recent study [15] of the same authors, they reported that even irregular shaped Ca doped lanthanum chromite powders produced under hydrothermal conditions exhibited good sinterability at 1400 °C in air atmosphere.

4. Summary

In the present study, it was found that pure LaCrO_3 and $\text{La}_{0.8}\text{Sr}_{0.2}\text{Cr}_{0.9}\text{Al}_{0.1}\text{O}_3$ with pseudo-cubic morphology were crystallized in NaOH solution. In contrast, particles with pseudo-hexagonal morphology were obtained in potassium mineralizers (KOH or KF). Microstructural results suggest that LC and LSCA powders were formed by homogeneous nucleation during the earlier stage of the hydrothermal treatment, because the synthesized powders were nearly monosized. However, a second stage of the reaction led to particle coarsening which was achieved by the Ostwald ripening mechanism. In general,

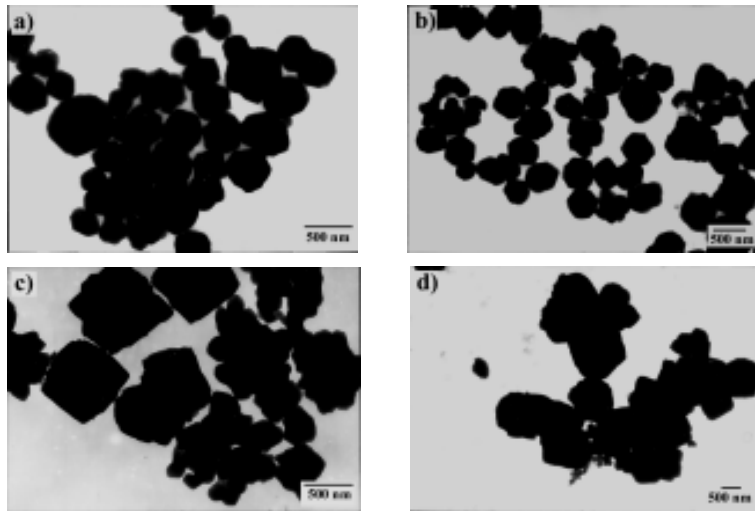


Fig. 5 TEM. micrographs of $\text{La}_{0.8}\text{Sr}_{0.2}\text{Cr}_{0.9}\text{Al}_{0.1}\text{O}_3$ powders obtained under hydrothermal conditions at $475\text{ }^\circ\text{C}$ in KOH (a,b) and NaOH (c,d) solutions 1 M, respectively, These powders were obtained for reaction intervals of 0.5 h (a,c) and 1.5 h (b,d).

a marked particle coarsening occurred when a NaOH solution was employed for the hydrothermal crystallization process. Hence, we surmise that the differences on the morphology and the significant coarsening of the particles might be associated with a relative increase of precursor gel solubility and the stable oxide phase in alkaline mineralizers (NaOH or KOH).

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