Synthesis and properties of $\text{La}_{1-x}\text{Ca}_x\text{AlO}_3$

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$\text{La}_{1-x}\text{Ca}_x\text{AlO}_3$ ($0 \leq x \leq 0.6$) perovskite-type oxides were prepared by co-precipitation method using metal nitrate salts as cation precursors and NaOH solution as the precipitating agent. Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) results indicate that decomposition of the precursor to the oxide begins at $\sim 800^\circ\text{C}$. Powder X-ray diffraction (XRD) patterns confirm the formation of the perovskite phase. Both undoped and doped lanthanum aluminates show two IR active vibrational modes at 450 and 670 cm^{-1} which are assigned to AlO_6 octahedra of the oxide matrix. The microstructure and morphology of the compounds show that the particles are nearly spherical in shape and are agglomerated. Electrochemical measurements indicate that the catalytic activity is strongly influenced by lanthanum doping. The highest electrode performance is achieved with large calcium content.

Keywords: perovskite oxide, chemical co-precipitation, powder diffraction, electrochemical properties

Síntesis y propiedades de $\text{La}_{1-x}\text{Ca}_x\text{AlO}_3$

Se prepararon diferentes óxidos tipo perovskita con formulación $\text{La}_{1-x}\text{Ca}_x\text{AlO}_3$ ($0 \leq x \leq 0.6$) mediante método de coprecipitación empleando sales nitrato como precursores catiónicos y NaOH como agente precipitante. Los resultados de análisis térmico diferencial (DTA) y análisis termogravimétrico (TGA) indican que la descomposición del precursor del óxido comienza a $\sim 800^\circ\text{C}$. Los patrones de difracción de rayos-X de polvo (XRD) confirman la formación de la fase perovskita. Los aluminatos de lantano, tanto dopado como no dopado, muestran dos modos vibracionales activos a 450 y 670 cm^{-1} que se asignan a octaedros AlO_6 de la matriz del óxido. La microestructura y morfología de los compuestos muestran que las partículas son de forma próxima a la esférica y aparecen en forma de aglomerados. Las medidas electroquímicas indican que actividad catalítica se ven fuertemente influenciadas por el dopaje con lantano. La mayor actividad del electrodo se alcanza con altos contenidos de calcio.

Palabras clave: óxido perovskítico, coprecipitación química, difracción de polvo, propiedades electroquímicas.

1. INTRODUCTION

Perovskite-type oxides have attracted great interest in both applied and fundamental areas of solid state chemistry, physics, advanced materials, and catalysis (1). In particular, perovskites have been widely studied in recent years as deep oxidation catalysts due to their relatively low cost, high activity and thermal stability, which make them potential alternatives to noble metals in environmental power generation (NO_x and UHC control) and exhaust clean-up (VOC removal, automobile converters). The properties of perovskites ABO_3 can be easily modified by the substitution of the A site cation, by another cation of different oxidation state. When the substituting cation has lower oxidation state, anionic vacancies or unusually high oxidation states of B cation are generated to maintain the structure electroneutrality. The electrical properties of La- and/or Al- site substituted LaAlO_3 compounds have been the subject of several studies (2-5). The catalytic properties of $\text{La}_{1-x}\text{M}_x\text{AlO}_{3-\delta}$ ($\text{A} = \text{Na}, \text{K}, \text{Ca}, \text{Sr}, \text{Ba}$, $x = 0.1$) oxides have been studied towards methane coupling reaction (6). It has been shown that a partial substitution of trivalent lanthanum ions by metals with lower oxidation state

improves the reactivity of these catalysts, activating methane towards total or partial oxidation. The catalytic activity performance of perovskite oxides depends on many factors such as: (i) the presence of oxygen vacancies (7, 8) and (ii) the electronic and semiconducting properties (9). On the other hand, addition of divalent cations in LaAlO_3 and a better control of the morphology can improve physical properties of these oxides (10). For this purpose, several synthesis methods have been developed for SOFC cathode materials and clearly the SOFC electrode performance is correlated with the materials processing. Recent work has shown that the solubility limit of calcium in lanthanum aluminate reached 5 % using the solid-state reaction as a synthesis method (4). To our best knowledge for higher compositions ($x > 0.05$) there was no study on the characterization of these oxides.

From these points of view, in this paper, we have studied the effect of partial substitution of lanthanum on structural, grain morphology, electric and electrochemical properties of $\text{La}_{1-x}\text{Ca}_x\text{AlO}_3$ oxides prepared by the co-precipitation method.

2. EXPERIMENTAL

A series of $\text{La}_{1-x}\text{Ca}_x\text{AlO}_{3-\delta}$ perovskites ($0 \leq x \leq 0.6$) were synthesized by the co-precipitation method. Aqueous solutions of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ were first dissolved in distilled water separately with the desired La/Ca ratio. NaOH 12 M was quickly added to the precursors under vigorous stirring until $\text{pH} = 10.5$. The precipitates were washed with distilled water and ethanol for several times, heated at 110°C for 12 h to obtain the dry precursors by evaporating the solvent. The obtained precursors were then ground into powders and heat-treated from 600 to 1000°C in air, respectively. TGA and DTA analyses of the precursor were carried out using a Linseis STA PT1600 thermal analyzer with a heating rate of 10°C per minute and under atmospheric conditions. XRD characterization of samples was carried out with a D8 Advance-Brucker using a $\text{Cu K}\alpha$ line at 0.1540 nm in the range of 10 – 65° in steps of 0.025 at a scan speed $2^\circ/\text{min}$. IR spectra were recorded by using FTIR-Shimadzu 8400S spectrometer. SEM photographs were taken in order to examine the particle morphology of the perovskite by using a JEOL scanning electron microscope (model JSM6390LV). The electrochemical experiments for O_2 reduction and evolution were performed using a Volta Lab 40 potentiostat/galvanostat. The measurements were carried out in a three-compartment cell. Potassium hydroxide electrolyte solution (1M) was prepared by dissolving the required amount of KOH (Merck) into bidistilled water. The working electrodes (1cm^2) were obtained by painting, with an oxide suspension. The counter electrode used was a Pt plate. The reference electrode was $\text{Hg}/\text{HgO}/1\text{ M KOH}$. All potentials in the text have been referred to this reference electrode.

3. RESULTS AND DISCUSSIONS

3.1. TG/DTA analysis

A typical TGA and DTA curves heating from 25 to 1000°C for the $\text{La}_{0.8}\text{Ca}_{0.2}\text{AlO}_3$ is shown in Fig. 1. The TGA curve exhibits four weight loss stages at the temperature ranges of 25–280, 420–630, 630–760 and 760 – 830°C . The DTA curve

Fig. 1- TG and DTA curves of $\text{La}_{0.8}\text{Ca}_{0.2}\text{AlO}_3$ precursor heated in air at $10^\circ\text{C}/\text{min}$.

exhibits one broad endothermic peak at 113°C , two weak endothermic peaks at about 500, 690°C and apparently one small exothermic peak at 818°C . The first gradual weight loss step from 25 to 280°C accompanying with a broad endothermic peaks can be ascribed to the removal of the residual water. The second weight loss stage at the temperature range of 420 – 630°C accompanied with a weak endothermic peak corresponds to the dehydration of the lanthanum, aluminum and calcium hydroxides. The third small weight loss from 630 to 760°C associating with the endothermic peak at about 690°C correspond probably to the decomposition of residual nitrates. A very weak weight loss up to 830°C was detected. It was accompanied with an exothermic peak which can be attributed to the formation of the $\text{La}_{0.8}\text{Ca}_{0.2}\text{AlO}_3$ crystal. This latter small exothermic peak attributable to the formation of the oxide was also found for LaAlO_3 synthesized through the in situ polymerization route (12). The temperature at which the perovskite phase was obtained appears higher in the calcium doped oxide ($\sim 820^\circ\text{C}$) than for the undoped case ($\sim 800^\circ\text{C}$) (13). This is due to the substitution of lanthanum with calcium which raises the temperature of reaction to form the oxide.

3.2. X-ray diffraction

The X-ray powder diffraction patterns displayed in Fig. 2 confirm that all samples are included in the series $\text{La}_{1-x}\text{Ca}_x\text{AlO}_{3-\delta}$ ($0 \leq x \leq 0.6$) after calcination at 1000°C for 6 h. These results depend on the amount of Ca doping the site A of the perovskite structure. In each case, below this temperature, the formation of the phase-pure perovskite did not proceed as exposed below. The X-ray diffraction patterns of the powders obtained by co-precipitation show that $\text{La}_{1-x}\text{Ca}_x\text{AlO}_3$ oxides

Fig. 2- X-ray diffraction patterns of perovskite samples $\text{La}_{1-x}\text{Ca}_x\text{AlO}_3$ ($0 \leq x \leq 0.6$).

exhibit a single phase with rhombohedral structure (JCPDS card 085-0848), with no detectable secondary phase. The unit cell dimensions 'a' and 'c', estimated assuming $a = b \neq c$ and $\alpha = \beta = 90^\circ$ and $\gamma = 120^\circ$ were very close to those reported for LaAlO_3 ($a = 5.364 \text{ \AA}$ and $c = 6.548 \text{ \AA}$). The lattice parameters in $\text{La}_{1-x}\text{Ca}_x\text{AlO}_3$ compounds are calculated in the 2θ range corresponding to diffraction peaks of {111} and {220}.

In addition, the gradual shifting to high angle observed on the X-ray diffraction pattern peaks for doped calcium lanthanum aluminum powders (figure 3), is due to the incorporation of Ca ions with a small ionic radius ($1.34 \text{ \AA}$) in comparison with La ($1.36 \text{ \AA}$) (14,15).

Indeed, the decrease of lattice parameters of Ca-doped powders (table 1) from that of pure LaAlO_3 powder, agrees with the statement done above. The lattice volume change does not follow Vegard's law (figure 4). This disagreement suggests a more complex structure than a simple solid solution. This result implies also the existence of two regimes, one for $x < 0.1$ and another for $x \geq 0.1$ where a linear dependency of the lattice volume with calcium content is observed.

Figure 5 presents XRD patterns of $\text{La}_{0.8}\text{Ca}_{0.2}\text{AlO}_3$ calcined at different temperatures. After being heated at 600°C in air, the powder is almost amorphous and the characteristic peaks of the perovskite phase appear with low intensity, which indicated an incipient onset of transformation of amorphous phase to the crystalline phase. In addition to the perovskite phase, few peaks were identified to resemble those of lanthanum oxide La_2O_3 (JCPDS 083-1344), aluminium oxide Al_2O_3 (JCPDS 016-0435), calcium oxide CaO (JCPDS 017-0912). Indeed at 600°C , the main peaks were attributed to these three phases together with weak peaks at about 33° in 2θ attributed to the perovskite oxide were observed.

Fig. 3- Evolution of the position of the highest X-ray diffraction peak

TABLE I. VALUES OF UNIT CELL PARAMETERS FOR PURE AND SUBSTITUTED LaAlO_3 .

Ca content x	a=b (Å) (± 0.002)	c(Å) (± 0.004)	V(Å ³)
0	5.3640	6.5525	163.189
0.1	5.3562	6.5402	162.491
0.2	5.3560	6.5369	162.397
0.3	5.3558	6.5347	162.333
0.4	5.3557	6.5325	162.269
0.5	5.3555	6.5303	162.205
0.6	5.3555	6.5281	162.150

Fig. 4- Lattice volume dependence on calcium content (x) for $\text{La}_{1-x}\text{Ca}_x\text{AlO}_{3-b}$

Fig.5- XRD patterns of the $\text{La}_{0.8}\text{Ca}_{0.2}\text{AlO}_3$ powder calcined at different temperatures: (a) La_2O_3 ; (b) Al_2O_3 ; (c) CaO ; (d) rhombohedral phase; (x) unidentified.

Fig. 6- Infrared spectra of $\text{La}_{1-x}\text{Ca}_x\text{AlO}_{3-\delta}$ ($0 \leq x \leq 0.6$) samples calcined at 1000°C.

Fig.7- Crystallite size of $\text{La}_{1-x}\text{Ca}_x\text{AlO}_{3-\delta}$ powder ($0 \leq x \leq 0.6$).

(a)

(b)

Fig.8- SEM micrograph of LaAlO_3 (a) and $\text{La}_{0.8}\text{Ca}_{0.2}\text{AlO}_3$ (b) calcined at 1000°C.

This is in good agreement with DTA results which show the peak corresponding to the dehydration of the lanthanum, aluminum and calcium hydroxides at $\sim 500^\circ\text{C}$. This means that the temperature range 500°C (DTA) to 600°C (XRD) is sufficient so that all metallic hydroxides are dehydrated and appear at 600°C on the X-ray diffractogram as oxides. When the powder is calcined at $700\text{--}900^\circ\text{C}$, the amorphous phase disappears gradually whereas the crystallinity of the $\text{La}_{0.8}\text{Ca}_{0.2}\text{AlO}_3$ phase is improved with increasing calcination temperature in the presence of the phases mentioned above. The formation of the $\text{La}_{0.8}\text{Ca}_{0.2}\text{AlO}_3$ perovskite oxide was clearly recognized at the calcining temperature above 800°C . The intensity of CaO , (Al_2O_3) O and La_2O_3 peaks decreased with the increasing calcining temperature.

3.3. IR Spectroscopy

The perovskite structure is characterized by IR spectra of these compounds recorded in the range $400\text{--}1200\text{ cm}^{-1}$ (figure 6). The spectra of substituted $\text{La}_{1-x}\text{Ca}_x\text{AlO}_3$ perovskites are similar to that of the rhomboedric LaAlO_3 structure. From the spectra, two bands are observed around 670 and 450 cm^{-1} . They are assigned to AlO_6 octahedra of the oxide matrix and the characteristic of a pure perovskite phase (19). Two additional bands for $\text{La}_{0.5}\text{Ca}_{0.5}\text{AlO}_3$ and $\text{La}_{0.4}\text{Ca}_{0.6}\text{AlO}_3$ samples are observed around 800 and 880 cm^{-1} . These bands probably correspond to the vibrations of tetrahedron AlO_4 (20, 21). It is observed that the band positions are composition-dependent. From pure to doped LaAlO_3 , the two bands shift to higher wavenumber. This displacement is so light that it is only noticed when comparing the end members LaAlO_3 and $\text{La}_{0.4}\text{Ca}_{0.6}\text{AlO}_3$. This may be due to the distribution of Ca^{2+} which replaces La^{3+} of A-site. The dependence of band position and intensity as a function of calcium content runs in parallel with the slight shift observed in the XRD patterns.

3.4. Structural and Morphological characterization

The peak broadening at lower angle is more meaningful for the calculation of particle size, therefore size of nanocrystals

has been calculated using Debye-Scherrer formula (Eq.1) (22). This formula for crystallite size determination is given by:

$$D = 0.89 \lambda / \beta \cos \theta \quad \text{Eq.1}$$

Where D is the crystallite size, λ is the wavelength of x-ray, β is the full width at half maximum (β expressed in radians), θ is the Bragg's angle. The particle size obtained from XRD for different compositions is presented in figure 7. From this figure, the oxides present an average crystallite size in the range of 31-74 nm. It is observed that the crystallite size increases with increase in content of calcium. This is probably due to the incorporation of Ca^{2+} into the LaAlO_3 lattice which leads to the crystallite growth. A similar result was found for Mn-doped BaTiO_3 (23). It has been shown that growth of Mn-doped BaTiO_3 crystallite is promoted due to the increase in oxygen vacancies.

The SEM micrographs of LaAlO_3 and $\text{La}_{0.8}\text{Ca}_{0.2}\text{AlO}_3$ after calcination (Figure 8) respectively reveal the microstructure of the ceramic samples. rains of various dimensions and forms are observed. In $\text{La}_{0.8}\text{Ca}_{0.2}\text{AlO}_3$ sample particles are nearly spherical in shape and the powder is partially agglomerated.

After heating at 1000°C for 6 h, the ceramics are made of small grains. The average grain sizes of the powders are approximately 0.15–0.6 μm . However some particles agglomerate as shown in Figure 8b. The formation of agglomerate is probably due to the nature of the solvent used in the preparation of the precipitate. The same result was also found for samarium-doped ceria powders (24). It has been shown that treating the precipitate with water and ethanol allows interactions between particles which lead during drying to the formation of chemical bonds.

3.5. Electrochemical properties

The electrochemical activity for oxygen reduction and evolution reactions was investigated on $\text{La}_{1-x}\text{Ca}_x\text{AlO}_3$ coated nickel substrate according to:

The critical properties to consider when choosing an electrocatalyst support include its electrical conductivity surface area macromorphology microstructure corrosion resistance and cost (25). The substrate of nickel satisfies these criteria and is often used in literature (26, 27).

Polarization studies under potentiostatic conditions were carried out. Figures 9 and 10 show the cathodic and anodic current-potential curves of air electrode with different substitutions of calcium. The coated electrode films showed good adherence during polarization. The voltammetric profile is rather featureless, showing a wide plateau region. It is clear that the coated perovskite electrodes present a wide range of electrochemical stability and a composition dependency of the current intensity. Electrode reactions over the surface of the oxides exhibit high currents. Compounds with large x values show higher cathodic and anodic currents than those with smaller x . Compared to all compositions, the $\text{La}_{0.4}\text{Ca}_{0.6}\text{AlO}_3$ one appears to be most active. Calcium, a divalent cation increases the catalytic activity and provides a catalyst with high structural stability due to the similarity of its ionic radius with that of La^{3+} . At the same voltage, the highest electrode performance is achieved, for oxygen reduction and evolution, with $x = 0.6$.

4. CONCLUSIONS

Perovskite-type $\text{La}_{1-x}\text{Ca}_x\text{AlO}_3$ oxides with x varying from 0.0 to 0.6 were prepared by the co-precipitation method. This study shows that the calcium content affects the physico-chemical properties of the oxide system. These materials exhibit a single phase perovskite-type at $x < 0.1$ and a more complex structure at $x \geq 0.1$. The microstructure and morphology of the compounds show that the particles are nearly spherical in shape and are agglomerated. Compared

Fig.9- The i - E polarization curves of oxygen reduction for $\text{La}_{1-x}\text{Ca}_x\text{AlO}_3$ electrodes in 1M KOH.

Fig.10- The i - E polarization curves of oxygen evolution for $\text{La}_{1-x}\text{Ca}_x\text{AlO}_3$ electrodes in 1M KOH.

to all studied compositions, $\text{La}_{0.4}\text{Ca}_{0.6}\text{AlO}_3$ electrode exhibits significantly greater electroactivity, indicating that this material is among the analyzed series the best electrocatalyst for oxygen reduction and evolution.

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