

Synthesis and electrical conductivity of perovskite $\text{Gd}_{1-x}\text{Ca}_x\text{CrO}_3$ ($0 \leq x \leq 0.3$) by auto-ignition process

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Abstract

In order to develop interconnect ceramics for intermediate temperature solid oxide fuel cells (IT-SOFCs), perovskite compounds, $\text{Gd}_{1-x}\text{Ca}_x\text{CrO}_3$ ($x=0\sim 0.3$), were prepared by an auto-ignition process and characterized. XRD analysis indicated that a single perovskite phase was obtained as Ca^{2+} content (x value) was lower than 0.3, while a second phase appeared at $x=0.4$. The lattice parameters of the unit cell decrease with increasing the substitution Ca^{2+} for Gd^{3+} . The particle sizes of $\text{Gd}_{0.7}\text{Ca}_{0.3}\text{CrO}_3$ powders are in the range of 20–50 nm observed by TEM. The powders exhibited better sintering ability and could reach 94.8% relative density at 1400 °C for 4 h in air. The DC four probe technique measurement indicated that the electrical conductivities of the specimens increased with increasing Ca^{2+} content as $x \leq 0.3$ but remarkably dropped when $x=0.4$, which might be attributed to the formation of the second phase with lower conductivity in the materials. $\text{Gd}_{0.7}\text{Ca}_{0.3}\text{CrO}_3$ with a density of 94% showed an electrical conductivity of 24 Scm^{-1} in air and 7.5 Scm^{-1} in H_2 (99.999%) at 700 °C respectively, which is about 50% more than that of the commonly used lanthanum chromite ($\text{La}_{0.7}\text{Ca}_{0.3}\text{CrO}_3$). It will be suitable to be interconnect material for IT-SOFCs.

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1. Introduction

The solid oxide fuel cell (SOFC) attracts more and more attention because of its high efficiency of power conversion and low pollution. The interconnector is one of the key components for SOFC stacks (SOFCs). The sufficient high electrical conductivity of the interconnector plays a significant role in determining a SOFCs performance [1]. The perovskite lanthanum chromite substituted with alkaline earth metals (Ca or Sr) have been widely accepted as the candidate for interconnection material in present generation SOFCs. It satisfies most of the requirements of SOFC such as high electronic and negligible ionic conductivity, chemical stability in both oxidizing and reducing atmospheres as well as chemical and thermo-mechanical compat-

ibility with other cell components under operating conditions (800–1000 °C) [2]. But, intermediate temperature SOFCs have attracted much more attention in recent years because of the potential to dramatically reduce the cost of the materials and cell fabrication besides improving reliability and operational life. To find a kind of new interconnect material with superior electrical properties for IT-SOFCs, the perovskite family of materials has been widely studied because of its unique electronic conductivity [3]. In $\text{Ln}(\text{AE})\text{CrO}_3$ ($\text{Ln}=\text{La}, \text{Y}$ and Gd , $\text{AE}=\text{alkaline earth element}$) perovskite system, many investigations have been focused on pure and doped materials of the former two. Little attention has been given to the synthesis and electrical conductivity of $\text{Gd}_{1-x}\text{Ca}_x\text{CrO}_3$ ($0 \leq x \leq 0.4$). Unfortunately, $\text{Gd}(\text{Ca})\text{CrO}_3$, as well as other lanthanide chromites, shows poor sinter-ability and is very difficult to densify under atmospheric conditions. Usually, two heating steps have been required for the fabrication of dense $\text{La}(\text{Ca})\text{CrO}_3$ and $\text{Y}(\text{Ca})\text{CrO}_3$ materials with high electrical conductivities:

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sintering under reduced pressure and annealing in air in order to fully oxidize the samples.

An auto-ignition process is a self-combustion method using citric acid as fuel and the nitrates of the metal components of the material to be synthesized as oxidant, and this procedure could enhance the density and phase purity of the sample at lower temperature. In this study, we tried to employ this technique to obtain highly active $Gd_{1-x}Ca_xCrO_3$ powders. Perovskite compounds $Gd_{1-x}Ca_xCrO_3$, where $x=0\sim 0.4$, were formed by this method. Dense materials could be fabricated without any control of oxygen pressure. The present paper deals with synthesis and electrical conductivities of such $Gd_{1-x}Ca_xCrO_3$ in high pure H_2 and in air.

2. Experimental

The fine powders with composition of $Gd_{1-x}Ca_xCrO_3$ ($x=0, 0.1, 0.2, 0.3$, and 0.4) were synthesized by auto-ignition process. The starting materials are (analytically pure) calcium nitrate with quadruple-hydrate ($Ca(NO_3)_2 \cdot 4H_2O$), gadolinium oxide (Gd_2O_3) and chromic nitrate with sextuple-hydrate ($Cr(NO_3)_3 \cdot 6H_2O$), which were mixed with treble citric acid and distilled water. Then it formed a gel by heating and the wet gel was further heated to about $120^\circ C$ to remove the solvents. The dried gel was put into an oven at $650^\circ C$, then the combustion reaction took place within a few seconds, forming the primary powders. The as-synthesized powders were calcined at $650^\circ C$ for 2 h. The powders were ball milled in isopropanol medium overnight with subsequent drying and then compacted to form small pellets using a pressure of 360 MPa. The pressed samples were sintered in air at $1400^\circ C$ for 4 h. Both heating and cooling rates were fixed at $100^\circ C h^{-1}$.

Particle size was observed by transmission electron microscopy (TEM). Identification of various phases of the powders and sintered samples were carried out by X-ray diffraction analysis in a Philips PW 1730 diffractometer using $Cu K_\alpha$ radiation. The bulk densities of all the sintered samples were measured by liquid displacement method using toluene. Fractured surfaces of the sintered specimens were examined with a scanning electron microscope (SEM). The electrical conductivity of the material had been studied from 500 to $800^\circ C$ by standard DC four probe technique using H.P. multimeter (Model 34401). Rectangular bar specimens ($34 \times 5 \times 1.8$ mm) were used for this purpose.

3. Results and discussion

3.1. Formation of perovskite $Gd_{1-x}Ca_xCrO_3$

X-ray diffraction (XRD) patterns for $Gd_{0.7}Ca_{0.3}CrO_3$ after heating at different temperatures for 2 h are shown in

Fig. 1. The XRD patterns show an orthorhombic structure for the as-synthesized powders after heating for 2 h at 650 and $900^\circ C$ respectively, which contain small amount of the second phase that may be $CaCrO_4$ [4,5]. Fig. 1(c) shows a single-phase with perovskite structure after calcination at $1000^\circ C$ for 2 h. It may be ascribed to $CaCrO_4$ decomposing in air at high temperature to yield perovskite $CaCrO_3$:



XRD patterns of the prepared powders of the system $Gd_{1-x}Ca_xCrO_3$ ($x=0.1, 0.2, 0.3, 0.4$ and 0.5) are shown in Fig. 2. The XRD patterns of the compositions in the range of $0.1 \leq x \leq 0.5$ were indexed in the orthorhombic perovskite $GdFeO_3$ -type structure. The samples with $x \leq 0.3$ took on single phase, while in the case of $x=0.4$ and 0.5 , traces of a second phase were observed, which means the solubility of Ca^{2+} in $GdCrO_3$ is lower than 0.4 ($1000^\circ C$). The introduction of Ca^{2+} into the lattice caused a small peak shift towards higher value of 2θ .

From Fig. 3 it is apparent that the unit cell lattice parameters of $Gd_{1-x}Ca_xCrO_3$ change with x value variety. It can be seen that the lattice parameter of the unit cell decreases with increasing the substitution Ca^{2+} for Gd^{3+} , and there are sudden turns of all three curves as $x > 0.3$, which indicates that there maybe exist small amount of a second phase, as Fig. 2 shows. The dots derived from crossed two broken lines show the solubility of Ca^{2+} in $GdCrO_3$ is $0.32\sim 0.34$ ($1000^\circ C$). From a, b and c, (Fig. 3) it can be concluded that the cell volume decreases along with the increase substitution of Ca^{2+} for Gd^{3+} . This results from many factors such as the ionic radius of the acceptor dopant (Ca^{2+}), the mixed valence state of the chromium ion, and the oxygen deficiency [6]. The substitution of the larger Ca^{2+} (0.099 nm) for Gd^{3+} (0.094 nm) at lattice positions should cause an increase in the unit cell volume. But the introduction of Ca^{2+} into

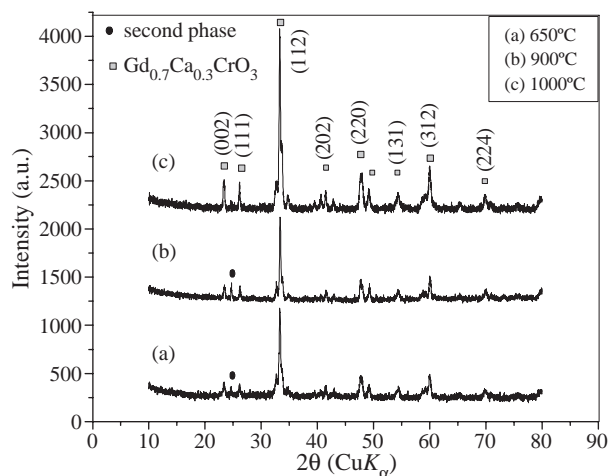


Fig. 1. XRD patterns for $Gd_{0.7}Ca_{0.3}CrO_3$ after heating for 2h at different temperatures.

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