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Journal of Solid State Chemistry 170 (2003) 68–74

JOURNAL OF
SOLID STATE
CHEMISTRY

<http://elsevier.com/locate/jssc>

Phase stability of $\text{La}_{1-x}\text{Ca}_x\text{CrO}_{3-\delta}$ in oxidizing atmosphere

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Received 28 March 2002; received in revised form 19 June 2002; accepted 27 August 2002

Abstract

The chemical stability of perovskite-type $\text{La}_{1-x}\text{Ca}_x\text{CrO}_{3-\delta}$ ($x=0.1, 0.2, 0.3$) in high oxygen partial pressure, P_{O_2} , was investigated with three methods: thermogravimetry, XRD analysis, and thermodynamic calculation. The second phase, CaCrO_4 was observed by XRD analysis on the powder equilibrated in high P_{O_2} . Thermogravimetry under fixed temperatures sensitively detected the segregation of the second phase in the form of oxygen incorporation, because oxidation of chromium ion accompanies the segregation. The second phase tended to appear in high P_{O_2} and at low temperature. The single-phase regions of $\text{La}_{1-x}\text{Ca}_x\text{CrO}_{3-\delta}$ obtained from the two experimental methods well agreed with each other. The results of thermodynamic calculation on the assumption of ideality of the solid solution also agreed with the experimental results. These results suggested the sufficient chemical stability of $\text{La}_{1-x}\text{Ca}_x\text{CrO}_{3-\delta}$ in high P_{O_2} concerning the application to an interconnector of high-temperature solid oxide fuel cells; for example, $\text{La}_{0.7}\text{Ca}_{0.3}\text{CrO}_{3-\delta}$ is stable at 1273 K in air.

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Keywords: $\text{La}_{1-x}\text{Ca}_x\text{CrO}_{3-\delta}$; Perovskite; Chemical stability; Solubility limit; Solid oxide fuel cell; Interconnector

1. Introduction

The perovskite-type $\text{La}_{1-x}\text{Ca}_x\text{CrO}_{3-\delta}$ has been applied to an interconnector material in high-temperature solid oxide fuel cells (SOFCs) based on YSZ electrolyte because of its high electronic conductivity, good compatibility with other materials in SOFCs, and excellent stability against reducing and oxidizing atmospheres. As to the chemical stability of doped lanthanum chromite in the operating condition, it is well known that the composition of the oxide varies in a reducing atmosphere owing to oxygen nonstoichiometry [1,2] which may cause electrochemical leakage of oxygen and also volume expansion. In addition, there is a possibility of the precipitation of the second phase [3–8]. The formation of the second phase in the interconnector of SOFCs can induce serious problems; for example, the

decrease in the electronic conductivity and the mechanical strength. Also, the second phase probably reacts with the other SOFC components such as YSZ electrolyte, yielding undesirable products [9].

According to Carter et al. [3], the second phase coexisting with $(\text{La}, \text{Ca})\text{CrO}_{3-\delta}$ in an oxidative atmosphere was identified as CaCrO_4 . They also reported the maximum of Ca content in $(\text{La}, \text{Ca})\text{CrO}_{3-\delta}$ in air as 30% ($x=0.3$) at 1273 K and 20% ($x=0.2$) at 1173 K, respectively. Yokokawa et al. [4,5,10,11] carried out thermodynamic calculation to construct the chemical potential diagrams related to $\text{La}_{1-x}\text{Ca}_x\text{CrO}_{3-\delta}$, and showed a possibility for segregation of CaCrO_4 and other phases. Peck et al. [6] experimentally obtained the phase diagrams of $\text{CaO-La}_2\text{O}_3\text{-Cr}_2\text{O}_3$ system and determined the solubility limit of calcium at 1223 K in air as 0.31. However, those experiments were performed only in air, where the concerned oxygen partial pressure was fixed at 0.21 bar. In order to understand the chemical stability of $\text{La}_{1-x}\text{Ca}_x\text{CrO}_{3-\delta}$ in oxidative atmospheres, it is required to elucidate the detailed

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phase relationship as a function of oxygen partial pressure, temperature, and dopant content.

In the present study, two independent experimental methods and thermodynamic calculation were employed to determine the precise single-phase region of $\text{La}_{1-x}\text{Ca}_x\text{CrO}_{3-\delta}$ ($x = 0.1, 0.2, 0.3$) in high oxygen partial pressures.

The first experimental method was thermogravimetry, which enabled to detect the phase separation from the solid solution which was previously prepared in a single phase. We measured the weight change of the solid solution with the variations of oxygen partial pressure, P_{O_2} , at fixed temperatures. In the single-phase region, the weight of the specimen changed in dependence on the oxide-ion vacancy concentration. When the second phase(s) appeared in high P_{O_2} , the weight of the specimen apparently exceeded the stoichiometric composition ($\delta = 0$) since the formation of the second phase(s) was accompanied by oxidation of Cr ion to a higher valence. Consequently, we successfully detected the phase separation from the solid solution with high sensitivity.

In contrast to the first method, the second one was the direct synthesis of the stable solid solution. The precursors, which were prepared at relatively low temperature and thereby consisted of perovskite and the other phase including Ca, were equilibrated at controlled P_{O_2} and temperature. It is expected that dissolution of Ca into the perovskite phase proceeds during the equilibration, until the Ca content in the perovskite reaches the solubility limit or the second phase disappears. We avoided a previous calcination at the temperature higher than that for the equilibration; such a calcination probably make a single phase before the equilibration. The existing phase(s) in the equilibrated powder were identified with X-ray diffractometry.

The third method was thermodynamic calculation. The stable phase(s) under the conditions of interest were evaluated by SOLGASMIX [12,13] combined with thermochemical database, CTC (Chemical Thermodynamic Computation System) [14].

In the present paper, the three methods described above will be referred to as thermogravimetry (TG), XRD, and thermodynamic calculation, respectively. The single-phase regions of $\text{La}_{1-x}\text{Ca}_x\text{CrO}_{3-\delta}$ obtained from the three methods will be compared with each other, and the reliability will be discussed.

2. Experimental

2.1. Specimen preparation for thermogravimetry

The powders of $\text{La}_{1-x}\text{Ca}_x\text{CrO}_{3-\delta}$ ($x = 0.10, 0.20, 0.30$) for thermogravimetry (TG) were prepared by a

simplified Pechini method [15]. The appropriate amounts of La_2O_3 (mass fraction > 0.9999 , Guaranteed reagents, Nakarai Chemical), $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (mass fraction as hydrate > 0.98 , Guaranteed reagents, Nakarai Chemical), and CaCO_3 (mass fraction > 0.99 , Guaranteed reagent, Kishida Chemical) were respectively dissolved in dilute HNO_3 . The concentration of cation in each nitrate solution was determined by a chelate titration. Three solutions were then mixed together in the appropriate ratio, and an excess amount of citric acid was added. After mixing well, the solution was heated with a hot plate to become a glassy gel. The gel was dried at about 460 K, and thoroughly ground for 6 h using 3 (m/o)-YSZ ball mill with ethanol. The ethanol was removed by heating slowly to 573 K, and the powder was subsequently calcined at 1473 K for 10 h in air. XRD analyses confirmed that all the calcined powders consisted of a single phase of perovskite. The powders were also analyzed by X-ray fluorescence spectroscopy to confirm that no impurity owing to preparation procedure was found. Each calcined powder about 1 g was pressed into a rod and sintered at 1673 K for 2 h in air. The relative densities of the rods were about 50–65%.

2.2. Thermogravimetry—observation of the phase separation from $\text{La}_{1-x}\text{Ca}_x\text{CrO}_{3-\delta}$

The weight changes of the $\text{La}_{1-x}\text{Ca}_x\text{CrO}_{3-\delta}$ specimen caused by oxygen nonstoichiometry, δ , or the separation of the second phase(s) were measured with stepwise P_{O_2} changes at each fixed temperature. The experimental setup consisted of an electronic microbalance (M25D-P, Sartorius) connected to an alumina reaction tube and a gas mixing system, as shown in Fig. 1. The specimen was wound with a platinum wire to be suspended in the

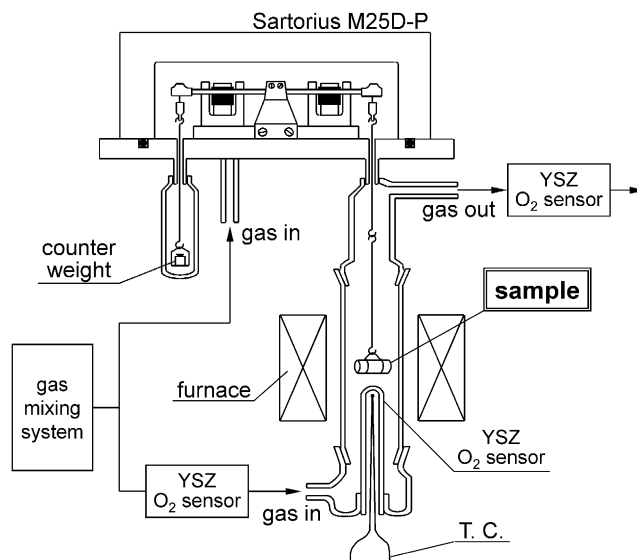


Fig. 1. Schematic of the apparatus for thermogravimetry.

reaction tube with alumina and silica sticks from the microbalance. The specimen temperature was kept within 1 K of the programmed temperature. The ambient oxygen partial pressure was controlled by the use of Ar–O₂, CO–CO₂ and H₂–H₂O–Ar gas mixtures, and monitored with a zirconia-based oxygen concentration cell which was placed below the specimen at a distance of 10–12 mm. Two concentration cells were also set to monitor the P_{O_2} of the inlet gas and that of the outlet gas of the reaction tube, respectively. We judged the specimen to be equilibrated with the gaseous phase, when both the weight of the specimen and the P_{O_2} in the reaction tube became constant.

The dependence of buoyancy upon the composition of the introduced gas was measured with a dense alumina specimen, which exhibits no oxygen nonstoichiometry. The weight after compensation for the buoyancy effect was reproducible to within ± 30 μ g. The accuracy of the obtained δ in about 1 g of La_{1-x}Ca_xCrO_{3- δ} is considered to be within 0.0006.

2.3. XRD—direct synthesis of stable phase(s) and characterization

The precursors of La_{1-x}Ca_xCrO_{3- δ} ($x=0.10, 0.20, 0.30$) for the phase investigation with XRD analysis were also prepared by the simplified Pechini method [15]. The starting materials were La₂O₃ (mass fraction >0.9999, Rare Metallic), CaCO₃ (mass fraction > 0.9999, Kanto Chemical), and Cr(NO₃)₃•9H₂O (0.980 ≤ mass fraction as hydrate ≤ 1.030, mass fraction of chloride <0.0001, that of sulfate <0.0001, that of iron <0.0001, Cica-Reagent, Kanto Chemical). They were dissolved in HNO₃ to prepare the solution mixtures of the appropriate composition. The concentration of each cation was determined with ICP-AES (SPS7700, Seiko Instrument). An excess amount of citric acid was added to the mixed nitrate solution and mixed well. The mixture was heated up to about 723 K to remove water and nitric oxides, and subsequently to start self-burning, which brought ash-like solid. The obtained precursor was ground with a mortar.

Each precursor was equilibrated in various P_{O_2} (10^{-2} –1 bar) and temperature (1073–1373 K), and the equilibrated powders were subsequently characterized at room temperature by XRD analysis as follows. In order to confirm complete removal of carbon, which remained in the precursors, we used TG-DTA/Q-MS (TG-DTA2000S, Mac Science/Thermolab, VG Gas Analysis Systems) for the equilibration. In the case of the equilibration in high P_{O_2} (≥ 0.1 bar), a gas mixture of O₂–Ar(N₂) with P_{O_2} of interest was introduced from the outset, and the precursor was heated up directly to the temperature for the equilibration at the rate of 20 K/min. For the equilibration in the lower P_{O_2} ($= 10^{-2}$ bar), a calcination process was inserted so as to complete the

oxidation of the residual carbon. In this case, an oxidative gas ($P_{O_2} = 0.21$ or 1 bar) was introduced at first, and the precursor was heated up to 973 K and kept at that temperature for several hours. The complete removal of the carbon at this stage was confirmed by both the weight loss and the mass signal of CO₂ in the outlet gas. Then, the flowing gas was shifted to that for the equilibration. After gas exchange in the chamber was completed, temperature was elevated from 973 K to that for the equilibration at the rate of 20 K/min. In both the cases with and without calcination process, the precursor was kept for 10 h under the condition of the equilibration, and subsequently cooled down to room temperature with natural cooling, which took about 15 min. The stable phase(s) under the condition were determined by XRD analysis with CuK α radiation (RAD IR, Rigaku) on the obtained powder.

2.3.1. Thermodynamic calculation—evaluation of stable phase(s)

The stable phase(s) under various conditions (oxygen partial pressure, temperature, and Ca content) were estimated with SOLGASMIX [12,13], which evaluates the equilibrium state to minimize overall Gibbs energy in the system. In this evaluation, the solid solution was assumed to be an ideal solution of the constituent perovskites: LaCrO₃ and CaCrO₃. Hypothetical compounds, La_{2/3}CrO₃ and LaCa_{0.5}Cr_{0.5}O₃ were taken into account to examine the possibilities of A-site deficiency and substitution of B-site by Ca ion in the solid solution. The thermodynamic data for the compounds were taken from thermodynamic database CTC [14], or estimated as reported in the literature [4].

3. Results and discussion

3.1. Thermogravimetry—observation of the phase separation from La_{1-x}Ca_xCrO_{3- δ}

Fig. 2 shows the relationship between the measured oxygen nonstoichiometry of La_{1-x}Ca_xCrO_{3- δ} ($x = 0.3$) and log P_{O_2} over the temperature range of 1073–1373 K. On the P_{O_2} dependence of the specimen weight, a plateau was observed in a high P_{O_2} region. The weight corresponding to the stoichiometric composition ($\delta = 0$) was assigned to the inflection point of the plateau [16]. At 1073 and 1173 K, the oxygen content measured in CO–CO₂ gas mixture obviously deviated from the behavior which is expected from the measurement in H₂–H₂O–Ar gas mixture. Though a possible reason for the deviation is the formation of CaCO₃ in CO–CO₂ atmosphere, the existence of calcium carbonate has not been confirmed by XRD analysis. Further details on the oxygen nonstoichiometry in a low P_{O_2} region will be reported elsewhere [2].

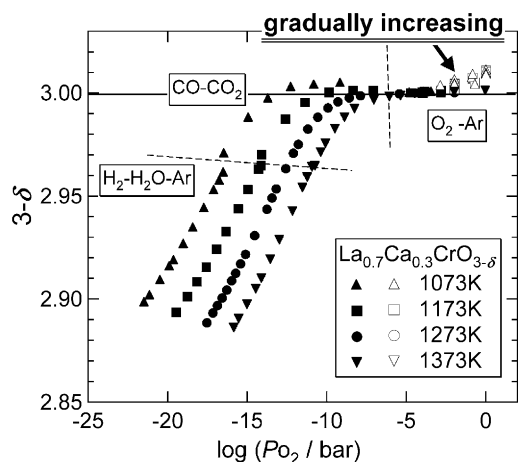


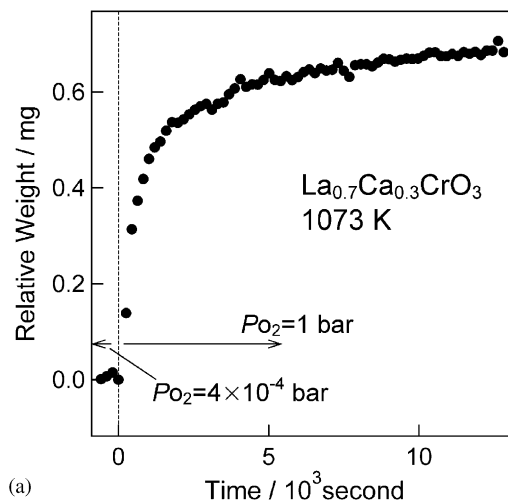
Fig. 2. Oxygen nonstoichiometry of $\text{La}_{1-x}\text{Ca}_x\text{CrO}_{3-\delta}$ ($x=0.3$). The gas mixtures used for the control of P_{O_2} are indicated in the small frames. Data denoted by open symbols above the stoichiometry line ($\delta = 0$) were not measured in equilibria.

Under some conditions in high P_{O_2} , the specimen weight gradually increased over the stoichiometric composition; in other words, negative δ 's ($3-\delta > 3$) were observed. Since the second phase is regarded as a compound with Cr^{6+} according to the literature [3–6] and as described later, the negative δ is attributed to the oxygen incorporation caused by the phase separation. In addition, the weight changes involving the negative δ were much slower than those in the low P_{O_2} region where oxygen-deficient nonstoichiometry appears, and new equilibria were not attained within our experimental period of 12 h. The difference in the rate of the weight change is illustrated in Fig. 3(a) and (b). The slow kinetics is regarded as controlled by the diffusion rate of cations for the phase separation, while the diffusion of oxide ions determines the rate of the weight change in the oxygen-deficient region.

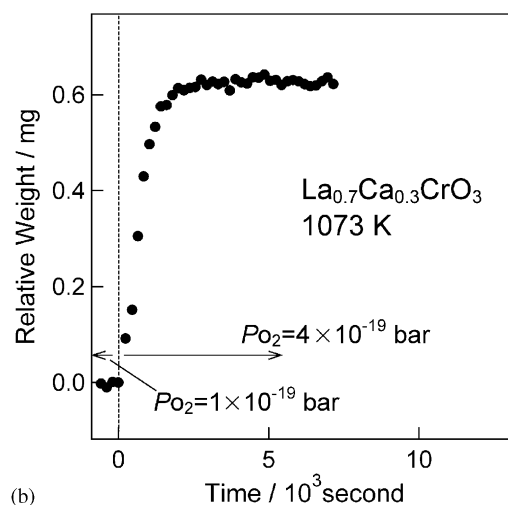
Thus, the conditions under which the negative δ was observed and/or the weight change was extraordinarily slow were judged to be in the multi-phase region. The obtained phase relationships of $\text{La}_{1-x}\text{Ca}_x\text{CrO}_{3-\delta}$ are shown in Fig. 4(a–c) as a function of P_{O_2} and temperature. In this figure, the open circle (○) and the cross (+) represent the single phase and multi-phase in the results of the thermogravimetry (TG), respectively. The second phase formed more easily in the higher P_{O_2} , at the lower temperature, and with the larger Ca content.

3.2. XRD—direct synthesis of stable phase(s) and characterization

Fig. 5 shows typical XRD patterns for the samples of the nominal composition of $\text{La}_{0.7}\text{Ca}_{0.3}\text{CrO}_{3-\delta}$. In this figure, the bottom pattern arose from the precursor after



(a)



(b)

Fig. 3. Typical temporal variation in the weight of the specimen after abrupt changes of P_{O_2} : (a) in an oxidizing atmosphere which caused the negative δ and (b) in a reducing atmosphere.

the preparation via the simplified Pechini method. The middle and upper ones were obtained from the powders which were equilibrated in $P_{\text{O}_2} = 1$ bar at 1273 and 1373 K, respectively. The upper one shows the single phase of the perovskite, while the middle one shows the coexistence with CaCrO_4 . The precursor as-prepared consisted mainly of a perovskite phase and CaCrO_4 .

In Fig. 4(a–c), the closed circle (●) and the diagonal cross (×) represent the conditions under which the single phase of $\text{La}_{1-x}\text{Ca}_x\text{CrO}_{3-\delta}$ and multi-phase appeared in the results of the XRD, respectively. Only CaCrO_4 was observed as the second phase, which agrees with the investigations by Carter et al. [3] and Peck et al. [6]. The single-phase regions obtained by means of the XRD well agreed with those suggested by the thermogravimetry (TG). The slight difference between the extent of the stable region obtained by the XRD and that obtained by the TG is understood as follows.

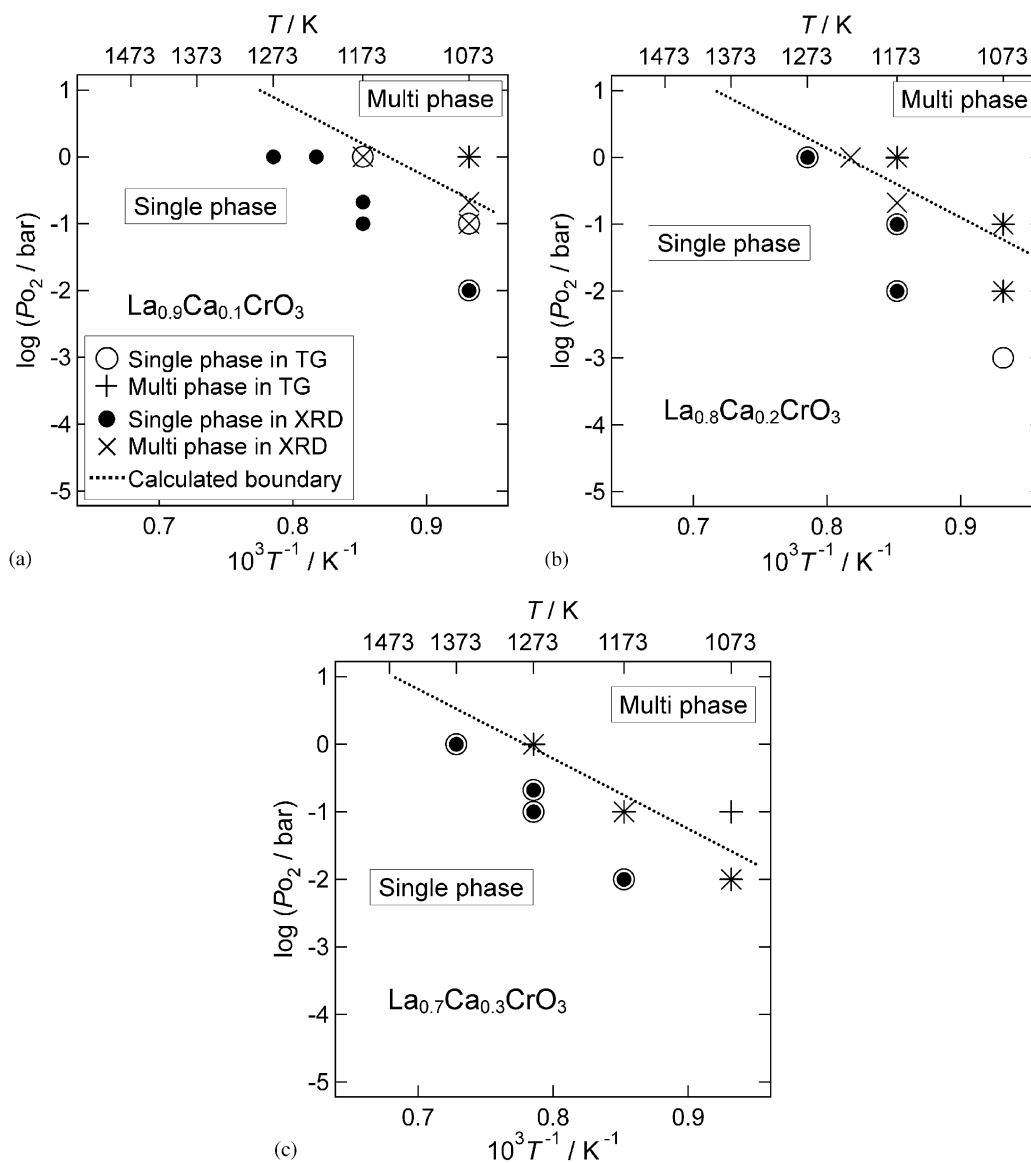


Fig. 4. Phase relationships of $\text{La}_{1-x}\text{Ca}_x\text{CrO}_{3-\delta}$ in high oxygen partial pressure: (a) $x = 0.1$; (b) $x = 0.2$; and (c) $x = 0.3$. (○) and (+) Represent the single phase and multi-phase in the results of the thermogravimetry (TG), respectively. (●) and (×) Represent the conditions under which the single phase and multi phase appeared in the XRD experiment, respectively. Dotted lines are the phase boundaries obtained from thermodynamic calculation, Eq. (5).

The essential difference between our two experimental methods, the TG and the XRD, is direction of the reaction observed. In the first method named thermogravimetry (TG), the specimen was previously prepared in a single phase. When the specimen is placed under conditions out of the stable region, the second phase separates from the $\text{La}_{1-x}\text{Ca}_x\text{CrO}_{3-\delta}$ solid solution. In the second method named XRD, the precursors of $\text{La}_{1-x}\text{Ca}_x\text{CrO}_{3-\delta}$ prepared at low temperature were directly equilibrated under the conditions of interest. The precursors consisted mainly of perovskite and CaCrO_4 , and it is expected that calcium-doping proceeds as the temperature goes up. Therefore, calcium dissolves into the perovskite during the equilibration up

to the solubility limit under the condition; this is the reaction opposite to that of the first method. Ideally, the single-phase regions obtained with the two experiments exactly agree with each other. In reality, there is a possibility that ideal equilibria were not attained due to a kinetic reason in both the experiments. If this is the case, the TG and the XRD tend to give larger and smaller single-phase regions than the true one, respectively. It is therefore certain that the true phase boundary exists between those obtained with the two experiments.

Moreover, the difference in the extent of stable region was small. The agreement between the results of the two experimental methods thus confirms the

sufficient certainty of the single-phase regions obtained in the present study. In addition, the determined single-phase regions are almost consistent with the reported solubility limit of Ca in air: $x = 0.3$ at 1273 K and $x = 0.2$ at 1173 K (3), and $x = 0.31$ at 1223 K [6].

3.3. Thermodynamic calculation—evaluation of stable phase(s)

The evaluation by SOLGASMIX and CTC also suggested the formation of the second phase(s) in high P_{O_2} . The main second phase was $CaCrO_4$. Additionally, a very small amount of La_2CrO_6 and $Ca_{10}(CrO_4)_7$, the proportion of which in molar ratio is 0.5% to the entirety at most, was also proposed. The evaluated stable phase(s) under each condition are summarized in Table 1. The behavior of the chemical stability of

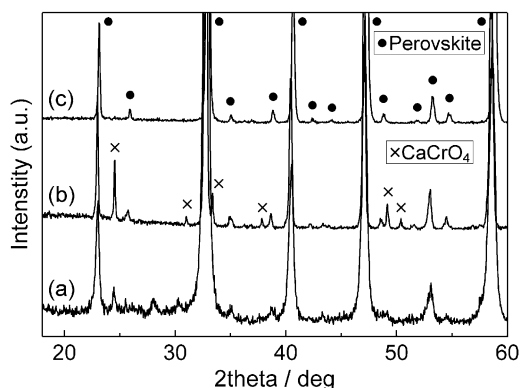
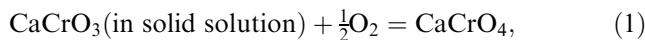


Fig. 5. Typical XRD patterns of the samples, the nominal composition of which was $La_{1-x}Ca_xCrO_3$ ($x=0.3$): (a) precursor as-synthesized; (b) and (c) equilibrated in $P_{O_2} = 1$ bar at 1273 and 1373 K, respectively.

$La_{1-x}Ca_xCrO_{3-\delta}$ suggested by SOLGASMIX is consistent with the results of the two experimental methods, that is, the second phase(s) tend to appear in high P_{O_2} , at low temperature, with larger x .

Regarding the two minor second phases, the XRD experiment did not detect them at all, which is possibly explained by the supposition that the amount of those compounds was less than the detection limit of XRD. However, the more probable interpretation is as follows: since the segregation of the suggested minor second phases, La_2CrO_6 and $Ca_{10}(CrO_4)_7$, involves the formation of a considerable amount of vacancies on A-site in the perovskite, the result that those compounds have not been observed implies that the formation of A-site vacancy in $La_{1-x}Ca_xCrO_{3-\delta}$ is negligible.

Therefore, the second phase of $La_{1-x}Ca_xCrO_{3-\delta}$ in high P_{O_2} is practically considered to be only $CaCrO_4$. On the basis of the assumptions, the reaction of the phase separation is the oxidation of $CaCrO_3$ in the solid solution; consequently, the following equilibrium must be achieved on the phase boundaries:



$$\mu(CaCrO_3) + \frac{1}{2}\mu(O_2) = \mu(CaCrO_4). \quad (2)$$

The chemical potential of $CaCrO_3$ is reduced by ideal mixing with $LaCrO_3$ as follows:

$$\mu(CaCrO_3) = \mu^\circ(CaCrO_3) + RT \ln x. \quad (3)$$

Since the standard pressure is defined as 1 bar in the thermodynamic database, the activity of oxygen gas is equal to oxygen partial pressure, P_{O_2} .

$$\mu(O_2) = RT \ln P_{O_2}. \quad (4)$$

Table 1

Second phases of $La_{1-x}Ca_xCrO_{3-\delta}$ evaluated with thermodynamic computation system, SOLGASMIX/CTC

Initial composition	$\log(P_{O_2}$ (bar))	$T(K)$			
		1373	1273	1173	1073
$La_{0.9}Ca_{0.1}CrO_3$	0	SP	SP	La_2CrO_6	$CaCrO_4$, La_2CrO_6
	-0.68	SP	SP	SP	La_2CrO_6
	-1	SP	SP	SP	La_2CrO_6
	-2	SP	SP	SP	SP
$La_{0.8}Ca_{0.2}CrO_3$	0	SP	SP	$CaCrO_4$, La_2CrO_6	$CaCrO_4$
	-0.68	SP	SP	SP	$CaCrO_4$, La_2CrO_6
	-1	SP	SP	SP	$CaCrO_4$, La_2CrO_6
	-2	SP	SP	SP	SP
$La_{0.7}Ca_{0.3}CrO_3$	0	SP	$CaCrO_4$	$CaCrO_4$, La_2CrO_6	$CaCrO_4$, La_2CrO_6
	-0.68	SP	SP	$CaCrO_4$, $Ca_{10}(CrO_4)_7$	$CaCrO_4$, La_2CrO_6
	-1	SP	SP	$CaCrO_4$, $Ca_{10}(CrO_4)_7$	$CaCrO_4$, La_2CrO_6
	-2	SP	SP	SP	$CaCrO_4$, $Ca_{10}(CrO_4)_7$

SP: Single phase of perovskite.

Finally, the relationship between oxygen partial pressure and temperature is derived as

$$\begin{aligned} \frac{2.303R}{2} \log P_{\text{O}_2} = & [\Delta_f H^\circ(\text{CaCrO}_4) \\ & - \Delta_f H^\circ(\text{CaCrO}_3)] \frac{1}{T} \\ & - [\Delta_f S^\circ(\text{CaCrO}_4) \\ & - \Delta_f S^\circ(\text{CaCrO}_3)] - R \ln x. \end{aligned} \quad (5)$$

The phase boundaries calculated with Eq. (5) are shown in Fig. 4(a–c) with dotted lines. The consistency in the extent of the single-phase region holds between the results of the experimental methods and that of thermodynamic calculation. The small deviation of the calculated boundaries from the experimental results can be attributed to the uncertainty of the thermodynamic data on CaCrO_4 , that on CaCrO_3 , and nonideality of the solid solution.

4. Conclusions

The second phase of $\text{La}_{1-x}\text{Ca}_x\text{CrO}_{3-\delta}$ was observed to form in oxidative atmospheres, and the compound was identified as CaCrO_4 with XRD analysis. The second phase tended to appear at low temperature, in high P_{O_2} , and with large Ca content. The extent of the single-phase regions suggested by the two independent experiments, which undergo the separation and the dissolution of the second phase, respectively, well agreed with each other to support the certainty of the experimental results. The thermodynamic calculation assuming $\text{La}_{1-x}\text{Ca}_x\text{CrO}_{3-\delta}$ to be an ideal solution essentially reproduced the experimental results. From the viewpoint of the chemical stability in high oxygen partial pressure, $\text{La}_{1-x}\text{Ca}_x\text{CrO}_{3-\delta}$ has sufficient durability for an interconnector of high temperature solid oxide fuel cells; for example, the solid solution of $x = 0.3$ is stable in a single phase at 1273 K in air.

Acknowledgments

This study was supported by “The basic research and development of micro solid oxide fuel cells” in ’00 from the New Energy and Industrial Technology Development Organization (NEDO) of Japan.

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