AIR-SINTERING CHARACTERISTICS OF
TI-DOPED LANTHANUM STRONTIUM CHROMITES
WITH B-SITE DOPING

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ABSTRACT

The effects of B-site dopants in the La_{1-x}Sr_{x}Cr_{0.9}Ti_{0.1-y}Co_{y}O_{3} perovskites (0.15 ≤ x ≤ 0.20 and 0 ≤ y ≤ 0.02) and La_{0.8}Sr_{0.2}Cr_{1-x}Ti_{0.1+y}M_{x}O_{3} perovskites (M = V and Ni; 0 ≤ x ≤ 0.05) on their air-sintering characteristics and thermal expansion behaviors have been studied using the fine powders made by the Pechini method. After heating at 1600°C for 10 h, the Ni-doped or Co-doped samples showed a single perovskite phase with the hexagonal symmetry, whereas 5 mol%V-doped one contained a very small amount of Sr_{3}(VO_{4})_{2} phase in the hexagonal perovskite phase. The V-, Co- and Ni-doping in the perovskites enhanced their air-sintering characteristics, and in particular, the V-doped samples showed the highest relative density. It was found that the V-doping in the perovskites was an effective way of decreasing the average linear thermal expansion coefficient (TEC). TEC of the La_{0.8}Sr_{0.2}Cr_{0.88}Ti_{0.1}V_{0.02}O_{3} sample in the temperature range from 50 to 1000°C was 10.2 × 10^{-6}/°C in air and 10.6 × 10^{-6}/°C under a H_{2} atmosphere, and showed a linear behavior.

INTRODUCTION

High-temperature solid oxide fuel cells (SOFCs) with Y_{2}O_{3} stabilized ZrO_{2} (YSZ) electrolyte are electrochemical and ceramic devices that convert the energy of a fuel directly into electricity without the need for an intermediate combustion stage. Because of their highly efficient and clean conversion of energy, the SOFC system can be applied to a wide variety of electric power generation systems ranging from small cogeneration systems to large power plants. Of all cell configurations, planar cell design is high in power density per volume (W/cm^{3}), short in electric conductivity paths and low in production cost [1]. However, in the planar type SOFC, the most significant problem is imposed by the generation of thermal stresses in the stack, since this cell configuration tends to produce large temperature difference in the plane direction. In addition, following thermal expansion problems inherent in alkaline earth metal (AE = Mg, Ca and Sr)-doped lanthanum chromite separator are the major technology barriers to the development of the SOFC [2]: (1) non-linear thermal expansion behavior related to a phase transformation between orthorhombic and rhombohedral symmetries, (2) large expansion under reducing atmospheres caused by an oxygen vacancy formation, and (3) average linear thermal expansion coefficient (TEC) mismatch between the LaCrO_{3}-based separator and YSZ electrolyte.

To solve the thermal expansion problems, La_{0.8}Sr_{0.2}Cr_{0.9}Ti_{0.1}O_{3} perovskite has
been considered for a SOFC separator [3]. The TEC of this material is the same as that of YSZ electrolyte, constant regardless of oxygen partial pressure under the SOFC operating conditions, and shows linear thermal expansion behavior. By the use of the La$_{0.8}$Sr$_{0.2}$Cr$_{0.9}$Ti$_{0.1}$O$_3$ separator, no stress among the cell components, which is caused by the TEC mismatch, should be observed during thermal cycles and under long-term operation. On the other hand, the SOFC separators should be gastight, because they separate fuel gas from the oxidizing gas. However, La$_{0.8}$Sr$_{0.2}$Cr$_{0.9}$Ti$_{0.1}$O$_3$ perovskite has poor sintering characteristics in air, and it is of crucial importance to devise an appropriate way of fabricating dense plates of this material in air.

Several attempts have been made to densify lanthanum chromites with B-site dopants [4-11]. In this study, the sintering characteristics of the La$_{1-x}$Sr$_x$Cr$_{1-y}$Ti$_y$O$_3$ perovskites (0.15 $\leq x \leq$ 0.20 and 0 $\leq y \leq$ 0.02) and La$_{0.8}$Sr$_{0.2}$Cr$_{1-x}$Ti$_{14}$M$_x$O$_3$ perovskites (M = V and Ni; 0 $\leq x \leq$ 0.05) have been investigated using fine powders made by the Pechini method. The aim of this study is to clarify the relationships between the B-site dopant of Ti-doped lanthanum strontium chromite and its sintering characteristics in air and its thermal expansion behavior.

**EXPERIMENTAL**

The Ti-doped lanthanum strontium chromite powders used for sintering characteristics in this study were prepared using the Pechini synthesis method. Aqueous solutions of La(NO$_3$)$_3$·6H$_2$O, Sr(NO$_3$)$_2$, Cr(NO$_3$)$_3$·9H$_2$O, Co(NO$_3$)$_3$·6H$_2$O, VC$_l$, Ni(NO$_3$)$_3$·6H$_2$O, and the organometallic Ti-compound were used for the synthesis. The nitrates, chlorides and organometallic compounds were mixed in desirable proportions, and citric acid (HO$_2$CCH$_2$C(OH)(CO$_2$H)CH$_2$CO$_2$H) was added to the solution in equivalent molar proportion to the amount of metal cations present, and then the mixture was heated to 100°C to form a viscous gel. The gel was then dried and fired at 800°C for 5 h to remove any remaining organic materials with a heating rate of 400°C/h.

In this study, the compositions of the samples with the perovskite structure were confirmed by ICP analysis and were in good agreement with the starting compositions within experimental error $\pm$ 2%. The typical compositions of the samples are summarized in Table I. All the samples were confirmed by powder X-ray diffractometry (XRD) (18 kW, Mac Science, M18XHF$^{22}$). A scanning rate of 0.02 °/s was used.

The sample powders calcined at the selected temperatures were used after milling with ethanol in a Y$_2$O$_3$-partially stabilized ZrO$_2$ ball mill with Y$_2$O$_3$-partially stabilized ZrO$_2$ balls. After drying, the powders were pressed into pellets with 20 mm diameter and approximately 2 mm thickness under a pressure of 70 MPa, and then sintered at selected temperatures with a heating rate of 200°C/h in air. The holding time at the selected temperatures was varied from 0 to 80 h. Zero hour means no holding time in this paper. Relative density was derived using the theoretical value determined from the experimental lattice parameters and unit formula.

Differential thermal analysis (DTA) measurement was carried out by a Mac Science TG-DTA5000S system in the temperature range from room temperature to 1600°C in air. A heating/cooling rate of 20°C/min was used. Reference used for the present measurements was $\alpha$-Al$_2$O$_3$ powder.
TEC was measured using a Mac Science TD5000S system. Samples were cut into rectangular shapes of 5 mm × 5 mm × 20 mm length. The reference used for the present measurements was a rod of fused silica in air, while a sapphire reference was used in H₂ atmosphere with a flow rate of 50 mL/min H₂ gas. H₂ gas was used during these measurements after it had been bubbled through pure water at 10°C. Measurement of the TECs was performed at a heating/cooling rate of 2°C/min from 50 to 1000°C in air. Although not strictly accurate from the academic viewpoint, the TECs of the materials in this study are calculated by the following equation (1):

\[ \alpha = \left( \frac{L_2 - L_1}{L_1} \right) \left( \frac{T_2 - T_1}{T_2 - T_1} \right) \]

where \( \alpha \) is the TEC, \( T_1 \) is the starting temperature, \( T_2 \) is the terminal temperature of an experiment, \( L_1 \) and \( L_2 \) are initial and final gauge lengths, respectively. We have confirmed that this dilatometer has an experimental error within ±0.06 x 10⁻⁶/°C for the measurement made in air and within ±0.1 x 10⁻⁶/°C for the measurement made in the H₂ atmosphere.

RESULTS AND DISCUSSION

Figures 1(a) and (b) show the relative density of the La₀.₈Sr₀.₂Cr₀.₉Ti₀.₁O₃ perovskite powder after heating at 800°C for 5 h, as a function of firing temperature with no holding time and as a function of holding time at selected temperatures. A green body had a relative density of approximately 39%. It is seen that the relative density of the perovskite was approximately 55% after 1600°C for 10 h, although a slight dependence was seen on the firing temperature and the holding time at selected temperatures. Generally, an acceptable relative density of the ceramic SOFC separator has been reported to be ≥ 94% [12]. Even using the fine powder with the average particle size of approximately 0.2 μm, the poor sintering characteristics of La₀.₈Sr₀.₂Cr₀.₉Ti₀.₁O₃ perovskite were not improved.

Figures 2, 3 and 4 show the XRD patterns of La₀.₈₊xSr₀.₂₋xCr₀.₉₋yTi₀.₀₈M₀.₀₂O₃ and La₀.₈Sr₀.₂₋xCr₀.₉₋yTi₀.₀₈M₀.₀₂O₃ (M = Ni and V) perovskites after heating at 1600°C for 10 h. It is clear in these figures that the (111) reflection, which is related to the orthorhombic perovskite structure, was not observed for all the perovskites. In addition, the main peak at around 32.5°, which corresponds to the (112) reflection of the orthorhombic phase, was split into the (104) and (110) ones of the hexagonal (rhombohedral) phase. Note that the (112) reflection is not strictly true, and the strict expression is the (200)(112)(002) reflections. As indicated in the literature [13], these XRD results suggest that all the perovskites showed the hexagonal cell, which was isostructural with the LaAlO₃ structure (Space group R-3c). In the systems of La₀.₈Sr₀.₂₋xCr₀.₉₋yTi₀.₀₈Ni₀.₀₂O₃ and La₀.₈Sr₀.₂₋xCr₀.₉₋yTi₀.₀₈Co₀.₀₂O₃, all the samples showed the single perovskite phase. In the La₀.₈Sr₀.₂₋xCr₀.₉₋yTi₀.₀₈V₀.₀₂O₃ system, the La₀.₈Sr₀.₂₋xCr₀.₉₋yTi₀.₀₈V₀.₀₂O₃ sample contained a very small amount of Sr₁(VO₄)₂ in addition to the hexagonal perovskite phase. It should be concluded that La₀.₈Sr₀.₂₋xCr₀.₉₋yTi₀.₀₈VₓO₃ perovskites form a solid-solution in the region of 0 ≤ x < 0.05.

Figures 5 and 6 show the lattice parameters and the cell volume of La₀.₈₊xSr₀.₂₋xCr₀.₉₋yTi₀.₀₈Co₀.₀₂O₃ and La₀.₈Sr₀.₂₋xCr₀.₉₋yTi₀.₀₈M₀.₀₂O₃ (M = Ni and V) perovskites after heating at 1600°C for 10 h. In Figure 5, the open and closed symbols represent x =
0.18 and x=0.15, respectively. In these figures, all the perovskites crystallized in a rhombohedral-hexagonal unit. Although it has been reported that the lattice parameters of La$_{0.9}$Sr$_{0.1}$Cr$_{0.9}$Co$_{0.1}$O$_3$ perovskites have a tendency to decrease with increasing Co content [11], the reverse results were observed for La$_{0.8+x}$Sr$_{0.2-x}$Cr$_{0.9}$Ti$_{0.1}$Co$_{0.1}$O$_3$ perovskite samples in this study. For the V-doped or Ni-doped perovskite samples, their lattice parameters increased with increasing B-site dopant content. When considering the TEC mechanism, the relationship between the type of B-site ions and TEC is very important. The effect of ionic radius of B-site dopant on the lattice parameters of the perovskite is rather complicated, and the study of the relationship is in progress.

Figures 7(a) and (b) show the relative density of the B-site doped perovskites after heating at 1000°C for 10 h as a function of firing temperature, and as a function of holding time at 1600°C. The B-site (Co, Ni and V) doping of the perovskite was effective in enhancing sintering characteristics. In particular, the V-doping provided remarkable improvement in sintering. For La$_{0.8}$Sr$_{0.2}$Cr$_{0.88}$Ti$_{0.1}$V$_{0.02}$O$_3$, a green body had relative density equal to approximately 49%. The densification of this material started at around 1200°C, and the main shrinkage took place in the temperature range from 1400°C to 1600°C. The relative density increased with increasing holding time and reached 85% at 1600°C for 40 h.

Figures 8(a) and (b) show the relative densities of the Ni-doped or V-doped perovskite samples after heating at 800°C for 5 h as a function of the B-site dopant content and the firing temperature. For the Ni-doped perovskite samples, their relative densities have a tendency to increase with increasing Ni content. On the other hand, the relative density of the V-doped samples at 1400°C and 1500°C increased with increasing V-content up to 2 mol%, and then decreased. For the firing temperature of 1600°C, their densities increased with increasing V content.

Figure 9 shows the DTA curves of La$_{0.8}$Sr$_{0.2}$Cr$_{0.9-y}$Ti$_{0.1}$V$_{y}$O$_3$ powders in air. Although it is not an easy task to clarify sintering mechanisms from the DTA data, no endothermic peaks, which are related to an appearance of a liquid phase, were observed. In addition, the sintering characteristics of the V-doped perovskite powders had a tendency to decrease with firing temperature: for the La$_{0.8}$Sr$_{0.2}$Cr$_{0.85}$Ti$_{0.1}$V$_{0.05}$O$_3$ powders, the relative density of the samples after heating at 1600°C for 40 h was 93% for the calcinations condition of 800°C for 5 h and 83% for the calcination condition of 1000°C for 10 h. These results suggest that V-doping suppresses the chromium-vapor component of the LaCrO$_3$ particles and the densification of the material occurs by a bulk ionic diffusion mechanism.

Figure 10 shows the XRD patterns of La$_{0.8}$Sr$_{0.2}$Cr$_{0.9-y}$Ti$_{0.1}$V$_{y}$O$_3$ powders after heating at 800°C for 5 h. All the samples contained a small amount of SrCrO$_4$. Because of the TEC mismatch between SrCrO$_4$ and the LaCrO$_3$, the densification of the LaCrO$_3$ perovskite is hindered more and more with increasing SrCrO$_4$ content [15]. In this case, since the content of SrCrO$_4$ was quite small, the influence of the phase on sintering should be negligible. It was noted that the XRD pattern of the La$_{0.8}$Sr$_{0.2}$Cr$_{0.85}$Ti$_{0.1}$V$_{0.05}$O$_3$ sample showed a small amount of Sr$_3$(VO$_4$)$_2$ second phase.

As described in the previous section, the La$_{0.8}$Sr$_{0.2}$Cr$_{0.85}$Ti$_{0.1}$V$_{0.05}$O$_3$ sample sintered at 1600°C for 10 h contained the Sr$_3$(VO$_4$)$_2$ phase. This means that the solubility limit of vanadium oxide into the LaCrO$_3$-based perovskite is < 0.05 even at 1600°C. This result indicates that the delay of the densification would be caused by the
formation of \( \text{Sr}_3(\text{VO}_4)_2 \). Therefore, the sintering mechanism of the V-doped lanthanum chromites should be as follows: Doping V metal at the B-site of perovskite structure remarkably enhances the sintering characteristics. Although the relative density of \( \text{La}_{0.8}\text{Sr}_{0.2}\text{Cr}_{0.9-x}\text{Ti}_{0.1}V_x\text{O}_3 \) perovskites has a tendency to increase with V-content, these perovskites form a solid-solution in the region of \( 0 \leq x < 0.05 \). For the case of \( \text{La}_{0.8}\text{Sr}_{0.2}\text{Cr}_{0.85}\text{Ti}_{0.1}V_{0.05}\text{O}_3 \), the excess vanadium oxide reacts with \( \text{SrO} \) in the perovskite and forms \( \text{Sr}_3(\text{VO}_4)_2 \). Initial atomic ratio of chromium, titanium and vanadium to combined lanthanum and strontium, \( [N(\text{Cr})+N(\text{Ti})+N(V)]/[N(\text{La})+N(\text{Sr})] \), was fixed at 1.00 in the present samples. By the appearance of \( \text{Sr}_3(\text{VO}_4)_2 \) phase, the stoichiometric composition of \( \text{La}_{0.8}\text{Sr}_{0.2}\text{Cr}_{0.85}\text{Ti}_{0.1}V_{0.05}\text{O}_3 \) sample should shift to an A-site lean region, and the excess chromium oxide starts the vaporization of chromium oxide and maintains the vaporization-condensation transport sintering mechanism. Therefore, \( \text{La}_{0.8}\text{Sr}_{0.2}\text{Cr}_{0.85}\text{Ti}_{0.1}V_{0.05}\text{O}_3 \) sample showed lower sintering characteristics when compared to \( \text{La}_{0.8}\text{Sr}_{0.2}\text{Cr}_{0.9}\text{Ti}_{0.1}V_{0.01}\text{O}_3 \) and \( \text{La}_{0.8}\text{Sr}_{0.2}\text{Cr}_{0.8}\text{Ti}_{0.1}V_{0.02}\text{O}_3 \) ones. At 1600°C, the reverse results were observed. The solubility limits of V metal into the perovskites should increase with increasing temperature and the A-site lean region in the perovskites should become smaller. Therefore, for \( \text{La}_{0.8}\text{Sr}_{0.2}\text{Cr}_{0.88}\text{Ti}_{0.1}V_{0.02}\text{O}_3 \), V-doping had an enhancing effect on densification.

\( \text{La}_{0.8}\text{Sr}_{0.2}\text{Cr}_{0.9-x}\text{Ti}_{0.1}V_x\text{O}_3 \) perovskite has been considered for the separator material in high-temperature solid oxide fuel cells (SOFC) from the viewpoint of thermal expansion compatibility between oxidizing and reducing atmospheres. Therefore, the effect of V-doping of the perovskite on its thermal expansion behavior is very important. Figure 11 shows the thermal expansion curves of the \( \text{La}_{0.8}\text{Sr}_{0.2}\text{Cr}_{0.88}\text{Ti}_{0.1}V_{0.02}\text{O}_3 \) perovskite in air or the \( \text{H}_2 \) atmosphere in comparison with \( \text{8YSZ} \) electrolyte. Although a large expansion in thermal curve of this material during the first heating cycle in the \( \text{H}_2 \) atmosphere was observed, it was not dramatic. It is seen in this figure that, during the measurement made in air and in the second heating cycle of the \( \text{H}_2 \) atmosphere, the thermal expansion curves of \( \text{La}_{0.8}\text{Sr}_{0.2}\text{Cr}_{0.88}\text{Ti}_{0.1}V_{0.02}\text{O}_3 \) perovskite had no anomaly and were quite similar to that of \( \text{8YSZ} \) electrolyte.

Figure 12 shows the TECs of \( \text{La}_{0.8}\text{Sr}_{0.2}\text{Cr}_{0.9-x}\text{Ti}_{0.1}V_x\text{O}_3 \) in the temperature range from 50 to 1000°C in air or the \( \text{H}_2 \) atmosphere. The TEC of \( \text{8YSZ} \) electrolyte was \( 10.3 \times 10^{-6}/°C \) in air and the TEC values are shown with the broken lines in Fig. 12. The TECs of V-doped perovskites have a tendency to decrease with increasing V content. The TEC of \( \text{La}_{0.8}\text{Sr}_{0.2}\text{Cr}_{0.88}\text{Ti}_{0.1}V_{0.02}\text{O}_3 \) perovskite was \( 10.2 \times 10^{-6}/°C \) in air, \( 10.6 \times 10^{-6}/°C \) during the first heating cycle and \( 10.4 \times 10^{-6}/°C \) during the second heating cycle in the \( \text{H}_2 \) atmosphere (oxygen partial pressure : \( 4 \times 10^{-19} \text{ atm} \) at 1000°C). For the measurements made in air, the thermal expansion behaviors of the V-doped perovskite samples during the second heating cycle were similar to those during the first one, and for the measurements made in the \( \text{H}_2 \) atmosphere, the behaviors during the third heating cycle were almost similar to those during the second one. It is well known that the large TEC in the \( \text{H}_2 \) measurement is related with the oxygen vacancy formation in the perovskites by the release of oxygen. In the second heating cycle, the TEC was smaller when compared to that during the first heating cycle. The reason for this is that the oxygen vacancies of the perovskites remained unchanged at 50°C and the difference in the vacancies between 50 and 1000°C was smaller when compared to that of the first heating cycle.

**CONCLUSIONS**
The effects of B-site dopants (V, Co and Ni) in the La$_{0.8}$Sr$_{0.2}$Cr$_{0.88}$Ti$_{0.10}$O$_3$–based perovskites with a B-site dopant content ≤ 5 mol% on their air-sintering characteristics and thermal expansion behaviors have been studied using the fine powders made by the Pechini method. It was found that the fine perovskite powders show a remarkable improvement in their sintering characteristics by V-doping. The thermal expansion behaviors of La$_{0.8}$Sr$_{0.2}$Cr$_{0.88}$Ti$_{0.1}$V$_{0.02}$O$_3$ perovskite were quite similar to those of the 8YSZ electrolyte in air or in the H$_2$ atmosphere. La$_{0.8}$Sr$_{0.2}$Cr$_{0.88}$Ti$_{0.1}$V$_{0.02}$O$_3$ perovskite is a promising candidate material for the SOFC separators with respect to thermal expansion and sintering characteristics.

REFERENCES

1. H. Itoh, M. Mori, N. Mori, and T. Abe, J. Power Sources, 49, 315(1994).
2. Y. Hiei, T. Yamamoto, H. Itoh, and M. Mori, Proc. 3rd European Solid Oxide Fuel Cell Forum/1998, P. Stevens, Editors, Nantes, France, (1998)p.89-96.
3. M. Mori and Y. Hiei, J. Am. Ceram. Soc., Published in 2001.
4. G. M. Christie, P. H. Middleton, B. C. H. Steele, J. Eur. Ceram. Soc., 14, 163(1994).
5. R. Koc and H. U. Anderson, J. Eur. Ceram. Soc., 9, 285(1992).
6. R. Koc and H. U. Anderson, J. Mater. Sci., 27, 5837(1992).
7. S. Hayashi, K. Fukaya, and H. Saito, J. Mater. Sci. Lett., 7, 457(1988).
8. P. S. Devi and M. S. Rao, Mater. Res. Bull., 28[10], 1075(1993).
9. H. Hayashi, K. Fukaya and H. Saito, J. Ceram. Soc. Japan, 100[8], 1078(1992).
10. H. Zhou, H. Taira, H. Takagi, and K. Tomono, J. Soc., Mat. Sci., Japan, 45[6], 604(1996).
11. M. Mori, Y. Hiei, and N. M. Sammes, in Proceedings of 3rd International Fuel Cell Conference, Japan, 437(1999).
12. B. K. Flandermeyer, J. T. Desek, P. E. Blackburn, D. W. Dees, C. C. McPheeters, and R. B. Poeppele, Abstract Fuel Cell Seminar, Tucson, Arizona, (1986)p.68-71.
13. O. Muller and R. Roy, “The Major Ternary Structural Families”, Chap. 4, Springer-Verlag, Berlin, (1974).
14. R. D. Shannon and C. T. Prewitt, Acta. Crystallogr., B25, 925(1969).
15. M. Mori, Y. Hiei, and N. M. Sammes, Solid State Ionics, Published in 2001.

Table I Typical compositions of the B-site-doped lanthanum strontium chromite perovskites before and after heating at 1600°C for 10 h.

| Perovskites | La$_{0.8}$Sr$_{0.2}$Cr$_{0.88}$Ti$_{0.1}$V$_{0.02}$O$_3$ | La$_{0.8}$Sr$_{0.2}$Cr$_{0.85}$Ti$_{0.1}$V$_{0.05}$O$_3$ |
|-------------|---------------------------------|---------------------------------|
| Treatment   | Before                          | After                           | Before                          | After                           |
| La          | 0.80                            | 0.80                            | 0.80                            | 0.80                            |
| Sr          | 0.20                            | 0.20                            | 0.20                            | 0.20                            |
| Cr          | 0.88                            | 0.88                            | 0.85                            | 0.86                            |
| Ti          | 0.10                            | 0.10                            | 0.10                            | 0.10                            |
| V           | 0.02                            | 0.02                            | 0.05                            | 0.04                            |
Fig. 1 Relative densities of the La$_{0.8}$Sr$_{0.2}$Cr$_{0.9}$Ti$_{0.1}$O$_3$ perovskite, (a) as a function of temperature with no holding time and (b) as a function of holding time at selected temperatures.

Fig. 2 XRD patterns of the perovskites after heating at 1600°C for 10 h in air.
(a) La$_{0.8}$Sr$_{0.2}$Cr$_{0.9}$Ti$_{0.1}$O$_3$
(b) La$_{0.85}$Sr$_{0.15}$Cr$_{0.8}$Ti$_{0.05}$Co$_{0.02}$O$_3$
(c) La$_{0.82}$Sr$_{0.18}$Cr$_{0.9}$Ti$_{0.08}$Co$_{0.02}$O$_3$

Fig. 3 XRD patterns of the perovskites after heating at 1600°C for 10 h in air.
(a) La$_{0.8}$Sr$_{0.2}$Cr$_{0.85}$Ti$_{0.1}$Ni$_{0.01}$O$_3$
(b) La$_{0.8}$Sr$_{0.2}$Cr$_{0.8}$Ti$_{0.1}$Ni$_{0.02}$O$_3$
(c) La$_{0.8}$Sr$_{0.2}$Cr$_{0.85}$Ti$_{0.1}$Ni$_{0.05}$O$_3$
Fig. 4 XRD patterns of the perovskites after heating at 1600°C for 10 h in air.
(a) La_{0.8}Sr_{0.2}Cr_{0.89}Ti_{0.1}V_{0.01}O_3
(b) La_{0.8}Sr_{0.2}Cr_{0.88}Ti_{0.1}V_{0.02}O_3
(c) La_{0.8}Sr_{0.2}Cr_{0.85}Ti_{0.1}V_{0.05}O_3

Fig. 5 Lattice parameters and cell volumes of the perovskites after heating at 1600°C for 10 h in air.
The open symbols : x = 0.18
The closed symbols : x = 0.15

Fig. 6 Lattice parameters and cell volumes of (a) La_{0.8}Sr_{0.2}Cr_{0.9-x}Ti_{0.1}Ni_{x}O_3 and (b) La_{0.8}Sr_{0.2}Cr_{0.9-x}Ti_{0.1}V_{x}O_3 perovskites after heating at 1600°C for 10 h in air.
Fig. 7 Relative densities of La$_{0.85}$Sr$_{0.15}$Cr$_{0.5}$Ti$_{0.05}$Co$_{0.02}$O$_3$ and La$_{0.85}$Sr$_{0.2}$Cr$_{0.5}$Ti$_{0.1}$M$_{0.02}$O$_3$ (M = Ni and V) perovskite, (a) as a function of temperature with no holding time and (b) as a function of holding time at selected temperatures.

Fig. 8 Density of La$_{0.8}$Sr$_{0.2}$Cr$_{0.9}$Ti$_{0.1}$Ni$_x$O$_3$ (a) and La$_{0.8}$Sr$_{0.2}$Cr$_{0.9}$Ti$_{0.1}$V$_x$O$_3$ (b) after heating at selected temperatures for 20 h.
Fig. 9 DTA curves of the perovskite powders calcined at 800°C for 5 h.

Fig. 10 XRD patterns of La$_{0.8}$Sr$_{0.2}$Cr$_{0.9-x}$Ti$_{0.1}$V$_x$O$_3$ perovskites after heating at 800°C for 5 h in air.

- : Sr$_3$(VO$_4$)$_2$
- : SrCrO$_4$

Fig. 11 Expansion behaviors of La$_{0.8}$Sr$_{0.2}$Cr$_{0.9-x}$Ti$_{0.1}$V$_x$O$_3$ perovskites in air or in a H$_2$ atmosphere.

Fig. 12 TECs of La$_{0.8}$Sr$_{0.2}$Cr$_{0.9-x}$Ti$_{0.1}$V$_x$O$_3$ in the temperature range from 50 to 1000°C in air or a H$_2$ atmosphere as a function of V content.