JOURNAL OF MATERIALS SCIENCE **38** (2003) 3431 – 3435

Formation, densification, and electrical conductivity of air-sinterable $(Sm_{1-x}Ca_x)CrO_3$ prepared through citric acid route

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In Ca^{2+}-substituted $SmCrO_3$, single-phase perovskite $(Sm_{1-x}Ca_x)CrO_3$, where $x = 0$ to 0.27, have been formed at low temperatures by a citric acid processing. $(Sm_{1-x}Ca_x)CrO_3$ powders consisting of submicrometer-size particles are sinterable; dense materials can be fabricated by sintering for 2 h at 1700°C under atmospheric pressure. The relative densities, grain sizes, and electrical conductivities increase with increased Ca^{2+} content. $(Sm_{0.73}Ca_{0.27})CrO_3$ materials show an excellent electrical conductivity of 2.6×10^3 $S \cdot m^{-1}$ at 1000°C. © *2003 Kluwer Academic Publishers*

1. Introduction

Refractory ABO_3 perovskite materials exhibit relatively high electrical conductivities at elevated temperatures by substitution of either A or B sites with acceptor- or donor-type cations. Consequently, there has been considerable interest in them as high-temperature electrochemical devices. In $ACrO_3$ (A = La, Y, Nd and Sm) perovskite system, many investigations have been focussed on pure and doped materials of the former two. Little attention has been given to the sintering and electrical conductivity of the last two, especially in $SmCrO_3$. Pure $SmCrO_3$ has been prepared by a solid-state reaction [1] and a combustion synthesis [2, 3]. Schneider *et al.* [1] studied the solid-state reaction of an equimolar mixture between Sm_2O_3 and Cr_2O_3 and reported that single-phase $SmCrO_3$ was obtained when heated at 1600°C. On the other hand, combustion synthesis resulted in the formation of $SmCrO_3$ at very low temperatures. Kingsley and Pederson [2] prepared $SmCrO_3$ powders with the crystallite size of ∼30 nm by the exothermic redox decomposition of ammonium dichromate, samarium nitrate, and glycine mixtures at ∼175°C. Moreover, $SmCrO_3$ powders with fine particles of ∼0.1 μm were prepared by the combustion of corresponding metal nitrate and tetraformal trisazine ($C_4H_{16}N_6O_2$) in a few minutes at ∼425°C under ambient conditions [3]. However, no studies on sintering were performed. Unfortunately, $SmCrO_3$, as well as other lanthanide chromites, shows poor sinterablity and is very difficult to densify under atmospheric conditions. Tripathi and Lal [4, 5] studied the AC electrical conductivity of $SmCrO_3$ with the relative density of ∼67% and reported that the value was as low as 2.1×10^{-1} $S \cdot m^{-1}$ at 500 K and 1 kHz. Palguev *et al.* [6] fabricated $Sm_{0.8}Ca_{0.2}CrO_3$ materials[1] by heating for 3 h at 1500°C in air. They showed the DC electrical conductivity of 6.3×10^2 and 1.0×10^1 $S \cdot m^{-1}$ at 1000°C in air and a wet hydrogen atmosphere (2.5% H_2O), respectively.

Two heating steps have been required for the fabrication of dense $LaCrO_3$ and $YCrO_3$ materials with high electrical conductivities [7, 8]: (i) sintering under reduced pressure and (ii) annealing in air in order to fully oxidize the samples. $NdCrO_3$ materials[1] were fabricated by sintering for 24 h at 1300°C in an oxygen atmosphere [9]. As will be described, they gave a much lower electrical conductivity, in comparison with that of $LaCrO_3$ and $YCrO_3$. This might be explained in terms of lower densities due to their poor sinterabilty in an oxidation atmosphere. Therefore, air-sinterable powders are required for the preparation of lanthanide chromites.

A solution technique using citric acid as a gelling agent has been developed to produce air-sinterable powders [10, 11]. This method has some features as follows: (i) formation of gel free from pH values, (ii) easy preparation of stoichiometric composition powders, and (iii) no requirement of washing.

In this study, we tried to apply this method to obtain reactive $SmCrO_3$ and $(Sm_{1-x}Ca_x)CrO_3$ powders. Single-phase perovskite $(Sm_{1-x}Ca_x)CrO_3$, where $x = 0$–0.27, were found to form at low temperatures. Dense materials could be fabricated without any control of oxygen pressure. The present paper deals with the formation, sintering, and conductivity of such $(Sm_{1-x}Ca_x)CrO_3$.

2. Experimental procedure

Samarium chloride ($SmCl_3 \cdot 6H_2O$, 99.9% pure), chromium chloride ($CrCl_3 \cdot 6H_2O$, 99.9% pure), calcium

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[1] No data for densification was described.

TABLE I Starting compositions and characteristics of $(Sm_{1-x}Ca_x)CrO_3$ $(0 \leq x \leq 0.27)$ materials sintered for 2 h at 1700°C in air

Sample	x in $(Sm_{1-x}\ Ca_x)\ CrO_3$	Bulk and relative densities $(Mg \cdot m^{-3}, \%)$	Grain size G_s (μm)	Activation enegry E_a (eV)	Electrical conductivity σ at 1000°C $(S \cdot m^{-1})$
A	0	7.02 (95.1)	2.2	0.23	1.6×10^2
B	0.05	6.91 (95.4)	2.4	0.22	2.4×10^2
C	0.10	6.78 (95.5)	2.8	0.21	4.4×10^2
D	0.15	6.81 (97.8)	3.6	0.21	7.3×10^2
E	0.20	6.68 (97.8)	4.2	0.20	1.4×10^3
F	0.25	6.56 (98.2)	5.1	0.19	2.2×10^3
G	0.27	6.54 (98.6)	5.4	0.19	2.6×10^3
H	0.30	–	–	–	–
I	0.35				

chloride $(CaCl_2 \cdot 2H_2O$, 99.9% pure), and citric acid $(C(CH_2COOH)_2(OH)(COOH))$ were used as starting materials. Table I shows the starting compositions. Appropriate amounts of starting materials corresponding to each composition were dissolved into a 0.5 L distilled water. A four-necked flask was equipped with a dropping funnel, a stirring rod, a thermometer and a thermocontroller. A mixed solution with the concentration of 2 mol/L (pH 2) was introduced into the flask and then heated to 70°C. Citric acid was added to the mixed solution at the same temperature, with stirring, to concentrate to the gelatinous state. The resulting gel product was dried for 12 h at 120°C. Differential thermal analysis (DTA) was performed in air at a heating rate of 10°C/min; α-Al_2O_3 was used as the reference in DTA. The as-prepared powders and specimens, obtained from DTA runs after cooling, were examined by X-ray diffraction (XRD) using Cu K_α radiation and a goniometer scanning speed of 0.25°/min. Interplanar spacings were measured with the aid of an internal standard of high-purity Si, and unit-cell values were determined by a least-squares refinement. Particle size was observed with a transmission electron microscope (TEM). Before sintering calcined powders (1000°C/2 h)[2] were pressed into pellets at 196 MPa and then isostatically cold-pressed at 392 MPa. The compacts (diameter ∼15 mm^{ϕ} and thickness ∼5 mm^{h}) covered with the powders, in which each as-prepared was heated for 2 h at 1750°C were put on the high-purity alumina setter and then sintered for 2 h at 1700°C in air. Bulk densities after polishing with diamond paste (nominal size 1 to 3 μm) were determined by the Archimedes method. Scanning electron microscopy (SEM) was used for microstructural observations. Direct current (DC) electrical conductivity was measured from 400° to 1000°C by the van der Pauw method [12]. Platinum leads (diameter 0.2 mm^{ϕ}) were fixed onto the disk-shaped specimen (diameter ∼13 mm^{ϕ} and thickness ∼1 mm^{h}) with platinum paste and then heated for 1 h at 1100°C. Each measuring run was performed in air.

3. Results and discussion

3.1. Formation of perovskite $(Sm_{1-x}Ca_x)CrO_3$

As-prepared powders A through I were amorphous to X-ray. DTA curves revealed broad exothermic peaks resulting from a combustion of citric acid at ∼350° to ∼500°C. No significant change in structure was observed up to ∼780°C. Although no peaks were detected in the DTA, the XRD lines of the perovskite phase began to appear when heated at 800°C, and they increased in intensities to 1000°C. The formation was completed by heating for 1 h at 1000°C. Single-phase perovskite compounds were obtained in powders A through G. For powders H and I, small amounts of $CaCrO_4$ [13] were presented in the specimens after heating at 1000°C; the specimens heated at temperatures ≥1000°C were mixtures of $(Sm_{1-x}Ca_x)CrO_3$[3] and $CaCrO_4$. All diffraction lines for pure $SmCrO_3$ were indexed as an orthorhombic unit cell with $a = 0.5368$, $b = 0.5496$ and $c = 0.7647$ nm, which were in good agreement with earlier data ($a = 0.53697$, $b = 0.54947$ and $c = 0.76489$ nm) [14]. Compositional changes result in a significant variation in cell dimensions. Fig. 1 shows the variation of lattice parameters for $(Sm_{1-x}Ca_x)CrO_3$ prepared by heating for 1 h at 1000°C. Up to 27 mol% Ca^{2+} content the values of the $(Sm_{1-x}Ca_x)CrO_3$ phase decreased linearly: a $(0.5368 \rightarrow 0.5356$ nm), b $(0.5496 \rightarrow 0.5426$ nm) and c $(0.7647 \rightarrow 0.7583$ nm). Thus, single-phase $(Sm_{1-x}Ca_x)CrO_3$, where $x = 0$–0.27, was found to be formed by the citric acid processing.

Fig. 2 shows TEM photographs of $SmCrO_3$ powders heated to various temperatures, indicating round-shape morphology consisting of submicrometer-size particles with a considerable degree of agglometry. The particles grew to 280 nm (1000°C), 340 nm (1100°C) and 450 nm (1200°C) with increased temperature.

3.2. Sintering and microstructure

The as-prepared powders A through G were calcined. The calcined powders were sintered as already described. XRD analysis showed that the materials thus obtained consisted of only perovskite phase. Table I shows the bulk and relative densities of $(Sm_{1-x}Ca_x)CrO_3$ materials. The relative densities were estimated using theoretical densities calculated from molecular weights, $Z = 4$ [14], Avogadro's number, and lattice parameters. Pure $SmCrO_3$ materials had

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[2] No chloride ions (tested by adding a $AgNO_3$ solution) were detected.

[3] The evidence that Ca^{2+} was substituted into the A-site was confirmed by X-ray Rietveld analysis [15]; the indicators S (goodness-of-fit) for samples A ($x = 0$) and F ($x = 0.25$) gave the smallest values of 1.2 and 1.4, respectively when the distribution of Sm^{3+}/Ca^{2+} was presumed to be 1/0 and 0.75/0.25 on the A-site of the perovskite structure.

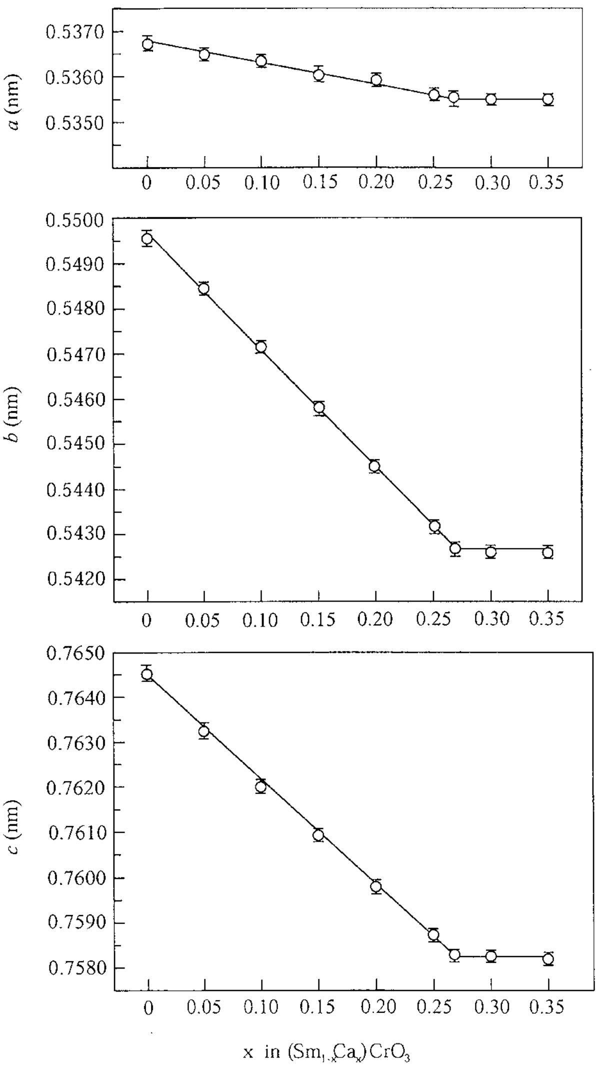

Figure 1 Lattice parameters of orthorhombic $SmCrO_3$ phase obtained by heating for 1 h at 1000°C in air.

a bulk density of 7.02 Mg/m^3, corresponding to 95.1% of theoretical density (7.38 Mg/m^3) [14].[4] The relative densities increased with increased Ca^{2+} content. Finally, $(Sm_{0.73}Ca_{0.27})CrO_3$ materials had 98.6% of theoretical.

Fig. 3 shows SEM photographs for fracture surfaces of $(Sm_{1-x}Ca_x)CrO_3$ materials. Their textures were of a homogeneous structure consisting of well-sintered octahedral grains. Average grain sizes were determined by direct SEM observation. As shown in Table I, they increased from 2.2 to 5.4 μm with increased Ca^{2+} content. Note that the dense materials could be fabricated by sintering in air. This result suggests that the present powders were sinterable.

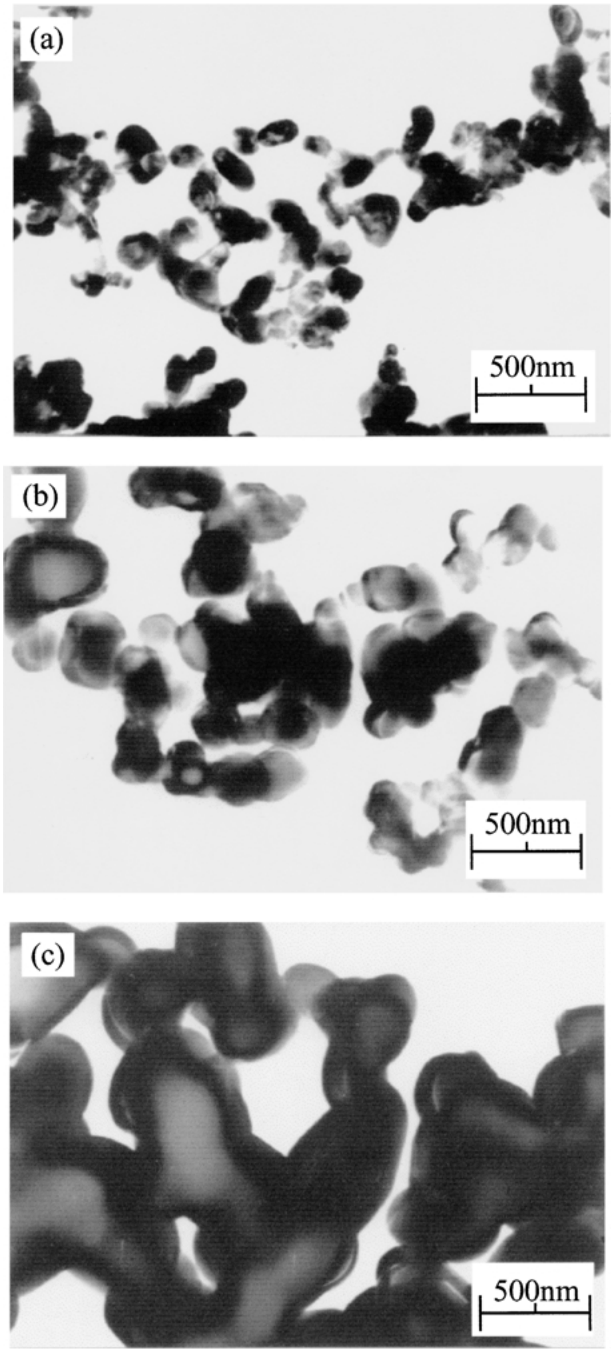

Figure 2 TEM photographs of $SmCrO_3$ powders heated to (a) 800°, (b) 1000°, and (c) 1200°C.

3.3. Electrical conductivity

The temperature dependence of electrical conductivity (σ) of $SmCrO_3$ materials in a plot of log (σT) against reciprocal absolute temperature $1/T$ is shown in Fig. 4 and compared with those of dense $LaCrO_3$ [7] and $YCrO_3$ [8] materials which gave the best data and porous $NdCrO_3$ materials [9][5] described earlier. These materials have been indicated that they were *p*-type semiconductors and their electrical conductivities were essentially due to the *3-d* band of the ions through the formation of cation vacancies [16, 17]. In addition, small-polarons seemed to be responsible for the conduction in rare earth ortho-chromites [17]. The conductivities of pure rare-earth chromites are well represented by the function of $(1/T) \cdot \exp(-E_a/kT)$, where T is the absolute temperature, E_a the activation energy, and k the Boltzmann constant. The value of $1.6 \times 10^2\ S \cdot m^{-1}$ was obtained at 1000°C. This value was

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[4] Sintering for 2 h at 1500° and 1600°C gave the materials with the relative densities of 72.5 and 83.3%, respectively.

[5] No densification occurred in the same powder preparation and sintering conditions as described in the literature [9].

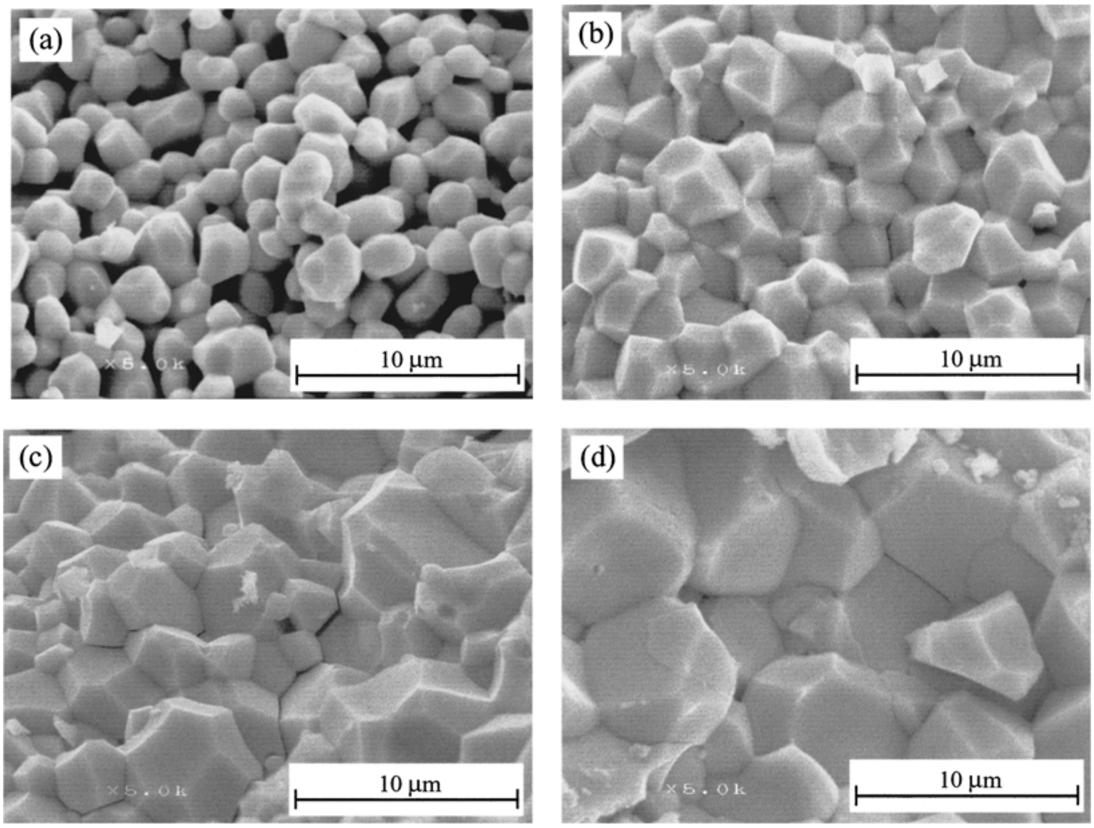

Figure 3 SEM photographs for fracture surfaces of (a) $SmCrO_3$, (b) $(Sm_{0.95}Ca_{0.05})CrO_3$, (c) $(Sm_{0.85}Ca_{0.15})CrO_3$, and (d) $(Sm_{0.75}Ca_{0.25})CrO_3$ materials.

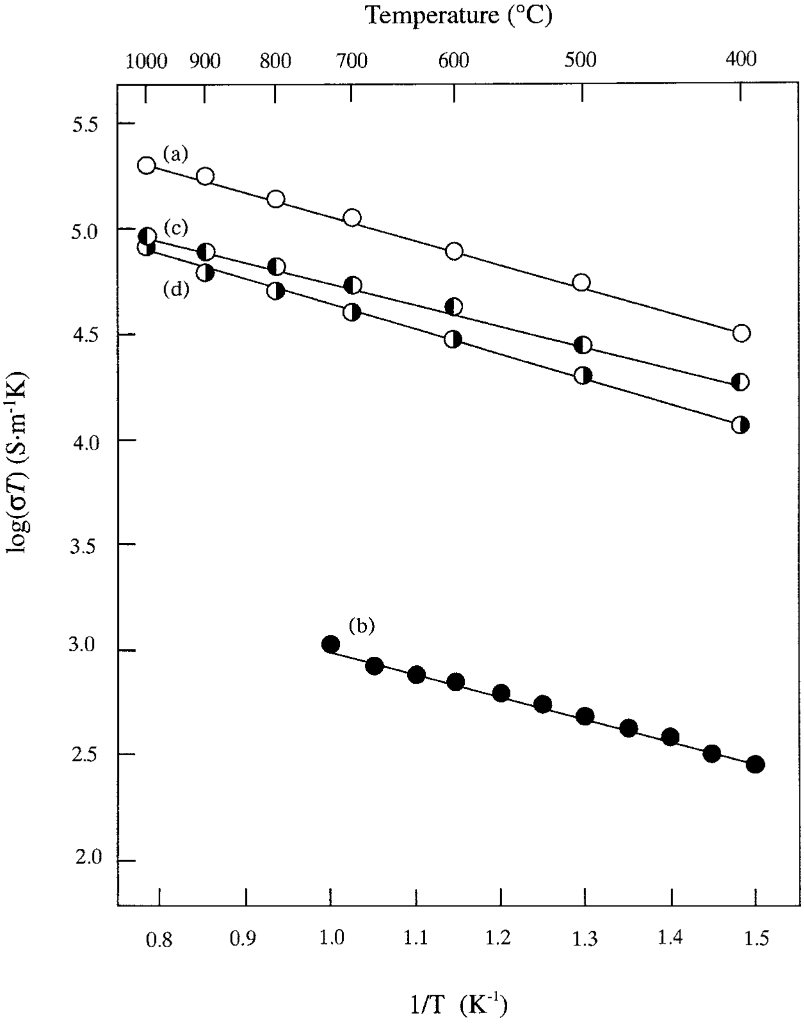

Figure 4 Log(σT) for (a) $SmCrO_3$, (b) $NdCrO_3$, (c) $LaCrO_3$, and (d) $YCrO_3$ materials as a function of $1/T$.

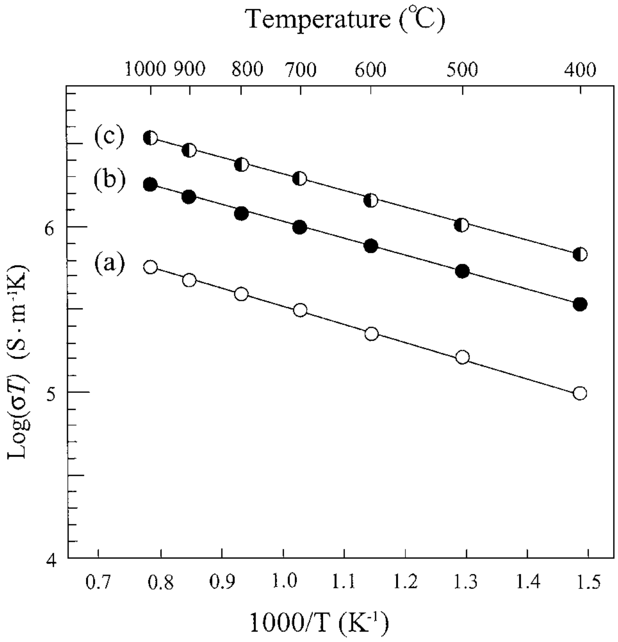

Figure 5 Log(σT) for (a) ($Sm_{0.90}Ca_{0.10}$)CrO_3, (b) ($Sm_{0.80}Ca_{0.20}$)CrO_3, and (c) ($Sm_{0.73}Ca_{0.27}$)CrO_3 materials as a function of $1/T$.

higher >2 times than those of $LaCrO_3$ (70.3 $S \cdot m^{-1}$) and $YCrO_3$ (61.1 $S \cdot m^{-1}$) materials. Thus, the electrical conductivity of $SmCrO_3$ must be originated from the 3 *d*-electrons. The activation energy (E_a) was determined to be 0.23 eV.

Fig. 5 shows the temperature dependences of σ for ($Sm_{1-x}Ca_x$)CrO_3 materials ($x = 0.10$, 0.20 and 0.27). Sakai *et al.* [18] studied the sinterability of calcium-doped lanthanum chromites (($La_{1-x}Ca_x$)-($Cr_{1-y}Ca_y$)O_3) and their electrical conductivity and reported that the linear dependence of log(σT) vs. $1/T$ at 770 to 1400 K was characteristic of the small-polaron hopping transport which was often observed in chromium-based perovskites [19, 20]. Table I shows σ data at 1000°C. The σ value increased with increased Ca^{2+} content. Finally, the ($Sm_{0.73}Ca_{0.27}$)CrO_3 materials showed the value of 2.6×10^3 $S \cdot m^{-1}$, in which the magnitude of σ is comparable to those of Sr^{2+}- and Ca^{2+}-substituted $LaCrO_3$ [7, 16–18]. Our structural[6] and electrical[7] data were applied to a model for hopping transport [21]. Hole mobility μ_p in the highest conductivity material was calculated to be 3.31×10^{-6} m^2/Vs. Then, ω_0 the frequency of a characteristic optical phonon was determined to be 3.53×10^{13} s^{-1}, which the value satisfied such condition as ω_0 ($h/2\pi$) $\ll kT$, where h is the Planck constant, k the Boltzmann constant, and T the absolute temperature. This condition has been required for small-polaron hopping mechanism [22]. Thus increase in the conductivity up to the Ca^{2+}-substituted level of $x \leq 0.27$ must be attributed to the formation of Cr^{4+} ions as a result of charge compensation caused by the hopping polarons between Cr^{3+} and Cr^{4+} ions.

4. Conclusion

Little attention has been given to the sintering and electrical conductivity of $SmCrO_3$. The citric acid gel processing results in the formation of ($Sm_{1-x}Ca_x$)CrO_3 at ~800° to ~1000°C. An extensive region up to $x = 0.27$ occurs in which the perovskite structure is present as a single phase. ($Sm_{1-x}Ca_x$)CrO_3 powders are sinterable. Dense sintered materials can be obtained without any control of oxygen pressure. Pure $SmCrO_3$ materials are higher >2 times than $LaCrO_3$ and $YCrO_3$ materials in electrical conductivity at 1000°C. Electrical conductivity increases with increased Ca^{2+} content. ($Sm_{0.73}Ca_{0.27}$)CrO_3 materials exhibit an excellent electrical conductivity at elevated temperatures.

Acknowledgments

This work was supported by a grant to Research Center for Advanced Science and Technology at Doshisha University from the Ministry of Education, Japan.

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Received 6 November 2002
and accepted 5 June 2003

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[6] The equilibrium lattice parameter $\langle a \rangle = (abc)^{1/3} = 0.6041$ nm was calculated from the measured lattice parameters ($a = 0.5356$, $b = 0.5426$, and $c = 0.7583$ nm).

[7] The concentration of charge carrier (hole) $p = 4.90 \times 10^{27}$ m^{-3} and the activation energy $E_a = 0.19$ eV were used.