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Thermal Expansion and Electrical Conductivity of $CaTi_{0.9}M_{0.1}O_{3-\delta}$ (M = Fe, Cu, Al)

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Abstract—The thermal expansion of $CaTi_{0.9}M_{0.1}O_{3-\delta}$ (M = Fe, Cu, Al) samples has been measured, and their lattice parameters have been refined in space group *Pnma*. The three materials are shown to be mixed conductors, *p*-type at high oxygen partial pressures and *n*-type at low oxygen pressures. At intermediate oxygen partial pressures, the conductivity varies little. The acceptor dopants studied are shown to raise the conductivity of calcium titanate in the order Al < Cu < Fe.

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INTRODUCTION

Perovskite oxides with mixed oxygen-ionic/electronic conductivity may find application as oxygen-permeable membranes in electrochemical converters for hydrogen production from hydrogen-containing gases, oxygen generation via air separation, and conversion of methane to syngas [1]. Doped calcium titanate is potentially attractive as membrane material [2] since it possesses sufficient stability in reducing atmospheres [3], high ionic and electronic conductivity [4, 5], and acceptable oxygen permeability [6].

Precise knowledge of the structural, electrical, and thermomechanical properties of materials is crucial for deciding in what area they can be applied. The purpose of this work was to study the effect of acceptor doping on the properties of calcium titanate.

EXPERIMENTAL

Samples for this investigation were prepared by a standard ceramic processing route, using analytical-grade $CaCO_3$, Fe_2O_3, TiO_2, Al_2O_3, and CuO as starting materials. Appropriate oxide mixtures were reacted at 1470 K for 2 h. Next, the samples were thoroughly ground and pressed into pellets, which were sintered at 1740 K for 2 h and then quenched to room temperature.

The phase composition of the samples was determined by x-ray diffraction (XRD) on a DRON-UM1 automated diffractometer ($2\theta = 20°–80°$). The phases present were identified using JCPDS Powder Diffraction File data and the fpeak.exe software package [7]. The lattice parameters of individual phases were refined by the Rietveld profile analysis method [8, 9]. The algorithm proposed by Rietveld was implemented in many programs, some of which can be found on the IUCr server [10]. We used the Fullprof program [11].

Electrical conductivity was measured by a four-probe dc method, using the client.exe software. The sample, placed in a holder with Pt pressure contacts, was mounted in a Y_2O_3-stabilized ZrO_2 tube, the walls of which were fitted with electrodes for an electrochemical oxygen pump and oxygen sensor, and the tube was tightly sealed. The temperature was monitored with a Pt/Pt–Rh thermocouple. The temperature and oxygen partial pressure were varied from 298 to 1270 K and from 10^{-9} to 0.21×10^5 Pa using a Zirkonia-318 microprocessor controller [7].

Thermal expansion was measured in air ($p_{O_2} = 0.21 \times 10^5$ Pa) during heating from 298 to 1170 K using an AF-1 dilatometer. Bar-shaped ceramic samples were prepared in the same manner as those for conductivity measurements. The heating/cooling rate was typically ~200 K/h. The linear thermal expansion coefficient at constant pressure, α, was determined using the well-known relation

$$\alpha = \frac{1}{L_0}\left(\frac{\partial L}{\partial T}\right)_p, \qquad (1)$$

as the slope of the $\Delta L/L(T)$ curve.

RESULTS AND DISCUSSION

XRD examination showed that the samples with the nominal compositions $CaTi_{0.9}M_{0.1}O_{3-\delta}$ (M = Fe, Cu, Al) were single-phase and had an orthorhombically distorted perovskite structure (sp. gr. *Pnma*). Figure 1 shows the XRD pattern of $CaTi_{0.9}Fe_{0.1}O_{3-\delta}$. The refined lattice parameters are listed in Table 1. It can be seen from these data that the lattice parameters of our

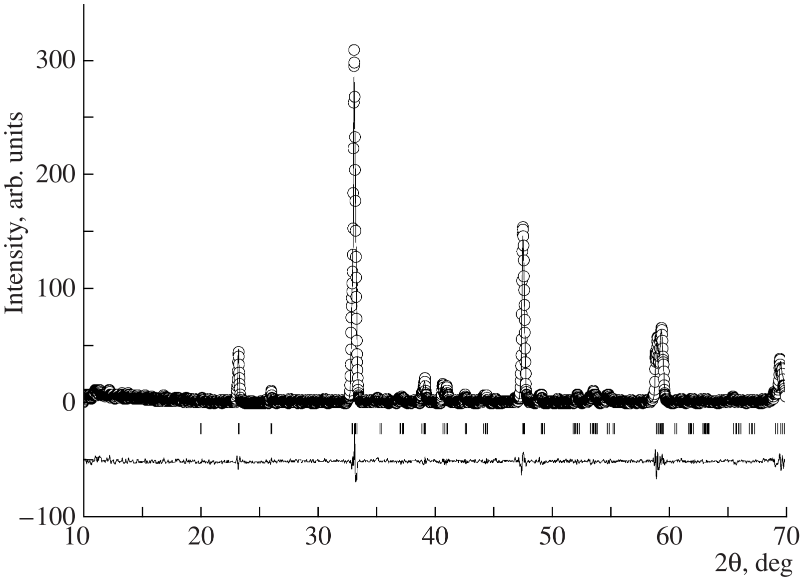

Fig. 1. XRD pattern of $CaTi_{0.9}Fe_{0.1}O_{3-\delta}$.

samples are governed not by the size of solute ions [12] but by some other factors, e.g., by oxygen stoichiometry.

The conductivity data for $CaTi_{0.9}M_{0.1}O_{3-\delta}$ (M = Fe, Cu, Al) are presented in Fig. 2. The log–log plots of conductivity versus oxygen partial pressure for calcium titanate acceptor-doped with Fe, Cu, and Al are characteristic of mixed conductors [13]. At high oxygen partial pressures, the conductivity is nearly proportional to $p_{O_2}^{1/4}$ since oxygen incorporation into lattice sites increases the carrier (hole) concentration according to the scheme [14]

$$V_O^{\bullet\bullet} + \frac{1}{2}O_2 = O_O^{\times} + 2h^{\bullet}. \quad (2)$$

Here, the concentration of oxygen vacancies $V_O^{\bullet\bullet}$ is a constant determined by the doping level. Therefore, the hole concentration and, hence, the conductivity vary as $p_{O_2}^{1/4}$:

$$\sigma \sim p = \mathrm{const}\, p_{O_2}^{1/4}. \quad (3)$$

At intermediate oxygen partial pressures, the plots in Fig. 2 have a broad plateau, indicating that ionic conduction prevails:

$$[(\mathrm{Fe, Al})'_{Ti}] = 2[V_O^{\bullet\bullet}]; \quad [\mathrm{Cu}''_{Ti}] = [V_O^{\bullet\bullet}]. \quad (4)$$

At low oxygen partial pressures, the conductivity increases because of the increase in electron concentration:

$$O_O^{\times} = \frac{1}{2}O_2 + V_O^{\bullet\bullet} + 2e'. \quad (5)$$

Here, the vacancy concentration varies, $n = 2[V_O^{\bullet\bullet}]$, and the conductivity is proportional to $p_{O_2}^{-1/6}$:

Table 1. Lattice parameters of undoped and doped calcium titanate

a, Å	b, Å	c, Å	V, Å^3	R_p	R_{wp}	R_{exp}	χ^2	R_{Br}	R_f
$CaTiO_3$									
5.379(5)	7.641(5)	5.441(8)	222.63(3)	22.9	26.3	15.0	3.1	4.1	3.1
$CaTi_{0.9}Fe_{0.1}O_{3-\delta}$									
5.378(7)	7.630(1)	5.428(6)	222.75(5)	19.4	25.0	42.1	0.4	3.7	2.6
$CaTi_{0.9}Al_{0.1}O_{3-\delta}$									
5.382(3)	7.625(4)	5.434(4)	223.04(1)	24.8	33.6	22.9	2.3	1.8	2.5
$CaTi_{0.9}Cu_{0.1}O_{3-\delta}$									
5.379(9)	7.633(2)	5.435(9)	222.63(3)	26.4	31.1	50.0	0.4	2.4	2.3

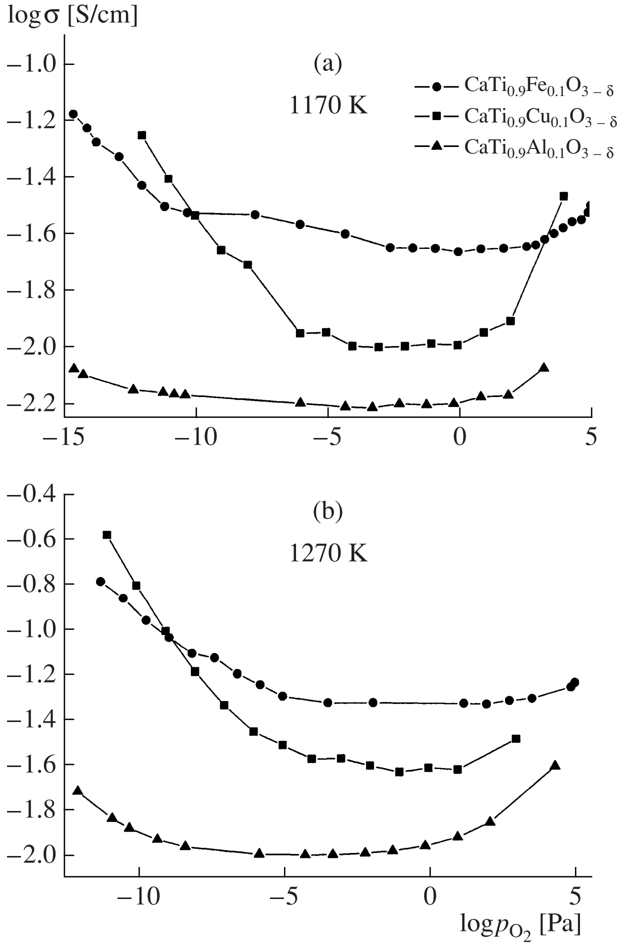

Fig. 2. Log–log plots of conductivity vs. oxygen partial pressure for $CaTi_{0.9}M_{0.1}O_{3-\delta}$.

$$\sigma \sim n = \mathrm{const}\, p_{O_2}^{-1/6}. \qquad (6)$$

The dopants raise the conductivity of $CaTiO_3$ in the order Al < Cu < Fe.

The thermal expansion data for our samples in different temperature ranges are presented in Table 2.

Table 2. Thermal expansion of $CaTi_{0.9}M_{0.1}O_{3-\delta}$

M	ΔT, K	$\alpha \times 10^{-6}$, K^{-1}	$\Delta\alpha \times 10^{-7}$, K^{-1}
Fe	290–770	14.5	0.83
	770–1270	10.6	3.3
Al	290–570	4.8	6.8
	570–800	10.6	2.2
	800–1270	8.5	2.9
Cu	290–1270	10.01	0.95

CONCLUSIONS

We refined the lattice parameters of the $CaTi_{0.9}M_{0.1}O_{3-\delta}$ (M = Fe, Cu, Al) compounds (orthorhombic perovskite structure, sp. gr. *Pnma*).

The electrical conductivity of $CaTi_{0.9}M_{0.1}O_{3-\delta}$ was measured in wide ranges of oxygen partial pressures and temperatures. The Fe-, Cu-, and Al-doped materials are mixed conductors, *p*-type at high p_{O_2} and *n*-type at low p_{O_2}. At intermediate oxygen partial pressures, the conductivity varies little. The acceptor dopants studied are shown to raise the conductivity of calcium titanate in the order Al < Cu < Fe. The thermal expansion of the three materials was measured.

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