

Journal of Alloys and Compounds 419 (2006) 271-280

Journal of ALLOYS AND COMPOUNDS

www.elsevier.com/locate/jallcom

A-site deficient perovskite-type compounds in the ternary CaTiO₃-LaCrO₃-La_{2/3}TiO₃ system

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Received 29 June 2005; accepted 9 September 2005 Available online 28 November 2005

Abstract

Phase equilibriums in the CaTiO₃-LaCrO₃-La_{2/3}TiO₃ quasi-ternary system have been studied by means of high-resolution powder diffraction technique using X-ray and synchrotron radiation. Over 50 $La_{(2+y-2x)/3}Ca_xCr_yTi_{1-y}O_3$ compounds were synthesized by solid-state reactions in air at 1350 °C using La₂O₃, CaCO₃, Cr₂O₃ and TiO₂. Based on the results of X-ray phase and structural analysis, the isothermal section of the CaTiO₃-LaCrO₃-La_{2/3}TiO₃ phase diagram at room temperature is constructed. The A-cation deficient $La_{(2+y-2x)/3}Ca_xCr_yTi_{1-y}O_3$ solid solution with different perovskite-type structures (space groups *Pbnm, Imma, I4/mcm* and *Cmmm* or *P2/m*) is formed in the CaTiO₃-LaCrO₃-La_{2/3}TiO₃ quasi-ternary system in air conditions. The compounds show high stability at high temperatures at reducing as well as at oxidizing conditions. The substances with y = 0 and y = 0.2 show n-type conductivity at 900 °C at $pO_2 = 10^{-15}$ to 10⁵ Pa and with y = 0.5 show conductivity minima these shift to the oxygen reach region with increasing A-site deficiency. The A-site deficient $La_{(2+y-2x)/3}Ca_xCr_yTi_{1-y}O_3$ samples have higher sintering ability in comparison with the cation stoichiometric $La_{1-x}Ca_xCr_{1-y}Ti_yO_3$ compositions and, in contrast to the latter, can be prepared as gas dense ceramics in air at temperatures lower as 1300 °C. Thermal expansion of the A-site deficient $La_{(2+y-2x)/3}Ca_xCr_yTi_{1-y}O_3$ ceramics us to 1300 °C was observed. Oxygen mobility in these ceramics can be characterised with chemical diffusion coefficients (1–9) × 10⁻⁹ cm² s⁻¹ at 900 °C and $pO_2 = 1000-21,000$ Pa. © 2005 Elsevier B.V. All rights reserved.

Keywords: Perovskites; Chromites; Titanates; Crystal structure; A-site deficiency; Oxygen stoichiometry; Electrical conductivity; Oxygen mobility; Thermal expansion; Chemical stability

1. Introduction

The optimal variant of realization of SOFC consist is the application of light hydrocarbon fuel (CH₄) with its direct electrochemical oxidation at the anode to carbon dioxide and water vapour [1]. Unfortunately, no optimal anode materials were found for the internal oxidation of dry fuel in the SOFC up to now. The basic imperfection of the most widespread SOFC anode material (composition Ni/NiO + YSZ) is the restricted possibility to use it in systems with internal reforming [2–4], because of the relative high catalytic activity for pyrolysis or

cracking of hydrocarbon fuel (CH₄ \rightarrow C + 2H₂) and for reforming (CH₄ + H₂O \rightleftharpoons CO + 3H₂) in comparison with the electrochemical reaction. Other disadvantages of the Ni/NiO + YSZ composites as SOFC-anode material are discrepancies between the thermal expansion coefficients (TEC) of metallic nickel and yttrium stabilized zirconia [1,5], changes of the catalytic activity during operation time in consequence of sintering of the nickel particles [6], or nickel sulfide (NiS) formation [7], and mechanical destruction of the anode by nickel oxidation.

Recently, a lot of new compounds have been offered as alternative anode materials: $La_{1-x}(Sr,Ca)_xCrO_3$ [5,8,9], $La_{0.8}$ $Sr_{0.2}Cr_{0.97}V_{0.03}O_3$ [10], $ZrO_2(Y_2O_3 + Nb_2O_5)$ [11], $(Sr_{1-x}Ba_x)_{0.6}Ti_{0.2}Nb_{0.8}O_3$ [12], $La_2Sr_4Ti_6O_{19-\delta}$ [13], $(Ti_{1-y}Mo_y)_2$ O_7 [14], $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$ [15,16], some individual compositions in the system $La_{1-a}Ca_aCr_{1-b}Ti_bO_{3-\delta}$ [17] and others.

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^{0925-8388/\$ -} see front matter © 2005 Elsevier B.V. All rights reserved. doi:10.1016/j.jallcom.2005.09.063

None of the proposed compounds fulfils the requirements of SOFC anodes completely [18].

Complex perovskite-type oxides (ABO₃) based on rare earth and alkaline earth oxides with 3d-transition metal oxides are interesting candidates in search of materials with electrocatalytic properties. Subjects of investigation in this field are lanthanum chromites and titanates substituted with alkaline earth ions.

Pudmich et al. [17] prepared and investigated a series of lanthanum chromites partially substituted with alkaline-earth elements in the A-position of the perovskite-type structure and with transition metals like Ti, Co, or Fe in the B-position with regard to their application as anodes in solid oxide fuel cells. A broad range of variation of the physical properties such as electrical conductivity and thermal expansion was observed. van Hassel et al. [19] published the first results on oxygen partial pressure dependence of the electrical conductivity and oxygen ionic transport in La_{1-a}Ca_aCrO_{3-x}.

It is known, that both lanthanum chromite (LaCrO₃) and calcium titanate (CaTiO₃) with perovskite structure are thermodynamically stable compounds at high temperatures in a wide oxygen partial pressure range of $(10^5 \text{ to } 10^{-15} \text{ Pa})$. Thermal expansion coefficients of some of the investigated compounds of this system are close to that of yttrium stabilized zirconia [17]. The sizes of La-Ca and Cr-Ti cations are close to each other which raise hopes to achieve solubility in a wide range of cation concentrations. By changing ratios of cations with various oxidation states in the separate sublattices of the perovskite structure, the concentrations both of cation and anion vacancies in the compounds of this system can be adjusted at the desirable level. The expected stability of chromium cations with oxidation states 3+ and 4+ in oxidizing environments and titanium cations with oxidation states 4+ and 3+ in reducing environments can provide the different types of electronic conductivity, depending on temperature and oxygen partial pressure, by varying cationic compositions.

Recently, the reduction stability of the $La_{1-x}Ca_xCr_{1-y}$ Ti_yO_{3- δ} compositions in H₂/H₂O/Ar gas flows with $pO_2 = 10^{-15}$ Pa at temperatures 800–1000 °C as well as the chemical compatibility with YSZ up to 1300 °C in air were demonstrated [20–25]. Depending on cationic composition and oxygen partial pressure, the compounds exhibit high (up to 100 S/cm) p- or n-type conductivities in oxidizing or reducing environments, respectively. Substances with alternating electronic conductivity types, depending on oxygen partial pressure, were found as well as substances with high electrical conductivities in both oxidizing and reducing atmospheres.

It was found, that the $La_{1-x}Ca_xCr_{1-y}Ti_yO_3$ mixed oxides with cation stoichiometry have various degrees of oxygen allocation within the region of structure stability at temperatures of 700–1000 °C and identical oxygen partial pressures [20–25]. The degree of dissociation is defined by the Ca/Ti ratio. The increase of this ratio is connected with an easier dissociation of the oxides and with the approximation of their behaviour to the properties of the $La_{1-x}Ca_xCrO_3$ solid solution. At decreasing Ca/Ti ratios the dissociation of these oxides is reduced. In case of Ca/Ti = 1, oxygen release was found only under very high reducing conditions. In accordance with results reported by Pudmich et al. [17], the most perovskite-type compounds in the system La-(Ca, Sr)-Cr-Ti-O, have a low catalytic activity concerning hydrocarbon oxidation reactions. At the same time, catalytic activity varies notably with changing compositions within the cation stoichiometric series $La_{1-x}Ca_xCr_{1-y}Ti_yO_3$. The correlation between total conductivity and catalytic activity was observed for some solid solutions, while such correlation was not found for some other solid solutions of these series [20].

Preliminary results demonstrate, that cation nonstoichiometric compounds with perovskite-type structure exist in the system $La_{(2.2-b)/3}Ca_{0.4}Cr_{1-b}Ti_bO_3$, and the cationic deficiency in the A-sub-lattice can reach up to 0.3 atomic indexes [20].

The A-site deficient lanthanide titanates $Ln_{1-x}TiO_3$ (Ln = La, Nd, Sm) with x = 0.0-0.33, so-called partial vacancy doped titanates, are known for a sufficiently long time. They can be prepared by solid-state reactions either at the presence of some alkaline, alkaline-earth or transition metals, or under oxygen pressures lower than that of air. For the first time the existence of La_{2/3}TiO₃ was reported by Kestigian et al. in 1955 [26]. Some of the compositions of the $La_{1-x}TiO_3$ solid solutions were obtained and investigated by Leonov et al. [27,28] and Basuev et al. [29]. According to literature data, the structure of La_{2/3}TiO₃ is orhtorhombic [30,31], tetragonal or cubic [32]. MacEachern et al. [33] studied the La_{1-x}TiO₃ system at $0.0 \le x \le 0.33$ and showed that three different orhtorhobmic structures are formed in this concentration range: *Pban* at $0.25 \le x \le 0.33$, *Ibmm* at $0.20 \le x \le 0.25$ and *Pbnm* at $0.0 \le x \le 0.20$. The cationdeficient La_{2/3}TiO₃ compound is thermodynamically unstable in air below 1400 °C, but could be stabilized by low-level substitution by PbTiO₃ [34,35,30], Ti³⁺ [30], alkali metals [36,37], Ca, Sr [38,39], Sc, Cr, Al [40,41], Nb [42] and Co [43]. The structure of $La_{2/3}TiO_{3-\delta}$ could be stabilized also with the formation of oxygen vacancies [28,30]. The A-cation deficient compounds R_{1-x} TiO₃ with the perovskite-like structure are known in the systems of Ce, Pr and Nd [28,29,40,44-47]. Many other investigations of physical and chemical properties of the A-site deficient titanates were performed in the last years [48–52].

The correlations between the composition of the $La_{(2+y-2x)/3}Ca_xCr_yTi_{1-y}O_3$ solid solution on the one hand and crystal structure as well as electrical conductivity, oxygen nonstoichiometry, oxygen mobility, thermal expansion on the other hand are the objects of interest of this article.

2. Experimental

2.1. Powder preparation and crystal structure

Calcium carbonate, lanthanum oxide, titanium dioxide and chromium(III) oxide, all of Analytical Reagent grade having purity >99.5%, were used as initial materials for preparation of the $La_{(2+y-2x)/3}Ca_xCr_yTi_{1-y}O_3$ (x, y=0.0-1.0) powders and slightly modified compositions. The appropriate mixtures were milled with ethanol in an agate ball mill for 24 h. The mixed powders were dried and calcined in air at 1100 °C for 20 h in alumina crucibles. After cooling to room temperature the products were milled again and finally annealed in air at 1350 °C for 20 h. The cooling and heating rates were about 5 °C/min. The obtained substances were repeatedly milled and the obtained powders were used for further experiments. Before XRD and oxygen nonstoichiometry inves-

tigations were carried out, the powders were treated at 1000 °C during 10 h and cooled to room temperature with a rate 2 °C/min.

The crystal structures were investigated at room temperatures by means of the powder diffraction technique using a Siemens D5000 powder X-Ray diffractometer (Cu K α -radiation; $\theta/2\theta$: scanning mode; step width of 0.02°; counting time per step: 7 s). High temperature behaviour of the crystal structures was studied by means of high-resolution powder diffraction technique and synchrotron radiation in the temperature range of 20–1000 °C in air. In situ diffraction experiments were carried out at the Hamburg Synchrotron Radiation Laboratory (HASYLAB) by using powder diffractometer at beam line B2, equipped with STOE furnace.

The crystal structures were refined by the full-profile Rietveld analysis method, including refinement of lattice parameters, positional and displacement parameters, site occupancy, scaling factor, sample shift, background and Bragg-peak profile parameters. The atomic displacement parameters are refined anisotropically for La(Ca) cations and isotropically for all other atoms. All calculations were performed using the WinCSD (Crystal Structure Determination) program package [53].

2.2. Oxygen nonstoichiometry

The initial oxygen content in compounds was determined by iodometry method after digestion of powders in KJ/HCl solution at elevated temperatures in sealed glass ampoules [25]. Oxygen nonstoichiometry changes were measured by solid-electrolyte technique using a PC-controlled device OXYLYT (SensoTech Magdeburg, Germany) [25]. The concept of combined coulometric–potentiometric arrangement for the investigation of solid–gas interactions in the carrier gas mode was described earlier in [54,55].

The investigation of oxygen nonstoichiometry was performed on some powders, the preparation of which is described in Section 2.1, in the temperature range of 20–1000 °C and at oxygen partial pressures from 10^{-15} to 21,000 Pa. The ceramic samples were used for simultaneous measurements of oxygen nonstoichiometry and the electrical conductivity. Air, Ar/O₂ with 1 Pa O₂, and Ar/H₂/H₂O with *p*H₂O/*p*H₂ = 0.01 gas mixtures were utilised as initial reagents.

2.3. Electrical conductivity

The electrical conductivity of ceramic samples was measured in gas atmospheres with controlled oxygen partial pressures by a dc four-point method described elsewhere [56]. The powders were pressed into bars $1 \text{ mm} \times 3 \text{ mm} \times 10 \text{ mm}$ together with four Pt wires (0.1 mm thickness) and sintered for 20 h in air at temperatures of 1250–1400 °C depending on composition. Heating and cooling rates during sintering were 5 °C/min. The conductivity was measured at 20–1000 °C in air and in the flowing gas mixtures of Ar/O₂ (1–100 Pa O₂) and Ar/H₂/H₂O with *p*H₂O/*p*H₂ = 0.01–50. The equilibrium values of the conductivity at 900 °C and different oxygen partial pressures can be achieved after 1–100 h exposition depending on composition and ceramic structures of the samples and the oxygen partial pressure range. The temperature dependencies of the electrical conductivity in air and in gas flow of Ar/H₂O/H₂ with *p*H₂O/*p*H₂ = 0.01 were recorded during cooling at a rate of 5 °C/min.

2.4. Thermal expansion

Along with the high-resolution powder diffraction technique on synchrotron radiation (Section 2.1), the thermal expansion some of ceramic samples was also investigated in a LINSEIS dilatometer in air in the temperature range of 293–1123 K.

2.5. Chemical diffusion coefficients

As presented elsewhere [57], chemical diffusion coefficients were determined at 900 °C by measurements of the electrical conductivity relaxation of the gas dense ceramic samples after an abrupt change of the oxygen partial pressures around the samples. Relaxation data were presented in the form of fractional conductivity changes versus elapsed time after pO_2 jumps [58].

3. Results and discussion

3.1. Powder preparation and investigation of the crystal structure

All prepared compositions as well as their crystal structures at room temperatures are shown in Fig. 1 and Table 1. Fig. 2 represents an example of profile fitting for $La_{0.13}Ca_{0.8}TiO_3$. The continuous solid solution with orthorhombic *Pbnm* structure is formed in the $(1 - x)LaCrO_3 - xCaTiO_3$ pseudo-binary system (Fig. 3). As the distorted cubic lattices of $LaCrO_3$ and $CaTiO_3$ have different ratios of cell parameters within the same GdFeO₃-type structure (a > b and a < b, respectively), some of the samples from this system display the tetragonal or cubic lattices. The diffraction data from the in situ high-temperature synchrotron experiments indicate that the orthorhombic (pseudo-cubic) *Pbnm* structure of $La_{0.5}Ca_{0.5}Cr_{0.5}Ti_{0.5}O_3$ transforms into the *Imma* one above 1070 K.

In the (1 - x)LaCrO₃-xLa_{2/3}TiO₃ pseudo-binary system, two kinds of the perovskite-like structures are found. LaCrO₃-rich compositions have the GdFeO₃-type *Pbnm* structure, whereas in the La_{2/3}TiO₃ rich region of the system the solid solution with the ordered A-cation vacancies and *P2/m* structure is formed. Both La_{(3-x)/3}Cr_{1-x}Ti_xO₃ perovskite-type phases co-exist in a wide concentration range of x = 0.2-0.8 (Fig. 4).

A-cation deficient perovskite-type solid solutions $La_{2(1-x)/3}$ Ca_xTiO₃ with four different crystal structures are formed in the pseudo-binary system $(1 - x)La_{2/3}TiO_3 - xCaTiO_3$ depending on composition. Similar to CaTiO₃, the samples with molar fraction of $La_{2/3}TiO_3$ 0/0.4 display the GdFeO₃-type structure. A-cation vacancies in these structures are statistically distributed in Ca(La) cation positions. At intermediate concentration of $La_{2/3}TiO_3$ (0.4/0.7) the solid solution with body-centered orthorhombic (pseudo-tetragonal) *Imma* structure is formed. The continuing increase of $La_{2/3}TiO_3$ content and the following A-cation deficiency lead to the formation of the tetragonal



Fig. 1. Phase diagram of the perovskite-type system $La_{(2+y-2x)/3}Ca_xCr_y$ $Ti_{1-y}O_3$.

Table 1 La_{(2+y-2x)/3}Ca_xCr_yTi_{1-y}O₃ compositions prepared in the system xCaTiO₃ – yLaCrO₃ – (1 – x – y)La_{2/3}TiO₃

	System	Formula	x	Compositions	Structure
1	(1-x)LaCrO ₃ $- x$ CaTiO ₃	$La_{1-x}Ca_xCr_{1-x}Ti_xO_3 \text{ or}$ $La_{(2+y-2x)/3}Ca_xCr_yTi_{1-y}O_3 \text{ at } y = 1-x$	x = 0	LaCrO ₃	Pbnm
			x = 0.2	La _{0.8} Ca _{0.2} Cr _{0.8} Ti _{0.2} O ₃	Pbnm
			x = 0.4	La _{0.6} Ca _{0.4} Cr _{0.6} Ti _{0.4} O ₃	Pbnm
			x = 0.5	La _{0.5} Ca _{0.5} Cr _{0.5} Ti _{0.5} O ₃	Pbnm
			x = 0.6	La _{0.4} Ca _{0.6} Cr _{0.4} Ti _{0.6} O ₃	Pbnm
			x = 0.8	La _{0.2} Ca _{0.8} Cr _{0.2} Ti _{0.8} O ₃	Pbnm
			x = 1	CaTiO ₃	Pbnm
2	(1-x)LaCrO ₃ $- x$ La _{2/3} TiO ₃	$La_{(3-x)/3}Cr_{1-x}Ti_xO_3$ or $La_{(2+y-2x)/3}Ca_xCr_yTi_{1-y}O_3, x=0; y=1-x$	x = 0	LaCrO ₃	Pbnm
			x = 0.1 x = 0.2 - 0.8	La _{0.967} Cr _{0.9} Ti _{0.1} O ₃ Multiphase region	Pbnm
			x = 0.82	La _{0.727} Cr _{0.18} Ti _{0.82} O ₃	P2/m
			x = 0.84	La _{0.72} Cr _{0.16} Ti _{0.84} O ₃	P2/m
			x = 0.86	La _{0.714} Cr _{0.14} Ti _{0.86} O ₃	P2/m
			x = 0.88	La _{0.707} Cr _{0.12} Ti _{0.88} O ₃	P2/m
			x = 0.9	La _{0.7} Cr _{0.1} Ti _{0.9} O ₃	P2/m
			x = 0.92	La _{0.693} Cr _{0.08} Ti _{0.92} O ₃	P2/m
			x = 0.94	La _{0.687} Cr _{0.06} Ti _{0.94} O ₃	P2/m
			x = 0.96	La _{0.68} Cr _{0.04} Ti _{0.96} O ₃	?
			x = 0.98	La _{0.673} Cr _{0.02} Ti _{0.98} O ₃	?
			x = 1	La _{0.667} TiO ₃	?
3	(1-x)La _{2/3} TiO ₃ – xCaTiO ₃	$La_{2(1-x)/3}Ca_x TiO_3$ or $La_{(2+y-2x)/3}Ca_x Cr_y Ti_{1-y}O_3$, $y = 0$	x = 0	La _{0.667} TiO ₃	?
			x = 0.02	La _{0.653} Ca _{0.02} TiO ₃	Cmmm
			x = 0.04	La _{0.64} Ca _{0.04} TiO ₃	Cmmm
			x = 0.06	La _{0.63} Ca _{0.06} TiO ₃	Cmmm
			x = 0.08	La _{0.613} Ca _{0.08} TiO ₃	Cmmm
			x = 0.1	La _{0.6} Ca _{0.1} TiO ₃	Cmmm
			x = 0.12	La _{0.587} Ca _{0.12} TiO ₃	Cmmm
			x = 0.16	La _{0.56} Ca _{0.16} TiO ₃	Cmmm
			x = 0.18	La _{0.556} Ca _{0.18} TiO ₃	Cmmm
			x = 0.2	La _{0.553} Ca _{0.2} TiO ₃	Cmmm
			x = 0.25	La _{0.5} Ca _{0.25} TiO ₃	14/mem
			x = 0.3	La _{0.467} Ca _{0.3} TiO ₃	14/mem
			x = 0.4	La _{0.4} Ca _{0.4} TiO ₃	Imma
			x = 0.5	La _{0.333} Ca _{0.5} TiO ₃	Imma
			x = 0.6	La _{0.267} Ca _{0.6} TiO ₃	Imma
			x = 0.7	La _{0.2} Ca _{0.7} TiO ₃	Pbnm
			x = 0.8	La _{0.133} Ca _{0.8} TiO ₃	Pbnm
			x = 0.9	La _{0.067} Ca _{0.9} TiO ₃	Pbnm
			x = 1	CaTiO ₃	Pbnm
4	xCaTiO ₃ - y LaCrO ₃ - $(1 - x - y)$ La _{2/3} TiO ₃	$La_{(2+y-2x)/3}Ca_xCr_yTi_{1-y}O_3$	x = 0.2; y = 0.6	La _{0.333} Ca _{0.6} Cr _{0.2} Ti _{0.8} O ₃	Pbnm
			x = 0.5; y = 0.3	La _{0.433} Ca _{0.5} Cr _{0.3} Ti _{0.7} O ₃	Pbnm
			x = 0.4; y = 0.4	La _{0.533} Ca _{0.4} Cr _{0.4} Ti _{0.6} O ₃	Pbnm
			x = 0.3; y = 0.5	La _{0.633} Ca _{0.3} Cr _{0.5} Ti _{0.5} O ₃	Pbnm
			x = 0.4; y = 0.5	La _{0.567} Ca _{0.4} Cr _{0.5} Ti _{0.5} O ₃	Pbnm
			x = 0.2; y = 0.6	La _{0.733} Ca _{0.2} Cr _{0.6} Ti _{0.4} O ₅	Pbnm
			x = 0.2; y = 0.6	La _{0.733} Ca _{0.2} Cr _{0.6} Ti _{0.4} O ₃	Imma
			x = 0.5; y = 0.2	La _{0.4} Ca _{0.5} Cr _{0.2} Ti _{0.8} O ₃	Pbnm
			x = 0.5; y = 0.2	La _{0.4} Ca _{0.5} Cr _{0.2} Ti _{0.8} O ₃	Imma
			x = 0.4; y = 0.2	La _{0.467} Ca _{0.4} Cr _{0.2} Ti _{0.8} O ₃	Imma
			x = 0.3; y = 0.3	La _{0.567} Ca _{0.3} Cr _{0.32} Ti _{0.7} O ₃	Imma
			x = 0.3; y = 0.2	La _{0.533} Ca _{0.3} Cr _{0.2} Ti _{0.8} O ₃	Imma
			x = 0.2; y = 0.2	La _{0.6} Ca _{0.2} Cr _{0.2} Ti _{0.8} O ₃	Imma
			x = 0.1; y = 0.2	La _{0.667} Ca _{0.1} Cr _{0.2} Ti _{0.8} O ₃	Imma
			x = 0.05; y = 0.2	La _{0.7} Ca _{0.05} Cr _{0.2} Ti _{0.8} O ₃	Imma

structure (space group *I4/mcm*). In the La_{2/3}TiO₃-rich range of the system (molar fraction of La_{2/3}TiO₃ 0.8/0.96) the ordered perovskite-like structure is formed. The alternation of fully and partially (~40%) occupied layers of A-cations is observed in these structures. Fig. 5 illustrates the changes of lattice parame-

ters of the perovskite phases, formed in the $CaTiO_3$ - $La_{2/3}TiO_3$ system, in dependence on the $La_{2/3}TiO_3$ content.

Increasing Cr- and La-contents in the $La_{(2+y-2x)/3}Ca_xCr_yTi_{1-y}O_3$ series, that is characterised with the orthorhombic perovskite-type structure (*Pbnm*) and constant



Fig. 2. Calculated (line) and observed (dots) patterns of the difference spectrum for La_{0.13}Ca_{0.8}TiO₃.



Fig. 3. Concentration dependence of the lattice parameters in the $La_{1-x}Ca_xCr_{1-x}Ti_xO_3$ (LaCrO₃-CaTiO₃) system. Lattice parameters and cell volume are transformed to perovskite-type cell.



Fig. 4. Concentration dependence of the lattice parameters in the $La_{(3-x)/3}Cr_{1-x}Ti_xO_3$ (LaCrO₃-La_{2/3}TiO₃) system. Lattice parameters and cell volume are transformed to perovskite-type cell.

A-site deficiency 0.07 (solid solution $La_{0.13}Ca_{0.8}Ti_{1.0}O_3$ -L $a_{0.93}Cr_{0.8}Ti_{0.2}O_3$), are accompanied with increasing lattice parameters and cell volumes. Fig. 6 indicates that the separate lattice parameters change with different slopes. The highest increase shows the *a*- and the lowest the *b*-parameter.

Fig. 7 presents crystal structures and lattice parameters changing with decreasing A-site deficiency (growing La_{0.5}Ca_{0.5}Cr_{0.5}Ti_{0.5}O₃ content) in the system "La_{2/3}TiO₃"-La_{0.5}Ca_{0.5}Cr_{0.5}Ti_{0.5}O₃. The compositions with large A-site deficiency have tetragonal *Cmmm* or *P2/m* structures and the same lattice parameters at increasing La_{0.5}Ca_{0.5}Cr_{0.5}Ti_{0.5}O₃ content. The sample with 0.24 mol fraction of La_{0.5}Ca_{0.5}Cr_{0.5}Ti_{0.5}O₃ in this system can be refined in both tetragonal and cubic structures. Nevertheless, there are traces of peaks at the pattern, which could not be indexed in body-centered lattices. These may indicate a beginning of ordering of A-cation vacancies. The change of slope of the cell volume occurs at ~0.3 and ~0.7 mole fractions of La_{0.5}Ca_{0.5}Cr_{0.5}Ti_{0.5}O₃ and may be associated with the existence areas of different perovskite structures and ordering of A-cation vacancies.



Fig. 5. Concentration dependencies of the lattice parameters in the $La_{2(1-x)/3}Ca_xTiO_3$ (CaTiO₃-La_{2/3}TiO₃) system. Lattice parameters and cell volumes are reduced to perovskite-like cell.



Fig. 6. Lattice parameters in the $La_{(2+y-2x)/3}Ca_xCr_yTi_{1-y}O_3$ (La_{0.13} $Ca_{0.8}Ti_{1.0}O_3$ -La_{0.93}Cr_{0.8}Ti_{0.2}O_3) quasi-binary system with constant A-cation deficiency (0.07 of A atomic index).

3.2. Oxygen nonstoichiometry and electrical conductivity

No oxygen release was observed during heating of the compounds of the system LaCrO₃-CaTiO₃-La_{2/3}TiO₃ from room temperature up to 1000 °C in Ar/O₂ gas flow with $pO_2 \ge 1$ Pa. For example, Fig. 8 illustrates no changes of the both titration current and calculated oxygen atomic index $(3 - \delta)$ for La_{0.6}Ca_{0.1}TiO₃. Only small oxygen release (δ =0.002–0.015) was observed in H₂/H₂O/Ar gas flow, as it is shown in Fig. 9 for La_{0.6}Ca_{0.1}TiO₃ and two other compounds of this series La_{0.33}Ca_{0.6}Cr_{0.2}Ti_{0.8}O₃ and La_{0.5}Ca_{0.5}Cr_{0.5}Ti_{0.5}O₃. The initial oxygen content in compounds was estimated as 2.99 ± 0.01 by iodometry method. High reduction stability of the investigated compositions indicates absence or presence of indefinable small amounts of chromium cations in oxidation states higher as 3+, as for example in LaCrO₃ [25].

The electrical conductivity some of the $La_{(2+y-2x)/3}Ca_x$ Cr_yTi_{1-y}O₃ compounds with different x and y measured in air



Fig. 7. Concentration dependencies of the lattice parameters in the $La_{(2+y-2,y)/3}Ca_xCr_yTi_{1-y}O_3$ ("La_{2/3}TiO₃"-La_{0.5}Ca_{0.5}Cr_{0.5}Ti_{0.5}O₃) system. Lattice parameters and cell volumes are transformed to perovskite-like cell.



Fig. 8. Titration current of the cell 2 and oxygen content of the $La_{0.6}Ca_{0.1}TiO_{3-\delta}$ powder during heating–exposition–cooling in Ar/O₂ gas flow with oxygen partial pressure 1 Pa.



Fig. 9. Change of oxygen content some of the $La_{(2+y-2x)/3}Ca_xCr_yTi_{1-y}O_3$ powder compounds during heating–exposition–cooling in H₂/H₂O/Ar gas flow $pH_2O/pH_2 = 0.53$.

and presented in Fig. 10 is relatively low and increases with temperature like by typical semiconductors. Chromites–titanates show much lower activation energy (0.35–0.37 eV) in comparison with pure titanates (1.55–1.65 eV). The conductivity level



Fig. 10. Temperature dependence of the electrical conductivity some of the $La_{(2+y-2x)/3}Ca_xCr_yTi_{1-y}O_3$ ceramic samples measured in air.



Fig. 11. pO_2 -dependence of the electrical conductivity some of the La_{0.567±Y}Ca₄Cr_{0.5}Ti_{0.5}O₃ ceramic samples at 900 °C.

below 1000 °C increases with increasing Cr-content on the Bsites of the perovskite-type structures. Changing La/Ca-ratio and corresponding A-site deficiency of titanates influence only a little the conductivity level and activation energy.

The pO_2 dependencies of the conductivity of the La_{(2-2x)/3}Ca_xTiO₃ compounds at 900 °C presented in [57] demonstrate very good linearity in logarithmic coordinates with a slope around -1/4. Only small slope increase was observed at changed structures from *Cmmm* at x = 0.1 to *Imma* at x = 0.4and to Pbnm at x=0.8. The La_{(2+v-2x)/3}Ca_xCr_vTi_{1-v}O₃ compounds with y=0 and 0.2 show linear dependences, but the samples of this series with y = 0.5 demonstrate conductivity minima in the pO_2 region 10^{-4} to 10^2 Pa. Fig. 11 presents the pO_2 -dependences for three La_{0.567 $\pm\gamma}Ca_4Cr_{0.5}Ti_{0.5}O_3$ samples} with different A-site deficiency near $La_{(2+y-2x)/3}Ca_xCr_yTi_{1-y}O_3$ nominal composition. Decreasing A-site deficiency shifts conductivity minima to higher pO_2 from $10^{-3.5}$ to 10^{-3} and $10^{-1.5}$ Pa, respectively. Due to this strong compositional influence, the solid-state synthesis of the compounds with comparable Cr and Ti contents can result in the formation of materials with noticeable different electrical properties.

Increasing from 0.547 to 0.597 La-content in La_{0.567± γ} Ca₄Cr_{0.5}Ti_{0.5}O₃ changes colour of the powders from deep-green to chlorine. The corresponding ceramic samples sintered in air at 1250 °C and cooled to room temperature at 7 °C/min showed changing surface colour from light-grey to deep-yellow. The grey colour was probably caused by the presence of the Cr⁴⁺-cations. Increasing La-content apparently reduces the content of Cr⁴⁺-cations in these compositions.

As majority of the single phase La_{(2+y-2x)/3}Ca_xCr_yTi_{1-y}O₃ compositions prepared in the quasi-ternary system CaTiO₃-LaCrO₃-La_{2/3}TiO₃ in air had yellow colour, the oxidation states of chromium and titanium cations in these compositions can be assumed near 3+ and 4+, respectively. The general formula for the A-site deficient compounds of the series La_{(2+y-2x)/3}Ca_xCr_yTi_{1-y}O₃ synthesized in air can be written as La³⁺_{(2+y-2x)/3}Ca²⁺_xCr³⁺_yTi⁴⁺_{1-y}O²⁻₃. Probable, the A-site vacancies in the cationic sub-lattice are distributed statistically.

Due to reduction of Ti⁴⁺-cations to Ti³⁺ at elevated temperatures in reducing conditions, the yellow coloured compounds change their colour to black. The observed n-type conductivity of the prepared samples in terms of the Kröger–Vink notation [59] can be explained with oxygen release:

$$O_{O}^{\times} + 2Ti_{Ti}^{\times} \rightleftharpoons V_{O}^{\bullet \bullet} + 2Ti_{Ti}^{/} + 0.5O_2$$

$$\tag{1}$$

assuming that conduction electrons are located on Ti³⁺-cations. The observed $\log(\sigma)/\log(pO_2)$ slope was near -1/4.

Most likely, appearing oxygen vacancies cannot annihilate with La,Ca-vacancies, because all the B-site positions in the perovskite-type structure stay occupied with Cr^{3+} , Ti^{4+} and Ti^{3+} cations and no other compounds enriched with Cr or Ti were detected by XRD method after reduction processes.

The p-type conductivity of the $La_{(2+y-2x)/3}Ca_xCr_{0.5}Ti_{0.5}O_3$ compounds in the relatively high oxygen partial pressure region (Fig. 11) can be explained with existence of Cr^{4+} cations:

$$2\mathrm{Cr}_{\mathrm{Cr}}^{\times} + V_{\mathrm{O}}^{\bullet} + 0.5\mathrm{O}_{2} \rightleftharpoons 2\mathrm{Cr}_{\mathrm{Cr}}^{\bullet} + \mathrm{O}_{\mathrm{O}}^{\times}$$
(2)

assuming that conduction holes are located on Cr^{4+} -cations. The experimental slope $log(\sigma)/log(pO_2) = +1/6$ was observed. The formation of Cr^{4+} states may be understood as result of the partial disproportionation of Cr^{3+} cations into $Cr^{2+}-Cr^{4+}$ pairs. This possibility for perovskite and perovskite-related structures was shown theoretical by Goodenough [60] and then suggested for stabilization of Mn^{3+} ions into $Mn^{2+}-Mn^{4+}$ pairs in $La_{1-x}Sr_xMnO_3$ [61] and Bi^{4+} cations into $Bi^{3+}-Bi^{5+}$ pairs in BaBiO₃ [62,63], for example.

The observed shift of the conductivity minima to oxygen reach site with increasing A-site deficiency may be related with changing Cr^{4+} and Ti^{3+} cation concentrations at these experimental conditions.

3.3. Thermal expansion

Thermal expansions of $La_{0.4}Ca_{0.4}TiO_3$ in the *a*-, *b*- and *c*-directions determined by synchrotron radiation are practically similar up to ~550 °C (Fig. 12). A slope change of the *a*-



Fig. 12. Temperature dependence of the lattice parameters and the cell volume of $La_{0.4}Ca_{0.4}TiO_3$ powder determined by diffraction of synchrotron radiation.



Fig. 13. Temperature dependence of the relative expansion ($\Delta L/L_0$), thermal expansion coefficient (TEC) and the first derivative of the relative expansion of the La_{(1.2+y)/3})Ca_{0.4}Cr_yTi_{1-y}O₃ ceramics.

parameter is observed at temperatures above 550 °C. The difference between *a*- and *c*-parameters at temperatures higher than 550 °C decreases and disappears at 900 °C indicating a transition to the cubic structure. The slope changes of the *a*-parameter and the cell volume of the La_{0.4}Ca_{0.4}TiO₃ sample correspond with the observed anomalies of the thermal expansion, obtained by dilatometric method (Fig. 13). The derivative of the relative expansion with respect to temperature was used for more visibility of the anomalies registered by dilatometry.

Fig. 13 represents the linear thermal expansion of the $La_{(1,2+y)/3}Ca_{0,4}Cr_yTi_{1-y}O_3$ ceramic samples with x=0.4 and y=0, 0.2 and 0.5 measured in air by dilatometry in comparison with the YSZ ceramics. The thermal expansion coefficients of the $La_{0,4}Ca_{0,4}TiO_{3-\delta}$ (x=0.4, y=0) and YSZ samples measured by dilatometric method are almost equal. Increasing Cr-content (y) is accompanied by decreasing thermal coefficients of the corresponding ceramics.

The agreement of the thermal expansions of $La_{0.4}Ca_{0.4}$ TiO_{3- δ} and YSZ in air within the temperature range 20– 950 °C is typical for all others compounds of the series $La_{2(1-x)/3}Ca_xTiO_3$. Thermal expansion of $La_{0.47}Ca_{0.4}$ $Cr_{0.2}Ti_{0.8}O_3$ and YSZ in the temperature range 20–900 °C in air has only small difference. Properly, no thermo-mechanical compatibility problems should appear at stable contact between lanthanum–calcium titanates and solid electrolyte membranes based on YSZ.

The differences of the thermal expansion of the $La_{0.47}Ca_{0.4}Cr_{0.2}Ti_{0.8}O_3$ samples observed by using dilatometry and diffraction of synchrotron radiation are negligible small (Fig. 14).

3.4. Oxygen mobility

The gas dense ceramic samples could not be prepared on the basis of A-site stoichiometric compounds $La_{1-x}Ca_xCr_{1-y}Ti_yO_3$ [25] by sintering in air up to 1350 °C. Even small A-site defi-



Fig. 14. Relative thermal expansion of $La_{0.47}Ca_{0.4}Cr_{0.2}Ti_{0.8}O_3$ determined by dilatometry and diffraction of synchrotron radiation.



Fig. 15. Time dependence of the conductivity of the gas dense $La_{0.47}$ $Ca_{0.4}Cr_{0.2}Ti_{0.8}O_{3-\delta}$ ceramic sample after the corresponding gas flow switches.



Fig. 16. X-ray diffractograms of $La_{0.47}Ca_{0.4}Cr_{0.2}Ti_{0.8}O_{3-\delta}$ before and after annealing at 900 °C for 100 h in H₂/H₂O/Ar gas flow with $pH_2O/pH_2 = 0.01$.



Fig. 17. X-ray diffractograms of $La_{0.47}Ca_{0.4}Cr_{0.2}Ti_{0.8}O_{3-\delta}$ and $(La_{0.47}Ca_{1.4}Cr_{0.2}Ti_{1.4}Cr$ $Ca_{0.4}Cr_{0.2}Ti_{0.8}O_{3-\delta} + YSZ$) powder mixture after annealing at 1300 °C for 200 h in air.



gas dense ceramic samples was estimated by using the conductivity relaxation method [64]. Fig 15 demonstrates the conductivity relaxation of the La_{0.3}Ca_{0.4}Cr_{0.2}Ti_{0.8}O₃ specimen with density 4.10 g/cm3 (93% of the theoretical density) at 900 °C after abrupt change of the oxygen partial pressure around the ceramic sample between air and Ar/O₂ gas mixture with $pO_2 = 916$ Pa. The chemical diffusion coefficient of this ceramic sample at the mentioned conditions was estimated as $(5-9) \times 10^{-9}$ cm² s⁻¹. Similar values between $(1-10) \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$ were found for the samples of the series $La_{0.6-\gamma}Ca_{0.4}Cr_{0.2}Ti_{0.8}O_3$ with y = 0.05-0.3. No essential changes of the chemical diffusion coefficients for samples with different A-site deficiency were observed.

ciency gives this opportunity. The oxygen mobility in selected

3.5. Chemical stability

All prepared single-phase $La_{(2+v-2x)/3}Ca_xCr_vTi_{1-v}O_3$ compositions were phase stable at 20–1000 °C and $pO_2 = 10^{-15}$ to 10^5 Pa. For example, Fig. 16 demonstrates identity of the X-ray difractogramms of the La_{0.47}Ca_{0.4}Cr_{0.2}Ti_{0.8}O₃ powder before and after annealing at 900 °C in H₂/H₂O/Ar gas flow with $pH_2O/pH_2 = 0.01$ and Fig. 17 shows no reactivity between La_{0.47}Ca_{0.4}Cr_{0.2}Ti_{0.8}O₃ and YSZ after annealing up to 1300 °C in air. No interaction was detected by scanning and raster electron microscopy, too (Fig. 18). The corresponding smooth concentration profiles of the separate elements were observed in the range of 1-2 µm.

4. Conclusions

A-site deficient $La_{(2+v-2x)/3}Ca_xCr_vTi_{1-v}O_3$ solid solution with different perovskite-type structures (space groups Pbnm, Imma, I4/mcm and Cmmm or P2/m) is formed in the CaTiO₃-LaCrO₃-La_{2/3}TiO₃ quasi-ternary system in air conditions. Stabilization of the La_{2/3}TiO₃ structure by low-level substitution of the both A- and B-cation sites is observed. Continuous phase transitions from orthorhombic (*Cmmm*) or monoclinic (P2/m), to tetragonal (I4/mcm), orthorhombic (Imma) and orthorhombic (*Pbnm*) are registered for the Ca- and Cr-stabilized La_{2/3}TiO₃ structures. The compounds show high stability at high temperatures and reducing as well as oxidizing conditions. No reactivity between A-site deficient chromites-titanates and YSZ was observed in air up to 1300 °C. At 900 °C, the compositions with y = 0, 0.2 are n-type semiconductors, and with y = 0.5 show conductivity minima versus oxygen partial pressure these shift to oxygen reach region with the increasing, A-site deficiency. The A-site deficient samples have higher sintering ability in comparison with the cation stoichiometric $La_{1-x}Ca_xCr_{1-y}Ti_yO_3$ compositions and in contrast to the latter can be prepared in gas dense state in air at temperatures 1200-1300 °C. Thermal expansion of the A-site deficient ceramics is comparable with YSZ. The oxygen mobility can be characterised with chemical diffusion coefficients $(1-9) \times 10^{-9}$ cm² s⁻¹ at 900 °C and $pO_2 = 1000-21,000$ Pa. It seems that the relatively low oxygen mobility of the A-site deficient chromites-titanates serves as the only disadvantage of these compositions with

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3

Length / µm

100

50

Zr

Ca

Ti

La

- Cr

AND THE REAL PROPERTY AND

5

4

respect to their application as ideal anode material for SOFC.

Acknowledgements

The authors gratefully acknowledge the financial support of Deutsche Forschungsgemeinschaft (project GU 484/1-3). One of the authors (LV) acknowledges the support of Ukrainian Ministry of Education and Science (project "Cation") and ICDD Grant-in-Aid program.

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