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# Solid state synthesis, structure and transport properties of compositions in the $CaRu_{1-x}Ti_xO_{3-\delta}$ system

### V. Vashook<sup>a, c, \*</sup>, D. Nitsche<sup>a</sup>, L. Vasylechko<sup>b</sup>, J. Rebello<sup>a</sup>, J. Zosel<sup>c</sup>, U. Guth<sup>a, c</sup>

<sup>a</sup> Dresden University of Technology, D-01062 Dresden, Germany

<sup>b</sup> Lviv Polytechnic National University, 79013 Lviv, Ukraine

<sup>c</sup> Meinsberg Kurt-Schwabe Research Institute, Kurt-Schwabe-Straße 4, D-04720 Ziegra-Knobelsdorf, Germany

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#### ABSTRACT

Double *B* perovskite-type CaRu<sub>1-x</sub>Ti<sub>x</sub>O<sub>3-δ</sub> series with *x* = 0, 0.1, 0.2. . . 0.9, 1.0 were synthesized in air by solid state reactions from simple ruthenium and titanium oxides and CaCO<sub>3</sub>. Crystal structures of CaRu<sub>1-x</sub>Ti<sub>x</sub>O<sub>3</sub> samples have been refined in space group *Pnma* (GdFeO<sub>3</sub>-type of structure) assuming statistical distribution of Ru and Ti species over the octahedral sites. Electrical conductivity and thermal expansion were investigated at *t* = 20–1000 °C and *p*O<sub>2</sub> = 1–21000 Pa. Apart from CaRuO<sub>3</sub> with a combined p-/n-type conductivity depending on temperature and *p*O<sub>2</sub>, all other compositions are n-type semiconductors. The conductivity of CaRuO<sub>3</sub> decreases with increasing temperature (metal-type). The Ti-containing compositions with *x* = 0.1–0.2 change their conductivity dependence from metal-type at relatively low oxygen partial pressures (*p*O<sub>2</sub>) to semi-conducting-type at relatively high ones. The materials with *x* > 0.2 have the semi-conducting-type dependence at all investigated *p*O<sub>2</sub>. Disproportionation of Ru<sup>4+</sup> into Ru<sup>3+</sup> and Ru<sup>5+</sup> cations is considered for explanation of the conductivity dependences on temperature and *p*O<sub>2</sub>. The investigated compositions show high catalytic activity for propene oxidation and no activity for NO<sub>2</sub> reduction.

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#### 1. Introduction

Oxygen reduction reaction at the SOFC cathode is often the main limiting factor of the performance of the whole SOFC system [1]. Therefore, search for new cathode materials, which offer a sufficient electrochemical performance already at intermediate temperatures (500–750 °C), is one of the most important goals of SOFC research. Cathode materials must have high phase stability at high temperatures in air and at some lower oxygen partial pressures in contact with solid electrolyte, high electrical conductivity, oxygen mobility and catalytic activity. Additionally, their thermal expansion has to be compatible with that of solid electrolyte.

Ruthenium has long been recognized as an efficient catalyst in both metallic and oxide forms for a large number of reactions of commercial and environmental importance [2–4]. The perovskitetype CaRuO<sub>3</sub>, SrRuO<sub>3</sub> and BaRuO<sub>3</sub> compositions were synthesized and described for the first time in 1958 [5]. The conductivity of CaRuO<sub>3</sub> and SrRuO<sub>3</sub> under room temperatures was later found to be metal-type (decreasing conductivity at increasing temperature) [6,7]. Their room temperature conductivity ranges near 1000 S/cm. Recently the electrical conductivity of CaRuO<sub>3</sub> was unsystematically measured in air and argon [8].

In 1972, the conductivity of CaRuO<sub>3</sub> and SrRuO<sub>3</sub> single crystals was measured at 0–300 K in air [9]. The metal-type conductivity published earlier could be confirmed in both substances. An anomaly of the conductivity can be observed on SrRuO<sub>3</sub> at the Curie temperature. The conductivity of CaRuO<sub>3</sub> shows no anomalies near the Neel temperature. Generally the conductivities of both perovskites behave very similar. The differences between the magnetic parameters of both substances could not be clarified completely until date.

The formation of continuous  $CaRu_{1-x}Ti_xO_3$  solid solution with orthorhombic GdFeO<sub>3</sub>-type perovskite structure has been recently reported in [10,11]. It was mentioned, that impure phases, such as  $Ca_3Ru_2O_7$ , were observed in a few cases, without any relationship to the *x* value. No information was provided on the structure peculiarities of the solid solution. Lattice parameters are given only for some selected compositions of solid solution. Some of these recent publications indicate that the magnetic behaviour of the  $CaRu_{1-x}Ti_xO_3$ [11–13] system is not completely clarified till now.

Based on the above mentioned peculiarities and also the high thermal stability of  $CaTiO_3$  and its good thermal compatibility with yttrium stabilized zirconia, this work was directed on the investigation of solid state synthesis of the  $CaRu_{1-x}Ti_xO_3$  compositions from  $CaCO_3$ ,  $TiO_2$ , and  $RuO_{2-x}$ , the determination of thermal

<sup>\*</sup> Corresponding author. E-mail address: Vladimir.Vashook@chemie.tu-dresden.de (V. Vashook).

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expansion coefficients and crystal structure parameters of these solid solutions depending on Ti concentration, the measurement of the electrical conductivity ( $\sigma$ ) and oxygen non-stoichiometry at high temperatures up to 1000 °C in air and inert gas atmospheres with oxygen concentration down to 1 Pa, and the characterization of the catalytic activity of selected compounds for hydrocarbon oxidation and NO<sub>2</sub> reduction.

#### 2. Experimental

#### 2.1. Powder preparation and crystal structure investigation

 $CaRu_{1-x}Ti_xO_3$  (x = 0.0, 0.1, 0.2...10) specimens were prepared by solid state reactions using  $RuO_{2-x}$  (Fluka, 60% Ruthenium content), TiO<sub>2</sub> (Riedel-de Haen, 99.9% purity) and CaCO<sub>3</sub> (Grüssing GmbH, 99% purity) powders. The stoichiometric mixtures of initial powders were milled in ethanol in an agate ball mill for 24 h. After drying the mixtures were heated in air at different temperatures from 800 to 1300 °C for10–130 h in alumina crucibles. After cooling to room temperature the products were milled again and analyzed by powder X-ray diffractometry PXRD. The cooling and heating temperature rates during syntheses at these stages were 5 °C/min.

Phase composition and crystal structure were investigated by means of the powder diffraction technique using a Siemens D5000 powder X-ray diffractometer (Cu K<sub>\alpha</sub> radiation,  $\theta/2\theta$ -scanning mode, step width of 0.02°, counting time per step-7 s). The crystal structures were refined by the full-profile Rietveld method, including refinement of lattice parameters, positional and displacement parameters of atoms, site occupancy, scaling factor, sample shift, background and Bragg-peak profile parameters. The atomic displacement parameters were refined isotropically for all atoms. All calculations were performed using the WinCSD (Crystal Structure Determination) program package [14].

#### 2.2. Electrical conductivity

The electrical conductivity was measured using ceramic bars with rectangular cross section in gas atmospheres with defined oxygen partial pressures by a DC four-point method described elsewhere [15]. The powders were pressed into shapes of 1 mm × 3 mm × 10 mm together with 4 Pt wires (0.1 mm by diameter) and sintered for 20–130 h in air at 1300 °C. Heating and cooling rates during sintering were 5 K/min. The conductivity was measured at 20–1000 °C in air and in flowing gas mixtures of Ar/O<sub>2</sub> (1–100 Pa O<sub>2</sub>) and at heating rate 7 K/min and cooling rate 1.7 K/min. The temperature cycles were carried out in air, then in Ar gas flow at oxygen concentration 46, 4.6, 1 Pa, and then finally in air again. Similar measurements were repeated for all members of the CaRu<sub>1-x</sub>Ti<sub>x</sub>O<sub>3</sub> solid solution.

#### 2.3. Oxygen content

Changes in oxygen content were measured by solid electrolyte titration technique with PC-controlled Zirox-System device (Zirox, Greifswald, Germany). The concept of a combined coulometric-potentiometric arrangement for the investigation of interactions between solids and the gaseous phases in the carrier gas mode has been described earlier in [16,17]. The investigation of oxygen non-stoichiometry was performed on ceramic samples prepared as described in Section 2.2. Air and Ar/O<sub>2</sub> (1Pa) were used as the initial gas mixtures. The observed resolution of this method is better than 0.005 of change of the oxygen atomic index.

#### 2.4. Thermal expansion

The dilatometric analysis was performed by a L76/11C device (Linseis, Germany) on the  $3 \text{ mm} \times 3 \text{ mm} \times 20 \text{ mm}$  bars sintered in air at  $1300 \degree C$  for 20 h. The length

measurements were collected during heating up to  $900 \,^{\circ}$ C with the rate  $10 \,\text{K/min}$ . The measurements were carried out in nitrogen flow ( $12 \,\text{l/min}$ ) as well as in air atmosphere.

#### 2.5. Catalytic activity

The catalytic activity of the mixed oxide powders (surface area ~0.4 m<sup>2</sup>) was measured for propene oxidation and NO<sub>2</sub> decomposition between 100–850 °C. Reactive gas mixtures of  $0.5\%C_3H_6 + 2.5\%O_2$  in nitrogen and  $2\%NO_2$  in N<sub>2</sub> were used in catalytic tests. Due to temperature change the gas velocity ranged between 0.4 and 0.9 cm s<sup>-1</sup>. The conversion was determined by change in the peak areas of the C<sub>x</sub>H<sub>y</sub> absorption using a FTIR spectrometry at  $\nu = (2635-3225) \text{ cm}^{-1}$  (R–CH<sub>3</sub> peak) or at  $\nu = (1782-1955) \text{ cm}^{-1}$  (N–O peak). The FTIR-data were analyzed with program MERLIN Version 1.

#### 3. Results and discussions

#### 3.1. Synthesis of $CaRu_{1-x}Ti_xO_3$

X-ray diffraction examinations of the specimens from the (1–x)CaRuO<sub>3</sub>–xCaTiO<sub>3</sub> systems after treatment at 800 °C (1 h) + 1000 °C (5 h) show that these samples consist of mixtures of CaRuO<sub>3</sub> and CaTiO<sub>3</sub> in the ratio corresponding to the nominal composition. Remarkable broadening of the diffraction maxima was observed, indicating a poor crystallinity of the phases. No formation of CaRu<sub>1-x</sub>Ti<sub>x</sub>O<sub>3</sub> solid solution could be detected. Further heat treatment of the specimens at 1300 °C for 17 h led to significant changes in the phase compositions. X-ray diffraction examination revealed perovskite-like structure for all samples. No traces of non-perovskite phases were detected. Crystal structures of the end members of the system-CaRuO<sub>3</sub> and CaTiO<sub>3</sub>—were successfully refined in space group *Pnma* (Fig. 1). The main features of the diffraction profiles of all other compositions within the CaRuO<sub>3</sub>-CaTiO<sub>3</sub> system could be also satisfactorily reproduced in the GdFeO<sub>3</sub>-type of structure, assuming formation of  $CaRu_{1-x}Ti_xO_3$  solid solution. However, the examination of the diffraction profiles revealed, that starting from the  $CaRu_{0.9}Ti_{0.1}O_3$ nominal composition, a broadening of the selected diffraction maxima is observed at the patterns of the samples with "mixed" compositions. Besides, weak satellite peaks are observed near the (200), (301) and (321) reflections at the patterns of the samples with x = 0.2 - 0.6 (Fig. 2, top). In contrast to the main diffraction maxima, which are shifted to the higher angles with increasing Ti content in nominal sample compositions, the positions of satellite peaks remain unchanged. Besides, the intensities of satellite maxima diminish with increasing Ti concentration, becoming undetectable in the samples with x > 0.7. These observations could be explained by a coexistence of two perovskite phases with the same structure and slightly different lattice dimensions, mainly *a*-parameter. Two-phase Rietveld refinement of the samples with nominal composition x = 0.1 - 0.7 confirms this assumption. Signif-



Fig. 1. Graphical results of the Rietveld refinement of CaRuO<sub>3</sub> and CaTiO<sub>3</sub> structures. Observed and calculated profiles, differential curves (in the bottom of figures), as well as vertical bars indicating positions of diffraction maxima are shown.



(200), (121) and (002) reflections

(321), (240), (042) and (123) reflections

Fig. 2. Fragments of diffraction pattern of CaRu<sub>0.7</sub>Ti<sub>0.3</sub>O<sub>3</sub>, refined in single-phase (top) and two-phase models (bottom).

icantly better fits between experimental and calculated profiles were achieved by using refinement of two perovskite structures instead of single-phase one (Fig. 2). From the obtained results it is evident, that the samples with nominal compositions with x=0.1-0.7 consist of two perovskite phases **P1** and **P2** with the same GdFeO<sub>3</sub>-type structure. Being almost equal in the sample with the nominal composition CaRu<sub>0.9</sub>Ti<sub>0.1</sub>O<sub>3</sub>, the amount of **P1** phase systematically increases with increasing Ti content, whereas that of phase **P2** decreases. Lattice parameters and cell volume of **P1** phase change systematically with Ti content, whereas only minor changes in the lattice parameters were observed for **P2** phase. Moreover, the lattice dimensions of **P2** phase are very close to those of CaRuO<sub>3</sub>. From these observations it might be concluded that **P1** phase corresponds to CaRu<sub>1-x</sub>Ti<sub>x</sub>O<sub>3</sub> composition, and **P2** phase is almost pure CaRuO<sub>3</sub>.

Additional heat treatment of the samples at 1300 °C for 17 h led to an improved coincidence of the experimentally collected and fitted XRD-patterns of the specimens, shown by decreasing intensity of satellite maxima and narrowing of some diffraction peaks of the main perovskite phase. Single-phase compositions were found for CaRu<sub>1-x</sub>Ti<sub>x</sub>O<sub>3</sub> samples with x = 0.6-0.9. Nevertheless, Ru-rich specimens (x = 0.1-0.5) remain two-phase, although a relative amount of minor perovskite phase **P2** has been reduced at about 10–20% in comparison with the previous series (Fig. 3).

Improved phase and structural quality of  $CaRu_{1-x}Ti_xO_3$  specimens with x < 0.5 has been achieved only after long-term annealing at 1300 °C for 100 h. No signs of the presence of minor perovskite phase, which was observed in the previous series, are visible now at the patterns of all  $CaRu_{1-x}Ti_xO_3$  samples. According to XRD examination, the  $CaRu_{1-x}Ti_xO_3$  samples with x = 0.3-1 display single-phase compositions with orthorhombic perovskite structure. Only at the patterns of two Ru-rich specimens (x = 0.1 and 0.2) the parasitic peaks of  $Ca_3Ru_2O_7$  (or  $Ca_3(Ru,Ti)_2O_7$ ) phase(s) with relative intensities less than 5% are observed. Besides, 2-3 residual

peaks of unidentified phase with relative intensities less than 1% are visible at these patterns. The presence of  $Ca_3Ru_2O_7$  as an impure phase in the  $CaRu_{1-x}Ti_xO_3$  system without any relationship with the *x* value has been also mentioned by Hardy et al. [11].

Crystal structures of all CaRu<sub>1-x</sub>Ti<sub>x</sub>O<sub>3</sub> specimens have been successfully refined in space group *Pnma* (GdFeO<sub>3</sub>-type of structure) assuming statistical distribution of Ru and Ti species over octahedral sites. As an example, graphical results of the Rietveld refinement of CaRu<sub>0.7</sub>Ti<sub>0.3</sub>O<sub>3</sub> and CaRu<sub>0.3</sub>Ti<sub>0.7</sub>O<sub>3</sub> structures are presented in Fig. 4. Refined values of structural parameters of all the CaRu<sub>1-x</sub>Ti<sub>x</sub>O<sub>3</sub> specimens are collected in Table 1. It has to be noticed that for Ru-rich specimens the values of the atomic displacement parameters of oxygen atoms are 3–4 times higher than correspond-



**Fig. 3.** Relative amount of **P1** and **P2** perovskite phases in the  $CaRu_{1-x}Ti_xO_3$  samples after heat treatment at 1300 °C for 17 h (open symbols) and 2 × 17 h (solid symbols).



Fig. 4. Graphical results of the Rietveld refinement of CaRu<sub>0.7</sub>Ti<sub>0.3</sub>O<sub>3</sub> (left) and CaRu<sub>0.3</sub>Ti<sub>0.7</sub>O<sub>3</sub> (right) structures. Observed (circles) and calculated (lines) profiles and differential curves (in the bottom of figures) are shown. Vertical bar profiles below indicate positions of diffraction maxima.

ing values for Ca and Ru/Ti species, which might indicate some deficiency in oxygen sublattice of these compounds. Lattice parameters and cell volumes of the samples in the CaRuO<sub>3</sub>–CaTiO<sub>3</sub> system change systematically with composition and vary between corresponding lattice dimensions of pure CaRuO<sub>3</sub> and CaTiO<sub>3</sub> (Fig. 5). Excellent agreement is observed between these results and those reported in [11].

Analysis of the obtained results clearly proves the formation of continuous solid solution with perovskite structure in the CaRuO<sub>3</sub>–CaTiO<sub>3</sub> pseudo-binary system. Gradual substitution of Ti for Ru sites in CaRu<sub>1-x</sub>Ti<sub>x</sub>O<sub>3</sub> series leads to an almost linear decrease of the cell volume, in accordance with reducing average ionic radii (rRu<sup>4+</sup> = 0.62 Å and rTi<sup>4+</sup> = 0.605 Å for octahedral sites, according to Shannon's scale). Dependence of the lattice parameters on concentration displays strongly anisotropic non-linear behavior. The decrease of the *a*- and *b*-parameters in CaRu<sub>1-x</sub>Ti<sub>x</sub>O<sub>3</sub> series is accompanied by an increase of the *c*-parameter (Fig. 5). This anisotropy is especially pronounced for the compositions with  $0 \le x \le 0.5$ , whereas for the Ti-rich specimens the character of the



**Fig. 5.** Concentration dependences of the lattice parameters and cell volume of perovskite phase in the samples with nominal composition CaRu<sub>1-x</sub>Ti<sub>x</sub>O<sub>3</sub>. For a comparison, literature data for CaRu<sub>0.3</sub>Ti<sub>7</sub>O<sub>3</sub> [11] are shown as well (crossed symbols). Lattice parameters of the orthorhombic cell are normalized to perovskite-like cell parameters as follows:  $a_p = a_0/\sqrt{2}$ ,  $b_p = b_0/2$ ,  $c_p = c_0/\sqrt{2}$ ,  $V_p = V_0/4$ .

lattice expansion is more or less regular. In this respect, two ranges of the solid solution can be distinguished in the system.

#### 3.2. Electrical conductivity

#### 3.2.1. Electrical conductivity and oxygen exchange

The time dependencies of the conductivity of the CaRu<sub>0.7</sub>Ti<sub>0.3</sub>O<sub>3</sub> ceramic sample (line 1), temperature (line 2) and voltage in the potentiometric cell of a Zirox-System device before reactor (line 3) are presented in Fig. 6. The Ti content dependencies of the conductivity measured during cooling in air with a rate 1.7 K/min for different temperatures are presented in Fig. 7. CaRu<sub>0.9</sub>Ti<sub>0.1</sub>O<sub>3</sub> has the highest conductivity at 400, 700, and 1000 °C, but CaRuO<sub>3</sub> shows the highest one at 100 °C.

Fig. 8 illustrates an extremely small oxygen exchange between even the Ru-richest CaRuO<sub>3</sub> composition and gas phase during heating–cooling process in Ar/O<sub>2</sub> gas mixture flow (51/h) with  $pO_2 = 2.5$  Pa. The sample was pretreated in air. Not the slightest deviation from the base line was observed for titration current on the cell 2 (line 1) of a Zirox-System device in the temperature range 20–1000 °C.

On the other hand, Fig. 9 illustrates visible dependence of conductivity from oxygen concentration in the ambient atmosphere around the sample. Line 1 shows the temperature dependence of the conductivity during cooling in  $Ar/O_2$  gas flow with  $pO_2 = 1$  Pa, line2 corresponds to the following heating treatment of that sample in air. At last line 3 corresponds to the following cooling down of the sample in air. Starting at 300–350 °C, the conductivity of the sample during heating in air (line 2) deviates from the line 1 (initial



**Fig. 6.** Time dependences of the conductivity (line 1), temperature (2), and voltage (3) in potentiometric cells of a Zirox-System device.

Table 1
Refined values of structural parameters of $CaRu_{1-x}Ti_xO_3$ in the space group Pnma.

Atom sites	Parameters	x in CaRu <sub>1-x</sub> Ti <sub>x</sub> O <sub>3</sub>										
		0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
	a, Å b, Å c, Å	5.52849(4) 7.66516(5) 5.36270(4)	5.51714(6) 7.66507(9) 5.36910(6)	5.50405(5) 7.66366(6) 5.37391(4)	5.49351(5) 7.66270(6) 5.37843(4)	5.48232(5) 7.65972(7) 5.38083(5)	5.47444(4) 7.65963(6) 5.38421(4)	5.46650(6) 7.65679(8) 5.38526(5)	5.45890(4) 7.65186(6) 5.38379(4)	5.45315(3) 7.64901(4) 5.38369(3)	5.44893(3) 7.64651(5) 5.38335(3)	5.44079(5) 7.64246(7) 5.38135(4)
Ca, 4c	x y z B <sub>iso</sub> , Å <sup>2</sup>	$\begin{array}{c} 0.9437(2)\\ \frac{1}{4}\\ 0.0162(4)\\ 0.62(3) \end{array}$	0.9557(3) $\frac{1}{4}$ 0.0180(5) 0.71(4)	$\begin{array}{c} 0.9522(2) \\ \frac{1}{4} \\ 0.0137(5) \\ 0.75(3) \end{array}$	$\begin{array}{c} 0.9527(2) \\ \frac{1}{4} \\ 0.0112(6) \\ 0.72(3) \end{array}$	$\begin{array}{c} 0.9544(2) \\ \frac{1}{4} \\ 0.0120(6) \\ 0.67(3) \end{array}$	$\begin{array}{c} 0.9574(1) \\ \frac{1}{4} \\ 0.0111(4) \\ 0.66(2) \end{array}$	0.9593(2) $\frac{1}{4}$ 0.0159(4) 0.66(3)	0.9599(1) <sup>1</sup> ⁄ <sub>4</sub> 0.0120(3) 0.73(2)	$\begin{array}{c} 0.9612(1)\\ \frac{1}{4}\\ 0.0080(2)\\ 0.77(1) \end{array}$	$\begin{array}{c} 0.9623(1) \\ \frac{1}{4} \\ 0.0079(2) \\ 0.82(1) \end{array}$	0.9645(1) <sup>1</sup> / <sub>4</sub> 0.0103(3) 0.91(2)
Ru/Ti, 4b	x y z B <sub>iso</sub> , Å <sup>2</sup>	0 0 ½ 0.67(1)	0 0 ½ 0.63(1)	0 0 ½ 0.75(1)	0 0 ½ 0.75(1)	0 0 ½ 0.78(2)	0 0 ½ 0.70(1)	0 0 ½ 0.90(1)	0 0 ½ 0.75(1)	0 0 ½ 0.750(9)	0 0 ½ 0.69(1)	0 0 ½ 0.63(2)
01, 4c	x y z B <sub>iso</sub> , Å <sup>2</sup>	0.0214(10) $\frac{1}{4}$ 0.5925(8) 3.16(12)	0.024(2) 1⁄4 0.5927(13) 3.8(2)	$0.0218(11) \\ \frac{1}{4} \\ 0.5925(10) \\ 4.3(2)$	$\begin{array}{c} 0.0248(13)\\ \frac{1}{4}\\ 0.5905(10)\\ 3.41(15) \end{array}$	$\begin{array}{c} 0.0191(13)\\ \frac{1}{4}\\ 0.5900(10)\\ 2.9(2) \end{array}$	0.0278(7) $\frac{1}{4}$ 0.5852(6) 1.51(9)	0.0327(8) <sup>1/</sup> 4 0.5825(7) 1.13(11)	0.0200(6) <sup>1/</sup> 4 0.5791(5) 1.09(7)	$\begin{array}{c} 0.0184(4) \\ \frac{1}{4} \\ 0.5777(4) \\ 1.08(5) \end{array}$	$\begin{array}{c} 0.0151(4) \\ \frac{1}{4} \\ 0.5752(4) \\ 0.97(6) \end{array}$	0.0199(6) 1⁄4 0.5699(6) 1.75(8)
O2, 8d	x y Z B <sub>iso</sub> , Å <sup>2</sup> R <sub>1</sub> R <sub>P</sub>	0.2077(6) 0.4506(4) 0.2010(6) 2.49(9) 0.0500 0.0994	0.2070(10) 0.4512(7) 0.2062(11) 2.70(14) 0.0565 0.1331	0.2112(7) 0.4560(5) 0.2074(7) 3.62(11) 0.0519 0.1102	0.2094(7) 0.4584(5) 0.2013(7) 2.30(11) 0.0661 0.1195	0.2117(9) 0.4626(6) 0.2069(9) 2.91(12) 0.0625 0.1048	0.2077(5) 0.4617(4) 0.2094(5) 2.00(7) 0.0613 0.0937	0.2054(7) 0.4610(5) 0.2091(8) 2.46(10) 0.0851 0.1227	0.2102(4) 0.4612(3) 0.2113(5) 1.30(6) 0.0601 0.0878	0.2096(3) 0.4615(2) 0.2108(3) 1.32(4) 0.0511 0.0762	0.2106(4) 0.4628(3) 0.2127(4) 1.27(4) 0.0526 0.0752	0.2083(4) 0.4630(3) 0.2097(5) 1.04(5) 0.0741 0.1138





**Fig. 8.** Time dependences of the conductivity (line 1), temperature (2), titration current in the coulometric (3) and voltage (4) in potentiometric cells of a Zirox-System device.



Fig. 7. Ti content dependences of the conductivity of the CaRu<sub>1-x</sub>Ti<sub>x</sub>O<sub>3</sub> solid solution at 100, 400, 700 and 1000  $^\circ$ C in air.





Fig. 10. Temperature dependences of the conductivity for some  $CaRu_{1-x}Ti_xO_3$  compounds at different oxygen partial pressures.

cooling process in Ar/O<sub>2</sub> gas flow). This behavior points indirectly to oxygen exchange between the solid sample and the gas phase at temperatures above 300–350 °C. The coincidence between the heating (line 2) and cooling (line 3) conductivities in air at temperatures above 700 °C indicate the establishment of equilibrium states between sample and gas phase at the used treatment conditions. This oxygen exchange cannot be detected, because variation of oxygen atomic index is much smaller than 0.005.

#### 3.2.2. Temperature dependences of the conductivity

The temperature dependences of the conductivity in gas flows with different oxygen concentrations for some of the  $CaRu_{1-x}Ti_xO_3$ 

samples are shown in Fig. 10a–e. Fig. 10f presents the conductivity versus temperature for all investigated compositions in air, for comparison.

Conductivity type of the CaRu<sub>1-x</sub>Ti<sub>x</sub>O<sub>3</sub> compositions changes with Ti content. CaRuO<sub>3</sub> shows metal-type behavior in the temperature range 20–1000 °C at  $pO_2 = 1$ , 4.5, 46 and 21000 Pa, CaRu<sub>0.9</sub>Ti<sub>0.1</sub>O<sub>3</sub> is metal-type at 1–46 Pa but semiconductor-type in air, CaRu<sub>0.8</sub>Ti<sub>0.2</sub>O<sub>3</sub> shows metallic properties at  $pO_2 = 1$  Pa (t > 100 °C) and 4.5 Pa (t > 500 °C), but semiconducting ones at higher oxygen partial pressure, and at last the CaRu<sub>1-x</sub>Ti<sub>x</sub>O<sub>3</sub> compositions with x = 0.3-1.0 are semiconductors in the entire investigated temperature– $pO_2$  area.



Fig. 11.  $pO_2$  dependences of the conductivity for some CaRu<sub>1-x</sub>Ti<sub>x</sub>O<sub>3</sub> compounds at different temperatures.

#### 3.2.3. $pO_2$ dependences of the conductivity

The  $pO_2$  dependences of the conductivity for some CaRu<sub>1-x</sub>Ti<sub>x</sub>O<sub>3</sub> compositions are shown in Fig. 11. Apart from CaRuO<sub>3</sub> all other compositions are the n-type semiconductors showing very small slopes of the conductivity versus  $pO_2$  (Fig. 11e and f). The CaRuO<sub>3</sub> sample shows feebly marked p-type conductivity at 500–1000 °C in low oxygen pressure region. The changing temperature dependences of the conductivity from metal- to semiconductor-type, which are shown for CaRu<sub>0.9</sub>Ti<sub>0.1</sub>O<sub>3</sub> and CaRu<sub>0.8</sub>Ti<sub>0.2</sub>O<sub>3</sub> in Fig. 10b and c, are also presented in the conductivity vs. oxygen partial pressure dependences in Fig. 11b and c, respectively.

#### 3.2.4. Defect model of the $CaRu_{1-x}Ti_xO_3$ compounds

Very weak dependences of the conductivity on oxygen partial pressure (Fig. 11) and changes between n- and p-type conductivity of some of the  $CaRu_{1-x}Ti_xO_3$  compositions point to possible coexistence of negative and positive electronic defects in these samples. Because  $Ca^{2+}$  and  $Ti^{4+}$  cations and  $O^{2-}$  anions are very stable, only

Ru-cations can be considered as possible defects sites for an explanation of the observed conductivity dependences.

Disproportionation of the Ru<sup>4+</sup> cations to Ru<sup>3+</sup> and Ru<sup>5+</sup> can be considered for explanation of changing conductivity type. In terms of the Kröger-Vink notation this process can be written as:

$$2Ru_{Ru}^{\times} \Leftrightarrow Ru_{Ru}^{\prime} + Ru_{Ru}^{\prime} \tag{1}$$

The excess electrons (e<sup>*l*</sup>) are localized on the Ru<sup>3+</sup> cations (Ru<sup>*l*</sup><sub>Ru</sub>) and the holes ( $h^{\bullet}$ ) on the Ru<sup>5+</sup> cations (Ru<sup>*i*</sup><sub>Ru</sub>). The conductivity, which decreases with oxygen partial pressure (n-type) can be explained by the defect reaction:

$$2Ru_{Ru}^{\prime} + 0.5O_2 + V_0^{\bullet\bullet} \Leftrightarrow 2Ru_{Ru}^{\times} + O_0^{\times}$$

$$\tag{2}$$

and conductivity increasing with pO<sub>2</sub> (p-type) by the reaction:

$$2\mathrm{Ru}_{\mathrm{Ru}}^{\times} + 0.5\mathrm{O}_2 + \mathrm{V}_0^{\bullet} \Leftrightarrow 2\mathrm{Ru}_{\mathrm{Ru}}^{\bullet} + \mathrm{O}_0^{\times} \tag{3}$$

Probably, both electronic defects are responsible simultaneously for the observed low  $log(\sigma)$  vs.  $log(pO_2)$  slopes, and only excess



Fig. 12. Thermal expansion of CaRu<sub>0.7</sub>Ti<sub>0.3</sub>O<sub>3</sub>, CaRu<sub>0.5</sub>Ti<sub>0.5</sub>O<sub>3</sub> and CaRu<sub>0.3</sub>Ti<sub>0.7</sub>O<sub>3</sub> in air (a) and nitrogen flow (b).

of one of these defects determines the conductivity type of the  $CaRu_{1-x}Ti_xO_3$  compositions (Fig. 11). That means that apart from  $CaRuO_3$  at low oxygen partial pressures all other compositions with n-type conductivity at all investigated oxygen partial pressures and at 400–1000 °C must have an excess of  $Ru^{3+}$  cations. This assumption is also supported by the structure analysis data, given in Section 3.1, indicating some oxygen deficit in Ru-rich compounds.

#### 3.3. Thermal expansion

Thermal expansion coefficients of CaRu<sub>0.7</sub>Ti<sub>0.3</sub>O<sub>3</sub>, CaRu<sub>0.5</sub>Ti<sub>0.5</sub>O<sub>3</sub> and CaRu<sub>0.3</sub>Ti<sub>0.7</sub>O<sub>3</sub> in the temperature range 20–900 °C do not depend on oxygen partial pressure but they increase with the Ti content (Fig. 12a and b). No anomalies were observed, which might indicate absence of the phase transformations in these compounds in the temperature range investigated. The small increase of the temperature slope of the expansion curves might be probably connected with small desorption of oxygen. The deviations of linearity are observed over 300 °C, which correlates with conductivity behavior (Fig. 9).

Table 2 presents the calculated thermal expansion coefficients (TEC) for the separate  $CaRu_{1-x}Ti_xO_3$  ceramics together with literature data for solid electrolyte ceramics. The TEC's of the investigated samples differ from that of CeO<sub>2</sub> between 4.4 and 10.1% and from that of YSZ between 64.1 and 76.0% at 700 °C. After [18] materials with less than 9% TEC difference are thermal-mechanically compatible during heating–cooling processes.

#### 3.4. Catalytic activity

#### 3.4.1. Propene oxidation

Fig. 13 shows propene conversion vs. temperature on the different  $CaRu_{1-x}Ti_xO_3$  powders. Total propene conversion was observed

Table 2	
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TEC va	lues for	some of	the CaRu1	$-xTi_xO_2$	ceramics.
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	TEC at 700 °C in 10 <sup>-6</sup> K <sup>-1</sup>	TEC at 900 °C in 10 <sup>-6</sup> K <sup>-1</sup>	TEC at 1000 °C in 10 <sup>-6</sup> K <sup>-1</sup>
YSZ	6.8	9.7	10.9
Doped CeO <sub>2</sub> CaRu <sub>0.7</sub> Ti <sub>0.3</sub> O <sub>3</sub>	12.5 [18] 11.24 in air 11.16 in N <sub>2</sub>	- 11.69 in air 11.60 in N <sub>2</sub>	12.1–13.6 [19] – –
CaRu <sub>0.5</sub> Ti <sub>0.5</sub> O <sub>3</sub>	11.58 in air 11.57 in N <sub>2</sub>	11.98 in air 12.00 in N <sub>2</sub>	- -
CaRu <sub>0.3</sub> Ti <sub>0.7</sub> O <sub>3</sub>	11.97 in air 11.95 in N <sub>2</sub>	12.41 in air 12.36 in N <sub>2</sub>	-



Fig. 13. Catalytic activity of some of the  $\text{CaRu}_{1-x}\text{Ti}_x\text{O}_3$  powders for propene oxidation.

with all powder samples at 850 °C. The rapid increase of the conversion rate starts at 630 °C on CaTiO<sub>3</sub> and at 500 °C on the Rucontaining compositions. The high catalytic activity is connected with Ru species as catalytic centres. The concentration of the Ru in the compositions does not play a big role.

#### 3.4.2. NO<sub>2</sub> decomposition

The CaRu<sub>0.3</sub>Ti<sub>0.7</sub>O<sub>3</sub>, CaRu<sub>0.5</sub>Ti<sub>0.5</sub>O<sub>3</sub> und CaRu<sub>0.7</sub>Ti<sub>0.3</sub>O<sub>3</sub> powders show no catalytic activity for the reduction of nitrogen dioxide. No differences were observed in conversion of NO<sub>2</sub> between empty quartz reactor and the reactor contained the CaRu<sub>1-x</sub>Ti<sub>x</sub>O<sub>3</sub> powders.

#### 3.5. Conclusions

Single-phase double *B* perovskite-type  $CaRu_{1-x}Ti_xO_{3-\delta}$  series were synthesized in air by solid state reactions at 1300 °C from simple ruthenium and titanium oxides and CaCO<sub>3</sub>. Crystal structures of these compositions can be refined in space group *Pnma* assuming statistical distribution of Ru and Ti species over the octahedral sites. Apart from CaRuO<sub>3</sub> all other investigated compositions are n-type semiconductors with a relatively small slope of the  $log(\sigma) - 1/T$  dependences. A metal-type temperature dependence of conductivity was found for CaRuO<sub>3</sub> at  $pO_2 = 1-21000$  Pa and for CaRu<sub>0.9</sub>Ti<sub>0.1</sub>O<sub>3</sub> and CaRu<sub>0.8</sub>Ti<sub>0.2</sub>O<sub>3</sub> at low oxygen partial pressures. The CaRu<sub>1-x</sub>Ti<sub>x</sub>O<sub>3- $\delta}$ </sub> ceramics with x > 0.2 are semiconductors. The highest conductivity in air was found for CaRu<sub>0.9</sub>Ti<sub>0.1</sub>O<sub>3</sub>. Changing with temperature and oxygen partial pressure the conductivity of  $CaRu_{1-x}Ti_xO_3$  ceramics was explained with the coexistence of electron and hole defects formed by disproportionation of  $Ru^{4+}$  into  $Ru^{3+}$  and  $Ru^{5+}$  cations. Very small oxygen exchange that cannot be registered directly by solid state coulometry was proposed for the explanation of the  $pO_2$  dependences of conductivity. Ru-containing compositions show high catalytic activity for propene oxidation but no measurable activity for NO<sub>2</sub> reduction.

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