High-temperature crystal structure and transport properties of the layered cuprates $Ln_2CuO_4$, $Ln=$ Pr, Nd and Sm

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**ABSTRACT**

High-temperature crystal structure of the layered cuprates $Ln_2CuO_4$, $Ln=$ Pr, Nd and Sm with tetragonal $T$-structure was refined using X-ray powder diffraction data. Substantial anisotropy of the thermal expansion behavior was observed in their crystal structures with thermal expansion coefficients (TEC) along $\alpha$- and $c$-axis changing from TEC($\alpha$)/TEC($c$) $\approx$ 1.37 (Pr) to 0.89 (Nd) and 0.72 (Sm). Temperature dependence of the interatomic distances in $Ln_2CuO_4$ shows significantly lower expansion rate of the chemical bond between Pr and oxygen atoms ($O_1$) belonging to CuO$_2$-planes (TEC($Pr$–$O_1$) $=$ 11.7 ppm K$^{-1}$) in comparison with other cuprates: TEC ($Nd$–$O_1$) $=$ 15.2 ppm K$^{-1}$, and TEC ($Sm$–$O_1$) $=$ 15.1 ppm K$^{-1}$. High-temperature electrical conductivity of Pr$_2$CuO$_4$ is the highest one in the whole studied temperature range (298–1173 K): 0.1–108 S/cm for Pr$_2$CuO$_4$, 0.07–23 S/cm for Nd$_2$CuO$_4$ and 4–9 S/cm for Sm$_2$CuO$_4$. The trace diffusion coefficient ($D_T$) of oxygen for Pr$_2$CuO$_4$ determined by isotopic exchange depth profile (IEDP) technique using secondary ion mass spectrometry (SIMS) varies in the range $7.2 \times 10^{-15}$ cm$^2$/s (973 K) and $3.8 \times 10^{-10}$ cm$^2$/s (1173 K) which are in between those observed for the manganese and cobalt-based perovskites.

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1. Introduction

Nowadays solid oxide fuel cells (SOFCs) are considered as one of the alternative to traditional hydrocarbons sources of energy due to their high efficiency and excellent fuel flexibility [1,2]. They are operating at high temperature up to 1273 K and this creates numerous problems such as chemical stability, matching of the thermal expansion coefficients (TEC) between the components of the SOFC, etc. [3–5]. Therefore, efforts are directed to the creation of the so-called intermediate temperature SOFC (IT-SOFC) with operation temperatures down to 773 K [6]. However, at such low temperature efficiency of the traditional electrode materials ($La_xSr_yMnO_3$ (LSM) for cathode and $Ni-(Zr,Y)O_2$ (YSZ) for anode) dramatically decreases and novel electrode materials with improved properties are needed.

A number of efforts were made to prepare oxide compounds having superior characteristics in comparison with the widely used LSM cathode material. Recently, layered cuprates have attracted attention for the application in high-temperature electrochemical devices. Some of them show high total conductivity up to $\approx 800$ S/cm at 1073 K as, for example, $La_{2/3}Sr_{1/3}CuO_2$ [7]. Main drawbacks of the cuprates as cathode materials in SOFC are high TEC up to 17.9 ppm K$^{-1}$ for $La_{1-x}Sr_xCu_2O_4$ [8] or 16.0 ppm K$^{-1}$ for $La_2Sr_2CuO_5$ [9] and high chemical activity toward reaction with electrolyte [8]. One of the reasons for such behavior could be instability at high temperature of oxides with copper in higher oxidation state $>+2$. Therefore, it is expectable that cuprates with Cu$^{2+}$ only could have better properties for high-temperature applications. Indeed, $La_2CuO_4$ has average TEC as low as 12.3 ppm K$^{-1}$, however, exhibits quite low conductivity at high temperature ($\sim 15$ S/cm at 1200 K) [10].

Depending on the ionic radius of the rare-earth cation, $Ln_2CuO_4$ cuprates are known to crystallize in different structure types. $La_2CuO_4$ with large $La^{3+}$ cation (Fig. 1A) crystallizes in the $K_{2}NiF_4$-type structure (so called T-phase), while other cuprates with smaller $Ln^{3+}$ cations, have $Nd_2CuO_4$-type structure (T-phase) (Fig. 1B). Although the high-temperature properties of the $La_2CuO_4$ are well studied, much less information is available for other $Ln_2CuO_4$ cuprates. However, one can expect that these compounds could be...
of interest since Ce-doped Nd$_2$CuO$_4$ with T-structure was found to exhibit promising properties for SOFC cathode application [11].

In the present paper, we report on the study of the thermal expansion, high-temperature electrical conductivity and high-temperature crystal structure of the cuprates Ln$_2$CuO$_4$, Ln=Pr, Nd and Sm performed in order to evaluate their possible use as cathode materials in SOFC. For Pr$_2$CuO$_4$ we have also determined oxygen trace diffusion and surface exchange coefficients using the diffusion of the isotope $^{18}$O detected by secondary ion mass spectrometry (SIMS).

2. Experimental

Ln$_2$CuO$_4$, Ln=Pr, Nd and Sm were synthesized by annealing of the stoichiometric mixtures of Nd(Sm)$_2$O$_3$ or Pr$_4$O$_{11}$ and CuO in air at 1273 K, 20 h (Ln=Pr, Nd) and 1323 K, 50 h (Sm). Copper oxide was prepared by decomposition of (CuOH)$_2$CO$_3$ at 573 K. Oxygen content of the cuprates was determined by iodometric titration.

Phase purity of the compounds was checked by X-ray powder diffraction (XRD) recorded in Huber G670 Guinier diffractometer (Cu$K_a$ radiation, image foil detector). High-temperature X-ray powder diffraction (HT XRD) data were collected in air using Bruker D8–Advance diffractometer (CuK$\alpha_1$ radiation, Vanlec PSD) in reflection mode equipped with high-temperature camera XKR-900 (Anton Paar). Crystal structures of the cuprates at different temperatures were refined by Rietveld method using TOPAS-3 program package.

Netzsch 402C dilatometer operated in air (298–1173 K, 10 K/min) was used for the thermal expansion coefficient measurements. For the thermal expansion measurements oxide powders were pressed into pellets 8 mm in diameter and 5–5.5 mm in height and annealed at 1343 K.

High-temperature electrical conductivity of the ceramic samples was measured in air by a standard 4-probe method in the temperature range of 298–1173 K. The samples have a typical shape of a disk with ~20 mm diameter and 1–2 mm thickness. The contacts were made from platinum wire (~0.2 mm) placed in alumina tube and were pressed independently to the surface of the sample by separate individual springs situated at the top of the quartz sample holder kept at room temperature. The contacts were arranged in a line with 5–6 mm spacing between them. The influence of undesirable thermoelectric power was omitted by subtracting two successive voltage values on the potential contacts (the inner pair) measured at opposite current directions. The resulting resistivity value was recalculated into specific resistance using the approach developed in [12].

Dense ceramic samples for SIMS study were prepared by spark plasma sintering (SPS), 2–2.4 g of Pr$_2$CuO$_4$ powders were filled into a graphite die with an inner diameter of 12 mm. The temperature was measured with an optical pyrometer focused on the surface of the graphite die and automatically regulated from 873 to 1273 K or 1323 K at a heating rate of 50 K/min. The temperature of 873 K was reached via a preset heating program by 4 min. The holding time was set to 5 min at the final temperature. A constant uniaxial pressure of 50 MPa was applied during the whole sintering period. After sintering, a surface layer (about 0.5 mm) of the ceramic sample was removed by polishing with sandpaper and ultrasonically cleaned in acetone to remove polish residues. Phase purity of the ceramic sample was checked by XRD.

The $^{18}$O penetration profiles were determined on a TOF-SIMS 5 instrument operated in depth profile mode, with a 45° incidence 25 keV Bi$^+$ primary ion beam; the crater depth was measured after the SIMS analysis by surface profilometry (Taylor–Hobson Talystep).

3. Results and discussion

3.1. Thermal expansion properties and high-temperature crystal structure of Ln$_2$CuO$_4$, Ln=Pr, Nd and Sm

XRD patterns of Ln$_2$CuO$_4$, Ln=Pr, Nd and Sm at room temperature were fully indexed in tetragonal f-centered unit cells with parameters $a=3.9608(1)$ Å; $c=12.1626(1)$ Å (Ln=Nd); $a=3.9414(1)$ Å; $c=12.1626(1)$ Å (Ln=Nd); $a=3.9136(2)$ Å; $c=11.9708(5)$ Å (Ln=Sm), which correspond to the literature data for these phases [13]. A clear decrease of the unit cell dimensions is observed with decreasing of the ionic radius of the rare-earth cation from Pr$^{3+}$ to Sm$^{3+}$ ($r_{Pr}^{3+} = 1.14$ Å, $r_{Nd}^{3+} = 1.12$ Å, $r_{Sm}^{3+} = 1.09$ Å, CN=8 [14]). Oxygen content of the phases, as determined by iodometric titration, corresponds within e.s.d. to the stoichiometric composition.

Thermal expansion curves for Ln$_2$CuO$_4$, Ln=Pr, Nd and Sm ceramic samples obtained by dilatometry are shown in Fig. 2. Calculated linear thermal expansion coefficients (TEC) are given in Table 1. Temperature dependences of the unit cell parameters

![Fig. 1. The crystal structures of T-(K$_2$NiF$_4$) (A) and T-phases (B).](image)

![Fig. 2. Thermal expansion curves for Ln$_2$CuO$_4$, Ln=Pr, Nd and Sm.](image)
of Ln2CuO4, Ln=Pr, Nd and Sm, as determined from high-temperature XRD data, are shown in Figs. 3A and B. TEC values of the cuprates calculated from the temperature dependence of unit cell volume (VT/3) correspond well to those from the dilatometry data (Table 1). It should be mentioned that they are higher in the comparison with those determined using dilatometry in the same temperature range by Kharton et al. [15] for Pr2CuO4 (10.21(7) ppm K−1) and Nd2CuO4 (10.12(2) ppm K−1).

Calculated TEC values along a-axis (TEC(a)) and c-axis (TEC(c)) of Ln2CuO4 are given in Table 1. Decreasing of TEC(a) from Pr to Sm is correlated with decreasing copper–oxygen in-plane bond length as can be observed from the unit cell dimensions of Ln2CuO4 given above. At the same time, TEC(c) increases from Pr2CuO4 to Sm2CuO4. Moreover, for Pr2CuO4 TEC(a) is substantially higher in comparison with TEC(c): TEC(a)/TEC(c) ≈ 1.37 (Table 1). Opposite situation is observed for Nd2CuO4 and Sm2CuO4 where TEC(a)/TEC(c) ≈ 0.89 (Nd) and 0.72 (Sm).

In order to reveal structural reason for such behavior, high temperature crystal structures of Ln2CuO4 were refined. Initial atomic coordinates were taken from the room-temperature data for Pr2CuO4 (S.G. I4/mm/m) [16]. As an example, results of the Rietveld refinement’s for Ln2CuO4, Ln=Pr, Nd and Sm using XRD data recorded at 298 and 1123 K are given in Table 2. Observed, calculated and difference XRD profiles for Ln2CuO4 at the selected temperatures are given in Fig. 4.

The sequence of layers in T-structure can be represented as CuO2–□Ln–□O2–□Ln–□O2Cu–… (Fig. 1B). There are two crystallographically distinct oxygen atoms in the T-structure belonging to CuO2 (oxygen O1) layers and to Ln2O2 block (oxygen O2). Both oxygen atoms occupy special positions in S.G. I4/mmm and the only refinable atomic parameter is z-coordinate of Ln2+ cation. Temperature dependences of the Ln–O1 and Ln–O2 interatomic distances are shown in Fig. 5, corresponding values of the temperature expansion rates are given in Table 1. One can observe that temperature induced expansion rate of Pr–O1 bond length is considerably smaller in comparison with the Nd–O1 and Sm–O1 ones. Moreover, at T > 873 K the difference between the Pr–O1 and Nd–O1 distances practically disappears. TEC of the long Pr–O1 bond (~2.68 Å at 298 K) is comparable with that for the shorter Pr–O2 one (~2.34 Å at 298 K), while for both Sm2CuO4 and Nd2CuO4 TEC of Ln–O1 bond is about 40% higher in comparison with Ln–O2 one (Table 1). It indicates to the presence of the stronger, in comparison with other rare-earth cations, interactions between praseodymium and oxygen atoms from the CuO2 layer. Such conclusion could have been supported by band structure calculations but to our knowledge no data are available for Pr2CuO4. However, detailed band structure calculations were performed for the layered cuprate PrBa2Cu3O7 [17,18]. In the band structure of PrBa2Cu3O7, in comparison with analogs with other rare-earth cations, interactions between praseodymium and oxygen atoms from the CuO2 layer. Such conclusion could have been supported by band structure calculations but to our knowledge no data are available for Pr2CuO4. However, detailed band structure calculations were performed for the layered cuprate PrBa2Cu3O7 [17,18].

### 3.2. High-temperature electrical conductivity of Ln2CuO4

High-temperature electrical conductivity behavior of the Ln2CuO4 ceramic samples was studied in air in the temperature range of 298–1173 K by four-probe method. Conductivity of all samples increases with temperature thus indicating a semiconductor-like behavior (Fig. 6). Conductivity of Pr2CuO4 is the highest one among studied cuprates in the whole temperature range: 0.1–108 S/cm for Pr2CuO4, 0.072–23 S/cm for Nd2CuO4 and 2 × 10−9–9 S/cm for Sm2CuO4. In contrast, at 298–1273 K La2CuO4 with T-structure exhibits temperature-independent type of conductivity with σ ~ 15 S/cm [10,19].

Two temperature ranges (298–773 and 773–1173 K) with activation-like behavior can be observed for all σ(T) dependences (Fig. 6). Their existence can be explained by the change from p- to n-type conductivity with increasing temperature as observed by Scavini et al. [20] in the high-temperature study of Nd2CuO4.

### Table 1

<table>
<thead>
<tr>
<th></th>
<th>Pr2CuO4</th>
<th>Nd2CuO4</th>
<th>Sm2CuO4</th>
</tr>
</thead>
<tbody>
<tr>
<td>TEC(dil)</td>
<td>11.8</td>
<td>12.6</td>
<td>12.6</td>
</tr>
<tr>
<td>VT/3</td>
<td>11.9</td>
<td>13.0</td>
<td>12.9</td>
</tr>
<tr>
<td>TEC(a)</td>
<td>13.0</td>
<td>12.5</td>
<td>11.5</td>
</tr>
<tr>
<td>TEC(c)</td>
<td>9.5</td>
<td>14.0</td>
<td>15.9</td>
</tr>
<tr>
<td>TEC(Ln–O1)</td>
<td>11.7</td>
<td>15.2</td>
<td>15.1</td>
</tr>
<tr>
<td>TEC(Ln–O2)</td>
<td>11.9</td>
<td>10.7</td>
<td>11.1</td>
</tr>
</tbody>
</table>
et al. [19]. The reason for anomalous high-temperature conduc-
tion behavior at high temperature. Increasing of the transition
temperature between ranges from Pr to Sm is likely to correlate
with the value of charge-transfer gap, which increases from
iso(Pr) ¼ 12.3096(2) 0.0623, 0.0494, 1.04
iso(Nd) ¼ 12.3207(1) 0.0665, 0.0527, 1.08
iso(Sm) ¼ 12.3194(5), c ¼ 12.3096(2)

Table 2
Results of the Rietveld refinement’s for Ln2CuO4 Ln ¼ Pr, Nd and Sm using XRD data recorded at 298 and 1123 K.

<table>
<thead>
<tr>
<th>Compound</th>
<th>T (K)</th>
<th>Unit cell parameters (Å)</th>
<th>Rwp, Rp, χ²</th>
<th>Atomic coordinates, Bmax (Å²)¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pr2CuO4</td>
<td>298</td>
<td>a ¼ 3.96072(3), c ¼ 12.2200(1)</td>
<td>0.0679, 0.0535, 1.05</td>
<td>z(Pr) ¼ 0.35187(8), Bmin(Pr) ¼ 0.26(6); Bmin(Cu) ¼ 0.59(8)</td>
</tr>
<tr>
<td></td>
<td>1123</td>
<td>a ¼ 4.00323(3), c ¼ 12.3208(1)</td>
<td>0.0665, 0.0527, 1.08</td>
<td>z(Pr) ¼ 0.35174(9), Bmin(Pr) ¼ 1.23(8); Bmin(Cu) ¼ 1.63(1)</td>
</tr>
<tr>
<td>Nd2CuO4</td>
<td>298</td>
<td>a ¼ 3.94357(3), c ¼ 12.1708(1)</td>
<td>0.0655, 0.0519, 1.04</td>
<td>z(Nd) ¼ 0.35118(9), Bmin(Nd) ¼ 0.34(7); Bmin(Cu) ¼ 0.3(1)</td>
</tr>
<tr>
<td></td>
<td>1123</td>
<td>a ¼ 3.98425(4), c ¼ 12.3096(2)</td>
<td>0.0623, 0.0494, 1.04</td>
<td>z(Nd) ¼ 0.3510(1), Bmin(Nd) ¼ 1.2(1); Bmin(Cu) ¼ 1.0(2)</td>
</tr>
<tr>
<td>Sm2CuO4</td>
<td>298</td>
<td>a ¼ 3.91445(6), c ¼ 11.9727(3)</td>
<td>0.0517, 0.0412, 1.03</td>
<td>z(Sm) ¼ 0.3508(1), Bmin(Sm) ¼ 0.7(1); Bmin(Cu) ¼ 0.5(1)</td>
</tr>
<tr>
<td></td>
<td>1123</td>
<td>a ¼ 3.95151(5), c ¼ 12.1278(2)</td>
<td>0.0481, 0.0382, 1.04</td>
<td>z(Sm) ¼ 0.3503(2), Bmin(Sm) ¼ 1.4(1); Bmin(Cu) ¼ 1.2(2)</td>
</tr>
</tbody>
</table>

* Ln and Cu are at 4e position (0, 0, z) and 2a (0, 0, 0) positions, respectively; oxygen atoms O1 and O2 are at special positions 4c (0, 1/2, 0) and 4d (0, 1/2, 1/4), respectively. Atomic displacement parameters for O1 and O2 were fixed at Bmax ¼ 1 Å² and were not refined.

Fig. 4. Observed, calculated and difference between them XRD profiles for Ln2CuO4 Ln ¼ Pr (T ¼ 973 K), Nd (T ¼ 1123 K) and Sm (T ¼ 1123 K).

In both ranges temperature dependencies of conductivity are perfectly fitted by Arrhenius law with activation energies (Ea) listed in Table 3. The conductivity of Pr2CuO4 rapidly increases with temperature in low temperature range and shows a saturation behavior at high temperature. Increasing of the transition temperature between ranges from Pr to Sm is likely to correlate with the value of charge-transfer gap, which increases from Pr2CuO4 to Sm2CuO4 [21]. Substantial increase of the activation energy is observed for Nd2CuO4 and Sm2CuO4 in high-temperature range in comparison with low-temperature one. For Pr2CuO4 the situation is opposite where Ea decreases nearly by −50% in comparison with low temperature range. These results are in good agreement with the data by Goodenough [22] and George et al. [19]. The reason for anomalous high-temperature conductivity behavior of Pr2CuO4 could also be connected with the specific feature of the electronic structure mentioned above.

3.3. Oxygen diffusion and surface exchange coefficients of Pr2CuO4

The oxygen diffusion coefficient D and the surface exchange coefficient k for Pr2CuO4 were determined by the isotopic exchange depth profile (IEDP) technique using SIMS after isotopic exchange of 18O for 16O in the ceramic samples.

Dense ceramic samples of Pr2CuO4 for SIMS study were prepared by SPS technique. Since the graphite was used as a pressure transmitting medium in SPS experiment, color of the surface of the pellet after the sintering was non-uniform indicating the partial reduction of cuprate. XRD study of the pellet with the surface cleaned by sandpaper, showed an absence of the admixture phases. Density of the ceramic samples of Pr2CuO4 prepared by SPS sintered at 1123 K. Prior to 18O exchange annealing, samples were held at 973, 1073, 1123 and 1173 K in air of normal isotopic abundance for a period of time approximately one order of magnitude longer than the tracer annealing time. This was carried out to ensure that the material was in chemical equilibrium at the desired temperature and oxygen partial pressure (in this study all annealings were carried out at a nominal oxygen pressure of 0.2 atm). The air was then removed, and labeled oxygen (95% enriched 18O2) introduced. Annealing time was 10–12 min for the samples studied at 1073, 1123 and 1173 K and 9 h for 973 K.

As an example, the 18O isotopic concentration depth profile of Pr2CuO4 annealed at 1073 K is given in Fig. 7. The oxygen tracer diffusion (D) and surface exchange (k) coefficients were determined by non-linear least squares regression based on fitting of the diffusion profiles using the Crank relation, solution of the...
Fick’s second law of the diffusion, similar to the procedure described in Refs. [10,23]. Calculated values of $D_T$ and $k$ are given in Table 4. Dependences of bulk oxygen tracer diffusion and surface exchange coefficients on reverse temperature are given in Fig. 8. They can be perfectly fitted by Arrhenius law with activation energies ($E_A$) for oxygen tracer diffusion and for surface exchange coefficients 290 ± 7 and 28 ± 197 kJ mol$^{-1}$, respectively.

Calculated value of activation energy for oxygen trace diffusion in Pr$_2$CuO$_4$ is much closer to that for the perovskites with low oxide-ion mobility like lanthanum–strontium manganate (250–300 kJ mol$^{-1}$) in comparison with cobaltates (100–200 kJ mol$^{-1}$) [23,24]. At the same time, the observed values of $D_T$ are by several orders of magnitude lower in comparison with strontium doped manganese La$_{1-x}$Sr$_x$MnO$_3$ for which they are $10^{-10}$–$10^{-12}$ cm$^2$/s at 1173 K and $10^{-14}$–$10^{-15}$ cm$^2$/s at 1073 K [24,25]. However, values of $D_T$ for Pr$_2$CuO$_4$ are much lower in comparison with good oxide-ion conductors like cobaltates ($4 \times 10^{-8}$ cm$^2$/s (1173 K); $2 \times 10^{-8}$ cm$^2$/s (1073 K)) and Ln$_2$NiO$_4$+1, $Ln$=La, Pr and Nd~$10^{-10}$ cm$^2$/s at 1073 K [26–28]. Moreover, observed values of the tracer diffusion coefficient for Pr$_2$CuO$_4$...
are much lower in comparison with La$_2$CuO$_4$ for which a value of \( \sim 10^{-8} \text{ cm}^2/\text{s} \) was reported already at 973 K [10]. One can explain it by substantial difference in the crystal structures of T and T'-phases which influences on the mechanism and energetics of the oxygen diffusion in the compounds. In both crystal structures there are slabs formed by Ln$^{3+}$ cations in which there are tetrahedral and octahedral voids for oxygen atoms. In the crystal structure of T-phase octahedral voids are fully occupied by oxygen atoms while tetrahedral sites are empty or partially occupied like in the case of La$_2$NiO$_4$ [30, 31]. Opposite situation is observed for the T'-phase where tetrahedral sites are fully occupied by oxygen while octahedral sites remain empty. This leads to the different coordination of copper in T- and T'-phases: octahedron for T- and square for T (see Fig. 1A and B). In the T'-structure the distances between transition metal cation and axial oxygen anion are much longer in comparison with the equatorial ones. For example, in La$_2$CuO$_4$ $d_{\text{Cu-O(eq)}}$ = 1.90 Å, $d_{\text{Cu-O(ax)}}$ = 2.43 Å [30] and in La$_2$NiO$_4$ $d_{\text{Ni-O(eq)}}$ = 1.95 Å, $d_{\text{Ni-O(ax)}}$ = 2.26 Å [31]. This weakens interactions between transition metal and axial oxygen atoms and makes easier migration of oxygen in the structure. Recently, it was established that migration of oxygen between octahedral and tetrahedral sites in La$_2$O$_2$ block plays a major role in the mechanism of oxygen diffusion in La$_2$NiO$_4$ [32, 33]. In the crystal structure of T-phase the distance between copper and empty octahedral site in the La$_2$O$_2$ block is substantially shorter (for example, in Pr$_2$CuO$_4$ it is equal to 1.81 Å which is much smaller in comparison with typical Cu$^{2+}$-O bond length). This should hamper oxygen diffusion in T-phases by the migration of oxygen between octahedral and tetrahedral sites in the La$_2$O$_2$ block. The lower diffusibility of oxygen in T-phases in comparison with T'-phases is supported by the substantially lower oxygen permeation fluxes observed through ceramic membranes of Nd$_2$CuO$_4$ and Pr$_2$CuO$_4$ in comparison with La$_2$CuO$_4$ [15].

Unfortunately, it is hard to compare the observed data for Pr$_2$CuO$_4$ with other T'-phase since, to our knowledge, no data for the oxygen tracer diffusion determined by SIMS is available for them. However, some years ago Idemoto et al. [34, 35] reported on the study of the oxygen chemical diffusion on both poly- and single crystal samples of Nd$_2$CuO$_4$ by means of thermomicrobalance. They have reported high values of the chemical oxygen diffusion coefficient \( \sim 10^{-5} \text{ to } 10^{-6} \text{ cm}^2/\text{s} \) at 923–1173 K and calculated values of self-diffusion coefficient are \( \sim 10^{-8} \text{ cm}^2/\text{s} \) at 1073–1173 K. However, due to the high dependence of the chemical diffusion coefficient on the microstructure of the sample, these values could be overestimated and it would be valuable to obtain values of the oxygen tracer diffusion for Nd$_2$CuO$_4$ by SIMS.

4. Conclusions

Our work showed that the high-temperature properties of the cuprates with T'-type structure (Ln$_2$CuO$_4$, Ln = Pr, Nd, Sm) depend strongly on the type of the rare-earth cation. Study of the thermal expansion behavior of the layered cuprates Ln$_2$CuO$_4$, Ln = Pr, Nd and Sm with T'-structure revealed its anisotropy along the a- and c-axis of the tetragonal structure. However, this anisotropy is different for Ln = Nd, Sm with TEC(a) < TEC(c) and for Pr$_2$CuO$_4$ with TEC(a) > TEC(c). High-temperature XRD study of the crystal structures of these layered cuprates, leads to the conclusion that anomalous behavior of Pr$_2$CuO$_4$ in comparison with Nd and Sm-based cuprates is due to the stronger bonding between Pr$^{3+}$ cations and oxygen atoms from the CuO$_2$-planes. High-temperature electrical conductivity of the studied cuprates increases with the rare-earth cation size from Sm to Pr. Measurements of the oxygen tracer diffusion coefficient for Pr$_2$CuO$_4$ by IEDP SIMS revealed values between those reported for the LSM and cobalt-based perovskites (La$_2$SrCoO$_4$) [36]. From the viewpoint of the application as cathode in IT-SOFC, rare-earth cuprates Ln$_2$CuO$_4$, Ln = Pr, Nd and Sm have advantages over other layered cuprates due lower TEC (\( \sim 12–13 \text{ ppm} \text{ K}^{-1} \)). However, conductivity of Ln$_2$CuO$_4$, Ln = Pr, Nd and Sm at T < 973 K is high enough (\( > 10^3 \text{ S/cm} \)) for Pr$_2$CuO$_4$ only. At the same time the “compressed” Pr$_2$O$_2$ slab in the Pr$_2$CuO$_4$ crystal structure with small separation between available empty octahedral sites and Pr cations hamper oxygen anion diffusion and results in small value of the oxygen tracer diffusion coefficient in this phase compared to those values obtained for the T-phases (La$_2$CuO$_4$ and Nd$_2$NiO$_4$) where this separation is significantly larger. This property seems to be one of the main drawbacks of the cuprates with T'-type structure and should limit their use as cathode in IT-SOFC. The possible way to overcome this problem can be cation replacements in both sites of the structure, which can extend the Pr$_2$O$_2$ slab resulting in higher oxygen mobility.

Acknowledgments

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