# RSC Advances

This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. This *Accepted Manuscript* will be replaced by the edited, formatted and paginated article as soon as this is available.

You can find more information about *Accepted Manuscripts* in the **Information for Authors**.

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/advances
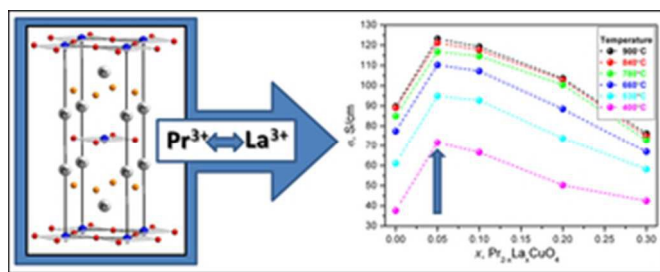
Graphical Abstract
27x11mm (300 x 300 DPI)

Journal Name

COMMUNICATION

Drastic change of electrical conductivity in Pr$_2$CuO$_4$ by isovalent La doping†

L. M. Kolchina,[a] N. V. Lyskov,[a,b] S. M. Kazakov,[a] G. N.Mazo*[a] and E. V. Antipov[a]

The uncommon way to affect transport properties of complex oxides through the example of Pr$_{2-x}$La$_x$CuO$_4$ was considered. It was established that the appropriate La doping in Pr$_2$CuO$_4$ leads to noticeable increase in high-temperature electrical conductivity. The reason for such changes are discussed from the viewpoint of possible charge redistribution in the Pr$_{2-x}$La$_x$CuO$_4$.

Complex transition metal oxides attract much attention as a consequence of a wide variety of physical and chemical properties, which stipulate their application as functional materials in different electrochemical devices such as solid-state sensors, oxygen permeation membranes and solid oxide fuel cells (SOFCs).[1] During the last years the interest in SOFCs development and commercialization keeps on rising due to their high efficiency, fuel flexibility and economic expediency. According to this background, lowering of operating temperature is an essential step in further SOFC implementation, which provides new opportunities for improving long-term stability and using cheaper sealing materials. Reduction of the main energy losses at lower temperatures associated with cathode performance is possible via implementation of new materials with high catalytic activity in oxygen reduction reaction and compatibility with solid electrolyte.[2-5]

Ln$_2$CuO$_4$ oxides, where Ln is a rare-earth element, commonly La-Sm, successfully proved themselves as promising cathodes for SOFCs operating below 750 °C.[6,7] These oxides with an exception of La$_2$CuO$_4$ have so-called T'-structure, which can be presented as the alternation of Ln$_2$O$_2$ slabs with fluorite structure and CuO$_2$ sheets.[8] Since the best cathode characteristics such as high conductivity, catalytic activity and compatibility with commonly used Ce$_{0.9}$Gd$_{0.1}$O$_{1.95}$ (GDC) electrolyte among the considered cuprates had been demonstrated by Pr$_2$CuO$_4$, attempts were made to improve efficiency of the cathode material by means of the heterovalent substitution of strontium for praseodymium, which was intended to increase of oxygen mobility in the crystal structure.[9] However, such heterovalent substitution in Pr$_2$CuO$_4$

leads to dramatic changes in the crystal structure depending on a doping level and, as a result, in physical and chemical properties of Pr$_{2-x}$Sr$_x$CuO$_4$ oxides.[9] Moreover, strontium-containing materials, as a rule, display higher thermal expansion coefficients (TECs) in comparison with their analogues without strontium and are less resistive to CO$_2$. As a consequence, those materials do not provide required long-term stability and must be replaced with more effective ones.[10] In this communication the uncommon way to affect transport properties, notably, electrical conductivity is considered with the example of Pr$_{2-x}$La$_x$CuO$_4$ system. Changes in electrical conductivity with the dopant concentration in Pr$_{2-x}$La$_x$CuO$_4$ complex oxides as well as reasons for these changes are reported for the first time to our knowledge. The choice of La as a dopant was inspired by an aspiration to extend an Ln$_2$O$_2$ fluorite slab by means of large cation incorporation in Pr$_2$CuO$_4$ without dramatic changes of structure type and physical properties. However, as it was revealed, electrical conductivity of Pr$_{2-x}$La$_x$CuO$_4$ is quite sensitive to lanthanum content and can be enhanced under an appropriate doping level.

In order to ensure the attainment of phase equilibrium in synthesized solid solutions, all Pr$_{2-x}$La$_x$CuO$_4$ powder samples were additionally annealed at 1000 °C for 50 hours. XRPD analysis confirmed that all La-doped samples (x = 0.05; 0.1; 0.2; 0.3) as well as undoped Pr$_2$CuO$_4$ were single-phase and had the T'-structure with a tetragonal symmetry (space group I4/mmm). No additional peaks were detected on the XRPD pattern of Pr$_{2-x}$La$_x$CuO$_4$ (ESI). The calculated lattice parameters of Pr$_{2-x}$La$_x$CuO$_4$ as a function of La-content are presented in Fig. 1a. As is clear from Fig. 1a, unit cell parameters of Pr$_{2-x}$La$_x$CuO$_4$ change unsteady with La content. Since non-linear dependences of the parameters vs. the solid solution composition (x) were observed, both c/a parameter ratio and cell volume were calculated and plotted together (Fig. 1b) to clarify this tendency. The unit cell volume rises monotonically with increase in La-content as it is expected for solid solution where a smaller cation is substituted with a larger one (r(Pr^{3+}) = 1.28 Å, r(La^{3+}) = 1.32 Å for 8-coordinated cations).[11] Otherwise, even small La addition induces elongation of the unit cell along the c-axis. The substitution of 2.5 at. % Pr (i.e., Pr$_{1.95}$La$_{0.05}$CuO$_4$ contains only 1 atom of lanthanum per 10 unit cells) provokes elongation along the c axis at 0.03 Å, whereas further increasing of La content up to 15 at. % results in elongation along the c axis at approximately the same value. The c/a ratio for the La-containing cuprates is close, but the c/a ratio for

[a.] Department of Chemistry, Moscow State University, Moscow 119991, Russia.
[b.] Institute of Problems of Chemical Physics RAS, Acad. Semenov av. 1, Chernogolovka 142432, Russia.
*E-mail: mazo@inorg.chem.msu.ru
† Electronic Supplementary Information (ESI) available: Experimental methods, X-ray diffraction data and TECs for Pr$_{2-x}$La$_x$CuO$_4$. See DOI: 10.1039/x0xx00000x
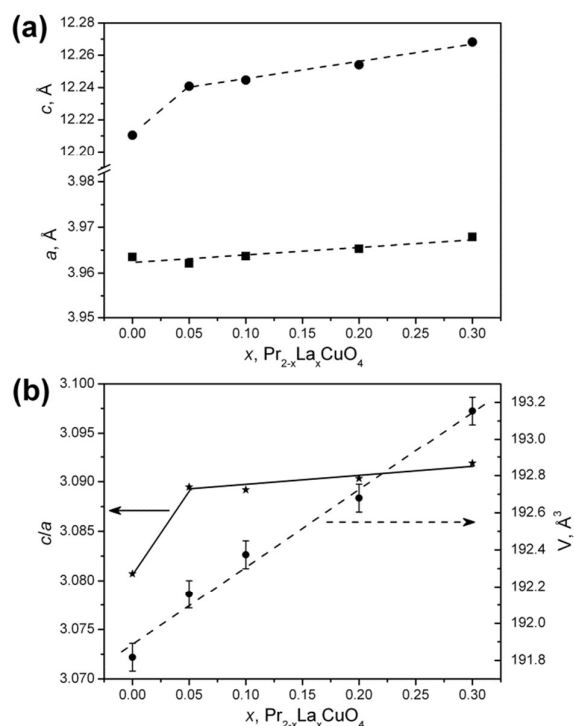
Fig. 1 (a, b) Variation of (a) unit cell parameters and (b) both c/a ratio and cell volume with La content (x) in $Pr_{2-x}La_xCuO_4$ at room temperature.

undoped Pr_2CuO_4 considerably differs. According to this background, the end-member (x = 0) of $Pr_{2-x}La_xCuO_4$ solid solution falls out from the principal trend.

High-temperature X-ray powder diffraction (HT XPRD) analysis of $Pr_{2-x}La_xCuO_4$ reveals no phase transitions in the temperature range of 25-800 °C (ESI). TECs calculated from HT XPRD vary within narrow limits of $11.9 \div 12.1 \cdot 10^{-6}$ K^{-1} (Table 1), which satisfies requirements for SOFC cathode materials[12].

High-temperature conducting properties of $Pr_{2-x}La_xCuO_4$ ($0 \leq x \leq 0.3$) were examined by a conventional DC four-probe technique in temperature range of 100-900 °C in air. The synthesis technique, temperature and time conditions were completely unified during a sample preparation process so that effect of ceramic microstructure on transport properties should be identical. Analysis of cross-section SEM images did not reveal any substantial

Table 1. Size variance and thermal expansion coefficients of $Pr_{2-x}La_xCuO_4$.

Composition	σ, $Å^2$	TEC*10^6, K^{-1}		
		$V^{1/3}$	Along a axis	Along c axis
Pr_2CuO_4	0	11.9	13.0	9.5
$Pr_{1.95}La_{0.05}CuO_4$	$3.90\cdot10^{-5}$	11.9	13.1	9.3
$Pr_{1.9}La_{0.1}CuO_4$	$7.60\cdot10^{-5}$	12.1	13.4	9.2
$Pr_{1.8}La_{0.2}CuO_4$	$1.44\cdot10^{-4}$	11.8	13.1	8.9
$Pr_{1.7}La_{0.3}CuO_4$	$2.04\cdot10^{-4}$	11.7	13.1	8.6

difference in samples microstructure (ESI). Fig. 2a shows temperature dependencies of electrical conductivity of $Pr_{2-x}La_xCuO_4$ ($0 \leq x \leq 0.3$). All studied materials exhibit thermoactivated (semiconducting) behavior in the low-temperature region (100-350 °C). In the high-temperature range of 350-900 °C conductivity of the materials tends to attainment of saturation. Temperature dependence of electrical conductivity in the low-temperature range can be satisfactory fitted by Arrhenius-like law modified for small polaron hopping:

$$\sigma(T) = \frac{A}{T}\exp(-\frac{E_a}{kT}) \quad (1),$$

where T is absolute temperature, k – the Boltzmann's constant, A - a pre-exponential factor, E_a - activation energy. The activation energy calculated in the temperature range of 100-350 °C is 0.37 eV for Pr_2CuO_4 and is a bit smaller (0.34±0.02 eV) for all La-doped samples. Thus, substitution of La for Pr does not significantly influence activation barrier.

Fig. 2b shows how electrical conductivity of $Pr_{2-x}La_xCuO_4$ varies with La content (x) at different temperature. The highest conductivity is achieved for the composition with the lowest La-content used in this work (2.5 at. %) at each temperature.

In many cases, oxygen stoichiometry, in particular, presence of interstitial oxygen atoms or vacancies, has a strong influence on
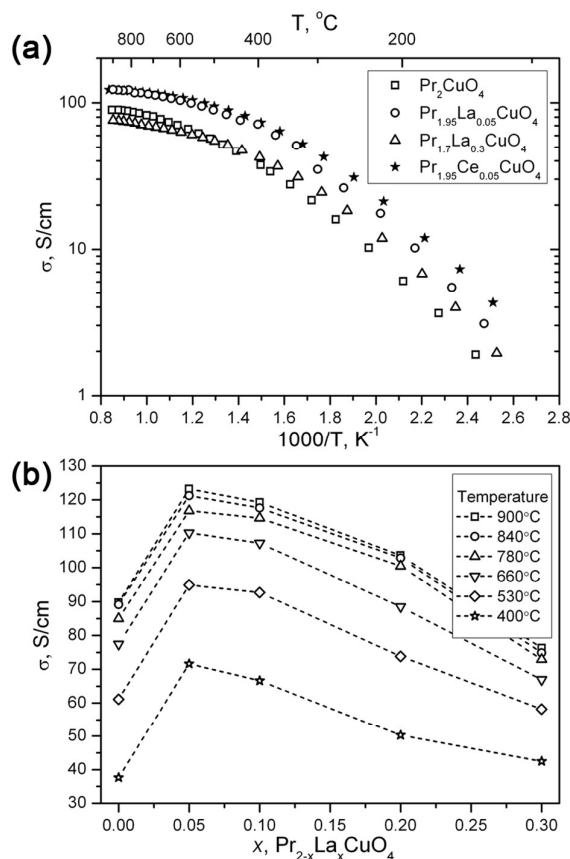

Fig. 2 (a, b) Electrical conductivity of $Pr_{2-x}La_xCuO_4$ samples in air: (a) – as a function of temperature and (b) – as a function of La content (x) at different temperatures. The conductivity of $Pr_{1.95}Ce_{0.05}CuO_4$ as a function of temperature is additionally inserted to Fig. 2a for comparison.

different physical properties, especially, on magnetic ordering and electronic transport in complex oxides, as it was demonstrated.[13] In spite of the fact that the apical oxygen atoms should not exist in the ideal Pr_2CuO_4 structure, their existence was proved by a number of investigators.[14,15] The presence of apical oxygen is extremely critical for Pr_2CuO_4 at low temperature (T < 25 °C).[16]

According to the results of the iodometric titration used for δ determination in $Pr_{2-x}La_xCuO_{4\pm\delta}$, oxygen content matches the stoichiometric value within a measurement error. No correlations between La content and oxygen stoichiometry were observed. Thermogravimetric studies also revealed no changes in oxygen stoichiometry under heating up to 950 °C in air. Therefore, oxygen content is not markedly varies neither with La content nor with temperature, and, as a result, cannot be a factor, which is responsible for conductivity rise.

Whereas the highest conductivity is attained for the composition in which 2.5 at. % of Pr positions occupied with La atoms, it is worth assuming that so small dopant concentration can induce local structure distortion only. Elimination of mutual interactions of La atoms is clear enough under the made assumption. However, it can be suggested that electron density redistribution expressing in changes in praseodymium and copper formal oxidation states occurs. This phenomenon can be described as follows. Substitution of Pr^{3+} by La^{3+} leads to appearance of local strains in the structure due to a size mismatch between Ln_2O_2 fluorite slab and CuO_2 sheets. One of possible ways to compensate the strains is an increase of a praseodymium formal oxidation state from +3 to +4 that results in depressing of praseodymium radius ($r(Pr^{4+})$ = 1.13 Å)[11]. A simple calculation shows that change in the oxidation state only of ~0.5 % praseodymium atoms is enough to maintain the average cation radius in the fluorite slab in case of $Pr_{1.95}La_{0.05}CuO_4$. This process, more likely, has thermoactivation nature. Supposing increase of the Pr oxidation state and taking into account absence of changes in oxygen stoichiometry, reduction of copper is transpired due to electron transfer from praseodymium to a CuO_2 sheet. Eventually, this leads to increase of charge carrier concentration in a CuO_2 sheet, where, according to commonly accepted model, charge transfer is realized by small polaron hopping.[17]

In order to confirm the assumption about charge redistribution in $Pr_{2-x}La_xCuO_4$ high-temperature properties of isostructural Ce-doped analogues of $Pr_{2-x}Ce_xCuO_4$ were investigated. Substitution of Ce for Pr is heterovalent and leads to electron transfer into CuO_2 sheet.[14,18] It is expected that La- and Ce-doped praseodymium cuprates should demonstrate similar behavior.

The study of high-temperature properties of $Pr_{2-x}Ce_xCuO_4$ shows that electrical conductivity has maximum for composition of x = 0.05 (Fig. 3) as well as in case of $Pr_{2-x}La_xCuO_4$. According to the data obtained (Fig. 2a), temperature dependencies of conductivity for the La- and Ce-doped (x = 0.05) cuprates are identical above 350 °C in comparison with undoped Pr_2CuO_4. In case of $Pr_{2-x}Ce_xCuO_4$ electron doping occurs. Similarity of the dependencies of electrical conductivity vs. La(Ce) content indicates that charge carrier generation in both cases should have the same nature that confirms the possible redistribution of electron density in $Pr_{2-x}La_xCuO_4$.

Experimental studies reveal that the highest conductivity is achieved for La-doped samples with 0.05 ≤ x ≤ 0.2. However, increasing of amount of La leads to reduction of electrical conductivity. Size variance $\sigma^2(r_A)$ can be used for explanation of observed physical properties for systems with isovalent doping.[19] Since systematic trends like as decrease of the normal state carrier
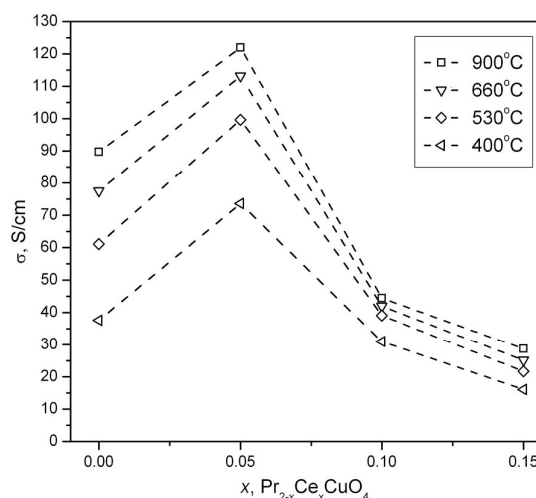

Fig. 3 Electrical conductivity of $Pr_{2-x}Ce_xCuO_4$ as a function of Ce content (x) at different temperatures in air.

density with $\sigma^2(r_A)$ increasing were observed in A_2CuO_4 superconductors,[20] one may conclude that isovalent substitution (in our case, substitution of La^{3+} for Pr^{3+}) leading to increase of $\sigma^2(r_A)$ (Table 1) should cause a reduction of conductivity. Traditionally, heterovalent substitution is used to influence transport properties of complex transition metal oxides. Nevertheless, the isovalent substitution, as shown in the present work, also has effect on conductivity due to possible redistribution of electron density between cations possessing in different oxidation state. Thus, "isovalent" substitution for cations, which can exist in various oxidation states, is an alternative approach to modifying properties of complex oxides. It is expected to be possible to implement this approach not only in the case of praseodymium cuprate, but in the case of other complex oxides of transition metals.

The proposed strategy of conductivity enhance can be effectively used to improve the electrochemical performance of SOFC cathode materials. Preliminary studies of polarization resistance of an electrode/electrolyte interface in the intermediate temperature range of 500-750 °C have showed that area specific resistance of the $Pr_{1.9}La_{0.1}CuO_4$/GDC interface is nearly twice as low as that for the undoped Pr_2CuO_4 electrode under the same conditions.[7] Detailed investigation of electrochemical behavior of the La-doped Pr_2CuO_4 electrode materials will be presented in subsequent reports.

Acknowledgments

Notes and references

1   P. Knauth and H. Tuller, *J. Am. Ceram. Soc.*, 2002, **85**, 1654-1680.
2   E. D. Wachsman and K. T. Lee, *Science*, 2011, **334**, 935-939.

3   J. G. Lee, J. H. Park and Y. S. Shul, *Nat. Commun.*, 2014, **5**, 4045-4054.

4   A. Orera and P. R. Slater, *Chem. Mater.*, 2010, **22**, 675-690.

5   T. A. Adams, J. Nease, D. Tucker and P. I. Barton, *Ind. Eng. Chem. Res.*, 2013, **52**, 3089-3111.

6   M. S. Kaluzhskikh, S. M. Kazakov, G. N. Mazo, S. Ya. Istomin, E. V. Antipov, A. A. Gippius, Yu. Fedotov, S. I. Bredikhin, Yi Liu, G. Svensson and Z. Shen, *J. Solid State Chem.*, 2011, **184**, 698-704.

7   N. V. Lyskov, M. S. Kaluzhskikh, L. S. Leonova, G. N. Mazo, S. Ya. Istomin, and E. V. Antipov, *Int. J. Hydrogen Energy,* 2012, **37**, 18357-18364.

8   D. E. Cox, A. I. Goldman, M. A. Subramanian, J. Gopalakrishnan and W.Sleight, *Phys. Rev. B*, 1989, **40**, 6998-7004.

9   G. N. Mazo, S. M. Kazakov, L. M. Kolchina, S. Ya. Istomin, E. V. Antipov, N. V. Lyskov, M. Z. Galin, L. S. Leonova, Yu. S. Fedotov, S. I. Bredikhin, Yi Liu, G. Svensson and Z. Shen, *Solid State Ionics*, 2014, **257**, 67-74.

10   S. Sønderby, P. L. Popa, J. Lu, B. H. Christensen, K. P. Almtoft, L. P. Nielsen and P. Eklund, *Adv. Energy Mater.*, 2013, **3**, 923-929.

11   R. D. Shannon and C.T. Prewitt, *Acta Cryst.*, 1969, **B25**, 925-946.

12   A. J. Jacobson, *Chem. Mater.*, 2010, **22**, 660-674.

13   P. Richard, G. Riou, S. Jandl, M. Poirier, P. Fournier, V. Nekvasil and M. Divis, *Phys. C*, 2004, **408**, 830-831.

14   G. Riou, P. Richard, S. Jandl, M. Poirier, P. Fournier, V. Nekvasil, S. N. Barilo and L. A. Kurnevich, *Phys. Rev. B*, 2004, **69**, 024511-024518.

15   Y. Tanaka, M. Karppinen, T. Kobayashi, T. S. Chan, R. S. Liu, J. M. Chen and H. Yamauchi, *Chem. Mater.*, 2008, **20**, 5414-5420.

16   Y. Krockenberger, H. Irie, O. Matsumoto, K. Yamagami, M. Mitsuhashi, A. Tsukada, M. Naito and H. Yamamoto, *Sci. Rep.*, 2013, **3**, 2235-2240.

17   P. A. Cox, *The Electronic Structure and Chemistry of Solids*, Oxford University Press, Oxford, 1987.

18   M. L. Sanjuin, M. A. Laguna, S. PiFiol, P. Canfield and Z. Fisk, *Phys. Rev. B*, 1992, **46**, 8683-8686.

19   J. P. Attfield, A. L. Kharlanov and J. A. McAllister, *Nature*, 1998, **394**, 157-159.

20   J. A. McAllister and J. P. Attfield, *Phys. Rev. B*, 2002, **66**, 014514-01523.