

Supplementary Information

Drastic Change of Electrical Conductivity in Pr₂CuO₄ by Isovalent La Doping

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Experimental

Synthesis: Pr_{2-x}La_xCuO_{4+δ} (x = 0; 0.05; 0.1; 0.2; 0.3) were prepared by a conventional solid-state route from pre-fired La₂O₃, Pr₆O₁₁ and CuO. Appropriate amount of these initial reagents with 99.99% purity were mixed by ball-milling under heptane. After drying during the 12 hours samples were pressed into pellet and annealed on Al₂O₃ crucibles at 1000 °C for 50 h in air. Oxygen content was determined by iodometric titration.

High-temperature X-ray powder diffraction (HT XRD): HT XRD data in air were collected by Bruker D8-Advance diffractometer (CuK_{α1} radiation, LynxEye PSD) in reflection mode equipped with high-temperature camera XRK-900 (Anton Paar). Unit cell parameters at 298-1073K were refined by Rietveld method using TOPAS-3 program package.

Sample preparation for DC conductivity measurements: For DC conductivity measurements single-phase powders were pressed into pellets under pressure of 5 tons per cm² and sintered at 1000 °C for 10 h in air. Relative density was ~90%. To create current collectors Pt-paste was placed on sides of a pellet. Potential electrodes were created with Pt-paste as two rings around a pellet. A distance between Pt-contacts was about 10 mm. Samples coated with Pt-paste were sintered at 900 °C for 10 h in air to eliminate organic binder.

DC conductivity measurements: Electrical conductivity measurements were performed by conventional four-point DC technique in the temperature range of 100–900 °C in air. DC conductivity was measured using a P-30 potentiostat/galvanostat (Elins Ltd, Russia) in cyclic voltamperometry (CVA) mode in the voltage range from –50 mV to 50 mV at the voltage scan rate of 20 mV/s. The resulting specific resistivity was recalculated from the slopes of CVA curves taking into account a current collector area and a distance between potential electrodes. The temperature of the sample was measured by a Pt–Pt/Rh thermocouple positioned close to the sample with an accuracy of ±1 °C.

Thermogravimetric analysis: TG studies were performed in artificial air (20% O₂(g), 80% Ar(g)) and argon from 100 to 950 °C with a heating rate of 10 °/min by Netzsch STA 449C thermoanalyser.

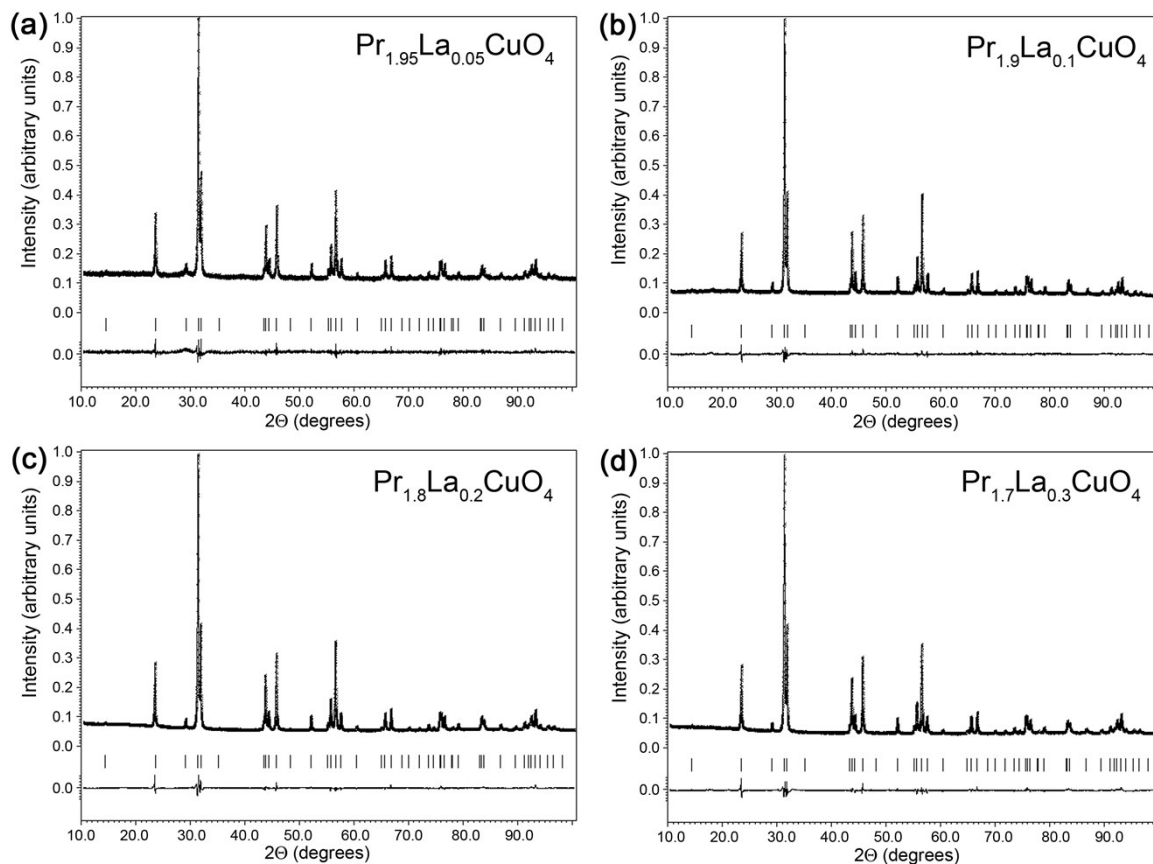


Figure S1. X-ray diffraction patterns of $Pr_{2-x}La_xCuO_4$.

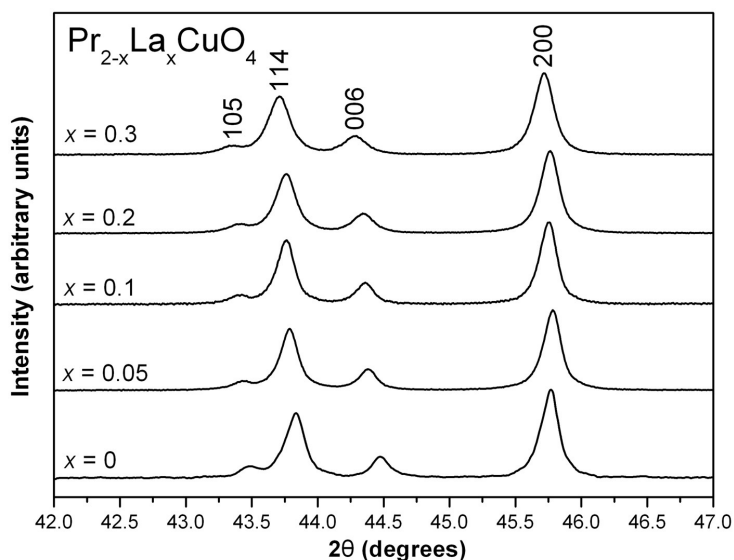


Figure S2. Overlay of XRPD patterns for $Pr_{2-x}La_xCuO_4$. The region with $h00$ and $00l$ reflections is shown to facilitate the comparison. Small La addition provokes greater shift of the 006 reflection than further increasing of La content. The position of the 200 reflex remains almost independent on La-doping.

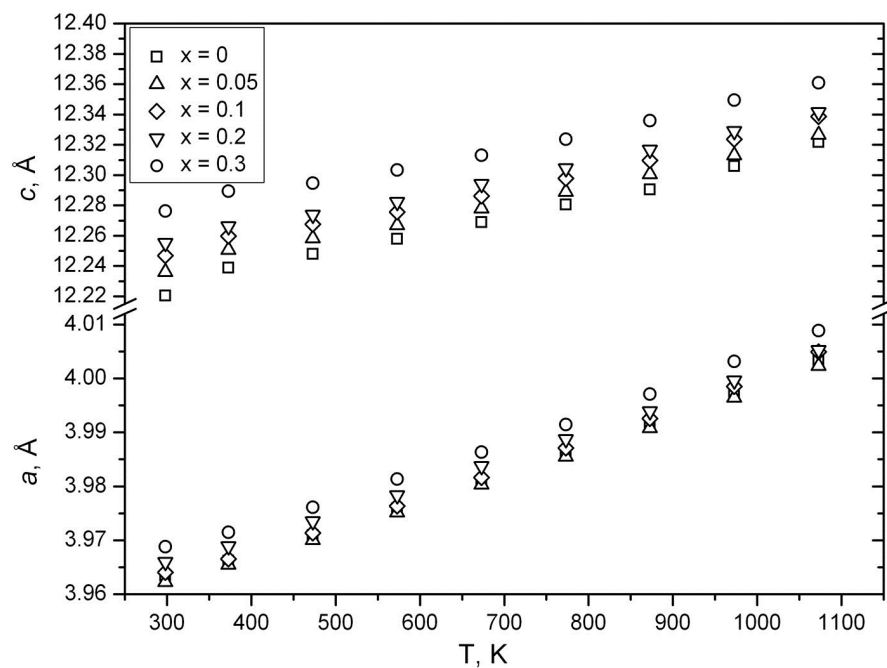


Figure S3. Temperature dependencies of $Pr_{2-x}La_xCuO_4$ unit cell parameters.

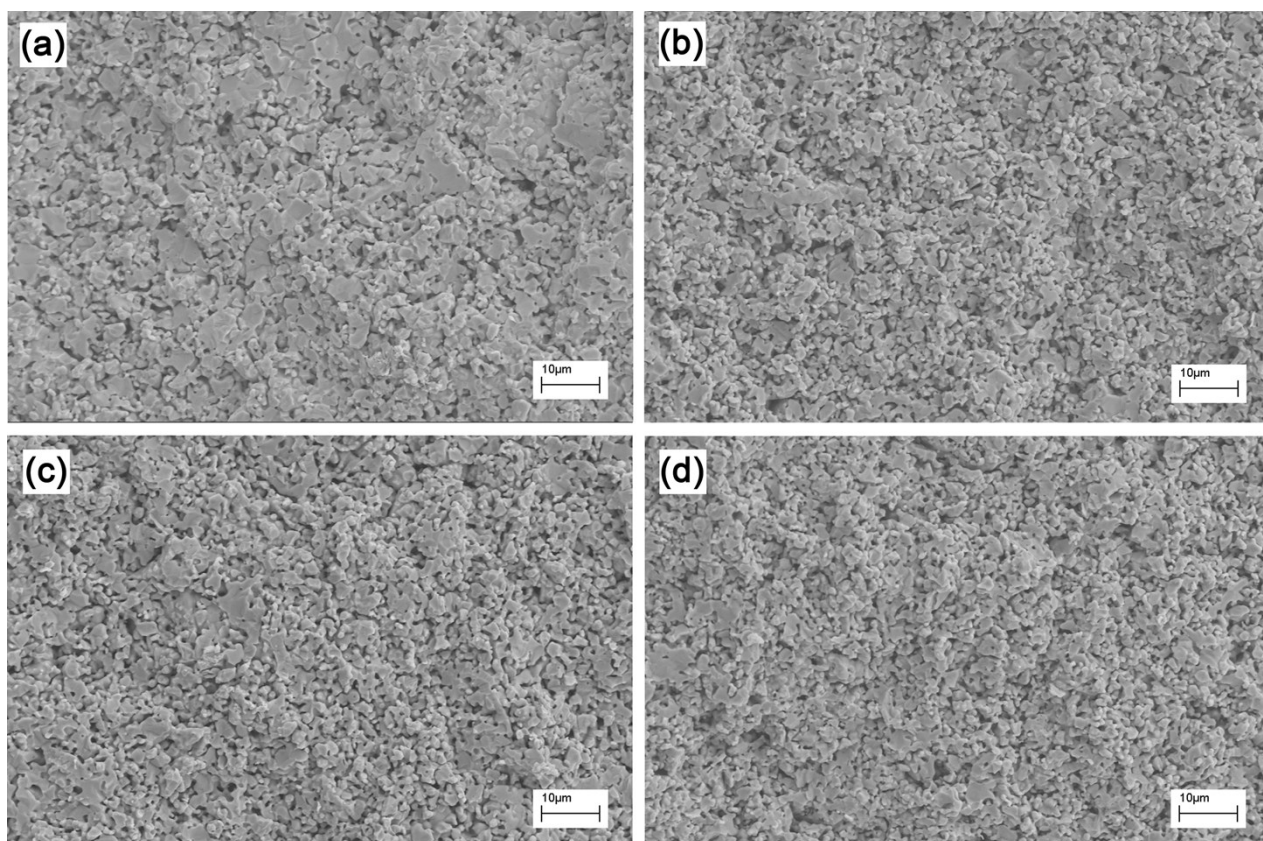


Figure S4. Cross section SEM images of $Pr_{2-x}La_xCuO_4$ samples: (a) – $x=0$; (b) – $x=0.05$; (c) – $x=0.1$; (d) – $x=0.3$.