

# Remarkable transition from rocksalt/perovskite layered structure to fluorite/rocksalt layered structure in rapidly cooled $\text{Ln}_2\text{CuO}_4$ .

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## Sample preparation for the phase diagram

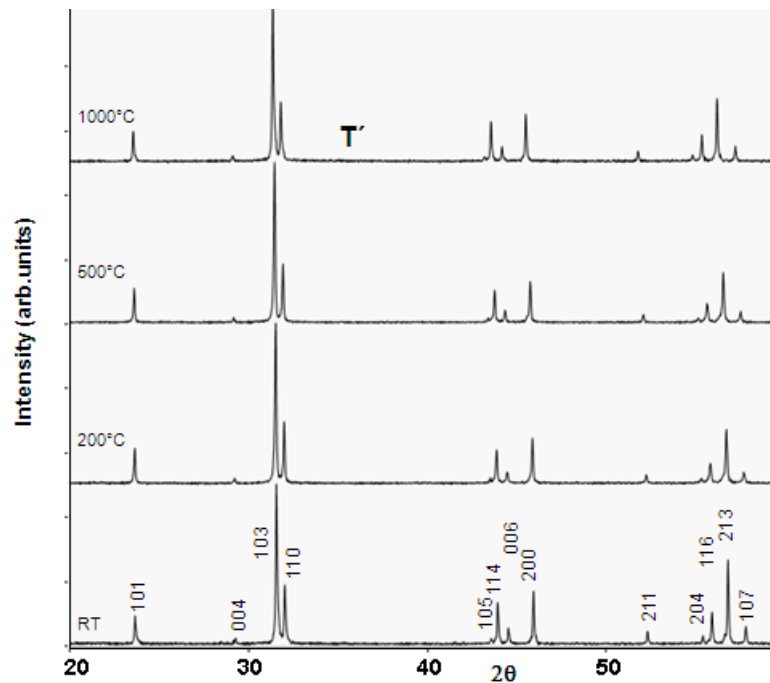
- Nineteen samples with different compositions were examined to construct the phase diagram of  $\text{Nd}_{1.8-x}\text{La}_x\text{Pr}_{0.2}\text{CuO}_4$  family. Materials have been produced, with varying La content over the range  $x=0$  to  $x=1.8$  with an increment of 0.1, by the solid state method.
- Hygroscopic powders ( $\text{Nd}_2\text{O}_3$ ,  $\text{Pr}_6\text{O}_{11}$ ,  $\text{La}_2\text{O}_3$ ) were dried for 30 minutes at temperature up to  $900^\circ\text{C}$ . Stoichiometric amounts of  $\text{Nd}_2\text{O}_3$  (Alfa-Aesar 99.9%),  $\text{Pr}_6\text{O}_{11}$  (Alfa-Aesar 99.9%),  $\text{CuO}$  (Aldrich 99+ %) and  $\text{La}_2\text{O}_3$  (Aldrich 99.99%) were then weighed and ground in acetone. These mixtures were then dried and calcined in air at  $850^\circ\text{C}$  for 36 hours. Following this, powders were reground using the planetary ball mill and the heat treatment ( $850^\circ\text{C}$  for 36 hours) repeated. Then sample was reheated at  $950^\circ\text{C}$  for 24 hours.
- In-situ X-ray diffraction analysis of powders were collected at room temperature on a Bruker axS D8 Advance diffractometer equipped with a solX energy dispersive detector in the  $10\text{--}90^\circ$  range with a step of  $0.02^\circ$  and counting time of 25 s per step ( $\text{CuK}\alpha = 1.5406 \text{ \AA}$ ). The high temperature diffraction data were collected in the  $10\text{--}90^\circ$  range, with a step of  $0.0148^\circ$  and a counting time of 1.5 s per step, on a Bruker axS D8 Advance diffractometer equipped with a high temperature Anton Paar HTK 1200N chamber and a one dimensional X-ray detector VANTEC-1 ( $\text{CuK}\alpha = 1.5406 \text{ \AA}$ ).

## T'' phase characterisation

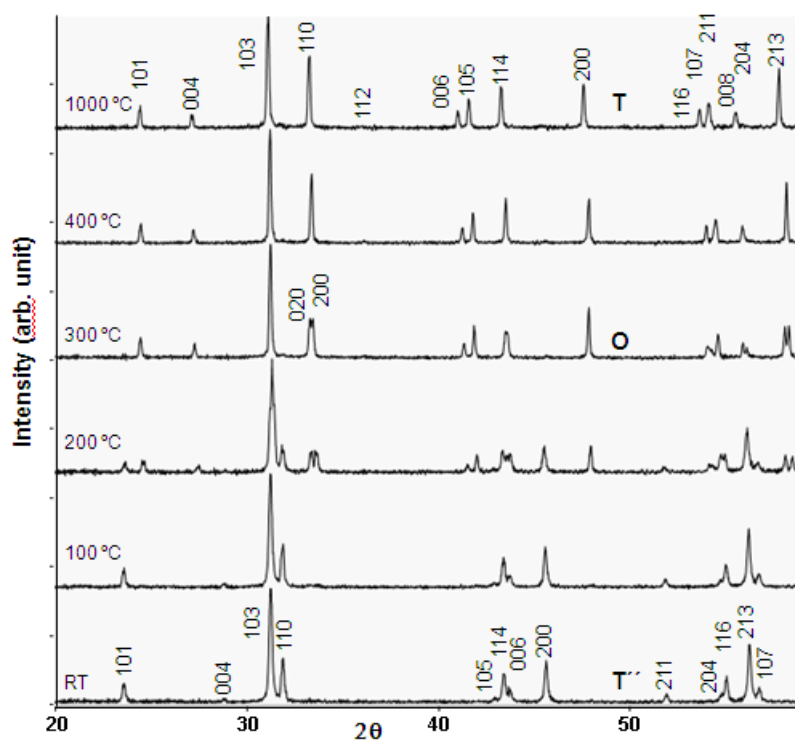
- The T'' phase was obtained by the solid state method with the composition  $\text{Nd}_{0.35}\text{La}_{1.45}\text{Pr}_{0.2}\text{CuO}_{4+\delta}$ . (Hygroscopic powders ( $\text{Nd}_2\text{O}_3$ ,  $\text{Pr}_6\text{O}_{11}$ ,  $\text{La}_2\text{O}_3$ ) were dried for 30 minutes at temperature up to  $900^\circ\text{C}$ . Stoichiometric amounts of  $\text{Nd}_2\text{O}_3$  (Alfa-Aesar 99.9%),  $\text{Pr}_6\text{O}_{11}$  (Alfa-Aesar 99.9%),  $\text{CuO}$  (Aldrich 99+ %) and  $\text{La}_2\text{O}_3$  (Aldrich 99.99%) were then weighed and ground in acetone. These mixtures were then dried and calcined in air at  $850^\circ\text{C}$  for 36 hours. Following this powders were reground using the planetary ball mill and the heat treatment ( $850^\circ\text{C}$  for 36 hours) repeated. Then sample was reheated at  $950^\circ\text{C}$  for 24 hours).
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- High resolution and high intensity time-of-flight neutron powder diffraction (NPD) data were collected using GEM diffractometer at the ISIS spallation source at Rutherford Appleton Laboratory, UK. The sample (ca. 5 g) was loaded into a thin-walled, cylindrical vanadium can and placed in the sample chamber in ambient condition. The diffraction data sets were analysed using GSAS package [2] in the Rietveld method [3, 4]. The background was fitted using an empirical Chebyshev polynomial and peak shapes were considered as pseudo-Voigt function.
- Selected area electron diffraction (SAED) patterns were collected in different orientations on a Jeol JEM-2011 electron microscope operated at 200 kV. The powder sample was ground using a mortar and pestle, and suspended in acetone. One drop of suspension was deposited on a copper grid with a holey carbon film.
- Thermogravimetric analysis (TGA) was carried out on a NETZSCH TG 209 instrument to evaluate the oxygen content (from weight loss) at different temperatures in air and to compare with neutron diffraction results. The initial weight of the sample was about 20 mg. The effect of buoyancy was corrected using empty crucible blank

runs under corresponding gas atmosphere and flow rates. The samples were heated up to 1000 °C in the TG furnace at a heating rate of 5 °C min<sup>-1</sup> in air and under flowing 5% Hydrogen/95% Argon (Flow rate: 30ml/min). The excess/deficiency of oxygen ( $\pm\delta$ ) was calculated from the detected mass change.

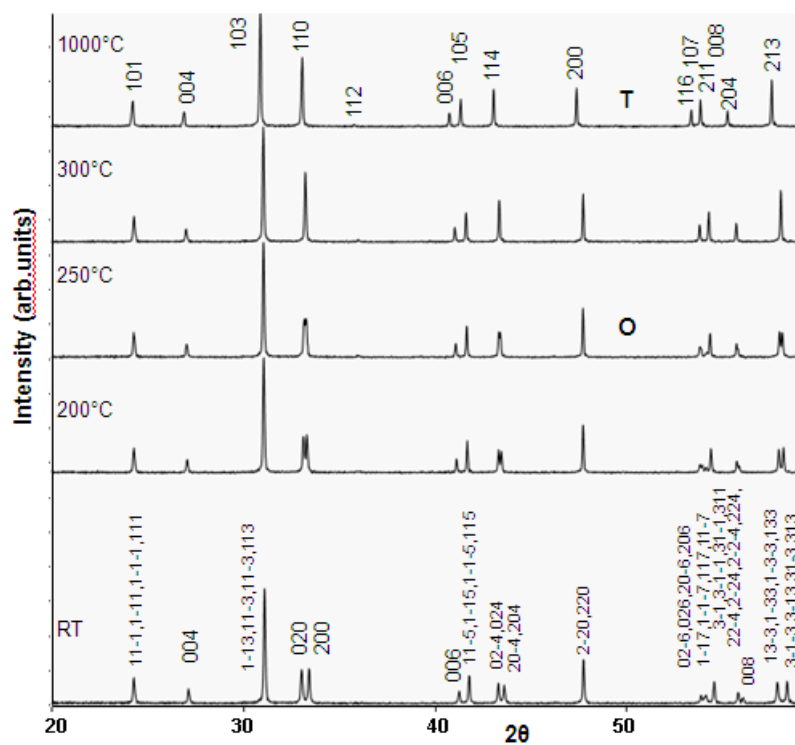
- Electrical properties were measured using small circular pellets. Powders were uniaxially pressed using a pressure of 120 MPa. The pellets had a diameter of 13 mm with a thickness of 1-2 mm and were fired in air for 10 hours at 850 °C. In-situ conductivity was measured using a four point DC technique from 900 °C to room temperature in air using Van der Pauw technique [5,6].



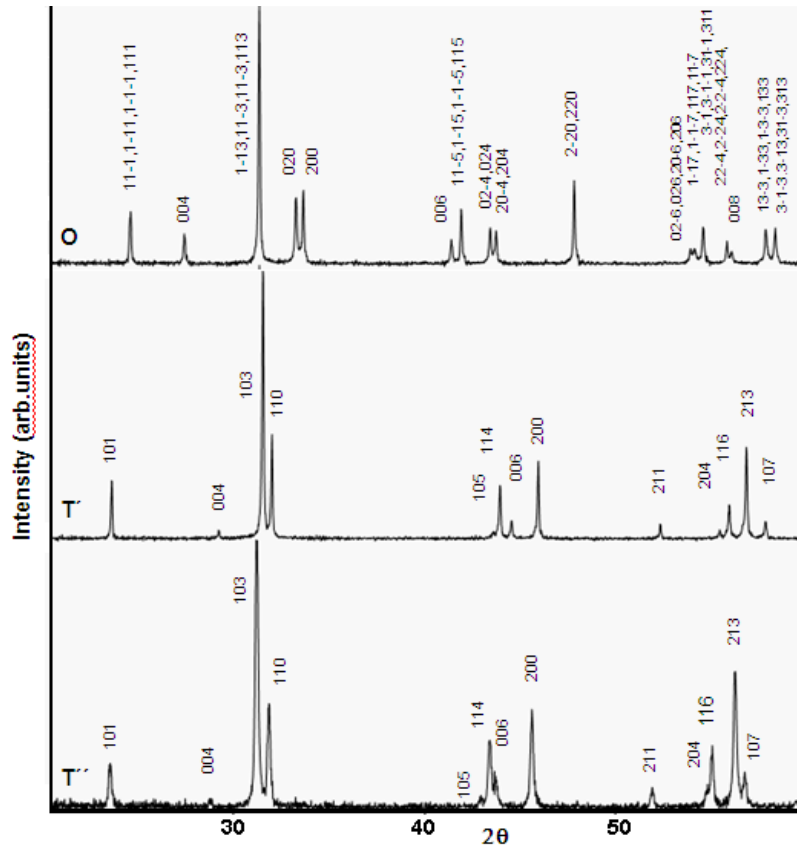
**Fig. S1:** In-situ XRD pattern for T' phase at different temperatures (RT, 200 °C , 500 °C , 1000 °C ) for x=0.1 composition.



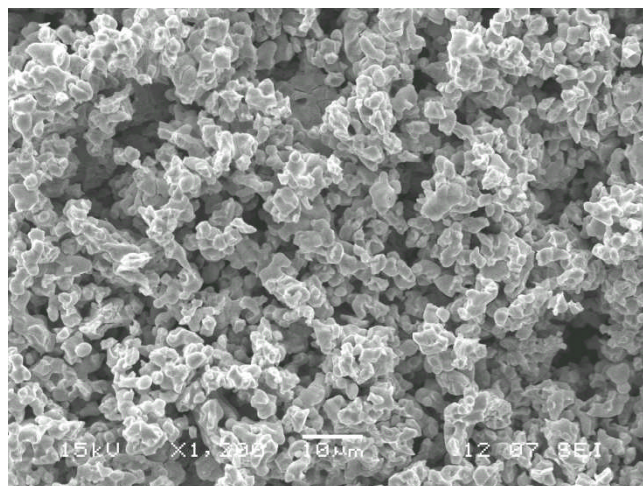
**Fig. S2:** In-situ XRD pattern for T'' phase at different temperatures (room temperature, 100 °C, 200 °C, 300 °C, 400 °C, 1000 °C) for x=1.45.



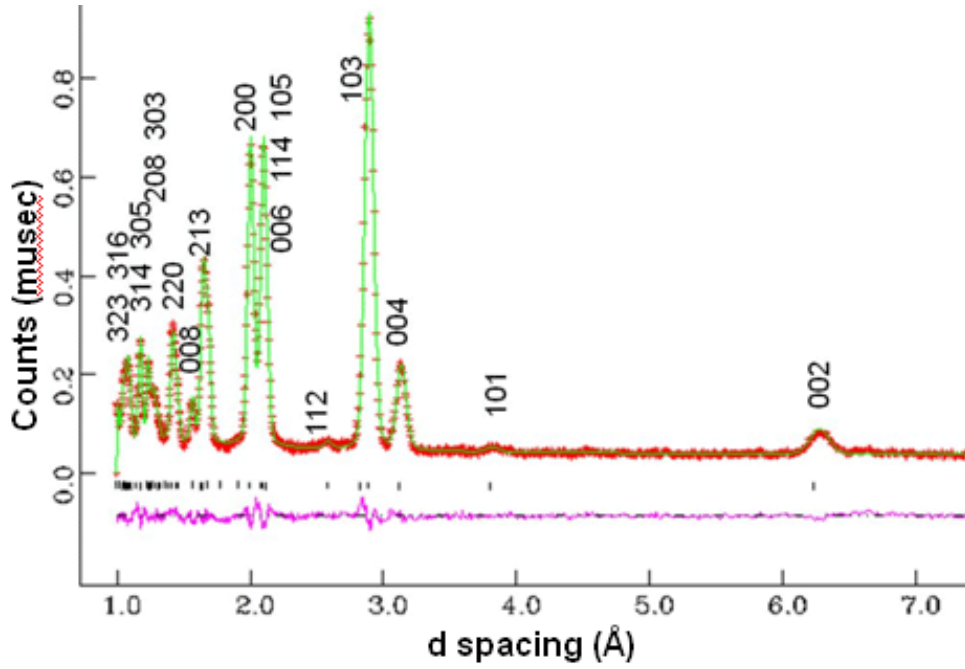
**Fig. S3:** In-situ XRD pattern for T phase at different temperatures (room temperature, 200 °C, 250 °C, 300 °C, 1000 °C) for x=1.7 composition.



**Fig. S4:** Comparison of XRD patterns for T' phase (x=0.1) T' phase (x=1.45) and O phase (x=1.7) for  $\text{Nd}_{1.8-x}\text{La}_x\text{Pr}_{0.2}\text{CuO}_4$  at room temperature.



**Fig. S5:** SEM image of the fine powder which was obtained from a dense pellet of  $\text{Nd}_{0.35}\text{La}_{1.45}\text{Pr}_{0.2}\text{CuO}_4$  after firing at  $950^\circ\text{C}$  for 10 hours and cooling to room temperature

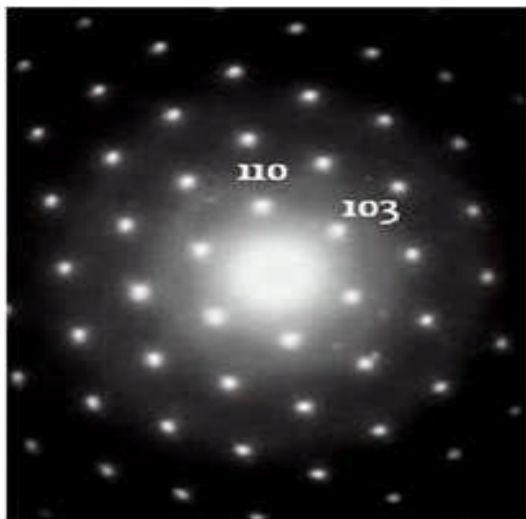


**Fig. S6:** Rietveld refinement neutron data profile of T'' at room temperature in the I4/mmm space group. Observed (plus sign), calculated (continuous line) and Bragg reflections (vertical lines) are shown

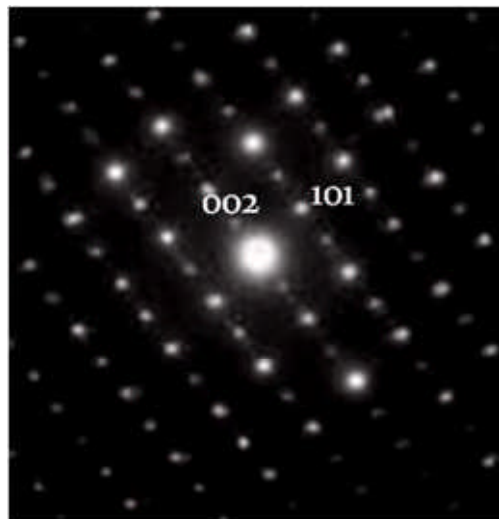
**Table S1:** Rietveld refined structural parameters of neutron powder diffraction data of Nd<sub>0.35</sub>La<sub>1.45</sub>Pr<sub>0.2</sub>CuO<sub>4</sub> at room temperature (22 °C). Chemical cell: s.g. I4/mmm,  $a = b = 4.0065(1)\text{Å}$ ,  $c = 12.5255(5)\text{Å}$ .  $R_p = 6.5\%$ ,  $R_{wp} = 4.34\%$ ,  $\chi^2 = 7.73$ .

Atom	Positions	$x$	$y$	$Z$	$B (\text{Å})^2$	Occupancy
La	4e	0	0	0.3520(1)	0.32(4)	0.725(3)
Nd	4e	0	0	0.3520(1)	0.32(4)	0.175(3)
Pr	4e	0	0	0.3520(1)	0.32(4)	0.100(5)
Cu	2a	0	0	0	0.58(6)	0.989(4)
O(1)	4c	0	0.5	0	1.02(6)	0.996(4)
O(2)	4d	0	0.5	0.25	0.84(5)	0.989(4)

(a)

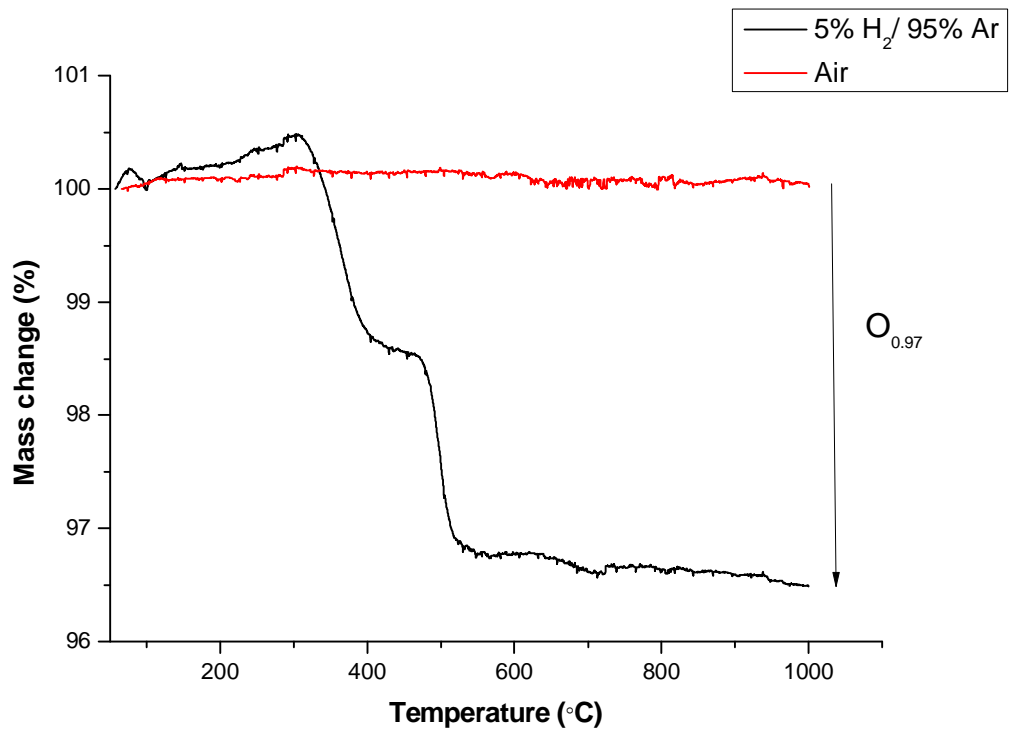


(b)



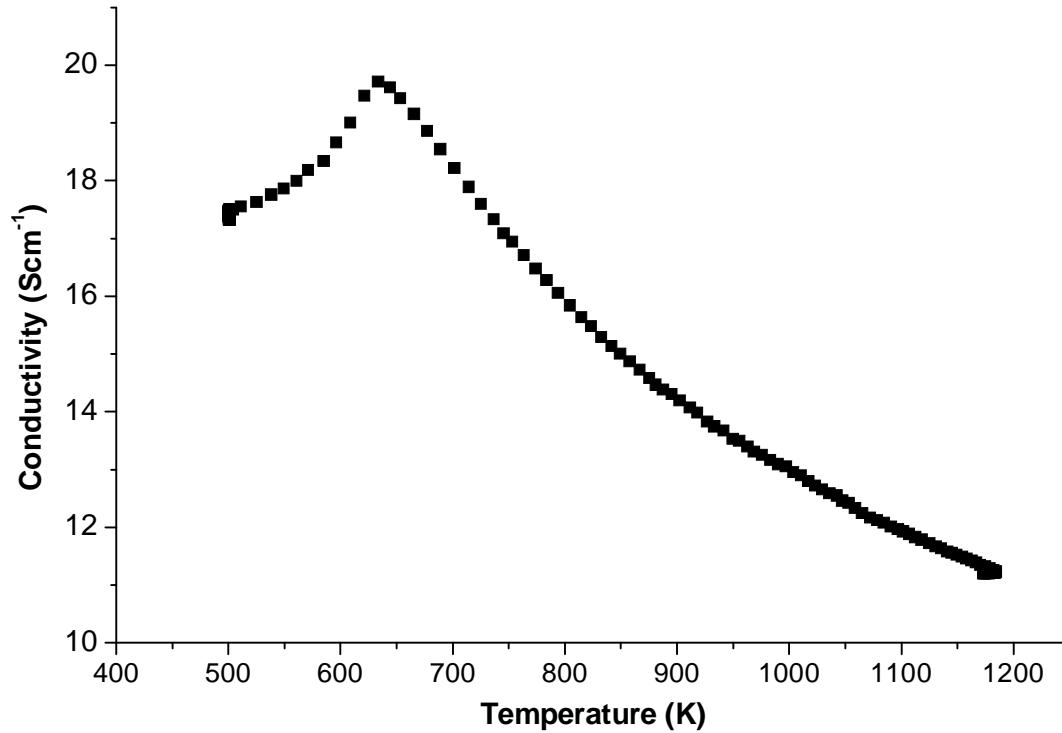
**Fig. S7:** SAED patterns for T'' phase at room temperature viewed down the  $\bar{3}31$  (a) and  $0\bar{1}0$  (b)

SAED patterns are in agreement with the NPD studies. Figure S7(a-b) shows a typical SAED pattern of the 4 coordinated tetragonal phase viewed down from two different directions  $\bar{3}31$  and  $0\bar{1}0$ . The phase is indexed according to the cell parameters from the  $d$ -spacings of the pattern and angle between each plane.



**Fig. S8:** Thermogravimetric analysis under air and 5% Hydrogen/95% Argon heating up to 1000 °C





**Fig. S9:** DC conductivity measurements for  $\text{Nd}_{0.35}\text{La}_{1.45}\text{Pr}_{0.2}\text{CuO}_4$

## References

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