High pressure synthesis of quasi-one-dimensional $GdFeO_3$-type perovskite $PrCuO_3$ with nearly divalent Cu ions

Journal:	*ChemComm*
Manuscript ID	CC-COM-06-2019-004656.R1
Article Type:	Communication

SCHOLARONE™
Manuscripts

ChemComm

COMMUNICATION

High pressure synthesis of quasi-one-dimensional $GdFeO_3$-type perovskite $PrCuO_3$ with nearly divalent Cu ions

Masaharu Ito,[a] Hidefumi Takahashi,[a,b] Hideaki Sakai,[a,c,d] Hajime Sagayama,[e] Yuichi Yamasaki,[d,f,g] Yuichi Yokoyama,[f,h] Hiroyuki Setoyama[i], Hiroki Wadati,[h] Kanako Takahashi,[a] Yoshihiro Kusano,[j] Shintaro Ishiwata*[a,b,d]

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

The new perovskite-type cuprate $PrCuO_3$ has been synthesized by high-pressure oxygen annealing. Synchrotron X-ray powder diffraction and absorption spectroscopy revealed that $PrCuO_3$ crystallizes in the $GdFeO_3$-type structure with cooperative Jahn-Teller distortion, forming one-dimensional chains of corner-shared CuO_4 plaquettes with nearly divalect Cu ions.

Discovery of high temperature superconductivity in layered perovskite cuprates has stimulated extensive studies on transition-metal oxides with perovskite-related structure.[1] So far, a wide range of perovskite-type transition-metal oxides ABO_3 including metastable phases has been explored with the help of high pressure technique.[2-4]

Among these metastable perovskite oxides, the compounds containing late 3d transition-metal ions with an unusually high valence state such as Fe^{4+}, Co^{4+}, and Ni^{3+} are known as unique systems showing various ground states, depending on the A-site ion.[5-11] For instance, as the A site of rhombohedral $LaNiO_3$ is substituted by Pr, which introduces the $GdFeO_3$-type distortion, the ground state changes from a paramagnetic metal to an antiferromagnetic insulator with charge disproportionation of the Ni ions.[6] On the other hand, when the A site of $LaNiO_3$ is substituted by Bi, the ground state becomes insulating because of the intersite charge transfer accompanying the charge disproportionation of Bi.[11-13] These unusual charge ordering phenomena can be interpreted as the manifestation of the strong orbital hybridizations inherent in the oxides with small or negative charge transfer energy.[14]

In contrast to the systematic studies on these perovskite oxides, $ACuO_3$ with unusually high valence Cu^{3+} ions has remained unexplored except for $LaCuO_3$, $La_{1-x}A_xCuO_3$ (A: Nd, Sr), and $NdCuO_{2.91}$,[15-18] despite the fact that $ACuO_3$ can be regarded as the three-dimensional analogue of the high-T_c cuprates. In this Communication, we report a high-pressure synthesis of a new highly distorted $GdFeO_3$-type cuprate $PrCuO_3$ with unusual oxidation state, in which square-planar CuO_4 units form quasi-one-dimensional chains.

Polycrystalline sample of $PrCuO_3$ was prepared by moderate temperature oxygen annealing at high pressures for the oxygen deficient perovskite $PrCuO_{2.5}$.[19] First, stoichiometric amounts of Pr_6O_{11} and CuO were dissolved in nitric acid, followed by drying

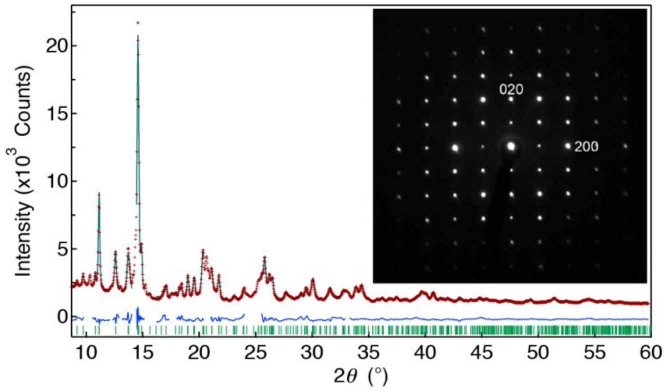

Fig.1 Observed synchrotron X-ray diffraction pattern (cross) and the calculated pattern (solid line) for $PrCuO_3$. The difference between them is plotted by blue solid lines (the data in the selected ranges are excluded from the fitting because of the presence of unknown impurities. The positions of the Bragg reflections are indicated by the green ticks. The inset shows an electron diffraction pattern taken with an incident beam parallel to [001].

---

[a] Department of Applied Physics and Quantum Phase Electronics Center (QPEC), University of Tokyo, Tokyo 113-8656, Japan.
[b] Division of Materials Physics, Graduate School of Engineering Science, Osaka University, Toyonaka, Osaka 560-8531, Japan.
[c] Department of Physics, Osaka University, Toyonaka, Osaka 560-0043, Japan.
[d] PRESTO, Japan Science and Technology Agency, Kawaguchi, Saitama 332-0012, Japan.
[e] Institute of Materials Structure Science, High Energy Accelerator Research Organization, Tsukuba, Ibaraki 305-0801, Japan.
[f] Research and Services Division of Materials Data and Integrated System (MaDIS), National Institute for Materials Science (NIMS), Ibaraki, Tsukuba 305-0047, Japan.
[g] RIKEN Center for Emergent Matter Science (CEMS), Wako, Saitama 351-0198, Japan.
[h] Institute for Solid State Physics, University of Tokyo, Chiba 277-8581, Japan.
[i] Kyushu Synchrotron Light Research Center, 8-7 Yayoigaoka, Tosu, Saga 841-0005, Japan.
[j] Department of Applied Chemistry and Biotechnology, Okayama University of Science, 1-1 Ridai-cho, Kita-ku, Okayama 700-0005, Japan
* E-mail: ishiwata@mp.es.osaka-u.ac.jp

at above 200 °C. The obtained sample was ground and heated at 900 °C in air, which is repeated for several times so that the sample becomes a precursor containing only Pr_2CuO_4 and CuO. The precursor was sealed in a gold capsule and heated at 1200 °C and 8 GPa for 30 min. The obtained polycrystalline sample of $PrCuO_{2.5}$ was mixed with an oxidizer $NaClO_3$ in a molar ratio of 2:1. The mixture was sealed in a gold capsule and heated at a moderate temperature of 440 °C and 7.5 GPa for 60 min (for details, see supporting information). The obtained sample was washed in distilled water to remove NaCl from $PrCuO_3$. Synchrotron X-ray diffraction (XRD) experiment was carried out at BL-8B, Photon Factory, KEK, Japan, for the fine polycrystalline sample prepared by the precipitation method.[11] The XRD data collected with a wavelength of 0.6872 Å were analyzed by Rietveld refinement using the RIETAN-FP program. Thermogravimetric (TG) analyses were performed on a Netzsch TG-DTA2500-IW thermal analyzer with a heating rate of 15 °C/min under a flow of mixed gas (96% Ar and 4% H_2). Energy dispersive X-ray spectroscopy (EDX) was performed by HORIBA EMAX X-act equipped with HITACH S-4300s scanning electron microscope. X-ray absorption near edge structure (XANES) at the Cu K-edge was measured in a transmission mode at BL4C of photon factory in KEK and BL11 of SAGA Light Source in Kyushu Synchrotron Light Research Center.

From the observation of transmission electron microscope shown in the inset of Fig. 1, $PrCuO_3$ was found to have an orthorhombic structure with lattice parameters, a~5.3 Å, b~6.3 Å, and c~7.3 Å. While the difference in the lattice parameters between a and b is significant as compared with that for $PrNiO_3$ with $GdFeO_3$-type structure (S.G.: *Pbnm*),[20] the structural parameters of $PrCuO_3$ were successfully determined by Rietveld refinement with adopting the structure of $PrNiO_3$ as an initial model (See Fig. 1 and Table 1). As illustrated in Figs. 2(a) and 2(b), CuO_6 octahedra expected for the $GdFeO_3$-type perovskite are considerably distorted to be virtually square-planar coordination in $PrCuO_3$ (one of the Cu-O bond lengths, 2.50(2) Å for Cu-O2, is much larger than the others). The square-planar CuO_4 plaquettes share the corner to form a quasi-one-dimensional chain along the c axis. As seen in Figs. 2(a) and 2(b), the CuO_4 plaquettes are largely tilted from the regular position (the bond angles for Cu-O1-Cu along the chain and for Cu-O2-Cu perpendicular to the chain are 140.2(6)° and 137.9 (4)°, respectively; see Table 2). $PrCuO_3$ is isostructural with $(Se,Te)CuO_3$ and similar to tetragonal $KCuF_3$, both of which contain Cu^{2+} ions and show the Jahn-Teller distortion with the ordering of the $d_{x^2-y^2}$ orbital. Therefore, contrary to our expectation for the Cu^{3+} state, it is presumable that $PrCuO_3$ contains the Jahn-Teller active, Cu^{2+} ions.[21-24] The presumption is supported by the bond-valence sums V_{BVS} calculated for Pr and Cu ions, which are +3.78 and +2.35, respectively (V_{BVS} was calculated by $\Sigma_i\{\exp(r_0\text{-}r_i)/0.37\}$, where r_0=2.135 and 1.679 for Pr and Cu, respectively). However, unlike the cases for $(Se,Te)CuO_3$ and $KCuF_3$, the calculated valence of Cu is significantly deviated from +2, suggesting the incomplete charge transfer between the Pr and Cu ions.

To check the oxygen contents in the polycrystalline samples of $PrCuO_{2.5}$ and $PrCuO_3$, TG measurements were performed with heating to 850 °C as shown in Fig. 3. For both measurements, distinct weight losses were observed around 400 °C. Both samples after the measurements were found to be a mixture of Pr_2O_3 and Cu by the XRD experiments. Thus, the weight losses can be ascribed to the oxygen releasing reactions as described in Fig. 3. The decreases in the mass (6.56 % for $PrCuO_{2.5}$ and 9.23 % for $PrCuO_3$) in the range from room temperature to 485 °C are fairly comparable to the theoretical values expected for each composition (6.55 % for $PrCuO_{2.5}$ and 9.51 % for $PrCuO_3$). The kink in the TG curve around 400 °C for $PrCuO_3$ can be explained by the oxygen reduction forming $PrCuO_{2.5}$. Note that the cation stoichiometry of $PrCuO_3$ was checked by the EDX analyses, giving the Pr/Cu ratio of 1.03, which is close to unity. The TG and EDX analyses confirmed the validity of the structural analyses performed with the nominal composition of $PrCuO_3$.

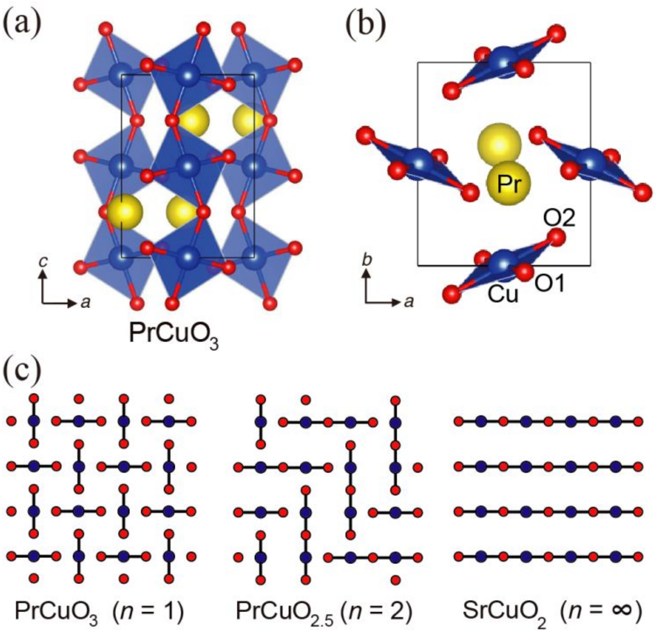

Fig.2 (a) Crystal structure of $PrCuO_3$ viewed along the b axis and (b) that along the c axis. (c) Schematics of Cu-O sublattices in the homologous series of $ACuO_{2+1/n}$ with A=Pr or Sr.

Table 1 Refined structural parameters of $PrCuO_3$. Space group; *Pbnm* (No. 62). a = 5.2979(6) Å, b =6.2532(8) Å, c =7.2829(8) Å, and V = 241.27 (5) Å^3. R_{wp}= 4.47 %, R_I= 1.17 %, S = 1.85. The equivalent isotropic atomic displacement parameters (B_{eq}) for Cu and O were fixed to be 0.8 and 1, respectively, during the refinements.

Atom	Site	x	y	z	B_{eq} (Å^2)
Pr	4c	0.0266(5)	0.0938(4)	0.25	0.74(6)
Cu	4b	0.5	0	0	0.8
O1	4c	0.618(4)	0.967(4)	0.25	1
O2	8d	0.306(4)	0.359(3)	0.053(3)	1

This journal is © The Royal Society of Chemistry 20xx

Table 2 Refined bond lengths and bond angles of $PrCuO_3$.

	lengths (Å)		angles (°)
Cu-O1 (×2)	1.936(8)	Cu-O1-Cu	140.2(6)
Cu-O2 (×2)	2.50(2)	Cu-O2-Cu	137.9(4)
Cu-O2 (×2)	1.89(2)	O1-Cu-O2 (×2)	92.0(3)
Pr-O1	2.46(3)	O1-Cu-O2 (×2)	88.0(3)
Pr-O1	2.30(2)	O1-Cu-O2 (×2)	85.2(3)
Pr-O2 (×2)	2.65(2)	O1-Cu-O2 (×2)	94.8(3)
Pr-O2 (×2)	2.24(2)	O2-Cu-O2 (×2)	92.0(3)
Pr-O2 (×2)	2.51(2)	O2-Cu-O2 (×2)	88.0(3)

Figure 4 shows XANES spectra of the Cu-K edge for polycrystalline samples of $PrCuO_3$, $PrCuO_{2.5}$, CuO, and $LaCuO_3$. CuO and $LaCuO_3$ were measured as references for the Cu^{2+} and Cu^{3+} states, respectively.[25] Although the difference in the local structure affects the shape of the XANES spectra, we can see the shifts of the position of the absorption edge, reflecting the difference of the oxidation state of Cu. Here, we define that the intersections of the horizontal line and each spectrum in the inset of Fig. 4 are the absorption edge energy for each compound (for details, see supporting information). The absorption edge energy of $PrCuO_{2.5}$ is comparable to that of CuO, indicating that the oxidation state of Cu in $PrCuO_{2.5}$ can be regarded as nearly +2. Considering the fact that the nominal oxygen content is supported by the TG measurement, the oxidation state of Pr in $PrCuO_{2.5}$ is expected to be +3. On the basis of the linear interpolation between the absorption edge energies for CuO and $LaCuO_3$, the oxidation state of Cu in $PrCuO_3$ was estimated to be +2.2(1). Provided that our sample of $PrCuO_3$ is free from the oxygen vacancy, the oxidation state of Pr is estimated to be +3.8, being consistent with the bond valence calculation.

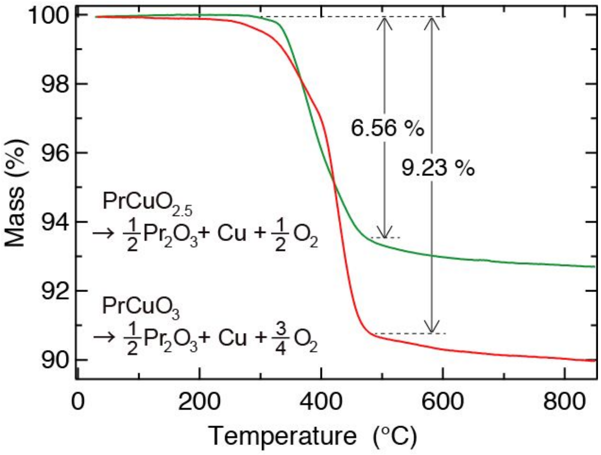

Fig.3 Thermogravimetric (TG) curves of $PrCuO_{2.5}$ (green) and $PrCuO_3$ (red).

In summary, we have succeeded in synthesizing a new perovskite cuprate $PrCuO_3$ and found the formation of the quasi-one-dimensional Cu-O chains embedded in the $GdFeO_3$-type structure. From the bond valence calculations, TG analyses, and XANES analyses, the oxidation state was found to be $Pr^{(4-d)+}Cu^{(2+d)+}O_3$. Having a look at the schematics of Cu-O sublattice viewed along the chains (see Fig. 2(c)), $PrCuO_3$ and $PrCuO_{2.5}$ can be regarded as the first (n = 1) and the second (n = 2) members of the homologous series of divalent cuprates $A^{2(1+1/n)+}Cu^{2+}O_{2+1/n}$, respectively. In $PrCuO_3$, the strong orbital hybridization between Pr, Cu, and O manifests itself as the unusual oxidation state with the cooperative Jahn-Teller distortion, giving rise to the formation of Cu-O chains. The quasi-one-dimensional structure with nearly divalent Cu ions promises that $PrCuO_3$ has a potential to be a nonlinear optical material as well as the one-dimensional cuprate Sr_2CuO_3.[26]

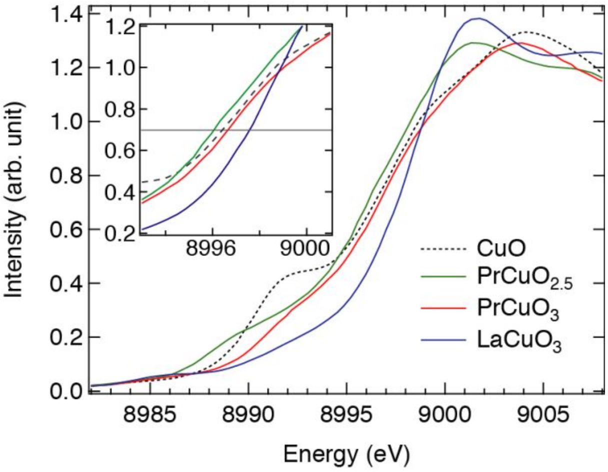

Fig.4 Normalized X-ray absorption spectra (Cu K-edge) for $PrCuO_{2.5}$, $PrCuO_3$, $LaCuO_3$, and CuO measured at room temperature. The inset shows the magnified view around the absorption edge energy.

The authors thank R. Arita, M. Ochi, and J. Fujioka for the fruitful comments. This work is partly supported by JSPS, KAKENHI (Grants No. 17H01195), JST PRESTO (JPMJPR1412), and Asahi Glass Foundation. The powder XRD measurement was performed with the approval of the Photon Factory Program Advisory Committee (Proposal No. 2015S2-007).

References

1 J. B. Goodenough, *Rep. Prog. Phys.*, 2004, **67**, 1915.
2 J. A. Rodgers, A. J. Williams and J. P. Attfield, *Zeitschrift für Naturforschung B*, 2006, **61**, 1515.
3 A. A. Belik and W. Yi, *J. Phys.: Condens. Matter*, 2014, **26**, 163201.
4 Y. Inaguma, *Handbook of Solid State Chemistry*, 2017, 49
5 M. Takano, N. Nakanishi, Y. Takeda, S. Naka and T. Takeda, *Mater. Res. Bull.* 1977, **12**, 923.
6 J. B. Torrance, P. Lacorre, A. I. Nazzal, E. J. Ansaldo and Ch. Niedermayer, *Phys. Rev. B* 1992, **45**, 8209.
7 I. Yamada, K. Takata, N. Hayashi, S. Shinohara, M. Azuma, S. Mori, S. Muranaka, Y. Shimakawa and M. Takano, *Angew. Chem. Int. Ed.* 2008, **47**, 7032.
8 T. Osaka, H. Takahashi, H. Sagayama, Y. Yamasaki and S. Ishiwata, *Phys. Rev. B*, 2017, **95**, 224440.
9 H. Sakai, S. Yokoyama, A. Kuwabara, J. S. White, E. Canévet, H. M. Rønnow, T. Koretsune, R. Arita, A. Miyake, M. Tokunaga, Y. Tokura and S. Ishiwata, *Phys. Rev. Mater.*, 2018, **2**, 104412.
10 A. E. Bocquet, A. Fujimori, T. Mizokawa, T. Saitoh, H. Namatame, S. Suga, N. Kimizuka, Y. Takeda and M. Takano, *Phys. Rev. B*, 1992, **45**, 1561.
11 S. Ishiwata, M. Azuma, M. Takano, E. Nishibori, M. Takata, M. Sakata and K. Kato, *J. Mater. Chem.*, 2002, **12**, 3733.

12 S. Ishiwata, M. Azuma, M. Hanawa, Y. Moritomo, Y. Ohishi, K. Kato, M. Takata, E Nishibori, M. Sakata, I. Terasaki and M. Takano, *Phys. Rev. B* 2005, **72**, 045104.
13 M. Azuma, S. Carlsson, J. Rodgers, M. G. Tucker, M. Tsujimoto, S. Ishiwata, S. Isoda, Y. Shimakawa, M. Takano and J. P. Attfield, *J. Am. Chem. Soc.* 2007, **129**, 14433.
14 T. Mizokawa, D. I. Khomskii and G. A. Sawatzky, *Phys. Rev. B*, 2000, **61**, 11263.
15 G. Demazeau, C. Parent, M. Pouchard and P. Hagenmuller, *Mater. Res. Bull.* 1972, **7**, 913.
16 J.-S. Zhou, W. Archibald and J. B. Goodenough, *Phys. Rev. B*, 2000, **61**, 3196.
17 S. Darracq, S. G. Kang, J. H. Choy and G. Demazeau, *J. Solid State Chem.*, 1995, **114**, 88.
18 B. H. Chen, D. Walker, E. Suard, B. A. Scott, B. Mercey, B. Mercey, M. Hervieu and B. Raveau, *Inorg. Chem.* 1995, **34**, 2077.
19 J. Fernández-Sanjulián, E. Morán and M. A. Alario-Franco, *High Press. Res.* 2010, **30**, 159.
20 J. L. García-Muñoz, J. Rodríguez-Carvajal, P. Lacorre and J. B. Torrance, *Phys. Rev. B*, 1992, **46**, 4414.
21 K. Kohn, K. Inoue, O. Horie, S. Akimoto, *J. Solid State Chem.* 1976, **18**, 27.
22 M. A. Subramanian, A. P. Ramirez and W. J. Marshall, *Phys. Rev. Lett.* 1999, **82**, 1558.
23 A. Okazaki and Y. Suemune, *J. Phys. Soc. Jpn.* 1961, **16**, 176.
24 M. T. Hutchings, E. J. Samuelsen, G. Shirane and K. Hirakawa, *Phys. Rev.* 1969, **188**, 919.
25 J.-H. Choy, D.-K. Kim, S.-H. Hwang and G. Demazeau, Phys. Rev. B 1994, **50**, 16631.
26 T. Ogasawara, M. Ashida, N. Motoyama, E. Eisaki, S. Uchida, Y. Tokura, H. Ghosh, A. Sulka, S. Mazumdar, and M. Kuwata-Gonokami, Phys. Rev. Lett. 2000, **85**, 2204.

This journal is © The Royal Society of Chemistry 20xx