6778 Inorg. Chem. 2010, 49, 6778–6780
DOI: 10.1021/ic100474x

Inorganic Chemistry
Communication

$CaCu_3Pt_4O_{12}$: The First Perovskite with the B Site Fully Occupied by Pt^{4+}

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Received March 11, 2010

A novel A-site ordered perovskite $CaCu_3Pt_4O_{12}$ was synthesized under high pressure and high temperature of 12 GPa and 1250 °C. $CaCu_3Pt_4O_{12}$ is the first perovskite in which the B site is fully occupied by Pt^{4+}. The crystal structure refinement based on the synchrotron powder X-ray diffraction data shows that $CaCu_3Pt_4O_{12}$ crystallizes in the space group $Im\overline{3}$ (cubic) with a lattice constant of $a = 7.48946(10)$ Å. The magnetic susceptibility data show the antiferromagnetic transition at $T_N = 40$ K, which is attributed to the magnetic ordering of Cu^{2+} spins with $S = {}^1/_2$.

Platinum oxides have been extensively investigated because of their excellent catalytic properties. Some of the platinum oxides crystallize in perovskite-related structures containing PtO_6 octahedra. $BaPtO_3$ has a hexagonal structure with face-sharing PtO_6 octahedra.[1] It has been reported that $CaPtO_3$ crystallizes in a postperovskite structure ($CaIrO_3$-type) with vertex- and edge-sharing PtO_6 octahedra.[2,3] Such face- and edge-sharing structures are generally considered unstable because of Coulomb repulsions between the metals in the short metal−metal distances. However, the metal−metal bonding of platinum probably exceeds the repulsion in these platinum oxides, leading to the face- and edge-sharing frameworks.

The perovskite phase has not been confirmed in $CaPtO_3$,[4] whereas two kinds of platinum-based mixed perovskites were reported. Ln_2MPtO_6 (Ln = lanthanides; M = Mg, Co, Ni, and Zn) has a random distribution of M and Pt ions at the B site.[5] Ba_2MPtO_6 (M = Ce and Pr) has a rock-salt-type ordering pattern of M and Pt ions at the B site.[6,7] In these mixed perovskites, the relaxation of metal−metal bonding of platinum by the insertion of other kinds of metal into the B site probably destabilizes the face- and edge-sharing frameworks. To our knowledge, perovskites with the B site fully occupied by platinum have not been reported.

In this Communication, we report a novel perovskite $CaCu_3Pt_4O_{12}$ (CCPO) with the B site fully occupied by Pt^{4+}. CCPO was synthesized under high pressure and high temperature of 12 GPa and 1250 °C. The crystal structure of CCPO is an A-site ordered perovskite with 1:3 ordering of Ca^{2+} (the A site) and Cu^{2+} (the A′ site) and with the vertex-sharing PtO_6 octahedra as shown in the inset of Figure 1.[8] CCPO demonstrates an antiferromagnetic transition at a Néel temperature (T_N) of 40 K because of the magnetic ordering of Cu^{2+} spins with $S = {}^1/_2$.

The polycrystalline sample of CCPO was synthesized from a mixture of CaO (99.9%), CuO (99.9%), and PtO_2 (99.9%) at a molar ratio of 1:3:4. The mixture was put into the gold capsule with an inner diameter of 2.8 mm and a height of 4.0 mm. The handling of the starting mixture was performed in a nitrogen-filled glovebox because of the hygroscopic property of CaO. The capsule was put into a high-pressure cell with a TiB_2−BN composite furnace. The cell was compressed to 12 GPa using a Kawai-type high-pressure apparatus at GRC, Ehime University. The capsule was heated to 1250 °C in 15 min, kept at this temperature for 30 min, and quenched to room temperature. The pressure was released slowly after the heat treatment. Synchrotron powder X-ray diffraction (SXRD) data were collected using the Debye−Scherrer camera installed at the BL02B2 beamline of SPring-8.[9]

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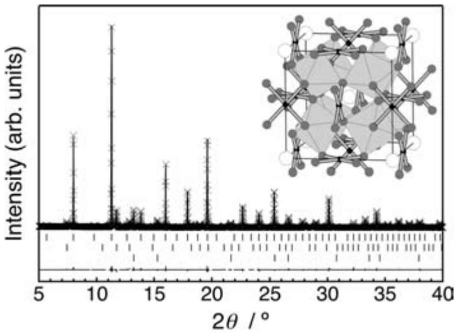

Figure 1. SXRD pattern and the Rietveld refinement results of CCPO. The dots and solid line indicate the observed and calculated patterns, respectively. The difference between the observed and calculated patterns is shown at the bottom. The vertical marks indicate the Bragg peak positions of CCPO, $M_xPt_3O_4$, and platinum metal, from top to bottom, respectively. The inset shows the refined crystal structure of CCPO. Large white spheres, small black spheres with 4-fold planar coordination, and medium gray spheres represent Ca, Cu, and O atoms, respectively. The octahedra represent PtO_6 octahedra.

The wavelength was 0.519 50 Å.[10] The crystal structure refinement was performed based on the SXRD data using a Rietveld program *RIETAN-FP*.[10] The magnetic susceptibility data were collected between 5 and 300 K in an external field of 1000 Oe upon zero-field cooling (ZFC) and field cooling (FC) using Quantum Design SQUID MPMS-XL.

Figure 1 shows the SXRD data and the calculated diffraction profile. The main phase is identified as a cubic perovskite of the $CaCu_3Ti_4O_{12}$ (CCTO) type with a lattice constant of $a \sim 7.49$ Å. Two impurities, a cubic phase with $a \sim 5.69$ Å and platinum metal and unknown phases, were found. The cubic phase is isostructural with $M_xPt_3O_4$ (M = Li, Na, Mg, Ca, and transition metals),[11] but details of the M ion were not clear in this study. We tentatively adopted a chemical formula of $Cu_{0.75}Pt_3O_4$ for this phase in the Rietveld refinement for a rough estimation of the weight ratios for each phase. The estimated weight ratios for CCPO, $M_xPt_3O_4$, and platinum are 83.74, 9.80, and 6.45 wt %, respectively.

The structural parameters obtained from the Rietveld refinement for CCPO are listed in Table 1. The small values of the reliability factors (R_{wp} and R_B) and the goodness of fit (S_{fit}) indicate that the refinement results are satisfactory. Structural disorder like an incorporation of platinum into the A′ site was examined for an initial structure model, but a significant amount of the disorder was not confirmed. The bond valence sum (BVS)[12] values are calculated from the bond lengths listed in Table 2. The BVS values of the Ca, Cu, and Pt sites are 2.04, 2.04, and 4.34, respectively.[13] These BVS values clearly demonstrate the valence state of $Ca^{2+}Cu^{2+}{}_3Pt^{4+}{}_4O_{12}$. Our structural analysis demonstrates that CCPO is the first perovskite in which the B site is fully occupied by Pt^{4+}.

The temperature dependence of the magnetic susceptibility measured upon ZFC and FC is shown in Figure 2. Almost no difference between ZFC and FC was observed. A cusp at 40 K clearly demonstrates an antiferromagnetic transition.

Table 1. Refined Structure Parameters of CCPO[a]

atom	site	g	x	y	z	$1000U$/Å^2
Ca	2a	1^b	0	0	0	6.9(3)
Cu	6b	1^b	0	$^1/_2$	$^1/_2$	6.9^c
Pt	8c	1^b	$^1/_4$	$^1/_4$	$^1/_4$	3.30(13)
O	24g	1^b	0.3036(10)	0.1736(9)	0	8.0(1.6)

[a] Space group $Im\bar{3}$ (No. 204), lattice constant $a = 7.48946(10)$ Å, $R_{wp} = 5.68\%$, $R_B = 1.72\%$, and $S_{fit} = 1.65$. [b] The site occupancy for all of the atoms was fixed to 1. [c] The following constraint was adopted: $U(Cu) = U(Ca)$.

Table 2. Selected Bond Lengths and Bond Angles for CCPO

	bond length/Å		bond angle/deg
Ca−O	2.619(8) × 12	O−Cu−O	83.0(5)
Cu−O	1.963(6) × 4	O−Cu−O	97.1(5)
Cu−O	2.853(8) × 4	O−Pt−O	88.7(3)
Pt−O	1.9986(19) × 6	O−Pt−O	91.3(3)
		Pt−O−Pt	139.1(3)
		Cu−O−Pt	81.8(2)

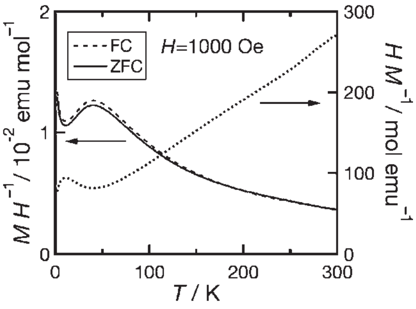

Figure 2. Temperature dependence of the magnetic susceptibility of CCPO measured in an external field of 1000 Oe. The solid, broken, and dotted curves represent the susceptibility upon ZFC and FC and the inverse susceptibility upon ZFC, respectively.

Because Pt^{4+} is expected to have an electron configuration of $t_{2g}{}^6e_g{}^0$ in a low-spin configuration due to the large crystal-field splitting of 5d orbitals,[2,3] only Cu^{2+} ions have localized spins in CCPO. Thus, the antiferromagnetic transition at $T_N = 40$ K is attributed to the ordering of the Cu^{2+} spins at the A′ site. This is in contrast to the ferromagnetic ordering of Cu^{2+} spins in $CaCu_3B_4O_{12}$ (B = Mn^{4+} and Fe^{4+}),[14,15] in which the antiferromagnetic interaction between A′ and B ions induces the ferromagnetic ordering of Cu^{2+} spins. The antiferromagnetism of CCPO can be explained by the superexchange interactions between the Cu^{2+} spins, as suggested in CCTO.[16,17] The Cu−O−Pt−O−Cu antiferromagnetic superexchange interaction pathway is dominant through the e_g orbitals of Pt^{4+}. It is interesting that antiferromagnetism of the Cu^{2+} spins is achieved not only through the d^0 ion (Ti^{4+} for CCTO) but also through the d^6 ion (Pt^{4+} for CCPO). T_N of CCPO is higher than that of CCTO ($T_N = 25$ K), indicating the strong superexchange interaction probably due to hybridization between Pt 5d and O 2p orbitals. The inverse magnetic

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susceptibility follows the Curie–Weiss law above T_N. The magnetic susceptibility data between 100 and 300 K are analyzed using the Curie–Weiss formula of $\chi^{-1} = C/(T - \theta)$, where C and θ are the Curie constant and Weiss temperature, respectively. C is 1.277(3) emu·K/mol, corresponding to the effective magnetic moment of 1.85 μ_B/Cu, if the magnetic contributions of the impurities are negligible. This value well explains the $S = {}^1/_2$ spin of Cu^{2+} (1.73 μ_B/Cu). θ is −44.0(5) K, showing the dominant antiferromagnetic interaction between Cu^{2+} spins in CCPO. The Curie–Weiss-like behavior remaining below T_N is probably attributed to the localized spins of the impurity phases such as $M_xPt_3O_4$.[18]

We consider the stabilizing factor for the vertex-sharing PtO_6 octahedra in this perovskite. In many alkaline-earth platinum oxide complexes, the PtO_6 octahedra are usually face- and edge-shared[1,19] or isolated.[20] This is explained by the strong metal–metal bonding property of platinum. Incorporation of the other metal ions into the B site relaxes the metal–metal bonding of platinum and tolerates the vertex-sharing PtO_6 octahedra network, leading to the mixed-metal perovskite containing platinum.[5,6] On the other hand, in CCPO, insertion of a CuO_4 square unit into the A site makes the vertex-sharing PtO_6 octahedra network favorable, leading to the perovskite structure with the B site fully occupied by Pt^{4+}. This finding could give us a strategy to obtain novel perovskites containing metal ions other than Pt^{4+}, which are unlikely at the B site within a simple perovskite structure.

Acknowledgment. The synchrotron radiation experiments were performed at the SPring-8 with the approval of the Japan Synchrotron Radiation Research Institute (Proposal Nos. 2008B1616, 2009B1298, and 2009B1322). The magnetic susceptibility experiments were performed using the facilities of the Institute for Solid State Physics, University of Tokyo. This work was partly supported by the Ministry of Education, Culture, Sports, Science and Technology of Japan for Grant-in-Aid for Young Scientist (B) No. 21750062.

Supporting Information Available: Crystallographic data of CCPO in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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