High-Pressure Synthesis of the Cobalt Pyrochlore Oxide Pb₂Co₂O₇ with Large Cation Mixed Occupancy

Junye Yang, Jianhong Dai, Zhehong Liu, Runze Yu, Hajime Hojo, Zhiwei Hu, Tunwen Pi, Yunliang Soo, Changqing Jin, Masaki Azuma, and Youwen Long

ABSTRACT: The novel A₂B₂O₇-type compound Pb₂Co₂O₇ was synthesized at 8 GPa and 1673 K. Synchrotron X-ray diffraction shows a cubic pyrochlore structure with space group Fd3m. Rietveld structural analysis reveals a large cation mixed occupancy at both A and B sites by about 40%, the greatest value found in the pyrochlore family. In combination with the X-ray absorption spectroscopy results, the specific chemical composition and charge states are determined to be (Co₀.₆Pb₀.₄)₃⁺(Pb₀.₆Co₀.₄)₄⁺O₇, in which both the A-site Co³⁺ and the B-site Pb⁴⁺ are low-spin. Due to the tetrahedral geometric frustration effects as well as the random Co⁴⁺ and Pb⁴⁺ distribution at the B site, spin glassy behavior is well observed following the conventional critical slowing down feature in Pb₂Co₂O₇.

I. INTRODUCTION

Pyrochlore oxides with chemical formula A₂B₂O₇ (or A₂B₂O₆O') have been attracting much attention due to their fascinating chemical and physical properties such as superconductivity observed in Cd₆Re₂O₇, giant magnetoresistance in Ti₃Mn₂O₇, unconventional anomalous Hall effect in metallic Nd₆Mo₂O₁₅, Kondo-like effect in Pr₃Ir₄O₁₁, etc. Pyrochlore often crystallizes in a face-centered cubic structure with space group Fd3m (No. 227). As shown in Figure 1a, the A-site cation in the pyrochlore with larger ionic size occupies the special atomic position 16d (1/2, 1/2, 1/2), which is coordinated by eight oxygens (6 O and 2 O'), while the smaller B-site cation is located at the special site 16c (0, 0, 0) with 6-fold oxygen coordination, forming distorted BO₆ octahedra. The two distinct oxygen positions are at 48f (x, 1/8, 1/8) for O and 8b (3/8, 3/8, 3/8) for O'. Moreover, when one considers the polyhedra composed of the nearest neighboring A-site or B-site cation, both OA₄ and OB₆ tetrahedra with geometric frustration can form. As a consequence, nontrivial spin properties such as spin liquid and spin ice may occur in pyrochlore oxides.

In past decades, the cobalt oxides have been investigated intensely due to their versatile functional properties. For example, high ferromagnetic Curie temperature is found in SrCo₃O₇ single crystals. On the other hand, the oxygen-deficient SrCoO₃ shows reversible redox reactions, making it promising for developing highly sensitive electrochemical sensors. The layered LiCoO₂ and the double perovskite (NdₓBaₓCa)₂Co₂O₆, a new compound studied widely in solid oxide fuel cells. In addition, a giant magnetoresistance effect is observed in LnBa₂Co₂O₆ (Ln = Eu, Gd) and collinear-magnetism-driven ferroelectricity is found in Sr₂CoMnO₆. In parallel to the study of Co-based oxides, the Pb-based oxides have also attracted much attention owing to their functional properties such as piezoelectricity, ferroelectricity, and multiferroicity. Unfortunately, however, as far as the Pb—Co—O ternary system is concerned, the number of compounds is extremely limited. It appears that the recently discovered perovskite PbCoO₃ (Pb²⁺Pb⁴⁺O₃Co²⁺Co⁴⁺O₁₂) with both A- and B-site charge orderings is the only known example of this ternary system to date. In this paper, we report the new finding of the Co-based pyrochlore Pb₂Co₂O₇, which can only be stabilized under high-pressure and low-temperature conditions probably due to the large cation mixed occupancy at both A and B sites.
were measured by using a Quantum Design physical property measurement system.

**III. RESULTS AND DISCUSSION**

Figure 1b shows the SXRD pattern of Pb$_2$Co$_2$O$_7$ measured at room temperature. All of the diffraction peaks can be well indexed on the basis of an $A_2B_2O_7$-type pyrochlore structure model with space group $Fd3m$. Since the high-resolution synchrotron X-ray is sensitive enough to distinguish the heavy atoms Pb and Co, the distribution for these two cations was examined by refining the occupancy parameter. When the Pb/Co atoms were constrained to fully occupy the $A$/$B$ sites or $B$/$A$ sites, a much higher agreement factor $R_p$ (>30%) was always obtained. In contrast, however, if we refined the occupancy parameter for these two sites by allowing Pb and Co to freely occupy the $A$ or $B$ site, the $R_p$ factor was sharply reduced to a satisfied value of less than 5%. The good agreement between the measurement data and the Rietveld refinement is shown in Figure 1b by considering the Pb/Co free occupancy but constraining the total occupancy factor to be unity for either the $A$ or $B$ site. Note that during the refinement the occupancy factor of oxygen is fixed to unity since the XAS results illustrate the almost stoichiometric oxygen content (discussed later).

Table 1 gives the related refined structural parameters. A

<table>
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<th>atom</th>
<th>site</th>
<th>g</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>$U_{eq}$ (Å$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
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<td>1ad</td>
<td>0.61(7)</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.387(3)</td>
</tr>
<tr>
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<td>16d</td>
<td>0.39(4)</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.387(3)</td>
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<tr>
<td>Pb2</td>
<td>16c</td>
<td>0.61(7)</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.145(3)</td>
</tr>
<tr>
<td>Co2</td>
<td>16c</td>
<td>0.39(4)</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.145(3)</td>
</tr>
<tr>
<td>O1</td>
<td>48f</td>
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<td>0.125</td>
<td>0.458(3)</td>
</tr>
<tr>
<td>O2</td>
<td>8d</td>
<td>1</td>
<td>0.375</td>
<td>0.375</td>
<td>0.375</td>
<td>0.515(2)</td>
</tr>
</tbody>
</table>

$^{*}$Crystal data: space group $Fd3m$ (No. 227), $Z = 8, a = 9.95776(2)$ Å, $\rho_{\text{calc}} = 5.0907(1)~g/cm^3$, $V = 987.30(1)$ Å$^3$, $R_{\text{wp}} = 8.9\%$, $R_p = 4.7\%$. g denotes the occupancy factor.

**II. EXPERIMENTAL DETAILS**

Polycrystalline Pb$_2$Co$_2$O$_7$ was prepared under high-pressure and high-temperature conditions using a cubic-anvil-type high-pressure apparatus. Highly pure (>99.9%) PbO$_2$ and CoO powders with a 1:1 mole ratio were used as starting materials. In addition, excess KClO$_4$ was used as an oxidizing agent. These reactants were thoroughly mixed in an agate mortar within an argon-filled glovebox and then sealed into a platinum capsule 2.8 mm in diameter and 4.0 mm in length. The capsule was treated at 8 GPa and 1673 K for 1/2 h. When the heat treatment was finished, the sample was quenched to room temperature, and the pressure was gradually released. The residual KCl in the final product was washed out by deionized water.

Synchrotron X-ray diffraction (SXRD) on powder samples was carried out using large Debye–Scherer camera on beamline BL02B2 in SPring-8 with the wavelength $\lambda = 0.4199$ Å. The SXRD data were analyzed using the Rietveld refinement program FullProf.$^{18}$ The soft X-ray absorption spectroscopy (XAS) at the Co L$_{2,3}$ edges was measured with total electron yield at the BL08B beamline of the National Synchrotron Radiation Research Center (NSRRC) in Taiwan. The hard XAS at the Pb L$_3$ edges was measured in the transmission geometry at the BL07A beamline of the NSRRC. The temperature-dependent dc magnetic susceptibility ($\chi_{dc}$) and field-dependent isothermal magnetization ($M$) were measured on a commercial superconducting quantum interference device magnetometer (Quantum Design). The magnetic susceptibility data were collected between 2 and 400 K at different magnetic fields with a temperature sweep model at a rate of 3 K/min. The temperature dependence of ac magnetization ($M'$), resistivity, and specific heat

Considerable Pb–Co mixed occupancy is found to occur, i.e. the $A$ site is occupied by about 60% Co and 40% Pb and vice versa for the $B$ site, indicating the detailed chemical composition to be ($Co_{0.6}Pb_{0.4}$)$_2$($Pb_{0.6}Co_{0.4}$)$_2$O$_7$. Although the mixed occupancy effect is also observed in other pyrochlores, the mixed occupancy degree is usually less than 25%.$^{19}$ The current Pb$_2$Co$_2$O$_7$ thus exhibits the greatest mixed occupancy in the pyrochlore family discovered so far. As shown later, the charge states of Pb and Co at different atomic sites are different to ensure that the $A$-site average ionic radius is larger than that of the $B$-site. This distinct charge distribution can effectively prevent the random $A$–$B$ antisolvent disorder of cations. In any event, Pb$_2$Co$_2$O$_7$ provides the first Co-based oxide possessing a cubic pyrochlore structure.

It is well-known that the multiplet spectral features in the XAS data at the 3d transition-metal $L_{2,3}$ edges are very sensitive to the valence and spin states as well as the local environment.$^{20,21}$ To identify the charge and spin states of Co, we performed the Co $L_{2,3}$ XAS measurements. Figure 2a shows the Co $L_{2,3}$ XAS of Pb$_2$Co$_2$O$_7$ together with that of EuCoO$_3$ and BaCoO$_3$ used as low-spin Co$^{3+}$ and Co$^{4+}$ references with CoO$_6$ octahedral coordination, respectively.$^{20}$ As shown in Figure 2a, Pb$_2$Co$_2$O$_7$ has an XAS profile similar to those of these two references, suggesting the presence of low-
spin Co ionic states in Pb₂Co₂O₇. Note that the XAS spectral feature of Pb₂Co₂O₇ is also similar to that observed in the Co³⁺ and Co⁴⁺ mixed system Na₂Co₄O₇, in which low-spin Co ions emerge as well. In addition, we find that the absorption spectrum of Pb₂Co₂O₇ displays an apparent energy shift relative to the references. For example, the L₁ edge peak position is located at 780.2 eV for EuCo³⁺O₃, 780.6 eV for Pb₂Co₂O₇, and 781.2 eV for BaCo⁴⁺O₃. By comparison, the valence state of Co ions in Pb₂Co₂O₇ is determined to be +3.4 on average, suggesting Co³⁺:Co⁴⁺ = 3:2 (i.e., Co³⁺:Co⁴⁺:O₃ in each formula unit). For the hard XAS of the heavier element Pb, the chemical shift of the Pb L₃ edge defined at μ ≈ 0.7–0.8 of the normalized intensity can be used to determine the valence state. In Figure 2b one can see that the Pb L₃ edge shifts to higher energy from the Pb⁴⁺ reference PbO to the current Pb⁴⁺ average Pb⁴⁺ site in Pb₂Co₂O₇. When the structural refinement and XAS results are combined, the detailed chemical and charge formula of Pb₂Co₂O₇ can be assigned to be (Co⁰₆Pb₀₄)₂⁺(Pb₀₆Co₀₄)⁴⁺O₇−₂, where Co³⁺ and the average Pb³⁺ occupy the pyrochlore A site with a mole ratio of 3:2, whereas Pb⁴⁺ and Co⁴⁺ occupy the B site with an identical ratio. This formula is also in accordance with the charge balance requirement for the stoichiometric oxygen content. Note that Pb is a valence skipper element; therefore, the average Pb³⁺ state occurring at the A site should be composed of Pb³⁺₀₄/Pb⁴⁺₀₅ in reality.

As mentioned above, although there exists a large Pb-Co mixed occupancy at both A and B sites, the A-B intersite disorder can be reduced significantly by the distinct charge states and ionic sizes of these two cations at different atomic sites. Moreover, both the A-site Co³⁺ and the B-site Co⁴⁺ are low-spin in nature. This means that the Co³⁺ is nonmagnetic and insulating. As a consequence, the magnetism and electrical transport will be dominated by the corner-sharing BO₆ octahedra in the current Pb₂Co₂O₇. Figure 3 presents the resistivity of Pb₂Co₂O₇ as a function of temperature. Since Pb⁴⁺ with a closed cell electronic configuration governs the B site, the compound exhibits electrical insulating behavior in the whole temperature region we measured, as featured by the increasing resistivity on cooling. Moreover, above 250 K, the temperature dependence of resistivity can be fitted on the basis of a 3D Mott variable range hopping model with the formula ρ(T) = ρ₀ exp(Tₐ/T)¹/₄, as shown in the inset of Figure 3, further revealing the insulating nature of Pb₂Co₂O₇, as expected from structural and charge state analysis.

Figure 2. XAS of (a) Co L₂,₃ edges and (b) Pb L₁ edge of Pb₂Co₂O₇. The XAS spectra of some related references are also shown for comparison.

Figure 3. Temperature dependence of resistivity of Pb₂Co₂O₇. The inset shows the fitting result by the 3D Mott variable range hopping model between 250 and 300 K.
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