Pressure Effect on Intersite Charge Transfer in A-site-Ordered Double-Perovskite-Structure Oxide

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ABSTRACT: The intersite charge transfer at room temperature was found to occur by applying pressure in the A-site-ordered double-perovskite-structure oxide LaCu$_3$Fe$_4$O$_{12}$. The pressure-induced charge transfer between the A-site Cu and B-site Fe causes a first-order-type transition from low-pressure LaCu$_3^{3+}$Fe$_3^{3+}$O$_{12}$ to high-pressure LaCu$_2^{2+}$Fe$_3^{2.75+}$O$_{12}$. The transition is accompanied by significant reduction of unit-cell volume, by unusual softening in bulk modulus, and by a change from an antiferromagnetic-and-insulating state to a paramagnetic-and-metallic state. The intersite charge-transfer transition in LaCu$_3$Fe$_4$O$_{12}$ is induced by changing pressure at ambient temperature as well as by changing temperature at ambient pressure. Besides, either physical pressure or chemical pressure, which is induced by cation substitution at the A′ site, decreases the intersite charge-transfer transition temperature, and reducing the unit-cell volume stabilizes Cu$^{2+}$ at the A site and unusual high-valence Fe$^{3.75+}$ at the B site in the A-site-ordered double-perovskite-structure oxides.

KEYWORDS: pressure effect, double-perovskite-structure oxides, intersite charge transfer, unusual high-valence state

1. INTRODUCTION

Perovskite-structure oxides, with the general formula ABO$_3$, usually contain alkaline metal, alkaline-earth metal, and lanthanide ions at the A site. An A-site-ordered double perovskite structure with the chemical formula A$'$$A_3$$B_4$$O_{12}$ can be formed by substituting a transition-metal ion such as Cu$^{2+}$ or Mn$^{3+}$ for 3/4 of the A-site ions in a simple ABO$_3$ perovskite.$^{1,2}$ This ordered perovskite usually has a cubic crystal structure with a space group Im$\overline{3}$ with A′ ions at the 2$a$ (0, 0, 0), A ions at the 6$b$ (0, 0.5, 0.5), B ions at the 8$c$ (0.25, 0.25, 0.25), and oxygen ions at the 2$4$ $g$ ($x$, $y$, 0) positions, as shown in Figure 1. This structure the BO$_6$ octahedron is rigid but significantly tilted, giving rise to a square-coordinated AO$_4$ unit. From a structural point of view, the flexibility for tilting the BO$_6$ octahedra in A$'$$A_3$$B_4$$O_{12}$ is rather limited because of the need to maintain the square-planar coordination at the originally 12-fold-coordinated A site in the simple perovskite structure. Thus, high-pressure synthesis is often useful to stabilize such a crystal structure.

Because both the A and B sites in A$'$$A_3$$B_4$$O_{12}$ can accommodate transition-metal ions, materials with this structure often exhibit intriguing properties due to A−B intersite interaction as well as A−A and B−B interactions.$^{3-5}$ For instance, a ferrimagnetic transition above room temper-
CaCu$_3$Mn$_3$O$_{12}$ induced valence mixing in the B-site Mn and gave (La/Bi)Cu$_3$Mn$_3$O$_{12}$, a half-metallic nature with spin-polarized conduction carriers, leading to a large magneto-resistance effect.8–10

Another phenomenon caused by the A-B intersite interaction in the A-site-ordered double-perovskite-structure oxide LaCu$_3$Fe$_4$O$_{12}$ was recently found; temperature-induced charge transfer.11 The compound was synthesized under a high-pressure and high-temperature condition. At room temperature the charge formula of the compound was LaCu$_{3.8}$Fe$_{3.2}$O$_{12}$, where an unusual Cu$^{3+}$ valence state at the square-planar-coordinated A site was stabilized. Heating induced the charge transfer at 393 K from the B-site Fe ions to the A-site Cu ions (4Fe$^{3+}$ – 3e$^-$ → 4Fe$^{2+}$ and 3Cu$^{3+}$ + 3e$^-$ → 3Cu$^{2+}$) and the charge formula changed to LaCu$_{2.8}$Fe$_{3.75+}$O$_{12}$. The high-temperature phase contained iron ions in the unusually high-valence state Fe$^{3+}$. The transition did not change the crystal-structure symmetry but drastically changed the unit-cell volume, leading to a negative-thermal-expansion-like volume contraction. This intersite charge transfer also associated with antiferromagnetism-to-paramagnetism and insulator-to-metal transitions.12

Like temperature, pressure can also modify the valence states of transition-metal ions in oxides. It is thus interesting to examine the effect of pressure on the intersite charge-transfer transition in LaCu$_3$Fe$_4$O$_{12}$ without changing the temperature. In this study, we measured the synchrotron X-ray diffraction (SXRD), Mössbauer spectra, and electric transport of LaCu$_3$Fe$_4$O$_{12}$ at room temperature and under high pressures ranging from ambient pressure to about 8 GPa. We found that pressure decreased the intersite charge-transfer transition temperature and induced the charge change between the A-site Cu and B-site Fe ions in LaCu$_3$Fe$_4$O$_{12}$ at room temperature. The observed physical pressure effect is also discussed with comparison of chemical pressure effect induced by the cation substitution.

2. EXPERIMENTAL SECTION

LaCu$_3$Fe$_4$O$_{12}$ was prepared by a solid-state reaction at 10 GPa and 1400 K in a way described in a previous report.11 A cubic anvil-type high-pressure apparatus was used for the reaction. The starting materials were La$_2$O$_3$, CuO and Fe$_2$O$_3$, and KClO$_4$ was used as an oxidizing agent. The sample synthesized was confirmed to be a single phase with the A-site-ordered double perovskite structure. No anomalies in the occupation factors for any sites were observed in the structure refinements, indicating that the compound had the stoichiometric composition.

The preliminary high-pressure SXRD experiment was done at the Beijing Synchrotron Radiation Facility. The detailed diffraction experiment was done at beamline BL22XU in SPring-8 by using a diamond anvil cell (DAC) with a stainless-steel gasket. A mixture of methanol and ethanol with a molar ratio of 4:1 was used as a pressure-transmitting medium in the DAC, and the applied pressure was calibrated using the ruby fluorescence method.15 The wavelength used in the detailed experiment was 0.49613 Å. The GSAS Rietveld program was used to analyze the SXRD data.14

The high-pressure $^{57}$Fe Mössbauer spectra were obtained on a Basset-type DAC with a Re gasket. $^{57}$Co in Rh and a control absorber consisting of α-Fe were used. Daphne 7474 was used as a pressure-transmitting medium. The resistivity under pressure was measured using a four-probe method with a cubic-anvil-type high-pressure apparatus. All the measurements were made at room temperature.

3. RESULTS AND DISCUSSION

Figure 2a shows the pressure dependence of SXRD patterns. The structure analysis from the diffraction data at 0.3 GPa confirms that the compound is crystallized with the charge formula LaCu$_{3.8}$Fe$_{3.2}$O$_{12}$, which is that of the low-temperature phase.11 When the pressure is increased to 3.6 GPa, additional diffraction peaks appear and two cubic phases coexist. Above that pressure, the low-pressure phase disappears and the high-pressure phase is stable up to 8.4 GPa, which is the maximum pressure used in this study. The refined structure parameters of phases at representative low pressure (2.7 GPa) and high pressure (4.2 GPa) are listed in Table 1. Note that the high-pressure phase is isostructural to the low-pressure one.

As shown by the pressure dependence of unit-cell volume (Figure 2b), this isostructural phase transition is associated with a roughly 1.7% volume contraction, revealing the first-order nature of the transition. The pressure dependence of cell volume ($V$) could be well fitted to an isothermal Birch–Murnaghan equation of state,

$$p(V) = 1.5B_0'(V_0/V)^{5/3} - (V_0/V)^{2/3}.$$  

where $B_0$ and $B'_0$ are the bulk modulus and its pressure derivative, respectively. $B'_0$ is fixed to be 4, which is a typical value for elastic lattices. The $B_0$ obtained for the low-pressure and high-pressure phases are respectively 133 ± 4 and 118 ± 2 GPa. When pressure induces a structural phase transition, the high-pressure phase usually has a larger $B_0$ than the low-pressure phase. The $B_0$ of the high-pressure phase of LaCu$_3$Fe$_4$O$_{12}$, however, is about 11% smaller than that of the low-pressure phase. Such unusual softening has been seen in crystalline gallium17 and a few other perovskite-structure...
changes of Fe charge and magnetic state under pressure. As 1.3 GPa are essentially the same as the spectra of the sextuplet decreases and the singlet becomes dominant (Figure further increasing pressure, the relative abundance of the singlet that coexists with the major sextuplet is seen. With b). When pressure increases to 1.9 GPa, a minor nonmagnetic one occurs around 3 GPa. This di transition from the low-pressure phase to the high-pressure the di one that heating does.

The Mössbauer spectra provide convincing evidence for the changes of Fe charge and magnetic state under pressure. As shown in Figure 3, the Mössbauer spectra observed at 0.5 and 1.3 GPa are essentially the same as the spectra of the LaCu$^{3+}$Fe$^{3+}$O$_{12}$ phase. The isomer shift (IS) $\approx 0.33$ mm s$^{-1}$ and the hyperfine field (HF) $\approx 46$ T indicate that Fe$^{3+}$ with a high-spin configuration orders antiferromagnetically (Figure 4a, b). When pressure increases to 1.9 GPa, a minor nonmagnetic singlet that coexists with the major sextuplet is seen. With further increasing pressure, the relative abundance of the sextuplet decreases and the singlet becomes dominant (Figure 4c). The singlet signals with IS $\approx 0.18$ mm s$^{-1}$ at high pressures are quite similar to the singlet signal seen in the spectrum of the high-temperature LaCu$^{3+}$Fe$^{3+}$O$_{12}$. Note that the IS and HF of the low-pressure phase are almost constant and the IS of the high-pressure phase also does not change with changing pressure. The transition is thus characterized by the first-order-type change in the relative abundance of the phases. The results clearly indicate that applying pressure causes the change of Fe from antiferromagnetically ordered Fe$^{3+}$ to paramagnetic Fe$^{2+}$. Although the two-phase coexistence region is slightly different from that observed in SXRD experiments, the transition from the low-pressure phase to the high-pressure one occurs around 3 GPa. This difference might originate from the difference in the experimental conditions.

It is therefore clear that pressure induces the intersite charge transfer at room temperature between the A-site Cu and B-site Fe ions. The insulator-to-metal transition observed in the resistivity measurement increasingly higher pressures is also consistent with the charge state transition, as shown in Figure 5. Because the electric transport properties of the A-site-ordered double-perovskite-structure materials are mainly governed by the nature of the BO$_6$ octahedra, the antiferromagnetically coupled Fe$^{3+}$ with high-spin configuration makes the low-pressure LaCu$^{3+}$Fe$^{3+}$O$_{12}$ phase being a Mott insulator. During the charge transfer, however, the resistivity decreases by about 4 orders of magnitude due to the formation of mixed valence state at the B site in the high-pressure LaCu$^{2+}$Fe$^{3+}$O$_{12}$ paramagnetic phase.

These results also imply that moderate pressure (about 3 GPa) reduces the charge-transfer transition temperature of LaCu$_2$Fe$_2$O$_{12}$ from 393 to 298 K (room temperature). This is similar to what occurs in the BiNiO$_3$ perovskite, where pressure induces the charge-transfer transition from Bi$^{3+}$Ni$^{2+}$O$_3$ to Bi$^{3+}$Ni$^{3+}$O$_3$ at room temperature. Because the charge-transfer transition in the pressure—temperature phase diagram for BiNiO$_3$ has a negative $dT_{C_{T}}/dp$ slope, applying pressure decreases the charge-transfer transition temperature. In the LaCu$_2$Fe$_2$O$_{12}$ A-site-ordered double perovskite, the unusual high-valence Fe$^{3+}$ state at the B site is stabilized at high temperature and high pressure while the unusual Cu$^{3+}$ state at the square-planar A site is stable at low temperature and low pressure. Because the energy levels of the high Fe$^{3+}$ and Cu$^{3+}$ states are comparable, a small external stimulus changes the energy balance between the states. We thus see the transition between the two states as the intersite charge-transfer transition in LaCu$_2$Fe$_2$O$_{12}$ either by changing pressure at ambient temperature or by changing temperature at ambient pressure. It is also important that such an intersite charge transfer occurs in the A-site-ordered double-perovskite-structure oxides in which both the A- and B-site transition-metal cations accept the transferred charge.

Note here that the intersite charge-transfer transition temperature of another A-site-ordered double-perovskite-structure oxide BiCu$_2$Fe$_2$O$_{12}$ (428 K) is higher than that of LaCu$_2$Fe$_2$O$_{12}$ (393 K). The lattice constant of BiCu$_2$Fe$_2$O$_{12}$ is

![Figure 3](image-url)

**Table 1. Refined Structure Parameters and Selected Bond Lengths of the LaCu$_2$Fe$_2$O$_{12}$ (Z = 2) Phases at Low Pressure (2.7 GPa) and High Pressure (4.2 GPa)**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Low Pressure (2.7 GPa)</th>
<th>High Pressure (4.2 GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure (GPa)</td>
<td>2.7</td>
<td>4.2</td>
</tr>
<tr>
<td>Space group</td>
<td>Im$\bar{3}$</td>
<td>Im$\bar{3}$</td>
</tr>
<tr>
<td>$\alpha$ (Å)</td>
<td>7.4012(1)</td>
<td>7.3428(1)</td>
</tr>
<tr>
<td>$V$ (Å$^3$)</td>
<td>405.41(2)</td>
<td>395.91(2)</td>
</tr>
<tr>
<td>$a$ (Å)</td>
<td>1.75(8)</td>
<td>1.34(8)</td>
</tr>
<tr>
<td>$b$ (Å)</td>
<td>2.73(7)</td>
<td>2.96(9)</td>
</tr>
<tr>
<td>$c$ (Å)</td>
<td>1.34(6)</td>
<td>1.03(8)</td>
</tr>
<tr>
<td>$x$ for O</td>
<td>0.3211(5)</td>
<td>0.3133(6)</td>
</tr>
<tr>
<td>$y$ for O</td>
<td>0.1695(6)</td>
<td>0.1744(7)</td>
</tr>
<tr>
<td>$U$ (100 x Ǻ$^2$)</td>
<td>0.05(1)</td>
<td>0.04(3)</td>
</tr>
<tr>
<td>Cu−O (Å) for CuO$_4$</td>
<td>1.824(4)</td>
<td>1.876(4)</td>
</tr>
<tr>
<td>Fe−O (Å) for FeO$_6$</td>
<td>2.014(1)</td>
<td>1.973(2)</td>
</tr>
<tr>
<td>$R_{wp}$ (%)</td>
<td>4.45</td>
<td>5.43</td>
</tr>
<tr>
<td>$R_p$ (%)</td>
<td>2.66</td>
<td>3.12</td>
</tr>
</tbody>
</table>

Numbers in parentheses are standard deviations of the last significant digit. $U$ is the isotropic thermal parameter. $R_{wp}$ and $R_p$ are agreement indices for the structure refinements by the Rietveld method.
7.4332 Å at room temperature, which is larger than that of LaCu₃Fe₄O₁₂ (7.4328 Å), and thus the charge-transfer transition temperature of the A-site-ordered double-perovskite-structure oxides decreases with decreasing volume. It implies that the charge-transfer transition temperature is reduced not only by physical pressure but also by chemical pressure due to cation substitution. Reducing the unit-cell volume of $\text{A}''\text{Cu}_3\text{Fe}_4\text{O}_{12}$ in either a physical or chemical way thus stabilizes Cu²⁺ and Fe³.75⁺ at the A and B sites and decrease the intersite charge-transfer transition temperature.

4. CONCLUSIONS

We found a pressure-induced intersite charge transfer at room temperature between the A-site Cu and B-site Fe in the A-site-ordered double-perovskite-structure oxide LaCu₃Fe₄O₁₂. Synchrotron X-ray diffraction, Mössbauer spectroscopy, and resistivity measurements under high pressure revealed that the first-order charge-transfer transition from low-pressure LaCu₃⁺³Fe³⁻⁴O₁₂ to high-pressure LaCu₂⁺³Fe³.75⁺⁴O₁₂ is accompanied by significant volume reduction with unusual softening in bulk modulus and a change from an antiferromagnetic-and-insulating state to a paramagnetic-and-metallic state. The intersite charge-transfer transition in LaCu₃Fe₄O₁₂ is induced either by changing pressure at ambient temperature or by changing temperature at ambient pressure. Besides, the intersite charge transfer is caused by not only physical pressure but also chemical pressure by substituting cations at the A’ site. Reducing the unit-cell volume stabilizes the unusual high-valence Fe³.75⁺ state at the B sites in the A-site-ordered double-perovskite-structure oxides.

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Author Contributions
Y.W.L., T.K., T.S., and Y.S. designed the study. All authors contributed the sample synthesis and property measurements. The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes
The authors declare no competing financial interest.

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■ REFERENCES


![Figure 4](image1.png)

Figure 4. Pressure dependence of (a) isomer shift (IS), (b) hyperfine field (HF), and (c) relative abundance of the LaCu₃Fe₄O₁₂ Mössbauer spectra. The squares and circles present the sextuplet Fe³⁺ ions and the singlet Fe³.75⁺ ions, respectively.

![Figure 5](image2.png)

Figure 5. Pressure dependence of LaCu₃Fe₄O₁₂ resistivity at room temperature. AFI = antiferromagnetic insulator; PM = paramagnetic metal.