

Title	Covalency Competition in the Quadruple Perovskite CdCu ₃ Fe ₄ O ₁₂
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7 **Covalency Competition in the Quadruple**
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11 **Perovskite CdCu₃Fe₄O₁₂**
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ABSTRACT

Cadmium ions (Cd^{2+}) are similar to calcium ions (Ca^{2+}) in size, whereas the Cd^{2+} tend to form covalent bonds with the neighboring anions because of the high electronegativity. The covalent Cd–O bonds affect other metal-oxygen bonds, inducing drastic changes in crystal structures and electronic states. Herein, we demonstrate high-pressure synthesis, crystal structure, and properties of a new quadruple perovskite $\text{CdCu}_3\text{Fe}_4\text{O}_{12}$. This compound exhibits an electronic phase transition accompanying a charge disproportionation of Fe ions without charge ordering below ~ 200 K, unlike charge-disproportionation transition with rock-salt-type charge ordering for $\text{CaCu}_3\text{Fe}_4\text{O}_{12}$. First-principle calculations and Mössbauer spectroscopy display that covalent Cd–O bonds effectively suppress the Fe–O bond covalency, resulting in the electronic state different from that of $\text{CaCu}_3\text{Fe}_4\text{O}_{12}$. This finding proposes covalency competition among constituent metal ions dominating electronic states of complex metal oxides.

1. INTRODUCTION

Chemical bonding is of fundamental interest in solid-state compounds.¹⁻⁴ Intrinsic properties of solids such as hardness, electrical conductivity, and thermal stability are strongly dependent on covalency between constituent atoms. Thus, in-depth understanding of covalency (or ionicity) is essential to elucidate structure-property relationships in solids. Chemical bonding of transition metal oxides has been widely investigated because of a great variety of their constituent elements, structures, and properties. The perovskite oxides ABO_3 have three-dimensional networks of $B-O$ bonds, whose characters are adjustable by ionic sizes of A - and B -site ions, thus being considered as a promising system for fundamental investigations and prospective applications.⁵⁻⁷ The B -sites for perovskite structure are usually occupied by smaller transition metal ions in the d-block, whereas the A -sites are occupied by larger cations in the s-block (e.g. Na^+ , Ca^{2+}) and rare-earth (e.g. Y^{3+} , La^{3+}) metal cations. On the other hand, several elements in the p- and d-blocks (e.g. Ag^+ , Pb^{2+} , Bi^{3+}) can occupy A -sites, and their relatively high electronegativities induce substantial changes in properties. For instance, stereochemical effects of Pb^{2+}/Bi^{3+} ions cause lattice distortions, leading to ferroelectricity,^{8,9} and covalent $Ag-O$ bonds serve to achieve high hole-mobility.¹⁰ The Cd^{2+} ions are almost isometric to the Ca^{2+} ions ($r_{Cd^{2+}} = 1.31 \text{ \AA}$; $r_{Ca^{2+}} = 1.34 \text{ \AA}$ in twelfefold coordination)^{11,12} while their Pauling electronegativities (χ) are quite different ($\chi_{Cd} = 1.69$; $\chi_{Ca} = 1.00$). The effects of different bonding characters between $Ca-O$ and $Cd-O$ bonds on properties were investigated in $ATiO_3$ ($A = Ca, Cd$) perovskites.^{13,14} $CaTiO_3$ crystallizes in the orthorhombic $GdFeO_3$ -type perovskite structure at room temperature and retains its symmetry down to the lowest temperature. Despite of the isomorphism at room temperature, $CdTiO_3$ undergoes a ferroelectric phase transition below 85 K, which is interpreted as effects of strong covalency of $Cd-O$ bonds on particular phonon

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3 modes.^{13,15,16} Further explorations for intriguing phenomena induced by Cd–O covalency have
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5 not been found probably because of the limited number of Cd-containing perovskites
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7 reported.^{17,18} Therefore, it is unclear how the formation of Cd–O covalent bonds affects the
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9 properties of B–O bonds in other systems.
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13 The quadruple perovskite series, $AA'_3B_4O_{12}$, is a derivative of the simple ABO_3
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15 perovskite. Three quarters of original A -sites (= A' -sites) are occupied by small transition metal
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17 ions (Cu^{2+} , Mn^{3+} , Fe^{2+} , Co^{2+} , Pd^{2+} , etc.) in pseudosquare coordination whereas the remaining
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19 fourth (= A -sites) are occupied by typical larger ions (Na^+ , Ca^{2+} , La^{3+} , etc.) in icosahedral
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21 coordination.¹⁹⁻²³ It was recently reported that the A -sites also tolerate a wide range of ions such
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23 as Mn^{2+} and Cu^+ ,²⁴⁻²⁶ in addition to smaller rare-earth metal ions (Y^{3+} , Lu^{3+} , etc.).²⁷ The Cd ions
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25 are also incorporated into A -sites in the quadruple perovskites such as $CdCu_3Ti_4O_{12}$,^{28,29}
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27 $CdCu_3Ru_4O_{12}$,³⁰ $CdCu_3Mn_4O_{12}$,³¹ and $CdMn_7O_{12}$.³² In any compounds, the covalency of Cd–O
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29 bonds does not seem to drastically change their properties because of insensitivity of electronic
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31 states to bonding properties. On the other hand, it was recently reported that the quadruple
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33 perovskites with unusual valence Fe ions (typically Fe^{4+}), $ACu_3Fe_4O_{12}$ ($A = Ca^{2+}$, Sr^{2+} , trivalent
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35 rare-earth metals R^{3+} , Bi^{3+} , and Ce^{4+}), demonstrate a wide range of intriguing properties strongly
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37 depending on the valences and/or sizes of A -site ions: charge disproportionation ($2Fe^{4+} \rightarrow Fe^{3+} +$
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39 Fe^{5+}), charge ordering/disordering of the Fe^{3+} and Fe^{5+} ions, bidirectional intersite charge
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41 transfers ($Cu^{2+} + Fe^{4+} \rightleftharpoons Cu^{3+} + Fe^{3+}$), negative thermal expansion, and high catalytic activity for
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43 oxygen evolution reaction.³³⁻⁴² Their electronic states are sensitive to the character of Fe–O
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45 bonds. There is a common correlation between Fe–O bond length and ^{57}Fe Mössbauer isomer
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47 shift (IS) in $Ca_{1-x}Sr_xCu_3Fe_4O_{12}$ and $RCu_3Fe_4O_{12}$ ($R =$ trivalent rare-earth metals).⁴³ The Fe–O
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49 bond covalency is flexibly controlled by the Fe–O bond elongation and can be reasonably
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3 estimated by *IS* values. The *IS* value of $\sim 0.17 \text{ mm s}^{-1}$ is a boundary of two distinct low-
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5 temperature electronic phases: (1) charge-disproportionated/ordered phase ($IS < \sim 0.17 \text{ mm s}^{-1}$)
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7 and (2) Cu-to-Fe electron-charge-transferred and/or charge-disproportionated/disordered phase
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9 ($IS > \sim 0.17 \text{ mm s}^{-1}$). The interatomic distances are typical factors determining covalency in
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11 transition metal compounds.⁴⁴ whereas Ca substitution by more electronegative Cd affects bond
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13 covalency and possibly induces a drastic change in electronic states.
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19 In this article, we demonstrate structural and electronic properties of $\text{CdCu}_3\text{Fe}_4\text{O}_{12}$, which
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21 was synthesized under ultra-high-pressure and high-temperature of 20 GPa and 1000 °C.
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23 Structural and spectroscopic data revealed that the low-temperature electronic phase
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25 transformation in $\text{CdCu}_3\text{Fe}_4\text{O}_{12}$ substantially differs from that in $\text{CaCu}_3\text{Fe}_4\text{O}_{12}$. Covalency
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27 competition between Cd–O and Fe–O bonds reasonably explain the differences in structures and
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29 properties between $\text{CdCu}_3\text{Fe}_4\text{O}_{12}$ and $\text{CaCu}_3\text{Fe}_4\text{O}_{12}$. This finding proposes that competition in
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31 covalent bond formation among constituent metal ions dominate electronic properties of solids.
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36 2. EXPERIMENTAL

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39 A precursor was obtained using the polymerized complex method.^{37,45} A mixture of
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41 $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (99.9%), $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (99.9%), and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (99.9%) at a molar ratio
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43 of 1:3:4 was dissolved in nitric acid solution (ca. 5 M), to which a five-fold excess of citric acid
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45 and a one-fold excess of 1,2-ethanediol were added while stirring. The resulting solution was
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47 heated to 573 K, while stirring, and maintained at this temperature for 1 h to dry. Subsequently,
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49 the dried powder was fired using a furnace at 673 K for 1 h and 948 K for 12 h in air with
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51 occasional grindings. The afforded precursor was mixed with an oxidizing agent KClO_4 (99.9%)
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53 in a mass ratio of 7:1. The sample mixture was sealed off during the treatment in a platinum
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3 capsule. The capsule was placed into a (Mg,Co)O pressure medium and compressed to pressures
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5 up to 20 GPa using a high-pressure apparatus. The sample was subsequently heated to 1273 K in
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7 20 min, maintained at this temperature for 30 min, and quenched to room temperature. During
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9 the heat treatment, the applied pressure was maintained. The pressure was slowly released after
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11 the heat treatment. The obtained polycrystalline sample was washed several times with distilled
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13 water.
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18 Synchrotron X-ray powder diffraction (SXRD) experiments were performed at the
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20 BL02B2 beamline of SPring-8 using samples contained in Lindemann glass capillary tubes with
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22 an inner diameter of 0.2 mm. The wavelength used was determined to be 0.42043 Å using a
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24 CeO₂ standard. Structure parameters were refined by Rietveld analysis using the program
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26 RIETAN-FP.⁴⁶ The crystal structures were drawn using the VESTA software.⁴⁷ The soft X-ray
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28 absorption spectrum (XAS) of Cu L₃-edge was collected at 300 K using the total electron yield
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30 method at the BL27SU beamline of SPring-8. The energy resolution was greater than 5000. The
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32 X-ray absorption near-edge structure (XANES) spectra of Cu K-edge for CdCu₃Fe₄O₁₂ were
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34 collected at 10 and 300 K at the BL14B1 beamline of SPring-8. The ⁵⁷Fe Mössbauer
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36 spectroscopy measurement was performed in transmission geometry using ⁵⁷Co/Rh as a radiation
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38 source and α-Fe as a control for the velocity calibration and isomer shift. The collected
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40 Mössbauer spectra were fitted computationally using the Lorentzian function. Magnetization
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42 measurements were conducted using a superconducting quantum interference device (SQUID,
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44 Quantum Design MPMS-XL) between 5 and 300 K under external magnetic fields between 0.1
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46 and 50 kOe. Since no well-sintered sample was obtained, the electric resistivity was not
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48 investigated in this study.
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3 Density functional theory (DFT) calculations of $\text{CaCu}_3\text{Fe}_4\text{O}_{12}$ and $\text{CdCu}_3\text{Fe}_4\text{O}_{12}$ were
4 performed using the projector augmented-wave method as implemented in VASP code.⁴⁸ The
5 exchange-correlation interaction was treated within the framework of the generalized gradient
6 approximation (GGA) with Perdew-Burke-Ernzerhof (PBE) functional.⁴⁹ The on-site Coulomb
7 interactions on the localized 3d electrons were treated with the GGA+ U approach⁵⁰ with $U_{\text{eff}} = 7$
8 and 4 eV for Cu and Fe, respectively, for both $\text{CaCu}_3\text{Fe}_4\text{O}_{12}$ and $\text{CdCu}_3\text{Fe}_4\text{O}_{12}$. The U values
9 were taken from the literature,⁵¹ in which the electronic structure of $\text{CaCu}_3\text{Fe}_4\text{O}_{12}$ was
10 investigated using DFT. The PAW data set with radial cutoffs 2.3 Å for Ca, Cd, Cu and Fe and
11 1.52 Å for O, where Ca-3s, 4s, 3p Cd-5s, 4d, Cu-3d, 4s, Fe-3d, 4s and O-2s, 2p were described
12 as valence electrons. The plane-wave cutoff energy was set to 500 eV. A $6 \times 6 \times 6$ k -point sampling
13 following the Monkhorst-Pack scheme was used.⁵² The lattice constants and internal coordinates
14 were optimized until the total energy difference and residual forces converge to less than 10^{-5}
15 and 10^{-2} eV/Å, respectively. Space groups of $\text{CaCu}_3\text{Fe}_4\text{O}_{12}$ and $\text{CdCu}_3\text{Fe}_4\text{O}_{12}$ are considered as
16 $Im\bar{3}$ to compare charge distribution at room temperature. $\text{CaCu}_3\text{Fe}_4\text{O}_{12}$ is reported to be
17 ferrimagnet, in which magnetic moments of Fe are ordered in the same direction and moments of
18 Cu are opposite to them.^{33,53} Thus, the electronic structure of $\text{CaCu}_3\text{Fe}_4\text{O}_{12}$ was calculated for the
19 ferrimagnetic phase. The magnetic structure of $\text{CdCu}_3\text{Fe}_4\text{O}_{12}$ was not able to be determined
20 precisely by experiment. In the present work, DFT calculations of $\text{CdCu}_3\text{Fe}_4\text{O}_{12}$ were made with
21 three different magnetic structures: i) the ferrimagnetic phase, ii) the ferromagnetic phase in
22 which all magnetic moments of Fe and Cu are ordered ferromagnetically, and iii) the G-type
23 antiferromagnetic phase in which Fe magnetic moments are arranged in the G-type
24 antiferromagnetic order while Cu ions have no magnetic moment. We found that the
25 ferrimagnetic phase was most stable among them. The calculated energy differences of the
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3 ferromagnetic and G-type antiferromagnetic phases when the ferrimagnetic phase is used as a
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5 reference were 0.49 and 0.11 eV per formula unit, respectively. Therefore, the ferrimagnetic
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7 structure was adopted for CdCu₃Fe₄O₁₂ in this study.
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10 11 12 3. RESULTS

13 14 15 **Crystal Structure**

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19 The samples obtained at pressures below 20 GPa contained much amount of impurity phases.
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21 In contrast, the sample synthesized at 20 GPa included insignificant amount of impurity phases.
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23 We adopted the sample obtained at 20 GPa in this study. Figure 1 displays the observed SXRD
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25 patterns of CdCu₃Fe₄O₁₂ at 100 and 300 K and Rietveld refinement results. The primary phase at
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27 300 K could be indexed in the cubic quadruple perovskite (space group: *Im* $\bar{3}$, No. 204) with a
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29 lattice constant *a* of ~7.30 Å. There were small amounts of impurity phases: α -Fe₂O₃ (~3 wt%)
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31 and CuO (~4 wt%). Since CdCu₃Fe₄O₁₂ exhibited no anomaly in temperature evolution of *a*-axis
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33 length, the crystal structures at all temperatures were refined using the same structure model as
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35 the RT phase. After the final refinements, we obtained satisfactory reliability factors: *R*_{wp} (~2%)
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37 and *R*_B (1.5–2%) at all temperatures. The structure parameters obtained from the refinement at
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39 100 and 300 K are listed in Table 1. The *a*-axis length of CdCu₃Fe₄O₁₂ (7.299 Å) at 300 K is
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41 almost identical to that of CaCu₃Fe₄O₁₂ (7.294 Å).⁴² The Cu–O and Fe–O bond lengths are also
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43 identical for CdCu₃Fe₄O₁₂ and CaCu₃Fe₄O₁₂ at this temperature. However, the Cd–O bond
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45 (~2.60 Å) was slightly longer than the Ca–O bond (~2.58 Å). This implies different bonding
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47 characters between them. The bond valence sums (BVSs) were calculated from the refinement
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49 results (Table 1). The BVS of Ca was +2.27,⁴² slightly larger than the value expected from
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51 divalency (+2), indicating that the Ca²⁺ ions are overbonded by the 12 neighboring oxide ions. In
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3 contrast, BVS of Cd was 1.82, slightly smaller than +2, exhibiting underbonding of Cd–O bonds
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5 for $\text{CdCu}_3\text{Fe}_4\text{O}_{12}$, as reported in $\text{CdMn}_7\text{O}_{12}$.³²
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9 The temperature dependence of Cu–O and Fe–O bond lengths displayed clear difference
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11 between $\text{CdCu}_3\text{Fe}_4\text{O}_{12}$ and $\text{CaCu}_3\text{Fe}_4\text{O}_{12}$ (Figure 2). The Cu–O bonds expanded and average Fe–
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13 O bond lengths decreased below 210 K for $\text{CaCu}_3\text{Fe}_4\text{O}_{12}$, which is attributed to the Fe-to-Cu
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15 electron charge transfer ($3\text{Cu}^{\sim 2.4+} + 4\text{Fe}^{\sim 3.65+} \rightarrow 3\text{Cu}^{\sim 2.2+} + 4\text{Fe}^{\sim 3.8+}$), as reported previously.⁴² In
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17 contrast, the Cu–O bonds shrank (~ 0.1 Å) and Fe–O bonds expanded very slightly below 200 K
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19 for $\text{CdCu}_3\text{Fe}_4\text{O}_{12}$. This indicates the opposite type of charge transfer (Cu-to-Fe electron charge
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21 transfer), compared to $\text{CaCu}_3\text{Fe}_4\text{O}_{12}$. This type of charge transfer is predominant for
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23 $\text{SrCu}_3\text{Fe}_4\text{O}_{12}$, not $\text{CaCu}_3\text{Fe}_4\text{O}_{12}$.⁴⁰
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28 29 Valence States

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32 Valence states of $\text{CdCu}_3\text{Fe}_4\text{O}_{12}$ were investigated by X-ray absorption and Mössbauer
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34 spectroscopies. Figure 3a shows the Cu L_3 -edge XAS at 300 K. The spectrum contained a
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36 shoulder ~ 932 eV, in addition to the main peak at ~ 930 eV. This ensures the mixed valence state
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38 of Cu ions (i.e. $\text{Cu}^{(2+\delta)+}$) for $\text{CdCu}_3\text{Fe}_4\text{O}_{12}$ as in $\text{CaCu}_3\text{Fe}_4\text{O}_{12}$ and $\text{SrCu}_3\text{Fe}_4\text{O}_{12}$.^{40,42} Figure 3b
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40 illustrates the Cu K-edge XANES spectra at 10 and 300 K for $\text{CdCu}_3\text{Fe}_4\text{O}_{12}$. The edge position at
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42 300 K was almost identical to those of $\text{CaCu}_3\text{Fe}_4\text{O}_{12}$ and $\text{SrCu}_3\text{Fe}_4\text{O}_{12}$ (Figure S1 in the
43
44 Supporting Information), estimating the Cu valence as ~ 2.4 . The Cu K-edge shifted to higher
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46 energy side on cooling down to 10 K, indicating the Cu oxidation by Cu-to-Fe electron charge
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48 transfer, as in $\text{SrCu}_3\text{Fe}_4\text{O}_{12}$. The magnitude of Cu oxidation was estimated to be ~ 0.13 valence
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50 unit (v.u.) from the edge shift of ~ 0.25 eV, in accordance to the reference data. Thus, the charge
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52 transfer process in $\text{CdCu}_3\text{Fe}_4\text{O}_{12}$ is represented as $3\text{Cu}^{\sim 2.4+} + 4\text{Fe}^{\sim 3.65+} \rightarrow 3\text{Cu}^{\sim 2.5+} + 4\text{Fe}^{\sim 3.55+}$.
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3 The ^{57}Fe Mössbauer spectra at temperatures between 4 and 300 K are illustrated in Figure
4 and the obtained hyperfine parameters are listed in Table 2. The spectrum at 300 K consisted of
5 a paramagnetic singlet (*B*-site Fe, 94 atom%) and a doublet (*A'*-site Fe, 3 atom%) from
6 $\text{CdCu}_3\text{Fe}_4\text{O}_{12}$, and a sextet (3 atom%) from the $\alpha\text{-Fe}_2\text{O}_3$ impurity. The primary singlet
7 component had an intermediate *IS* value (0.176 mm s^{-1}) between $\text{CaCu}_3\text{Fe}_4\text{O}_{12}$ (0.16 mm s^{-1}) and
8 $\text{SrCu}_3\text{Fe}_4\text{O}_{12}$ (0.20 mm s^{-1}).^{40,42} The spectrum split into multiple magnetic sextet components
9 below 200 K: one Fe^{5+} (29 atom%) and three Fe^{3+} (69 atom% in total). The spectrum at 4 K is
10 more similar to that of the solid solution $\text{Ca}_{0.6}\text{Sr}_{0.4}\text{Cu}_3\text{Fe}_4\text{O}_{12}$ [one Fe^{5+} (31 atom%) and three
11 Fe^{3+} (69 atom% in total)] rather than those of $\text{CaCu}_3\text{Fe}_4\text{O}_{12}$ [one Fe^{5+} (39 atom%) and two Fe^{3+}
12 (61 atom% in total)] and $\text{SrCu}_3\text{Fe}_4\text{O}_{12}$ [one Fe^{5+} (18 atom%) and one Fe^{3+} (82 atom%)].^{40,42,43}
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14 This observation ensures that the low-temperature electronic state of $\text{CdCu}_3\text{Fe}_4\text{O}_{12}$ is
15 distinguished from that of $\text{CaCu}_3\text{Fe}_4\text{O}_{12}$.
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33 **Magnetic Property**

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36 Figure 5a displays temperature dependence of the magnetic susceptibility for
37 $\text{CdCu}_3\text{Fe}_4\text{O}_{12}$. A clear magnetic transition at $\sim 190 \text{ K}$ was observed but the behavior below this
38 temperature was not simple. This is interpreted as coexistence of ferromagnetic (Curie
39 temperature $\sim 190 \text{ K}$) and antiferromagnetic (Néel temperature $\sim 170 \text{ K}$) domains. It is noted that
40 this behavior is very similar to the magnetic susceptibility of $\text{Ca}_{0.6}\text{Sr}_{0.4}\text{Cu}_3\text{Fe}_4\text{O}_{12}$,⁴³ in which
41 ferromagnetic charge-ordered and antiferromagnetic charge-disordered phases coexist. The
42 isothermal magnetization curve of $\text{CdCu}_3\text{Fe}_4\text{O}_{12}$ at 5 K was also similar to that of
43 $\text{Ca}_{0.6}\text{Sr}_{0.4}\text{Cu}_3\text{Fe}_4\text{O}_{12}$ (Figure 5b). The magnetization value of $\text{CdCu}_3\text{Fe}_4\text{O}_{12}$ at 50 kOe was much
44 smaller than the ferromagnetic saturation magnetization ($\sim 10 \mu_{\text{B}}$ per formula unit) of
45 $\text{CaCu}_3\text{Fe}_4\text{O}_{12}$ and rather close to that of $\text{Ca}_{0.6}\text{Sr}_{0.4}\text{Cu}_3\text{Fe}_4\text{O}_{12}$ ($\sim 3 \mu_{\text{B}}$ per formula unit). These
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3 features confirm that the low-temperature magnetic phase of $\text{CdCu}_3\text{Fe}_4\text{O}_{12}$ is different from the
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5 ferrimagnetic phase of $\text{CaCu}_3\text{Fe}_4\text{O}_{12}$.
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9 4. DISCUSSION

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12 The above-demonstrated experimental data reveal that $\text{CdCu}_3\text{Fe}_4\text{O}_{12}$ undergoes a charge
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14 disproportionation and a Cu-to-Fe electron charge transfer below 200 K as follows: $3\text{Cu}^{\sim 2.4+} +$
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16 $4\text{Fe}^{\sim 3.65+} \rightarrow 3\text{Cu}^{\sim 2.5+} + 4\text{Fe}^{\sim 3.55+}$; $\text{Fe}^{\sim 3.55+} \rightarrow \sim 0.3\text{Fe}^{5+} + \sim 0.7\text{Fe}^{3+}$. This feature is similar to that of
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18 $\text{Ca}_{0.6}\text{Sr}_{0.4}\text{Cu}_3\text{Fe}_4\text{O}_{12}$ and well distinguished from $\text{CaCu}_3\text{Fe}_4\text{O}_{12}$. $\text{Ca}_{0.6}\text{Sr}_{0.4}\text{Cu}_3\text{Fe}_4\text{O}_{12}$
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20 accommodates an intermediate Fe–O bonding character between ionic ($\text{SrCu}_3\text{Fe}_4\text{O}_{12}$) and
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22 covalent ($\text{CaCu}_3\text{Fe}_4\text{O}_{12}$) Fe–O bonds, which can be controlled by weight-averaged ionic size of
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24 A-site ions. The Fe–O bonding character of $\text{CdCu}_3\text{Fe}_4\text{O}_{12}$ was evaluated in the *IS* versus Fe–O
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26 bond length diagram, according to a previous study.⁴³ Figure 6 shows the *IS* as a function of Fe–
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28 O bond length at 300 K. It is noted that the data point of $\text{CdCu}_3\text{Fe}_4\text{O}_{12}$ is substantially deviated
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30 from $\text{CaCu}_3\text{Fe}_4\text{O}_{12}$ – $\text{SrCu}_3\text{Fe}_4\text{O}_{12}$ solid solution line, where the Fe–O bond covalency is primarily
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32 dependent on the Fe–O bond length. In other words, the Fe–O bonds of $\text{CdCu}_3\text{Fe}_4\text{O}_{12}$ have more
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34 ionic character despite of almost the same Fe–O bond lengths as $\text{CaCu}_3\text{Fe}_4\text{O}_{12}$. In this diagram,
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36 the electronic phases are divided at $IS \sim 0.17 \text{ mm s}^{-1}$ for $A\text{Cu}_3\text{Fe}_4\text{O}_{12}$ system ($A = \text{Ca/Sr}, R^{3+}$).⁴³
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38 $\text{CdCu}_3\text{Fe}_4\text{O}_{12}$ has an *IS* value similar to that of $\text{Ca}_{0.6}\text{Sr}_{0.4}\text{Cu}_3\text{Fe}_4\text{O}_{12}$, indicating near covalent
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40 character. The intermediate Fe–O bonding character for $\text{CdCu}_3\text{Fe}_4\text{O}_{12}$ is not apparently expected
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42 because similar Fe–O bond lengths to $\text{CaCu}_3\text{Fe}_4\text{O}_{12}$. To elucidate the difference between Cd–O
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44 and Ca–O bonds, we compared electronic states of $\text{CdCu}_3\text{Fe}_4\text{O}_{12}$ and $\text{CaCu}_3\text{Fe}_4\text{O}_{12}$ obtained
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46 from DFT calculations.
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Figure 7a displays density of states (DOS) of $\text{CdCu}_3\text{Fe}_4\text{O}_{12}$ and $\text{CaCu}_3\text{Fe}_4\text{O}_{12}$ obtained from DFT calculations. It is obvious that the valence bands for both compounds mainly consist of Cu, Fe, and O orbitals. In contrast, the Ca and Cd orbitals less contribute to the valence band. To examine their contribution in detail, the partial DOS of Ca-s, p and Cd-s, p, d orbitals are displayed in Figure 7b. The d orbital DOS of Cd ion is almost fully occupied in a range of -7 and 0 eV, which overlaps the valence band. The s and p (mainly 5s and 5p) orbitals of Cd ion are partially occupied below the Fermi level, although these orbitals are expected to be empty in a simple ionic model with $[\text{Kr}]4d^{10}$ electron configuration. This indicates that 5s and 5p orbitals of Cd ion are well hybridized with O 2p orbitals because of strong covalent character of Cd–O bond, as shown in Ti–O bond for TiMnO_3 .⁵⁴ In contrast, no substantial DOSs of s, p-orbitals were observed in the valence band of $\text{CaCu}_3\text{Fe}_4\text{O}_{12}$, indicating less covalency between Ca and O ions.

Figure 7c shows electron density distributions of $\text{CdCu}_3\text{Fe}_4\text{O}_{12}$ and $\text{CaCu}_3\text{Fe}_4\text{O}_{12}$ obtained from DFT calculations. Substantial electron density exists between Cu and O ions for both oxides, confirming strong covalency of Cu–O bonds, as demonstrated experimentally in a previous work.⁴¹ Little electron density is observed between Ca and O atoms as expected from strong ionic character of Ca–O bond. In contrast, remarkable electron density is confirmed between Cd and O atoms. This is well explained by orbital hybridization of Cd 5s, 5p orbitals with O 2p orbital, as shown in the DOS calculations. Thus, we conclude that the Cd ions form more covalent bonds with O ions, simultaneously weakening the covalency Fe–O bonds because of covalency competition.

CONCLUSION

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3 In summary, a new quadruple perovskite oxide $\text{CdCu}_3\text{Fe}_4\text{O}_{12}$ was synthesized under
4 ultra-high pressure of 20 GPa and its structural and electronic properties were investigated. The
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6 low-temperature charge-disproportionated electronic phase was different between nominally
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8 isoelectronic compounds, $\text{CdCu}_3\text{Fe}_4\text{O}_{12}$ and $\text{CaCu}_3\text{Fe}_4\text{O}_{12}$. Theoretical calculation and
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10 experimental spectroscopy study demonstrate that the covalent Cd–O bond suppresses the of Fe–
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12 O bond covalency. This derives clear differences in low-temperature electronic transformations.
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14 This finding proposes that competition of bond covalency play a crucial role in electronic
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16 properties of transition metal oxides.
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22 23 **ASSOCIATED CONTENT**

24 25 26 **Supporting Information.**

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30 Cu K-edge XANES spectra of $A\text{Cu}_3\text{Fe}_4\text{O}_{12}$ ($A = \text{Cd}, \text{Ca}, \text{and Sr}$) (PDF)
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42 43 **Notes**

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45 The authors declare no competing financial interest.
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Table 1. Structure Parameters, Selected Bond Lengths, and BVS at 100 and 300 K for CdCu₃Fe₄O₁₂.^a

Temperature (K)	100	300
Space group	<i>Im</i> $\bar{3}$	<i>Im</i> $\bar{3}$
<i>a</i> (Å)	7.29321(14)	7.29919(8)
<i>x</i> (O)	0.3105(3)	0.3091(3)
<i>y</i> (O)	0.1779(3)	0.1776(3)
<i>U</i> _{iso} (Cd)×1000 (Å ²)	2.4(3)	7.1(4)
<i>U</i> _{iso} (Cu)×1000 (Å ²)	4.4(2)	7.5(3)
<i>U</i> _{iso} (Fe)×1000 (Å ²)	0.88(19)	2.9(2)
<i>U</i> _{iso} (O)×1000 (Å ²)	5.8(5)	7.7(6)
Cd–O (×12) (Å)	2.610(2)	2.601(2)
Cu–O (×4) (Å)	1.8958(18)	1.9034(18)
Cu–O (×4) (Å)	2.726(3)	2.735(3)
Fe–O (×6) (Å)	1.9482(7)	1.9479(6)
Fe–O–Fe (deg.)	138.75(10)	139.02(10)
BVS(Cd) (v.u.)	1.78	1.82
BVS(Cu) (v.u.)	2.27	2.22
BVS(Fe) (v.u.)	3.73	3.72
<i>R</i> _{wp} (%)	2.181	2.182
<i>R</i> _B (%)	1.509	1.928
<i>S</i>	0.5622	0.5848

^aAtomic sites: Cd 2*a* (0, 0, 0), Cu 6*b* (0, 1/2, 1/2), Fe 8*c* (1/4, 1/4, 1/4), O 24*g* (*x*, *y*, 0); The occupancy factor *g* for Cd, Cu, Fe, and O sites was fixed at unity. ^bThe BVSs were calculated using the following parameters: *b*₀ = 0.37 for all atoms, *r*₀ = 1.904 for Cd, *r*₀ = 1.649 for Cu, and *r*₀ = 1.772 for Fe.^{55,56}

Table 2. Hyperfine Parameters for CdCu₃Fe₄O₁₂ at 4 and 300 K Deduced from Mössbauer Spectra.^a

Temperature (K)	Species	IS (mm s ⁻¹)	HF (kOe)	ΔE_q (mm s ⁻¹)	Abundance (%)
300	Fe (<i>B</i> -site)	0.176	0	0	94
	Fe (<i>A'</i> -site)	0.414	0	1.750	3
	Fe (α -Fe ₂ O ₃)	0.373	515	-0.175	3
4	Fe ⁵⁺	0.075	226	0	29
	Fe ³⁺ (1)	0.363	429	0	15
	Fe ³⁺ (2)	0.410	465	0	13
	Fe ³⁺ (3)	0.447	499	0	41
	Fe ³⁺ (α -Fe ₂ O ₃)	0.515	540	0.440	2

^a HF : hyperfine field; ΔE_q : quadrupole splitting (doublet) or quadrupole shift (sextet). Quadrupole shifts were calculated as follows: $\Delta E_q = (S_2 - S_1)/2$, where S_1 is the deference between the position of first and second peak, and S_2 is the deference between the position of fifth and sixth peak in the sextet.

FIGURE CAPTIONS

Figure 1. Observed SXRD patterns of $\text{CdCu}_3\text{Fe}_4\text{O}_{12}$ at 100 and 300 K and the Rietveld refinement results. Dots (black) and solid lines (red) represent observed and calculated patterns, respectively. The difference between the observed and calculated patterns is shown at the bottom (blue). The vertical marks (green) indicate the Bragg reflection positions of $\text{CdCu}_3\text{Fe}_4\text{O}_{12}$ (upper), $\alpha\text{-Fe}_2\text{O}_3$ (middle), and CuO (lower). The inset of upper panel shows the crystal structure of $A\text{Cu}_3\text{Fe}_4\text{O}_{12}$.

Figure 2. Temperature dependence of the lattice constant a and selected bond lengths for $\text{CdCu}_3\text{Fe}_4\text{O}_{12}$ (red) and $\text{CaCu}_3\text{Fe}_4\text{O}_{12}$ (black). The filled circles for Fe–O bond lengths represent average values of $\text{CaCu}_3\text{Fe}_4\text{O}_{12}$. The data for $\text{CaCu}_3\text{Fe}_4\text{O}_{12}$ were taken from reference.⁴²

Figure 3. X-ray absorption spectra of (a) Cu L₃-edge (300 K) and (a) Cu K-edge (10 and 300 K) for $\text{CdCu}_3\text{Fe}_4\text{O}_{12}$. The inset of (b) shows the enlarged spectra of the absorption edges.

Figure 4. Mössbauer spectra of $\text{CdCu}_3\text{Fe}_4\text{O}_{12}$ at temperatures between 4 and 300 K.

Figure 5. (a) Temperature dependence of the magnetic susceptibility and (b) isothermal magnetization for $\text{CdCu}_3\text{Fe}_4\text{O}_{12}$.

Figure 6. IS versus Fe–O bond length at ~ 300 K for $\text{CdCu}_3\text{Fe}_4\text{O}_{12}$ and $\text{Ca}_{1-x}\text{Sr}_x\text{Cu}_3\text{Fe}_4\text{O}_{12}$. The red and blue circles represent the type of low-temperature phase, red: charge-disproportionated and charge-ordered phase, blue: charge-disproportionated and charge-disordered phase. The $\text{Ca}_{0.6}\text{Sr}_{0.4}\text{Cu}_3\text{Fe}_4\text{O}_{12}$ (red circle with blue border) locates around phase boundary. The data for $\text{Ca}_{1-x}\text{Sr}_x\text{Cu}_3\text{Fe}_4\text{O}_{12}$ were taken from reference.^{40,42,43}

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3 **Figure 7.** (a) DOS of $ACu_3Fe_4O_{12}$ ($A = Cd, Ca$) and (b) Partial DOS of Cd and Ca ions. The
4 values averaged between majority and minority spins are shown. The zero energy is set to the
5 Fermi level. (c) Electron density distributions of $ACu_3Fe_4O_{12}$ ($A = Cd, Ca$). The equi-density
6 level is 0.025 e/Bohr^3 ($= 0.319 \text{ e/\AA}^3$).
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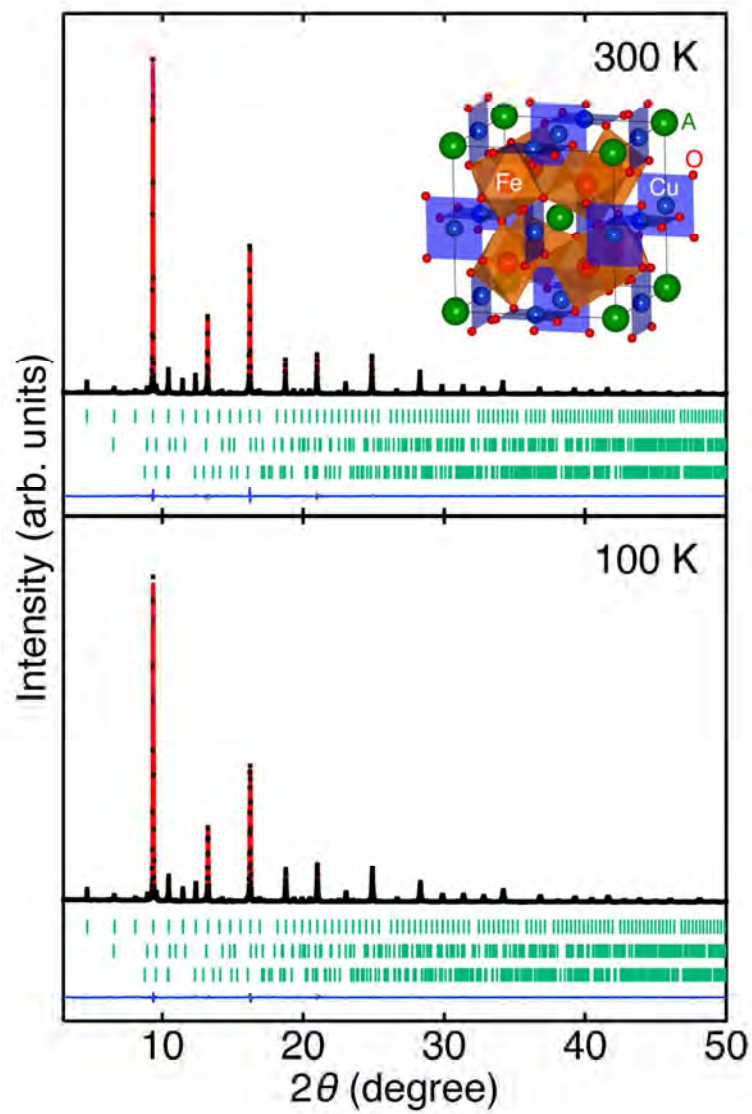


Figure 1

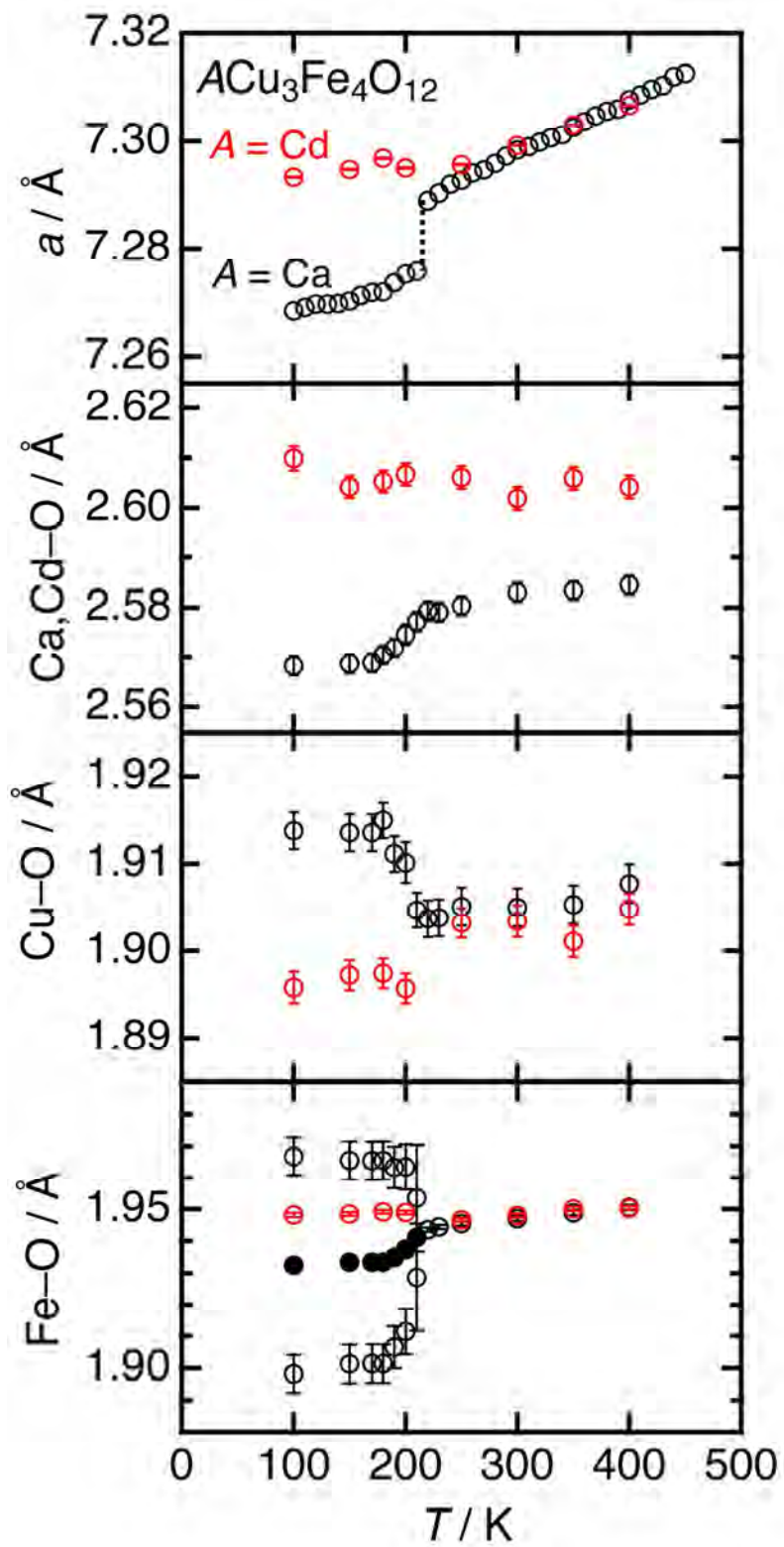
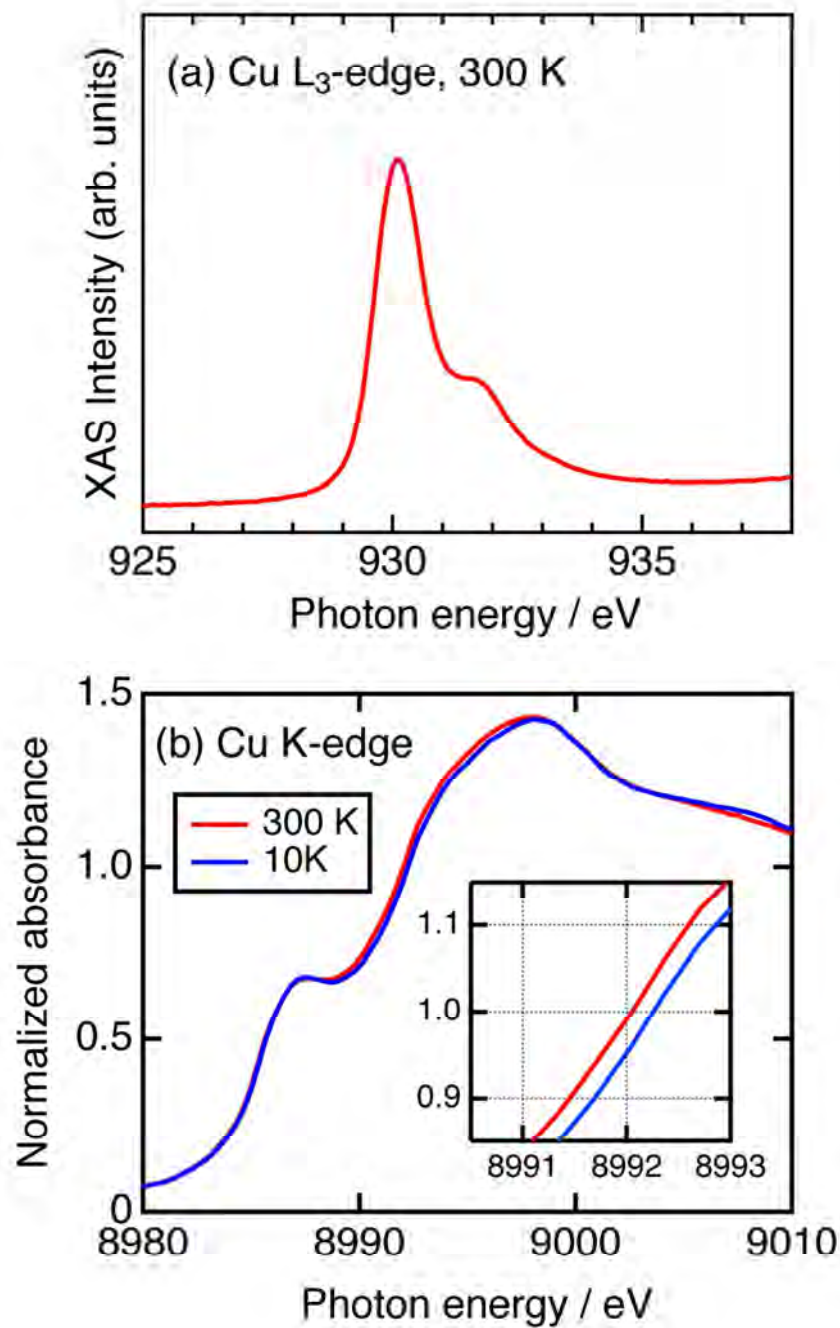


Figure 2

**Figure 3**

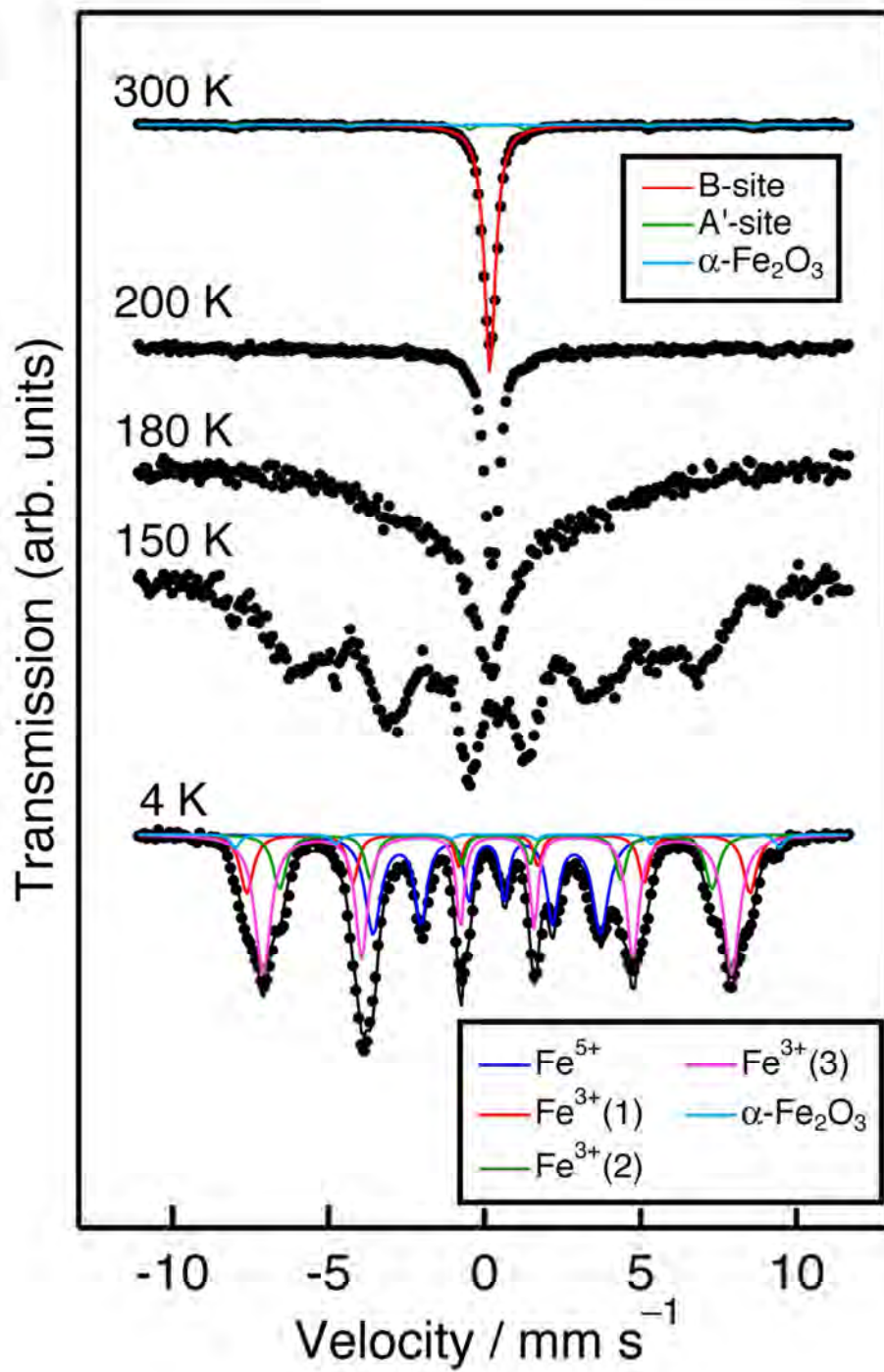


Figure 4

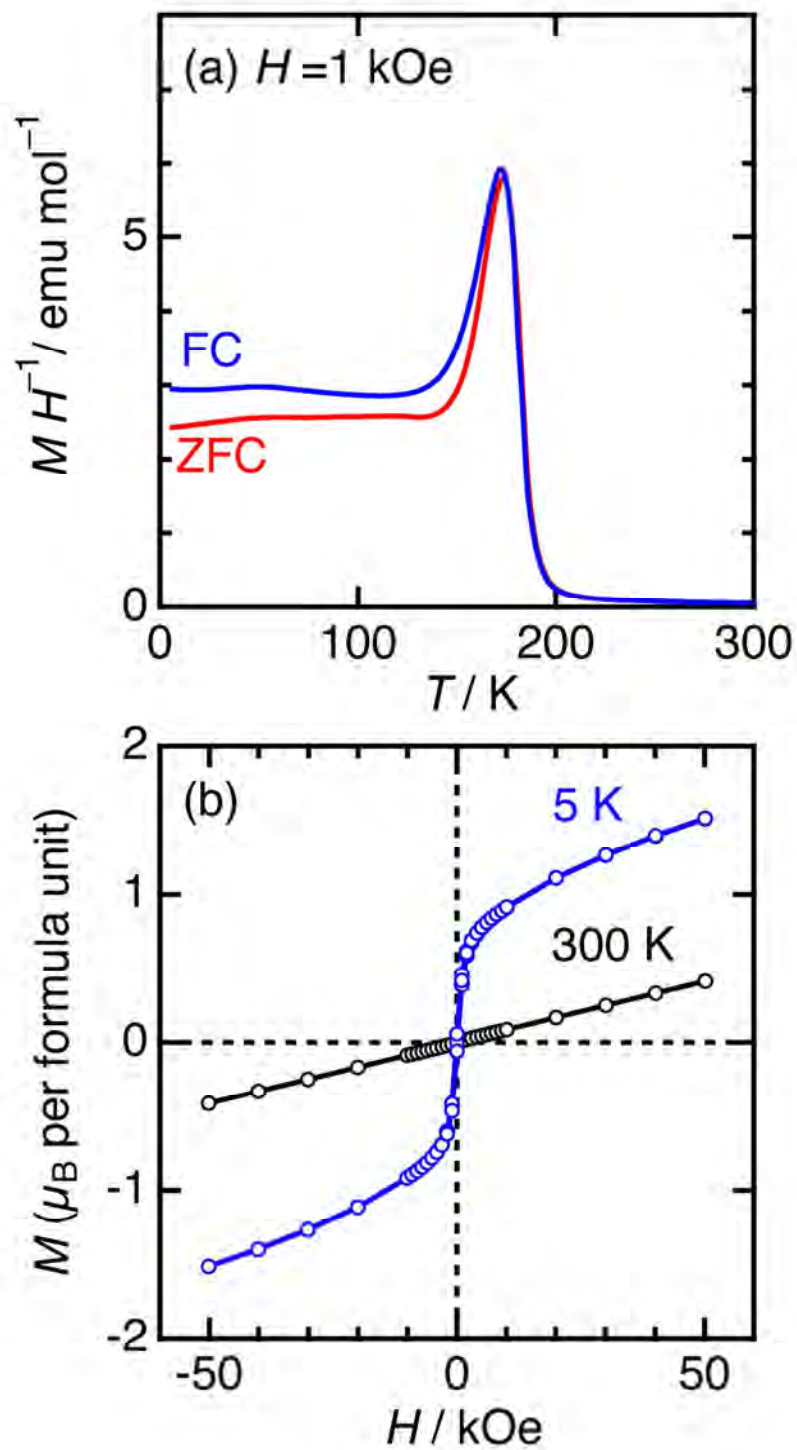


Figure 5

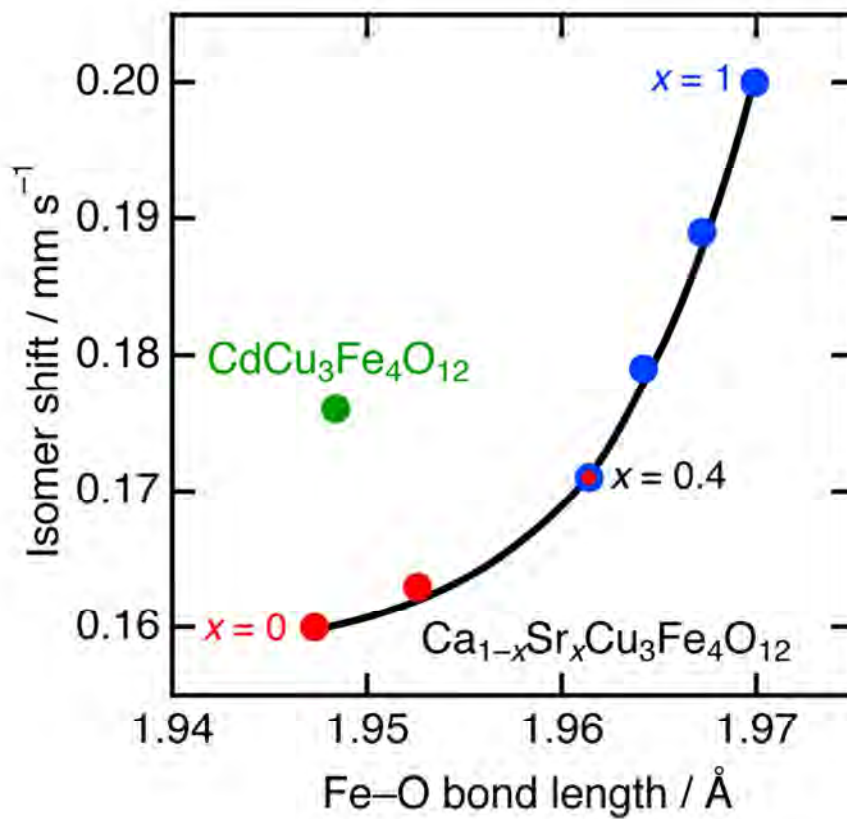


Figure 6

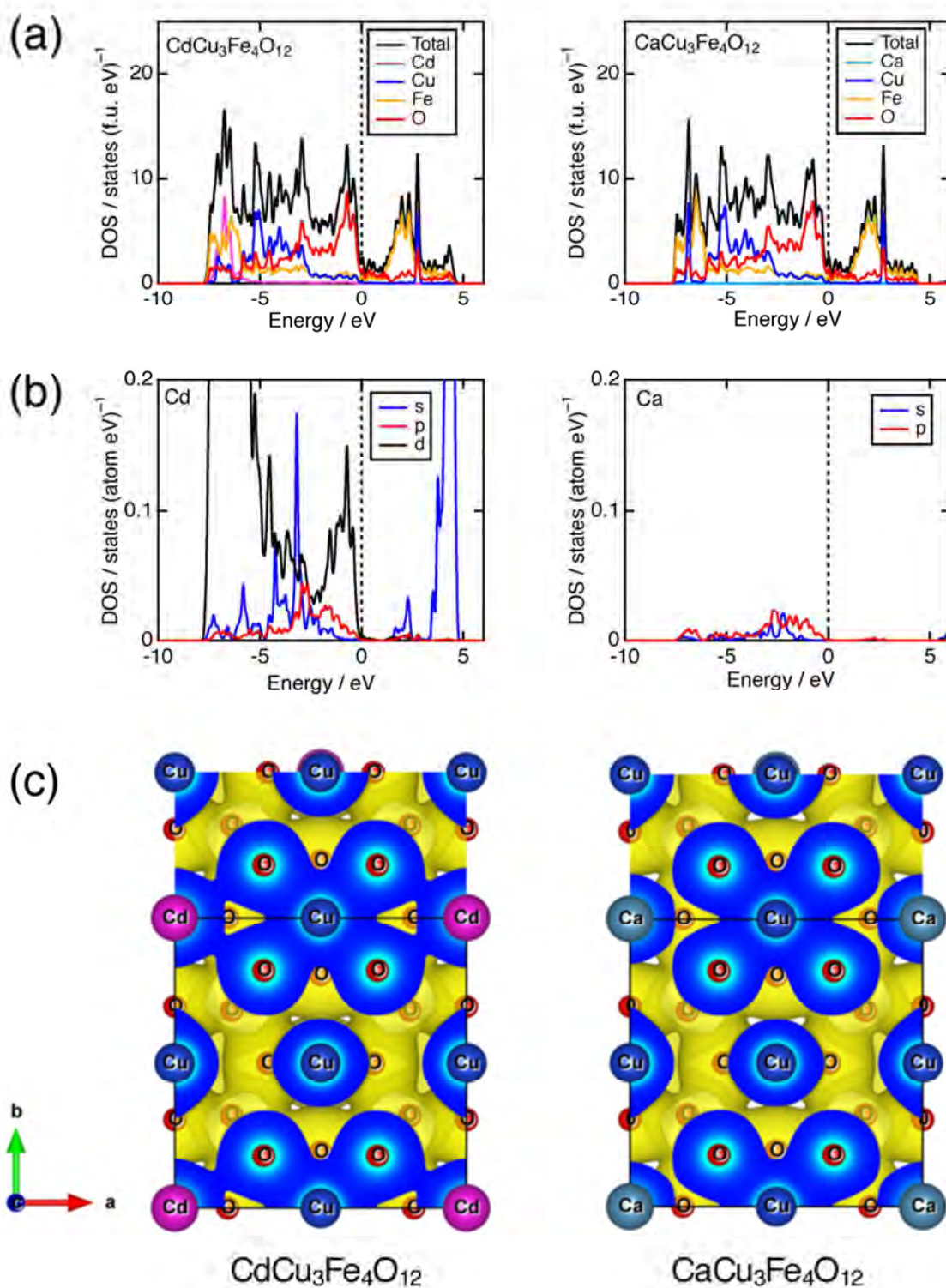
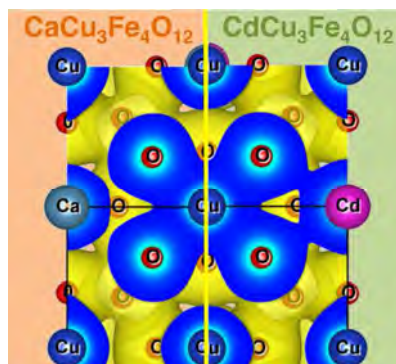


Figure 7

For Table of Contents Only



We demonstrate high-pressure synthesis, crystal structure, and properties of a new quadruple perovskite $\text{CdCu}_3\text{Fe}_4\text{O}_{12}$. $\text{CdCu}_3\text{Fe}_4\text{O}_{12}$ undergoes a charge disproportionation of Fe ions without charge ordering below ~ 200 K. First-principle calculations and Mössbauer spectroscopy display that covalent Cd–O bonds effectively suppress the Fe–O bond covalency, resulting in the electronic state different from that of the isoelectronic compound $\text{CaCu}_3\text{Fe}_4\text{O}_{12}$. This finding proposes covalency competition among constituent metal ions dominating electronic states of complex metal oxides.