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Negative Thermal Expansion

Giant Negative Thermal Expansion in the Iron Perovskite $SrCu_3Fe_4O_{12}$**

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The great discovery of high-temperature superconductivity in layered cupric oxides has provided opportunities to systematically reinvestigate the electronic properties of 3d transition-metal oxides theoretically and experimentally.[1] As a result, it has become possible to quantify a set of electronic parameters such as d–d electron correlation, p–d charge transfer, and others as a function of atomic number and valence (number of d electrons). We are interested in the comparison of Fe^{II}, Fe^{III}, and Fe^{IV} oxides such as $Fe^{II}O$, $LaFe^{III}O_3$ (LFO), and $SrFe^{IV}O_3$ (SFO) from this viewpoint. The effective d–d correlation energy U_{eff} has been found to be approximately 6 eV for FeO, 13.5 eV for LFO, and 7 eV for SFO, while the effective p–d charge-transfer energy Δ_{eff} varies as approximately 8 eV for FeO, 5.5 eV for LFO, and −3 eV for SFO.[2] In this case, "effective" indicates that multiplet effects were taken into account in these estimations, which makes use of these parameters in materials science more practical.

In Fe^{IV} oxides with large negative Δ_{eff}, the iron d levels are lowered down to below the oxygen p levels, justifying their consideration as $Fe^{III}(O_6)^{11-}$ (to be referred to hereafter as $Fe^{III}L$, where L stands for a ligand oxygen hole) rather than the usual $Fe^{IV}(O_6)^{12-}$ for the octahedral structural unit.[2] To our knowledge, Fe^{II} and Fe^{III} oxides are generally antiferromagnetic insulators in their ground states, while $Fe^{III}L$ oxides show a shift to metallicity and ferromagnetism. SFO maintains cubic symmetry and metallic conductivity down to low temperature.[3] It seems to be an antiferromagnet with $T_N \approx 134$ K, but the nearest-neighboring spins make a small angle of approximately 46° ($3.1\ \mu_B$ per Fe at 4 K) in its helicoidal spin structure with a long wavelength.[4] Moreover, genuine ferromagnetism appears when the specific volume is compressed to $V(7\ \text{GPa})/V(0\ \text{GPa}) = 0.95$.[5] These specific characteristics of $Fe^{III}L$ oxides should be considered to result from interplay of Fe d electrons and O p holes. Indeed, some of us previously reported that a single-crystalline film of SFO is a p-type metal.[6] Hereafter, however, we use the nominal valence of Fe^{IV} rather than $Fe^{III}L$ for brevity.

Experimental studies on Fe^{IV} oxides are currently expanding to the perovskite system $ACu_3Fe_4O_{12}$ (ACFO, A: alkaline earths and rare earths; the structure is shown in the inset to Figure 1),[7] where the Cu^{II} ions also equipped with deep d levels participate in various fashions. On cooling, $CaCu_3Fe_4O_{12}$ (CCFO) shows a charge disproportionation (CD) of $2\,Fe^{IV} \rightarrow Fe^{III} + Fe^{V}$ (or $2\,Fe^{III}L \rightarrow Fe^{III} + Fe^{III}L^2$)[2] accompanied by a volume contraction, and also ferrimagnetism resulting from antiferromagnetic coupling of the Cu and Fe sublattices at approximately 210 K.[8] On the other hand, $LaCu_3Fe_4O_{12}$ (LCFO) demonstrates an intersite charge transfer (CT) of $3\,Cu^{2+} + 4\,Fe^{3.75+} \rightarrow 3\,Cu^{3+} + 4\,Fe^{3+}$ accompanied by a sharp volume increase and antiferromagnetism, not ferrimagnetism, at approximately 400 K.[9] Thus intersite Cu-O-Fe interactions bring about a variety of intriguing electronic and structural phenomena. Herein, we report that the strontium analogue $SrCu_3Fe_4O_{12}$ (SCFO) exhibits negative thermal expansion (NTE) behavior with a linear expansion coefficient

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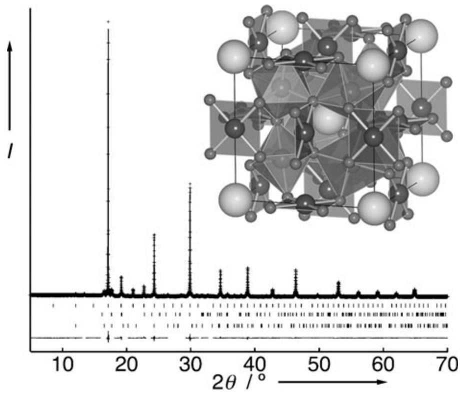

Figure 1. Observed (+) and calculated (——) SXRD profiles for SCFO. The vertical marks indicate the Bragg reflection positions of SCFO, CuO, and α-Fe_2O_3 in descending order. The bottom curve indicates the difference between the observed and calculated profiles. The inset shows the crystal structure of SCFO. The large spheres, pseudo-square planes, and octahedra represent Sr atoms, CuO_4 planar units, and FeO_6 octahedral units, respectively.

of $\alpha = -2.26 \times 10^{-5}\ K^{-1}$, which is comparable with the largest value reported to date.[10]

Polycrystalline SCFO samples were synthesized by treating starting oxide powder under a high pressure of 15 GPa at 1273 K. Homogeneous mixing of the constituent elements in the starting powder using a polymerized complex method[11] improved the product quality remarkably. Synchrotron X-ray powder diffraction (SXRD) data could be indexed with cubic $AA'_3B_4O_{12}$-type perovskite structure with $a = 7.34921(10)$ Å (Figure 1), though small amounts of CuO (4.28 mass%), α-Fe_2O_3 (3.02 mass%), and unidentified phase(s) (presumably a few mass percent) were detected as impurities. In the process of data analysis, the assumption of a different stoichiometry for any site did not improve the result within the present level of precision. The final results based on the stoichiometric composition and full site occupancies are summarized in Table S1 (see the Supporting Information). We note that, as will be discussed later, Mössbauer spectroscopy revealed a slight substitution of Fe for Cu at the A' site, as is known for the Ca analogue,[8] but this sort of minor stoichiometric deviation does not affect the experimental and analytical results described below.

The bond valence sum (BVS)[12,13] calculated from the structural data for Sr is +3.23, which is much larger than that expected from a simple ionic model of $Sr^{II}Cu^{II}_3Fe^{IV}_4O_{12}$. This result implies that the Sr–O unit is under a strong compression, even stronger than in $SrCu_3Ti_4O_{12}$ with a corresponding value of +2.95.[14] The BVS for Cu (+2.21) is also larger than expected, while that of Fe (+3.54) is smaller. SCFO may thus be considered to be a perovskite made of a compressed ($A + A'$) site and an expanded B site.

Comparison of the temperature dependence of the lattice constant as a function of element A is quite interesting. Shown in Figure 2a are those normalized at 300 K (a/a_{300K}).[8,15] An ordinary positive thermal expansion ($da/dT > 0$) is dominant for CCFO and LCFO, except for the abrupt volume changes induced by the CD and the CT for CCFO and LCFO, respectively. In regard to SCFO, it is convenient to divide the temperature range into three as ranges 1 (< 170 K), 2 (170–270 K), and 3 (> 270 K). In contrast to the others, SCFO shows a NTE in range 2 (see also Figure S1 in the Supporting Information). A linear fitting to the data in the 200–230 K range gives a large negative value of $\alpha = -2.26 \times 10^{-5}\ K^{-1}$. Note that this value exceeds common values of $-1 \times 10^{-5}\ K^{-1}$ or less[16] and is comparable with the known highest value of $-2.5 \times 10^{-5}\ K^{-1}$ for the giant NTE material, an antiperovskite nitride.[10]

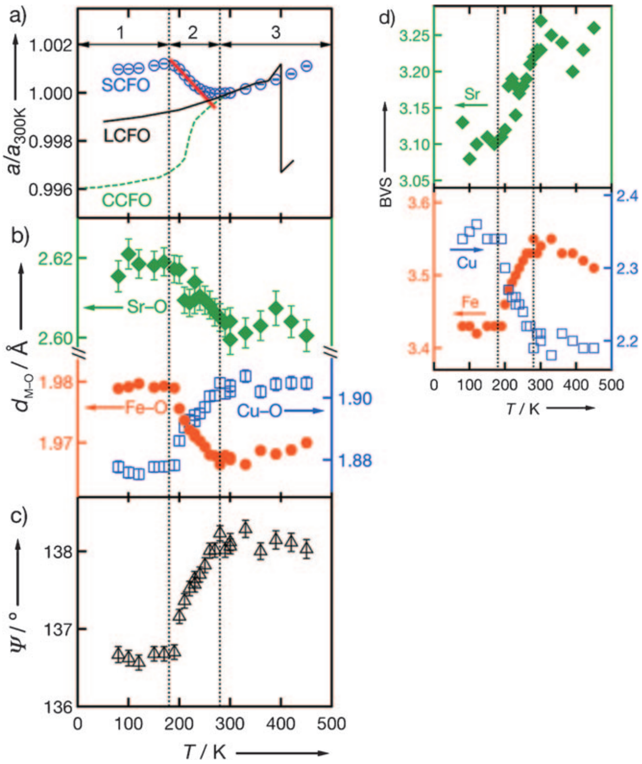

Figure 2. Temperature dependence of the structure parameters for SCFO. a) a/a_{300K} compared with those of CCFO and LCFO, b) metal–oxygen bond lengths (d_{M-O}), c) Fe-O-Fe bond angle (ψ), and d) bond valence sums for Sr, Cu, and Fe.

The NTE mechanism of SCFO was investigated using the results of SXRD and Mössbauer spectroscopy. On cooling in range 2, all the metal–oxygen bonds change their lengths considerably. The Fe–O separation gradually increases by approximately 0.6%, the Cu–O bond shrinks by about 1.4%, and the Sr–O bond is elongated by approximately 0.4% (Figure 2b). Note that the lattice constant depends only on the Fe-related parameters, d_{Fe-O} (Fe–O bond length) and ψ (Fe-O-Fe bond angle), in the manner $a = 4 d_{Fe-O} \sin(\psi/2)$. The NTE results from the predominance of the positive contribution by d_{Fe-O} over the counteraction by ψ (see Figure 2c).

Figure 3 shows the representative Mössbauer spectra of SCFO measured in ranges 1 (4 and 118 K), 2 (206 K), and 3 (293 K). The 293 K spectrum consists of 1) a singlet from the Fe ions located at the B site (B-Fe; isomer shift IS = 0.195 mm s^{-1}, 83 atom%), 2) a doublet arising from a small amount of Fe^{III} incorporated into the A' site (IS = 0.374 mm s^{-1}, 6 atom%), which was also detected in CCFO,[8] and 3) two magnetic sextets from impurities (α-

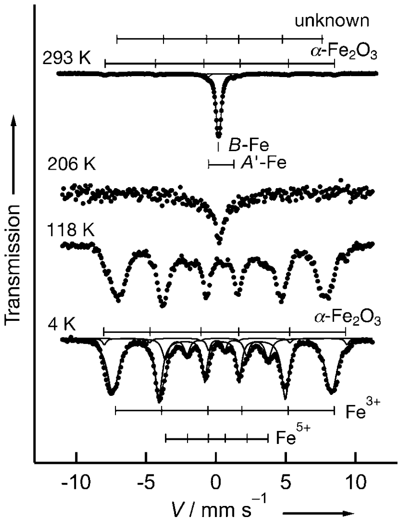

Figure 3. Mössbauer spectra collected at various temperatures. ● observed spectra, —— fittings.

Fe_2O_3 and an unknown phase). The IS of the *B*-Fe is very close to that of CCFO (IS = 0.15 mm s^{-1}).[8] Below approximately 200 K, this component is divided into a pair of components having largely different hyperfine parameters, thus indicating the occurrence of CD to Fe^{III} and Fe^{V}. The two important parameters, IS and magnetic hyperfine field, at 4 K are 0.44 mm s^{-1} and 484 kOe and 0.06 mm s^{-1} and 228 kOe for Fe^{III} and Fe^{V}, respectively. The relative abundance of Fe^{III}/Fe^{V} of 4:1 is, however, definitely different from the 1:1 ratio for CCFO.[8] This kind of deviation is known for $SrFe^{IV}O_3$ doped with electrons ($Sr_{1-x}La_xFeO_3$), and the present ratio of 4:1 is close to that for $Sr_{0.5}La_{0.5}FeO_3$.[17] In the present case, the electron donors are the Cu ions. Actually, the BVS for Cu increases from +2.20 to +2.35, while that for Fe decreases from +3.55 to +3.43 (see Figure 2d). Along with these changes, the overbonding of the Sr ions is relaxed from +3.25 to +3.10 in terms of BVS. Considering the gradual structural change in region 2, it is difficult to expect the prevalence of any well-defined charge ordering. Needless to say, the structure refinement based on the rock-salt-type ordering of Fe^{III} and Fe^{V} such as found for CCFO[8] did not give any improvement in the analysis of the SXRD data. Thus, the Fe^{III} and Fe^{V} cations are most probably randomly distributed in SCFO.

In consistency with the above results, the magnetism of SCFO is significantly different from that of CCFO. CCFO is a ferrimagnet with a large net moment, but the Sr analogue is an antiferromagnet with $T_N = 180$ K (see Figure S2 in the Supporting Information). However, short-ranged magnetic ordering seems to develop above the T_N, as suggested from the magnetic broadening of the Mössbauer spectrum at 206 K. The presence of a very small spontaneous magnetization has been suggested from the separation of the field-cooled magnetization (FC) from the zero-field-cooled (ZFC) magnetization below 90 K.

In summary, $ACu_3Fe_4O_{12}$ is a system equipped with a pair of complementary units: the octahedral $(FeO_6)^{8-}$ unit bearing p hole character, and the square-planar $(CuO_4)^{6-}$ unit, which can easily bear the same character. The linkage of these units by corner-sharing sets the stage for versatile charge distribution. It is the *A* cation that finely tunes the Cu-O-Fe framework so that it demonstrates the versatility. In regard to $SrCu_3Fe_4O_{12}$, the unusual gradual lattice expansion on cooling is caused by intersite charge transfer needed to relax the over compression of the Sr−O unit that gradually advances.

Experimental Section

A precursor was prepared from a stoichiometric mixture of $Sr^{II}(NO_3)_2\cdot 4H_2O$ (99.9%), $Cu^{II}(NO_3)_2\cdot 3H_2O$ (99.9%), and $Fe^{III}(NO_3)_3\cdot 9H_2O$ (99.9%) and a fivefold molar excess of citric acid. The mixture was dissolved in a mixture of water and ethanediol (5:1). The solution was heated at 433 K overnight, and the resulting solid was thermally decomposed at 723 and 973 K with intermediate grindings. The obtained precursor with a nominal chemical composition of $Sr^{II}Cu^{II}_3Fe^{III}_4O_{10}$ was mixed with $KClO_4$ (14 mass%, 99%, oxidizing agent) and treated at 1273 K and 15 GPa for 15 min. The obtained polycrystalline sample was washed with water and acetone several times. The washed powder was put into a glass capillary tube for SXRD measurements. SXRD data were collected at the BL02B2 beamline of SPring-8. The temperature was controlled by a nitrogen gas flow. The wavelength used was determined to be 0.77293 Å using a CeO_2 standard. Rietveld refinements were performed using the program RIETAN-FP.[18] Magnetic susceptibility measurements were conducted using a SQUID (Quantum Design MPMS-XL) between 5 and 300 K in an external field of 1000 Oe in FC and ZFC modes. ^{57}Fe Mössbauer spectroscopy measurements were performed using a ^{57}Co/Rh γ-ray source. The velocity scale and the isomer shift were determined by using α-Fe as a control material, and the resulting spectra were least-squares-fitted using the Lorentzian function.

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