Inorganic Chemistry
Article

Inorg. Chem. 2009, 48, 8489–8492 8489
DOI: 10.1021/ic901128k

Intermetallic Charge Transfer in A-Site-Ordered Double Perovskite $BiCu_3Fe_4O_{12}$

Youwen Long,* Takashi Saito, Takenori Tohyama, Kengo Oka, Masaki Azuma, and Yuichi Shimakawa

Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011, Japan

Received June 11, 2009

An A-site-ordered double perovskite $BiCu_3Fe_4O_{12}$ was synthesized at high-pressure and high-temperature conditions. Similar to the isostructural $LaCu_3Fe_4O_{12}$, the temperature-induced intermetallic charge transfer between the A′-site Cu and the B-site Fe ions occurs but at higher temperature (428 K) than $LaCu_3Fe_4O_{12}$ (393 K) does. This charge transfer causes an isostructural phase transition with volume contraction by 0.6% as well as semiconductor-to-metal and antiferromagnetism-to-paramagnetism transitions. Although the Bi cation at the A site does not take part in the charge transfer, it appears to enhance the charge-transfer temperature by stabilizing the square-planar coordinated Cu^{3+}.

1. Introduction

A-site-ordered $AA'_3B_4O_{12}$ double perovskites often crystallize with an $Im\overline{3}$ cubic lattice in which the A- and A′-site cations are ordered at the originally 12-fold-coordinated A site in a simple ABO_3 perovskite as shown in Figure 1. The materials with this special ordered structure display lots of intriguing physical properties such as high permittivity, colossal magnetoresistance, and both positive and negative magnetodielectricity.[1–5] The A′ site in $AA'_3B_4O_{12}$ can accommodate transition-metal ions such as Cu^{2+} unlike the A site in the simple ABO_3 perovskite. Because of the presence of transition-metal ions at the A′ site, the ordered $AA'_3B_4O_{12}$ perovskites provide opportunities to study interactions between the transition-metal ions at the A′ site and the B site.

A very rare intermetallic charge transfer (CT) between A′-site Cu ions and B-site Fe ions was recently found in an A-site-ordered perovskite $LaCu_3Fe_4O_{12}$, which was prepared under high pressure and temperature.[6] The unusually high valence states of Cu^{3+} at the square-coordinated A′ site and of $Fe^{3.75+}$ at the octahedrally coordinated B site compete with each other in the compound, and a temperature change induces the CT. Moreover, the CT accompanies antiferromagnetic and metal-to-insulator first-ordered isostructural transitions with a large volume contraction. When the A-site La is replaced by an aliovalent Ca in the compound, however, a completely different charge transition, that is, charge disproportionation, takes place in $CaCu_3Fe_4O_{12}$ along with structural and ferrimagnetic transitions.[7] In this compound, the instability of the unusually high oxidation state of Fe^{4+} is resolved by the charge disproportionation from Fe^{4+} to Fe^{3+} and Fe^{5+} ordered in the rock-salt manner ($CaCu_3Fe^{4+}{}_4O_{12} \rightarrow CaCu_3Fe^{3+}{}_2Fe^{5+}{}_2O_{12}$). Therefore, the valence change of A-site ions leads to essentially different charge states and physical properties in the $ACu_3Fe_4O_{12}$ family, though the A-site replacement here only corresponds to one-fourth substitution of the A site in a simple ABO_3 perovskite.

It is thus interesting to examine what happens when the La ions in $LaCu_3Fe_4O_{12}$ are replaced by isovalent Bi ions. Another interesting point in this substitution is whether the Bi ions can also be involved in the CT, since Bi is potentially capable of undergoing a CT as found in the intermetallic CT between Bi and Ni in $BiNiO_3$, where the charge-disproportionated $Bi^{3+}{}_{0.5}Bi^{5+}{}_{0.5}Ni^{2+}O_3$ transforms into a charge-uniform $Bi^{3+}Ni^{3+}O_3$ at about 4 GPa.[8]

2. Experimental Section

$BiCu_3Fe_4O_{12}$ was prepared using Bi_2O_3, CuO, and Fe_2O_3 (all > 99.9% pure) as starting materials with a mol ratio of 1:6:4. Appropriate $KClO_4$ was added as an oxidizing agent. These fine mixed reagents were treated at 10 GPa and 1373 K for 1 h using a cubic-anvil-type high-pressure apparatus. The residual KCl and a small amount of unreacted starting materials were washed out using a dilute acid solution.

Phase identification and crystal structure analysis of the resultant sample were carried out by high-resolution synchrotron X-ray diffraction (SXRD) at the beamline BL02B2 in

---

*To whom correspondence should be addressed. E-mail: ywlong@msk.kuicr.kyoto-u.ac.jp.

(1) Homes, C. C.; Vogt, T.; Shapiro, S. M.; Wakimoto, S.; Ramirez, A. P. *Science* **2001**, *293*, 673.

(2) Subramanian, M. A.; Li, D.; Duan, N.; Reisner, B. A.; Sleight, A. W. *J. Solid State Chem.* **2000**, *151*, 323.

(3) Zeng, Z.; Greenblatt, M.; Subramanian, M. A.; Croft, M. *Phys. Rev. Lett.* **1999**, *82*, 3164.

(4) Imamura, N.; Karppinen, M.; Motohashi, T.; Fu, D.; Itoh, M.; Yamauchi, H. *J. Am. Chem. Soc.* **2008**, *130*, 14948.

(5) Shimakawa, Y. *Inorg. Chem.* **2008**, *47*, 8562.

(6) Long, Y. W.; Hayashi, N.; Saito, T.; Azuma, M.; Muranaka, S.; Shimakawa, Y. *Nature* **2009**, *458*, 60.

(7) Yamada, I.; Takata, K.; Hayashi, N.; Shinohara, S.; Azuma, M.; Mori, S.; Muranaka, S.; Shimakawa, Y.; Takano, M. *Angew. Chem., Int. Ed.* **2008**, *47*, 7032.

(8) Azuma, M.; Carlsson, S.; Rodgers, J.; Tucker, G. M.; Tsujimoto, M.; Ishiwata, S.; Isoda, S.; Shimakawa, Y.; Takano, M.; Attfield, J. P. *J. Am. Chem. Soc.* **2007**, *129*, 14433.

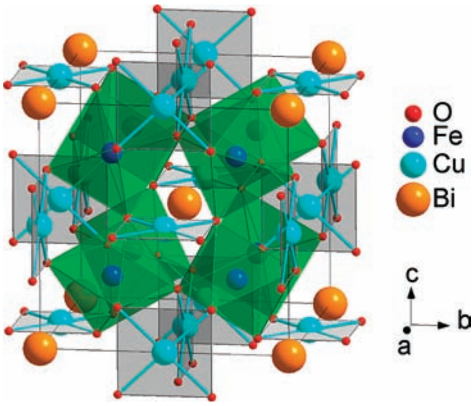

Figure 1. Crystal structure of the A-site-ordered $BiCu_3Fe_4O_{12}$.

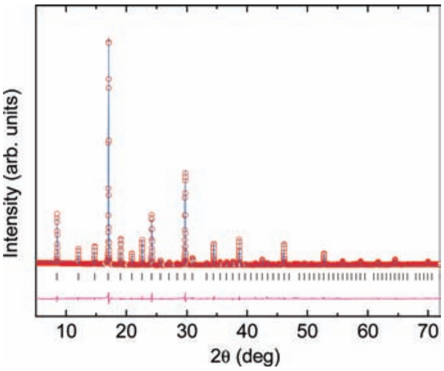

Figure 2. SXRD pattern of $BiCu_3Fe_4O_{12}$ at 300 K and the Rietveld refinement profile. The observed (circle), calculated (line), and difference (bottom line) patterns are shown. Bragg reflections are indicated by tick marks. Diffractions from a small amount of impurities are excluded.

SPring-8. A large Debye−Scherrer camera with an imaging plate detector was used. The powder sample was put into a glass capillary tube with an inner diameter of 0.2 mm and was rotated during the measurements. The wavelength used was 0.77785 Å. The SXRD data were collected at 300, 350, 375, 400, 420, 440, 460, and 480 K in a 2θ range from 1 to 75° with a 0.01° resolution. The GSAS Rietveld software was used to refine the structural parameters.[9]

The electrical resistance of the sample was measured using a conventional method during heating at 0.5 K/min. Magnetic susceptibility was measured with a superconducting quantum interference device magnetometer (Quantum Design, MPMS-2) at temperatures from 2 to 500 K. The applied magnetic filed was 0.1 T.

3. Results and Discussion

The as-made black product included a $BiCu_3Fe_4O_{12}$ phase, as well as a small amount of unreacted Fe_2O_3 impurity. As shown in Figure 2, the SXRD pattern at 300 K can be well fitted with a cubic $Im\overline{3}$ space group, revealing the A-site-ordered perovskite structure of $BiCu_3Fe_4O_{12}$, in which the Bi and Cu cations are ordered with a ratio of 1:3 in the A site of a simple ABO_3 perovskite. The refined structural parameters are listed in Table 1. The Bi cations are coordinated with 12 O atoms with the identical Bi−O distance, whereas the Cu cations form square-planar coordinated CuO_4 units because of the significant tilting of FeO_6 octahedra. Bond valence sum (BVS) calculations[10,11] showed that the valences of both Cu and Fe ions were very close to +3.0. The calculations gave a valence of +2.4 for Bi, but this should be due to an underbonded condition in Bi−O, which is usually seen in undistorted BiO_{12} polyhedra.[12] Such a condition is also consistent with the large thermal factor of Bi as shown in Table 1. Thus, the charge combination in the compound at 300 K should be $BiCu^{3+}{}_3Fe^{3+}{}_4O_{12}$, which is the same as that found in the low-temperature phase of $LaCu_3Fe_4O_{12}$.[6] It is noted that in the present compound we see no structural distortion from the cubic symmetry though many of the perovskites containing Bi at the A site have distorted crystal structures.

Table 1. Refined Structural Parameters of $BiCu_3Fe_4O_{12}$ at 300 K from the Rietveld Analysis of SXRD Data[a]

atom	site	x	y	z	U_{iso} (100 × Å^2)
Bi	2*a*	0	0	0	3.73(5)
Cu	6*b*	0	1/2	1/2	1.09(5)
Fe	8*c*	1/4	1/4	1/4	0.09(4)
O	24*g*	0.3187(8)	0.1742(5)	0	1.0

[a] Space group: $Im\overline{3}$; Lattice parameter: $a = 7.43322(8)$ Å; Bond angle: ∠Fe−O−Fe = 135.5(2)°; $R_{wp} = 4.63\%$; $R_p = 3.28\%$.

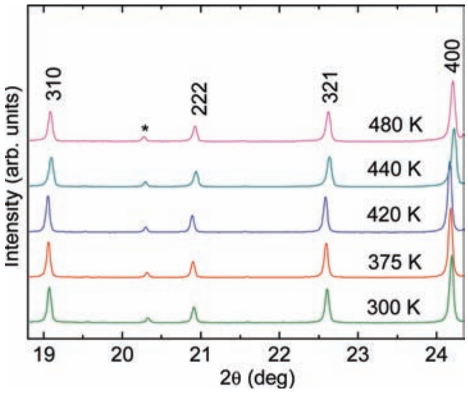

Figure 3. SXRD patterns of $BiCu_3Fe_4O_{12}$ obtained at various temperatures. The peak marked with an asterisk originates from Fe_2O_3 impurity.

As shown in Figure 3, the high-temperature SXRD patterns clearly show an unusual shift of the peak position between 420 and 440 K, but the absence of any symmetrical change indicates that this change is an isostructural phase transition. We refined the crystal structure at each temperature from the SXRD data, and the temperature dependence of Cu−O and Fe−O bond lengths are presented in Figure 4a. Corresponding to the isostructural phase transition, the Cu−O distance significantly increases with increasing temperature, whereas the Fe−O bond length decreases. As shown in Figure 4b, the valences of both Cu and Fe ions obtained from the BVS calculations were close to +3.0 below the transition, whereas the BVS values of Cu and Fe ions

---

(9) Larson, A. C.; von Dreele, R. B. *General Structure Analysis System* (*GSAS*), Report No. LAUR 86-748, Los Alamos National Laboratory, 1994.

(10) Brown, I. D.; Altermatt, D. *Acta Crystallogr.* **1985**, *B41*, 244.

(11) The BVS values (V_i) for Cu, Fe, and Bi ions were calculated using the formula $V_i = \sum_j S_{ij}$, and $S_{ij} = \exp[(r_0 - r_{ij})/0.37)]$. The following r_0 values reported in references 6 and 8 were used: 1.739 and 1.649 respectively for Cu^{3+} and Cu^{2+} with twelve coordinated oxygen atoms; 1.751 and 1.772 respectively for Fe^{3+} and $Fe^{3.75+}$ with six coordinated oxygen atoms ; 2.094 for Bi^{3+} with twelve coordinated oxygen atoms. In a strict sense, bond valence parameters should be temperature dependent. However, it is clear from the data between 300 and 420 K that the effect of temperature on the parameters is negligible. We thus used a single r_0 value for each oxidation state of the ion.

(12) Wang, X.; Liebau, F. *Acta Crystallogr.* **2007**, *B63*, 216.

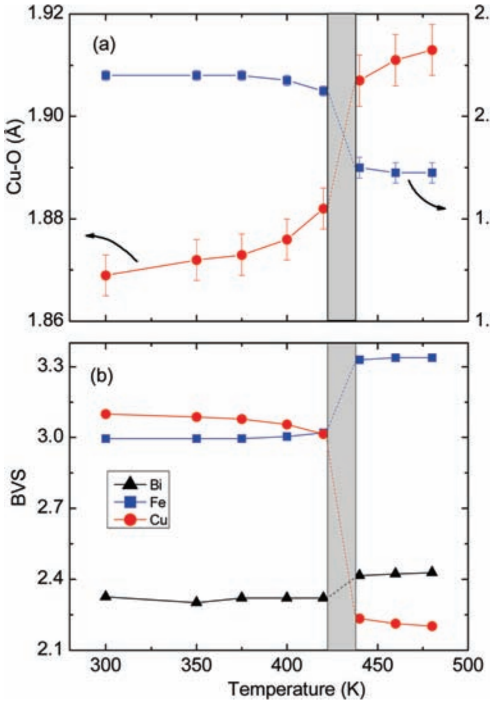

Figure 4. Temperature dependences of (a) Cu−O and Fe−O bond lengths and (b) BVS values for Bi, Cu, and Fe.

respectively change to about +2.2 and +3.4 above the transition. The valence state of the Bi ion, on the other hand, does not change significantly in the whole temperature range we measured. This implies that the charge formula changes to $BiCu^{2+}{}_3Fe^{3.75+}{}_4O_{12}$ above the transition, just like that of the high-temperature phase in $LaCu_3Fe_4O_{12}$.[6]

The above structural results clearly show that $BiCu_3Fe_4O_{12}$ undergoes an intermetallic CT between the A′-site Cu and the B-site Fe ions, similar to that occurred in $LaCu_3Fe_4O_{12}$, and that the A-site Bi ions are not involved in the CT. This CT accompanies a notable change in unit cell volume by about 0.6% as shown in Figure 5a, suggesting the first-order feature of the transition. The decrease of the Fe−O bond length in the transition is responsible for the volume contraction with increasing temperature.

This intermetallic CT also causes significant changes in both transport and magnetic properties. As shown in Figure 5b of the temperature dependence of electrical resistance, the low-temperature $BiCu^{3+}{}_3Fe^{3+}{}_4O_{12}$ phase shows a semiconducting behavior whereas the high-temperature $BiCu^{2+}{}_3Fe^{3.75+}{}_4O_{12}$ phase exhibits a metallic one. The intermetallic CT between the A′-site Cu and B-site Fe cations produces a mixed valence state in Fe, leading to the metallic property above the transition. This change in electronic structure can be viewed as a doping into the B-site Fe ions, but the doping in the present compound is essentially different from the conventional chemical doping by substitutions.

As shown in Figure 5c, the magnetic susceptibility increases when $BiCu_3Fe_4O_{12}$ changes from the low-temperature semiconducting phase to the high-temperature metallic phase. The transition temperature determined from the temperature derivative of the susceptibility is 428 K. The change in magnetic susceptibility is quite similar to that observed in the intermetallic CT in $LaCu_3Fe_4O_{12}$. Therefore, by analogy with $LaCu_3Fe_4O_{12}$, the low-temperature semiconducting phase of $BiCu_3Fe_4O_{12}$ is most probably in an antiferromagnetic ordered state, and the CT-induced magnetic change should be of an antiferromagnetism-to-paramagnetism transition.

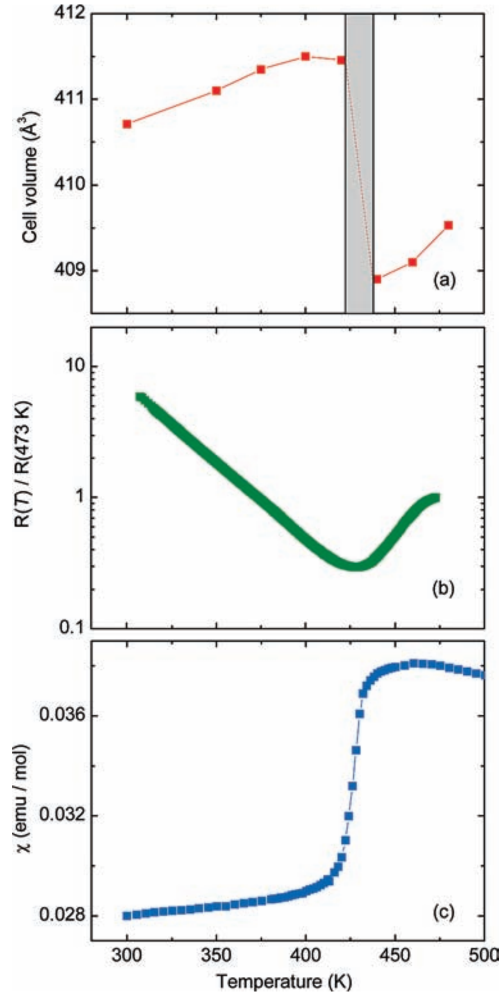

Figure 5. Temperature dependence of (a) unit cell volume, (b) normalized resistance, and (c) magnetic susceptibility χ.

It should be noted that the isovalent A-site substitution increases the transition temperature of the Cu−Fe intermetallic CT from 393 K in $LaCu_3Fe_4O_{12}$ to 428 K in $BiCu_3Fe_4O_{12}$. This is in sharp contrast to the change in the magnetic transition temperature in an isostructural system, in which the similar Bi substitution for La results in the slight decrease of ferrimagnetic transition temperature from 361 K in $LaCu_3Mn_4O_{12}$ to 350 K in $BiCu_3Mn_4O_{12}$.[13,14] The ferrimagnetic orderings in these two ordered perovskites with Mn at the B sites are caused by the antiferromagnetic couplings between the A′-site Cu and B-site Mn spins. Thus, the isovalent A-site ions with comparable ionic sizes[15] do not affect the magnetic interactions considerably. In the present Fe-containing compounds, however, the A-site Bi ions clearly affect the intermetallic CT transition temperature though they do not take part in the CT. The Bi ions at the A site in $BiCu_3Fe_4O_{12}$ seem to stabilize the A′-site ground

---

(13) Alonso, J. A.; Sánchez-Benítez, J.; De Andrés, A.; Martínez-Lope, M. J.; Casais, M. T.; Martínez, J. L. *Appl. Phys. Lett.* **2003**, *83*, 2623.

(14) Takata, K.; Yamada, I.; Azuma, M.; Takano, M.; Shimakawa, Y. *Phys. Rev. B* **2007**, *76*, 024429.

(15) Shannon, R. D. *Acta Crystallogr.* **1976**, *A32*, 751.

state of Cu^{3+} in the square-planar coordination, so the transition temperature of the intermetallic CT increases compared to that in $LaCu_3Fe_4O_{12}$. Since 6s and 6p orbitals in Bi often hybridize with 2p orbitals in O in oxides, the stabilization of Cu^{3+} may be mediated through the orbital hybridization in Bi−O−Cu bonds.

In conclusion, a new A-site-ordered $BiCu_3Fe_4O_{12}$ perovskite was prepared and was found to exhibit a temperature-induced Cu−Fe intermetallic CT similar to that found in $LaCu_3Fe_4O_{12}$. This CT is associated with significant transitions in crystal structure, electrical, and magnetic properties. The A-site Bi cation itself does not take part in the CT, but it stabilizes the A′-site square-coordinated Cu^{3+} and thereby increases the temperature at which the CT occurs.

Acknowledgment. We thank J. E. Kim for help with the SXRD experiments. This work was partly supported by Grants-in-Aid for Scientific Research (19GS0207, 19014010 and 19340098), by the Global COE Program "International Center for Integrated Research and Advanced Education in Materials Science" and by a grant for the Joint Project of Chemical Synthesis Core Research Institutions from the Ministry of Education, Culture, Sports, Science, and Technology (MEXT) of Japan.