High-pressure synthesis, electronic states, and structure–property relationships of perovskite oxides, $\text{ACu}_3\text{Fe}_4\text{O}_{12}$ ($A$: divalent alkaline earth or trivalent rare-earth ion)

Ikuya YAMADA$^\dagger$

Nanoscience and Nanotechnology Research Center, Osaka Prefecture University, 1–2 Gakuen-cho, Naka-ku, Sakai 599–8570, Japan

Recent investigations on the quadruple perovskite series, $\text{ACu}_3\text{Fe}_4\text{O}_{12}$ ($A$ = divalent alkaline-earth metal or trivalent rare-earth metal ion), have demonstrated anomalous electronic phase transformations such as charge disproportionation and charge transfer. These behaviors originate from the unusual high valence Fe$^{4+}$ (or Fe$^{3.75+}$) ions that are dominated by ligand holes. In this review, various structural transformations and electronic properties in $\text{ACu}_3\text{Fe}_4\text{O}_{12}$ perovskites are shown. Furthermore, intriguing structure–property relationships of the $\text{A}^{2+}\text{Cu}_3\text{Fe}_4\text{O}_{12}$ perovskites are presented. The local structural distortions on metal-oxygen bonds, which are represented as bond discrepancies and global instability indices, are closely related to the electronic phase transformations at low temperature generating a wide range of remarkable phenomena such as negative thermal expansion, ferromagnetism, and metal–nonmetal transitions.

Key-words: Charge disproportionation, Charge transfer, Unusual high valence Fe ion, High-pressure synthesis, Bond discrepancy, Global instability index, Negative thermal expansion

1. Introduction

Perovskite-type transition metal oxides demonstrate a rich variety of fascinating properties such as superconductivity, ferromagnetism, magnetotransport, and ferroelectricity. Among them, the Fe$^{4+}$-containing $\text{ABO}_3$-type perovskites, $\text{AFe}_2$O$_3$ ($A$: Ca, Sr, Ba), exhibit various electronic features with structural modifications. The simple cubic perovskite, SrFeO$_3$, has a metallic conductivity with complicated antiferromagnetic spin structures, which are different from the isoelectronic Mn$^{3+}$-based perovskites (with a 3d$^4$ electron configuration) because of the difference in the charge transfer energy (energy for ligand-to-metal charge transfer), $\Delta_C$. The $\Delta_C$ value is positive for Mn$^{3+}$ (+1.8 eV) but negative for Fe$^{4+}$ ions (~3 eV). This remarkable electronic state of the Fe$^{4+}$ ions also induces intriguing phenomena in other $\text{AFe}_2$O$_3$ perovskites, such as the charge disproportionation (CD) of $2\text{Fe}^{4+}\rightarrow\text{Fe}^{3+}+\text{Fe}^{5+}$ ($2\text{Fe}^{4+}L\rightarrow\text{Fe}^{3+}+\text{Fe}^{5+}+L^2$, where $L$ represents a ligand hole) in the orthorhombic GdFeO$_3$-type perovskite CaFeO$_3$, and the ferromagnetic alignment of Fe spins in the cubic perovskite BaFeO$_3$.

The quadruple $A$-site-ordered perovskite oxides with $A\text{A'}_2\text{B}_2\text{O}_{12}$-type formula have been attracting considerable interest because of their rich variety of physical properties such as magnetoresistance, charge/orbital/magnetic orderings, and giant dielectric constants. The $A\text{A'}_2\text{B}_2\text{O}_{12}$ perovskites, in which the original $A$-sites are divided into icosahedrally coordinated and pseudo-square planar coordinated sites (Fig. 1), allow us to investigate complex electronic interactions between $A'$- and $B$-site TM ions. In particular, the Fe$^{4+}$($\text{Fe}^{3.75+}$)-containing $\text{ACu}_3\text{Fe}_4\text{O}_{12}$ (ACFO) perovskites display interesting phenomena such as CD, charge transfer (CT), and negative thermal expansion.

1 Corresponding author: I. Yamada; E-mail: i-yamada@21c.osakafu-u.ac.jp

Fig. 1. Crystal structure of $\text{ACu}_3\text{Fe}_4\text{O}_{12}$ perovskites drawn using the program VESTA.

2. $A^{2+}\text{Cu}_3\text{Fe}_4\text{O}_{12}$

2.1 $\text{CaCu}_3\text{Fe}_4\text{O}_{12}$

$\text{CaCu}_3\text{Fe}_4\text{O}_{12}$ (CCFO) was reported as the first member of the ACFO perovskite series in 2008. CCFO was successfully synthesized under high pressures of above ~9 GPa, while the synthesis of high-purity samples required even higher pressures (up to ~15 GPa). CCFO crystallized in a cubic $A\text{A'}_2\text{B}_2\text{O}_{12}$-type structure with the Im$3$ space group (No. 204). In a simple ionic model, CCFO was expected to have a nominal valence state of $\text{Ca}^{2+}\text{Cu}^{3+}\text{Fe}^{4+}\text{O}_{12}$. $\text{Fe}^{57}$ Mössbauer spectroscopy and bond valence analysis revealed that this ionic model is appropriate at room temperature, arousing interest about the electronic phase transformation at low temperatures. Synchrotron X-ray and electron diffraction studies demonstrated that a first-order structural...
phase transition with a symmetry lowering to the $Pn\bar{3}$ space group (No. 201) occurred at 210 K (Fig. 2). Fe Mössbauer spectroscopy displayed that a CD transition of $2\text{Fe}^{3+} = \text{Fe}^{3+} + \text{Fe}^{5+}$ occurs simultaneously with the structural phase transition (Fig. 3). The resulting $\text{Fe}^{3+}$ and $\text{Fe}^{5+}$ ions form rock-salt-type charge ordering (CO). During the CD transition, the Cu valence remained at approximately $+2$, and was therefore not involved in the CD.

The electronic properties of the charge-disproportionated CCFO phase were investigated. The magnetization data of CCFO showed a ferromagnetic property below 210 K (Figs. 4 and 5), which was interpreted as the ferrimagnetic alignment of $2\text{Fe}^{3+} (S = 5/2) \rightarrow 2\text{Fe}^{5+} (S = 3/2) \rightarrow 3\text{Cu}^{2+} (S = 1/2)$. Later, neutron powder diffraction and X-ray magnetic circular dichroism measurements confirmed the detailed magnetic structure.

The magnetic property of CCFO is distinguishable from that of the antiferromagnetic-like $\text{CaFeO}_3$. The ferromagnetic alignment of Fe spins in CCFO is attributed to the antiferromagnetic superexchange interactions between the $A'$-site Cu and $B$-site Fe ions, whereas antiferromagnetic interactions between only Fe ions are predominant in $\text{CaFeO}_3$. The electrical conductivity of CCFO abruptly changed below 210 K (Fig. 6). This is derived from the localization of the charge carrier associated with the ligand holes in the charge-disproportionated CCFO phase.

The above-demonstrated electronic properties of CCFO are different from those of the simple perovskite $\text{CaFeO}_3$, in which metal-insulator, second-order CD, and structural phase transitions occur at 290 K, whereas an antiferromagnetic transition occurs at 115 K. Substantial differences between the properties of CCFO and $\text{CaFeO}_3$ suggest that the insertion of Cu ions into the $A$-sites may induce complex electronic interactions between the Cu and Fe ions, motivating the investigation of novel $A'CFO$ compounds.

2.2 SrCu$_3$Fe$_4$O$_{12}$

The synthesis of SrCu$_3$Fe$_4$O$_{12}$ (SCFO) required a high pressure of $\sim 15$ GPa. A precursor prepared by polymerization improved the purity of the resulting SCFO sample. It is noted that the electronic states, structural transitions, and physical properties of SCFO are entirely different from those of CCFO because of the difference in the ionic radii of $\text{Ca}^{2+}$ and $\text{Sr}^{2+}$ ions. This is in contrast to other $A'A'_2B_4O_{12}$-type systems, which show less $A$-site ion-size-related effects on electronic states and properties.

Interestingly, SCFO displayed a NTE between 170 and 270 K, with a minimum linear thermal expansion coefficient of $-2.3 \times 10^{-5}$ K$^{-1}$ (Fig. 2). The NTE of SCFO was induced by a continuous CT between Cu and Fe ions (Cu$^{2+} + \text{Fe}^{3+} \rightarrow \text{Cu}^{3+} + \text{Fe}^{2+}$ in a simplified model). The temperature evolution of the metal-oxygen bond lengths (Cu–O, Fe–O) indicated that upon
cooling the Cu valence tends to increase while the Fe valence decreases in the NTE temperature range.\(^{16,17}\)\(^{57}\)Fe Mössbauer spectroscopy revealed that Fe ions disproportionate into Fe\(^{3+}\) and Fe\(^{5+}\) below ~200 K, resulting in an Fe\(^{3+}\):Fe\(^{5+}\) abundance ratio of ~4:1 at 4 K (Fig. 3). The average Fe valence was calculated at approximately +3.4 in this phase, revealing that the Fe valence was reduced from nominally +4 at room temperature.

The CT in SCFO is associated with the steric strain of the elongated (or compressed) metal-oxygen bonds. The bond valence sum (BVS) for Fe sites of SCFO at room temperature is calculated at +3.54. This value is much lower than that expected for a simple ionic model of Sr\(^{2+}\)Cu\(^{3+}\)Fe\(^{5+}\)O\(_{12}\). This deviation implies the forced elongation of the Fe-O bonds. The tensile strain on Fe-O bonds can drive the observed decrease in Fe valence, resulting in positive charge (electron) transfer from Fe to Cu (and Cu to Fe). The Fe-O bond elongation with charge transfer leads to the continuous unit cell volume expansion based on the relationship between the bond length/angle and the a-axis length: 

\[ a = 4(\text{Fe-O}) \times \sin(\angle \text{Fe-O-Fe}/2). \]

The physical properties of CCFO and SCFO were also quite distinct. SCFO exhibited an antiferromagnetic-like transition at ~170 K, followed by a large deviation in the zero-field-cooling and field-cooling modes below ~80 K because of the short-range magnetic ordering (Fig. 4). The magnetic properties of SCFO primarily originate from the randomly distributed Fe\(^{3+}\) and Fe\(^{5+}\) ions in the charge-disproportionated phase. Ferromagnetic super-exchange interactions predominate between adjacent Fe\(^{3+}\)-Fe\(^{5+}\) ions, whereas antiferromagnetic interactions prevail between adjacent Fe\(^{3+}\)-Fe\(^{3+}\)/Fe\(^{5+}\)-Fe\(^{5+}\) ions. The electrical resistivity of SCFO appears to be semiconducting throughout the temperature range measured (Fig. 6).

3. \(A^{2+}\)Cu\(_3\)Fe\(_4\)O\(_{12}\)

LaCu\(_3\)Fe\(_4\)O\(_{12}\) (LaCFO) was reported as the second member of \(A\)CFO perovskites by Long et al. in 2009.\(^{21}\) LaCFO had a nominal valence state of La\(^{3+}\)Cu\(^{2+}\)+Fe\(^{3.75+}\)O\(_{12}\) above 393 K. This phase showed a first-order CT transition of 3Cu\(^{2+}\)+4Fe\(^{3.75+}\) \(\rightarrow\) 3Cu\(^{3+}\)+4Fe\(^{3+}\) (3Cu\(^{2+}\)+4Fe\(^{3+}\)+1L\(_{B}\) \(\rightarrow\) 3Cu\(^{2+}\)+1L\(_{B}\)+4Fe\(^{3+}\) in the ligand hole picture), resulting in a valence state of La\(^{3+}\)Cu\(^{3+}\)+Fe\(^{3+}\)+O\(_{12}\) in the low-temperature phase. The Fe valence transition with CT was confirmed by \(^{57}\)Fe Mössbauer spectroscopy. Because of the valence transition in Fe ions (Fe\(^{3.75+}\) \(\rightarrow\) Fe\(^{3+}\)) and their resulting expansion, the unit cell volume abruptly expanded at the CT transition temperature (Fig. 2). Antiferromagnetic, metal–insulator, and isostructural phase transitions coincided with the CT (Figs. 4–6). A subsequent report\(^{22}\) by Long et al. showed that the Bi-analog, BiCu\(_3\)Fe\(_4\)O\(_{12}\) (BCFO), simultaneously undergoes the CT, antiferromagnetic, and metal–insulator transitions at 432 K, which is similar to those occurring in LaCFO. The authors suggested that the reduced Fe valence in LaCFO and BCFO probably destabilized the charge-ordered state in the charge-disproportionated phase with a nonequivalent abundance ratio of Fe\(^{3+}\) and Fe\(^{5+}\) ions (8Fe\(^{3.75+}\) \(\rightarrow\) 5Fe\(^{3+}\)+3Fe\(^{5+}\)), leading to the conclusion that the CT transitions predominate within the \(A^{2+}\)Cu\(_3\)Fe\(_4\)O\(_{12}\) compounds, unlike the CD occurring in \(A^{3+}\)Cu\(_3\)Fe\(_4\)O\(_{12}\). However, their considerations could not be confirmed because of the use of only two examples of \(A^{3+}\)Cu\(_3\)Fe\(_4\)O\(_{12}\).
compounds possessing A-site ions with the same ionic radii (La$^{3+}$ and Bi$^{3+}$: 1.17 Å for Shannon’s ionic radius$^{24}$). The authors subsequently reported the electronic phase diagram of the Ca$_{1-x}$La$_x$Cu$_4$Fe$_2$O$_{12}$ solid solution$^{25}$; however, they did not demonstrate what determines the type of electronic phase transitions (CD or CT) in the $\text{ACFO}$ system.

### 3.2 $\text{YCu}_3\text{Fe}_4\text{O}_{12}$

$\text{YCu}_3\text{Fe}_4\text{O}_{12}$ (YCFO) reported in 2013$^{26}$ is formally isoelectronic to LaCFO and BCFO at high temperatures. YCFO was considered to be an appropriate compound for elucidating the structure–property relationships in perovskites with the formula $\text{A}^3\text{Cu}_4\text{Fe}_2\text{O}_{12}$, because the large differences in the ionic radii of A-site ions (Shannon’s ionic radius: $r_{\text{La}^{3+}} = 1.16\text{ Å}$, $r_{\text{Y}^{3+}} = 1.019\text{ Å}$) may affect the low-temperature electronic states and properties. High-pressure (15 GPa) and high-temperature (1273 K) conditions produced good-quality samples of YCFO.$^{26}$

The unit cell volume of YCFO changed almost monotonically with temperature, implying the absence of CT (Fig. 2). The valence states of the Fe and Cu ions in YCFO were investigated by $^{57}\text{Fe}$ Mössbauer and by soft X-ray absorption spectroscopy, respectively. A primary singlet component was found in the Mössbauer spectrum at room temperature, and its isomer shift value reached an Fe valence close to +4. The singlet component split into three components below ~250 K: Fe$^{3+}(1)$, Fe$^{2+}(2)$, and Fe$^{3+}$, showing that YCFO undergoes the CT transition of $8\text{Fe}^{2+}\text{Cu}^{3+} + 5\text{Fe}^{3+} + 3\text{Fe}^{\text{A}^s}$ type (Fig. 3). The abundance ratio of these three components was estimated at Fe$^{3+}(1)$:Fe$^{3+}(2)$:Fe$^{2+}$ = 4:1:3. The electron diffraction pattern showed a rock-salt-type CO structure (Fig. 2). The CT transition temperatures as in LaCFO (Fig. 2) are predominant in this case.$^{57}$The isothermal magnetization curves of several LaCFO samples showed complex behaviors because of the contributions of the 4f magnetic moments; the steep slopes in the vicinity of the zero field could be used to distinguish between the ferromagnetic and antiferromagnetic components. The electrical resistivity of low-temperature phase was strongly dependent on the temperature of the CT phases (Fig. 6). In contrast, the resistivity of the charge-disproportionated phases was less dependent on temperature (Fig. 6). These data can reasonably enable the distinction of $\text{LaCu}_3\text{Fe}_4\text{O}_{12}$ perovskites based on two types of electronic phases. The electronic phase diagram for $\text{LaCu}_3\text{Fe}_4\text{O}_{12}$ (Fig. 7) displays a clear boundary between the CT and CD phases. In addition, the $\text{LaCu}_3\text{Fe}_4\text{O}_{12}$ phase diagram successfully excluded the carrier-doping effect of Fe ions, thus enabling consideration of the structural features related to the electronic states.

In order to elucidate the determinants of the low-temperature electronic phase transitions (CT or CD) occurring in the $\text{LaCu}_3\text{Fe}_4\text{O}_{12}$ perovskites, structural analyses were performed. Crystal structures of all the $\text{LaCu}_3\text{Fe}_4\text{O}_{12}$ perovskites were refined using the Rietveld refinement program, Rietan-FP.$^{29}$ Based on the synchrotron X-ray powder diffraction data. The crystal structures of the LaCFO samples with room temperature (or the lowest temperatures above the CT transitions for LaCFO and PrCu$_3$Fe$_4$O$_{12}$) were compared based on the BVS analysis (Fig. 8)$^{29}$.

The BVS of Cu ions are close to +2 for all LaCFO. However, the BVS of $\text{LnCu}_3\text{Fe}_4\text{O}_{12}$ ions decreased almost monotonically from 3.60 (LaCFO) to 2.61 (LuCFO), whereas the BVS of Fe ions increases from 3.47 (LaCFO) to 3.80 (LuCFO) with decreasing $\text{Ln}$ ionic radii. The deviation of BVS from the nominal oxidation number ($\nu(M)$) of +3 is defined as the bond discrepancy$^{30}$, $\delta(M) = |\nu(M) - \nu(M)|$, and the root-mean-square of bond discrepancies of all the constituent atoms calculates global instability index (GII).$^{30}$ The GII versus $r_{\text{La}}$ plot in Fig. 8(d) displays that the GII has a quadratic-like dependence on the $r_{\text{La}}$, implying that the total structural distortions of $\text{LaCu}_3\text{Fe}_4\text{O}_{12}$ phases are strongly dependent on the $\text{La}$ ion sizes. The bond discrepancies calculated for the $\text{Ln}$ and Fe ions ($\delta(M)$ and $\delta(\text{Fe})$) have negative correlations, as seen in the bond discrepancy diagram in Fig. 9(a). The $\text{LaCu}_3\text{Fe}_4\text{O}_{12}$ samples that underwent CT transitions are included in the second quadrant, whereas those showing CD transitions are shown in the fourth quadrant. In the former series, compressive (tensile) strains on $\text{LnO}$ (Fe-O) bonds are expected to be relaxed in response to the CT transition. The relationship between the bond discrepancy and the CT transition temperature is evidenced by the GII.
Figure 9(b) shows an almost linear relationship between the GII and the CT transition temperature in LnCFO. The above-demonstrated relationships are the first examples revealing correlations between the bond discrepancy/GII and electronic phase transitions.

4. Summary

Exploratory studies on ACu3Fe4O12 perovskites prepared under high pressures and temperatures have demonstrated a rich variety of electronic states and properties originating from unusual high valence Fe ions. Systematic investigations on LnCu3Fe4O12 compounds have revealed intriguing structure–property relationships. The bond discrepancy and global instability indices offer efficient means for evaluating the electronic states and the resulting phase transformations in this system.

Acknowledgements

The author thanks all collaborators for their contributions. This work was financially supported by JST, JSPS KAKENHI (No. 21750062), Nippon Sheet Glass Foundation, and Murata Science Foundation.

References

1) J. B. MacChesney, R. C. Sherwood and J. F. Potter, J. Chem. Phys., 43, 1907–1913 (1965).
2) T. Takeda, Y. Yamaguchi and H. Watanabe, J. Phys. Soc. Jpn., 4, 967–969 (1972).
3) S. Ishiwata, M. Tokunaga, Y. Kaneko, D. Okuyama, Y. Tokunaga, S. Wako, K. Kakurai, T. Arima, Y. Taguchi and Y. Tokura, Phys. Rev. B, 84, 054427 (2011).
4) A. E. Bocquet, A. Fujimori, T. Mizokawa, T. Saitoh, H.
Namatame, S. Sugii, N. Kimizuka, Y. Takeda and M. Takano, Phys. Rev. B, 46, 1561–1570 (1992).
5) A. E. Bocquet, T. Mizokawa, T. Saitoh, H. Namatame and A. Fujimori, Phys. Rev. B, 46, 3771–3784 (1992).
6) M. Takano, N. Nakanishi, Y. Takeda, S. Naka and T. Takada, Mater. Res. Bull., 12, 923–928 (1977).
7) N. Hayashi, T. Yamamoto, H. Kageyama, Y. Watanabe, T. Kawakami, Y. Matsushita, A. Fujimori and M. Takano, Angew. Chem., Int. Ed., 50, 12547–12550 (2011).
8) Z. Zeng, M. Greenblatt, M. A. Subramanian and M. Croft, Phys. Rev. Lett., 82, 3164–3167 (1999).
9) J. A. Alonso, J. Sanchez-Benitez, A. De Andres, M. J. Martinez-Lope, M. T. Casais and J. L. Martinez, Appl. Phys. Lett., 83, 2623–2625 (2003).
10) A. Prodi, E. Gilioli, A. Gauzzi, F. Licci, M. Marezio, F. Bolzoni, Q. Huang, A. Santoro and J. W. Lynn, Nat. Mater., 3, 48–52 (2004).
11) M. A. Subramanian, D. Li, N. Duan, B. A. Reisner and A. W. Sleight, J. Solid State Chem., 151, 323–325 (2000).
12) I. Yamada, K. Takata, N. Hayashi, S. Shinohara, M. A. Subramanian, D. Li, N. Duan, B. A. Reisner and A. W. Sleight, J. Solid State Chem., 151, 323–325 (2000).
13) M. Mizumaki, W. T. Chen, T. Saito, I. Yamada, J. P. Attfield and Y. Shimakawa, Phys. Rev. B, 84, 094418 (2011).
14) P. M. Woodward, D. E. Cox, E. Moshopoulou, A. W. Sleight and S. Morimoto, Phys. Rev. B, 62, 844–855 (2000).
15) T. Ueda, M. Kodera, K. Yamada and T. Oguchi, J. Phys. Soc. Jpn., 82, 094718 (2013).
16) I. Yamada, K. Tsuchida, K. Ohgushi, N. Hayashi, J. Kim, N. Tsuji, R. Takahashi, M. Mizumaki, T. Saito, T. Tohyama, K. Oka, M. Azuma and Y. Shimakawa, Inorg. Chem., 49, 1561–1574 (2010).
17) J. Sanchez-Benitez, J. A. Alonso, M. J. Martinez-Lope, A. De Andres and M. T. Fernandez-Diaz, Inorg. Chem., 49, 5679–5685 (2010).
18) J. Sanchez-Benitez, J. A. Alonso, H. Falcon, M. J. Martinez-Lope, A. De Andres and M. T. Fernandez-Diaz, J. Phys.: Condens. Matter, 17, S3063–S3068 (2005).
19) A. Dittl, S. Krohns, J. Sebald, F. Schrettle, M. Hemmida, H. A. K. von Nidda, S. Riegler, A. Reisner, S. G. Ebbinghaus and A. Loidl, Eur. Phys. J. B, 79, 391–400 (2011).
20) I. Yamada, K. Shiro, K. Oka, M. Azuma and T. Irifune, J. Phys. Soc. Jpn., 121, 912–914 (2013).
21) Y. W. Long, N. Hayashi, T. Saito, M. Azuma, S. Muranaka and Y. Shimakawa, Nature, 458, 60–63 (2009).
22) Y. W. Long, T. Saito, T. Tohyama, K. Oka, M. Azuma and Y. Shimakawa, Inorg. Chem., 48, 8489–8492 (2009).
23) Y. W. Long and Y. Shimakawa, New J. Phys., 12, 063029 (2010).
24) R. D. Shannon, Acta Crystallogr. A, 32, 751–767 (1976).
25) W. T. Chen, T. Saito, N. Hayashi, M. Takano and Y. Shimakawa, Sci. Rep., 2, 449 (2012).
26) H. Etani, I. Yamada, K. Ohgushi, N. Hayashi, Y. Kusano, M. Mizumaki, J. Kim, N. Tsuji, R. Takahashi, N. Nishiyama, T. Inoue, T. Irifune and M. Takano, J. Am. Chem. Soc., 135, 6100–6106 (2013).
27) I. Yamada, H. Etani, K. Tsuchida, S. Marukawa, N. Hayashi, T. Kawakami, M. Mizumuki, K. Ohgushi, Y. Kusano, J. Kim, N. Tsuji, R. Takahashi, N. Nishiyama, T. Inoue, T. Irifune and M. Takano, Inorg. Chem., 52, 13751–13761 (2013).
28) F. Izumi and K. Momma, Solid State Phenom., 130, 15–20 (2007).
29) I. D. Brown and D. Altermatt, Acta Crystallogr. B, 41, 244–247 (1985).
30) I. D. Brown, Chem. Rev., 109, 6858–6919 (2009).
31) K. Momma and F. Izumi, J. Appl. Cryst., 44, 1272–1276 (2011).

Ikuya Yamada received his Master of Science in 2003 and Ph.D. in 2006 from Kyoto University. He was a postdoctoral fellow at Kyoto University from 2006 to 2007, and at University of Paris VI from 2007 to 2008. He was an Assistant Professor at Ehime University, Japan, from 2008 to 2012, and a researcher at Precursory Research for Embryonic Science and Technology, Japan Science and Technology Agency, from 2011 to 2014. He has been working as a special lecturer at Osaka Prefecture University, Japan, since 2012. His current fields of interest are high-pressure synthesis, crystal structure, and physical properties of novel functional materials.