Inorganic Chemistry
Communication
pubs.acs.org/IC

# $AgCu_3V_4O_{12}$: a Novel Perovskite Containing Mixed-Valence Silver ions

Yasuhide Akizuki,[†] Ikuya Yamada,*[,‡,§] Koji Fujita,*[,†] Hirofumi Akamatsu,[∥] Tetsuo Irifune,[⊥] and Katsuhisa Tanaka[†]

[†]Department of Material Chemistry, Graduate School of Engineering, Kyoto University, Katsura, Nishikyo-ku, Kyoto 615-8510, Japan

[‡]Nanoscience and Nanotechnology Research Center, Osaka Prefecture University, 1-2 Gakuen-cho, Naka-ku, Sakai, Osaka 599-8531, Japan

[§]JST-PRESTO, 4-1-8 Honcho, Kawaguchi, Saitama 332-0012, Japan

[∥]Materials Research Institute and Department of Materials Science and Engineering, Pennsylvania State University, MSC Building, University Park, State College, Pennsylvania 16802, United States

[⊥]Geodynamics Research Center, Ehime University, 2-5 Bunkyo-cho, Matsuyama, Ehime 790-8577, Japan

*Supporting Information*

**ABSTRACT:** A novel silver-containing perovskite, $AgCu_3V_4O_{12}$, was synthesized under high-pressure and high-temperature conditions. It crystallizes in an A-site-ordered perovskite structure (space group $Im\bar{3}$), in which silver ions occupy the 12-coordinated A sites forming regular icosahedra, and exhibits metallic behavior. Bond-valence-sum calculations and X-ray photoemission spectroscopy reveal that Ag ions are present in the mixed-valence state, most likely attributable to the coexistence of $Ag^+$ and $Ag^{3+}$, unlike the case of well-known perovskite-type $AgNbO_3$ and $AgTaO_3$ containing only $Ag^+$ ions. We discuss metallic conduction in relation to electronic structure calculations.

Silver-based perovskite oxides have been extensively studied in recent years because of the discoveries of their ultralow dielectric losses, photocatalytic properties, and large piezoelectric responses, which may find technological applications in the future. Despite these fascinating properties, only a limited number of silver-based oxides such as $AgNbO_3$ and $AgTaO_3$ have been reported to crystallize in the perovskite-type structure.[1,2] Silver belongs to 4d transition metals, and its electron configuration in the ground state is described by [Kr] $4d^{10}5s^1$. Although three kinds of Ag ions, i.e., monovalent, divalent, and trivalent, are known, the $Ag^+$ ion is the most stable because of its closed-shell structure ([Kr] $4d^{10}$). Because the ionic radius of $Ag^+$ is comparable to that of $Na^+$ ($Ag^+$ = 1.28 Å and $Na^+$ = 1.18 Å for 8-coordination), there are several isotropic or similar crystal structures between sodium- and silver-containing compounds including niobium oxides $NaNbO_3$[3] and $AgNbO_3$[4] (perovskite structure), copper oxides $NaCuO_2$[5] and $AgCuO_2$[6] (crednerite structure), vanadium oxides $\beta$-$Na_{0.33}V_2O_5$ and $\beta$-$Ag_{0.33}V_2O_5$[7] ($\beta$-vanadium bronze), and so forth.

On the other hand, a few compounds with Ag ions in oxidation states higher than +1 are known, such as $Ag_2O_2$ ($Ag^+Ag^{3+}O_2$),[8] $Ag_2O_3$ ($Ag^{3+}{}_2O_3$),[9] $Ag_3O_4$ ($Ag^{2+}Ag^{3+}{}_2O_4$),[10] and $AgCuO_2$ ($Ag^{(1+x)+}$ $Cu^{(2+y)+}O_2$).[11] For $AgCuO_2$, the electronic structure and physical properties are quite different from those for the isostructural $NaCuO_2$: $NaCuO_2$ ($Na^+Cu^{3+}O_2$) behaves as an insulator because of localization of the valence electrons,[12] while in $AgCuO_2$, the valence electrons of silver and copper in mixed oxidation states are delocalized, instead of $Ag^+$ and $Cu^{3+}$, resulting in high electrical conductivity.[11]

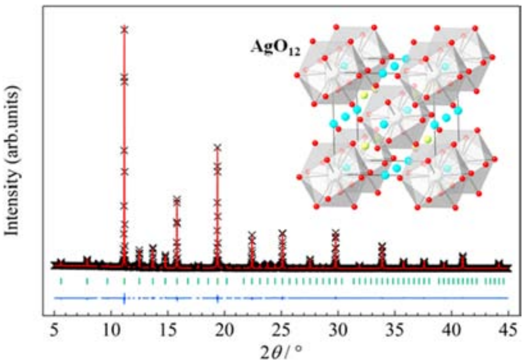

**Figure 1.** Rietveld refinement of the room-temperature SXRD pattern ($\lambda$ = 0.49941 Å) for $AgCu_3V_4O_{12}$, showing the observed (crosses), calculated (solid line), and difference (bottom line) profiles. The ticks indicate the Bragg reflection positions of $AgCu_3V_4O_{12}$. Inset: Refined crystal structure of $AgCu_3V_4O_{12}$ with $AgO_{12}$ icosahedra.

In this study, we focus on A-site-ordered perovskite oxides $AA'_3B_4O_{12}$. Many compounds in this family crystallize in an enlarged cubic $2a_p \times 2a_p \times 2a_p$ unit cell (space group $Im\bar{3}$) relative to its archetype with a lattice constant $a_p$ (see the inset of Figure 1). In $AA'_3B_4O_{12}$, three-quarters of the A sites (=A′ sites) are occupied by 3d transition metals, inducing a notable magnitude of $BO_6$ octahedral tilt to generate the pseudosquare $A'O_4$ configuration suitable for Jahn−Teller active ions such as $Cu^{2+}$ and $Mn^{3+}$. The remaining one-quarter of A sites is surrounded by 12 $O^{2-}$ ions, forming a regular icosahedron, which is typically filled with large cations such as alkali-metal, alkaline-earth-metal, and lanthanide ions similarly to simple

**Received:** October 11, 2013
**Published:** December 5, 2013

dx.doi.org/10.1021/ic402579v | *Inorg. Chem.* 2013, 52, 13824−13826

perovskite oxides. Although A-site-ordered perovskites with $Na^+$ occupying the 12-coordinated A sites have been reported such as $NaMn_7O_{12}$,[13] $NaCu_3V_4O_{12}$,[14] $NaCu_3Ru_4O_{12}$,[15] and so forth, no information is available on the existence of the silver analogues $AgA'_3B_4O_{12}$ until now. In this Communication, we report the synthesis and crystal and electronic structures of a novel A-site-ordered perovskite, $AgCu_3V_4O_{12}$, in which Ag ions occupy the 12-coordinated A sites to form regular icosahedra and are present as the mixed-valence state.

Polycrystalline $AgCu_3V_4O_{12}$ was synthesized by the solid-state reaction at 15 GPa and 1373 K. The experimental details including material synthesis and structural characterization are described in the Supporting Information, section 1. Figure 1 shows the room-temperature synchrotron powder X-ray diffraction (SXRD) pattern of $AgCu_3V_4O_{12}$ and the results of analysis by the Rietveld method. A few weak diffraction peaks from unidentified impurity phases were detected, but their amount was assumed to be a few weight percent. Rietveld refinement of the SXRD data for the main phase was performed by assuming as an initial model the structure in the space group $Im\overline{3}$ (No. 204) with Ag on 2*a* (0, 0, 0), Cu on 6*b* (0, $^1/_2$, $^1/_2$), V on 8*c* ($^1/_4$, $^1/_4$, $^1/_4$), and O on 24*g* (*x*, *y*, 0). Because no apparent vacancy was observed at any sites, the occupation factor ($g$) was constrained to unity. A good fit was obtained with the stoichiometric composition model (reliability factors $R_{wp}$ = 3.931% and $R_B$ = 2.626%; goodness of fit $S_{fit}$ = 0.8098). The refined crystal structure of $AgCu_3V_4O_{12}$ is illustrated in the inset of Figure 1, and the final structural parameters and selected bond lengths are listed in Table 1.

**Table 1. Rietveld Refinement Results and Selected Bond Distances of $AgCu_3V_4O_{12}$ at Room Temperature[a]**

| atom | site | $g$[b] | $U_{iso}/10^{-2}$ Å$^2$ | M−O/Å | BVS[c] |
|---|---|---|---|---|---|
| Ag | 2*a* | 1 | 0.93(4) | 2.635(2) × 12 | 1.33 |
| Cu | 6*b* | 1 | 0.454(18) | 1.9565(15) × 4 | 2.16 |
| V | 8*c* | 1 | 0.411(13) | 1.9216(5) × 6 | 4.16 |
| O | 24*g* | 1 | 0.21(4) | | |

[a] Space group: $Im\overline{3}$ (No. 204); $a$ = 7.27904(7) Å; atom positions Ag (0, 0, 0), Cu (0, $^1/_2$, $^1/_2$), V ($^1/_4$, $^1/_4$, $^1/_4$), and O (0.3088(3), 0.1889(3), 0); $R_{wp}$ = 3.931%, $R_B$ = 2.626%, and $S_{fit}$ = 0.8098. [b] The site occupancy $g$ for all sites was fixed to 1. [c] The bond valence sum (BVS)[16] was calculated using the following parameters: $b_0$ = 0.37 for all atoms, $r_0$ = 1.805 for $Ag^+$, $r_0$ = 1.679 for $Cu^{2+}$, and $r_0$ = 1.784 for $V^{4+}$.

$AgCu_3V_4O_{12}$ is a new member of the $AA'_3B_4O_{12}$-type perovskite family, and the Ag ions occupy the 12-coordinated regular icosahedral sites. The crystal structure with high-coordinated Ag ions has been scarcely observed except for the cubic phase of the simple perovskite $AgNbO_3$ at 873 K (space group $Pm\overline{3}m$), in which Ag ions occupy 12-coordinated regular cuboctahedral sites.[4] In the case of $AgNbO_3$, however, the crystal structure transforms into the orthorhombic perovskite (space group $Pmc2_1$) under ambient conditions because of $NbO_6$ tilting accompanied by a decrease in the coordination number of Ag ions to 8. To the best of our knowledge, $AgCu_3V_4O_{12}$ is the first compound in which Ag ions occupy 12-coordinated sites even under ambient conditions.

In $AgCu_3V_4O_{12}$, assignment of the formal oxidation states of three valence-variable transition metals is challenging. Because each oxygen is considered to be an $O^{2-}$ anion, the combined oxidation states of the three cations must be +24 to maintain charge neutrality. The bond valence sums (BVSs)[16] of silver, copper, and vanadium calculated from the structural parameters in Table 1 are +1.33, +2.16, +4.16, respectively, and the total of the BVS values is +24.45, close to the total cation charge expected from charge-balance consideration. This implies that $AgCu_3V_4O_{12}$ contains predominantly $Ag^+$, $Cu^{2+}$, and $V^{4+}$ ions, but some or all of the constituent cations are partially oxidized for charge balance. In the case of isostructural $ACu_3V_4O_{12}$ (A = Na, Ca, and Y), each of the Cu and V ions is present as the mixed-valence state, and the A-site substitution induces electron doping to modulate the charge distributions of the two cations at the A′ and B sites.[17]

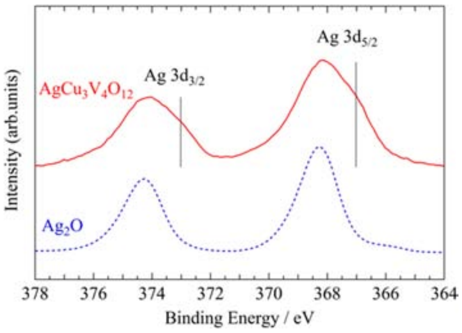

**Figure 2.** Ag 3d core-level XPS spectra of $AgCu_3V_4O_{12}$ and $Ag_2O$ at room temperature. The energy positions of the shoulder components relative to the main ones in the Ag $3d_{5/2}$ and $3d_{3/2}$ peaks for $AgCu_3V_4O_{12}$ are marked by vertical bars.

Figure 2 shows the X-ray photoelectron spectroscopy (XPS) results for Ag 3d core levels of $AgCu_3V_4O_{12}$. In the figure, the XPS results of $Ag_2O$ are also displayed for comparison. Both spectra consist of a spin−orbit coupling doublet, i.e., Ag $3d_{3/2}$ and Ag $3d_{5/2}$ peaks. The Ag $3d_{5/2}$ peak for $AgCu_3V_4O_{12}$ has one major component at ∼368 eV and a shoulder component at ∼367 eV. The major component of 368 eV corresponds to the binding energy of the Ag $3d_{5/2}$ peak for $Ag_2O$, and the shoulder component of 367 eV is in good agreement with the binding energy of the Ag $3d_{5/2}$ peaks for mixed-valence oxides $Ag_2O_2$ ($Ag^+Ag^{3+}O_2$)[18] and $AgCuO_2$[11] as reported previously. The binding-energy shift of the 3d peak from $Ag^+$ to $Ag^{3+}$ is negative, opposite to the usual case where the higher-valence cations tend to show the higher binding energy due to the electronegativity difference. The unusual shift for silver compounds may arise from other factors such as the lattice potential and work function.[19] We can also see from Figure 2 that the full width at half-maximum of the Ag $3d_{5/2}$ peak for $AgCu_3V_4O_{12}$ (∼2.0 eV) is much broader than that for $Ag_2O$ (∼1.0 eV),[18] while it is comparable to those for $Ag_2O_2$[18] and $AgCuO_2$[11] (∼1.5−2.0 eV). Thus, we conclude that the A-site Ag ions in $AgCu_3V_4O_{12}$ adopt average valence states higher than +1, or $Ag^{(1+x)+}$ in the mixed-valence state of $Ag^+$ and $Ag^{3+}$. This is in contrast with the pure $Ag^+$ state in perovskite-type $AgNbO_3$ and $AgTaO_3$. Analysis of Cu and V 2p core-level XPS for $AgCu_3V_4O_{12}$ in comparison to those for a reference compound, $CaCu_3V_4O_{12}$, demonstrates that Cu ions are present as $Cu^{2+}$ and $Cu^{3+}$ and V ions are mainly present as $V^{4+}$ (the detailed results are described in the Supporting Information, section 3 and Figure S1). From XPS analysis and BVS calculations, a plausible ionic model is described as $Ag^{(1+x)+}Cu^{(2+y)+}{}_3V^{(4+z)+}{}_4O_{12}$ ($x$ ∼ 0.3, $y$ ∼ 0.2, and $z$ ∼ 0.1).

Figure 3 shows the temperature dependence of the electric resistivity of $AgCu_3V_4O_{12}$. The low resistivity value ($\rho < 20$ m$\Omega$·cm) and positive slope ($d\rho/dT > 0$) are observed over the entire temperature range of measurement (2 K < $T$ < 300 K), indicating that $AgCu_3V_4O_{12}$ is metallic. To gain further insight into the electrical properties of $AgCu_3V_4O_{12}$, we performed electronic structure calculations (the computational details are described in the Supporting Information, section 2). The electronic density of states (DOS) of $AgCu_3V_4O_{12}$, as shown in Figure 4, clearly indicate its metallic behavior. The DOS at the Fermi level ($E_F$) consist of the Cu and V 3d and O 2p states. In the isostructural $ACu_3V_4O_{12}$ (A = Na, Ca, and Y), the Cu and V 3d electrons are delocalized to cause metallic conduction.[17] A similar behavior is expected for $AgCu_3V_4O_{12}$. In contrast to $ACu_3V_4O_{12}$ (A = Na, Ca, and Y), the Ag 4d states compose the DOS near $E_F$ (see the inset of Figure 4), implying their contribution to metallic conduction through hybridization with the O 2p states. This scenario is consistent with the presence of silver in the mixed-valence state, as demonstrated by BVS values greater than 1 and XPS analysis of the Ag 3d core levels. These results suggest that chemical substitution of the A sites with transition-metal ions can provide a versatile route for modifying the electronic structures in perovskite oxides.

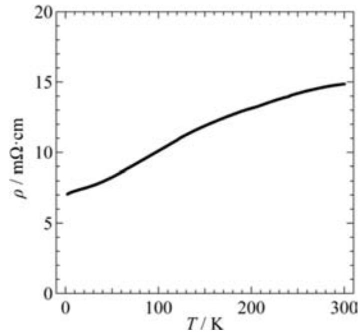

**Figure 3.** Temperature dependence of $\rho$ of $AgCu_3V_4O_{12}$.

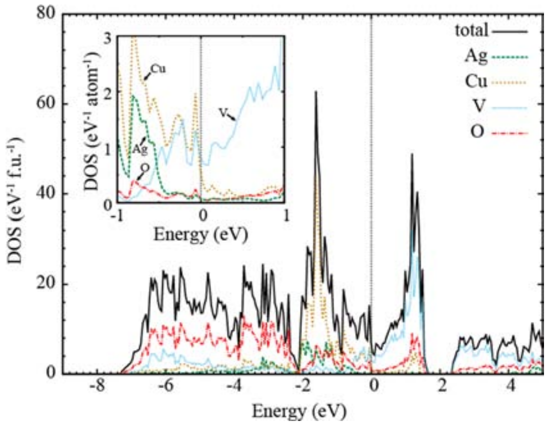

**Figure 4.** Calculated DOS for $AgCu_3V_4O_{12}$. Inset: Partial DOS near the Fermi energy.

## ■ ASSOCIATED CONTENT

### Supporting Information

Crystallographic data (CIF format), details of experiments and calculations, and Cu and V 2p core-level XPS results. This material is available free of charge via the Internet at http://pubs.acs.org.

## ■ AUTHOR INFORMATION

### Corresponding Authors

*E-mail: i-yamada@21c.osakafu-u.ac.jp.
*E-mail: fujita@dipole7.kuic.kyoto-u.ac.jp.

### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

The authors thank Isao Tanaka for his support in the electronic structure calculations. The synchrotron radiation experiments were performed at SPring-8 with approval of the Japan Synchrotron Radiation Research Institute (Proposal Nos. 2010B1667 and 2013A1683).

## ■ REFERENCES

(1) Fu, D.; Endo, M.; Taniguchi, H.; Taniyama, T.; Itoh, M. *Appl. Phys. Lett.* **2007**, *90*, 252907.
(2) Soon, H. P.; Taniguchi, H.; Itoh, M. *Appl. Phys. Lett.* **2009**, *95*, 242904.
(3) Glazer, B. A. M.; Megaw, H. D. *Acta Crystallogr., Sect. A* **1973**, *29*, 489.
(4) Sciau, P.; Kania, A.; Dkhil, B.; Suard, E.; Ratsuzna, A. *J. Phys.: Condens. Matter* **2004**, *16*, 2795.
(5) Brese, N. E.; O'Keeffe, M. *J. Solid State Chem.* **1989**, *83*, 1.
(6) Curda, J.; Klein, W.; Jansen, M. *J. Solid State Chem.* **2001**, *162*, 220.
(7) Tamauchi, T.; Ueda, Y. *Phys. Rev. B* **2008**, *77*, 104529.
(8) Jansen, M.; Fischer, P. *J. Less-Common Met.* **1988**, *137*, 123.
(9) Standke, B.; Jansen, M. *Angew. Chem.* **1985**, *97*, 114.
(10) Standke, B.; Jansen, M. *Angew. Chem.* **1986**, *98*, 78.
(11) Muñoz-Rojas, D.; Córdoba, R.; Fernández-Pacheco, A.; Teresa, J. M. D.; Sauthier, G.; Fraxedas, J.; Walton, R. I.; Casañ-Pastor, N. *Inorg. Chem.* **2010**, *49*, 10977.
(12) Mizokawa, T.; Namatame, H.; Fujimori, A.; Akeyama, K.; Kondoh, H.; Kuroda, H.; Kosugi, N. *Phys. Rev. Lett.* **1991**, *67*, 1638.
(13) Marezio, M.; Dernier, P. D.; Chenavas, J.; Joubert, J. C. *J. Solid State Chem.* **1973**, *6*, 16.
(14) Kadyrova, N. I.; Zakharova, G. S.; Zainulin, Y. G.; Volkov, V. L.; D'yachkova, T. V.; Tyutynnik, A. P.; Zubkov, V. G. *Dokl. Chem.* **2003**, *392*, 251.
(15) Tanaka, S.; Shimazui, N.; Takatsu, H.; Yonezawa, S.; Maeno, Y. *J. Phys. Soc. Jpn.* **2009**, *78*, 024706.
(16) Brown, I. D.; Altermatt, D. *Acta Crystallogr., Sect. B* **1985**, *41*, 244.
(17) Shiraki, H.; Saito, T.; Azuma, M.; Shimakawa, Y. *J. Phys. Soc. Jpn.* **2008**, *77*, 064705.
(18) Hoflund, G. B.; Hazos, Z. F.; Salatia, G. N. *Phys. Rev. B* **2000**, *62*, 11126.
(19) Gaarenstroom, S. W.; Winograd, N. *J. Chem. Phys.* **1977**, *67*, 3500.