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Superconducting Double Perovskite Bismuth Oxide Prepared by a Low-Temperature Hydrothermal Reaction

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Abstract: *Perovskite-type structures (ABO_3) have received significant attention because of their crystallographic aspects and physical properties, but there has been no clear evidence of a superconductor with a double-perovskite-type structure, whose different elements occupy A and/or B sites in ordered ways. In this report, hydrothermal synthesis at 220 °C produced a new superconductor with an A-site-ordered double perovskite structure, $(Na_{0.25}K_{0.45})(Ba_{1.00})_3(Bi_{1.00})_4O_{12}$, with a maximum T_c of about 27 K.*

The perovskite structure, ABO_3, and its derivatives have received significant attention because the structure can accommodate various metals with a wide range of valence and ionic radii. This has increased interest in the crystallographic aspects and physical properties of the perovskite structures. However, there is no clear evidence of a superconductor with a double-perovskite-type structure, whose different elements occupy A and/or B sites in ordered ways. After the cuprates, the fabrication of a perovskite superconductor family with the next highest transition temperature (T_c) is based on the bismuthates, $BaBiO_3$.[1] Superconductivity was first discovered in the perovskite-type $BaPb_{1-x}Bi_xO_3$ by Sleight et. al. in 1975;[2] it had a maximum T_c near 13 K. After that, by doping the semiconductive $BaBiO_3$ with K at the Ba sites, a new superconducting system, $Ba_{1-x}K_xBiO_3$ (BKBO), which showed a higher T_c (near 30 K), was reported by Cava et. al. and Matheiss et. al.[3–5] Moreover, the electronic properties of BKBO have been studied extensively to investigate metallicity at ambient conditions by several authors.[6–8] $BaBiO_3$ is a semiconductor and crystallizes in a monoclinic distorted order as a perovskite structure,[1] where the BiO_6 octahedra are tilted at a lower angle, in contrast to the 180° orientation in the perfect structure. Substituting K, Pb, and Sr atoms in the $BaBiO_3$ compound to form $Ba_{1-x}K_xBiO_3$, $Ba_{1-x}Pb_xO_3$, and $Sr_xK_{1-x}BiO_3$ causes a symmetry change, as well as the appearance of superconductivity. The noncuprate superconductor, BKBO, has a simple perovskite-type structure in which the A sites are occupied by K^+ and Ba^{2+} ions and the B sites are occupied by bismuth ions in mixed valence states with a BiO_6 octahedron. A superconductive perovskite-type oxide $(Ba_{0.75}K_{0.14}H_{0.11})BiO_3 \cdot n\,H_2O$, with $T_c = 8$ K, fabricated by hydrothermal synthesis at 180 °C has previously been reported.[9] The crystal structure of this reported compound was determined to be double perovskite whose A site has two crystallographic sites: *2a* and *6b*. The *2a* site is randomly occupied by a K atom and an H_2O molecule, and *6b* is fully occupied by a Ba atom. A Bi atom occupies one of the lattice sites (*8c*), with the BiO_6 octahedra being slightly tilted at the corner. However, its superconductivity remains obscure, as the volume fraction of this compound can be estimated to be less than 1 %. There is another report on the hydrothermal synthesis of a double perovskite with the structure $Ba_{1-x}K_xBi_{1-y}Na_yO_3$.[10] However, no crystal structural refinement was performed; it also does not show any superconducting transition, even at temperatures as low as 2 K. Therefore, detailed investigation is necessary to understand the effect of the synthesis conditions and crystal structures on the emergence of superconductivity in Bi-based double perovskite oxides.

Herein, we show a novel A-site-ordered superconductive double perovskite bismuthate, $(Na_{0.25}K_{0.45})(Ba_{1.00})_3(Bi_{1.00})_4O_{12}$, with a higher T_c (ca. 27 K); the compound was synthesized through a low-temperature hydrothermal method using $NaBiO_3 \cdot n\,H_2O$, $Ba(OH)_2 \cdot 8\,H_2O$, and KOH as starting materials. The crystal structure of this compound was determined and is shown in Figure 1. The A′ site is randomly occupied by a vacancy and both Na and K atoms, whereas the A″ site is occupied by Ba. A Bi atom fully occupies the B site and forms the network of corner-sharing BiO_6 octahedra. This report reveals the hydrothermal synthesis, magnetic and transport properties, crystal structure, and thermal behavior, as well as predicting the electronic band structure of this novel A-site-ordered double perovskite oxide, with a superconducting transition temperature up to 27 K.

XRD analysis of all the compounds synthesized using the five different molar ratios of Ba/Bi (1.00, 1.25, 1.50, 1.75, and 2.00) in the starting materials gave similar major peaks. The typical X-ray powder diffraction pattern of the hydrother-

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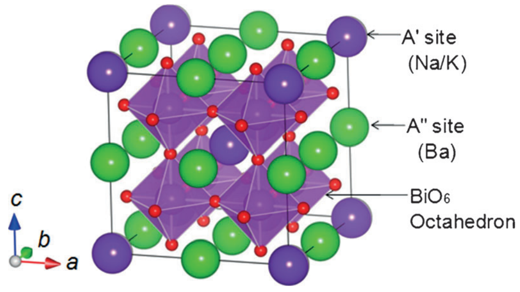

Figure 1. Crystal structure of A′A″$_3$B$_4$O$_{12}$-type perovskite. The spheres at the A′ site are for Na/K and for Ba atoms at the A″ site; they also indicate their respective positions. A network of corner-sharing BiO$_6$ octahedra is shown, with oxygen atoms are in the corner of octahedra.

mally synthesized products shows the peaks indexed with a cubic cell of $a = 8.550\ (2)$ Å with the space group $Im\bar{3}m$ (Supporting Information, Figure S1). Two small unknown impurity peaks between 26° and 28° were found for all the synthesized products.

The results of chemical analysis show that an increase in the Ba/Bi molar ratio of the starting materials increases the ratio of Ba/Bi in the final products from 0.87 to 1.24 (Table S1). The ratio of Na/Bi slightly increases from 0.08 to 0.11 as the Ba/Bi ratio increases; however, the K/Bi ratio slightly decreases from 0.15 to 0.13 when the Ba/Bi molar ratio is increased. Thus, we cannot deny the possibility that Na and/or K occupy not only the A site, but also the B site, especially for synthesized products from higher Ba/Bi molar ratios.[10] In addition, the iodometric titration results suggest that both Bi^{5+} and Bi^{3+} are present in the synthesized compounds. The average Bi valence increases from 4.35 to 4.70 with an increase in the Ba/Bi molar ratio of the starting materials.

Figure 2 shows the temperature dependence of magnetization susceptibility ($4\pi M/H$) of the hydrothermally synthesized products in zero field cooling (ZFC) mode. The susceptibility values start to drop between 13 and 27 K, except for one compound (Ba/Bi = 2.00). The transition temperature (T_c^{mag}) decreases as the molar ratio of Ba/Bi increases. Consequently, the compound with a Ba/Bi molar ratio of 1.00 exhibits the highest diamagnetic behavior, with an onset T_c^{mag} of about 27 K. The estimated shielding volume fraction of the compound with a Ba/Bi molar ratio of 1.00 is as large as roughly 60 % at 5 K. This volume fraction is an indication of the bulk superconducting nature. The smeared transition may be attributed to the inhomogeneous superconducting properties. On the other hand, the FC data for the compound with a Ba/Bi molar ratio of 1.00, which corresponds to a Meissner signal of approximately 6 % at 5 K (Figure S5), which is much lower than the ZFC data. This change may be due to vortex pinning. Thus, the double perovskite should be responsible for the appeareance of superconductivity.

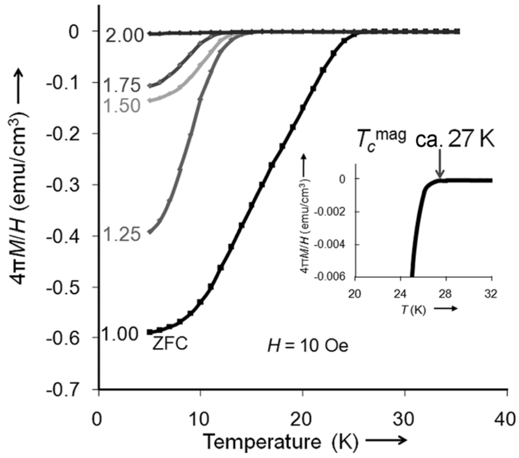

Figure 2. Temperature-dependence of DC magnetic susceptibility curves of superconducting samples prepared at different Ba/Bi molar ratios in an applied external field of 10 Oe in ZFC mode. The density of the sample was assumed (7.78 g cm^{-3}) from Rietveld refinement data. The highest diamagnetic signal appears at ca. 27 K for a compound with a Ba/Bi molar ratio of 1.00, as shown in the inset.

Figure 3 a shows the temperature dependence of electrical resistivity for a pellet of powder with a molar ratio of Ba/Bi = 1.00 pressed using a cubic-anvil-type high pressure facility (8 GPa/200 °C). The electrical resistivity increased with decreasing temperature and dropped at ca. 22 K (T_c^{onset}). Zero resistivity was observed below ca. 8 K. The broad transition between 8 and 22 K implies that the sample is inhomogeneous. With increasing magnetic field, T_c^{onset} decreased, but superconductivity persists up to 0.9 T (Figure 3 b). This behavior reveals that the synthesized compound is a type II superconductor. Zero resisitivity was detected in the sample prepared by pressing a 8 GPa, we could not find zero resistivity in the samples prepared by a uniaxial pressing or by a hot isostatic pressing as high as several tens of MPa. Heating above 400 °C led to decomposition (see below), thus it was hard to make a sintered pellet of the powder. The negative gradient of resistivity may be attributed to grain boundaries; similar phenomenon is also reported in the case of B-doped diamond, the HfNCl family, and LaO$_{1-x}$F$_x$BiS$_2$ superconductors.[11–16] The difference between T_c^{mag} and T_c^{onset} might be due to the effects of grain boundary and/or high-pressure pressing, even though we could not find a significant change in the laboratory XRD pattern (Figure S7). The

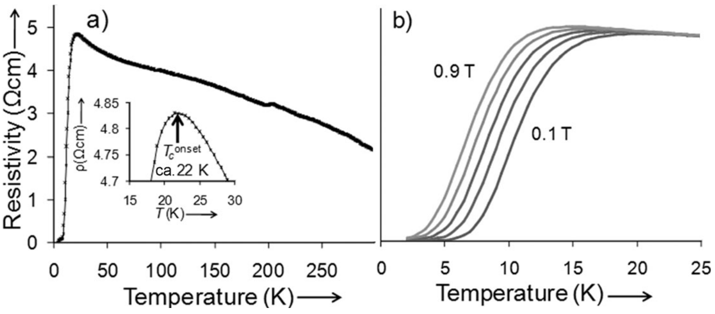

Figure 3. a) Temperature dependence of electrical resistivity $\rho(T)$ for the compound with a Ba/Bi molar ratio of 1.00; inset: the T_c^{onset} was estimated at ca. 22 K. b) Resistivity $\rho(T)$ curves for the Ba/Bi = 1.00 compound at applied fields (0.1 T–0.9 T) in intervals of 0.2 T.

reasons for the degradation of superconducting properties are still obscure. Therefore, improving the superconducting properties remains as a challenge for this double perovskite oxide.

Incorporation of Na may be important for the formation of a double perovskite structure. $Ba_{1-x}K_xBiO_3$ has a simple perovskite structure and is usually obtained via solid-state synthesis without the presence of Na in both the starting materials and final products.[3,17–19] On the other hand, the double perovskite structure was formed by hydrothermal synthesis using Na in the starting materials.[9,10] These reported double perovskites contain either H_2O or Na in the structure, which is consistent with our experimental results; Na was present in the starting materials and detected in the final products. The formation of double perovskite structures may be related to the different ionic and molecular radii of the components. The ionic radii of K^+ (149 pm) and Ba^{2+} (147 pm)[20] are comparable, which likely allows them to randomly occupy the A site and form a simple perovskite structure. Conversely, the ionic/molecular radii of Na^+ (117 pm)[20] and H_3O^+ (115 pm)[21] are different to those of K^+ and Ba^{2+}, which may restrict the random distribution and consequent formation of a simple perovskite structure. As described later, the TG analysis showed that H_2O incorporation is unlikely; therefore, incorporation of Na is the most likely reason for the formation of a double-perovskite-type structure.

We have summarized the products synthesized from different molar ratios of Ba/Bi in Table S1. The lattice parameters of all the compounds are comparable. On the other hand, T_c and the superconducting volume decrease with an increase in the bismuth valence. This suggests that the superconducting properties of the prepared samples are related to the bismuth valence and not to the lattice parameters. Another possibility is that the incorporation of Na and/or K into the B site degrades their superconductivity, as is observed in double perovskite structures of $Ba_{1-x}K_xBi_{1-y}Na_yO_3$.[10]

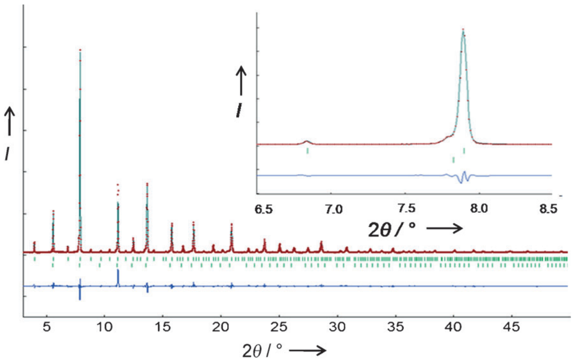

Figure 4. SXRD Rietveld refinement profile of hydrothermally synthesized product ($\lambda = 0.41336$ Å). Markers and lines indicate observed and calculated profiles, respectively. Upward and downward marks show positions of Bragg reflections for the double perovskite structure $(Na_{0.25}K_{0.45})(Ba_{1.00})_3(Bi_{1.00})_4O_{12}$), and the simple perovskite one ($BaBiO_3$). Residual errors are drawn at the bottom of figure. Inset shows an expansion between 6.5° and 8.5°, demonstrating the existence of a simple perovskite phase.

For further crystal structure investigation, we focused on the product hydrothermally synthesized with a Bi/Ba molar ratio of 1.00 in the starting materials, because such a product exhibits the highest T_c^{mag} (ca. 27 K). The existence of a double super cell is confirmed by observation of the 110 electron diffraction spots (Figure S2), which correspond well with the double-perovskite-type structure obtained from the XRD data. A detailed structural analysis of the product was carried out by Rietveld analysis using the SXRD data (Figure 4). The compound peaks have been indexed as an $A'A''_3B_4O_{12}$ double-perovskite-type structure with the $Im\bar{3}m$ space group, as shown in Figure 1. We observed shoulders on the peaks, which could be indicative of a simple perovskite structure. Accordingly, we assumed the existence of a simple perovskite bismuth oxide, comparable to hydrothermally synthesized cubic $Ba_{0.96}Bi_{0.86}O_{2.59}(OH)_{0.41}$,[22] as a second phase. Thus, the refinement was performed considering the two-phase model. The chemical composition of the double perovskite can be formulated as $(Na_{0.25}K_{0.45})(Ba_{1.00})_3(Bi_{1.00})_4O_{12}$. The total chemical composition calculated from this mixed model of double and simple perovskite-type structures (Bi/Ba/K/Na = 1.00:0.83:0.09:0.05) is close to the chemical analysis results (Bi/Ba/K/Na = 1.00:0.87:0.15:0.08) described in above. Moreover, the average bismuth valence of this compound from Rietveld refinement is determined to be about 4.36, which is very close to the value of the bismuth valence (4.35) determined by chemical analysis. These deviations may be due to either the small impurity peaks or different occupation possibilities of the *2a* site.

Next, we examined the thermal stability of the hydrothermally synthesized product with a starting Ba/Bi molar ratio of 1.00. No significant mass change was observed below 400 °C, but a total mass change of −1.9 % from 450 to 700 °C was found (Figure S3). The mass spectrometry data indicated that O_2 was the corresponding gas evolved in the temperature range 450–700 °C. Whereas the average valence of Bi in the sample heated to 400 °C (4.39) is close to that of the unheated sample, the valence of the sample heated to 600 °C decreases to 4.00. Therefore, the mass loss is caused by the release of O_2 molecules accompanied by the reduction of Bi^{5+} to Bi^{3+}. No significant peaks corresponding to the weight losses of H_2O, H_2, and CO_2 were found. Furthermore, the absence of any H_2O and OH groups were also confirmed by the FT-IR spectrum of the unheated sample (Figure S4).

High-temperature synchrotron X-ray powder diffraction patterns were collected to investigate the structural change for this prepared sample. The double perovskite structure is retained up to 400 °C (Figure S9). The sample heated to 600 °C has a simple cubic perovskite-type cell with $a = 4.3561(9)$ Å. The lattice parameter of the unit cell ($2a \times 2a \times 2a$) is $a = 8.7122$ Å, which is 1.87 % longer than that of the sample heated to 400 °C. This change is probably not only related to the thermal expansion, but also to the reduction of Bi (Bi^{5+} to Bi^{3+}) and O_2 evolution. Importantly, a sample heated to 400 °C showed superconductive transition similar to that of the sample before heat treatment (Figure S6). On the other hand, a sample heated to 600 °C no longer exhibits superconducting behavior. Therefore, heat treatment above

400 °C involves the reduction of Bi with the evolution of oxygen, phase transition from double perovskite to a simple perovskite structure, and loss of superconductivity. These results indicate that the synthesized double perovskite oxide with superconductivity is only obtained by a low-temperature reaction. This is different from simple perovskite compounds,[19] which were synthesized by solid-state reactions at approximately 500 °C. In contrast to our hydrothermally synthesized double perovskite oxides, the heat treatment of simple perovskite oxides does not cause phase transition and loss of superconductivity.

The compounds treated hydrothermally resulted in superconducting double perovskite structures. However, previous reports on the preparation of double perovskite compounds, $Ba_{1-x}K_xBi_{1-y}Na_yO_3$, by a hydrothermal reaction at 180 °C did not show any superconductivity.[10] For this report, no description of the bismuth valence in the product was reported. Another report describes the synthesis of a similar double-perovskite-type bismuthate at 180 °C with a lattice parameter of 8.5444 (3) Å.[9] Upon heating, it released H_2O and increased T_c from 8 to 15 K.[9] For the samples, bismuth valences of ca. 4.22–4.27 are reported.[9] Both compounds from the previous reports are synthesized at 180 °C, which is lower than the synthesis temperature of our prepared samples. Accordingly, the synthesis temperature may be an essential factor for the improvement of superconductivity.

We examined the relationship between the bismuth valence and T_c^{mag} in simple and double perovskite products (Figure 5). The highest T_c^{mag} (ca. 27 K) in this report appears at a bismuth valence of ca. 4.35–4.40 and further increased in the bismuth valence decreases T_c in double perovskite oxides (Figure 5 a). From Figure 5 b, it is also observed that a simple perovskite compound, $Ba_{1-x}K_xBiO_{3-\delta}$, becomes superconducting when the bismuth valence is higher than 4.2, with the highest T_c^{mag} appearing at a bismuth valence of ca. 4.3–4.4.[19] The trend observed between the bismuth valence and superconductivity in double perovskite compounds is similar to that observed in simple perovskite compounds. Therefore, even though ordering of A sites in the double perovskite structure differs from that of the simple perovskite structures, the bismuth valence and related carrier concentration are important factors for the appearance and control of superconductivity. Finally, we focused the calculated band structures of simple perovskite $Ba_{0.6}K_{0.4}BiO_3$ (BKBO) and our synthesized double perovskite $(Na_{0.25}K_{0.45})(Ba_{1.00})_3(Bi_{1.00})_4O_{12}$ compounds, as shown in Figure 6. The band structures reveal metallic character with dispersion bands crossing the Fermi level (E_F) for both structures. The bands crossing the Fermi level show strong hybridization between the Bi 6*s* and O 2*p* orbitals. In both structures, the O 2*p* contribution is higher than the Bi 6*s* one (Figure S8). Reportedly, the Bi 6*s* band is less than half filled at $Bi^{+4.4}$ in $Ba_{0.6}K_{0.4}BiO_3$.[6,7] A similar phenomenon is observed in our synthesized double perovskite structure where maximum carriers are generated at $Bi^{+4.39}$ (Figure 5 a) to form a less than half filled Bi 6*s* band. This supports the experimental finding of the relationship between the carrier concentration and T_c^{mag} of this double perovskite oxide, and this partially filled Bi 6*s* band confirms the metallic properties. As described above, the resistivity measurement shows that the synthesized double perovskite compound is semimetallic. This discrepancy may be due to the effects of grain boundary and/or high-pressure pressing.

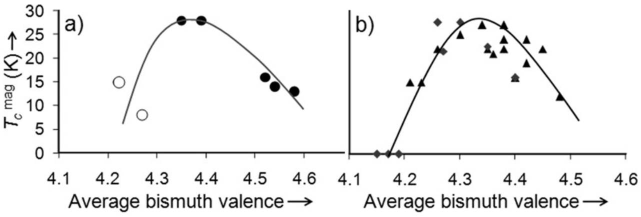

Figure 5. Dependencies of T_c^{mag} on average bismuth valence. a) For our double perovskite products (full circles) and for the reported double-perovskite-type bismuthate[9] (open circles). b) For a simple perovskite compound[19] (triangles) and another simple perovskite,[23] where no oxygen deficiency was assumed (diamonds).

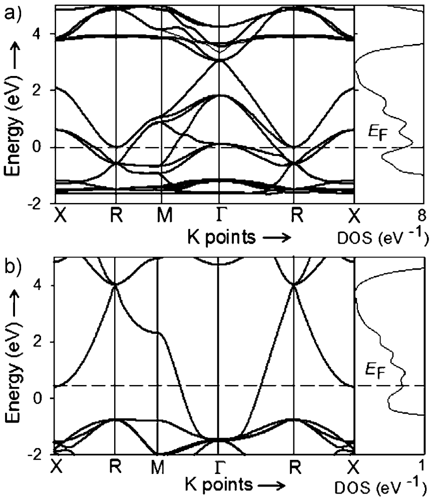

Figure 6. The calculated electronic band structure and atom-projected DOS for a) $(Na_{0.25}K_{0.45})(Ba_{1.00})_3(Bi_{1.00})_4O_{12}$ double perovskite and b) $Ba_{0.6}K_{0.4}BiO_3$ simple perovskite under ambient conditions.

In summary, a new A-site-ordered double-perovskite-type superconducting material $(Na_{0.25}K_{0.45})(Ba_{1.00})_3(Bi_{1.00})_4O_{12}$, with a maximum T_c^{mag} of ca. 27 K, was prepared by a facile hydrothermal reaction at 220 °C. To the best of our knowledge, this compound is the first example of double perovskite structures with a large superconducting shielding volume fraction (ca. 60 %) and zero resistivity. The starting materials, especially the molar ratio of Ba/Bi and the synthesis temperature of the hydrothermal reaction, are keys for fabricating products with superconducting properties. The thermal behavior reveals that the double-perovskite-type structure and superconductivity are retained up to 400 °C. Moreover, the superconductive properties of this compound are strongly related to the average bismuth valence. The highest T_c^{mag} (ca. 27 K) in this compound is found at a bismuth valence of ca. 4.35–4.39. Therefore, the bismuth valence and related carrier concentrations are the important factors for the appearance of superconductivity in this family of compounds. Furthermore, electronic band structure calculations confirm the metallic behavior of this synthesized double perovskite oxide.

We expect that this hydrothermal method will produce additional new superconductors.

Experimental Section

Hydrothermal synthesis was performed with a Teflon-lined autoclave (70 mL). The starting materials, $NaBiO_3{\cdot}n\,H_2O$, $Ba(OH)_2{\cdot}8H_2O$, and KOH, were combined and the autoclave was heated to 220°C. The resulting solid products were washed repeatedly with distilled water. The final black product was dried at 70°C.

The phase of the product was examined by X-ray powder diffraction (XRD) and transmission electron microscopy (TEM). The synchrotron X-ray powder diffraction (SXRD) was collected using a Debye–Scherrer camera installed at the BL02B2 powder diffraction beam line at SPring-8 with approval of the Japan Synchrotron Radiation Research Institute (JASRI: Proposal No. 2013A1299). Crystal structure refinement was performed using the Rietveld program RIETAN-FP.[24] The crystal structure was drawn with VESTA.[25] The thermal stability was investigated by thermogravimetric analysis (TGA) and mass spectrometry. The absence of OH groups was also confirmed by FT-IR spectra. Elemental analysis was carried out using inductively coupled plasma (ICP), atomic absorption spectroscopy (AAS) and iodometric titration using an automatic titrator (TOA DKK AUT-701). The temperature dependence of the DC magnetic susceptibility was measured using either a superconducting quantum interference device magnetometer (MPMS-5S, Quantum Design) or a vibrating sample magnetometer (PPMS, Quantum Design). The electrical resistivity measurement was carried out between 2 and 300 K using a standard four-probe method (PPMS, Quantum Design). The electronic band structure calculations were performed using the CASTEP code[26] in the framework of density functional theory (DFT) with generalized gradient approximations (GGA) and the Perdew–Burke–Ernzerhof (PBE) exchange correlation functional.[27]

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[1] B. A. Baumert, *J. Supercond.* **1995**, *8*, 175–181.
[2] A. W. Sleight, J. L. Gillson, P. E. Birstedt, *Solid State Commun.* **1975**, *17*, 27–28.
[3] R. J. Cava, B. Batlogg, J. J. Krajewski, R. Farrow, L. W. Rupp, A. E. White, K. Short, W. F. Peck, T. Kometani, *Nature* **1988**, *332*, 814–816.
[4] L. F. Mattheiss, D. R. Hamann, *Phys. Rev. Lett.* **1988**, *60*, 2681–2684.
[5] R. J. Cava, B. Batlogg, G. P. Espinosa, A. P. Ramirez, J. Krajewskij, W. F. Peck, Jr., W. Ruppl, Jr., S. Cooper, *Nature* **1989**, *339*, 291–293.
[6] D. Jung, E.-K. Choi, *Bull. Korean Chem. Soc.* **1999**, *20*, 1045–1048.
[7] V. Meregalli, S. Y. Savrasov, *Phys. Rev. B* **1998**, *57*, 14453–14469.
[8] M. Shirai, N. Suzuki, K. Motizuki, *J. Phys. Condens. Matter* **1990**, *2*, 3553.
[9] H. Jiang, N. Kumada, Y. Yonesaki, T. Takei, N. Kinomura, M. Yashima, M. Azuma, K. Oka, Y. Shimakawa, *Jpn. J. Appl. Phys.* **2009**, *48*, 010216–010218.
[10] G. Zhang, G. Li, F. Huang, F. Liao, K. Li, Y. Wang, J. Lin, *J. Alloys Compd.* **2011**, *509*, 9804–9808.
[11] Y. Mizuguchi, S. Demura, K. Deguchi, Y. Takano, H. Fujihisa, Y. Gotoh, H. Izawa, O. Miura, *J. Phys. Soc. Jpn.* **2012**, *81*, 114725–114729.
[12] E. A. Ekimov, V. A. Sidorov, E. D. Bauer, N. N. Mel'nik, N. J. Curro, J. D. Thompson, S. M. Stishov, *Nature* **2004**, *428*, 542–545.
[13] Y. Takano, M. Nagao, I. Sakaguchi, M. Tachiki, T. Hatano, K. Kobayashi, H. Umezawa, H. Kawarada, *Appl. Phys. Lett.* **2004**, *85*, 2851–2853.
[14] S. Yamanaka, K. Hotehama, H. Kawaji, *Nature* **1998**, *392*, 580–582.
[15] H. Kawaji, K. Hotehama, S. Yamanaka, *Chem. Mater.* **1997**, *9*, 2127–2130.
[16] T. Ito, Y. Fudamoto, A. Fukaya, I. M. Gat-Malureanu, M. I. Larkin, P. L. Russo, A. Savici, Y. J. Uemura, K. Groves, R. Breslow, K. Hotehama, S. Yamanaka, P. Kyriakou, M. Rovers, G. M. Luke, K. M. Kojima, *Phys. Rev. B* **2004**, *69*, 134522–134534.
[17] K. Hyun-Tak, K. Kwang-Yong, K. Won-Jeong, *J. Korean Phys. Soc.* **2001**, *39*, 1013–1018.
[18] Y. Idemoto, Y. Iwata, K. Fueki, *Phys. C* **1994**, *222*, 257–266.
[19] Y. Idemoto, Y. Iwata, K. Fueki, *Phys. C* **1992**, *201*, 43–49.
[20] R. D. Shannon, *Acta Crystallogr. Sect. A* **1976**, *32*, 751–767.
[21] B. E. Conway, *Ionic hydration in chemistry and biophysics*, Elsevier Publ. Co., Amsterdam, **1981**, pp. 312.
[22] H. Jiang, N. Kumada, Y. Yonesaki, T. Takei, N. Kinomura, *J. Ceram. Soc. Jpn.* **2009**, *117*, 214–216.
[23] D. G. Hinks, B. Dabrowski, J. D. Jorgensen, A. W. Mitchell, D. R. Richards, S. Pei, D. Shi, *Nature* **1988**, *333*, 836–838.
[24] F. Izumi, K. Momma, *Solid State Phenom.* **2007**, *130*, 15–20.
[25] K. Momma, F. Izumi, *J. Appl. Crystallogr.* **2008**, *41*, 653–658.
[26] S. J. Clark, M. D. Segall, C. J. Pickard, P. J. Hasnip, M. I. J. Probert, K. Refson, M. C. Payne, *Z. Kristallogr.* **2005**, *220*, 567–570.
[27] J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **1996**, *77*, 3865–3868.