

Differences of Structural and Electronic Properties in $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ ($x=0, 0.04, \text{ and } 0.4$)

Dongwoon Jung* and Eun-Kuk Choi

Department of Chemistry, Wonkwang University, Iksan, Jeon-Buk 570-749, Korea

Received June 23, 1999

Electronic structures calculated based upon the extended Huckel tight-binding method for $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ with $x = 0, 0.04, \text{ and } 0.4$ are reported. It is noticed that the commensurate ordering of Bi^{3+} and Bi^{5-} is responsible for the insulating and semiconducting behavior in BaBiO_3 and $\text{Ba}_{0.96}\text{K}_{0.04}\text{BiO}_3$. The band gaps of 3.2 eV and 1.4 eV for the former and the latter compounds, respectively, are consistent with the experimental results. Doping in Bi 6s-block band up to $x = 0.4$ causes the collapse of the ordering of Bi^{3-} and Bi^{5+} , thereby resulting in the superconductivity in the $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$ compound. Strikingly, the character of oxygen contributes to the conducting mechanism than that of the bismuth. This is quite different from the cuprate superconductors in which the character of copper dominates that of oxygen.

Introduction

The recent growth of interest in the copper-free superconductors is due to, in part, no further progress of raising the superconducting transition temperature during a past decade and limitations to apply for many electronic and electric devices in the copper-oxide high- T_c superconductors. In addition, the non-cuprate materials are attractive to many scientists since these materials may provide clues to understand the roles of the phonon-electron interactions in the microscopic pairing mechanism of high- T_c superconductors. As a consequence of the effort to discover the non-cuprate superconductors, the quaternary and ternary intermetallic compounds, such as $\text{LnLi}_2\text{B}_2\text{C}$ ($T_c = 16.6$ K),¹ $\text{YPd}_3\text{B}_3\text{C}_{0.3}$ ($T_c = 23$ K),² and lanthanum nickel boro-nitride ($T_c = 13$ K)³ were synthesized. Before the success of preparations of those three compounds, alkali metal doped fullerides, A_3C_{60} ($\text{A}_3 = \text{Na}_2\text{Cs}, \text{K}_3, \text{Rb}_3, \text{K}_2\text{Rb}, \text{Rb}_2\text{K}, \text{ and } \text{Rb}_2\text{Cs}$) were found to be superconducting with the T_c up to 31 K when $\text{A}_3 = \text{Rb}_2\text{Cs}$.⁴⁻¹¹ The T_c 's of these non-cuprate compounds are similar to or lower than that of $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ which was synthesized just after the discovery of high- T_c copper-oxide superconductors.¹²

$\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ is originated from the insulating BaBiO_3 compound. When Scholder *et al.* first synthesized BaBiO_3 ¹³ whose structure was closely related to that of perovskite, the substantial interest in this compound was made on the oxidation state of Bi. Upon the formal charges of Ba^{2+} and O^{2-} , the oxidation state of Bi is +4 which indicates that the electronic structure of Bi is $6s^1$ at the ground state. However, Scholder *et al.* assumed that the oxidation state of Bi was not Bi^{4+} but the mixture of Bi^{3+} and Bi^{5+} which were known to exist in many bismuth oxides. A similar opinion was proposed by Nakamura *et al.*¹⁴ that the oxidation states of Bi in the compound were either $\text{Ba}_2(\text{Bi}^{3+}\text{Bi}^{5+})\text{O}_6$ or the "filled Bi^{4+} band". On the other hand, de Hair and Blasse resolved the oxidation state of Bi by using infrared spectroscopy and concluded that Bi favored Bi^{3+} in the BaBiO_3 compound.¹⁵ Cox and

Sleight refined the structure of the compound with the use of neutron diffraction powder data.¹⁶ Analyzing the inequivalent Bi-O bond distances found in BaBiO_3 , they concluded that the compound consisted of Bi^{3+} and Bi^{5+} in equal amount rather than Bi^{4+} , and the Bi^{3+} and Bi^{5+} cations took on an ordered arrangement. The insulating property found in BaBiO_3 was supposed to be the result of a commensurate charge-density-wave (CDW) involving the ordering of Bi^{3+} and Bi^{5+} into distinct crystallographic sites.

Superconductivity was found in the perovskite-type $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$ by Sleight *et al.*¹⁷ which exhibited superconducting transition temperature varying from 0.45 K when $x = 0$ to 13 K when $x = 0.25$. The substitution of Bi with Pb results in the collapse of commensurate ordering made by Bi^{3+} and Bi^{5+} and consequently the compound becomes metallic (superconducting). When x became larger than 0.25 it showed semiconducting property. Likewise BaBiO_3 , the semiconducting behavior was thought to be the reason why Bi^{3+} and Bi^{5+} are ordered as the amount of Bi increases. In spite of having the low T_c , the discovery of superconductivity in the substituted BaBiO_3 compound encouraged to investigate the analogues of this system.

The success to synthesize the $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ system was motivated by the idea that an appropriate doping method might suppress the semiconducting property associated with the commensurate CDW found in BaBiO_3 and create a metallic (and superconducting) compound. The oxidation state of Bi in $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ is $4 + x$. As x increases the number of holes in the Bi 6s band increase. Superconducting state can be achieved when the balanced ordering of Bi^{3+} and Bi^{5+} is broken as x increases in this compound. Schneemeyer *et al.* reported¹⁸ the growth and structural characterization of single crystals of $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ when $x = 0, 0.04, \text{ and } 0.4$. The compound becomes superconducting when $x = 0.4$ with the T_c of 30.5 K. So far no systematic study on this compound with various x values has been made. It is important, therefore, to investigate the differences of structural and electronic properties between insulating (*i.e.*, $x = 0$), semi-

conducting (*i.e.*, $x = 0.04$), and superconducting (*i.e.*, $x = 0.4$) compounds. In this paper, electronic structures calculated based upon the extended Hückel tight-binding method¹⁹ for $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ with $x = 0, 0.04$, and 0.4 are reported.

Structure. The structure of the BaBiO_3 at room temperature is monoclinic which is made up of distorted perovskite units. In this compound, two different BiO_6 octahedra are connected alternatively by edge-sharing mode along the crystallographic *a*- and *c*-directions, as shown in Figure 1(a). One octahedron is tilted from the vertical *c*-axis and the next one is tilted in opposite direction to construct a zigzag structure with the angle of 159.9° (see Figure 1(a)). The Bi-O distances in one octahedron are 2.15 Å and 2.13 Å for axial and equatorial, respectively and those in the next octahedron are 2.25 Å and 2.27 Å, respectively. It was speculated that the short and long Bi-O distances indicate the charge disproportionation occurred in the way that $2\text{Bi}^{4+} \rightarrow \text{Bi}^{3+} + \text{Bi}^{5+}$, which results in the insulating property in this compound.

The structure of $\text{Ba}_{0.96}\text{K}_{0.04}\text{BiO}_3$ is similar to that of the pristine BaBiO_3 in that two different octahedra are connected alternatively along the *a*- and *c*-directions. Any octahedron is not tilted from the vertical *c*-axis in this compound, however, so that the axis line to connect the octahedra along the *c*-direction is straight. The Bi-O bond distances in an octahedron are 2.22 Å and 2.11 Å for axial and equatorial, respectively, and 2.11 Å and 2.23 Å, respectively in the next octahedron. Two short and four long Bi-O bonds construct the first octahedron, while two long and four short ones are the components of the next. In $\text{Ba}_{0.96}\text{K}_{0.04}\text{BiO}_3$ compound, therefore, two environmentally different Bi are still alternatively ordered as in the case of BaBiO_3 . This ordering is consistent with the fact that the compound exhibited semi-conducting property. Because of the existence of two structurally different octahedra, the unit cells of BaBiO_3 and $\text{Ba}_{0.96}\text{K}_{0.04}\text{BiO}_3$ consist of four octahedra as shown in Figure 1. Further substitution for Ba by K in $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ results in the cubic structure in which each unit cell is made up of one octahedron when $x = 0.4$ (*i.e.*, all octahedra are identical). The Bi-O distance in the BiO_6 octahedron in this compound is 2.1435 Å for both axial and equatorial bonds.

Results and Discussion

The Bi 6s-block bands of BaBiO_3 , $\text{Ba}_{0.96}\text{K}_{0.04}\text{BiO}_3$, and

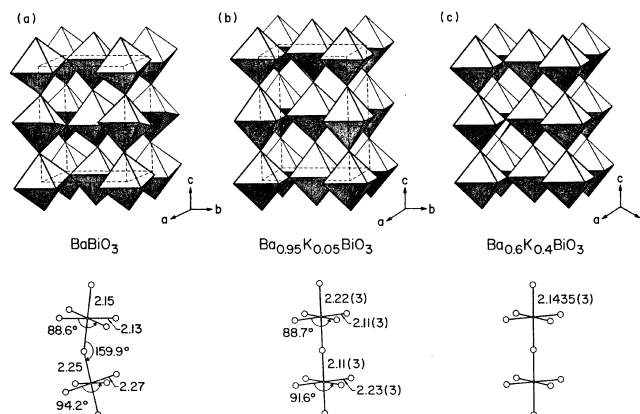


Figure 1. Structural representation of $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ for (a) $x=0$, (b) $x=0.04$, and (c) $x=0.4$. Dotted lines refer to the unit cell. Lower portions represent the bond distances and angles. [ref. 18]

$\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$ are shown in Figures 2a, 2b, and 2c. Four Bi 6s bands occur in BaBiO_3 and $\text{Ba}_{0.96}\text{K}_{0.04}\text{BiO}_3$ since four octahedra construct the unit cells of these two compounds. Similarly, only one Bi 6s band is shown in cubic $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$. It was found from the resistivity experiments that BaBiO_3 and $\text{Ba}_{0.96}\text{K}_{0.04}\text{BiO}_3$ exhibit insulating and semi-conducting property, respectively. Our calculation is consistent with the experimental results that the band gap of BaBiO_3 and $\text{Ba}_{0.96}\text{K}_{0.04}\text{BiO}_3$ are 3.2 eV and 1.4 eV, respectively (see Figures 2a and 2b). Differently from the two compounds, $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$ shows metallic property as shown in Figure 2c (*i.e.*, the Bi 6s-block band is cut by the Fermi energy). Since the oxidation state of Bi is -4.4 in this compound, the Bi 6s band is less than half-filled. It is clear from Figure 2c that the band is almost equally dispersive along the *a*-, *b*-, and *c*-directions which means the compound is a three-dimensional metal. In the band structure of BaBiO_3 , however, the valence and conduction bands are strongly dispersive along the crystallographic *a*-direction but it is almost flat along the *b*- and *c*-directions. This is reasonable because an BiO_6 octahedron is symmetrically connected to the neighboring one by edge-sharing mode along each direction in $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$, while different BiO_6 octahedra are ordered alternatively in BaBiO_3 and $\text{Ba}_{0.96}\text{K}_{0.04}\text{BiO}_3$ compounds. The amount of orbital interactions depend upon the symmetry of bonding orbitals. Highly symmetric

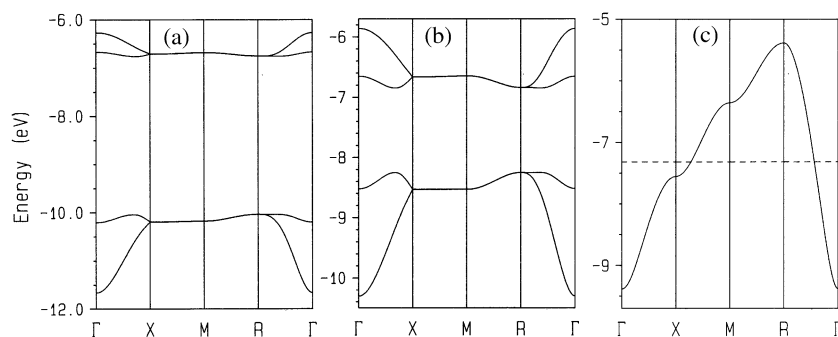


Figure 2. The Bi 6s-block bands of $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ for (a) $x=0$, (b) $x=0.04$, and (c) $x=0.4$. The dashed line refers to Fermi energy.

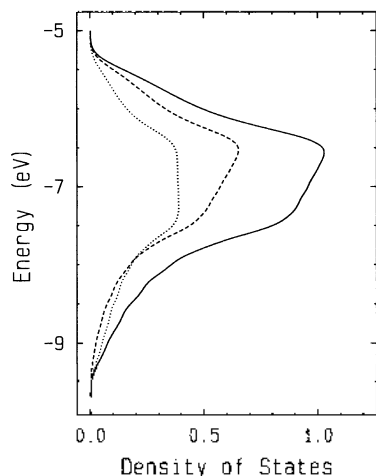


Figure 3. The density of states (DOS) calculated for $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$. The solid, dashed, and dotted lines refer to the projected DOS of total, Bi 6s, and O 2p contributions, respectively.

$\text{Ba}_{0.4}\text{K}_{0.6}\text{BiO}_3$ compound, therefore, show larger orbital interactions in every direction, thereby illustrating a strongly dispersive band. The width of the Bi 6s-block band is about 4 eV, which is close to the value obtained from the ab initio calculation. Metallic property found in this compound arises from the fact that the environments of all Bi are identical and each Bi contains same amount of holes upon the substitution for Ba with K. The shape of this band is similar to the highest lying d-block band (*i.e.*, x^2-y^2 band of Cu which is cut by the Fermi energy) found in the high- T_c copper-oxide superconductors.²⁰

The x^2-y^2 band in the cuprate superconductors consists of largely Cu d-orbitals and small amount of O p-orbitals. Holes generated in the hole superconductors (*i.e.*, high- T_c copper-oxide superconductors) are, therefore, mainly contributed by copper d-characters. The highest lying Bi 6s-block band of BaBiO_3 which is cut by the Fermi energy is composed of Bi 6s and O 2p characters. Strikingly the O 2p contribution to the partially filled band in $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$ is larger than the Bi 6s contribution, as shown in the projected density of states (see Figure 3). Consequently, the character of oxygen contributes to the conducting mechanism more than that of the bismuth in $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$ compound which is different from the copper-oxide superconductors. It is understandable when the Bi 6s-block band in superconducting $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$ is antibonding level between O 2p and Bi 6s since the energy level of O 2p is higher than that of Bi 6s, as

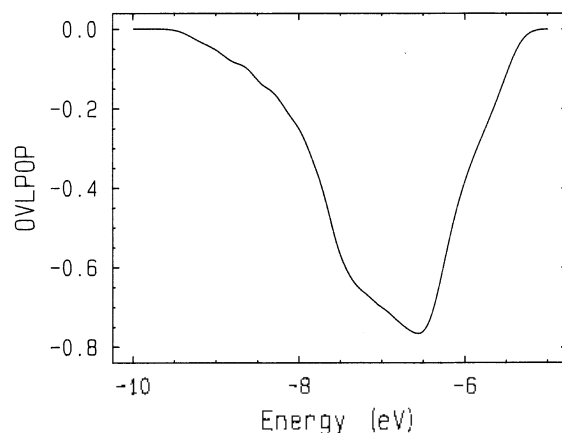
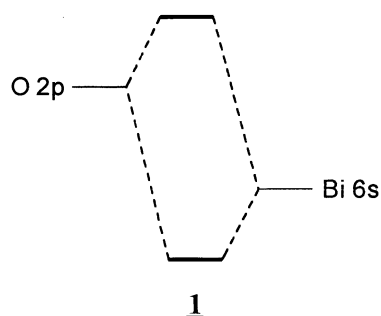


Figure 4. The atomic overlap population calculated for $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$.

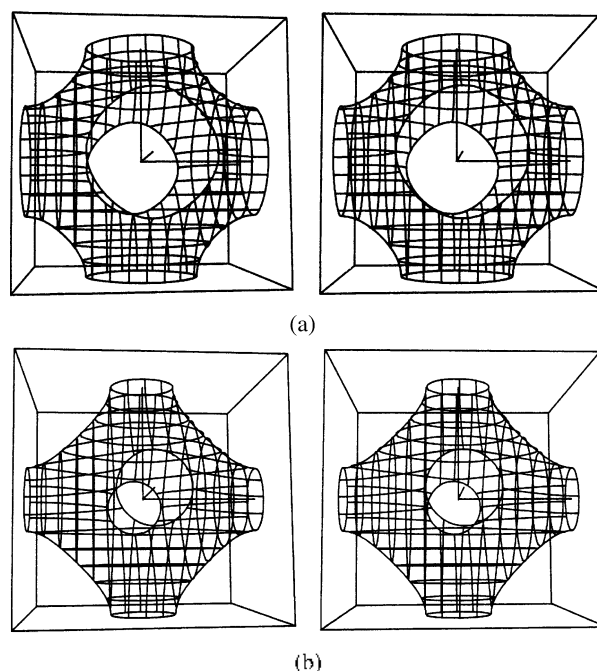


Figure 5. Fermi surfaces calculated for $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$ when (a) the Bi 6s-block band is half-filled, and (b) the Bi 6s-block band is less than half-filled.

illustrated in 1. The atomic orbital overlap population (see Figure 4) shows that the Bi 6s-block band has antibonding property between Bi 6s and O 2p, as expected.

The three dimensional Fermi surfaces associated with the band of $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$ for half-filled and less than half-filled (*i.e.*, real) situations are shown in Figures 5a and 5b. Upon the oxidation states of Ba^{2+} , K^+ , and O^{2-} , that of Bi in the $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$ compound becomes $\text{Bi}^{4.41}$ which means the Bi 6s band is less than half-filled in this case. The Bi 6s-block band is fully occupied when it is Bi^{3+} , but completely empty when Bi^{5+} . As mentioned earlier, the oxidation state of Bi in the pristine BaBiO_3 is not Bi^{4+} but Bi^{3+} and Bi^{5+} coexist by charge disproportionation. The Bi 6s-block band is half-filled, therefore, when Bi^{3+} and Bi^{5+} coexist with same

amount to make an average oxidation state of Bi^{3+} . As shown in Figure 5, the Fermi surface for the less than half-filled shows nesting-like behavior but that for the half-filled no nesting. Fermi surface nesting is susceptible to cause the metal-insulator transition *via* CDW. In general, the CDW and superconductivity competes with one another, with the CDW tending to suppress superconductivity and vice versa.²¹ A metal-superconductor transition is stronger in the $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$ compound although very weak Fermi surface nesting is observed. It means that the driving force is not enough to show a metal-insulator transition since the gap is not formed over the entire Fermi surface.

Conclusions

The commensurate ordering of Bi^{3+} and Bi^{5+} is responsible for the insulating and semiconducting behavior in BaBiO_3 and $\text{Ba}_{0.96}\text{K}_{0.04}\text{BiO}_4$. The band gaps of 3.2 eV and 1.4 eV for the former and the latter compounds, respectively, are consistent with the experimental results. Doping in Bi 6s-block band causes the collapse of the ordering of Bi^{3+} and Bi^{5+} , thereby resulting in the superconductivity in the $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$ compound. Strikingly, the character of oxygen contributes to the conducting mechanism than that of the bismuth. This is quite different from the cuprate superconductors in which the character of copper dominates that of oxygen.

Acknowledgment. This work was supported by Wonkwang University in 1998.

References

1. Cava, R. J.; Takagi, H.; Zandbergen, H. W.; Krajewski, J. J.; Peck Jr, W. F.; Siegrist, T.; Batlogg, B.; van Dover, R. B.; Felder, R. J.; Mizuhashi, K.; Lee, J. O.; Eisaki, H.; Uchida, S. *Nature* **1994**, *367*, 252.
2. Cava, R. J.; Takagi, H.; Batlogg, B.; Zandbergen, H. W.; Krajewski, J. J.; Peck Jr, W. F.; van Dover, R. B.; Felder, R. J.; Siegrist, T.; Mizuhashi, K.; Lee, J. O.; Eisaki, H.; Carter, S. A.; Uchida, S. *Nature* **1994**, *367*, 146.
3. (a) Cava, R. J.; Zandbergen, H. W.; Batlogg, B.; Eisaki, H.; Takagi, H.; Krajewski, J. J.; Peck Jr, W. F.; Gyorgy, E. M.; Uchida, S. *Nature* **1994**, *372*, 245. (b) Zandbergen, H. W.; Jansen, J.; Cava, R. J.; Krajewski, J. J.; Peck Jr, W. F. *Nature* **1994**, *372*, 759.
4. Hebard, A. F.; Rosseinsky, M. J.; Haddon, R. C.; Murphy, D. W.; Glarum, S. H.; Palstra, T. T. M.; Ramirez, A. P.; Kortan, A. R. *Nature* **1991**, *350*, 600.
5. Holczer, K.; Klein, O.; Huang, S.-M.; Kaner, R. B.; Fu, K.-J.; Whetten, R. L.; Diederich, F. *Science* **1991**, *252*, 1154.
6. Stephens, P. W.; Mihaly, L.; Lee, P. L.; Whetten, R. L.; Huang, S.-M.; Kaner, R.; Diederich, F.; Holczer, K. *Nature* **1991**, *351*, 632.
7. Rosseinsky, M. J.; Ramirez, A. P.; Glarum, S. H.; Murphy, D. W.; Haddon, R. C.; Hebard, A. F.; Palstra, T. T. M.; Kortan, A. R.; Zahurak, S. M.; Makhija, A. V. *Phys. Rev. Lett.* **1991**, *66*, 2830.
8. Fleming, R. M.; Ramirez, A. P.; Rosseinsky, M. J.; Murphy, D. W.; Haddon, R. C.; Zahurak, S. M.; Makhija, A. V. *Nature* **1991**, *352*, 787.
9. Tanigaki, K.; Ebbesen, T. W.; Saito, S.; Mijuki, J.; Tsai, J. S.; Kubo, Y.; Kuroshima, S. *Nature* **1991**, *352*, 222.
10. Keltz, S. P.; Chen, C.-C.; Lieber, C. M. *Nature* **1991**, *352*, 223.
11. Rosseinsky, M. J.; Murphy, D. W.; Fleming, R. M.; Tycko, R.; Ramirez, A. P.; Siegrist, T.; Dabbagh, G.; Barrett, S. F. *Nature* **1992**, *356*, 416.
12. Cava, R. J.; Batlogg, B.; Krajewski, J. J.; Farrow, R. C.; Rupp Jr, L. W.; White, A. F.; Short, K. T.; Peck Jr, W. F.; Kometani, T. Y. *Nature* **1988**, *332*, 814.
13. Scholder, R.; Ganter, K.; Glaser, H.; Merz, G. Z. *Anorg. Allg. Chem.* **1963**, *319*, 375.
14. Nakamura, T.; Saburo, K.; Sata, T. *J. Phys. Soc. Jpn.* **1971**, *31*, 1284.
15. de Haar, J. Th. W.; Blasse, G. *Solid State Commun.* **1971**, *12*, 727.
16. (a) Cox, D. E.; Sleight, A. W. *Solid State Commun.* **1976**, *19*, 969. (b) Cox, D. E.; Sleight, A. W. *Acta Cryst.* **1979**, *B35*, 1.
17. Sleight, A. W.; Gillson, J. L.; Bierstedt, P. E. *Solid State Commun.* **1975**, *17*, 27.
18. Schneemeyer, L. F.; Thomas, J. K.; Siegrist, T.; Batlogg, B.; Rupp, L. W.; Opila, R. L.; Cava, R. J.; Murphy, D. W. *Nature* **1988**, *335*, 421.
19. (a) Whangbo, M.-H.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 6093. (b) Ammeter, J. H.; Burgi, H.-B.; Thi-beault, J.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 3686.
20. (a) Whangbo, M.-H.; Evain, M.; Beno, M. A.; Williams, J. M. *Inorg. Chem.* **1987**, *26*, 1831. (b) Whangbo, M.-H.; Evain, M.; Beno, M. A.; Williams, J. M. *Inorg. Chem.* **1987**, *26*, 1832. (c) Whangbo, M.-H.; Evain, M.; Beno, M. A.; Geiser, U.; Williams, J. M. *Inorg. Chem.* **1987**, *26*, 2566. (d) Jung, D.; Whangbo, M.-H.; Herron, N.; Torardi, C. C. *Physica C* **1989**, *160*, 381.
21. Jung, D. *Bull. Korean Chem. Soc.* **1999**, *20*, 281.