

Pressure effect on $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ near the composition of Metal-Semiconductor transition

M. Shizuya ^{a,1}, S. Ueda ^a Y. Mogami ^a T. Nishio ^a H. Minami ^a H. Uwe ^a

^a*Institute of Materials Science, University of Tsukuba, Tsukuba, Ibaraki, 305-8573, Japan*

Abstract

The effect of the hydrostatic pressure up to 1 GPa to the resistivity of $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ has been investigated. Specimens are single crystals prepared by an electro-chemical method. Either the superconducting transition temperature T_c or the conductivity increases with pressure in the metallic phase. On the semiconducting sample ($x \sim 0.3$), which is near the metallic phase, we find that the temperature dependence of the resistivity changes to $\frac{d\rho}{dT} > 0$ below 20 K at above 0.4 GPa. This suggests that the new conducting phase, which may be superconducting, appears in the semiconducting sample under high pressure.

Key words: High pressure;Oxide superconductor; $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$

$\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ has attracted much attention because they show relatively high superconducting transition temperature ($T_C = 32$ K) in spite of having no two dimensional conducting plane. For the parent material BaBiO_3 , it is believed that the origin of the semiconductivity is from the three-dimensional charge density wave (CDW) formed by the lattice distortion and the charge disproportionation. The substitution of K for Ba removes the valence electron at the Bi site, and causes the change of the lattice structure and the decrease of the lattice parameter. $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ becomes metallic at $x = 0.3$ as K doped, and superconductivity with $T_C=32$ K appears simultaneously. The pressure effect for this material has been measured about superconducting transition in the metallic phase. For $x = 0.4$, the pressure coefficient dT_C/dP has been found to be positive below 4 GPa [1]–[4], which is in contrast with negative for $\text{BaPb}_x\text{Bi}_{1-x}\text{O}_3$ [2]. dT_C/dP turns negative above 4 GPa[3]. In the semiconducting phase, the pressure effect to the electronic structure is also interesting, because the pressure reduces the lattice volume as K-doping which changes this material to supercon-

ductor. In this work, we measured the resistivity of $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ in both the semiconducting phase and the metallic phase under hydrostatic pressure up to 1 GPa.

The single crystals of $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ grown by an electro-chemical method [5]. The composition x was determined by an Electron Probe Micro-Analyzer (EPMA). To measure the DC resistivity the crystals was cut to have typically sizes of 2 mm \times 0.7 mm \times 0.13 mm. The four gold probes were evaporated in vacuum as the sample was heated at 350°C. Subsequently, samples were heated at 350 \sim 400°C in O_2 for 1 hour.

The pressure was applied by using a piston-cylinder clamp cell. The pressure at low temperature, which is maximally 0.3 GPa smaller than at room temperature if the cell was clamped, was determined from the change of T_C of Sn situated next to the sample.

dT_C/dP equals 0.38 K/GPa at the mid point of the transition for the metallic sample $\text{Ba}_{0.60}\text{K}_{0.40}\text{BiO}_3$ as seen in fig 1. This value is comparable with previous works [3][4]. The normal state resistivity under high pressure(fig. 2) decreases as about 12 %/GPa. In fig. 3 the resistivity for $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ at $x = 0.3 \pm 0.03$ for several pressure is displayed. This crystal con-

¹ E-mail:s995304@ipe.tsukuba.ac.jp

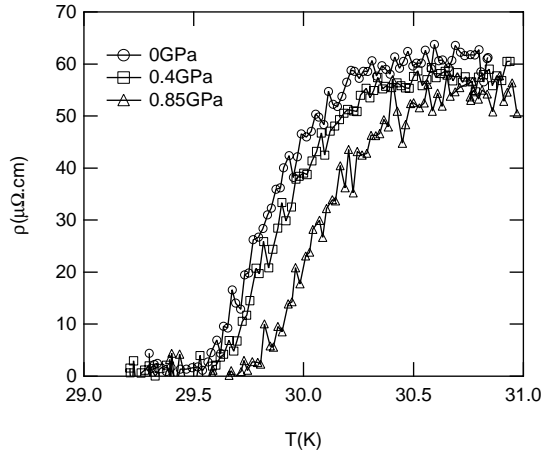


Fig. 1. Superconducting transition in resistivity for several pressures of $\text{Ba}_{0.60}\text{K}_{0.40}\text{BiO}_3$. The applied current was 0.1 mA to avoid heating of the sample.

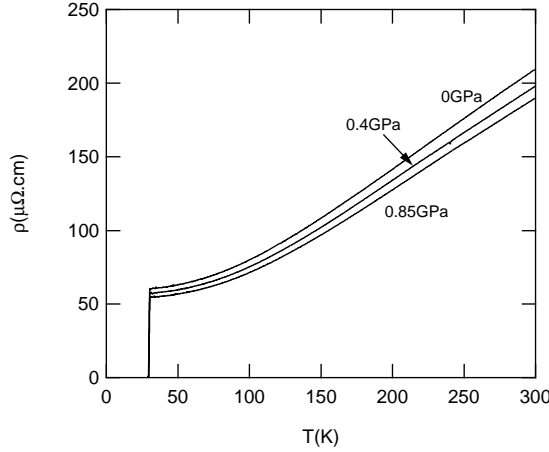


Fig. 2. Temperature dependence of resistivity under high pressure for $\text{Ba}_{0.60}\text{K}_{0.40}\text{BiO}_3$.

tains superconducting (metallic) part whose T_C measured by a SQUID magnetometer is 30 K. Although the temperature dependence of resistivity at 0 GPa is semiconductor-like, and the superconducting transition at 30 K could not be seen. Therefore we seems to measure the resistance of the semiconducting part in the sample. Under high pressure over 0.4 GPa the resistivity starts to decrease below 20 K. The minimum resistivity below 20 K for 0.61 GPa or 0.84 GPa increases with current (ex. The resistivity of current 0.1 mA at 4.5 K under 0.84 GPa is four times as large as at 0.01 mA).

For metallic $\text{Ba}_{0.60}\text{K}_{0.40}\text{BiO}_3$, the increase of both T_C and conductivity under pressure suggests that the pressure adds extra electrons to the conduction band. This will increase the Fermi level, for the electronic band, both the electron density and the density of

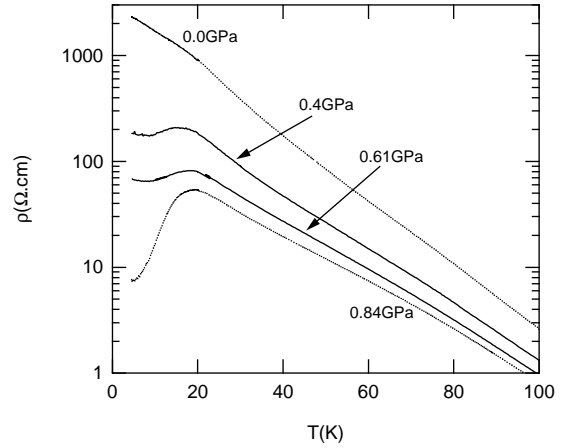


Fig. 3. Temperature dependence of resistivity under high pressure for $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ ($x \sim 0.3$). The composition of this crystal varies ± 0.03 depend on the position of the surface measured by EPMA. Therefore the crystal is mixed semiconducting phase and metallic phase whose T_C equals 30 K measured by SQUID magnetometer. The used current below 20 K is 0.01 mA.

state to increase. By the optical measurement, the existing of the localized electrons in superconducting $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ is suggested[6]. If the pressure reduces the number of localized electrons, these electrons will move to the conduction band as extra electrons under pressure. Moreover, the behavior of the semiconducting phase as seen in fig. 3 could be regarded as the appearance of a superconducting phase caused by moving of the localized electrons to the empty conduction band under pressure.

Acknowledgements

We thank Chemical Analysis Center for EPMA analysis.

References

- [1] J. E. Schirber, B. Morosin, D. S. Ginley, *Physica C* **157** (1989) 237.
- [2] H. Uwe, T. Osada, A. Iyo, K. Murata, T. Sakudo, *Physica C* **162-164** (1989) 743.
- [3] H. Takahashi, N. Môri, Y. Nagata, S. Nakamura, T. Uchida, J. Akimitsu, Y. Tokura, *Physica C* **210** (1993) 485.
- [4] J. Beille, C. Escribe-Filippini, J. Marcus, M. Affronte, *Physica B* **194-196** (1994) 1481.
- [5] T. Nishio, H. Minami, H. Uwe, *Physica C* **357** (2001) 376.
- [6] A. V. Puchkov, T. Timusk, M. A. Karlow, S. L. Cooper, P. D. Han, D. A. Payne, *Phys. Rev. B* **54** (1996) 6686.