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Single-Crystal Growth of the Superconducting $Ba_{1-x}K_xBiO_3$ by the Floating-Zone Method

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Abstract. We have successfully grown single crystals of $Ba_{1-x}K_xBiO_3$ with the volume of the order of 1 mm^3 by the floating-zone method. It was important to use a high-pressure reducing atmosphere and the “twice-scanning” method for the successful growth. The crystal growth was performed under argon pressure of 1.0 MPa. The potassium content of each single crystal is much smaller than that of the feed rod. Single crystals of $x = 0.32, 0.42, 0.50$ (estimated from the ICP-AES analysis) annealed in flowing oxygen gas show superconductivity with the transition temperature $T_c = 29\text{ K}, 25\text{ K}, 15\text{ K}$, respectively. From the powder x-ray diffraction analysis and electrical resistivity measurements, each obtained single-crystal has been found to be composed of at least two phases with different x values.

Keywords: $Ba_{1-x}K_xBiO_3$, single-crystal growth, floating-zone method

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Among oxide superconductors not containing copper, $Ba_{1-x}K_xBiO_3$ (BKBO) exhibits the highest superconducting transition temperature, $T_c = 30\text{ K}$ for $x \sim 0.4$, in spite of the low carrier concentration [1]. Single crystals of BKBO have been grown by the flux method and the electrochemical technique so far [2 - 4]. However, it has not yet been reported that the floating-zone (FZ) method is able to be applied to BKBO. In the FZ method, the control of the composition of a single crystal is comparatively easy. In general, the FZ method allows the growth of high-quality single crystals.

In this paper, we have tried the single-crystal growth of BKBO with various potassium contents by the FZ method. The superconducting properties have been investigated.

In order to prepare the feed rod for the FZ growth, first, we prepared the polycrystalline powder of $BaBiO_3$ by the solid-state reaction method. That is, the prescribed amount of BaO_2 and BiO_3 of 99.9 % purity was mixed, ground and pre-fired at $800\text{ }^\circ\text{C}$ in oxygen gas for 12 h. Next, K_2CO_3 of 99.8 % purity and Bi_2O_3 were added to the pre-fired powder of $BaBiO_3$ in order to prepare a feed rod with various ratios of Ba : K : Bi. After 1 h grinding, the powder was isostatically cold-pressed into a rod of 5 - 6 mm in diameter and ~

100 mm in length. Then, the rod was sintered at $650\text{ }^\circ\text{C}$ in air for 12 h. Single crystals were grown in an infrared radiation-convergence type furnace with halogen lamp using a premelted feed rod. That is, the so-called “twice-scanning” method was used [5]. The high-density premelted feed rod was prepared by the first scan. In the first scan, the lamp power was elevated gradually under argon pressure of 1 MPa until the feed rod melted. The molten zone passed through at a speed of $\sim 20\text{ mm/h}$. The premelted feed rod and the as-sintered rod were rotated at $\sim 20\text{ rpm}$ in the opposite direction. Next, the usual growing procedure was carried out under argon pressure of 1 MPa at the growth rate of 1.0 mm/h , using the premelted feed rod. Since the obtained rod was covered with potassium evaporating from the molten zone, single crystals were obtained by crushing the rod mechanically. In order to fill up oxygen vacancies and remove the strain, the as-grown crystals were post-annealed in flowing oxygen gas at $300\text{ }^\circ\text{C}$ for 150 h.

The products were identified by the powder x-ray diffraction analysis and the back-Laue photography. The composition was determined by the inductively coupled plasma atomic emission spectroscopy (ICP-AES). The magnetic susceptibility was measured using a SQUID magnetometer. Electrical resistivity measurements were carried out by the dc four-point probe method.

By using the “twice-scanning” method in a high-pressure reducing atmosphere, namely, under argon pressure of 1 MPa, a rod containing single crystals of BKBO was successfully obtained. This atmosphere was necessary to suppress the evaporation of potassium out of the molten zone and to keep the molten zone stable. It was hard to keep the molten zone stable in air and also in oxygen gas. The best growth rate was 0.8 – 1 mm/h. It was confirmed that single crystals were not obtained at the growth rate of 2 mm/h and that the molten zone was not keep stable at the rate slower than 0.5 mm/h on account of the penetration of the molten liquid into the feed rod.

The volume of the obtained single-crystals was the order of 1 mm³. Many spots were clearly observed in the Laue photograph, but we could take no photograph with only a single set of symmetric spots. The powder x-ray diffraction peaks of the obtained single-crystals have revealed that these are of the single phase with the cubic perovskite structure. Looking at each peak in detail, however, it was slightly split. These mean that each obtained single-crystal is composed of at least two phases with different x values. Table 1 shows the nominal composition of the feed rods and the composition of the obtained single-crystals determined by ICP-AES. It is found that the average of the potassium content of each single crystal is much smaller than that of the feed rod. This is due to evaporation of potassium during the two scans.

TABLE 1. Nominal composition of the feed rods and composition of the obtained single-crystals determined by ICP-AES.

	Ba	K	Bi
Feed rod A (Nominal)	0.60	0.50	1.00
Single crystal (ICP)	0.64	0.32	1.04
Feed rod B (Nominal)	0.60	0.80	1.00
Single crystal (ICP)	0.57	0.42	1.01
Feed rod C (Nominal)	0.50	1.00	1.00
Single crystal (ICP)	0.49	0.50	1.01

Figure 1 displays the typical temperature dependences of the magnetic susceptibility on field cooling and the electrical resistivity for single crystals obtained from the feed rod A, B and C. It is found from the susceptibility that single crystals of $x = 0.32, 0.42, 0.50$ show superconductivity with the transition temperature $T_c = 29, 25, 15$ K, which are comparable to T_c values of polycrystalline samples of BKBO, respectively [1]. The superconducting volume fraction of the single crystal ($x = 0.42$) grown from the feed rod B is estimated from the Meissner effect to be 30 – 45 % of the perfect diamagnetism. The superconducting volume fraction of single crystals (x

= 0.32, 0.50) grown from the feed rod A, C is smaller than that from B. Moreover, no resistance drop due to superconducting is observed for single crystals from the rod A and C, owing to the high resistivity value at low temperature. These results suggest that single crystals from the rod A and C are composed of a superconductor and an insulator with different x values so that superconducting paths are not connected with one another. It may be inevitable that single crystals of BKBO grown by the FZ method have a domain structure due to a kind of phase separation.

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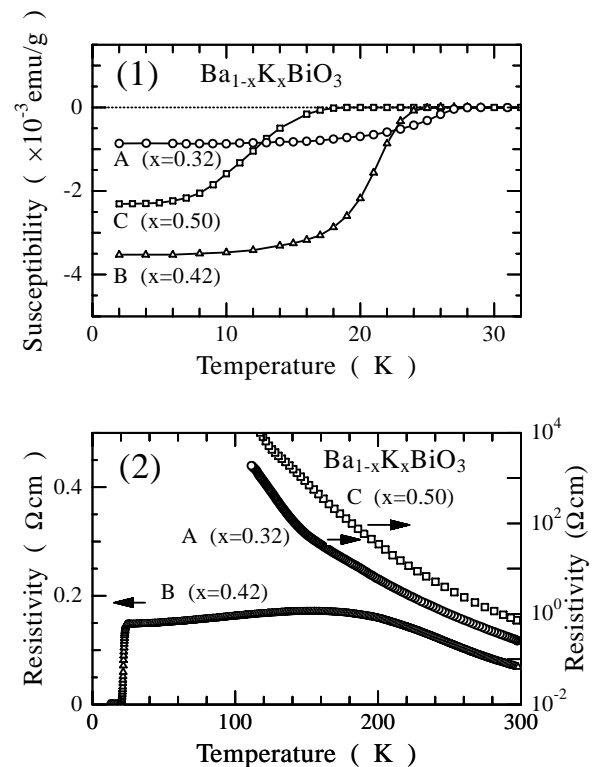


FIGURE 1. Temperature dependences of (1) the magnetic susceptibility on field cooling in a field of 3 Oe and (2) the electrical resistivity for single crystals of $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ obtained from the feed rod A, B and C.

REFERENCES

1. S. Pei *et al.*, *Phys. Rev. B* **41**, 4126 (1990).
2. J.P. Wignacourt *et al.*, *Appl. Phys. Lett.* **53**, 1753 (1988).
3. L.F. Schneemeyer *et al.*, *Nature* **335**, 421 (1988).
4. M.L. Norton, *Mat. Res. Bull.* **24**, 1391 (1989).
5. K. Oka and T. Ito, *Physica C* **227**, 77 (1994).