Rapid low-temperature synthesis of superconducting (Ba,Rb)BiO$_3$ using molten RbOH

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Abstract. Polycrystalline samples of perovskite (Ba,Rb)BiO$_3$ have successfully been synthesized in a short time of 2 h at a temperature as low as 310 ºC by the direct precipitation from molten RbOH. The powder x-ray diffraction pattern has revealed the formation of well-crystallized Ba$_{1-x}$Rb$_x$BiO$_3$ with 0.31 < x < 0.40. The appearance of superconductivity has been confirmed by the magnetic susceptibility measurements for all samples. The superconducting transition temperature $T_c$ has a maximum value of ~28 K at x ~ 0.37, which is quite similar to that of (Ba,K)BiO$_3$. These results are in good agreement with those of samples obtained by the conventional solid-state reaction method.

1. Introduction
The perovskite (Ba,A)BiO$_3$ (A=K, Rb) is known as a superconductor with a high value of the superconducting transition temperature $T_c$ ~ 30 K among oxides without copper. The synthesis of (Ba,A)BiO$_3$ by the solid-state reaction method requires a complicated process because of the phase separation and the volatility of A ions at high temperatures. On the other hand, the low-temperature synthesis of (Ba,K)BiO$_3$ using molten KOH offers advantages of a single-step preparation-process at temperatures much lower than those used in the solid-state reaction. Wignacourt et al. [1] have succeeded in preparing tiny crystals of non-superconducting Ba$_{0.87}$K$_{0.13}$BiO$_3$ at 360 ºC from the molten KOH-Ba(OH)$_2$-Bi$_2$O$_3$ system for the first time. Then, Liu and Fu [2] have prepared polycrystalline samples of superconducting Ba$_{0.5}$K$_{0.5}$BiO$_3$ at 260 ºC for several hours from molten KOH by using NaBiO$_3$ with Bi$^{5+}$ ions as one of starting materials. Very recently, we have successfully synthesized polycrystalline samples of Ba$_{1-x}$K$_x$BiO$_3$ in a considerably short heating-time of several minutes at a temperature as low as 290 ºC by the direct precipitation from molten KOH using strong oxidizer BaO$_2$ as one of starting materials. We have also succeeded in controlling the K-content x in a wide range between 0.24 and 0.51 by the addition of H$_2$O [3].

In this paper, we report the low-temperature synthesis of polycrystalline samples of superconducting Ba$_{1-x}$Rb$_x$BiO$_3$ with a wide range of x using molten RbOH. For comparison, synthetic results of Ba$_{1-x}$K$_x$BiO$_3$ are also shown.

2. Experimental
Polycrystalline samples of Ba$_{1-x}$Rb$_x$BiO$_3$ were synthesized as follows. A mixture of RbOH-H$_2$O of 20 g, BaO$_2$ of 0.698 g and Bi$_2$O$_3$ of 1.50 g (Rb:Ba:Bi=26:0.64:1 in the molar ratio) was put into a Teflon beaker on a hot plate, which was preheated at 310 ºC in air. Then, 0-1.5 ml of H$_2$O was added...
immediately with stirring at 300 rpm. The beaker was kept at 310°C with stirring continuously for only 2 h. The melt was quenched to room temperature by removing the Teflon beaker from the hot plate. After cooling, black polycrystalline powder was isolated by dissolving RbOH with distilled water and dried in air. Polycrystalline samples of Ba$_{1-x}$K$_x$BiO$_3$ were also synthesized in the same way. However, a mixture of KOH of 20 g, BaO$_2$ of 0.654 g, Bi$_2$O$_3$ of 1.50 g (K:Ba:Bi=55:0.6:1 in the molar ratio) and H$_2$O of 0-8 ml were used as starting materials and was heated at 290°C for only 1 h. All products were characterized by powder x-ray diffraction using CuKα radiation at room temperature. The contents of Rb and K were estimated from the lattice parameter $a$ using relations of $a = 4.3548 - 0.1370x$(Rb) and $a = 4.3548 - 0.1743x$(K) which were obtained from the results of samples synthesized by the conventional solid-state reaction method [4, 5], respectively. The magnetic susceptibility was measured using a SQUID magnetometer in a magnetic field of 5 Oe on field cooling.

3. Results

Figures 1 and 2 show the powder x-ray diffraction patterns at room temperature for Ba$_{1-x}$Rb$_x$BiO$_3$ and Ba$_{1-x}$K$_x$BiO$_3$ synthesized using molten AOH, respectively. The products are of the single phase of Ba$_{1-x}$Rb$_x$BiO$_3$ with $0.317 \leq x \leq 0.396$ and Ba$_{1-x}$K$_x$BiO$_3$ with $0.243 \leq x \leq 0.487$. With increasing amount of the additional H$_2$O, the A-content $x$ decreases. As can be seen especially in Figs. 1(b) and 2(b), all diffraction peaks are single for all products within the experimental accuracy in our powder x-ray diffraction measurements, indicating that the crystal structure is cubic for all products. Moreover, sharp peaks suggest that well-crystallized samples of Ba$_{1-x}$A$_x$BiO$_3$ are obtained.

**Figure 1.** (a) Powder x-ray diffraction patterns of Ba$_{1-x}$Rb$_x$BiO$_3$ at room temperature using CuKα radiation in a wide range of 2θ. (b) Dependence on $x$ of the (321) diffraction peak on an expanded scale.

**Figure 2.** (a) Powder x-ray diffraction patterns of Ba$_{1-x}$K$_x$BiO$_3$ at room temperature using CuKα radiation in a wide range of 2θ. (b) Dependence on $x$ of the (321) diffraction peak on an expanded scale.
Figures 3 and 4 show the temperature dependence of the magnetic susceptibility $\chi$ of Ba$_{1-x}$Rb$_x$BiO$_3$ and Ba$_{1-x}$K$_x$BiO$_3$, respectively. The value of $T_c$ is defined as the onset temperature where $\chi$ changes by 0.1% of the perfect diamagnetism from the normal-state value. Figure 5 shows the $x$ dependence of $T_c$ and the magnetic susceptibility at 2 K, $\chi_{2K}$, which is regarded as being related to the superconducting volume fraction.

First, as for Ba$_{1-x}$K$_x$BiO$_3$, a single-step diamagnetic response due to the Meissner effect is observed for $x \geq 0.287$. However, values of $|\chi_{2K}|$ for $x < 0.357$ are small, indicating that bulk superconductivity appears for $x \geq 0.36$. The $T_c$ has a maximum value of 29.8 K at $x = 0.357$ and then tends to decrease with increasing $x$. These results are in good agreement with those of Ba$_{1-x}$K$_x$BiO$_3$ samples obtained by the conventional solid-state reaction method [4]. To our surprise, however, it is found that both $T_c$ and $|\chi_{2K}|$ appear to decrease in a very narrow range of $x \approx 0.39$, suggesting that superconductivity is suppressed in this narrow region of $x$. In order to clear the reason for this suppression of superconductivity, further investigation is necessary.

Next, as for Ba$_{1-x}$Rb$_x$BiO$_3$, values of $T_c$ and its $x$-dependence are quite similar to those of Ba$_{1-x}$K$_x$BiO$_3$. Superconductivity is observed for all samples with $0.317 \leq x \leq 0.396$ and $T_c$ has a maximum value of 28.3 K at $x = 0.369$, which are in agreement with those of Ba$_{1-x}$Rb$_x$BiO$_3$ samples obtained by the conventional solid-state reaction method [5]. On the other hand, $x$ dependence of $|\chi_{2K}|$ in Ba$_{1-x}$Rb$_x$BiO$_3$ is almost coincident with that in Ba$_{1-x}$K$_x$BiO$_3$, though its values are smaller than those of Ba$_{1-x}$K$_x$BiO$_3$. The small values of $|\chi_{2K}|$ in Ba$_{1-x}$Rb$_x$BiO$_3$ may be due to the small size of grains constituting a sample, because the surface of a grain is penetrated by magnetic field, resulting in large reduction of the superconducting volume fraction for a sample composed of small grains. In fact, the
powder of Ba$_{1-x}$Rb$_x$BiO$_3$ obtained in the present work appears to be fine in comparison with that of Ba$_{1-x}$K$_x$BiO$_3$. As for the anomalous suppression of superconductivity as observed at $x \approx 0.39$ in Ba$_{1-x}$K$_x$BiO$_3$, it is not observed in Ba$_{1-x}$Rb$_x$BiO$_3$.

In conclusion, we have successfully synthesized superconducting perovskite Ba$_{1-x}$Rb$_x$BiO$_3$ with $0.31 < x < 0.40$ in a short heating time of 2 h at a temperature as low as 310 ºC by the direct precipitation from molten RbOH. This work indicates that the present method using molten hydroxide is simple and powerful for the preparation of BaBiO$_3$ system.

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