Controlled Growth of Bi-Based Cuprate Whiskers

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Cuprate whiskers with different crystal phases, $Bi_2Sr_2CuO_x$ (Bi-2201) and $Bi_4Sr_8Cu_5O_x$ (Bi-485), have been obtained by heating melt-quenched glass precursors. The crystal phase of the grown whiskers were controllable by changing the precursor composition and heating conditions. The Bi-2201 whiskers were identified to be of the R-phase, written in a general formula as $Bi_{2+x}Sr_{2-x}CuO_y$. The hole concentration of the as-grown Bi-2201 whiskers was also controlled from the underdoped to the overdoped state by changing the precursor composition. The temperature dependence of resistivity changed from a semiconducting to a metallic behavior corresponding to the hole concentration.

High-temperature superconducting cuprates have attracted much attention, not only due to their importance for practical applications, but also because of the superconducting mechanism which realizes such an unexpectedly high critical temperature (T_c). It is well established that the most important superconducting parameter, T_c, strongly depends on the hole concentration. As for the Bi–Sr–Ca–Cu–O system, which is one of the typical high-T_c superconductors, three isostructual compounds with different numbers of CuO_2 planes in a unit formula are known: $Bi_2Sr_2Ca_{n-1}Cu_nO_x$ ($n = 1$, 2, 3). Hereafter, the $n = 1$, 2, 3 materials are denoted as Bi-2201, Bi-2212, and Bi-2223, respectively. The T_c values of these phases are around 20,[1] 80,[2] and 110 K,[2] respectively. Many factors have been reported to change the hole concentration, that is to change T_c, in the Bi–Sr–Ca–Cu–O system. The oxygen content,[3—6] defects in the alkaline earth metal sites,[7] and substitution of Bi for alkaline earth metal,[8] influence the hole concentration. Because the superconducting phases of the Bi-system allow a wide range of compositional alternations for building themselves, such defects or intrasubstitution are observed. It is therefore important to achieve controlled growth, that is to control the crystal phase and chemical composition, in the synthesis of the Bi-system superconductors so as to obtain samples having the desired property.

It has been reported that Bi-2212 whiskers of single crystals can be grown by heating a melt-quenched Bi–Sr–Ca–Cu–Al–O glass precursor in a stream of O_2 gas (glass precursor method).[9—11] Because the whiskers are very flexible and show good superconducting properties, they are useful for both applications and measurements of the physical properties. The object of our study is to achieve controlled growth. In this paper we report that the crystal phase and chemical composition of the whiskers are controllable by using the glass precursor method. Whiskers of the Bi-2201 and $Bi_4Sr_8Cu_5O_x$ (Bi-485) phases have been successfully synthesized, and their chemical compositions can be controlled by changing the compositions of the glass precursors.

Experimental

To synthesize the Bi-2201 and Bi-485 whiskers, we prepared glass precursors without Ca. Five glass precursors with different Bi contents were prepared. The powders of Bi_2O_3, $SrCO_3$, and CuO were mixed to the nominal composition of $Bi_zSr_2CuO_y$ (z=1.0, 1.3, 1.5, 2.0, 3.0) using a ball mill for 30 min. A mixture of 15 g was melted in an alumina crucible at 1200 °C for 30 min in air. A box-type electric furnace with heating elements on the two side walls was used for the melting process. The melt was quenched to room temperature by pouring the melt on a copper plate and pressing with another copper plate. The cooling rate was estimated to be 10^3 K s^{-1} in this method.[12] The thickness of the quenched glass precursor plates was 0.5—1.0 mm. From the results of energy dispersive X-ray (EDX) spectroscopy measurements, each precursor was found to contain about 10 at. % of Al due to the dissolution of Al from the crucible during the melting process. The precursors were placed in an alumina boat and heated variously at between 870 and 915 °C in air. After heating, the samples were cooled to room temperature in the furnace.

The crystal phase of the grown whiskers was determined using a Rigaku X-ray diffractometer equipped with a Cu $K\alpha$ tube, and the morphology of whiskers was observed using a Hitachi scanning electron microscope (SEM, model S-2400). A compositional analysis was performed with a Horiba EMAX-5770 EDX system. A differential thermal analysis (DTA) was carried out using Rigaku TAS 100 equipment between room temperature and 1000 °C in a stream of $O_2/Ar = 1/4$ gas at a heating rate of 10 K min^{-1}. The temperature dependence of the electrical resistance was measured by a standard four-probe method.

Results and Discussion

Each glass precursor with different Bi-content is heated at various temperatures. Figure 1 shows the relationship between the precursor composition and the most appropriate temperature for whisker growth (open circles), together

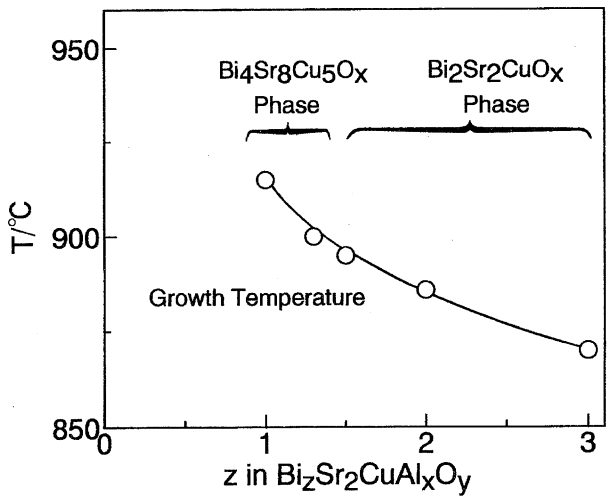

Fig. 1. Relationship between precursor composition and the most appropriate temperature (T) for the whisker growth together with the crystal phase of grown whiskers.

with the crystal phase of grown whiskers. The growth temperature increases with decreasing Bi content in the precursor from 870 °C ($Bi_3Sr_2CuAl_xO_y$ precursor) to 915 °C ($BiSr_2CuAl_xO_y$ precursor). The temperature range suitable for whisker growth is less than 5 degrees. The melting temperature of the precursor, defined as the highest endothermic peak in the DTA curve, is about 20 °C higher than the growth temperature, and shows a similar dependence against the precursor composition. This means that the growth temperature is closely related to the melting temperature of the precursor.

A typical example of the whisker growth is shown in Fig. 2. The whiskers grow upwards almost perpendicularly from the surface of the crystallized glass substrate. Each whisker has a ribbon-like shape and dimensions of ca. 5 μm thick, 10—100 μm wide, and ca. 4 mm long. The whiskers grow during the long period of heating, reaching a maximum length of 4 mm (200 h). The Bi-2212 whiskers grow to ca. 8 mm for the same heating period, indicating that the growth rate of the Bi-2201 and Bi-485 whiskers is reduced to about one-half for the Bi-2212 whiskers. The crystal phase of the whiskers

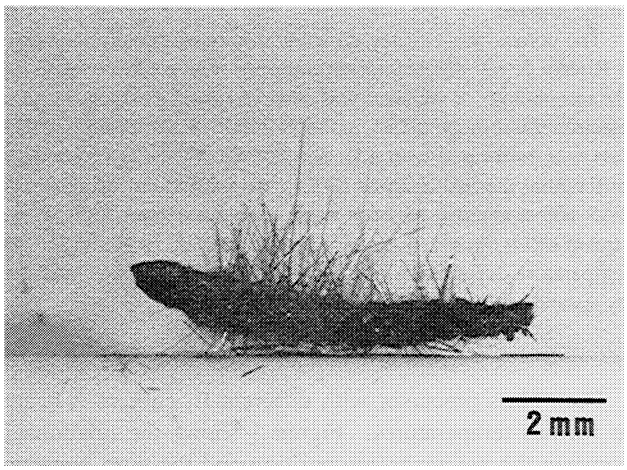

Fig. 2. Example of whisker growth from a glass precursor.

was determined by X-ray diffraction measurements, and was classified based on the Bi content in the precursor. As shown in Fig. 1, three precursors with a higher Bi content give Bi-2201 whiskers. On the other hand, the two precursors with a lower Bi content give whiskers of the Bi-485 phase. The Bi-485 phase, which is not a superconductor, was first reported as being a single phase by Ikeda et al.[13] These two kinds of whiskers can be separately prepared by controlling the precursor composition (Fig. 1).

There are two crystal phases in the Bi-2201 compound. One is the so-called R-phase, written according to the general formula $Bi_{2+x}Sr_{2-x}CuO_y$, and becomes a superconductor.[14] The other phase with a stoichiometry much closer to $Bi_2Sr_2CuO_y$ exists, but is not superconducting (so-called C-phase).[14] The two phases are distinguished by the c-axis lattice parameter. The c-axis lattice parameter of the R-phase and the C-phase is 24.4—24.8 and 23.4—23.6 Å, respectively.[1,15] All of the X-ray diffraction peaks obtained from the well-grown surface of the ribbon-like Bi-2201 whiskers can be indexed as (00n) lines, indicating that the ab plane is parallel to the well-grown surface, as in the case of the Bi-2212 whiskers. Since the c-axis lattice parameter of the Bi-2201 whiskers is 24.4—24.6 Å (Table 1), the whiskers are of the R-phase. The growing axis of the Bi-2212 whiskers has been reported to be the a-axis,[16] which can be explained by the modulation structure along the b-axis. Because the [100] plane shows a much larger deviation of atoms from their ideal position than does the [010] plane, due to the modulation structure, the [100] plane provides a more active site for growth of the Bi-2212 phase.[17] The Bi-2201 phase has the modulation structure along the b-axis in the same manner as the Bi-2212 phase. Therefore, it can be presumed that the Bi-2201 whiskers grow along the a-axis.

An energy-dispersive microprobe analysis was performed on each batch of the Bi-2201 whiskers to determine the stoichiometry. Typically, 5—8 whiskers from each batch were examined at three points on each whisker. The average compositions for the Bi-2201 whiskers are listed in Table 1. The experimental uncertainty for the composition in Table 1 is approximately ±0.8 at. % for each cation. The Bi-2201 whiskers do not contain a measurable amount of aluminum. The chemical composition of the Bi-2201 whiskers can be written according to the general formula $Bi_{2+x}Sr_{2-x}CuO_y$. The ratio of Bi to Sr in the Bi-2201 whiskers obtained from the higher Bi content precursor (sample A) is greater than that from the lower Bi content precursor (sample C), whereas the Cu content is nearly constant. Since the precursor composition influences the Bi-2201 whisker composition, the Bi/Sr ratio can be controlled by the precursor composition. Pb-doped Bi-2201 whiskers (sample D) are successfully obtained when a precursor with Pb, $BiPb_{0.5}Sr_2CuAl_xO_y$, is heated at 875 °C for 200 h in air. This means that an additional element can be introduced into the Bi-2201 whiskers using the glass precursor method. The Pb content of the whisker is 8.0 at. % and the (Bi+Pb)/Sr ratio is in agreement with that of the whiskers obtained from the $Bi_{1.5}Sr_2CuAl_xO_y$ precursor.

Table 1. List of Composition, Bi/Sr Ratio, and c-Axis Lattice Parameter of Bi-2201 Whiskers Grown from Various Precursors

Precursor	Bi-2201 whisker composition/at.%					c/Å	Sample
	Bi	Pb	Sr	Cu	Bi/Sr		
$Bi_3Sr_2CuAl_xO_y$	46.8	—	32.4	20.8	1.44	24.45	A
$Bi_2Sr_2CuAl_xO_y$	42.2	—	38.1	19.7	1.11	24.47	B
$Bi_{1.5}Sr_2CuAl_xO_y$	41.7	—	38.7	19.7	1.08	24.44	C
$BiPb_{0.5}Sr_2CuAl_xO_y$	34.1	8.0	38.4	19.5	1.09[a)]	24.55	D

a) (Bi+Pb)/Sr ratio.

The temperature dependence of the resistivity of the Bi-2201 whiskers is shown in Fig. 3. Samples A and C, without Pb, show a semiconducting behavior, although the R-phase is a superconducting phase. Assuming that the nonstoichiometry of oxygen is invariable for elemental substitution,[8)] the substitution of trivalent Bi for divalent Sr reduces the hole concentration. The semiconducting behavior is attributed to a lack of hole concentration. Even in such an underdoped state, the resistivity of sample C with the lower Bi/Sr ratio is about one order lower than that of sample A, due to the higher hole concentration arising from the lower Bi/Sr ratio. The Pb-doped sample (D) has a still lower resistivity, and shows a metallic behavior. Pb is thought to occupy the Bi site.[18,19)] Therefore, the substitution of Pb for Bi increases the hole concentration, assuming that Pb becomes a divalent cation in this compound. The superconducting transition is not observed down to 4.2 K for the as-grown whiskers. When sample D is annealed at 250 °C for 20 h under reduced pressure in order to reduce the oxygen content, it shows a superconducting transition at around 7 K. Therefore, the Pb-doped Bi-2201 whiskers are thought to be in an overdoped state. These results indicate that we can control not only the crystal phase, but also the hole concentration from the underdoped to the overdoped state in the as-grown Bi-2201 whiskers.

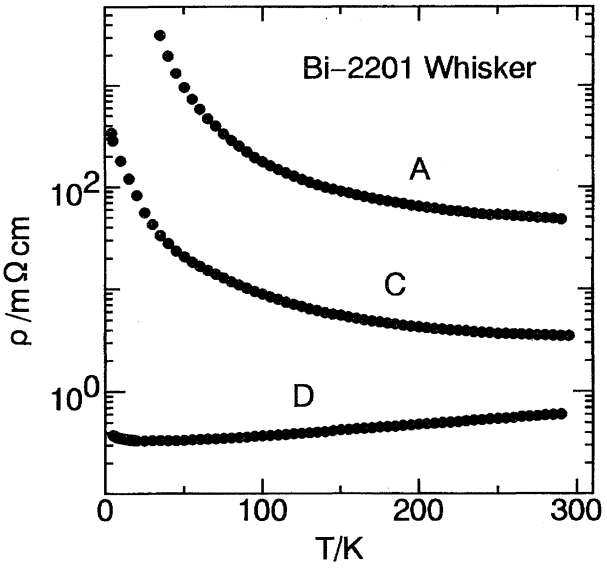

Fig. 3. Temperature (T) dependence of the resistivity (ρ) of Bi-2201 whiskers.

Bi-485 whiskers are grown from the lower Bi content precursors, and have a ribbon-like shape like the Bi-2212 and Bi-2201 whiskers. Figure 4 shows the X-ray diffraction pattern from a well-grown surface of the whiskers. Fuertes et al. have performed X-ray structure analyses using Bi-485 single crystals, and reported the following crystal structure and cell parameters: $a = 5.373$, $b = 33.907$, $c = 23.966$ Å.[20)] All of the diffraction peaks observed in the Bi-485 whisker can be indexed as ($0m0$) lines. The b-axis lattice parameter was calculated to be 33.93 Å. The well-grown surface of the whisker therefore corresponds to the ac plane of the Bi-485 phase. Figure 5 shows the temperature dependence of the resistivity of the Bi-485 whisker grown from the $BiSr_2CuAl_xO_y$ precursor. The resistivity is 44 mΩ cm at room temperature, and the whisker shows a semiconducting behavior.

In order to synthesize the whiskers of the Bi-2223 phase with a highest T_c of over 100 K in the Bi-system superconductors, we have variously changed the precursor composition and heating conditions. However, the Bi-2223 whiskers have not been obtained using the glass precursor method. The Bi-2223 whiskers are obtained by annealing the once-synthesized Bi-2212 whiskers in a Ca- and Cu-rich Bi–Sr–Ca–Cu–Pb–O calcined powder while retaining the outline of the form of the original crystals.[21)] The phase conversion from Bi-2212 to Bi-2223 is achieved by selecting a proper annealing conditions. Only the Bi-2223 whiskers do not grow directly from a glass precursor.

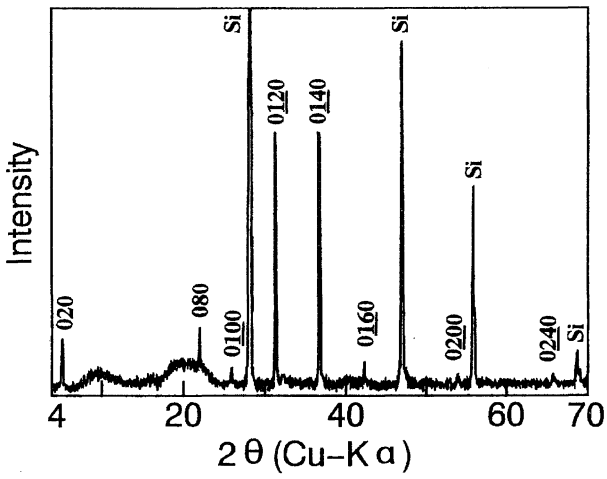

Fig. 4. X-Ray diffraction pattern from the well-grown surface of a ribbon-like Bi-485 whiskers. Silicon powder is used as a internal standard.

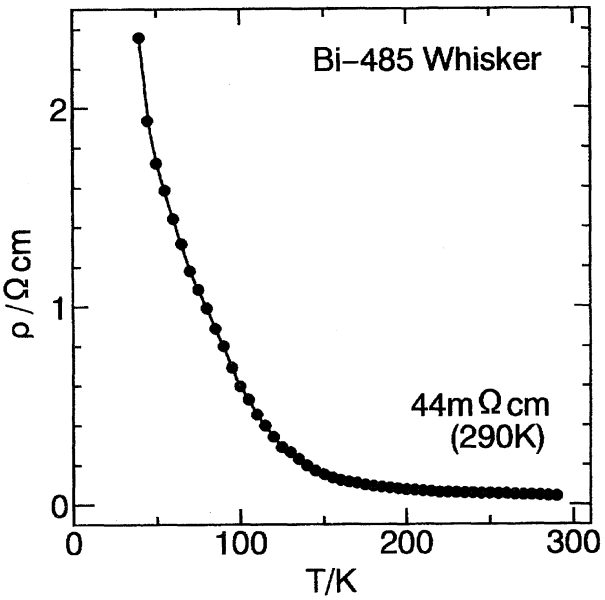

Fig. 5. Temperature (T) dependence of the resistivity (ρ) of Bi-485 whisker.

Regarding the growth mechanism of the Bi-2212 whiskers, a self-supporting micro-top-seeding mechanism has been proposed.[11] The growth site of the Bi-2212 whisker is the bottom, which is buried in the crystallized glass substrate several tens of micrometers deep. In the proposed model, the whisker growth takes place through precipitation from a melt closely surrounding the bottom of the whisker. The melt has the same composition as that of a melt equilibrated with the Bi-2212 phase. The growth temperature of the Bi-2201 whiskers is just below the melting temperature of the precursors. The temperature of the endothermic peaks in the DTA curve, regarded as partial melting, decreases in the same manner as does that of the melting temperature. The glass precursors are curved after whisker growth, as shown in Fig. 2, suggesting that the growth temperature is within the range of partial melting. The existence of a liquid phase is thought to be closely related to the Bi-2201 whisker growth, as in the case of the Bi-2212 phase. Shigematsu et al. have proposed a tentative phase relation in the pseudo-binary system between $Bi_2(Sr, Ca)O_4$ and $(Sr, Ca)CuO_2$.[22] The Bi-2201 and Bi-2212 phases are in equilibrium with a melt, whereas no liquid phase equilibrated with the Bi-2223 phase exists in the proposed relation. The Bi-485 single crystals were obtained by a self-flux method.[20] The crystal phases giving whiskers in the glass precursor method correspond to that equilibrated with a liquid phase. Therefore, the growth mechanism of the Bi-2201 and Bi-485 whiskers is thought to be the same as that of the Bi-2212 whiskers. The variation in the precursor composition would alter the composition of a melt surrounding the bottom of the whisker, resulting in a change in the Bi/Sr ratio of the whiskers.

Conclusion

Bi-2201 and Bi-485 whiskers have been successfully synthesized by controlling the precursor composition and heating temperature in the glass precursor method. An additional element, Pb, can be introduced into the Bi-2201 whiskers. The hole concentration of the as-grown Bi-2201 whiskers is also controlled from the underdoped to the overdoped state by changing the precursor composition. The temperature dependence of the resistivity changes from a semiconducting to a metallic behavior, corresponding to the hole concentration. The growth mechanism of the Bi-2201 and Bi-485 whiskers is thought to be the same as that proposed for the Bi-2212 whiskers.

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