Growth of Co-Based Oxide Whiskers

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Three kinds of single-crystalline whiskers of $Bi_2Sr_2CoO_6$ (BC-221), $(Bi_2Sr_2O_4)_x(CoO_2)_2$ (BC-222), and $(Ca_2CoO_3)_xCoO_2$ (Co-225) phases were grown from the surfaces of precursor plates by annealing in an O_2 gas flow. The phases of the whiskers can be controlled by the Co content of the precursor plates. The average compositions of the whiskers are $Bi_{2.5}(Sr, Ca)_{3.3}CoO_{6+\delta}$, $Bi_{3.0}(Sr, Ca)_{3.1}Co_{2.0}O_{9+\delta}$, and $(Ca, Sr, Bi)_{1.9}Co_{2.0}O_{5+\delta}$. Although the Co-225 whiskers are 1.2 mm at the longest, the BC-221 and the BC-222 whiskers reach lengths of as much as 8.0 mm. Microstructural observations indicate that the growth points of the whiskers are their bases. The length of the whiskers depends on the crystallization status of the precursor plates.

Introduction

The preparation of single-crystalline whiskers possessing a unique shape in the $Bi_2Sr_2CaCu_2O_9$ (Bi-2212) superconducting phase has been reported.[1] Because the whiskers were grown from the surfaces of glassy precursor plates toward free space by annealing in an O_2 gas flow, they have very high crystallinity without defects. Recently, Co-based oxide whisker growth was reported for $(Ca_2CoO_3)_xCoO_2$ (Co-225) and $(Bi_2Sr_2O_4)_x(CoO_2)_2$ (BC-222) whiskers grown from glassy precursor plates. They exhibited excellent thermoelectric properties at high temperatures in air.[2,3]

Thermoelectric power generation is expected to develop as a valuable energy source in the next few decades. Central to the realization of thermoelectric power generation are thermoelectric materials that exhibit not only high thermoelectric figures of merit ($ZT = S^2T/\rho\kappa$, where S is the Seebeck coefficient, T is the temperature, ρ is the electrical resistivity, and κ is the thermal conductivity) upward of 1.0 but also high chemical stabilities at high temperatures in air and no content of harmful elements. Recently, oxide compounds have attracted much attention as promising thermoelectric materials because of their potential to achieve the above-mentioned qualities. The shapes of the Co-225 and BC-222 whiskers are appropriate for thermoelectric applications; however, their lengths have thus far been limited to ca. 1.0 mm. Longer whiskers are required for both application and understanding of the mechanism of attaining high ZT values. Accordingly, elucidation of the Co-based whisker growth mechanism is a prerequisite for the growth of longer whiskers. In this paper, a necessary condition for preparing whiskers of ca. 1.0 cm in length is discussed.

Experimental Procedures

Co-based single crystalline whiskers were prepared using the glass-annealing method.[2,3] Bi_2O_3, $CaCO_3$, $SrCO_3$, and Co_3O_4 powders used as starting materials were mixed with the cationic compositions of Bi:Ca:Sr:Co = 1:1:1:y ($0.5 \le y \le 2.0$). The mixtures were melted in air using alumina crucibles at 1300 °C for 30 min. The crucibles were taken out of the furnace, and the melt was immediately quenched by insertion between two copper plates at room temperature to obtain glassy plates. The precursor plates were given abbreviated names according to their Co contents, e.g., the $y = 0.5$ plate is the 0.5-plate, and the $y = 1.0$ plate is the 1.0-plate. The precursor plates were annealed in a stream of O_2 gas at 880−940 °C for 100 h to grow the whiskers from their surfaces. After annealing, the whiskers grown from the surfaces of the precursor plates were "reaped" using tweezers.

The cationic compositions of the precursor plates and the whiskers were evaluated by energy-dispersive X-ray (EDX) analysis using sintered $BiSrCaCoO_z$ powder as the standard. c cell parameters for the well-grown plane of the whiskers were obtained by X-ray diffraction (XRD) measurements using Si powder as the internal standard. Transmission electron microscopic (TEM) observation was carried out at 300 kV (Hitachi H-9000UHR). Samples for TEM observation were prepared using an Ar ion-etching method.

Results and Discussion

Figure 1 shows scanning electronic microscopic (SEM) images of the whiskers grown from the 0.5- and 1.0-plates. The whiskers grew from the surfaces of the precursor plates and their phases depended on the Co contents of the precursors. From XRD measurements (Figure 2) and EDX analysis (Table 1) of the whiskers, it was found that three phases of the whiskers, $Bi_2Sr_2CoO_6$ (BC-221), BC-222, and Co-225, can be grown. The BC-221 whiskers grew under the conditions of low temperature and low Co content of the precursor plates. The whiskers with high Co contents, namely, in order, the BC-222 and Co-225 phases, were formed with

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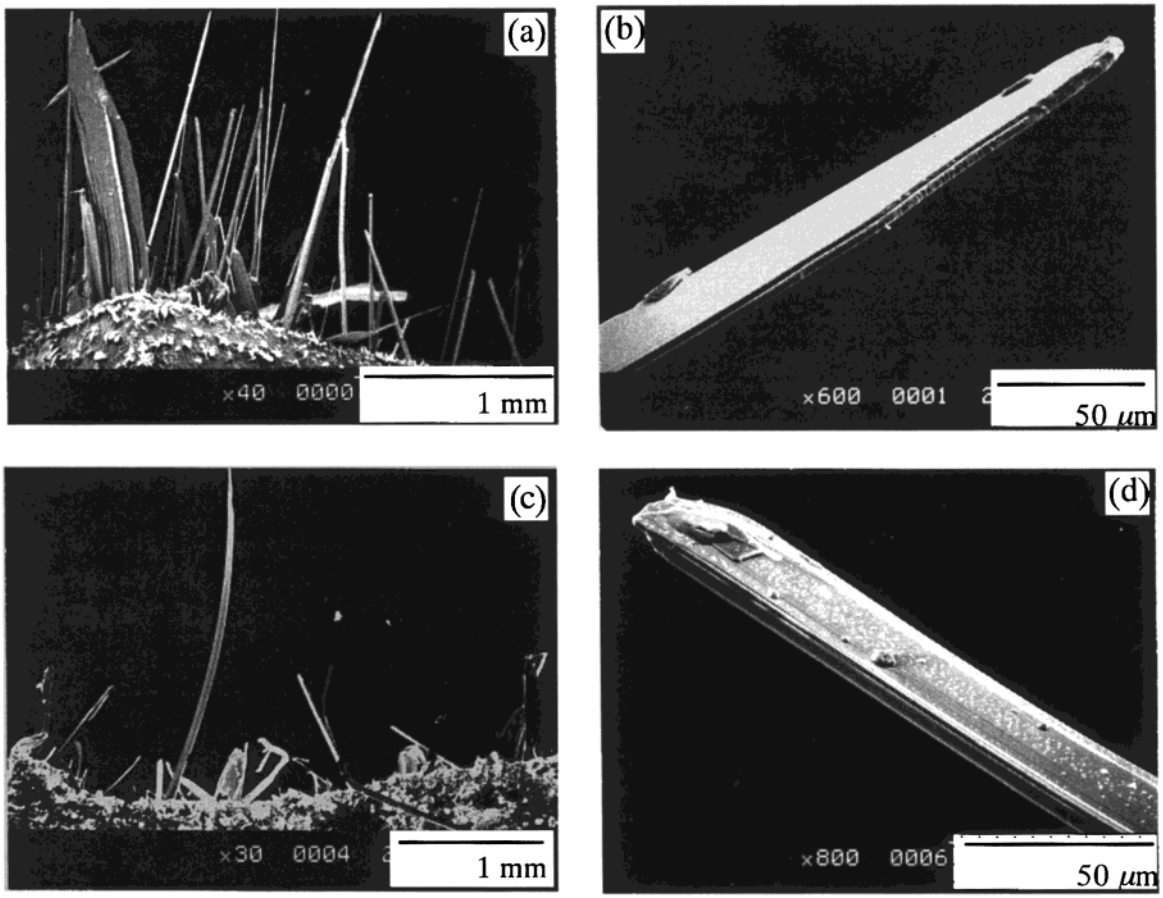

Figure 1. SEM images of the whiskers grown from (a,b) 0.5- and (c,d) 1.0-plates.

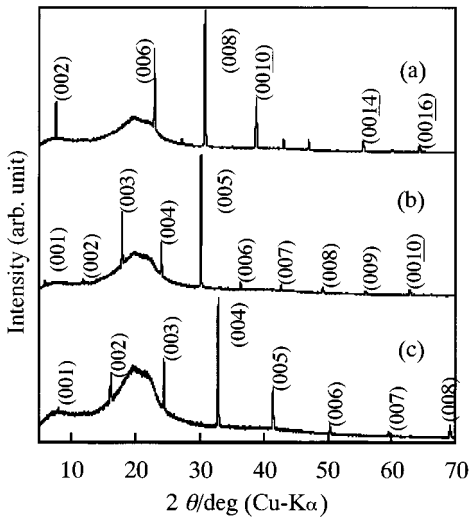

Figure 2. XRD patterns of the well-grown plane of whiskers grown from (a) 0.75-, (b) 1.0-, and (c) 2.0-plates. The broad peak around 20° is due to the glass sample holder.

increasing Co content of the precursor plates and increasing annealing temperature. Both BC-221 and BC-222 whiskers coexist in the 1.0-plate annealed at 880 °C, and both BC-222 and Co-225 coexist in the 1.5-, 1.75-, and 2.0-plates annealed at 920 °C. The two kinds of whiskers in the same plate can be distinguished easily by length. In the 1.0-plate, the BC-221 whiskers are longer than the BC-222 whiskers. On the other hand, the BC-222 whiskers are longer than the Co-225 whiskers in the 1.5-, 1.75-, and 2.0-plates. All whiskers exhibited ribbonlike shapes and measured 1.0−5.0 μm in thickness and 50−200 μm in width. The Co-225 whiskers were shorter than 1.2 mm, whereas the BC-221 and the BC-222 whiskers could be as long as 8.0 mm. All XRD peaks were indexed to (00*l*), except for some peaks in the BC-221 samples. This means that the well-grown plane of the whiskers corresponds to the crystallographic *ab* plane (Figure 2). In the BC-221 whiskers, the diffraction peaks that are not indexed to (00*l*) would be due to misalignment of the well-grown plane on the sample holder or incommensurate modulation structure along the *c* axis. The composition and the *c* cell parameters of the whiskers are almost independent of the annealing temperature and the starting Co content of the precursor plates in each phase. The *c* cell parameters are 23.18−23.22, 14.80−14.81, and 10.87−10.88 Å for BC-221, BC-222, and Co-225, respectively.

TEM images indicate that the three kinds of the whiskers consist of layered structures, as shown in Figure 3. The whiskers have very high crystallinities. Neither defects nor grain boundaries are present in the BC-221 and the Co-225 whiskers. Stacking faults are observed, and the BC-221 phase is included as an intergrowth phase in the BC-222 whiskers. In the BC-221 whiskers, a CoO_6 perovskite layer and a $Bi_2Sr_2O_4$ quadruple rock-salt layer alternate as in the $Bi_2Sr_2CuO_6$ structure.[4] Both BC-222 and Co-225 whiskers exhibit

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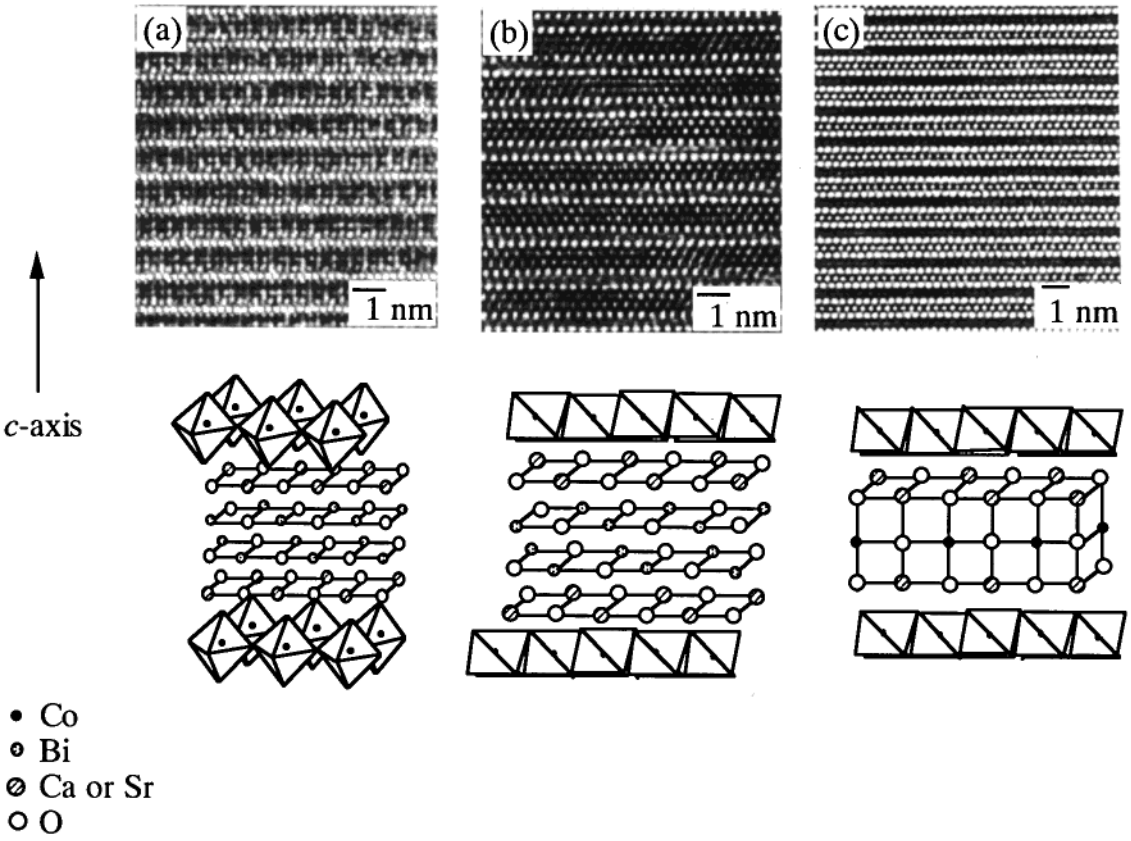
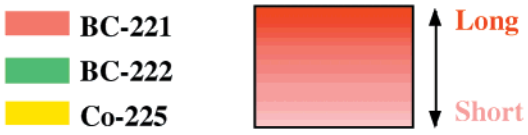


Figure 3. TEM images of the cross-sections and schematic crystal structures of (a) BC-221, (b) BC-222, and (c) Co-225 whiskers.

Table 1. Compositions of Whiskers Grown from $BiSrCaCo_y$ Precursor Plates

y	Annealing Temperature			
	880°C	900°C	920°C	940°C
0.5	$Bi_{2.5}(Ca, Sr)_{3.3}CoO_{6+\delta}$			
0.75	$Bi_{2.6}(Ca, Sr)_{3.3}CoO_{6+\delta}$			
1.0	$Bi_{2.4}(Ca, Sr)_{3.0}CoO_{6+\delta}$ $Bi_{3.0}(Ca, Sr)_{3.1}Co_{2.0}O_{9+\delta}$	$Bi_{3.0}(Ca, Sr)_{3.1}Co_{2.0}O_{9+\delta}$		
1.25	$Bi_{2.9}(Ca, Sr)_{3.0}Co_{2.0}O_{9+\delta}$	$Bi_{3.1}(Ca, Sr)_{3.2}Co_{2.0}O_{9+\delta}$		
1.5			$Bi_{2.9}(Ca, Sr)_{3.0}Co_{2.0}O_{9+\delta}$ $Bi_{0.3}(Ca, Sr)_{1.9}Co_{2.0}O_{5+\delta}$	
1.75			$Bi_{2.7}(Sr, Ca)_{2.8}Co_{2.0}O_{9+\delta}$ $Bi_{0.7}(Ca, Sr)_{2.6}Co_{2.0}O_{5+\delta}$	$Bi_{0.2}(Ca, Sr)_{1.8}Co_{2.0}O_{5+\delta}$
2.0			$Bi_{2.8}(Ca, Sr)_{3.1}Co_{2.0}O_{9+\delta}$ $Bi_{0.3}(Ca, Sr)_{1.9}Co_{2.0}O_{5+\delta}$	$Bi_{0.3}(Ca, Sr)_{2.0}Co_{2.0}O_{5+\delta}$



structures in which a CoO_2 layer composed of edge-sharing CoO_6 units and a $Bi_2Sr_2O_4$ quadruple rock-salt or a Ca_2CoO_3 triple rock-salt layer are piled alternately in the *c* axis direction.[5,6] Although the phase diagram of the Bi−Sr−Ca−Co−O system has not been determined, it is worthy of notice that three kinds of the whiskers with different crystallographic structures can

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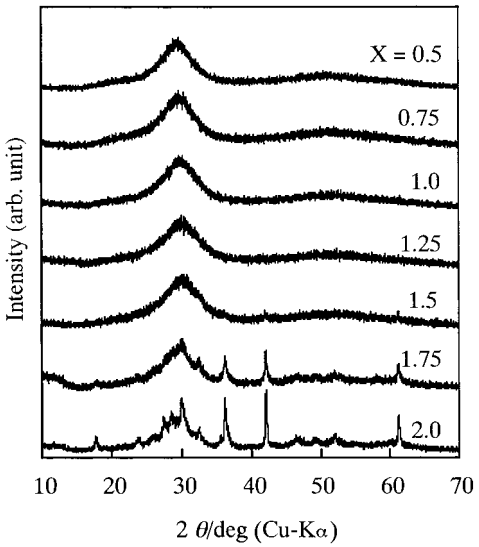

Figure 4. Powder XRD patterns for $BiSrCaCo_y$ precursor plates.

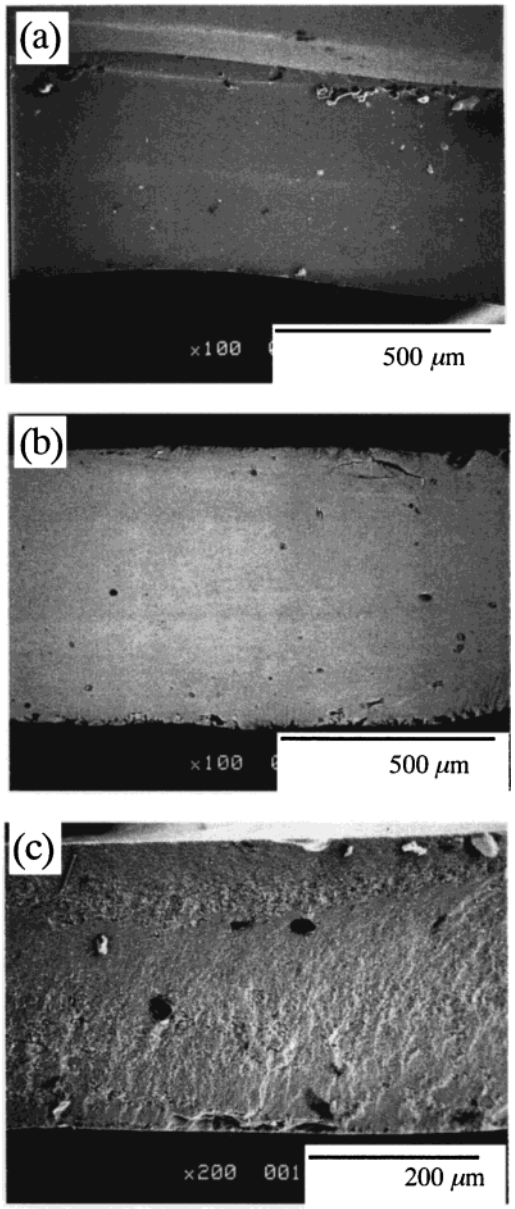

Figure 5. SEM images for cross-sections of (a) 0.5-, (b) 1.0-, and (c) 2.0-plates.

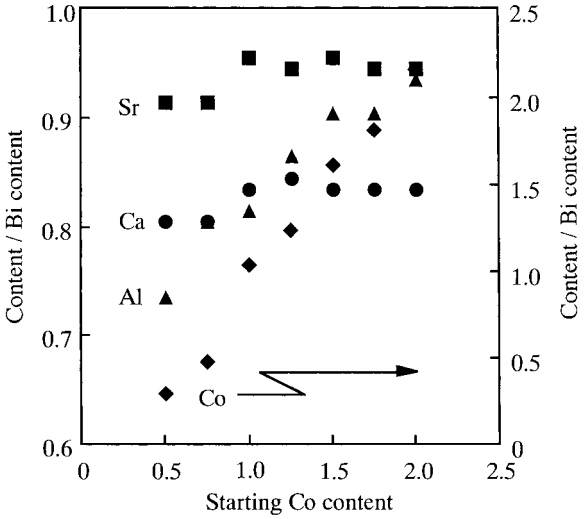

Figure 6. Contents of (■) Sr, (●) Ca, (♦) Co, and (▲) Al normalized by the Bi content of the precursor plates.

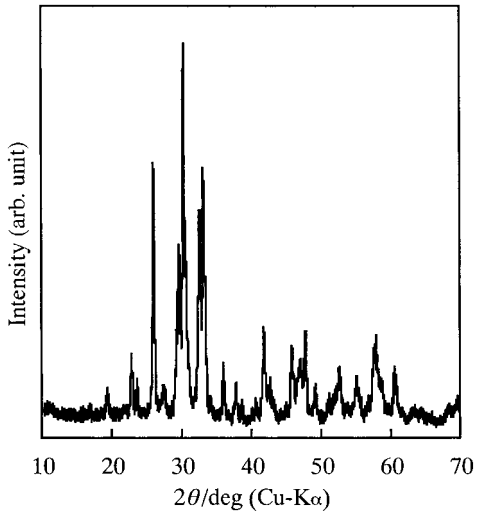

Figure 7. XRD pattern of Al-free 2.0-precursor plate melted in a Pt crucible.

be grown separately by changing only the Co content in the precursor plates.

The difference in whisker length between the Co-225 and BC-221 or BC-222 phases is due to the crystallization status of the precursor plates. The XRD patterns in Figure 4 indicate that there is no crystallization in the 0.5- to 1.5-plates. Diffraction peaks, however, appear in the 1.75- and 2.0-plates. The crystallization of the 2.0-plate is also verified by the SEM image (Figure 5). The cross-sectional surfaces of the 0.5- and 1.0-plates are smooth and shiny. In contrast, for the 2.0-plate, although the surface pressed by the copper plates at the quenching step is shiny, the cross-sectional surface has a turbid whitish appearance, and crystallized grains can be observed in the SEM image. This means that the melting point of the 2.0-plates is higher than those of the other plates.

The EDX analysis of the cationic content of the precursor plates normalized by Bi content is shown in Figure 6. The Ca and Sr contents are almost indepen-

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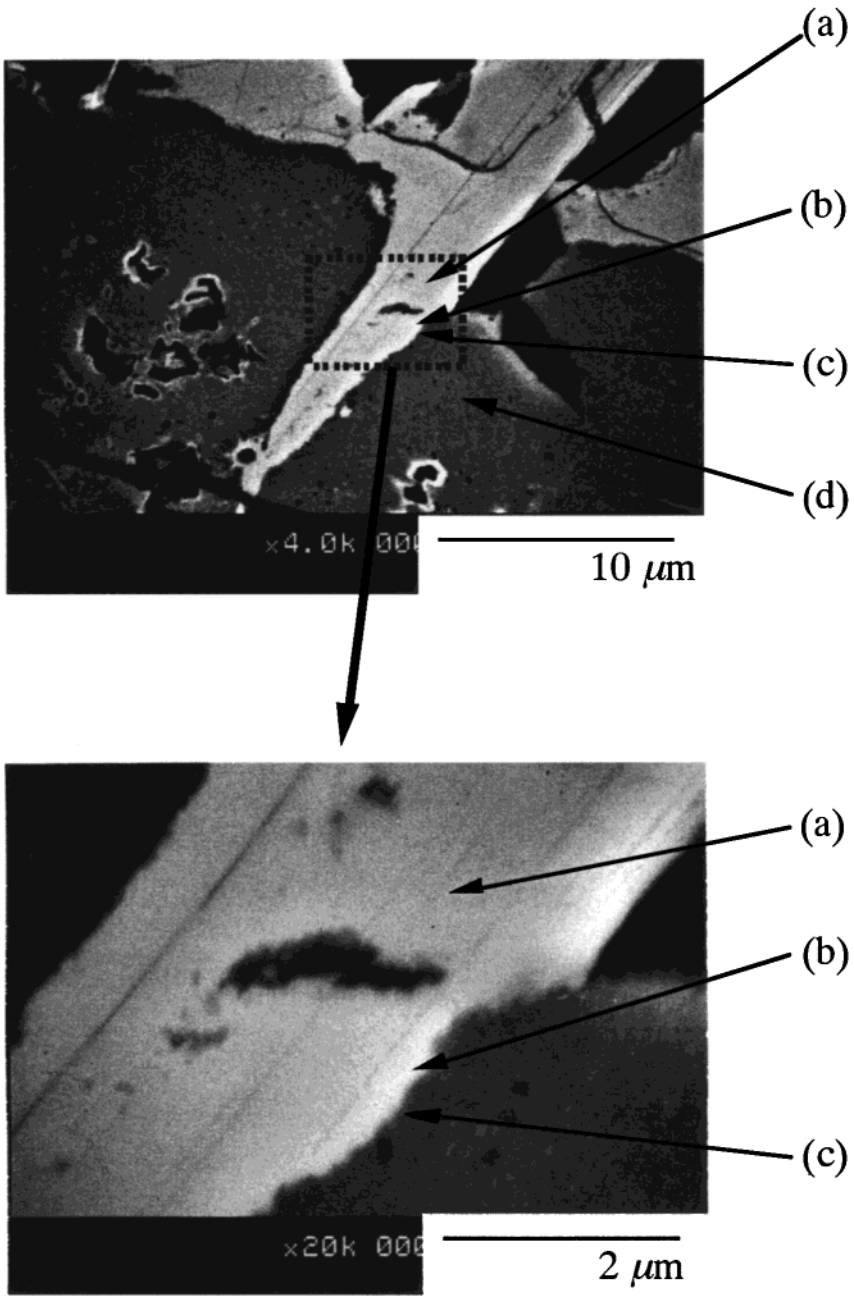

Figure 8. Backscattering image of cross-section of 1.0-plate after annealing. (a) BC-221 ($Bi_{2.2}(Sr, Ca)_{2.6}Co$) whisker, (b) $Bi_{2.7}(Sr, Ca)_{3.3}Al_{0.54}Co$, (c) $Bi(Sr, Ca)_{1.6}Al_{1.2}Co_{0.2}$, and (d) $Bi(Sr, Ca)_{2.0}Al_{1.3}$ regions.

dent of the starting Co content. Although Al was not mixed as a starting element, it entered the plates from the alumina crucible. The content of Al increases with the starting Co content. In the case of the Bi-2212 whisker, Al is also included in the precursor plates.[7] The reason for the rise in the melting point of the precursor plates with increasing Co content seems to be the increase in the Co or/and Al contents. The XRD pattern of an Al-free 2.0-plate prepared by using a Pt crucible gives a result of crystallization, as shown in Figure 7. The diffraction intensities of the peaks are larger than those for the 2.0-plate prepared by using the alumina crucible. No Pt contamination was detected by the EDX analysis. Because the Pt crucible has a higher thermal conductivity than the alumina crucible, a part of the melt in the Pt crucible would crystallize at the moment when the crucible was taken out from the furnace before quenching. The larger part of the melt, however, crystallized during quenching. That is, Al seems to promote glass formation rather than to increase the melting point. The crystallization of the precursor plates is caused by the increase in the starting Co content.

Matsubara et al. assumed a self-supporting micro-top-seeding mechanism in which the growth points of the whiskers are their bases inside the glass precursors for the Bi-2212 whiskers.[8] The growth of the whiskers from the glassy plates indicates that the growth mechanism of the Co-based oxide whiskers is similar to that of the

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(8) Matsubara, I.; Funahashi, R.; Ogura, T.; Yamashita, H.; Tsuru, K.; Kawai, T. J. *Cryst. Growth* **1994**, *141*, 131.

Bi-2212 whiskers. This conclusion is supported by microstructural observations of the bases of the BC-221 whisker (Figure 8). The morphology at the base of the BC-221 whisker is similar to that of the Bi-2212 whisker.[8] The bases of the BC-221 whiskers are surrounded by regions with cationic compositions of $Bi_{2.7}(Sr, Ca)_{3.3}Al_{0.5}Co$ that are richer in Bi and $Bi(Sr, Ca)_{1.6}Al_{1.2}Co_{0.2}$ that are poorer in Bi than the BC-221 phase and that seem to be in liquid and solid states at the annealing temperature, respectively. Although Al is detected in the precursor plates, the whiskers are Al-free because the material elements for the whisker growth are supplied from the liquid region, which includes a low content of Al, and the solid region acts as a support for the whiskers and as a micro-crucible storing the liquid phase. To obtain longer whiskers, preventing the crystallization of the precursor at the quenching step is an essential condition. The whiskers grow from the bases with the complex microstructure of a micro-crucible. Moreover, a large amount of liquid in the micro-crucible is necessary to obtain long whiskers. Glassy precursors are preferable to crystallized precursors for forming such a complex microstructure with a large amount of liquid. For the preparation of long Co-225 whiskers, the melting temperature and the quenching speed must be increased.

All Co-based whiskers have excellent electrical properties. The BC-222 and Co-225 whiskers have high thermoelectric performances at high temperatures.[2,3] The BC-221 whisker shows negative magnetoresistance at low temperatures.[9] Seven kinds of Cu- and Co-based whiskers, $Bi_4Sr_8Cu_5O_{19}$, $Bi_2Sr_2CuO_6$, Bi-2212,[10] BC-221, BC-222, Co-225, and Ca−Co−Cu−O (structure unidentified),[11] can be prepared using the glass-annealing method. Moreover, it seems possible to prepare other oxide single crystals using the glass-annealing method.

Conclusion

We succeeded in the preparation of the BC-221, BC-222, and Co-225 whiskers using the glass-annealing method. The phases of the whiskers can be controlled by the Co contents of the precursor plates. Although the Co-225 whiskers are 1.2 mm at the longest, the BC-221 and BC-222 whiskers reach lengths of as much as 8.0 mm. Because the growth points of the whiskers are their bases, preventing crystallization at the quenching step is very important for obtaining longer whiskers. All Co-based whiskers have excellent electrical properties. The success of the whisker growth of a variety of Cu- and Co-based oxides indicates that the glass-annealing method could function as a general preparation method for single crystals, such as the flux or floating zone methods.

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