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Phase control and growth of Y123 and Y124 crystals below 600 °C by molten KOH flux

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ABSTRACT

Phase formation temperatures of $YBa_2Cu_3O_{7-\delta}$ (Y123), $YBa_2Cu_4O_8$ (Y124) and $Y_2Ba_4Cu_7O_{15}$ (Y247) in a system containing molten KOH have been studied with respect to partial oxygen pressure. At the low oxygen partial pressure of approximately 10^{-5}–10^{-4} atm, crystalline Y123 phase was generated at as low as 550 °C with the superconducting transition temperature above 90 K. In the air atmosphere, Y124 phase was formed below 600 °C and Y123/Y124 phase boundary was observed approximately 775 °C. At the oxygen pressure of 1 atm, Y247 was formed between the regions of Y123 and Y124 formation. Phase formation relation among Y123, Y124 and Y247 is similar to that of the conventional system without KOH, however, phase boundary sifts toward lower temperature by 50–150 °C in the KOH contained system. The morphology of the obtained crystals indicates that they grew by the liquid phase growth mode. The process with the molten KOH has a potential to fabricate superconducting liquid phase epitaxial films at very low temperatures below 600 °C.

1. Introduction

Many crystal growth processes of high-temperature superconductor $YBa_2Cu_3O_{7-\delta}$ (Y123) and its rare-earth substituted series have been studied for device applications composed of superconducting thin films. The processes include, for example, pulsed laser deposition, vacuum evaporation, chemical vapor deposition and metal–organic deposition. They all can achieve good epitaxial growth on a single or crystallo-graphically oriented substrate with good superconducting properties. Unfortunately, the processing temperatures, however, is rather high to produce superconducting devices in a simple, reliable and efficient manner of production.

Crystal growth and liquid phase epitaxy (LPE) using molten BaO–CuO flux (so-called self-flux) is also well known as a formation process for Y123 superconducting films. This process provides an epitaxial film on various types of single crystalline substrate with high growth rate, large thickness and high crystalline perfection [1–4], and even on seeded metal tapes with transport supercurrent [5–9]. Self-flux process can also grow $YBa_2Cu_4O_8$ (Y124) crystals, whose transition temperature is comparable with Y123 phase when Ca is substituted for Y, at higher oxygen partial pressures [10–13]. The process temperature is also so high for Y123 and Y124 phases to easily react with many conventional materials and restricts the usage of various potential materials for substrate and buffer layers [14].

Recently, another flux, molten KOH, was reported for Y124 crystal growth in air at lower temperatures than BaO–CuO flux [15–20]. Furthermore, the molten KOH flux was revealed to synthesize Y123 phase in flowing N_2 atmosphere [21–24]. The synthesis temperature is below 600 °C, which is the lowest process temperature among the conventional preparation methods of Y123 series. This means that the KOH flux process has an advantage for the fabrication of superconducting thin film devices. To apply this process to the device applications, phase formation conditions of Y123 and Y124 should be well defined. Therefore, this paper focuses on the phase formation conditions with molten KOH involved and phase relations of Y123, Y124 and other related phases in relation with oxygen partial pressure and temperature. This paper also discusses a potential of KOH processed LPE growth of superconducting films.

2. Experimental

Y_2O_3, $BaCO_3$ and CuO were used as starting materials. The molar ratio of the metal composition of the raw materials was Y:Ba:Cu = 1:2:4. The raw materials were heated in an alumina crucible with the same weight of KOH to a target temperature in 3 h, kept at the temperature for 12 h and cooled down rapidly to the room temperature. The reaction of the raw materials with KOH is assumed as follows when Y124 is synthesized.

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$$\frac{1}{2}Y_2O_3 + 2BaCO_3 + 4CuO + xKOH + \frac{1}{4}O_2 \rightarrow YBa_2Cu_4O_8 + (x-4)KOH + 2K_2CO_3 + 2H_2O$$

As the result of the reaction, K_2CO_3 could be formed at high temperatures. This implies that the flux used in this experiment can be considered to be the mixture of KOH and K_2CO_3. Atmospheres examined were air and flowing gas of N_2, $O_2 + N_2$ and O_2 for the investigation of the dependence of oxygen partial pressure (PO_2), which was measured by an oxygen sensor during the heat treatment.

To remove KOH and K_2CO_3 form the synthesized phases, water and ethanol was used. The obtained powder was measured by X-ray diffraction for the phase identification and by superconducting quantum interference device (SQUID) for the determination of superconducting transition temperature after adequate oxygenation annealing. Temperature dependence of magnetization was measured under the applied field of 10 Oe by the zero-field-cooling procedure.

3. Results and discussion

The XRD patterns of the samples synthesized in N_2 gas flow ($PO_2 = 10^{-5}$–10^{-4} atm) were shown in Fig. 1. Starting materials were seen in 450 °C-sample, because of low synthesis temperature to form superconducting phases. At temperatures between approximately 500 °C and 700 °C almost single phase of Y123 was detected. The diffraction peaks of Y123 are indicated by solid lines in XRD patterns. *C*-axis lengths of the Y123 phases estimated from (00*l*) diffraction peaks are approximately 1.168 nm, which corresponds to the oxygen content of $7-\delta \approx 6.9$. The XRD line width of 500 °C-sample, however, is obviously broader than the other samples and the peak tops are shifted toward low angle. The corresponding *c*-axis length is estimated to be 1.171 nm. At 800 °C Y_2BaCu0_5 (Y211) phase, which is a high temperature stable phase in Y–Ba–Cu–O system, was intensely detected in XRD with $BaCO_3$ and some unidentified peaks. $BaCO_3$ was probably formed during the washing process, where Ba element dissolved in the residual solidified solution may react with water and CO_2 in air. Both Y123 and Y211 phases were detected at 750 °C.

Samples containing Y123 phase showed 90-K transition of superconductivity. Fig. 2 shows temperature dependence of magnetization measured by the SQUID magnetometer for the samples synthesized at 500 and 550 °C. The sample of the 550 °C-synthesis exhibited a sharp transition at 91 K, indicating the formation of high quality Y123 crystalline phase. On the other hand, the 500 °C-sample showed a broad transition even after the same oxygenation annealing. This indicates inferior crystalline perfection, which corresponds to the broader widths of XRD peaks than those detected on the other samples.

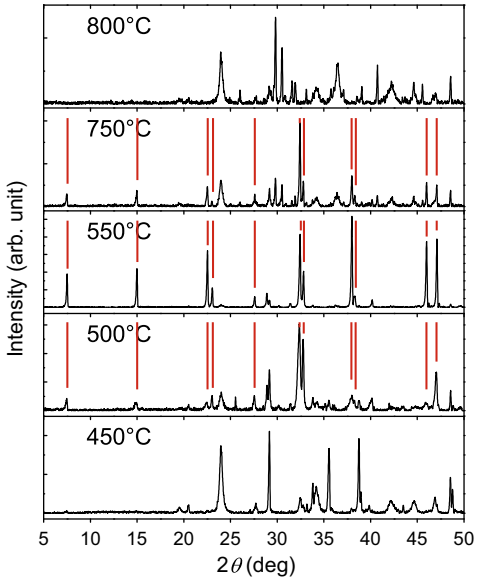

Fig. 1. XRD patterns of samples synthesized at $PO_2 = 10^{-5}$–10^{-4} atm for various preparation temperatures.

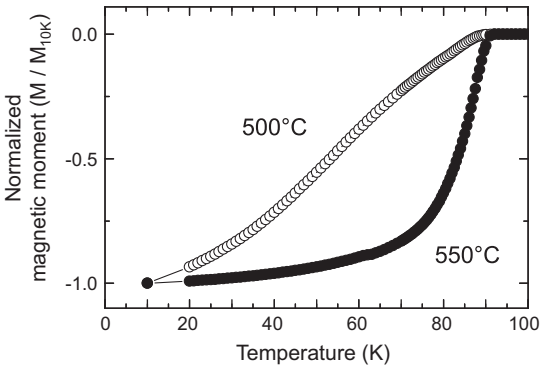

Fig. 2. Normalized magnetic moment of 500 °C- and 550 °C-samples prepared at $PO_2 = 10^{-5}$–10^{-4} atm.

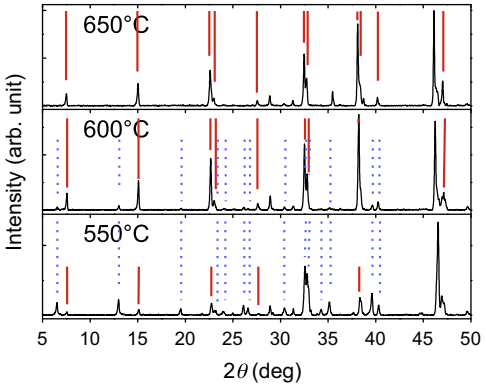

Fig. 3. XRD patterns of samples synthesized at $PO_2 = 0.01$ atm for various preparation temperatures.

The synthesis in the flowing gas of N_2 + 1%O_2 ($PO_2 = 0.01$ atm) at 550 °C generated Y124 phase in addition to Y123 phase as shown in Fig. 3. The diffraction peaks of Y124 are indicated by dotted lines. The magnetization of the 550 °C-sample as a function of temperature shows superconducting transition at approximately 90 K and around 70 K as shown in Fig. 4. These transition temperatures correspond to the existence of Y123 and Y124 phases, respectively. The transition drop at 70 K is larger than that at 90 K, indicating that Y124 phase was formed more in volume than Y123 phase. This corresponds to the XRD intensities of these phases. As the synthesis temperature increased to 650 °C, Y124 phase was diminished and only Y123 phase was formed as determined by the XRD and magnetization measurements. At 800 °C, formed phase changed from Y123 to Y211. At lower temperatures below about 500 °C, raw materials remained unreacted.

As oxygen partial pressure increased to 0.2 atm, the temperature range of Y124 phase formation became wider. The regions in which Y123 or Y124 phase was formed were clearly distinguished. The phase boundary exhibited between 750 °C and 790 °C. Y211 phase was formed above 900 °C.

When oxygen partial pressure was 1 atm, $Y_2Ba_4Cu_7O_{15-\delta}$ (Y247) phase was detected by XRD measurement at a region between