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## Large REBCO single crystals: growth processes and superconducting properties

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Abstract. A low solubility of yttrium in the Ba-Cu-O melt and a steep liquidus slope near the peritectic temperature  $T_p$  lead to a very slow growth rate of YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7- $\delta$ </sub> (YBCO or Y123) single crystals and this creates a problem in growth of large single crystals. To solve this problem, increasing the growth rate and extending the growth time are significant. Using the crystal pulling method, we have developed several processes and succeeded in growing large Y123 and Nd<sub>1-x</sub>Ba<sub>2+x</sub>Cu<sub>3</sub>O<sub>7- $\delta$ </sub> (NdBCO) single crystals with an edge size over 25 mm in the a-b plane and up to 20 mm in the *c*-axis direction. In this article, three methods of increasing growth rate are reviewed. They are (i) employing high oxygen partial pressure, (ii) choosing RE (rare earth) elements with higher solubilities in the Ba-Cu-O solution, and (iii) growing REBCO crystals including several RE elements. Using these methods the growth rate was effectively enhanced from two to five times that of Y123. The critical temperature  $T_c$  of 92.7 K was achieved from a Y123 single crystal grown under 1 atm oxygen partial pressure, indicating that  $T_c$  is insensitive to the oxygen pressure of the growth atmosphere in the YBCO system. A high  $T_c$ of about 95 K for NdBCO superconductors with a sharp transition was obtained by controlling the ratio of Ba to Cu (Ba/Cu) in the liquid, suggesting that the Ba/Cu ratio in the liquid composition has a significant importance in controlling  $T_c$ . By partial substitution of Sm at the Y sites up to 30%,  $Y_{1-x}Sm_xBa_2Cu_3O_{7-\delta}$ (Y(Sm)BCO) crystals show a  $T_c$  of 91  $\pm$  1 K and do not display  $T_c$  depression.

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#### 1. Introduction

It is well known that there are two types of melt for singlecrystal growth, i.e., congruent melting and incongruent melting. In the case of congruent melting, solid and melt have the same compositions, while in the case of incongruent melting they have different compositions as shown in table 1. Single crystals grown under congruent melting have a higher growth rate since a diffusioncontrolled solute transportation is not necessary. On the

**Table 1.** A comparison between congruent and incongruent melting for single-crystal growth.

Congruent melting	Incongruent melting	
Melt constitution Growth rate Example growth rate	solid = melt ∼mm h <sup>−1</sup> Si several tens mm/h	solid ≠ melt ~mm d <sup>-1</sup> YBCO 1–2 mm d <sup>-1</sup>

other hand, since the solid and the melt compositions are different in the case of incongruent melting, solute diffusion is required for single-crystal growth. In comparison with single-crystal growth under congruent melting, this solute diffusion process leads to a very slow growth rate. Table 1 lists two typical materials, the semiconductor Si and the superconductor Y123. Single-crystal Si grows in a congruent melt and possesses a very fast growth rate of several tens of millimetres per hour. In contrast, single-crystal Y123 grows in an incongruent melt and features a slow growth rate of superconductor Y123 is much lower than that of semiconductor Si.

The yttrium solubility limits at temperatures near the peritectic temperature were experimentally obtained by analysing the Y equilibrium concentration in the Ba-Cu-O solution [2]. The Y concentration is very low at about 0.6 at.% in the Ba-Cu-O solution for a given growth temperature [2], while it is nearly 16.7 at.% in the Y123 single crystal. In addition, a liquidus slope is steep. It is both low Y solubility and sharp liquidus slope that result in a very slow growth rate for Y123 single crystals, which is about two orders of magnitude lower than that of an Si single crystal. Because of this, it becomes crucial to achieve large Y123 single crystals for the practical application. There are two main aspects to the growth of large crystals. One is to increase the growth rate while the other is to extend the growth period. The second aspect related to a long growth period involves several problems:

(i) retaining a relatively constant amount of solution in the crucible and preventing the solution from creeping;

(ii) preventing the formation of floating 123 particles; and

(iii) keeping a relatively constant growth temperature.

As to these three problems, some methods [3] have been already reported and they are out of the scope of the present investigation. Our particular interest is the first aspect, regarding increasing growth rate, and this will be discussed below. The growth rate referred to in this article is the one in the *c*-axis direction ( $R_c$ ).

The flux method of growing Y123 single crystals has been widely reported [4–9]. Using this method, the crystal nucleation in the melt cannot be controlled. Therefore, it is quite difficult to stabilize the growth of a large single crystal. Normally, the size of single crystals obtained by the flux method is several square millimetres in the a-bplane and as thin as 1 mm or less in the *c*-axis direction. Sheel [4] and Wolf *et al* [5] reported that the thickness of Y123 crystals was greatly increased by adjusting the

rate  $R_c$  of the flux method is quite slow; it was found to be 0.004 mm h<sup>-1</sup> [6]. By stirring the melt, the thickness of the diffusion layer was reduced and the crystal growth rate could be increased [7, 8]. Moreover, by introducing a pin into the middle of the melt, a crystal growth rate of up to 0.016 mm h could be reached [6]. Yamada and Shiohara developed a solute-rich-liquid crystal-pulling method (SRL-CP method) [10] to solve

crystal-pulling method (SRL-CP method) [10] to solve the problem of low Y supersaturation at the growth temperature. In this method, Y2BaCuO5 (Y211) powder was settled at the bottom of the crucible and BaO-CuO composite  $(3BaCuO_2 \cdot 2CuO)$  was added to this layer of Y211 powder. For crystal growth, the  $3BaCuO_2$ . 2CuO solution was kept in a temperature gradient so that Y<sub>2</sub>BaCuO<sub>5</sub> (Y211) solid phase could exist at the bottom of the crucible as the Y supply source. With natural and forced convections in the flux, this Y solute could be transported to the surface of the solution, leading to a solute supersaturated solution growth. In contrast to the flux method, the growth rate was found to be above 0.05 mm  $h^{-1}$  [1]. Namikawa *et al* reported an optimized growth process [11] for continuous Y123 single-crystal growth. In this process, the crystal rotation rate was reduced with increasing crystal size in order to keep a nearly constant growth temperature since the increase in crystal size led to an increased interface temperature. A Y123 single crystal was successfully obtained with a size of  $17 \times 17 \text{ mm}^2$  in the *a*-*b* plane and 8 mm in the *c*-axis direction after a continuous growth period of 266 h [11]. Moreover, extended growth period processes have been reported in various ways, considering the convection of the melt, utilizing numerical calculation simulation to control growth conditions [3], and employing a lateral temperature gradient on the liquid surface to reduce the formation of Y123 on the crucible wall [3]. These successful methods have led to a long period for Y123 single-crystal growth. However, because of the low Y concentration and the steep liquidus slope near  $T_p$ , the crystal growth rate is not sufficiently high to produce a large Y123 single crystal even in the SRL-CP method. Therefore, it is crucial to increase the growth rate for a large high- $T_c$  superconductor.

cooling rate below 1 K h<sup>-1</sup>. Due to the low Y solubility

and the difficulty of increasing supersaturation, the growth

In this article, three methods of increasing growth rate are reviewed:

(i) employing high oxygen partial pressure [12, 13];

(ii) choosing RE elements with higher solubility in the solution [14, 16]; and

(iii) growing REBCO crystals including several RE elements [17].

Superconducting properties are strongly dependent on REBCO systems and processes [18–21], so the interests of the present work also cover superconductivity with enlarging single-crystal processes and related REBCO systems.

#### 2. Growth rate determining parameters

Based on Cochran flow analysis [22] and considering a mass flow balance, the growth rate of a Y123 single

crystal was estimated by Yamada *et al* [1]. Assuming the interface kinetics is negligible, i.e., the Y concentration at the interface  $C_i$  is equal to the Y equilibrium concentration at the temperature of the liquid surface  $C_l(T_s)$ , the growth rate at the maximum  $R_{max}$  is

$$R_{max} = \frac{D}{\delta} \frac{\{C_l(T_b) - C_l(T_s)\}}{\{C_{123} - C_l(T_s)\}}$$
(1)

where  $R_{max}$  is the maximum growth rate, D is the diffusion coefficient of the solute in the solution,  $C_l(T_b)$  is the equilibrium concentration at the bottom of the crucible,  $C_l(T_s)$  is the equilibrium concentration at the growth temperature, and  $C_{123}$  is the concentration of the solute in the Y123 phase.  $\delta$  is the thickness of the solute boundary layer in the solution given by the equation

$$\delta = 1.6D^{1/3} \nu^{1/6} \omega^{-1/2} \tag{2}$$

where  $\nu$  is the kinematic viscosity and  $\omega$  is the angular velocity of rotation. Substitution of equation (2) into equation (1) leads to

$$R_{max} = \frac{D^{2/3}\omega^{1/2}}{1.6\nu^{1/6}} \frac{\{C_l(T_b) - C_l(T_s)\}}{\{C_{123} - C_l(T_s)\}}.$$
 (3)

Assuming a linear relationship between the temperature and the RE element concentration near  $T_p$  in the Ba–Cu–O solution,  $C_l(T_b)$  and  $C_l(T_s)$  can be expressed by

$$C_l(T_b) - C_l(T_p) = \frac{T_b - T_p}{m_l^{211}}$$
(4)

$$C_l(T_s) - C_l(T_p) = \frac{T_s - T_p}{m_l^{123}}$$
 (5)

where  $m_l^{211}$  and  $m_l^{123}$  represent the liquidus slope above and below  $T_p$ , respectively. By substituting (4) and (5), (3) gives

$$R_{max} = \frac{D^{2/3}\omega^{1/2}}{1.6\nu^{1/6}} \frac{\{(T_b - T_p)/m_l^{211}\} + (T_p - T_s)/m_l^{123}}{\{C_{123} - C_l(T_s)\}}.$$
(6)

To enlarge the single crystal, several growth rate determining parameters can be discussed on the basis of (6). First, the RE concentration at the temperature of the surface  $C_l(T_s)$  increases with the enhancement of the solubility of the RE element  $C_l(T_p)$ , and this will lead to reduction of the difference  $[C_{123} - C_l(T_s)]$ . As a result, the growth rate increases as well. Second, a low liquidus slope of  $m_l^{211}$  and  $m_l^{123}$  may cause the high supersaturation when a liquid temperature gradient is given between the surface and bottom. In addition, a high temperature gradient between the liquid surface and bottom,  $\Delta T = T_b - T_s$ , also raises the supersaturation on the growth surface by forced and natural convection. Thus, these increased supersaturations result in a high growth rate. Third, using high rotation speed  $\omega$ , one can also effectively reduce the thickness of the solute boundary layer  $\delta$  (2) and consequently achieve a higher growth rate too. Moreover, a higher growth temperature will result in a higher solute diffusion coefficient D in the solution and a lower kinematic viscosity  $\nu$ . In accordance with the facts that D is higher and v is lower, the growth

rate becomes higher. As to the RE solute concentration in REBCO, it should be pointed out that  $C_{123}$  may not be constant at 16.7 at.%. When RE–Ba solid solution occurs, for instance for RE = Nd, Sm or Gd,  $C_{123}$  may be higher than 16.7 at.%. In this case, the supersaturation  $\Delta C = C_{123} - C_l(T_s)$ , should be considered instead of  $C_l(T_s)$ only.

### 3. RE element solubility graph and crystal growth rate

#### 3.1. Employing high oxygen partial pressure

Yttrium solubility limits were measured under different oxygen partial pressures [23] as shown in figure 1. First, the yttrium equilibrium concentrations at the peritectic temperature  $C_l(T_n)$  were approximately 0.60 and 0.70 at.% for oxygen pressures of 0.21 and 1 atm, respectively, i.e.,  $C_l(T_p)$  increased with increasing oxygen partial pressure. Correspondingly, the yttrium equilibrium concentration at the growth temperature of  $C_l(T_s)$  also increases. Further, there is a slight decline in the liquidus slope of  $m_l$  with an increase of the oxygen partial pressure. Moreover, a higher growth temperature should be applied at high oxygen partial pressure, which may cause higher solute diffusion coefficient D and lower kinematic viscosity v in the solution. As described above, based on (6) and figure 1, a higher oxygen partial pressure may facilitate Y123 singlecrystal growth. For the same reason, one can expect a high growth rate for other REBCO crystals as well using a high oxygen partial pressure. In this review, we will focus on the work associated with Y123 single-crystal growth under 1 atm oxygen pressure.

### **3.2.** Choosing RE elements with higher solubilities in the solution

Solubilities of several RE elements (Y, Nd, Sm, Gd, Dy, and Yb) have been investigated in Ba-Cu-O near the peritectic temperature [2] to understand the REBCO single-crystal growth. Among them, Sm and Nd feature the highest solubility and the smallest liquidus slope near  $T_p$  [2]. Sm and Nd solubility near  $T_p$  is about 1.8 and 3.2 at.%, respectively, in Ba-Cu-O solution, as shown in figure 2, which is several times higher than Y solubility. In addition, the slopes of the Sm and Nd liquidus are much lower than that of Y. Furthermore the SmBCO and NdBCO oxides have melting temperature about 1060 and 1086 °C, respectively, which is approximately 55 and 80 °C higher than that of Y123 [2]. Due to these high melting temperatures, either Sm or Nd is likely to have a high diffusion coefficient D and a low kinematic viscosity  $\nu$ . Because of these several merits, one can expect the highest growth rate of crystals in the NdBCO system, so we choose the NdBCO system for growth of large single crystals.



Figure 1. The temperature dependence of yttrium solubility in a solution with a Ba/Cu ratio of 3:5 under different oxygen partial pressures.



Figure 2. The temperature dependence of Y, Sm, and Nd solubilities in a solution with a Ba/Cu ratio of 3:5 in air.

### 3.3. Growing REBCO crystals including several RE elements

Since Sm and Nd have high solubility in the Ba–Cu–O melt as shown in figure 2 [2], we believed that a high growth rate could be achieved for crystal growth by partial

substitution of Sm or Nd at the Y site. Moreover, by controlling the Sm (or Nd) substitution content, the  $T_c$  may not be depressed.

In the present work, the growth of Y(Sm)BCO single crystals was investigated [17]. Figure 3 shows the temperature dependence of the Y + Sm content in the Ba–

	(i)	(ii)	(iii)
REBCO system	YBCO ( $P(O_2) = 1$ atm)	NdBCO	Y(Sm)BCO
Growth method	SRL-CP	TSSG	SRL-ĆP
Crucible	$Y_2O_3$	$Nd_2O_3$	$Y_2O_3$ or $Sm_2O_3$
Solution	Ba <sub>3</sub> Cu <sub>5</sub> O <sub>8</sub>	$Ba_x Cu_y O$ , x/y = 0.55 - 0.85	Ba <sub>3</sub> Cu <sub>5</sub> O <sub>8</sub>
Solute	Y from $Y_2BaCuO_5$	Nd from Nd <sub>2</sub> O <sub>3</sub> crucible	Y, Sm from $Y_2BaCuO_5$ , Sm <sub>2</sub> BaCuO <sub>5</sub>
Seed crystal	YBCO thin film	NdBCO thin film	YBCO or SmBCO thin film
Rotation speed (rpm)	70–120	70–120	70–120
Growth atmosphere Surface temperature (°C) Temperature difference $\Delta T^{a}$ (°C)	$P(O_2) \approx 1 \text{ atm}$ 1013–1018 ~10	air 1058–1070 2–5	21–100% <i>P</i> (O <sub>2</sub> ) 1000–1023 ~10

**Table 2.** Experimental conditions for REBa<sub>2</sub>Cu<sub>3</sub>O<sub>7- $\delta$ </sub> single-crystal growth.

<sup>a</sup> Temperature difference between the surface and bottom in the liquid.



**Figure 3.** The Y and Sm concentrations in the solution versus the growth temperature  $T_g$ .

Cu–O melt, indicating that Y + Sm concentration increased from 0.531 to 0.765 at.% at growth temperatures from 1000 to 1020 °C. In comparison with the YBCO system, this increased solubility and growth temperature could be expected to produce a high growth rate for single crystals.

#### 4. Growth conditions of REBCO single crystals

Experimental conditions for REBCO single-crystal growth are listed in table 2, including (i) a Y123 single crystal grown under 1 atm oxygen pressure, (ii) an NdBCO single crystal grown under air, and (iii) Y(Sm)BCO single-crystal growth.

First of all, we used  $Y_2O_3$ ,  $Sm_2O_3$ , and  $Nd_2O_3$  crucibles to prevent contamination. The rotation speed was set from 70 to 120 rpm according to the growing crystal size. Both air and 1 atm oxygen pressure were selected for the growth atmosphere. The high oxygen partial pressure was generated by flowing oxygen gas at a rate of approximately 450 ml min<sup>-1</sup>. Seed crystals used were YBCO, SmBCO, and NdBCO thin films deposited on MgO single crystals [24], which were prepared by rf thermal plasma evaporation. XRD patterns of the films show only (00l)(l = 1, 2, ..., 7) peaks of REBCO, indicating that these films grew with a *c*-axis orientation.

Secondly, the SRL-CP method as described in [11] was used for YBCO and Y(Sm)BCO crystal growth to enhance supersaturation.  $Y_2BaCuO_5 \ (Y211) \ and \ Sm_2BaCuO_5$ (Sm211) powders were settled at the bottom of the crucible and BaO-CuO composite was added above this layer. During crystal growth, the Y or Sm solute could be transported to the surface of the liquid by forced and natural convections so that a higher supersaturation could be achieved. In contrast, an ordinary top-seeded solutiongrowth (TSSG) technique was applied to grow NdBCO single crystals [14]. The Nd solute was supplied by the interaction between the molten solvent and the crucible Nd<sub>2</sub>O<sub>3</sub>. The reason is that it is not necessary to increase supersaturation for the NdBCO system due to the high Nd solubility and the low liquidus slope near  $T_p$ . For the same reason, in the case of NdBCO crystal growth the temperature gradient in the liquid was limited to less than 5 °C between the surface and bottom while a higher temperature gradient was applied in the SRL-CP method in order to achieve the high supersaturation.

Lastly, to study the effects of liquid composition on the  $T_c$ , the various xBaO + yCuO powders (the ratio of xto y is 1:1, 3:5, or 1:3) were introduced into the crucible to adjusting the Ba/Cu ratio in the solution from 0.55 to 1.00. When the Ba/Cu ratio ranged from 0.55 to 0.85 in the solution, a group of NdBCO single crystals was produced successfully [16].

#### 5. Growth rate of REBCO single crystals

Figure 4 displays the growth length in the *c*-axis direction versus the growth time for single crystals grown from the Ba–Cu–O solution with the Ba/Cu ratio of 3:5. The rotation speed was kept constant at 120 rpm for continuous pulling. Obviously, the growth length slope reflects the growth rate. The graphs display comparisons for (*a*) growing under air and 1 atm oxygen pressure for Y123 single crystals, (*b*) growing Y123 and NdBCO single crystals, and (*c*) Y123 single crystals with and without Sm addition.



**Figure 4.** The growth time dependence of growth length in the *c*-axis direction,  $L_c$ , for REBCO single crystals grown in the solution with the Ba/Cu ratio of 3:5: (a) Y123 crystals grown under air and 1 atm oxygen pressure; (b) Y123 and NdBCO single crystals grown under air; (c) Y123 and Y<sub>0.881</sub>Sm<sub>0.119</sub>Ba<sub>2</sub>Cu<sub>3</sub>O<sub>7- $\delta$ </sub> single crystals grown under air.

#### 5.1. Growing under air and 1 atm oxygen pressure

As shown in figure 4(a), it is clear that the singlecrystal growth is nearly 1.5–2.5 times faster under 1 atm oxygen pressure than under air atmosphere, indicating that the growth rate can be significantly enhanced using high oxygen partial pressure. By using this process, a large single crystal ( $19.8 \times 19.5 \text{ mm}^2$  in the *a*-*b* plane and 16.5 mm in the *c*-axis direction as shown in figure 5) was successfully produced from a small crucible of 50 mm diameter [12, 13]. These results are promising for future industrial applications that involve production of much larger REBCO single crystals in a larger crucible at a higher growth rate.

#### 5.2. Growing Y123 and NdBCO single crystals

The slope of the growth length curve of the NdBCO single crystal is four to five times that of the Y123 single crystal [14, 16] as shown in figure 4(*b*). A large NdBCO single crystal (with dimensions of  $24 \times 24$  mm<sup>2</sup> in the *a*–*b* plane and 21 mm in the *c*-axis direction as shown in figure 6) was achieved after crystal pulling for only 67 h. It takes about two weeks to obtain a YBCO single crystal of roughly the same size. To the best of our knowledge, this is the largest REBCO superconductor single crystal grown by the crystal pulling method. Such a high growth rate suggests that NdBCO oxide is the strongest candidate in the REBCO systems for producing large single crystals in a short time for a potential application.

#### 5.3. Y123 single crystals with and without Sm addition

An increased growth rate achieved by the Sm substitution for Y can be seen from figure 4(c). The Sm substitution content *x* was 0.119 and the growth temperature was  $1010^{\circ}$ C. The slope of the growth length curve for the Y<sub>0.881</sub>Sm<sub>0.119</sub>Ba<sub>2</sub>Cu<sub>3</sub>O<sub>7- $\delta$ </sub> single crystal was nearly twice that of the Y123 single crystal [17]. This enhanced growth rate should mainly be attributed to the high Y + Sm concentration in the Ba–Cu–O melt as shown in figure 3. Thus, it can be concluded that the growth rate could be effectively raised by partly substituting RE elements with higher solubility.

It should be pointed out that the growth rate is a function of either the growth temperature or the RE solubility as discussed above. In the growth temperature range from 1000 to  $1020 \,^{\circ}$ C, a series of Sm-substituted single crystals was grown with Sm content of *x* ranging from 0.059 to 0.303 as shown in figure 7. A higher growth temperature leads to a higher Sm concentration in the liquid. Thus this enhancement in both growth temperature and Sm concentration is responsible for the high growth rate. In brief, the growth rate depends on the extent of Sm substitution.

### 6. Superconducting properties of REBCO single crystals

Critical temperatures  $T_c$  were determined by measuring magnetic susceptibility. A field of 10 Oe was applied parallel to the *c*-axis ( $H \parallel c$ ). Y123 samples were oxygenated at 500 °C for 2 weeks, while NdBCO samples were oxygenated at 340 °C for 200 h. For Y(Sm)BCO samples, we chose oxygenating conditions of 500 °C for 3 d.



**Figure 5.** An as-grown Y123 single crystal was produced under 1 atm oxygen pressure. The size is  $19.8 \times 19.5 \text{ mm}^2$  in the *a*-*b* plane and 16.5 mm in the *c*-axis direction.



**Figure 6.** An as-grown NdBCO single crystal was produced in the solution with the Ba/Cu ratio of 3:5 under air. The size is  $24 \times 24$  mm<sup>2</sup> in the *a*–*b* plane and 21 mm in the *c*-axis direction.

### 6.1. High oxygen partial pressure and physical properties

Figure 8 displays the temperature dependence of magnetization for Y123 single crystals grown under air and 1 atm oxygen pressure.  $T_c$  values shown are 93.0 K for the crystal grown under air and 92.7 K for the crystal grown under 1 atm oxygen pressure [12, 25]. Both curves display a transition width as small as 2 K. This result suggests that the  $T_c$ is not sensitive to the growth atmosphere in the YBCO sys-



**Figure 7.** Sm substitution contents in Y(Sm)BCO single crystals versus the growth temperature  $T_{q}$ .

tem, while it was widely reported to be very sensitive in the case of the NdBCO and SmBCO systems [18–21] because of REBCO solid solution formation from relatively large ionic radii. For this reason, the high oxygen partial pressure seems to be ineffective for the single-crystal growth of REBCO with large ionic radii.

#### 6.2. Substitution of Nd for Ba and critical temperature

REBCO superconductors when RE = Nd and Sm show relatively low transition temperatures  $T_c$  in the conventional melt-textured process because these RE ions can easily enter the Ba sites [18–21]. The oxygen-controlled melt-textured method (OCMG) has been found to be beneficial to produce high- $T_c$  NdBCO and SmBCO bulk superconductors [18–21], suggesting that the low oxygen partial pressure is an effective  $T_c$ -controlling parameter for producing REBCO superconductors.



**Figure 8.** The temperature dependence of magnetization for Y123 single crystals grown under air and 1 atm oxygen pressure.



**Figure 9.** The temperature dependence of magnetization for NdBCO single crystals grown under air in different ratios of Ba to Cu in the solution.

In our recent work [16], we presented the result of the 95 K NdBCO superconductors, which were grown in air by controlling liquid composition. Figure 9 shows the temperature dependence of magnetization for NdBCO single crystals grown in solutions with different Ba/Cu ratios. Obvious effects of Ba/Cu ratio in the solution on superconducting transition behaviours are exhibited. With raised Ba/Cu  $T_c$  increases and the transition width  $\Delta T$ becomes narrow, indicating that the Ba to Cu ratio in the solution plays a significant role in controlling the  $T_c$  of the NdBCO superconductor. There are obvious advantages over the method of growing crystals by means of low oxygen partial pressure since one can simply produce high- $T_c$  NdBCO superconductor in air. Furthermore, figure 10 shows the temperature dependence of magnetization in the temperature range of 87–97 K for crystals grown in solution with a Ba/Cu ratio of around 0.8. The onset temperature of about 95 K is clearly exhibited. This proves that a high  $T_c$  (>90 K) with a sharp transition can be achieved using a Ba/Cu ratio in the solution of approximately 0.8.

The NdBCO quasi-ternary phase diagram in the



**Figure 10.** The temperature dependence of magnetization for the NdBCO single crystals grown under air in solution with the Ba/Cu ratio at approximately 0.8.

vicinity of the Nd123–liquid coexistence region at different temperatures was presented by Kambara *et al* [26]. It was clarified that the different points on the liquidus are connected by tie lines with certain points on the solid solution line. What is more, with higher Ba/Cu ratio in the solution the corresponding NdBCO crystal becomes closer to the stoichiometric 123 composition, in other words, the extent of Nd substitution is reduced. Thus high  $T_c$  could be achieved.

#### 6.3. Sm substitution and superconductivity

High critical temperatures  $T_c$  of  $91 \pm 1$  K were obtained from oxygenated Y(Sm)BCO single crystals grown under air as shown in figure 11, suggesting that there is no depression in  $T_c$  with Sm substitution up to 30% [17]. Moreover, for comparison, the high oxygen pressure of 1 atm was used to investigate the effect of oxygen partial pressure on  $T_c$ . A high critical temperature  $T_c$  of 92.4 K with a transition width less than 1 K was also obtained from a  $Y_{0.785}Sm_{0.215}Ba_2Cu_3O_{7-\delta}$  single crystal grown under 1 atm oxygen pressure at 1023 °C as shown in figure 12 [17], indicating that  $T_c$  tends to be insensitive to the oxygen partial pressure of the growth atmosphere for Y(Sm)BCO single crystals with Sm substitution up to 20%, while it is very sensitive in the SmBCO system [27, 28]. For this reason, the crystal growth of Y(Sm)BCO needs no control of the oxygen partial pressure in the said x range. There are obvious advantages over the other two processes. One is to use the high-oxygen-pressure (1 atm) technique of increasing growth rate in the YBCO system and the other is to use the low-oxygen-partial-pressure method of superconductivity enhancement in the SmBCO and NdBCO systems. Similarly, other RE elements with high solubility in the Ba-Cu-O melt (such as Nd and Gd) can also be expected to provide the same results as Sm in the YBCO single crystal, that is, high growth rate and high superconducting properties grown under air atmosphere.



**Figure 11.** The temperature dependence of magnetization for  $Y_{1-x}Sm_xBa_2Cu_3O_{7-\delta}$  single crystals grown under air with different Sm substitution contents.

Table 3. Growth conditions, growth rates, and critical temperatures.

	Growth atmosphere	Growth temperature (°C)	Ba/Cu ratio in the liquid	RE solubility (at.%)	Growth rate (mm h <sup>-1</sup> )	Critical temperature (K)
YBCO YBCO	air $P(O_2) = 1$ atm	997–1002 1013–1018	3:5 3:5	~0.6 ~0.7	0.04–0.08 0.08–0.2	$\begin{array}{c} 91\pm2\\ 91\pm2 \end{array}$
Y(Sm)BCO NdBCO	air air air	1000–1023 1068–1070 1058–1063	3:5 3:5 4:5	~0.8 ~3.2 ~2.6	0.06–0.14 0.2–0.3 0.1~0.15	$91 \pm 2$ $90 \pm 5$ $94 \pm 2$



**Figure 12.** The temperature dependence of magnetization for a  $Y_{0.785}Sm_{0.215}Ba_2Cu_3O_{7-\delta}$  single crystal grown at 1023 °C under 1 atm oxygen pressure.

#### 7. Discussion

This paper reviews three ways of facilitating crystal growth to achieve large REBCO single crystals. Superconducting properties are also associated with different processes



**Figure 13.** A comparison of crystal growth rate in different REBCO systems grown under air and 1 atm oxygen pressure.

and REBCO systems. The growth rate comparison is exhibited by figure 13 for several REBCO systems employed to grow large single crystals. Growth processes and superconducting properties are summarized in table 3. First, the Y123 has a low growth rate in air because of the low Y solubility in the Ba-Cu-O solution. High oxygen partial pressure considerably facilitates the Y123 growth, the rate of which rises 1.5-2.5-fold under 1 atm oxygen pressure against ambient air. This high growth rate is mainly attributed to the increased Y solubility in the Ba-Cu–O solution. Using this high oxygen partial pressure,  $T_c$ will not be depressed for the YBCO system. However, for REBCO systems with large-ionic-radius RE elements, the RE elements may enter at the Ba site under high oxygen partial pressure. As a result,  $T_c$  becomes low. Second, the NdBCO oxide has an extremely fast growth rate compared with other REBCO systems because of the high solubility of Nd in the Ba-Cu-O solution. Either a high ratio of Ba/Cu in the solution or a low oxygen partial pressure could be used for an effective depression of the RE-Ba substitution, then achieving a high  $T_c$  value at nearly 95 K with a sharp transition. Third, by substituting Sm (or Nd) for Y up to 30%, the crystal growth rate is obviously increased compared with that of Y123 since the mixed RE element solubility becomes higher in the Ba-Cu-O solution. Critical temperature values exhibit the almost same level as that of Y123 for Sm substitution for Y in the said x range. With such an Sm substitution, the  $T_c$ value tends to be insensitive to the oxygen partial pressure of the growth atmosphere.

In brief, many factors could affect the REBCO growth rate for achieving large REBCO single crystals; we believe that the main rate controlling factor is the RE solubility in the Ba-Cu-O solution. There are essentially two methods to enhance the RE solubility. One is to use high oxygen partial pressure, while the other is to partly or completely replace Y by RE elements with higher solubilities in the Ba-Cu-O solution. In addition, high growth temperature normally leads to high solubility of RE elements in the solution, high diffusion coefficient D, and low kinematic viscosity  $\nu$  in the solution. As a result, the crystal growth is facilitated. On the other hand, when the superconducting property  $T_c$  is considered, one should be careful in choosing the REBCO system and the growth process, including growth atmosphere, liquid composition, and other growth conditions. In other words, both high growth rate and high superconductivity should be taken into account for selecting a favourite candidate to achieve large REBCO single crystals.

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