Crystal growth of Bi$_2$(Sr$_x$Ca$_{3-x}$)Cu$_2$O$_y$ with traveling solvent floating zone method

K.W. Yeh$^{a,*}$, Y. Huang$^b$, J.Y. Gan$^a$, Y.S. Chang$^a$

$^a$Department of Materials Science and Engineering, National Tsing Hua University, Hsinchu, Taiwan, ROC
$^b$Materials Science Center, National Tsing Hua University, Hsinchu, Taiwan, ROC

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Abstract

The traveling solvent floating zone method was employed within an infrared radiation furnace to grow crystals of Bi$_2$(Sr$_x$Ca$_{3-x}$)Cu$_2$O$_y$, $x = 1.5–2$. Crystals of various Sr/Ca ratios were obtained with lowest value approximately 1.32. The ratio of the temperature gradient $G$ over the growth rate $R$, i.e., $G/R$, directly relates to the occurrence of constitutional supercooling. The minimum critical value of $G/R$ in a stable growth condition is $4.5 \times 10^{11}$ K/s/m$^2$ from this experimental result and fundamental estimation. A rotation rate of 30 rpm produced a slightly convex growth front and therefore enhanced the morphological stability of the growing crystal. Compositional analysis of the steady-state solvent zone indicated a primary crystallization field (PCF) located at the bismuth-rich and copper-deficient region relative to the 2212 stoichiometry, and this compositional range equaled proximal to Bi$_{2.425}$Sr$_{1.911}$Ca$_{0.807}$Cu$_{1.857}$O$_y$. Meanwhile this PCF composed a corresponding tie-line relationship with a slightly copper-deficient 2212 single-phase region.

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1. Introduction

Since the discovery of the oxide superconductors, the mechanism and origin of superconductivity have been investigated extensively [1–3]. Further understanding of not only the development of higher $T_c$ materials, but also of structural and physical properties of alternate similar systems, such as YBa$_2$Cu$_3$O$_{7+\delta}$ (YBCO) and Bi$_2$Sr$_2$CaCu$_2$O$_y$ (Bi-2212), is required. Recently for the consideration on applications, the focus has been on either increasing the Sr/Ca ratio or substitution of Fe [4], Co [5], Ni [6] and Li [7] at the Cu atomic sites within a Bi-2212 crystal lattice in order to enhance $T_c$ of Bi-2212 compounds. In contrast, the breakdown of
the superconductivity was studied by decreasing $T_c$ through a decrease in the mole ratio of strontium divided by calcium (Sr/Ca), or through the doping of Y [4] or rare earth ions [8] into Ca atomic sites. However, owing to poor crystallinity and poor phase purity of the specimen, limitations occurred when measuring the polycrystalline samples of sintering or small crystals obtained from the slow cooling method. Therefore, larger and higher quality single crystals can increase the reliability of physical measurements. Thus, in recent years, single crystal growth has become a significant issue in the field of superconductor materials research.

Being a peritectic compound, single phase Bi-2212 cannot be obtained by solidification from its stoichiometric melt. Flux growth from KCl or KOH [9] has been applied to obtain single crystalline Bi-2212. However, a growth method from a self-flux system is desirable to avoid unintentional doping of impurities from the flux salt [10,11]. Our earlier study on the primary crystalization field (PCF) of Bi-2212 [12] has indicated that using a bismuth-rich and copper-deficient off-stoichiometric composition as a solvent, Bi-2212 crystals free of inclusion can be obtained successfully.

In this work the traveling solvent floating zone method (TSFZ) was utilized to perform the growth of Bi-2212 single crystal. A stable solution is suspended between the polycrystalline rods by surface tension, thereby preventing the reaction of Bi-compound with crucible at high temperature. In addition, major growth parameters, including atmosphere, growth rate and rotation rate, can be controlled easily. Owing to the higher temperature gradient introduced by this heat source, the intergrowth of impurity phases can be reduced at a reasonable slow growth rate. Furthermore, the composition of liquidus can be easily obtained by quenching the melt. A full understanding of the influence of growth parameters and the details of phase diagram yielded larger uniform single crystals. Additionally, crystals of various Sr/Ca ratios were obtained and their compositions as well as structure were also discussed herein.

2. Experimental procedure

An infrared radiation furnace (model SC-15HD, NEC Nichiden Machinery) equipped with two ellipsoidal mirrors and two 1.5kW halogen lamps positioned at the foci of the mirrors were applied in the experiments herein. The heating area forming the molten zone was at the foci of each mirror and approximately 4mm in width. The melt with solvent composition was suspended by surface tension between two rods. Two rods were counter-rotated at a certain rate to introduce sufficient forced convection (and mixing) within the melt. As a result, a favorable slightly convex growth interface was maintained during the growth. Crystallization occurred at the growth front between the lower rod and the melt, as both rods were lowered simultaneously. Growth atmosphere within the quartz chamber was maintained at 1 atm. Lower oxygen pressure was controlled by the flow of a mixed gas (Ar:O$_2$ = 13:1).

Powders of Bi$_2$O$_3$, SrCO$_3$, CaCO$_3$, and CuO with 3N purity were weighted with desired ratios and mixed, calcined at 750°C for 12h in an aluminum oxide crucible and subsequently heated at 800°C for 24h. After calcinations, the specimen was ground into 1µm particles and was pressed into a rubber tube under hydrostatic pressure of 600 kg/cm$^2$, thereafter it was sintered at 850°C for 24h in air. For a thorough reaction, this grinding, pressing and sintering process were repeated. Thereafter, the typical diameter of sintered rods was about 5mm. Large voids within the sintered rod are detrimental to the stability of the growth process. Due to capillary effect, the melt was partially absorbed by the voids within the feed rod and the volume of the melt was reduced. Excess reduction of the zone volume lead to instability of the liquid zone, which zone composition was therefore changed when excess amount of the feed rod was dissolved into the zone, consequently resulted in growth failure. This problem could be avoided by performing a zone-passing procedure at a faster growth rate, such as 20mm/h of melting and solidification, which thereby increases the rod density. While growth condition of the molten zone was stabilized, growth rate was decreased gradually to 0.2mm/h or slower to obtain larger
crystals. For a successful growth process, more than 30 mm length of crystal grown at a rate below 0.2 mm/h was obtained before we terminated the growth. In order to extract more information about the conditions for a stable growth, we quenched the molten zone by switching off the lamp power.

Platelets of Bi-2212 single crystal were obtained by cleaving the as-grown boule along its grain boundary. The major surface of the crystal was perpendicular to (001) direction. A Rigaku Rotaflex RU-300 X-ray powder diffractometer with CuKα X-ray source was employed to investigate the lattice constant of crystal. By applying the method of Nelson–Riley extrapolation[13], we may obtain the c-axis length of the crystal to an accuracy of within 0.001 Å 20 values of (0020), (0022), (0026), (0028), and (0030) diffraction peaks were applied in this calculation. To analyze the surface morphology and the composition of each crystal, a Joel JSM-840A high-resolution scanning electron microscope equipped with a Link MK6B energy dispersive X-ray analyzer (EDX) was employed. An amorphous specimen of known composition of Bi2.150Sr1.950Ca0.975-Cu1.950Oy was prepared by splash quenching to avoid phase separation. It was used as a standard specimen with which to calibrate the correlation between the profile intensity and the calculated composition. In order to improve the peak to noise ratio, we chose the characteristic peaks of each element, Bi3+-L, Sr2+-L, Ca2+-K, and Cu2+-K such that the overlap of the energy peaks could be avoided and its relative error was reduced to below 2%. To confirm the accuracy of the off-stoichiometric melt from EDX, the inductively coupled plasma atomic emission spectrometer analyzer (abbreviated as ICP), Perkin-Elmer 300DV, was employed. The standard specimen described above also confirmed the accuracy of this analysis. A quantum design superconducting quantum interference device (SQUID) was applied to measure the temperature dependence of the magnetic molar susceptibility $\chi_m$. Furthermore, a comparison of the susceptibility curves within the field cooled and zero field cooled measurements provided the onset superconducting temperature $T_c$. Herein, a low magnetic field of 5 G was applied.

3. Results

3.1. Characterization of Bi-2212 single crystals

For a successful growth, it is essential to understand the solvent composition that corresponds to the target crystal composition. In this study we applied the optimal composition in PCF of previous LPE growth [12], which is Bi0.325Sr0.29-Ca0.145Cu0.24Oy (abbreviated as 325240-2.0), as the starting solvent composition for the crystal growth experiment of Sr/Ca ratio at 2.0. Furthermore, starting with the same mole fraction of Bi = 0.325 and Cu = 0.240 for the solvent composition, we proceeded growth experiments for lower Sr/Ca ratios at 1.8, 1.5 and 1.0. In float zone growth, the average compositions of the solid (i.e. the so-called “solids”) and liquid (the liquidus) adjust at steady state so that the composition of the Bi-2212 crystal is the same as the composition of the feed rod. Thus, the composition Bi2.05Sr2Ca0.89-Cu2.02Oy (abbreviated as F-2.25) was selected from the crystals of LPE experiments as the feed rod of Sr/Ca ratio at 2.25. The nominal compositions of the feed rods and the solvents with different Sr/Ca ratios are listed in Table 1. For crystal growth experiment at lower Sr/Ca ratio, the solid solution range proposed by Müller et al. [14] was considered herein for the starting composition of the feed rod. The single-phase region of Bi-2212 was shaped like a triangular pyramid on their graph. Based on the thermodynamic principle of tie–line relationship, we believed the solute should be proximal to the Cu-deficient face of the pyramid when grown with nominal Cu-deficient solvents in our study. Therefore, the middle point of the line intersected by the imaginary cross-section of a specific Sr/Ca ratio and the copper-deficient face of the pyramid, was chosen as the composition of the feed rods F-1.88, F-1.78, F-1.67 and F-1.0 within the series.

Growth results with different starting compositions and their growth parameters are summarized in Table 2. Owing to the strongly anisotropic growth habit, an as-grown boule consists of a bounty of plate-like crystals with their c-axis perpendicular to the growth direction. Single crystals with typical dimensions of
6 x 3 x 0.2 mm³ were cleaved from the as-grown boule. No secondary phase was detected by X-ray diffraction analysis. The composition was determined by EDX analysis on the cleavage surface of a crystal and the standard deviation from 20 points of EDX measurements was typically Bi < 1.7%, Sr < 1.0%, Ca < 2.0% and Cu < 1.5%.

The compositional uniformity of an as-grown boule was confirmed through a comparison of several cleaved crystals from the same boule. Typically, the relative variation within a boule was found to be Bi < 1.5%, Sr < 1.0%, Ca < 2.0% and Cu < 0.7%, which was within the accuracy of our measuring technique. Crystals of the Sr/Ca ratios from 2.0 to 1.5 were obtained with a growth rate of 0.2 mm/h and a rotation rate of 30 rpm. However, we found it difficult to grow sufficient area size of crystals with Sr/Ca ratio lower than 1.32, due to their unstable growth behavior. Much smaller size crystals of Sr/Ca ratio of approximately 1.32 were obtained from growth run G14, which began with Sr/Ca ratio of 1.0.

Fig. 1 presents the isothermal sections of (SrO, CaO)–BiO1.5–CuO pseudo-ternary phase diagram at 0.07 bar of oxygen pressure and at approximately 900°C of temperature. Fig. 1a illustrates

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Table 1
The starting compositions of the feed rod and the solvent rod of different Sr/Ca ratios

<table>
<thead>
<tr>
<th>Feed rod</th>
<th>Composition (total = 7)</th>
<th>Sr/Ca ratio</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi</td>
<td>Sr</td>
<td>Ca</td>
<td>Cu</td>
</tr>
<tr>
<td>F-2.25</td>
<td>2.09</td>
<td>2</td>
<td>0.89</td>
</tr>
<tr>
<td>F-1.9</td>
<td>2.027</td>
<td>1.966</td>
<td>1.036</td>
</tr>
<tr>
<td>F-1.88</td>
<td>2.074</td>
<td>1.888</td>
<td>1.005</td>
</tr>
<tr>
<td>F-1.78</td>
<td>2.092</td>
<td>1.852</td>
<td>1.040</td>
</tr>
<tr>
<td>F-1.67</td>
<td>2.115</td>
<td>1.808</td>
<td>1.083</td>
</tr>
<tr>
<td>F-1.0</td>
<td>2.142</td>
<td>1.484</td>
<td>1.484</td>
</tr>
<tr>
<td>FZ0-1.38</td>
<td>1.940</td>
<td>1.787</td>
<td>1.292</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Solvent rod</th>
<th>Composition (mole%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>325240-2.0</td>
<td>32.5 29 14.5 24 2</td>
</tr>
<tr>
<td>335250-2.0</td>
<td>33.5 27.7 13.8 25 2</td>
</tr>
<tr>
<td>346265-2.4</td>
<td>34.65 27.30 11.53 26.52 2.37</td>
</tr>
</tbody>
</table>

The nomenclature of the feed rod was abbreviated as F-(Sr/Ca ratio). And the nomenclature of the solvent rod was abbreviated as (Bi-%)(Cu-%)-(Sr/Ca ratio).

Table 2
The growth conditions and the characteristics of as-grown single crystals

<table>
<thead>
<tr>
<th>Run no.</th>
<th>Feed rod composition</th>
<th>Solvent rod composition</th>
<th>Growth rate (mm/h)</th>
<th>Rotation rate (rpm)</th>
<th>Crystal composition Bi:Sr:Ca:Cu</th>
<th>Sr/Ca ratio</th>
<th>T_onset (K)</th>
<th>c-axis length (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>G1</td>
<td>F-2.25</td>
<td>335250-2.0</td>
<td>0.2</td>
<td>12</td>
<td>30.683:26.769:14.022:28.527</td>
<td>1.91</td>
<td>91.5</td>
<td>30.886</td>
</tr>
<tr>
<td>G2</td>
<td>F-2.25</td>
<td>335250-2.0</td>
<td>0.15</td>
<td>12</td>
<td>29.678:27.572:14.505:28.245</td>
<td>1.90</td>
<td>92</td>
<td>30.893</td>
</tr>
<tr>
<td>G7</td>
<td>F-1.90</td>
<td>346265-2.4</td>
<td>0.2</td>
<td>30</td>
<td>30.324:27.132:14.131:28.413</td>
<td>1.92</td>
<td>93</td>
<td>30.909</td>
</tr>
<tr>
<td>G9</td>
<td>F-1.88</td>
<td>325240-1.8</td>
<td>0.2</td>
<td>30</td>
<td>30.576:25.702:14.992:28.730</td>
<td>1.71</td>
<td>89</td>
<td>30.869</td>
</tr>
<tr>
<td>G10</td>
<td>F-1.78</td>
<td>325240-1.5</td>
<td>0.2</td>
<td>30</td>
<td>29.806:26.001:15.884:28.310</td>
<td>1.64</td>
<td>92</td>
<td>30.856</td>
</tr>
<tr>
<td>G11</td>
<td>F-1.67</td>
<td>325240-1.5</td>
<td>0.2</td>
<td>30</td>
<td>29.211:25.666:16.806:28.316</td>
<td>1.53</td>
<td>88</td>
<td>30.804</td>
</tr>
<tr>
<td>G14</td>
<td>F-1.0</td>
<td>325240-1.0</td>
<td>0.2</td>
<td>30</td>
<td>28.777:24.837:18.868:27.517</td>
<td>1.32</td>
<td>88</td>
<td>30.768</td>
</tr>
</tbody>
</table>
the compositional range of Sr/Ca ratio near 1.9 determined from our study, and Fig. 1b demonstrates the range of Sr/Ca ratio from 1.5 to 1.7. The triangles in these two figures are drawn by taking the cross section of the single-phase regions determined by Müller et al. [14] for Sr/Ca ratio of 1.9 and 1.6, respectively. According to the diagram, the lower left side of this triangle is Cu-deficient. While grown from Cu-deficient solvents, our crystals’ compositions fall to the left side of the triangle, consistent with the tie-line principle in the phase diagram. Therefore the solid ellipse, enclosing this compositional range in the diagram, represents the 2212 solidus that ties to the liquidus. In addition, the long axis of this ellipse indicates a larger range of bismuth distributions within the compound [20]. Comparing to crystal compositions of various reports [15–19], however, their compositional deviation spanned a wide range of approximately 10% particularly in the Bi content. This discrepancy was probably owing to measurements without calibrating by a compound standard. In Fig. 1c, we propose a schematic pseudo-ternary phase diagram at 0.07 bar of oxygen pressure and approximately 900°C of temperature. This diagram presents the solidus field of Sr/Ca ratio 1.9, 1.6, and 1.3 as well as the liquidus. Moreover, to connect the solidus field with the PCF, a tie line is drawn when the Sr/Ca ratio equals to 1.9. Due to insufficient information, the analogous range of crystal compositions of Sr/Ca ratio at 1.3 is then plotted as a dotted ellipse. As we can see that at a smaller Sr/Ca ratio of a single crystal, the decrease of Cu content occur along with a slight decrease of Bi content.

Fig. 2 indicates that the structural modification, induced by the cation substitutions of Bi\(^{3+}\), Sr\(^{2+}\),

![Diagram](image-url)

Fig. 1. (a) Isothermal section of (SrO, CaO)–BiO\(_{1.5}\)–CuO pseudo-ternary phase diagram at oxygen pressure of 0.07 bar in about 900°C. The triangle is drawn by taking the Sr/Ca ratio of 1.9 section of the single-phase region, determined by Müller et al. [14]. Various symbols represent the compositions of single crystals obtained by different groups [15–19]. (b) Isothermal section of (SrO, CaO)–BiO\(_{1.5}\)–CuO pseudo-ternary phase diagram at oxygen pressure of 0.07 bar in about 900°C. The triangle is drawn by taking the Sr/Ca ratio of 1.6 section of the single-phase region, determined by Müller et al. [14]. Hollow circles represent the compositions of single crystals obtained by Gu et al. [19]. (c) The tie-line relationship between the solidus field and the corresponding PCF of Sr/Ca ratio around 1.9 in Bi\(_2\)(Sr,Ca)\(_3\)Cu\(_2\)O\(_y\) system. This graph presents the shifting of the solidus field of different Sr/Ca ratios.
Ca\(^{2+}\) is simplified only from the influence of Sr/Ca ratios. The dotted line in this graph represented the decreasing behavior of c-axis length facilitated by the decrease of Sr/Ca ratios within the sintered specimen [14]. Our data, listed in the last column in Table 2 in the range of Sr/Ca ratio from 1.32 to 2.05, the solid circles, correlate well with their results. The solid line represents the regression result of our data and the slope is apparently steeper. As described above when the Sr/Ca ratio decreases, the Bi content in the crystal decreases slightly, thus, the c-axis length of crystals decreases more sharply. Additionally, as seen in Fig. 2, a significant discrepancy in c-axis length was found between our work and other TSFZ-grown crystals [17,18]. This may be partially due to the less oxygen content within our crystals, which were grown under lower oxygen atmosphere.

The typical temperature dependence of the magnetic susceptibility of a TSFZ crystal yields a sharp superconducting transition with a width of less than 4 K. The onset superconducting temperature \(T_{c,\text{onset}}\) correlates well with the cation ratios and oxygen contents. Specimens with controlled cation ratios could be prepared by sintering method [21] at will. On the contrary, to obtain single crystals with a wide compositional range is very difficult from a TSFZ growth experiment. The linearity between \(T_{c,\text{onset}}\) and Bi or Ca content thereby cannot be clarified. Nevertheless, as seen in Table 2, \(T_{c,\text{onset}}\) of our crystals, within the range of 92–93.5 K, is relatively higher for Sr/Ca ratios of approximately 2.0. This discrepancy is due to the modifications of \(T_{c,\text{onset}}\) are predominately controlled by the transformations of the c-axis length [22,23], irrespective of the difference in cation concentrations or a small variation of oxygen contents.

### 3.2. Optimal G/R values

In order to characterize the temperature distribution in our TSFZ growth system, we probed the axial temperature variation of a Bi-2212 ceramic heated at around 80% of power at its melting. Temperature under molten condition could not be measured directly in our system because bismuth compound react easily with thermocouple materials. To simulate a similar thermal conductive condition, a piece of Bi-2212 ceramic cylinder rod, 15 cm long 8 mm in diameter, was employed here. The junction of a Pt/Pt–Rh13% thermocouple was placed in contact with the midpoint of the rod. Temperature distribution along the growth axis was measured by sampling data as the rod was moved longitudinally at a slow rate. Fig. 3 plots two curves measured from two different directions perpendicular to the growth axis. The parameter of interest in analyzing the stability of the growth is the temperature gradient in front of the growth interface. For the TSFZ growth in this study, the growth interface generally locates at approximately 2 mm below the optical focus. Thus, the temperature gradient was 262°C/
cm in the direction facing the lamp, and it was 234°C/cm in the direction perpendicular to the optical axis. This asymmetry of the temperature distribution was smeared out from the rapid rotation during the growth. Therefore, an average value of 248°C/cm is taken for the gradient parameter \( G \), which is slightly greater than the reports of the other group [24].

The growth instability of interface depends heavily upon the \( G/R \) factor. That is, when \( G/R \) value is greater than certain critical value, constitutional supercooling can be avoided. However, the fundamental determination of the maximum stable growth rate is difficult because several critical thermodynamic parameters, such as the diffusion coefficient \( D_L \) of the melt and the slope of liquidus curve \( m_L \) near the 2212 composition, remain unknown in this system. The experimental results proposed by Cima et al. [25] with the laser heated float zone (LHFZ) method suggested that the \( G/R \) ratio should be greater than \( 3 \times 10^{11} \) K s/m². Considering the temperature gradient is approximately 248°C/cm in our TSFZ system, our growth rate should be slower than 0.3 mm/h. Our earlier growth experiences at higher growth rates, such as 0.5 and 1 mm/h, resulted in cellular interface that was a clear indication for unstable growth. Intergrowth with the inclusion of (SrCa)-CuO\(_x\) (011)-phase was typically found at the cellular interface under such high growth rate conditions. (SrCa)CuO\(_x\) (011)-phase was also the major impurity phase found in the LPE growth study of Bi-2212 film [12]. Three growth rates of 0.2, 0.15 and 0.1 mm/h at a constant rotation rate of 12 rpm with the same starting solvent composition were then attempted. Fig. 4 is a photograph demonstrating the cross-section of the solvent zone, which was quenched from the growth run G1. As seen in Fig. 4, a nearly planar solid–liquid (S/L) interface was obtained at a rate of 0.2 mm/h. From a comparison with interfaces of 0.15 mm/h (G2) and 0.1 mm/h (G3), the interfaces behaved nearly planar and there was no difference between the interface of 0.2 mm/h and interfaces of lower than 0.2 mm/h. These results suggest that 0.2 mm/h is under the maximum value for a stable growth, as a result, a critical value of \( G/R \) is proposed herein as \( 4.46 \times 10^{11} \) K s/m².

3.3. Optimal rotation rate

Various rotation rates of the feed rod and the solvent rod were applied to induce alternate magnitudes of forced convection, thereby altering the shape and curvature of the growth interface. Indeed, to engage the leave of grain boundaries from the free surface of the boule, a slightly convex growth interface is favored, which in turn increases the crystal size. Thus, Fig. 5 plots a variety of interface shapes at rotation rates of 12, 30 and 39 rpm, respectively. As the rotation rate is increased, the tendency toward a flat interface becomes obvious. However, the interface of 39 rpm is too flat to become a concave front at the peripheral region, which is created by the coupling of the forced convection and the significant thermocapillary flow within larger temperature gradient of the TSFZ apparatus [26]. In addition, decreasing the thickness of the diffusion boundary layer can be achieved by increasing the counter rotation rate from 12 to 30 rpm, thereby improving the interface stability. This phenomenon will be discussed in the subsequent section.
3.4. Determination of boundary layer thickness and PCF

The compositional variation in front of the growth interface was studied by EDX measurement, which was conducted in a $5 \times 5 \, \text{mm}^2$ sampling area with $5 \, \mu\text{m}$ spacing on SEM. The mole ratios of Bi and Cu ions, rather than Sr and Ca were selected as the $y$-axis due to their significant variance in composition between the solvent and the crystal region. Moreover, due to invisibility of the two-phase boundary, the zero line was determined from the variations within the ZAF factors of each element in the SEM technique. As seen in Fig. 6a, comparing mole ratios of Bi and Cu with distance from interface, the compositional change is observed at approximately $30 \, \mu\text{m}$ from Bi-2212 crystal composition to roughly Bi-2201 composition at a rotation rate of 12rpm. At a rotation rate of 30rpm, whereas Fig. 6b indicates that the transitional boundary is about $20 \, \mu\text{m}$. With sufficient measurements, the boundary layer thickness equals $30–35 \, \mu\text{m}$ at a rate of 12rpm, and the thickness is around $20 \, \mu\text{m}$ at a rate of 30rpm. Based upon steady-state growth conditions, only the influence of rotation rates is considered for low growth rates. For a rotating disc on the melt surface as proposed by BPS theory [27], the correlation between the rotation rate $\omega$ and the boundary layer thickness $\delta$ is $\delta \propto \omega^{-0.5}$, while the kinematics viscosity was assumed constant for a similar flow pattern within the molten zone. The boundary layer thickness $30–35 \, \mu\text{m}$ at 12rpm and $\sim 20 \, \mu\text{m}$ at 30rpm correlates well with the above relationships. Moreover, decreasing the boundary layer thickness, namely, decreasing the diffusion path of a solute can therefore enhance the stable growth rate by raising rotation rates from 12 to 30 rpm [28].

If this condition is satisfied, the melt will adjust from the starting composition to an equilibrium liquidus at a slow growth rate, hence, the bulk composition of the quenched zone of a stable growth will be close to the liquidus. The cross-sections of G2 and G3 quenched zone were

Fig. 5. Varied curvature of growth interface resulted from different rotation rates, 39rpm (G6), 30rpm (G9) and 12rpm (G3), respectively from top to bottom.

Fig. 6. The behavior of transiting from 2212 crystal composition to a nearly 2201 composition in one dendrite of varied rotation rate, G3 (12rpm) in (a) and G8 (30rpm) in (b). The origin of the $x$-axis indicates the position of the growth interface determined by the difference of the EDX signals. Left side of the zero line represents the crystal.
analyzed quantitatively in an area of roughly 20 × 30 μm. Thus, the average composition from 20 points of measurement was Bi$_{2.425}$Sr$_{1.911}$Ca$_{0.807}$Cu$_{1.857}$O$_y$ (346265), which was confirmed by ICP as having a less than 3% relative error as compared to EDX data. Therefore in Fig. 1c, this compositional range is marked as a circle, which is connected with the crystal compositions of Sr/Ca around 1.9. This composition, slightly richer in Bi and Cu than the starting solvent 325240, locates within the region of liquids, that is, the PCF based on the growth parameters 0.2 mm/h and 30 rpm of the TSFZ growth. Compared to other previous studies, the zone composition determined by chemical analysis was 35.5:22.4:14.9:26.9 with 1 mm/h and 30 rpm of the FZ method [10]. Cima et al. [25] applied the LHFZ method to produce fibers with different growth rates, and their zone composition was 40:23:13:24 at the rate of 3.96 mm/h. Accordingly, these two studies confirmed that the PCF is bismuth-rich and copper-deficient. Gazit et al. used a similar LHFZ apparatus [29] and obtained the composition 32.1:23.5:12.3:32.1 at their lowest growth rate (2.52 mm/h), nevertheless, the measurements were probably not taken in the steady-state region of the boule due to the inconsistency between the crystal composition and the feed rod composition.

4. Discussion

The constitutional supercooling criterion proposed by Tiller [30] can be applied to the solution growth herein. Instability of a solution containing a number (j) of solute constituents may be expressed by writing the growth rate as:

$$ R > D_0 G / \sum_{i=1}^{j} \left\{ \frac{m_i (k_i - 1) n_i}{D_i / D_0} \right\}, $$

where $D_0$ is the diffusion coefficient of the solvent, and $D_i$ refers to the diffusion coefficient of solute constituent $i$. $m_i$ is the slope of liquidus curve, $k_i$ is the segregation coefficient, and $n_i$ is the solute concentration. None of these parameters were clearly known in this material system. For the sake of a clear discussion on the $G / R$ value, we propose certain numbers for a reasonable estimation as follows. To simplify the case, assuming that $D_i$ equals $D_0$ and a typical value of $10^{-9}$ m$^2$/s in the flux of oxide systems [31] is employed. The composition of the solute $C_S$ and the solvent $C_L$ were adopted from the growth run G6, subsequently, $C_S$ was Bi$_{2.146}$Sr$_{1.865}$Ca$_{0.961}$Cu$_{2.028}$O$_y$ and $C_L$ was Bi$_{2.425}$Sr$_{1.911}$Ca$_{0.807}$Cu$_{1.857}$O$_y$. From this, the segregation coefficients of the cations, $k_{Bi} = 0.885$, $k_{Sr} = 0.975$, $k_{Ca} = 1.191$ and $k_{Cu} = 1.09$, are obtained. Furthermore, the slope of liquidus curve is calculated from dividing the concentration difference by the temperature difference. Assuming the similar slope at above and below the peritectic point of 2212 compound, the temperature difference equals approximately 100°C between the partial melting point of the solvent (~900°C) and the total melting point of the 2212-phase (~1000°C). As a result, the $G / R$ value from this estimation is $4.5 \times 10^{11}$ K s/m$^2$. This value agrees well with the experimental results when previously discussed in Section 3.2.

5. Conclusions

A successful growth of Bi-2212 crystal requires appropriate optimization among various growth parameters. The determination of PCF provides a direct route from phase diagram in a solution growth system. A reasonable growth rate obtained good single crystal can be derived from the critical ratio of $G / R$ when the temperature gradient $G$ of certain growth system is characterized. Therefore, $G / R$ parameter can be applied as a checkpoint for stable growth of Bi-2212 via different techniques. Both our experimental result and fundamental estimation indicated that the $G / R$ ratio should exceed $4.5 \times 10^{11}$ K s/m$^2$. That is, since the temperature gradient is approximately 248°C/cm at the position of the growth interface, the growth rate $R$ should be equal or lower than 0.2 mm/h to stabilize the planar growth front. Growth parameters of 30 rpm and 0.2 mm/h are optimal, therefore good single crystals with a wide range of Sr/Ca ratio can be obtained reproducibly with crystal size of approximately $6 \times 3 \times 0.2$ mm$^3$. The primary crystallization field (PCF) was determined through
analyzing the composition of the solvent zone. Quantitative EDX analysis indicates that this PCF is bismuth-rich and copper-deficient relative to 2212 solid solution region.

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