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Review

Crystal Growth Techniques for Layered Superconductors

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Abstract: Layered superconductors are attractive because some of them show high critical temperatures. While their crystal structures are similar, these compounds are composed of many elements. Compounds with many elements tend to be incongruent melting compounds, thus, their single crystals cannot be grown via the melt-solidification process. Hence, these single crystals have to be grown below the decomposition temperature, and then the flux method, a very powerful tool for the growth of these single crystals with incongruent melting compounds, is used. This review shows the flux method for single-crystal growth technique by self-flux, chloride-based flux, and HPHT (high-pressure and high-temperature) flux method for many-layered superconductors: high-T_c cuprate, Fe-based and BiS_2-based compounds.

Keywords: flux method; incongruent melting compounds; solution growth; high-T_c cuprate superconductor; Fe-based superconductor; BiS_2-based superconductor

1. Introduction

This review presents the single-crystal growth of high-T_c cuprate, Fe-based and BiS_2-based superconductors as typical layered superconductors. These layered superconductors form many analogous compounds and show other interesting properties. Additionally, layered superconductors have high anisotropy. In order to reveal such intrinsic properties, their single crystals are necessary. However, layered superconductors are composed of multiple elements and they are incongruent melting compounds. This suggests that the growth of single crystals cannot use the melt-solidification process and, thus, the solution-growth process is necessary. During the single-crystal growth process, the temperature must be lower than the decomposition temperature of the layered superconductors. Hence, the flux method is useful for single-crystal growth of layered superconductors. In this review, the single-crystal growth technique for high-T_c cuprate, Fe-based and BiS_2-based compounds using various fluxes are introduced.

2. Single-Crystal Growth Techniques for Incongruent Melting Compounds

In order to grow single crystals, their raw materials of layered superconductors have to become solution (liquid phase) below the decomposition temperatures of the products. The solvent of that solution (liquid phase) is called "flux". Flux plays a role as a solvent in the solution-growth process. Therefore, flux should be composed of low-melting compounds, such as metals, alkali chlorides, and other compounds with a eutectic composition. The conventional flux method, the traveling solvent floating-zone (TSFZ) method, the top-seeded solution growth (TSSG) method, and the high-pressure and high-temperature (HPHT) flux method are briefly explained in this chapter. The conventional flux method does not have to use a special apparatus, but obtained crystals are small. On the other hand, TSFZ and TSSG methods use special apparatuses which are expensive. However, these methods

can grow large-sized crystals, and the HPHT flux method is necessary for single-crystal growth under high pressure.

2.1. (Conventional) Flux Method

There are two kinds of flux methods. The components of the flux are the elements in the products; this is called as "self-flux method". The other is the use of flux which does not include the same element in the products.

The flux and raw materials for target compounds are mixed using a mortar, and put in the crucible. The mixed powder is heated for the solution-growth process, and then the single crystals are obtained. Generally, oxide materials (e.g., high-T_c cuprate compounds) are heated in open atmosphere, and non-oxide materials (e.g., Fe-based and BiS_2-based compounds) are performed in a closed atmosphere, such as sealed in a quartz tube in vacuum. Finally, the important point of flux selecti is the following: flux should not react with the target materials, and should be easily separated from the grown single crystals. Examples of single-crystal growth of a layered superconductor using the flux method are shown below.

2.1.1. High-T_c Cuprate Superconductor

Many compounds are reported as high-T_c cuprate superconductors. This review shows high-T_c cuprate of $(R,A_e)_2CuO_4$ ((R,A_e)-214 phase) (R: rare earth element, A_e: Ba,Sr,Ce) [1], $RBa_2Cu_3O_x$ (R-123 phase) [2], $Bi_2Sr_2Ca_{n-1}Cu_nO_x$ (n = 1: Bi-2201, n = 2: Bi-2212, n = 3: Bi-2223 phase) [3] single crystals. CuO-based (self-flux) or alkali chloride-based compounds are generally employed for flux in the single-crystal growth of high-T_c cuprate. Single crystals several millimeters (mm) in size are obtained by the flux method.

When nominal compositions of precursors are $(La,Sr)_2CuO_4$:CuO = 1:4 (molar ratio) and $YBa_2Cu_3O_x$:CuO = 3:2 (molar ratio), (La,Sr)-214 and Y-123 single crystals are grown from CuO flux (self-flux) [4]. Another example is the growth of Y-123 single crystals using $7BaCuO_2$11CuO as a flux. Y-123 single crystals are grown from the precursor of Y-123:$7BaCuO_2$11CuO = 16:9 (molar ratio) [5]. In contrast, Bi-2212 single crystals are obtained from the precursor of the cation ratio Bi:Sr:Ca:Cu = 2:2:1:2 which are weighed from Bi_2O_3, $SrCO_3$, $CaCO_3$, and CuO. This precursor is put in a crucible with a weight on the cover (cap), and then the precursor is melted for Bi-2212 single-crystal growth. The cation ratio of this precursor is the stoichiometric composition for Bi-2212, and their melt acts as flux (self-flux) [6].

Alkali chloride-based compounds are also useful for flux. Y-123 and Bi-2212 single crystals are grown using KCl-based flux. The melting point of KCl is 776 °C although eutectic composition exists between KCl and NaCl. Its composition is KCl:NaCl = 1:1 (weight ratio) and eutectic temperature is 657 °C. This eutectic composition (KCl/NaCl) has the advantage for the growth of single crystals by lowering the melting points. Y-123 single crystals with sizes of several millimeters (mm) are grown from 2 wt % KCl/NaCl added Y-123 raw materials [7]. In Bi-2212 single crystals, some reports show using only KCl for flux [8–10]. In one instance, much KCl flux is added in Bi-2212 raw materials for single-crystal growth, which nominal composition is Bi-2212:KCl = 1:99 (weight ratio) [9].

Finally, I introduce the growth of single-crystalline whiskers. Whisker is a special morphology of the single crystal. They have high aspect ratio (needle shape) with perfect crystallinity. However, the growth mechanism is not completely clear. Growth of whiskers of high-T_c cuprate layered superconductors is reported [11]. Those growth methods use glassy precursor and/or special flux. High-T_c cuprate superconductors are composed of many elements. Therefore, growth of high crystallinity single crystals is difficult. However, the whiskers have perfect crystallinity, and are free of dislocation. Figure 1 shows a typical scanning electron microscope (SEM) image of a Y-123 single-crystal whisker. The growth method of high-T_c cuprate single crystal whiskers has two routes, which use a glassy precursor and a TeO_2/Sb_2O_3-doped precursor. When using the glassy precursor method, Al_2O_3-doped Bi-2212 raw materials are melted and quenched, thus, the glassy precursor

(Bi–Sr–Ca–Cu–Al–O) is obtained. Bi–Sr–Ca–Cu–Al–O glassy precursor is heat-treated and then Bi-2212 whiskers are grown on the precursor [11]. However, this method can grow only Bi-2212 whiskers in high-T_c cuprate superconductors. Whiskers of Bi-2212, Bi-2201, Bi-2223, and R-123 phases can be grown by TeO_2/Sb_2O_3 doping method. For Bi-2212 and Bi-2201, TeO_2-doping and Ca-rich precursors are used for whisker growth of which nominal compositions are $Bi_2Sr_2Ca_nCu_nTe_{0.5}O_x$ (n = 1 for Bi-2201, n = 2 for Bi-2212). Those precursors are pressed into pellets and heated. Whiskers are obtained on the pellets [12,13]. $Bi_{1.6}Pb_{0.4}Sr_{2.0}Ca_{2.0}Cu_{3.0}O_x$ single phase powder (1.0 mol) and TeO_2 (0.5 mol) are mixed and pelletized. This pellet is heated, and then (Bi,Pb)-2223 whiskers are obtained [14]. On the other hand, R-123 whiskers can also be grown from TeO_2/Sb_2O_3 doped precursor pellets. TeO_2 or Sb_2O_3 doping and R and Ba-rich precursors ($R_{1.5–2.0}Ba_3Cu_3Te_{0.5}O_x$ or $R_{1.5–2.0}Ba_{2.75}Cu_3Sb_{0.5}O_x$) are used and the same treatment is applied. R-123 with R = Y, Sm, Eu, Gd, Dy, Ho, Er, Tm, and Yb whiskers can be grown from the precursor pellet [15–17]. Additionally, Ca-substituted R-123 with R = Y, La, Nd, Sm, Eu, Gd, Dy, Ho, Er, Tm, Yb, and Lu whiskers are grown from $RBa_{2-3}Cu_3Ca_{1.00–1.75}Te_{0.5}O_x$ precursor pellets [18–20]. We assume that TeO_2 and Sb_2O_3 play a role as flux.

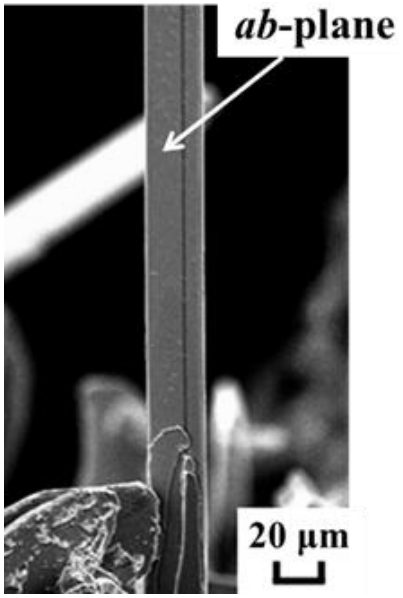

Figure 1. Typical SEM image of a Y-123 single crystal whisker.

2.1.2. Fe-Based Superconductors

Fe-based superconductors include R(O,F)FeAs (1111) (R: rare earth elements) [21], $A_eFe_2As_2$ (122) (A_e: alkaline earth metal) [22], AFeAs (111) (A: alkali metals) [23], β-FeSe (11) [24], and $(A,A_e)_2Fe_4Se_5$ (245) [25], Fe-based with perovskite oxide layer compounds (so-called 42622) [26], and so on. Some types of Fe-based superconductors are reported as single crystals which are grown by the flux method. Typical fluxes are As-based self-flux, Sn flux and chloride-based flux. Especially, growth of 122 single crystals have been intensively reported.

$(A_e,K)Fe_2As_2$ (A_e = Ba, Sr) single crystals can be grown using FeAs as a self-flux [27]. One of the growth methods is as follows. The starting materials of Ba or Sr, K, and FeAs in a molar ratio of 0.5:1:4 are put into an alumina crucible and sealed in a welded Ta crucible under 1.6 atm of Ar. This product is sealed in an evacuated quartz ampoule and is heated for the growth of single crystals [28]. In addition to the growth of KFe_2As_2 single crystals [29], $Ba_{0.6}K_{0.4}Fe_2As_2$ single crystals are obtained from a stoichiometric compound, which plays a role of self-flux [30].

Growth of 111 single crystals can also be applied to the growth of LiFeAs and $NaFe_{1-x}Co_xAs$ (x = 0–0.3). In LiFeAs, Li metal added Fe-As mixture is placed into an Al_2O_3 crucible. The crucible is inserted into the Nb container, covered by a Nb cap with outlets for the flux (for a sieve). The Nb

container is welded in an Ar atmosphere with a base pressure of 1.5 atm, and the sealed Nb container is sealed in a quartz tube under 0.25 atm of Ar to prevent any oxidation. This product is heated for single-crystal growth. Figure 2 shows optical and SEM images of obtained LiFeAs single crystals [31]. On the other hand, $NaFe_{1-x}Co_xAs$ (x = 0–0.3) single crystals are grown using NaAs self-flux. NaAs, Fe, and Co powders are weighed to the molar ratio of NaAs:Fe:Co = 4:(1 − x):x, and ground. The mixtures are put into Al_2O_3 crucibles, then sealed in iron crucibles under 1.5 atm of high-purity Ar gas. Then the crucible is heated for single-crystal growth [32].

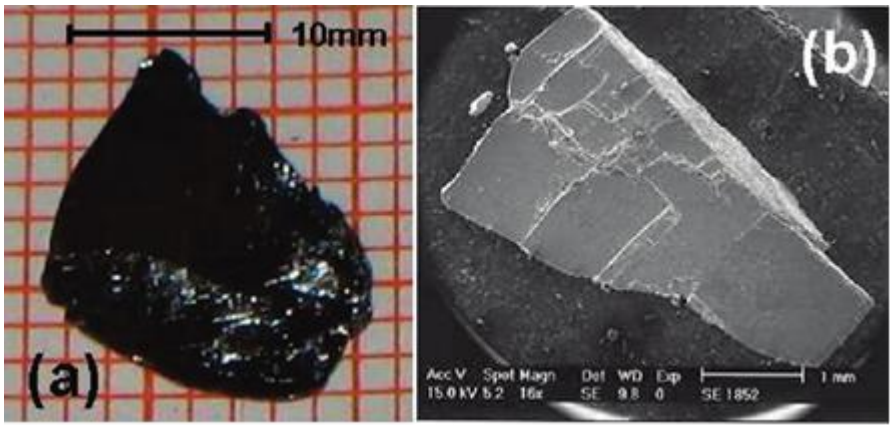

Figure 2. Optical image of a LiFeAs crystal (**a**) and a SEM image (**b**) [31]. Single-Crystal Growth and Characterization of Superconducting LiFeAs.

There are reports about the growth of $Sr_4V_2O_6Fe_2As_2$ single crystals, which is a FeAs self-flux method. The nominal composition of the raw materials is FeAs:$Sr_4V_2O_6Fe_2As_2$ = 2:1 (molar ratio). The mixture is sealed in a quartz tube in vacuum, then heated [33]. Moreover, growth of nano-sized whiskers is reported. The $Ca_{10}(Pt_4As_8)(Fe_{1.8}Pt_{0.2}As_2)_5$ precursor with 10 wt % CaAs self-flux is put into a Ta capsule and sealed in a quartz tube in vacuum. This product is heated, and the $Ca_{10}(Pt_4As_8)(Fe_{1.8}Pt_{0.2}As_2)_5$ nano-sized whiskers are obtained. SEM images are shown in Figure 3. The whiskers have lengths of 0.1–2.0 mm, widths of 0.4–5.0 μm, and thicknesses of 0.2–1.0 μm [34].

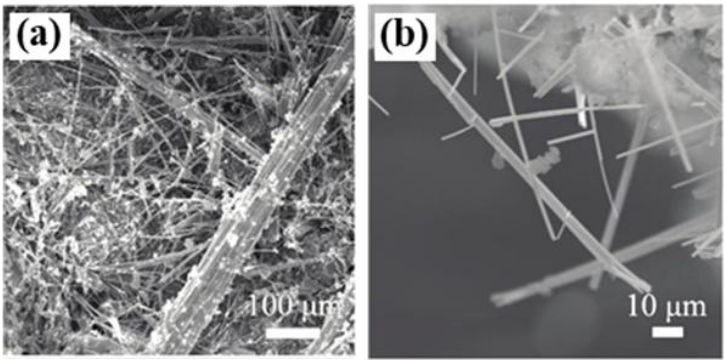

Figure 3. SEM images of $Ca_{10}(Pt_4As_8)(Fe_{1.8}Pt_{0.2}As_2)_5$ whiskers [34]. Growth of Single-Crystal $Ca_{10}(Pt_4As_8)(Fe_{1.8}Pt_{0.2}As_2)_5$ Nanowhiskers with Superconductivity up to 33 K. (**a**) Wide field of view, (**b**) Enlarged image.

Sn flux is also effective for 122 single-crystal growths, since Sn has a low melting point (232 °C). $BaFe_2As_2$ and $Ba_{0.55}K_{0.45}Fe_2As_2$ single crystals can be grown using Sn flux. Ba, K, Fe, and As are added to Sn in the molar ratio of (Ba/K)Fe_2As_2:Sn = 1:48 and put into MgO crucible. The crucible containing silica wool is placed on top of the growth crucible and these are sealed in a silica tube

under approximately 0.33 atm of Ar. Then this silica tube is heated for single-crystal growth. Sn flux is decanted from the obtained single crystals at 500 °C [35]. Nevertheless, the remaining Sn at the single crystal surfaces is subsequently dissolved at room temperature for a few days in liquid Hg. The obtained single crystals are heated for one hour at 190 °C in vacuum to evaporate the remaining traces of Hg [36].

Finally, growth of 11 (β-FeSe) single crystals is exhibited, for which chloride-based flux is effective. β-FeSe decomposes into Fe and a hexagonal phase (α-FeSe) at 457 °C. This suggests that single-crystal growth has to be perform at low temperature (less than 457 °C). Therefore, the eutectic chloride composition is useful for flux. Some reports are shown in the following. A eutectic temperature of LiCl:CsCl = 29:21 (molar ratio) composition is 326 °C, which can use the flux for 11 (β-FeSe) single-crystal growth. After the growth, this flux can be removed by water wash. 11 (β-FeSe) single crystals are grown by LiCl/CsCl flux [37]. The eutectic composition of $KCl/AlCl_3$ is also used for 11 (β-FeSe) single-crystal growth [38]. $AlCl_3$-based compositions have low eutectic temperature. However, their handling should be done carefully to prevent an explosion hazard. The eutectic temperature of NaCl:KCl = 1:1 (molar ratio) composition is higher than β-FeSe decomposition temperature, but β-FeSe single crystals are obtained by rapid cooling between the NaCl/KCl eutectic temperature and room temperature [39].

2.1.3. BiS_2-Based Superconductors

BiS_2-layered superconductors include $Bi_4O_4S_3$ [40], $R_n(O,F)BiS_2$ (R_n: La, Ce, Pr, Nd, Yb) [41–45], A_bFBiS_2 (A_b: Sr, Eu) [46–48], (La,M)$OBiS_2$ (M: Ti, Zr, Hf, Th) [49], and $Eu_3F_4Bi_2S_4$ [50] and $Bi(O,F)BiS_2$ [51,52]. Especially, $R_n(O,F)BiS_2$ shows similarity to the crystal structure of superconducting R(O,F)FeAs (1111) [21], and S-site can be substituted by Se, which also becomes superconductive [53]. In contrast, substitution of Sb in Bi sites depress superconductivity. Single crystals of those superconductors can be grown using alkali metal chloride flux. CsCl-based composition is extensively used as a flux for $R_n(O,F)BiS_2$ single-crystal growth, since CsCl exhibits little reactivity to the quartz tube at high temperature. Figure 4 shows the reactivity between each alkali chloride (LiCl, NaCl, KCl, RbCl, CsCl) and the quartz tube at high temperature (800 °C 10 h). The quartz tube is slightly reacted to CsCl, RbCl, and KCl. Furthermore, a melting temperature of CsCl (645 °C) is lower than those of RbCl and KCl, which is advantageous as a flux. This review focuses on growth of $R_n(O,F)BiS_2$ single crystals using CsCl-based flux. A eutectic CsCl/KCl flux with CsCl:KCl = 5:3 molar ratio (eutectic temperature: 616 °C) is mainly used for $Rn(O,F)BiS_2$ single-crystal growth [54]. Concretely, raw materials of $R_n(O,F)BiS_2$ with nominal composition (0.8 g) and the CsCl/KCl flux (5.0 g) are mixed using a mortar, and then sealed in a quartz tube under vacuum (~10 Pa). This mixed powder is heated for single-crystal growth, and then furnace-cooled to room temperature. The quartz tube is opened in air, and the flux is dissolved using distilled water. The remaining product is filtered. Therefore, $R_n(O,F)BiS_2$ single crystals are obtained [55,56]. Figure 5 shows a typical SEM image of $R_n(O,F)BiS_2$ (R_n = Nd) single crystals. For comparison, F-free R_nOBiS_2 single crystals are grown by CsCl flux [57,58]. Since the heat-treatment temperature for the growth of F-free single crystals is higher than that of $R_n(O,F)BiS_2$, thus, the quartz tube corrosion from KCl is enhanced at high temperature. Review of $R_n(O,F)BiS_2$ superconducting single crystals is available [59]. With another flux, a eutectic composition of KCl:LiCl = 3:2 (molar ratio) can use the flux for $R_n(O,F)BiS_2$ single crystals. The molar ratio of KCl/LiCl flux and $Nd(O,F)BiS_2$ raw materials is KCl/LiCl:$Nd(O,F)BiS_2$ = 25:1. The heat-treatment for single-crystal growth is performed at a lower temperature, below 750–450 °C to prevent corrosion of a quartz tube [60]. $La(O,F)BiSe_2$ is similar compound for $La(O,F)BiS_2$; these single crystals are also obtained using CsCl flux. The weight ratio of raw materials and CsCl flux is same for $La(O,F)BiS_2$ case [61]. Moreover, $R_n(O,F)SbS_2$ are non-superconducting compounds, those single crystals can be grown by the same growth method used for $R_n(O,F)BiS_2$ [62].

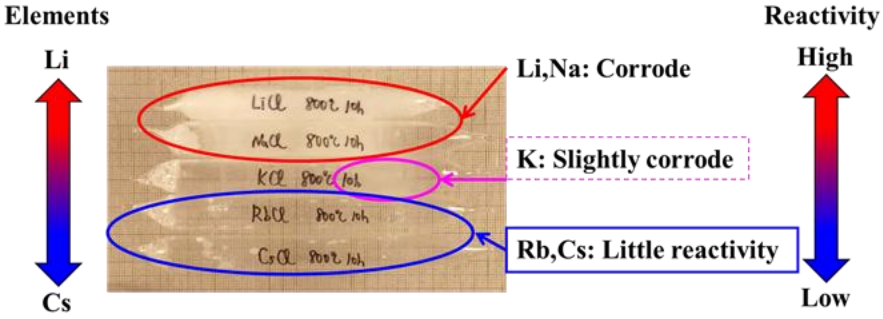

Figure 4. Reactivity between each alkali chloride (LiCl, NaCl, KCl, RbCl, CsCl) and quartz tube at 800 °C for 10 h.

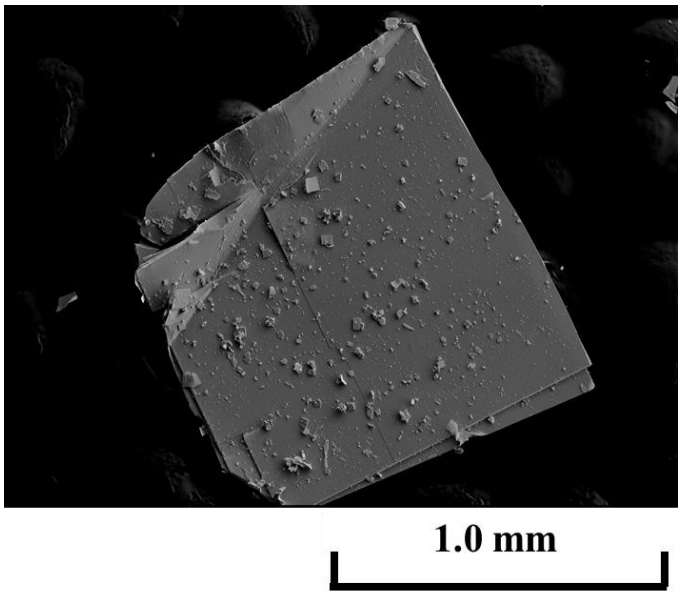

Figure 5. Typical SEM image of an R(O,F)BiS_2 (R = Nd) single crystal.

2.2. Traveling Solvent Floating-Zone (TSFZ) Method

The traveling solvent floating-zone (TSFZ) method [63] is based on the floating-zone (FZ) method, which is one of the single-crystal growth methods for congruently melting compounds. This method does not use a crucible, which means that the reaction with a crucible does not need to be considered. The schematic image of the FZ method is shown in Figure 6a. The bottom of the feed rod and seed crystal are partially melted by the local heating, and the feed rod and seed crystal are connected via the melt by surface tension. Then, the molten zone is formed between the melt of the feed rod and the seed crystal. The feed rod and seed crystal move down for the single-crystal growth. In the TSFZ method, the solvent is welded to the bottom of the feed rod (Figure 6b). The solvent plays a role as flux. Figure 7 shows the typical phase diagram of incongruent melting. The target phase (α) becomes melts incongruently at T_d. α cannot be grown by the simple melt growth, whereas the composition on X-Y liquidus line (β_1 to β_2) is selected for the solvent, and the liquid/melt of β is slowly cooled, just below the X-Y liquidus line, it begins to freeze into a crystal of α [64]. In other words, a feed rod is dissolved in the molten zone with the solvent, and then the feed rod becomes a liquid solution below the incongruent melting temperature. Subsequently, it is slowly cooled and the single crystal of the incongruent melting compound is obtained.

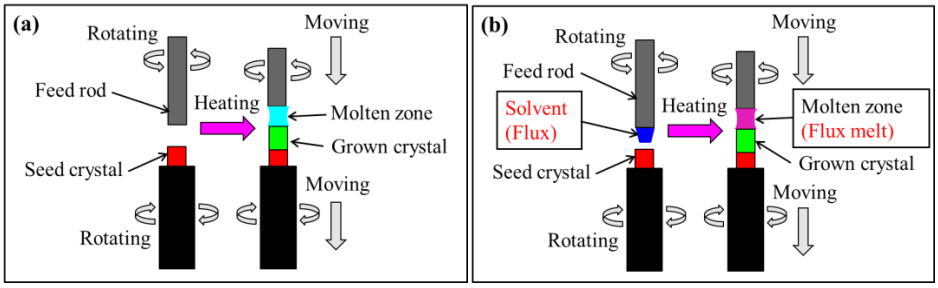

Figure 6. Schematic image of (**a**) floating zone (FZ) and (**b**) traveling solvent floating zone (TSFZ) methods.

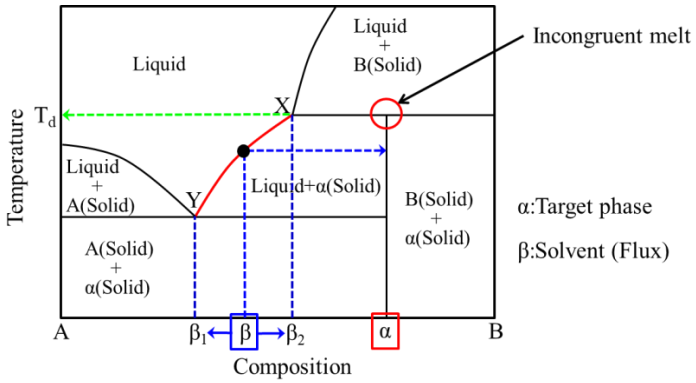

Figure 7. Typical phase diagram of an incongruently melting compound.

The TSFZ method is very effectual for single-crystal growth of high-T_c cuprate superconductors. Large (centimeter size) single crystals of high-T_c cuprate superconductors were successfully grown for the first time by the TSFZ method in [65]. For (R,A_e)-214 single crystals, the solvent for the TSFZ method is the compounds with CuO-rich composition. For instance, a (La,Sr)-214 single crystal is grown from solvent of CuO with a composition from 78 mol % [66], growth of (Nd,Ce)-214 single crystal also uses CuO-rich solvent with 85 mol % CuO [67]. Figure 8 shows a (Nd,Ce)-214 single crystal grown by TSFZ method. Single crystals of Bi-based high-T_c cuprate superconductors are also grown by the TSFZ method. For Bi-2212 single crystals, the nominal composition of the feed rod is $Bi_{2.2}Sr_{1.8}Ca_{1.0}Cu_{2.0}O_8$, and that of the solvent is $Bi_{2.4}Sr_{1.5}Ca_{1.0}Cu_{1.8}O_x$, which is Bi-rich and Sr-poor [68]. Bi-2223 has the highest T_c in Bi-based high-T_c cuprate superconductors. A Bi-2223 single crystal is grown by using a Bi-rich and Sr-poor feed rod and a very slow growth rate (0.05 mm/h). Nominal composition of the Bi-rich and Sr-poor feed rod is $Bi_{2.1}Sr_{1.9}Ca_{2.0}Cu_{3.0}O_x$ which plays a role as the solvent for the TSFZ method [69].

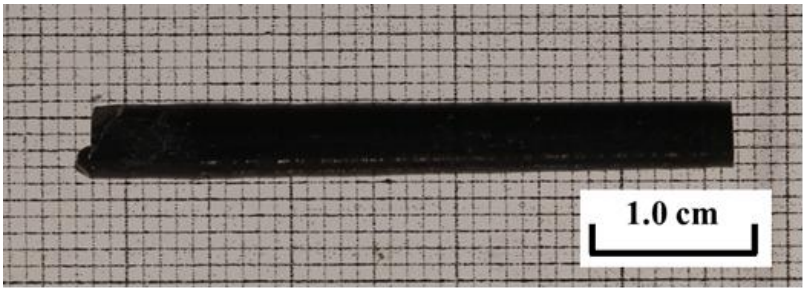

Figure 8. A (Nd,Ce)-214 single crystal grown by the TSFZ method.

2.3. Top-Seeded Solution Growth (TSSG) Method

The op-seeded solution growth (TSSG) method is like a combination of the single-crystal growth technique for flux method and the Czochralski (CZ) method. A seed crystal is placed in the solution feed with a flux, and single crystals of the target material are slowly pulled from the bottom of the seed crystal. The schematic image of the TSSG method is shown in Figure 9. In the modified TSSG method, the temperature and/or concentration gradient are given between the top and bottom of the crucible [70].

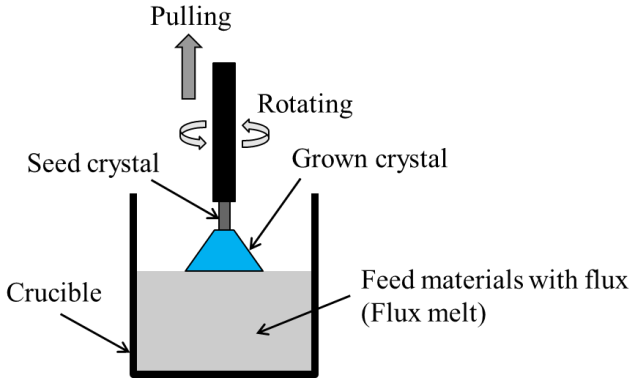

Figure 9. Schematic image of the top-seeded solution growth (TSSG) method.

(La,Ba)-214 single crystal is grown from a CuO flux solution of which the nominal composition of the solution is La(Ba)-214:CuO = 3:17 (molar ratio) [71]. Actually, the TSSG method mainly uses R-123 for single-crystal growth. Y-123 single crystals are grown from Y-123:$Ba_3Cu_7O_{10}$ = 17:83 (molar ratio) [72] and Y:Ba:Cu = 5:36:59 (cation ratio) [70] solution by the TSSG method. Additionally, BaO/CuO flux is employed for Nd-123 single-crystal growth, of which the nominal composition is Nd-123:$Ba_3Cu_5O_8$ = 1:3 (molar ratio) [73].

2.4. High-Temperature and High-Pressure (HPHT) Flux Method

This flux method (See Section 2.1) is performed in a cubic anvil high-pressure apparatus under high-temperature and high-pressure (HPHT), which is named as the HPHT flux method. The typical schematic image of the sample cell assembly for the HPHT flux method is shown in Figure 10. This method is a powerful method for single-crystal growth. The HPHT flux method can avoid the vaporization from raw materials. Therefore, this method enables difficult single-crystal growth under ambient pressure. It can grow single crystals, not only layered superconductors, but also other superconductors. For instance, β-ZrNCl and β-HfNCl superconducting single crystals are grown using NH_4Cl flux at 900–1200 °C under 3 GPa [74]. MgB_2 single crystals are successfully grown by the HPHT flux method [75,76].

Some reports exhibit the single-crystal growth of Fe-based superconductors by the HPHT flux method. L_n(O,F)FeAs (L_n = Pr, Nd, Sm) single crystals are grown using NaAs or KAs flux by the HPHT flux method. The molar ratio of L_n(O,F)FeAs raw materials and NaAs or KAs flux are weighed as between 1:1 and 1:10, respectively. That mixture puts in boron nitride (BN) container, and then pressure is applied at 3 GPa. This anvil is heated for single-crystal growth. The remaining NaAs or KAs fluxes are dissolved in water [77]. By the same method, NaCl/KCl flux is used for Sm(O,F)FeAs single-crystal growth, and a nominal composition of Sm(O,F)FeAs raw materials and NaCl/KCl flux are between 1:1 and 1:3, respectively [78]. O-deficient SmOFeAs ($SmO_{0.85}FeAs$) single crystals are grown from stoichiometric compound at 3.3 GPa, which is the HPHT self-flux method [79]. Furthermore, the HPHT flux method can also grow Pr(O,F)FeAs single-crystalline whiskers. Flux is NaAs, and the molar ratio of Pr(O,F)FeAs precursor to NaAs flux is 1:1, respectively. This mixture is put into a BN

container and pressure is applied at 3 GPa. The product is heated and then whiskers with various lengths (400–1300 μm), widths (40–70 μm), and thicknesses (5–10 μm) are obtained [80]. A review of single-crystal growth of Fe-based superconductors by the HPHT flux method is available in [81].

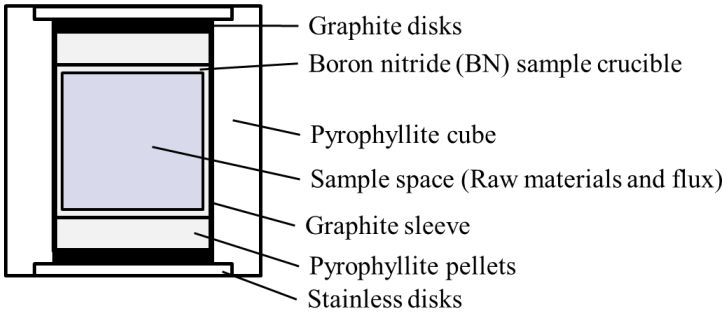

Figure 10. Schematic image of the sample cell assembly for the high-temperature and high-pressure (HPHT) flux method.

3. Summary

Flux is necessary for the growth of single crystals of layered superconductors. Small (mm size) single crystals can be grown by the conventional flux method. Low melting point metals (e.g., Sn), chloride-based compounds (e.g., KCl) and self-flux are used for the flux. Furthermore, the particular flux can grow single-crystalline whiskers with perfect crystallinity. In contrast, large (cm size) single crystals are obtained by TSFZ and TSSG methods. The HPHT flux method makes single-crystal growth possible, which is difficult under ambient pressure.

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