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Flux growth utilizing the reaction between flux and crucible

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ABSTRACT

Flux growth involves dissolving the components of the target compound in an appropriate flux at high temperatures and then crystallizing under supersaturation controlled by cooling or evaporating the flux. A refractory crucible is generally used to contain the high temperature melt. The reaction between the melt and crucible materials can modify the composition of the melt, which typically results in growth failure, or contaminates the crystals. Thus one principle in designing a flux growth is to select suitable flux and crucible materials thus to avoid any reaction between them. In this paper, we review two cases of flux growth in which the reaction between flux and Al_2O_3 crucible tunes the oxygen content in the melt and helps the crystallization of desired compositions. For the case of La_5Pb_3O, the Al_2O_3 crucible oxidizes La to form a passivating La_2O_3 layer which not only prevents further oxidization of La in the melt but also provides [O] to the melt. For the case of $La_{0.4}Na_{0.6}Fe_2As_2$, it is believed that the Al_2O_3 crucible reacts with $NaAsO_2$ and the reaction consumes oxygen in the melt thus maintaining an oxygen-free environment.

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1. Introduction

Materials synthesis and crystal growth in molten fluxes are compelling routes to novel materials with intriguing physical properties important for both scientific research and technological applications. Flux growth is also known as high temperature solution growth; the flux melts at high temperatures and acts as the solvent in a solution growth. In a typical flux growth, first the components of the target compound are dissolved in a flux, which is usually molten salt, oxide, or metal inside of a refractory crucible. Then, crystal growth takes place under supersaturation controlled by cooling or evaporating the flux. By dissolving the components of a desired compound in a flux with a low melting temperature, sometimes in controlled atmosphere or sealed ampoule, flux growth is good for the growth of a large variety of materials, such as compounds that would sublimate, compounds with a high melting temperature, volatile components, poisonous components, or a phase transition below the melting temperature.

Flux growth of oxides has been well developed in the last century. A good text book about this topic is "Crystal Growth from High-Temperature Solutions" by Elwell and Scheel [1]. There are also some good review articles [2–4]. Crystal growth and materials exploration from metallic flux were mainly developed in recent years with a major contribution from Canfield and Fisk [4–12]. Compared to the flux growth of oxides which is normally performed in air or flowing gas (O_2, N_2, or Ar), growth of intermetallic compounds from metallic flux or salt is more challenging because most intermetallics tend to oxidize in air and some are moisture sensitive, volatile, and/or poisonous.

In many cases, more than one kind of flux can mediate the crystal growth of one desired compound. Crystals of the same nominal composition but grown out of different fluxes might exhibit different physical properties, which could lead to confusions in understanding the intrinsic properties. One good example is the physical properties of K-doped $BaFe_2As_2$, one important member of FeAs-based superconductors. Kim et al. [13] studied the low temperature specific heat of $Ba_{0.6}K_{0.4}Fe_2As_2$ single crystals grown out of Sn, In, and FeAs fluxes, and found that the physical properties depend on the preparation method. This illustrates the importance of growing crystals out of an appropriate flux. There are some important factors that have to be considered in selecting the right flux [1,6,14]. One of them is that the reaction between flux and crucible should be negligible.

In a flux growth, a refractory crucible is needed to hold the melt at high temperatures. Depending on the composition of the desired compound, the properties of flux, and the temperature profile, crucible materials can be metals (Fe, Ni, Ta, W, Mo, Pt), quartz, graphite, nitrides (BN), or oxides (Al_2O_3, MgO, ZrO_2). At high temperatures, a serious reaction between flux and crucible can destroy the crucible and ruin the growth. A minor reaction can modify the composition of the melt, which leads to the failure of the growth, or, in most cases, contaminates the crystals as a substitution or an inclusion. Crystal contamination from crucible materials can significantly affect the physical properties. This is well illustrated by the growth of YBCO superconductors in an Al_2O_3 crucible. The BaO–CuO flux attacks Al_2O_3 crucibles and Al_2O_3 dissolved into the flux contaminates the crystals as substituent that suppresses the superconducting transition temperature by over 20 K [15]. Thus, when

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designing a flux growth, a good combination of flux and crucible is normally selected so that no or negligible reaction between flux and crucible is expected at high temperatures.

In this paper, we provide a different view of the reaction between flux and refractory crucible materials: in some special cases, the reaction can be employed to facilitate the growth of desired compositions. Specifically, we review the flux growth of La_5Pb_3O and $La_{0.4}Na_{0.6}Fe_2As_2$ in which the reaction between flux and Al_2O_3 crucible helps control the oxygen content in the melt for the growth of desired crystals.

2. Crystal growth of La_5Pb_3O

La_5Pb_3O single crystals were grown out of a mixture of La, Co, and Pb. Starting materials La (99.999% Ames Laboratory), Co (99.999%, Alfa Aesar), and Pb (99.9999%, Alfa Aesar) were placed in a 2 ml Al_2O_3 crucible with a molar ratio of 7:2:1. A catch crucible containing quartz wool was mounted on top of growth crucible and both were sealed in a silica ampoule under approximately 1/3 atmosphere of high pure argon gas. The sealed ampoule was heated to 1150 °C, stayed at 1150 °C for 4 h, and then cooled to 850 °C over 60 h. Once the furnace reached 850 °C, the excess flux was decanted from the rectangular crystals with the typical dimension of $0.5 \times 0.5 \times 2$–$4\ mm^3$. Room temperature X-ray powder diffraction of pulverized single crystals confirmed single phase of as-grown crystals. The stoichiometry of as-grown crystals was confirmed with elementary analysis as well as single crystal X-ray and neutron diffraction performed at room temperature. Detailed crystal characterization and physical properties will be reported elsewhere.

A similar procedure was previously employed to grow Ce_5Pb_3O single crystals [16]. Once Co is absent in the starting materials, no Ce_5Pb_3O crystals could be obtained. This, together with the fact that no Co contamination was found in the as-grown crystals, suggests that Co is an important component in forming a proper flux mediating the growth of Ce_5Pb_3O. The successful growth of Co-free La_5Pb_3O in our study suggests a similar role of Co in the growth. Investigation of the La–Co and La–Pb binary phase diagrams suggests that Co is important in lowering the melting temperature of the mixture. Fig. 1 shows the La–Co binary phase diagram [17]. In a wide composition range $10 < x_{Co} < 55\%$at, $La_{1-x}Co_x$ alloy melts below 850 °C. Even though Pb melts at a low temperature of 320 °C, the melting temperature of La–Pb alloys increases rapidly when introducing La into Pb melt; the line compound La_5Pb_3 melts congruently at 1450 °C.

It is interesting to note that no oxygen was introduced in the starting materials but the resulting crystals contain oxygen. After decanting, a thin layer of La_2O_3 was always observed inside of the alumina growth crucible and it takes the shape of the crucible. Fig. 2 shows a SEM picture of part of the La_2O_3 layer. The high pure starting materials are not expected to introduce that much oxygen. The growth was performed in a sealed quartz tube with the highest homogenizing temperature of 1150 °C which is below the softening temperature of quartz. So it is unlikely that significant amount of oxygen diffuses into the quartz tube during crystal growth. As shown in Fig. 2, some quartz wool in the catch crucible fall down into the melt, which might provide oxygen to oxidize La. However, in a growth performed without using quartz wool inside of the catch crucible, both the La_2O_3 layer and La_5Pb_3O single crystals were obtained. Therefore, the alumina growth crucible, which has direct contact with the melt, is expected to be the only source for oxygen in La_5Pb_3O crystals and the La_2O_3 layer. As a rule of thumb, rare earth concentrations over 12% in a wide variety of intermetallic fluxes react with Al_2O_3 [18]. In the growth of La_5Pb_3O, there are 70%at La in the melt and oxidization of La metal in the melt by the growth crucible is expected. This oxidization leads to the formation of La_2O_3 layer and also explains why the La_2O_3 layer takes the shape of the growth crucible.

As shown in Fig. 2, the rectangular La_5Pb_3O grains nucleate on the surface of La_2O_3 layer. We believe that the oxidization layer is critical for the growth of La_5Pb_3O crystals: (1) it serves as the source of oxygen to the melt and controls the oxygen content in the melt by the reaction $2[La]+3[O]=La_2O_3(s)$; (2) it also serves as the passivating layer to prevent further oxidization of rare earth metal. The La/Co ratio in the starting materials stays close to the eutectic with the melting temperature about 640 °C (see Fig. 1). Oxidization of La metal will modify the composition of the melt. The melting temperature of the melt increases when the flux becomes more Co-rich, and in the worst case La–Co binary compounds might precipitate. A decanting temperature of 850 °C was selected considering the composition change of the melt due to the oxidization of La during the growth. The lowest decanting temperature used in our growths is 825 °C. The successful decanting at 825 °C suggests that Co should be less than 55%at without considering the effect of alloying with Pb on the melting temperature of La–Co binary alloy.

Fig. 3 illustrates how the reaction between growth crucible and flux helps the growth of La_5Pb_3O: at high temperatures, Al_2O_3 oxidizes La metal forming La_2O_3 passivating layer which controls the oxygen content in the melt; La_5Pb_3O crystals nucleate on the surface of La_2O_3 passivating layer. With a similar procedure, we have been able to grow R_5Pb_3O (R=La, Ce, Pr, Nd, and Sm) crystals. However, we failed to grow R_5Pb_3O crystals with heavier rare earth ions even though a rare earth oxide layer also forms. This might signal limited oxygen solubility and/or diffusivity in R–Co–Pb melt with heavy rare earth ions.

3. Crystal growth of $La_{0.4}Na_{0.6}Fe_2As_2$

The growth and physical properties of $La_{0.4}Na_{0.6}Fe_2As_2$ single crystals were reported elsewhere [19]. When looking for proper crucible materials for the growth of LaFeAsO superconductors out of NaAs flux, it was noticed that $La_{0.4}Na_{0.6}Fe_2As_2$ crystals were always obtained once the Al_2O_3 crucible is used to hold the melt but LaFeAsO crystals result when the Ta crucible is used, even though we started with the same starting materials and used an identical heat treatment process. The difference is illustrated in Fig. 4. For the growth of LaFeAsO single crystals, the starting materials of a homogeneous mixture of LaAs, ($1/3Fe+1/3Fe_2O_3$) or FeO, and NaAs with the molar ratio of 1:1:15 was loaded into a Ta tube [20]. For the growth of $La_{0.4}Na_{0.6}Fe_2As_2$ single crystals, the same homogeneous mixture was loaded into an Al_2O_3 crucible, which was further sealed inside of a Ta tube under 1/3 atmosphere of argon gas. The use of Ta tube in both cases is necessary to protect the quartz tube from NaAs at high temperatures.

As shown in Fig. 4, the only difference between the above two growths is the use of an Al_2O_3 crucible which has a direct contact with the flux. The dramatic difference in the crystal composition forces us to consider the possibility that the Al_2O_3 crucible absorbs oxygen introduced by iron oxide into the melt. The formation of $NaAsO_2$ has been proposed to account for the solubility of oxygen in an NaAs flux. $NaAsO_2$ has a low melting temperature of about 600 °C, which is similar to that of NaAs [21]. After crystal growth, the Al_2O_3 crucible turns to be gray and reaction between the crucible and flux was always observed. Sometimes, the Al_2O_3 growth crucible cracks after growth. Residual flux was found both inside and outside of the growth crucible. Unfortunately, we did not further investigate the reaction mechanism for the following two reasons: (1) in a typical growth, about 0.10 g Fe_2O_3 was used in a 3 g mixture of charge and flux. This can lead to the formation of 0.12 g $NaAsO_2$. With that little amount of $NaAsO_2$, it is difficult to find the reacting product in the ampoule; and

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