Flux requirements for the growth of RFeAsO (R = rare earth) superconductors

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Abstract
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Keywords
Materials Science and Engineering, crystal growth from melt, crystal structure, diffusion, iron compounds, lanthanum compounds, solubility, superconducting materials, X-ray diffraction

Disciplines
Condensed Matter Physics | Metallurgy

Comments

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Flux requirements for the growth of $R$FeAsO ($R$=rare earth) superconductors

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Millimeter-sized LaFeAsO single crystals have been successfully grown out of NaAs flux starting with (LaAs+1/2Fe$_2$O$_3$):20NaAs. The factors which allow the growth of these crystals out of NaAs but not out of many other fluxes, such as FeAs, have been investigated. X-ray powder diffraction found that NaAs synthesized for the growth of RFeAsO superconductors has monoclinic LiAs structure. Thermal analysis confirmed that NaAs melts congruently at about 600 °C. The ability to extract RFeAsO crystals from this NaAs flux suggests that NaAs has a significant oxygen solubility, possibly due to the formation of the ternary compound NaAsO$_2$, and enough oxygen diffusivity to transport solute to the growth front. Oxygen solubility and diffusivity are two important factors in searching for an alternative environmentally benign flux for the growth of RFeAsO superconductors. © 2011 American Institute of Physics. [doi:10.1063/1.3555632]

Since the discovery of superconductivity in LaFeAsO$_1-x$F$_x$,$^1$ extensive work has been carried out to synthesize high purity polycrystalline materials and to grow sizeable single crystals of FeAs-based superconductors in order to explore the intrinsic as well as anisotropic physical properties and superconducting mechanism. The successful growth of centimeter-sized single-crystals of the $AFe_2As_2$ system ($A=$Ca, Sr, Ba, and Eu) has enabled significant advancement in our understanding of these iron pnictides intermetallic superconductors and elucidated the important structural, magnetic, thermodynamic, and transport features of these novel superconductors.$^2$ In contrast, the growth of RFeAsO ($R$=rare earth) has been found to present several challenges which have made developing a synthesis protocol difficult. There are no reports available on the multicomponent phase diagram and the melting/solidification mode of RFeAsO compounds, which would facilitate design and optimization of growth processes. Moreover, the high vapor pressure at relative low temperatures and poisonous nature of arsenic require special precautions during the crystal growth.

Small (up to 600 μm) single crystals of RFeAsO were initially grown out of NaCl flux under ambient or high pressure.$^5,6$ The low solubility of RFeAsO starting materials in NaCl flux requires the growth at high temperatures under high pressure for larger crystals. Later, we identified that NaAs is a suitable flux for the growth of plate-like LaFeAsO single crystals with typical dimensions of $3 \times 4 \times 0.05$–0.3 mm$^3$. This growth protocol has since been applied to other RFeAsO compounds with magnetic rare earth ions. The availability of millimeter-sized high quality single crystals enables various structural and physical property studies of the RFeAsO compounds to be conducted by different techniques.$^8$–$^{11}$ However, the separation of crystals from flux by washing and cleaning processes generates a large amount of hazardous waste water containing sodium arsenate hydrate. From this point of view, an environmentally friendly flux for the growth of RFeAsO compounds is still needed. Motivated by this, in this letter we report our understanding of why NaAs is a proper flux and what criteria could be used in looking for new, environmentally benign fluxes.

Since no Na–As binary phase diagram is available, we synthesized NaAs and measured the melting characteristics with differential scanning calorimetry (DSC). NaAs was first synthesized by firing Na metal and As chunks in a Ta tube at 565 °C for 15 h. X-ray powder diffraction was performed in protected atmosphere to determine the phase purity and lattice parameters. The diffraction experiments were carried out on a PANalytical Xpert PRO MPD x-ray diffractometer with monochromatic Cu K$_\alpha$ radiation at room temperature by step scanning in the angle range 10°–80° in increments of 0.02° and dwell times of 60 s. Silicon powder was added to the sample as an internal standard and the diffraction pattern was analyzed with the software JADE. For DSC measurements of the melting and solidification behavior, about 30 mg NaAs powder was loaded into a 1/8" diameter Ta capsule which was sealed in 1/3 atmosphere Ar with a laser welder. The detailed description of the sealing and laser welder is reported elsewhere.$^{12}$ DSC was performed using a NETZSCH DSC 404 C Pegasus thermal analyzer with a heating rate of 10 °C/min in the temperature range of 25–700 °C.

Figure 1 shows a representative diffraction spectrum for NaAs. Two different structures have been reported for NaAs: NaP structure with the space group $P2_12_12_1$,$^{13}$ and LiAs structure with the space group $P$1/c.$^{14}$ The diffraction pattern shown in Fig. 1 could be indexed with monoclinic LiAs structure. The lattice parameters determined with JADE are $a=6.237(1)$ Å, $b=5.865(2)$ Å, $c=11.583(6)$ Å, and $\beta =116.88(3)$°, which all agree well with the previous report.$^{14}$

As illustrated in Fig. 1, reflections from Na$_2$As were also observed. The presence of Na-rich phase might be induced by the reaction between As vapor and Ta.

Figure 2 shows the DSC heating and cooling traces for NaAs. NaAs melts congruently at about 600 °C, which agrees with the prediction by Sangster and Pelton.$^{15}$ The
weak feature around 400 °C indicates that the sample is slightly off stoichiometric so that a eutectic with an adjacent phase is observed. The low melting temperature facilitates the growth of RFeAsO compounds in low temperature range, for example at a temperature below 1200 °C which is around the softening point of quartz. We also studied the mixtures of NaAs and prefired RFeAsO at the molar ratio of 10:1, 15:1, and 20:1, respectively. However, no features other than the melting/solidification of NaAs were observed.

FeAs has been widely used to grow AFe2As2 compounds. Attempts to synthesize RFeAsO compounds from various Fe–As binary liquids, such as FeAs, FeAs2, Fe2As, Fe3As, and Fe5As2, were not successful when the highest homogenizing temperature is below 1200 °C (limitation of quartz). A comparison of the materials which have been grown from FeAs with the RFeAsO compounds suggest that either the rare earth element or oxygen is not soluble in the Fe–As based flux. However, as we have successfully grown Sr1−LaFe2As2 and Sr1−NdFe2As2 from Fe–As based fluxes we hypothesize that the failure in growing RFeAsO crystals out of FeAs flux is due to insufficient solubility and/or mobility of oxygen in the flux below 1200 °C.

The crystal growth from high temperature solution involves the dissolution of starting materials in flux, nucleation, and growth of desired compositions from the supersaturated solution.16 The successful growth of RFeAsO crystals from NaAs flux suggests that liquid NaAs has reasonable solubility and diffusivity of oxygen at high temperatures. We note that the ternary compound NaAsO2 also melts at about 600 °C which might suggest a wide range of oxygen content in Na–As–O melt.17 Unfortunately, there are no reported data on either the solubility or diffusivity of oxygen in liquid NaAs. Moreover, the reactive nature of Na and the vapor pressure and toxicity of As place the determination of these factors beyond the scope of this work. Thus, we cannot give a quantitative measure of the required solubility or diffusivity of oxygen in the melt in searching for new fluxes. However, we can expect that as long as the oxygen activity is sufficiently low that the rare earth is not oxidized, thus avoiding the precipitation of rare earth oxides, an Na–As–O melt is suitable for the growth of RFeAsO compounds.

To confirm the above hypothesis and check possible critical oxygen content beyond which rare earth oxides precipitate, we tried the growth of LaFeAsO single crystals starting with (1) LaAs+1/2 Fe2O3, and (2) La3O3+Fe2O3, respectively. For direct comparison with our standard protocol that uses elemental iron as a starting material, LaAs+1/3 Fe2O3+1/3 Fe, other growth parameters, such as homogenizing temperature and time, cooling rate, etc., were kept the same as reported before.7 Figure 3 shows a picture of a LaFeAsO single crystal grown starting with LaAs+1/2 Fe2O3. Careful characterization observed that the extra oxygen or absence of elemental Fe did not affect the growth habit, the yield, nor the physical properties of LaFeAsO crystals. Magnetization and electrical resistivity measurements (not shown) confirmed the structural and magnetic transitions at 155 K and 141 K, respectively.7 This suggests that it is unlikely to tune the oxygen stoichiometry in RFeAsO crystals by varying the oxygen content in the melt.

For the growth starting with La3O3 and Fe2O3, small crystals with the largest dimension up to 200 μm were obtained with small overall yield. Residual La2O3 was also present and found intermixed with the crystals after washing away the flux. While it is tempting to assume that the allowable oxygen activity in the flux was exceeded, it should be noted that the dissolution rate of the La2O3 in the liquid might be considerably different than that of LaAs and the residual La2O3 is actually undissolved starting material. Since the growth protocol was determined for LaAs, we cannot rule out kinetic factors. If the former case, the upper limit of oxygen content in flux is calculated to be in the range of 3–7 at. %. The failure to obtain a homogenous liquid during the dissolution process will affect both the yield and the size...
of the crystals. Further experiments are in progress to determine the upper limit of the oxygen activity suitable for growth of LaFeAsO.

Based on the growths conducted in this study, the ability to synthesize LaFeAsO from melts is a function of the oxygen solubility of the liquid. Growth of Fe–As fluxes were unsuccessful even though these fluxes could be utilized to incorporate rare earth elements into the intermetallic AFe2As2 compounds. Liquid NaAs, on the other hand, shows a high degree of versatility in the preparation of RFeAsO compounds in that a variety of starting materials were used successfully. It is believed that the ability of NaAs to dissolve the oxide starting materials, and especially the highly stable rare earth oxides, is related to the solubility of oxygen in liquid NaAs. High solubility of oxygen is also supported by the existence of the low melting compound NaAsO2. The similarity in melting points between the melting temperatures of NaAs and NaAsO2 suggests that the liquidus between the compounds extends across the phase diagram. However, while oxygen solubility is important, transport of oxygen to the growing interface (diffusion limited growth) is also a necessary component.

With the idea that oxygen solubility and diffusivity are important factors in selecting the proper flux for the growth of RFeAsO, we checked the oxygen solubility and diffusivity in various low melting metals. Figure 4 shows the oxygen solubility and diffusivity at 1100 °C in some metals which are normally considered as flux for the growth of intermetallic compounds.18–22 Obviously, In, Ga, and Cu have limited solubility of oxygen which disqualifies them as the flux. Ag has a good solubility and diffusivity of oxygen. Unfortunately, at temperatures below 1200 °C, it has limited solubility of Fe. Sn exhibits finite solubility and diffusivity of oxygen, thus growth at higher temperature is necessary. Pb has a very good solubility of oxygen. However, crystal growth of RFeAsO might be limited by the poor oxygen diffusivity. Melt agitation might be needed to enhance the solute transportation to facilitate the growth of RFeAsO nuclei.

We noticed that CeFeAsO single crystals with the largest dimension up to 800 μm have been successfully grown out of Sn flux homogenized at 1400 °C.23 This confirms the above analysis. When looking for other fluxes for the growth of RFeAsO crystals, the solubility and diffusivity of oxygen in liquid Sn can be used as a reference. At 1100 °C, Pb melt has a much larger oxygen solubility but a negligible diffusivity. Crystal growth in Pb with liquid agitation is desired to further confirm the above analysis.

In summary, we studied the properties of NaAs and synthesized LaFeAsO single crystals starting with LaAs and Fe2O3. The experiments suggest that NaAs can have a significant solubility of oxygen possibly due to the formation of ternary compound NaAsO2. The variation in oxygen content in the flux does not change the oxygen stoichiometry in RFeAsO crystals. Oxygen solubility and diffusivity are two important factors one needs to consider when looking for alternative, environmentally benign flux for the growth of RFeAsO single crystals.

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