Physical properties optimization of polycrystalline LiFeAs

CrossMark

Shiv J. Singh [a,b,*], Uwe Gräfe [a], Robert Beck [a], Anja U.B. Wolter [a], Hans-Joachim Grafe [a], Christian Hess [a,c], Sabine Wurmehl [a,d], Bernd Büchner [a,c,d]

[a] Leibniz-Institute for Solid State and Material Research, IFW-Dresden, 01171 Dresden Germany
[b] Research Center for Environmentally Friendly Materials Engineering, Muroran Institute of Technology, 27-1 Mizumoto-cho, Muroran, Hokkaido, 050-8585, Japan
[c] Center for Transport and Devices of Emergent Materials, Technische Universität Dresden, 01069 Dresden, Germany
[d] Institut für Festkörperphysik, Technische Universität Dresden, 01069 Dresden, Germany

ARTICLE INFO

ABSTRACT

We present a study of parameter optimization for synthesizing truly stoichiometric polycrystalline LiFeAs. Stoichiometric LiFeAs has been prepared in a very broad range of synthesis temperature (200–900 °C) under otherwise exactly the same conditions, and has been characterized by structural, magnetic, transport, nuclear quadrupole resonance (NQR), and specific heat measurements. Our study showed that the LiFeAs phase is formed at 200 °C with a large amount of impurity phases. The amount of these impurity phases reduces with increasing synthesis temperature and the clean LiFeAs phase is obtained at a synthesis temperature of 600 °C. Magnetic susceptibility and resistivity measurements confirmed that the superconducting properties such as the critical temperature T_c, and the upper critical field H_{c2} do not depend on the synthesis temperature (≤ 700 °C), remaining at almost the same value of $\sim$19 K and $\sim$40 T, respectively. However, the width ΔT_c of the transition and the NQR line width decrease with increasing the synthesis temperature and reached to minimum value for the synthesis temperature of 600 °C. Our careful analysis suggests that the best sample obtained at 600 °C is optimal concerning the low resistivity, high residual resistivity ratio (RRR), low ΔT_c, high T_c and H_{c2}, and a small NQR line width with values which are comparable to that reported for LiFeAs single crystals. Specific heat measurements confirmed the bulk superconducting nature of the samples. The H_{c2} value estimated from the specific heat is consistent with that of the resistivity measurements. Concisely, 600 °C synthesis temperature yields optimal high quality polycrystalline LiFeAs bulk samples. Further improvement of the quality of the sample prepared at 600 °C could be obtained by a controlled slow cooling process. Microstructural analysis reveals that the abundance of micro-cracks becomes strongly reduced by the slow cooling process, resulting in an increase in clean and well-connected grain boundaries.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

The discovery of iron-based superconductors [1] in 2008 is the most exciting example of high-temperature superconductivity since the emergence of cuprates and generated a great interest in the scientific community. Following the pioneering work of Kamihara et al., [1], more than 200 superconducting compounds have been reported [2] in which the superconducting compounds REFeAsO$_{1-x}$F$_x$ with RE = rare earth (1111 phase), AEFe$_2$As$_2$ with AE = alkali earth (122 phase), AFeAs with A = alkali metal (111 phase) and FeSe (11 phase) have attracted tremendous attention. All these sub-families of iron-based superconductors have a layered structure with the same building blocks, namely tetrahedrons, which consist of an alternate stacking of blocking and superconducting layers. The superconducting transition temperature (T_c) has been raised up to a maximum of 58 K in the '1111' compound (Sm1111) substituted with fluorine at oxygen sites [3,4]. A particular family is the 111 phase, such as LiFeAs [5–9] and NaFeAs [10–12], which have the simple crystal structure among the iron arsenides. LiFeAs, of particular focus in this study, shows $T_c \sim$18 K and has a tetragonal PbFCl (Cu$_2$Sb)-type structure (space group $P4/nmm$) [5–9], possessing within a unit cell, a single FeAs tetrahedral layer sandwiched between two Li layers. Whereas the closely related compound NaFeAs is reported to undergo three successive phase transitions around 55, 45, and 10 K corresponding to the structural transition from tetragonal to orthorhombic, antiferromagnetic and superconducting transitions, respectively [10–12], no experimental evidence for structural or magnetic

---

* Corresponding author. Tel.: +49 0 351 4649 157; fax: +49 0 351 4659 313.
  E-mail address: s.j.singh@ifw-dresden.de, sjsingh@mmm.muroran-it.ac.jp, shivjees@gmail.com (S.J. Singh).

transitions has been found for LiFeAs down to low temperature [7–8,13–16]. This means, the superconductivity appears in stoichiometric LiFeAs without any additional doping or external pressure. However, it seems that the physical and magnetic properties depend in a very subtle manner on the precise stoichiometry. Furthermore, off-stoichiometry of 111 has been reported to greatly suppress the superconductivity [8]. The understanding of the sensitivity of Li concentration on the superconducting properties of LiFeAs is still under debate.

There are several methods for the synthesis of LiFeAs using a wide heating temperature range 700–1500 °C with different conditions [5,6,17–18]. However, the most common synthesis [14,15] temperature is ~800 °C. Most of the studies on LiFeAs are based on the single crystal growth at ~1050–1500 °C by different methods like self-flux [9], Sn flux [19] and Bridgman technique [17]. However, the synthesis of the doping series of single crystals, especially off-stiochiometric LiFeAs, is very difficult because of the corresponding thermodynamic phase diagram which is not truly known. Another difficulty is that the actual composition at a very high synthesis temperature is hard to control due to the volatile nature of Li. This problem can be avoided in the polycrystalline samples, especially if prepared at low temperature. In the literature, there are only few papers available based on the synthesis of polycrystalline samples. Wang et al., [5], Tapp et al., [6] and Pitcher et al., [7] reported on the synthesis of LiFeAs polycrystalline samples which can be exhibited nearly the LiFeAs phase with a small amount of off-stoichiometries. The reported values for T_c and the upper critical field (H_{c2}) have a very broad range from 14 to 19.2 K [5,6,9,17–19] and 13 to 80 T [20–24], respectively. This spread of data is likely to be caused by the different synthesis conditions and processes which easily could lead to off-stoichiometry or impurity phases. Therefore, it is obviously important to optimize the synthesis of LiFeAs for revealing its intrinsic properties, and to define a starting point for controlled doping and off-stoichiometry experiments.

One of the difficulties in growing high-quality stoichiometric LiFeAs is without any doubt connected with the use of Li. Li is a very reactive alkali element with a low melting point (~180 °C), which is also highly volatile, easily oxidized in air, and highly reactive with crucible walls at very high sintering temperatures [8]. In this respect, a low temperature synthesis can be helpful to control the Li content, similar to the case of oxypnictide superconductors where a low-temperature synthesis has proven an effective method to improve the superconducting properties by controlling the fluorine content [4,25]. To optimize the synthesis temperature, we have synthesized the stoichiometric LiFeAs (1:1:1) compound in the very broad range of synthesis temperature between 200 °C and 900 °C under otherwise exactly the same conditions. A broad spectrum of characterization by XRD, magnetization, resistivity, NQR and specific heat measurements have been done for each set of samples under the again exactly the same conditions for studying and comparing the quality of polycrystalline samples. Different types of characterization on each set of samples depicts that a synthesis temperature of 600 °C is at optimum for synthesizing phase-pure polycrystalline LiFeAs samples with the highest onset T_c value of 19.2 K with a very sharp transition width ΔT_c ~1.2 K. The superconducting properties of our best samples are well characterized by different measurements which are consistent with those of earlier reported LiFeAs single crystals [9,17,19].

2. Experimental details

To optimize the synthesis process, we have prepared polycrystalline stoichiometric LiFeAs bulk samples at synthesis temperature T_{synth} = [200, 900 °C]. For each set of samples prepared at a particular temperature, the same synthesis process is followed as given in the block diagram of Fig. 1. In the first step, the purity of the starting reagents, i.e. Li rods (99.99%) and FeAs (FeAs using starting materials Fe powder (99.99%) and As powder (99.99%) prepared by heating at 700 °C for 12 h) corresponding to a stoichiometric LiFeAs ratio, were mixed in an agate mortar, which was then placed into an alumina (Al_2O_3) ceramic crucible. Other possible crucible materials such as quartz and Nb have not been used in order to minimize the possible side reactions of Li and As, respectively. The crucible was inserted into an Nb container, covered by an Nb cap. The Nb crucible was welded in an Ar atmosphere to prevent any oxidation. The sample was then heated at 200 °C for 12 h (Step 1). This step is used because of the high reactivity and the low melting point (180 °C) of Li. The resultant powder was homogenized, pressed into pellets by applying a uniaxial pressure of 5 MPa, put into an alumina crucible and sealed in an evacuated Nb tube which was inserted in an evacuated quartz tube and then heated at the considered synthesis temperature T_{synth} for 45 h (Step 2). After this reaction, the obtained pellets had a lot of cracks and were very brittle. Hence, the synthesized pellets were again thoroughly reground and the powder was pressed by applying a pressure of 5 MPa. These pellets were again put into an alumina crucible which was placed in an Nb tube that was sealed afterwards. Finally, this Nb tube was inserted in an evacuated quartz tube and put in a furnace at the same T_{synth} for 2 h (Step 3). The furnace was then cooled down to room temperature by furnace cooling. These steps were done separately for each considered synthesis temperature T_{synth} under the same conditions. After finding the best T_{synth}, we have also optimized the cooling process by investigating the effect of cooling rates of 1, 0.3 and 0.1 K/min in the third step. In all these slow cooled samples, we shall focus only on the sample prepared by a cooling rate of 0.1 °C/min in this paper.

The resulting samples were characterized by powder XRD where the data were collected on a Stoe Stadi P diffractometer in transmission geometry with Mo K_α-radiation, equipped with a Ge monochromator and a DECTRIS MYTHEN 1 K detector. For some samples, such as the samples prepared at 200 and 300 °C, a Huber G670 Guinier imaging plate diffractometer with Co K_α-radiation and a Ge 111 monochromator has been used. The samples were protected against degradation in air by sealing them inside a glass capillary. The powder diffraction patterns were scanned over the angular range 0–55° or 10–100° with a very small step size through Mo K_α-radiation and Co K_α-radiation, respectively. The profile analysis and the lattice parameters were obtained from Rietveld refinements on the XRD data employing the Fullprof software suite [26]. Microstructural characterizations were performed using a field-emission scanning electron microscope (FEI: Nova-SEM 200). Inductively coupled plasma mass spectroscopy (ICP-MS, Agilent 7500C Quadrupole ICP-MS with dynamic reaction cell) was used to confirm the 1:1:1 composition of LiFeAs. For the ICP-MS analysis, about 10–20 mg of the LiFeAs polycrystal was dissolved in a leak-free glass ampule in 300 mg of nitric acid. Complete dissolution was ensured by stirring for 48 h. One should note that the error bar for ICP-MS is around 1–2%.

Nuclear quadrupole resonance (NQR) spectroscopy was measured using a commercial Tecmag Apollo spectrometer. Due to the extreme sensitivity of the sample to air and moisture, the pellets were powdered and sealed in a quartz tube in an Argon atmosphere to avoid any contact of the sample with air. A copper coil was wrapped around the quartz tube. The spectra were taken by sweeping the frequency point by point with a standard Hahn–Spin-Echo-Pulse sequence [27]. A Fourier transformation of the received time signals had been done for each frequency and the results were summed up to obtain the overall NQR spectrum. From the spectra, the center of spectral weight (called NQR frequency ν) and the full width at half maximum (called NQR line width $\Delta\nu$) were extracted.