High Efficient Synthesis of Iron-based Superconductors

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Abstract

We have performed systematic investigations aimed at high efficient synthesis of the 1111 family iron-based superconductors. By using meta-stable reactive starting materials of \( \text{LnAs} \) and \( \text{FeO} \), assisted by mechanical alloying and fast heating, high purity samples with \( T_{c}^{\text{onset}} \) greater than 50K can be made with sintering temperatures between 1433K-1073K, and sintering time from 20 min to 40 h. High purity phase with sintering temperature as low as 973K was demonstrated successfully although \( T_{c}^{\text{onset}} \) fall below 50K and weak grain boundary suppressed greatly the zero resistance temperature. Ultra fast microwave sintering brings the sintering time further down to 5 min. Samples prepared by the above high efficient methods typically posses submicron grain and very high upper critical field, indicating very high pinning power. Besides offering cost advantages, the developed methods may play important roles in the exploit of novel superconductors.

1. Introduction

The discovery of \( \text{LaFeAsO}_{1-x}\text{F}_{x} \) superconductors with \( T_{c} \) up to 26 K [1] has stimulated extensive research in this field. Many new families of iron based superconductors were soon found with highest \( T_{c} \) of 55K achieved [2,3]. Compared to cuprates, the iron based superconductors show high critical magnetic field \( H_{C} \), high critical current density \( J_{c} \) [4] but with much smaller anisotropy [5], which make them very attractive for high field applications.

The \( \text{SmFeAsO} \)-based superconductors were of particular interests for application due to its relatively higher \( T_{c} \). Superconductivity can be easily induced by doping \( \text{F} \) at \( \text{O} \) site. However, sample preparation by conventional solid state sintering usually needs high temperature and long time (typical above 1433K...
and longer than 40h) [1], which causes excessive loss of fluorine, results in degradation of the superconducting properties [6]. We have reported previously a fast synthesis method by using meta-stable starting materials, high energy ball milling of individual material and fast heating, high purity samples were successfully prepared with temperature lowered to 1173K and sintering time down to 20 minutes [7].

In this work, we report our latest results on high efficient synthesis of the SmFeAsO-based superconductors. To further increase the efficiency of sample preparation, we replaced the time consuming ball milling of individual starting materials by mechanical alloying (MA). Ultra fast microwave synthesis was also demonstrated with which high purity samples can be obtained within 5 minutes. Besides offering cost advantages, the developed methods may play important roles on the exploit of novel superconductors.

The crystal structure of the samples were studied by the powder X-ray diffraction patterns measured on a diffractometer (Bruker D8 Focus) using Cu Kα radiation at 40 KV and 40 mA. The temperature dependant resistivity was measured using the standard four point method in a physical property measurement system (Quantum Design, PPMS-9T). Upper critical fields \( H_{c2} \) were determined from the temperature dependant resistivity under different magnetic fields using the Werthamer-Helfand-Hohenberg formula [8].

2. Mechanical alloying synthesis

Mechanical alloying (MA) is a powder processing technique that allows for preparation of homogeneous materials starting from blended powder mixtures. From the repeated cold welding and fracture of the powder particles, this powder metallurgical process was successfully used in the preparation of many unique materials, including nanostructure alloys, amorphous materials and non-equilibrium phases etc, which cannot be synthesized via conventional routes [9, 10].

Stoichiometric amounts of the intermediate compounds of LnAs, Fe2As, FeO and LnOF were loaded into a cylindrical container with preliminary grinding in a glove box filled with high purity Ar atmosphere. The mixtures were then mechanical alloyed for 3 h on a shake mill. The resulted powders were pressed to pellets, sealed in silica tubes. The detailed sintering process are the same as described in [7].

The XRD patterns of Sm0.85Nd0.15FeAsO0.85F0.15 MA-samples, sintered at 1433K, 1253K, 1193K, 1073K, and 973K from 20 min to 40 h, are shown in Fig. 1. Nearly phase-pure samples were obtained at 1193K and 1253K except minute impurities of oxyfluoride, which were usually observed in the F-doped samples [1, 2, 11-13]. Their diffraction peaks can be fully indexed by the ZrCuSiAs structure type with the space group of P4/nmm. The higher temperature (1433 K) sintered samples contained a small amount of SmOF, SmAs and Fe2As impurities (marked by Δ, * and □, respectively), and the amount of SmAs increased at longer sintering time. The impurities of the arsenide and oxides might result from the phase
separation due to fluorine loss, which is more severe at 1433K. Low sintering temperatures of 1193/1253K are thus preferred, which allowed relatively phase pure samples to be reproducibly obtained for sintering time from 20 min up to 40h. XRD patterns in Fig. 1b show that almost pure tetragonal phase of SmFeAsO was obtained for the 1073K-sintered samples except minor SmOF. Rather pure tetragonal phase is also evidently prepared at 973K with minor amounts of SmAs appeared in the 973K-2h sample, and the impure phase decreased with increasing sintering time. For comparison, the sample sintered at 1273K for 2 h but from un-milled coarse powders shows more SmAs impurities.

Tab. 1 summarizes material properties of samples prepared at different conditions. Samples sintered for 40 h at 1433K, 1253K and 1193K have similar \( T_c \), around 51K and narrow transition widths (Fig. 2a). It is found that 1253K, which lies slightly above the melting point of Fe\(_2\)As (1213K) [14], is especially favorable, since samples sintered at this temperature for different times — from 20 min to 40 h — show only slight variation of \( T_c \), from 51.4K to 50.3K. For comparison, samples sintered at the same temperature using un-milled powders showed lower \( T_c \) with larger variation (46.9K to 49.8K, Tab. 1). For sintering temperature of 1073K, \( T_{\text{onset}} \) = 50.2K and \( T_{\text{zero}} \) = 21.3K were observed for sample 1073K-2h. With increasing of sintering time up to 40 h, \( T_{\text{onset}} \) monotonically increased to 52.5K and \( T_{\text{zero}} \) increased to 39.3K. Since fluorine loss at such low sintering temperature can be ignored, thus the enhancement of \( T_c \) is due to the improved fluorine diffusion and better crystallization. With sintering condition of 973K-2h, \( T_{\text{onset}} \) was observed at 39.6K but no zero resistance was found until 5K. Increasing the sintering time to 40h, \( T_{\text{onset}} \) increased to 48.3K and zero resistivity was observed at 14.3K. The effect of sintering time is obviously due to improved grain linkage.

Tab. 1. Superconducting properties of Sm\(_{0.85}\)Nd\(_{0.15}\)FeAsO\(_{0.85}\)F\(_{0.15}\) sintered at different conditions: critical temperature \( T_c \), upper critical field \( H_{c2} \), slope of temperature dependence of critical field \( dH/dT \) near \( T_c \) using the criteria of \( \rho_{90\%} \), normal state resistivity \( \rho_{300K} \), normal-state residual resistivity ratio \( RRR = \rho_{300K}/\rho_{55K} \).

<table>
<thead>
<tr>
<th>Sample</th>
<th>( T_c ) (K)</th>
<th>( -dH_{90%}/dT ) (T/K)</th>
<th>( H_{c2} ) (T)</th>
<th>( \rho_{300K} ) (m( \Omega )-cm)</th>
<th>RRR</th>
</tr>
</thead>
<tbody>
<tr>
<td>1193K-40h</td>
<td>50.1</td>
<td>10.8</td>
<td>375</td>
<td>4.71</td>
<td>4.0</td>
</tr>
<tr>
<td>1253K-20min</td>
<td>51.4</td>
<td>10.2</td>
<td>363</td>
<td>2.44</td>
<td>3.8</td>
</tr>
<tr>
<td>1253K-2h</td>
<td>51.3</td>
<td>10.6</td>
<td>377</td>
<td>2.66</td>
<td>4.1</td>
</tr>
<tr>
<td>1253K-40h</td>
<td>50.3</td>
<td>10.3</td>
<td>359</td>
<td>1.05</td>
<td>4.1</td>
</tr>
<tr>
<td>1433K-20min</td>
<td>49.0</td>
<td>8.7</td>
<td>295</td>
<td>2.90</td>
<td>3.6</td>
</tr>
<tr>
<td>1433K-2h</td>
<td>50.1</td>
<td>8.0</td>
<td>278</td>
<td>4.53</td>
<td>3.5</td>
</tr>
<tr>
<td>1433K-40h</td>
<td>50.4</td>
<td>7.7</td>
<td>272</td>
<td>0.47</td>
<td>3.8</td>
</tr>
<tr>
<td>1073K-2h</td>
<td>50.2</td>
<td>N/A</td>
<td>N/A</td>
<td>9.0</td>
<td>3.1</td>
</tr>
<tr>
<td>1073K-40h</td>
<td>52.5</td>
<td>12.1</td>
<td>440</td>
<td>4.8</td>
<td>4.4</td>
</tr>
<tr>
<td>973K-2h</td>
<td>39.6</td>
<td>N/A</td>
<td>N/A</td>
<td>12.5</td>
<td>1.2</td>
</tr>
<tr>
<td>973K-40h</td>
<td>48.3</td>
<td>N/A</td>
<td>N/A</td>
<td>11.1</td>
<td>2.4</td>
</tr>
<tr>
<td>1253K-2h*</td>
<td>46.9</td>
<td>7.1</td>
<td>215</td>
<td>5.55</td>
<td>3.1</td>
</tr>
<tr>
<td>1253K-40h*</td>
<td>49.8</td>
<td>6.6</td>
<td>228</td>
<td>0.83</td>
<td>3.6</td>
</tr>
</tbody>
</table>

*, samples sintered from unmilled coarse powders.

The normal state resistivity at 300K (\( \rho_{300K} \)) drops from 4.71 m\( \Omega \)-cm for the 1193K-40h sample to 1.05 m\( \Omega \)-cm for the 1253K-40h sample, as shown in Fig. 2(a) and Tab. 1. However, despite the substantial drop of the normal state resistivity, the residual resistivity ratio (\( RRR = \rho_{300K}/\rho_{55K} \)) in the normal state remains around 4.1 for both samples. Further increasing the sintering temperature to 1433K decreases the
$\rho_{300K}$ to 0.47 m$\Omega$-cm. Therefore, sintering conditions have a strong and uniform effect on the normal state resistivity over a wide range of temperatures, likely by affecting the connectivity of the conducting paths related to grains and grain boundaries.

![Fig. 2.](image) 

**Fig. 2.** (a) Temperature dependent resistivity of Sm$_{0.85}$Nd$_{0.15}$FeAsO$_{0.85}$F$_{0.15}$ samples sintered for 40 hours at different temperature from mechanical alloyed powders. (b) Temperature dependent resistivity of Sm$_{0.85}$Nd$_{0.15}$FeAsO$_{0.85}$F$_{0.15}$ sample sintered at 1253K/40h under different magnetic field. The inset shows the $H_{c2}$ vs. $T_c$ curve.

The critical fields $H_{c2}$ were determined from the temperature dependant resistivity at different magnetic fields (Fig. 2(b)) according to the WHH formula [8] and the common standard $\rho_{90\%}$. The results, listed in [Tab. 1](#), indicate that all the MA-samples annealed at lower temperatures (1193K, 1253K) had very high $H_{c2}$. The highest value of 377 T was obtained in the sample sintered at 1253K/2h, which is much higher than those prepared by conventional solid state reaction [12,15], also higher than those prepared by high pressure reactions [11]. With sintering temperature of 1253K, increasing the sintering time did not lead to an obvious variation of $H_{c2}$. On the other hand, when the sintering temperature was raised to 1433K, $H_{c2}$ quickly dropped to 295 T after 20 min and to further lower values of 272T at longer time of 40h. For comparison, the samples prepared from *un-milled* powders had lower values of $H_{c2}$ (~220T), when sintered at 1253K for either 2 h or 40 h.

### 3. Microwave synthesis

To further increase the synthesis efficiency, we propose here a microwave sintering process. Mechanical alloyed powders of SmFeAsO$_{0.85}$F$_{0.15}$ were sealed in an evacuated silica tube. The tube was then wrapped by microwave transparent porous refractory ceramics in order to reduce thermal radiation loss. The whole assembly was put into a household microwave oven (Galanz P70D20TLK-D4) for reaction sintering for 2-10 min. Two experimental configurations were used as illustrated in [Fig. 3a](#), one is directly microwave sintering and the other is similar but with a SiC ceramic board placed underneath the silica tube as a heater due to its high microwave absorption ability.

[Fig. 3b](#) shows the XRD patterns of the typical samples. After mechanical alloying for 6 h, the mixture was transformed mostly into amorphous state with only very weak and much broadened peaks from SmAs (\*) and SmOF (\%). The alloyed mixtures were pressed into pellets and microwave cooked for different times at 700W. During the microwaves sintering, the sample flashed purple glow at the very beginning, quickly turned to red, lasted for up to 4-5 minutes and then dimmed, indicating different microwave absorptions at different reaction stages. At 2 min sintering time, tetragonal SmFeAsO phase formed as the major phase with small amount of SmAs and SmOF remained as minor impurities. The SmAs impurity can be largely reduced by extending the sintering time to 5 min. Longer reaction time up to 10 min was investigated but showing no further improvement in phase purity. Apparently, the microwave coupling efficiency dropped significant when the tetragonal SmFeAsO phase was formed, consistent with the observation of sample color variation during the sintering process. Comparisons were
made by microwave sintering of un-milled samples, no obvious microwave absorption was observed, the powders remained un-reacted after sintering for 5 min. It is thus evident that mechanical alloying, which produced severe lattice deformation, is one of the key factors contributing to the success of microwave sintering.

Fig. 3. (a) The schematic of the thermal insulation container with the SiC-assisted ceramic board. (b) XRD patterns of the microwave-sintered SmFeAsO$_{0.85}$F$_{0.15}$ samples. The impurities of SmAs and SmOF are indicated by * and ¨, respectively.

Normalized temperature dependant resistivity ($\rho/\rho_{300K}$) of the samples, reacted at 700 W for different times were shown in Fig. 4a. Rather high $T_c^{\text{onset}}$ of 51.5K was observed for 2 min sintering, but $T_c^{\text{zero}}$ was only 20K showing rather broad residual resistance tail. At longer sintering time of 5 min, the $T_c^{\text{onset}}$ slightly decreased to 50.4K, while $T_c^{\text{zero}}$ moved upwards to ~ 30K accompanied by gradually decrease in the residual resistance. However, no obviously difference was observed in the resistivity curve when the sintering time was further increased to 10 min due to significantly drop in microwave coupling, consistent with the observed color change during sintering and the results of XRD analysis.

Fig. 4. Temperature dependant resistivity for SmFeAsO$_{0.85}$F$_{0.15}$ samples: (a) directly sintered at 700 W for different time or (b) with the SiC assistance.

The tail-like behavior of resistivity curve in Fig. 4a is apparently due to weak link at the grain boundaries. To improve the grain boundary linkage, a piece of SiC board was placed underneath the silica tube. Due to the high microwave absorption, the board will act as a heat reservoir, offering longer sintering time. With the SiC board present, the $T_c^{\text{onset}}$ decreased to 46.1K for 2 min at 700 W, and further decreased to 45.2K and 41.8K when sintering time was increased to 5 and 10 min, respectively. However, the grain linkage was much improved as indicated clearly by the disappeared resistance tail. The improved grain linkage can also be seen from the room temperature resistivity values. While the normal state resistivity $\rho_{300K}$ of a typical sample (5min) directly microwave reacted was about 8.2 m$\Omega$·cm, sample prepared with a SiC heater show a much lower value of 2.3 m$\Omega$·cm (5min-SiC). The drop of $T_c^{\text{onset}}$ is most likely resulted from the fluorine sublimation under vacuum at rather high temperature. The effect of
SiC heat reservoir is also evidenced by the significantly reduced impurity of SmAs when reacted at 700W for 2 min. The SmAs impurity diminished completely for 5 min reaction.

The preliminary results of microwave sintering with domestic microwave cooker are very promising. By using more advanced microwave sintering equipment, such as those with higher and controllable microwave power density, adjustable microwave frequency and proper absorption materials, SmFeAsO-based superconductors with better quality can be expected with synthesis time in the range of minutes rather than hours or tens of hours.

4. Summary

In summary, by using meta-stable LnAs, FeO, Fe2As starting materials, and mechanical alloying, the kinetics of reaction can be greatly improved. As a result, SmFeAsO-based superconductors were successfully synthesized at lower temperatures and in shorter times. Synthesis of high purity samples was achieved at 1253K with a typical sintering time of 20min to 40 h. The sintering time can be lowered to as low as 973K although poor grain linkage reduced greatly the zero resistance of the sample. In order to further shorten the synthesis time, microwave sintering was applied. It was observed that the highly deformed powders prepared by mechanical alloying show high microwave absorption. As a result, synthesis time for SmFeAsO-based superconductors can be reduced to 2-5 minutes. To overcome the difficulties of reduced microwave absorption during microwave sintering, the SiC board which has high microwave absorption was introduced as a heat reservoir, which improved significantly the grain boundary linkage.

All the samples prepared by the high efficient method show high Tc around 50K and high critical field, which made it very attractive for applications. The high Hc2 may be understood by the small grains containing many nano-sized crystal defects induced by the mechanical alloying.

Acknowledgement

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Reference