Processing and Characterization of Bulk FeSe

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Abstract: We investigated the effect of processing conditions on the structure and physical properties of the polycrystalline samples of $\text{Ca}_{0.8}\text{Fe}_2\text{Se}_2$ prepared via solid state reaction. X-ray diffraction showed that the main phase became FeSe when the sintering temperature increased above 350 °C. The temperature dependence of magnetization (M - T curves) recorded in zero-field-cooled mode by SQUID magnetometer showed some bumps at around 120 K to 140 K. These bumps moved to lower temperatures when the processing temperature increased above 550 °C. On the other hand, pure FeSe materials produced at 900 °C for 24 h showed a sharp superconducting transition $T_{c,\text{onset}} = 8.16$ K and the critical current density of 6,252 A/cm² at 5 K, self-field. SEM results indicated an enhanced grain connectivity.

Key words: $\text{Ca}_{0.8}\text{Fe}_2\text{Se}_2$, FeSe, X-ray diffraction, magnetization measurements, SEM, EDX analysis.

1. Introduction

The discovery of superconductivity in Fe-based quaternary oxypnictide $\text{LaFeAsF}_x\text{O}_{1-x}$ with the transition temperature $T_c \approx 26$ K [1] has motivated researchers in the endeavor to improve performance of this compound for practical applications. The substitution of La by smaller RE (rare earth) elements led to up to now the highest transition temperature in this class of compounds, $T_c \approx 56$ K [2, 3]. Researchers have until now identified eleven systems of pnictides. Among them, the greatest interest has been devoted to FeSe, $\text{FeTe}_{1-x}\text{Se}_x$, and $\text{FeTe}_{1-x}\text{S}_x$, due to their simple crystal structure and absence of the toxic As [4]. The onset T_c of 15 K was found in $\text{FeSe}_{0.5}\text{Te}_{0.5}$ [5-7], while in the bulk $\text{K}_{0.8}\text{Fe}_2\text{Se}_2$ T_c was 31 K and in the single crystal of $\text{Cs}_{0.8}\text{Fe}_2\text{Se}_2$ T_c reached 27.4 K [8]. Note that besides the very promising values of the upper critical field, comparable to those of the cuprate RE-123 superconductors, the iron-pnictide materials offer several advantages in the preparation as compared to the cuprate high- T_c superconductors: no oxygenation

process is required, “clean” chemistry can be used to obtain large and homogeneous samples. There is no twinning complicating interpretation of the magnetization data [9, 10]. This makes the pnictides very interesting for applications, where large and homogenous samples are needed. Among the As-free pnictide superconductors the recently reported $\text{X}_y\text{Fe}_2\text{Se}_2$ ones, with $X = \text{Yb}, \text{Li}, \text{Ca}, \text{Na}, \text{Eu}, \text{Ba}$ etc., belong to the most promising materials. The system offers high T_c and H_{c2} values and a simple chemistry [11]. E.g., in the CaFeSe system, T_c as high as 40 K was reported. For applications, a material with high super-currents and a reproducible performance is required. In order to improve the critical current density of this material, we studied the processing conditions.

In the present work, high quality polycrystalline samples of $\text{Ca}_{0.8}\text{Fe}_2\text{Se}_2$ were prepared and the effect of Ca addition on microstructure, and magnetic performance was investigated. There is a large difference between the melting point of Fe and Se. We prepared the first batch of the $\text{Ca}_{0.8}\text{Fe}_2\text{Se}_2$ samples at various, rather low sintering temperatures. Eventually, the same material was produced at a high temperature.

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For comparison, pure FeSe material was produced by utilizing the 6 h ball milled powders processed at 900 °C for 24 h. All samples were measured by the *M-T* measurements. Further, SEM (scanning electron microscopy) and SEM by EDX (energy dispersive X-ray) analyses were performed.

2. Experimental

The $\text{Ca}_{0.8}\text{Fe}_2\text{Se}_2$ material was produced from the commercial powders of Fe (99.9% purity), Se (99.5 % purity) and CaO (99% purity). The powders were mixed in a nominal ratio $\text{Ca:Fe:Se} = 0.8:2:2$ in a glove box and thoroughly ground there in argon atmosphere. The powder mixture was then pressed into pellets 5 mm in diameter and 2 mm thick using a uniaxial pressure of 200 MPa. The consolidated pellets were wrapped into Nb foil, then sintered in two steps. In the first step, utilizing a quartz tube furnace, the samples were sintered in a high purity Ar gas at 250 °C for 10 hours. Then, the sintered pellets were once more thoroughly ground and mixed in a glove box and again pressed into the pellets similar to the first step. In the second step, the samples were placed in an alumina crucible in a quartz tube furnace and there kept in a high purity argon atmosphere for 10 h at different sintering temperatures from 250 °C to 550 °C with increment of 50 °C. Eventually, the furnace was cooled to room temperature. Some of the samples were sealed in quartz tubes and sintered at high temperatures at 700 °C for 10 h, and at 900 °C for 15 h. Finally, the temperature was lowered to room temperature at a cooling rate of 50 °C/h. For the pure FeSe material was produced.

The constituent phases of the samples were identified with a high-resolution automated X-ray powder diffractometer (RINT2200), using $\text{Cu-K}\alpha$ radiation generated at 40 kV and 40 mA. Small specimens with dimensions of $1 \times 1 \times 0.5 \text{ mm}^3$ were cut from the bulk FeCaSe pellets and subjected to the measurements of magnetization vs. temperature, using a SQUID magnetometer (Quantum Design, model

MPMS5) in the temperature range 5 K to 300 K. The microstructure of the samples sintered at high temperatures was studied using the SEM and the chemical composition of various phases was analyzed by EDX spectroscopy.

3. Results and Discussion

Fig. 1 presents the X-ray diffraction patterns of the $\text{Ca}_{0.8}\text{Fe}_2\text{Se}_2$ compounds produced at different low temperatures. In the samples sintered below 350 °C the dominant phases were FeSe, $\text{Ca}_4\text{Fe}_9\text{O}_{17}$ and SeO_2 . With increasing temperature the peak of SeO_2 disappeared and the main phase became $\beta\text{-FeSe}$, with a small minority of $\text{Ca}_4\text{Fe}_9\text{O}_{17}$. X-ray diffraction indicated that FeSe samples were polycrystalline, similar to the earlier reports [1, 12]. The main $\text{Ca}_4\text{Fe}_9\text{O}_{17}$ peak decreased with increasing temperature, indicating that Ca could enter the Fe sublattice site of FeSe. More details will be discussed further.

The temperature dependence of the dc magnetization curves of $\text{Ca}_{0.8}\text{Fe}_2\text{Se}_2$ recorded in ZFC (zero-field-cooled) mode showed a significant bump at 133 K to 135 K. This high temperature bump shifted to lower temperatures with the sintering temperature increasing above 500 °C, and reached 123 K for the sintering temperature of 750 °C (see Fig. 2). Similar bumps were observed by Yoshikazu et al. in

Fig. 1 X-ray diffraction patterns of $\text{Ca}_{0.8}\text{Fe}_2\text{Se}_2$ material.

the FeSe material under high pressure at around 50 and 200 K, and attributed them to the structural phase transition and the magnetic transition, respectively [13]. According to Li et al. [14], a similar anomaly near 125 K was observed also in sintered bulk $\text{FeSeCr}_{0.05}$ materials in magnetization versus temperature dependence near 125 K, in both the zero-field-cooled and field cooled (20 Oe) modes.

The micro structure and chemical composition of the newly prepared $\text{Ca}_{0.8}\text{Fe}_2\text{Se}_2$ material were studied by means of SEM and SEM by EDX analyses.

The morphology and chemical composition of $\text{Ca}_{0.8}\text{Fe}_2\text{Se}_2$ samples sintered at high temperatures, 750 °C and 900 °C, were carried out utilizing the SEM, SEM by EDX analyses. The typical scanning electron micrographs for the polished sample surface of as grown $\text{Ca}_{0.8}\text{Fe}_2\text{Se}_2$ material treated for 10 hours at

750 °C were depicted in Fig. 3. According to the SEM images and element mapping, the sample contained only a few distinct structures distinguished by 3 colors, black, gray and white (see Fig. 3). However, the SEM by EDX analysis showed many structures (Table 1, see spectra A to I). It indicated that we have not yet reached a homogenous FeSe or FeSeCa compound (see Table 1). On the sample sintered for 15 h at 900 °C the SEM micrographs are similar to those of the samples sintered at 750 °C (see Fig. 4). Further, the elemental mapping exhibits only a few structures containing mainly iron, selenium and calcium (Table 2, spectra a-e).

Note that in the samples sintered for 15 hours at high temperature, around 900 °C, the major phase was FeSe (see Table 2). Based on the experience with FeSe materials produced by low and high temperature

Fig. 2 Magnetization versus temperature curves for the $\text{Ca}_{0.8}\text{Fe}_2\text{Se}_2$ samples sintered in argon atmosphere at 250 °C, 350 °C, 450 °C, and 750 °C for 10 hours.

Fig. 3 The SEM images of the $\text{Ca}_{0.8}\text{Fe}_2\text{Se}_2$ samples sintered for 10 h at 750 °C.

sintering, one can expect that the high-temperature processing is crucial for growing good quality FeSe material with high density. Until now, several researchers have tried to produce the FeSe material at

around 750 °C. However, they found rather low critical current densities, in the range of 10^3 A/cm^2 at 5 K, the samples becoming normal even at external magnetic field around 0.4 T [15]. In the attempt to improve properties of these materials, we mixed the commercial powders of Fe (99.9% purity) and Se (99.9% purity) in the nominal ratio Fe:Se = 1:1, thoroughly ground and ball-milled them in glove box for 6 h. The powder mixture was pressed into pellets of 5 mm in diameter and 2 mm thickness using a uniaxial pressure of 200 MPa. The samples were sealed in quartz tubes and sintered at 600 °C for 24 h. Then, the pellets were again thoroughly ground and ball-milled in a glove box and pressed into pellets and eventually final sintering was performed at 900 °C for 24 h. The phase purity and the superconducting performance were characterized by x-ray diffractometer and SQUID, respectively.

The phase composition of the final bulk FeSe material sintered at 900 °C for 24 h is shown in Fig. 5 (top). For comparison, we also show the structure of the $\text{Ca}_{0.8}\text{Fe}_2\text{Se}_2$ sample sintered at 750 °C for 10 h. The FeSe material sintered at 900 °C for 24 h showed mainly the $\beta\text{-FeSe}$ phase with tetragonal structure (Fig. 5, top) with a minor amount of impurity of the $\text{Ca}_{0.8}\text{Fe}_2\text{Se}_2$ sample contains several phases and only isolated FeSe islands as indicated by SEM by EDX analysis (see Table 1). The X-ray diffraction proved that with an optimum sintering process combined with ball-milling FeSe phase formation appears also in the $\text{Ca}_{0.8}\text{Fe}_2\text{Se}_2$ samples.

Table 1 The SEM by EDX analysis of $\text{Ca}_{0.8}\text{Fe}_2\text{Se}_2$ sample sintered 10 h at 750 °C.

	Fe (%)	Se (%)	Ca (%)	O (%)	Others	Color
(A)	0.1	0.1	21.9	55.1	22.9	Black
(B)	1.2	47.9	47.7	0	3.3	White
(C)	94.2	0.2	0.7	0	4.9	Gray
(D)	41.1	44.2	1	11.9	1.8	White
(E)	46.9	51.8	0	0	1.3	White
(F)	1.9	44.6	43.2	7.8	2.4	White
(G)	96.2	0.2	0.8	0	2.8	Gray
(H)	1.3	30.4	23.9	40.9	3.5	Gray
(I)	71.6	3.3	5.1	15.5	4.5	Gray

Table 2 The SEM by EDX analysis of $\text{Ca}_{0.8}\text{Fe}_2\text{Se}_2$ sample sintered 15 h at 900 °C.

	Fe (%)	Se (%)	Ca (%)	O (%)	Color
(a)	46.9	51.8	0	0	White
(b)	1.9	44.6	43.2	7.8	White
(c)	96.2	0.2	0.8	0	Gray
(d)	1.3	30.4	23.9	40.9	Black
(e)	71.6	3.3	5.1	15.5	Gray

Fig. 4 The SEM images of $\text{Ca}_{0.8}\text{Fe}_2\text{Se}_2$ samples sintered for 15 h at 900 °C. **Fig. 5** X-ray diffraction spectra of bulk FeSe sample sintered at 900 °C for 24 h (top) and 750 °C for 15 h (bottom).

Fig. 6 (left) shows the temperature dependence of the magnetic susceptibility of FeSe sample sintered at

900 °C for 24 h. The superconducting transition temperature was 8.16 K. No high temperature bumps were observed. The M-H loop was measured at 5 K on the same sample and the critical current density was estimated from it using Bean model (Fig. 6, right). The critical current densities (J_c) recorded at 5 K at self-field and 2 T were 6,253 A/cm² and 2,597 A/cm², respectively. The present J_c and H_{irr} values are clearly improved as compared to the bulk FeSe materials previously produced by the sintering process [15, 16]. Further, the low field J_c values were also good as compared to the recently reported FeSe wire prepared by diffusion process [16]. The critical current densities of 350 A/cm² and 1,027 A/cm² were reported for FeSe tapes and several-core FeSe wires with Fe tapes, respectively [17].

The improved J_c results can originate from a better grain connectivity due to the higher sintering temperature used in the present synthesis process. The results indicate a possibility to further improve the process by a synthesis at high temperatures. To obtain more information on the FeSe material composition, we studied the microstructure and chemical composition by SEM and SEM-EDX analyses (Fig. 7).

Fig. 7 shows the scanning electron micrograph images of the polished surface of the FeSe material sintered at 900 °C for 24 h. On the top figure, a high density of FeSe grains can be seen. The SEM-EDX analysis clarified that all white grains were of FeSe. The average grain size of 1-3 micrometers, similar to earlier reports [15], was observed. In a higher magnification (the bottom figure) one can see also small grains of some secondary impurity phases at grain boundaries, marked by black arrows.

Fig. 6 Temperature dependence of DC magnetic susceptibility for FeSe samples produced by sintering at 900 °C for 24 hours and ball milling time 6 h (left) and the field dependence of the critical current density (right) for the same material at 5 K.

Fig. 7 The SEM images of FeSe samples produced by a sintering at 900 °C for 24 hours and ball milling time 6 h.

We expect that further improvement in J_c in the bulk FeSe material can be realized by a further improving the grain boundary connection without impurities. The present results indicate that the optimization of high temperature sintering is crucial for improving the bulk FeSe performance, which can be very useful for the development of superconducting super-magnet applications.

4. Summary

In summary, we fabricated bulk polycrystalline $\text{Ca}_{0.8}\text{Fe}_2\text{Se}_2$ via solid state reaction at different low and high temperatures. X-ray diffraction results clarified that at temperature above 350 °C the major phase was FeSe. Magnetization vs. temperature measurements showed a bump at temperatures between 133 K and 135 K, which for very high sintering temperatures shifted downwards, up to 125 K. Further, bulk FeSe pellets were produced utilizing ball-milled powders sintered at 900 °C for 24 hours. These samples showed a sharp superconducting transition at around 8.16 K and J_c value of 6,253 A/cm² at 5 K in self field. The SEM analysis indicated a dense structure of grains of about 2 μm in size, SEM by EDX analysis proved that the grains are mostly of FeSe. A further optimization of the sintering process is still needed to obtain good quality superconducting FeSe that could be utilized as a rare-earth-free superconducting

super-magnet in industrial applications, e.g. in medicine.

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