Low-temperature synthesis of FeTe$_{0.5}$Se$_{0.5}$ polycrystals with a high transport critical current density

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Abstract
We have prepared high-quality polycrystalline FeTe$_{0.5}$Se$_{0.5}$ at temperature as low as 550°C. The transport critical current density evaluated from the current–voltage characteristics is over 700 A cm$^{-2}$ at 4.2 K under zero field, which is several times larger than that for FeTe$_{0.5}$Se$_{0.5}$ superconducting wires. The critical current density estimated from magneto-optical images of flux penetration is also similar to this value. The upper critical field of the polycrystalline FeTe$_{0.5}$Se$_{0.5}$ at $T = 0$ K estimated using Werthamer–Helfand–Hohenberg theory is 585 kOe, which is comparable to that of single crystals. This study gives some insight into how to improve the performance of FeTe$_{0.5}$Se$_{0.5}$ superconducting wires.

With motivation from the discovery of superconductivity in oxypnictide LaFeAsO$_{1-x}$F$_x$ with a critical temperature $T_c \sim 26$ K, a series of iron-based superconductors have been synthesized in a short time [1–8]. Among these compounds, FeSe and FeTe$_{1-x}$Se$_x$ (the 11 system) have attracted great attention because of the planar crystal structure being simpler than that of layered iron pnictides. Therefore, they are better candidates for use in investigating the underlying mechanism of superconductivity in the iron-based system. The lower toxicity and sensitivity to the atmosphere of the starting materials also make the 11 system more promising compared with iron pnictide superconductors. Although the transition temperature, $T_c$, is not very high in this 11 system, it can be enhanced to as high as 37 K by applying pressure [9, 10]. Recently, by introducing alkali metal K (Cs, Rb) into this 11 system to form a ternary compound, $T_c$ increased to 30 K [11–13]. In addition to the very simple crystal structure, just as in iron pnictide superconductors, the very high values of upper critical field make this system a potential candidate for practical applications [14–18]. Also the critical current densities, $J_c$, of high-quality single crystals are reported to be over $1 \times 10^5$ A cm$^{-2}$ [18–20]. Superconducting wires made from FeTe$_{0.5}$Se$_{0.5}$ have been reported, but the transport critical current density is restricted to $\sim 230$ A cm$^{-2}$ at 4.2 K even under zero field [21–23]. Polycrystalline samples of iron-based superconductors in general have the problem of weak links. In order to improve the performance of FeTe$_{1-x}$Se$_x$ wires, it is essential to investigate the performance of FeTe$_{1-x}$Se$_x$ polycrystals and how to reduce the weak-link features. We have reported on FeTe$_{1-x}$Se$_x$ polycrystals prepared at higher temperatures, 600–680°C, with less impurities [24]. Since the grain sizes of samples prepared at higher temperatures are too large, weak links between grains are particularly obvious. Here we report the low-temperature synthesis and characterization of a high-quality FeTe$_{1-x}$Se$_x$ polycrystalline sample. The characterizations through x-ray diffraction, magnetization, resistivity, transport critical current density, and magneto-optical measurements are discussed.

FeTe$_{0.5}$Se$_{0.5}$ polycrystalline samples were synthesized by the solid-state reaction method. Stoichiometric amounts of Fe powder (Kojundo Chemical Laboratory, 99.9%), Te grains (the same as above, 99.9999%), and Se grains (the same as above, 99.9%) were weighed, mixed and ground with an agate mortar and pestle. The mixing and grinding processes were carried out in a nitrogen-filled glove box. The ground powder was cold-pressed into pellets with 600 kg cm$^{-2}$ uniaxial pressure.
The pellets were sealed in an evacuated quartz tube, and slowly ramped to 550 °C in 5 h from room temperature, and kept there for 24 h. After cooling to room temperature naturally, the reacted pellets were reground, pressed (1800 kg cm\(^{-2}\) uniaxial pressure), sealed in a quartz tube, sintered again at 550 °C for 24 h, and finally annealed at 400 °C for 24 h, and this was followed by quenching. When the sintering temperature is lower than 500 °C and higher than 400 °C, although the 11 phase can be formed, there are more impurities, and the superconducting volume fraction is very small.

The phase identification of the sample was carried out by means of powder x-ray diffraction (M18XHF, MAC Science) with Cu Kα radiation generated at 40 kV and 200 mA. The bulk magnetization is measured by a superconducting quantum interference device (SQUID) magnetometer (MPMS-5XL, Quantum Design). The microstructures were characterized using a scanning electron microscope (SEM, Hitachi S-4300) operated at 15 kV. The resistivity measurements were performed within the sample chamber of a SQUID magnetometer. The I–V measurements were performed using a bath type cryostat (Spectromag, Oxford Instruments). For local magnetic characterization, we applied magneto-optical (MO) imaging. For this purpose, the sample was cut using a wire saw, and the surface was polished with a lapping film. A Bi-substituted iron garnet indicator film is placed in direct contact with the sample, and the whole assembly is attached to the cold finger of a He-flow cryostat (Microstat-HR, Oxford Instruments) and cooled down to 5 K. MO images are acquired by using a cooled CCD camera with 12-bit resolution (ORCA-ER, Hamamatsu). To enhance the visibility of the local magnetic induction and eliminate the signals from the impurity phases, a differential imaging technique is employed [25, 26].

Figure 1(a) shows the x-ray diffraction pattern of the as-prepared polycrystalline sample. All the peaks were well indexed using a space group of P4/ nmm except for the small peaks for an impurity phase marked with asterisks. The compound crystallizes in a tetragonal structure and the impurity phase is identified as hexagonal Fe\(_7\)Se\(_8\). The calculated lattice constants are \(a = 0.3799 \text{ nm}\) and \(c = 0.5980 \text{ nm}\), which are slightly smaller than those for samples prepared at higher temperatures (\(a = 0.3800 \text{ nm}\) and \(c = 0.6011 \text{ nm}\)) and single crystals [19, 27]. Figure 1(b) shows the SEM image of this sample. From this image, we see that the typical grain size is \(\sim 10 \mu m\) or less, although with a broad size distribution. The grains are sheet-like, but the ratio of width (\(w\)) to thickness (\(t\)) may be larger than 10. Although the amount of impurity of this sample is higher than that for samples prepared at the commonly used higher temperatures of 600–680 °C [24], the average grain size has been reduced from 50–100 \(\mu m\) to less than 10 \(\mu m\). Temperature dependences of the zero-field-cooled (ZFC) and field-cooled (FC) magnetization at 5 Oe for the FeTe\(_{1-x}\)Se\(_x\) polycrystalline sample are shown in figure 1(c).

which is due to weak links between grain boundaries and has appeared for many FeTe\(_{1-x}\)Se\(_x\) polycrystalline samples prepared at higher temperatures [22, 24], is suppressed for our present sample. So we think that the reduction of grain size is beneficial to the grain boundaries.

Figure 2(a) shows the temperature dependence of the resistivity of the sample. The room temperature resistivity is 690 \(\mu \Omega\) cm. The resistivity shows semiconducting behaviour above 150 K, and shows metallic behaviour in
Figure 2. (a) Temperature dependence of the resistivity of the FeTe$_{0.5}$Se$_{0.5}$ polycrystalline sample. The inset shows the resistivity around $T_c$. (b) Field dependence of the resistivity of the FeTe$_{0.5}$Se$_{0.5}$ polycrystalline sample around $T_c$. The inset shows the upper critical field $H_{c2}$ versus temperature determined as the mid-point of the resistive transition.

Figure 3. (a) Magnetic field dependence of the magnetization at different temperatures for the FeTe$_{0.5}$Se$_{0.5}$ polycrystalline sample. The inset shows the $M$–$H$ curves at 15 K. (b) Magnetic field dependence of the critical current densities calculated from the data in (a).

the normal state below 150 K. A sharp drop in resistivity was observed at about 14.3 K, which indicates the onset of superconductivity. Zero resistance occurs at 12.5 K and the transition width is 1.8 K. The residual resistivity ratio $\rho(300\, K)/\rho(T_{\text{onset}})$ is 2.06. A similar temperature dependence of the resistivity is reported for samples with compositions close to FeTe$_{0.5}$Se$_{0.5}$ [19, 22, 27–31]. This behaviour has been attributed to weak charge-carrier localization due to a large amount of excess Fe in Fe$_{1+y}$Te$_{1-x}$Se$_x$ system [27]. The value of the resistivity of our polycrystalline sample is larger than that reported in [27], but similar to that reported in [19], and lower than that reported in [22, 28, 29]. The intrinsic microscopic inhomogeneities of the polycrystalline sample and impurity phase may be the reason for this higher value of the resistivity. The variation of $T_c$ with the magnetic field is shown in figure 2(b) for $H = 0, 10, 20, 30, 40$ and 50 kOe. With increasing field, the resistive transition shifts to lower temperatures, and this is accompanied by a slight increase in the transition width. The inset of figure 2(b) shows the variation of the upper critical field $H_{c2}$ with reduced temperature $t = T/T_{\text{onset}}$ for the FeTe$_{0.5}$Se$_{0.5}$ polycrystalline sample. The value of $H_{c2}$ was defined as the field at the mid-point of the resistive transition. The slope of $H_{c2}$ at $T_c$ is $-60.6\, kOe\, K^{-1}$. The value of $H_{c2}$ at $T = 0\, K$ estimated using the Werthamer–Helfand–Hohenberg formula [32], $H_{c2}(0) = -0.69T_c|dH_{c2}/dT|_{T=T_c}$, is 585 kOe. This value is comparable to that for the single crystals [14–18].

In order to extract the superconducting parameters, we have used the Ginzburg–Landau (GL) formula for the coherence length ($\xi$), $\xi = (\Phi_0/2\pi H_{c2})^{1/2}$, where $\Phi_0 = 2.07 \times 10^{-7}\, G\, cm^2$; the coherence length $\xi$ at the zero temperature is calculated as 2.38 nm. It is well known that, for the two-gap superconductivity in the dirty limit, the impurity scattering could strongly enhance the upper critical field $H_{c2}$. This phenomenon has been clearly observed in MgB$_2$, a dirty two-gap superconductor, where the $H_{c2}$ increases remarkably on alloying MgB$_2$ with some impurities [33]. Therefore, the very high $H_{c2}$ value observed for our polycrystals could be reasonably attributed to the strong impurity scattering effect from the impurities in such a new multi-band superconductor.

Figure 3(a) shows magnetic hysteresis curves for this sample. A small amount of Fe$_7$Se$_8$ impurity may be the reason for the ferromagnetic background in the $M$–$H$ curves. Shown in the inset is the $M$–$H$ curve at 15 K, which is higher than $T_c$. Since the curves at 12.5 K (not shown) and 15 K are almost identical, we assumed that this background is temperature independent at low temperatures. In these hysteresis loops, the ratio of superconducting signals to the ferromagnetic background is not as strong as that for the sample prepared at higher temperatures [24]. This is because the magnetization is proportional to the grain sizes if the intragranular critical current density ($J_{\text{intra}}$) is fixed, and the grains prepared at higher temperatures are much larger. From the magnetization hysteresis loops, we can evaluate the intragranular critical
current density $J_{c\text{ intra}}$ for polycrystalline samples using Bean’s model with the assumption of field-independent $J_c$. According to Bean’s model, $J_{c\text{ intra}}$ (A cm$^{-2}$) is given by

$$J_{c\text{ intra}} = \frac{30\Delta M}{d},$$

with the assumption that intergranular critical current is zero, where $\Delta M$ (emu cc$^{-1}$) is $M_{\text{down}} - M_{\text{up}}$, $M_{\text{up}}$, and $M_{\text{down}}$ are the magnetizations when sweeping the field up and down, respectively, and $d$ (cm) is the average diameter of the grains in the polycrystalline sample [34]. The $\Delta M$ used here is obtained after subtracting the ferromagnetic background. Figure 3(b) shows the field dependencies of the $J_c$ obtained for this sample, calculated from the data shown in figure 3(a) using equation (1) and the typical dimension. $J_c$ calculated from the $M–H$ curve is estimated to be $2 \times 10^4$ A cm$^{-2}$ at 5 K under zero field; this value is a little smaller than that for the single crystal [19], but still in the range for applications. $J_c$ values in excess of $5 \times 10^4$ A cm$^{-2}$ are sustained up to 10 kOe.

Figures 4(b)–(e) depict MO images of the FeTe$_{0.5}$Se$_{0.5}$ polycrystalline sample in the remanent state after applying a 500 Oe field for 0.25 s which was subsequently reduced to zero. Figure 4(a) shows the polished surface of the FeTe$_{1-x}$Se$_x$ polycrystalline sample for MO measurements. The sample dimensions are $895 \times 555 \times 200$ μm$^3$. Shown in figures 4(b)–(e) are MO images of the remanent state recorded at several different temperatures. These images are similar to the MO images of 1111 polycrystals [35–37]. In these figures, the bright regions correspond to the trapped flux in the sample. The dots in these images are due to defects in the indicator garnet film. At all temperatures, the field profile is inhomogeneous, which implies that the intergranular current density is much smaller compared with the intragranular current density. The intragranular current density decreases gradually as the temperature is increased towards $T_c$. We calculated the intragranular critical current density from the magnetic induction profile. Figure 4(f) shows the magnetic induction profiles along the dotted line in figure 4(b). In this calculation, we roughly estimate the intragranular critical current densities as $J_c \sim dB/dx$. For typical grains, $J_c$ thus estimated is $\sim 1 \times 10^4$ A cm$^{-2}$ at 5 K. This value is much smaller than that estimated from the $M–H$ curve, as shown in figure 3(b). This is because the formula that we adopted here is based on the condition with infinite thickness of the sample, but from the SEM image, the ratio of width to thickness is very large. So the real $J_c$ should be obtained by multiplying by $w/t$, which is roughly 10.
dislocations located along the boundary [40] or competing the weak-link feature is common in these systems. This symmetry [41]. We investigated the transport orders, low carrier density and unconventional pairing mechanism, the global critical current density $J_c$ should be investigated. For iron-based superconductors, the global $J_c$ values for polycrystalline samples were less than $10^5 \text{ A cm}^{-2}$, and very sensitive to the magnetic field [38, 39]. Namely, the weak-link feature is common in these systems. This has usually been ascribed to the tensile strain generated by dislocations located along the boundary [40] or competing orders, low carrier density and unconventional pairing symmetry [41]. We investigated the transport $J_c$ of the FeTe$_{0.5}$Se$_{0.5}$ polycrystalline sample. The polycrystalline sample dimension for this measurement is $1200 \times 180 \times 75 \mu m^3$, and the distance between the two voltage contacts is $470 \mu m$. In superconductors, the driving force competes with the pinning force. If the former wins over the latter, measurable voltages could be observed. The inset of figure 5(a) shows the zero-field $I$–$V$ characteristics at different temperatures ranging from 4.2 to 10 K. Here we adopt $E = 1 \mu V \text{cm}^{-1}$ as a criterion for the $I$–$V$ curve to define the transport $J_c$. Figure 5(a) shows the temperature dependence of the transport $J_c$ at zero field. At 4.2 K, a transport $J_c$ as high as 724 $\text{A cm}^{-2}$ was observed for the FeTe$_{1-x}$Se$_x$ polycrystalline sample. The transport $J_c$ does not increase as fast below $T_c$. The transport $J_c$ as a function of field at 4.2 K is shown in figure 5(b). Like for YBa$_2$Cu$_3$O$_{7-\delta}$ and other iron-based superconductors, the transport $J_c$ shows a strong field dependence at low fields. For example, $J_c$ (0 Oe) is ten times as large as $J_c$ (0.5 kOe). When the field is more than 0.5 kOe, the field dependence of $J_c$ is not as strong as that in the low-field region. The value of the transport $J_c$ is more than two orders less than the intragranular $J_c$, as shown in figure 3(b) and by that obtained from the magnetic induction profile in figure 4(e). This implies the presence of weak links between superconducting grains. The transport $J_c$ of the FeTe$_{1-x}$Se$_x$ polycrystalline sample is smaller than those for SmFeAsO$_{0.7}$F$_{0.3-\delta}$ wires (1300 $\text{A cm}^{-2}$) [38] and Ag doped Sr$_{0.67}$K$_{0.4}$Fe$_2$As$_2$ wires (3750 $\text{A cm}^{-2}$) [39], but of the same order as that for randomly oriented polycrystalline YBa$_2$Cu$_3$O$_{7-\delta}$ [42], but several times larger than that for FeTe$_{0.5}$Se$_{0.5}$ wires [21–23].

In conclusion, x-ray diffraction, magnetization, resistivity, transport critical current density and magneto-optical measurements were performed on high-quality polycrystalline FeTe$_{0.5}$Se$_{0.5}$ prepared at 550°C compared with the samples prepared at higher temperatures. By using higher static pressure to make denser pellets and increasing the annealing time, or using the high-pressure synthesis method, we can obtain more pure and homogeneous samples with higher transport critical current density. Alternatively, we can utilize the powder-in-tube method to make the sample more dense and well-connected. This is the subject of ongoing research.
polycrystalline FeTe$_{0.5}$Se$_{0.5}$ is 585 kOe, which is comparable to that for single crystals. Our low-temperature synthesis is promising for the development of practical FeTe$_{1-x}$Se$_x$ systems, with potential higher transport critical current density, for applications, especially in superconducting wires.

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