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Direct Microwave Synthesis of 11-Type Fe(Te,Se) Polycrystalline Superconductors with Enhanced Critical Current Density *

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We report a direct microwave synthesis method for the preparation of 11-type high quality Fe(Te,Se) polycrystalline superconductors. The bulk samples are rapidly synthesized under the microwave irradiation during several minutes, with a subsequent annealing process at 400°C. The samples exhibit a nearly single phase of the tetragonal PbO-type crystal structure with minor impurities. Morphology characterization shows high density, tight grain connectivity and large grain sizes around 100 μm with small cavities inside the sample. Resistivity and magnetization measurements both show similar superconducting transitions above 14 K. The magnetic hysteresis measurements display broad and symmetric loops without magnetic background, and a high critical current density J_c about 1.2×10^4 A/cm^2 at 2 K and 7 T is estimated by the Bean model. Compared with the solid-state reaction synthesized samples, these superconducting bulks from microwave-assisted synthesis are possibly free of the interstitial Fe due to smaller c-axis, higher T_c in magnetic transitions, better M–H loops without magnetic background and greatly enhanced J_c, and are promising as raw materials for the non-toxic Fe-based superconducting wires for large currents and high field applications.

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Since the discovery of high-temperature superconductivity in Fe-based pnictides and chalcogenides (FeSCs), extensive efforts have been focused on the search of new materials, research of the superconducting mechanism and development of practical applications.[1−5] The main structural prototypes of these FeSCs include the 1111-type LaFeAsO, the 122-type $BaFe_2As_2$, the 111-type LiFeAs, the 11-type FeSe and several others.[6−12] Due to their intrinsic advantages of high upper critical field H_{c2}, low anisotropy, metallic parent compounds and large critical grain boundary angle and so on, FeSCs have superior potentials for high field applications of superconducting wires and tapes with large critical current density J_c.[13−16] Among them, 122-type superconductors can be easily synthesized by the convenient powder-in-tube (PIT) method, and a practical transport $J_c \sim 10^5$ A/cm^2 at 10 T and 4.2 K has been successfully obtained in $Sr_{0.6}K_{0.4}Fe_2As_2$ tapes, a 100-m-class superconducting wire was also achieved.[17−19] However, the toxic arsenic and active alkali elements in these 122-type superconductors are still difficult to process for practical applications.

The 11-type Fe(Te,Se) has also attracted a great deal of attention due to its non-toxic chemical composition without arsenic and simple crystal structure in FeSCs, its superconducting T_c is about 15 K in bulks and near 20 K in thin films with the H_{c2} above 50 T, and the monolayer FeSe thin film on $SrTiO_3$ even shows the highest T_c above 65 K.[16,20−25] However, due to the very delicate chemical stoichiometry when forming the 11-type superconducting phase, the Fe(Te,Se) bulks prepared by the solid-state reaction method always exhibit poor superconducting properties, which are generally believed to be caused by the severe magnetic pair-breaking effect from the inevitable interstitial Fe atoms near the chalcogen planes. This leads to very low J_c about 10^2 A/cm^2 in the fabricated Fe(Te,Se) superconducting wires.[26−30] Meanwhile, the epitaxially grown $FeSe_{0.5}Te_{0.5}$ thin film with a CeO_2 buffer layer exhibits a superior high field performance with J_c exceeding 10^5 A/cm^2 under the magnetic field of 30 T at 4.2 K, which are much higher than the conventional superconductors currently in use.[25,31] To solve the interstitial Fe problems in Fe(Te,Se) bulks, post-annealing processes by oxygen (or iodine etc.) have been developed on high quality single crystals of thin slices, which could expel the excess interstitial Fe atoms out of the single crystal and thus significantly enhance J_c to around 10^5 A/cm^2 in self-field at 2 K.[32−35] However, this annealing process is not applicable for polycrystalline bulks that can be used to fabricate Fe(Te,Se) superconducting wires, which still requires new synthesizing approaches to be

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developed.

Microwave synthesis has been widely used in chemical reactions for the acceleration of reaction rate, rapid processing, selective reactions, direct and volumetric heating with energy saving, and the nonthermal effects from a focused electromagnetic field often yield highly dense products.[36–38] Here, we report a direct microwave synthesis method for the preparation of 11-type Fe(Te,Se) polycrystalline superconductors within very short reaction duration of several minutes. We are able to obtain high quality polycrystalline bulks with much higher critical current density comparing with the samples from the solid-state reaction method.

The polycrystalline $FeTe_{0.6}Se_{0.4}$ bulk samples were synthesized by the direct microwave synthesis method and the common solid-state reaction method separately for comparison. The raw materials of Fe powders (99.99%, Alfa Aesar), Te powders (99.999%, Alfa Aesar) and Se powders (99.999%, Alfa Aesar) with stoichiometric ratio as $FeTe_{0.6}Se_{0.4}$ were mixed and thoroughly ground in an agate mortar, and then pressed into cylinder pellets of 0.5 g each in weight and 8 mm in diameter under 400 MPa uniaxial pressures. All of the preparation processes were carried out in an argon-filled glove box (the content of water and oxygen is below 0.5 ppm). The pellets were subsequently sealed into the evacuated quartz-glass ampoules ($\sim 10^{-3}$ Pa). The pellets were then divided into two groups for synthesis by the direct microwave synthesis method or the solid-state reaction method, respectively. For the direct microwave synthesis, the sealed ampoules were placed at the center of a microwave oven (EM-310BX, Sanyo), then the microwave irradiation was carried out at the electric power level of 1000 W with a frequency of 2.45 GHz for 2–5 min. Under direct microwave irradiation, the samples reacted dramatically and emitted blue light during the exothermic reaction; however, the temperature of the sample cannot be measured directly. The obtained ampoules were annealed at 400℃ for 40 h subsequently to obtain more homogeneous samples. As a comparison, the other batch of samples were synthesized by the common solid-state reaction method by heating at 680℃ for 40 h twice with intermediate grinding in a muffle furnace, and then annealed at 400℃ for 40 h. Hereinafter, the synthesized $FeTe_{0.6}Se_{0.4}$ samples by the solid-state reaction and the direct microwave synthesis are referred as FTS680 and FTSM, respectively.

The crystal structure of all of the samples was characterized by PXRD using a PAN-analytical x-ray diffractometer with Cu-K_α radiation at room temperature. The sample morphology analysis was carried out by a scanning electron microscope (Phenom ProX). The temperature dependence of resistivity was measured in the range of 1.8–300 K by a standard four-probe method on a physical property measurement system (PPMS, Quantum Design). Magnetic measurements were performed on a magnetic property measurement system (MPMS, Quantum Design).

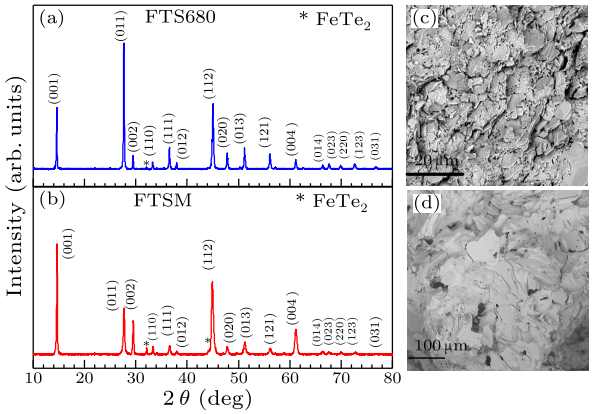

Fig. 1. XRD patterns for the $FeTe_{0.6}Se_{0.4}$ samples of the FTS680 (a) and FTSM (b), and SEM images for the FTS680 (c) and FTSM (d).

The PXRD patterns of both the FTS680 and the FTSM samples are shown in Figs. 1(a) and 1(b), which exhibit nearly pure phase of the 11-type tetragonal PbO-type structure for all of the samples. The reflection peaks were well indexed by the space group of $P4/nmm$ (No. 129) and trace amount of impurity peaks for $FeTe_2$ can be observed as marked with asterisks. The FTSM sample contains more impurity because of the very short reacting duration. The calculated lattice constants are $a = 3.80264$ Å and $c = 6.05631$ Å for the FTS680 sample, and $a = 3.80202$ Å and $c = 6.05194$ Å for the FTSM sample, respectively. It is worth noting that the lattice parameter of c axis of the FTSM sample is clearly smaller than the FTS680 one. Moreover, a preferred orientation along c axis can be seen in the PXRD pattern of the FTSM sample which is actually due to the larger sizes of crystal grains. The SEM photograph on the fracture surface of the two different samples is shown in Figs. 1(c) and 1(d). The FTS680 sample consists of flake-like grains with an average size of 1–10 μm with random orientation, and clear grain boundaries can be observed in the SEM images. Comparatively, the FTSM sample contains much larger crystal grains with the sizes of more than 100 μm inside the sample. These grains are arranged tightly together without obvious grain boundaries but small cavities exist inside all over the sample, which are formed due to the decrease of sample density from the powders during the quick microwave assisted reaction. From the chemical phase and sample morphology characterizations, it is quite surprising that the combination reaction among Fe, Te and Se happens extremely quickly by direct microwave synthesis, which can be finished in several minutes and is greatly energy saving. This yields nearly phase-pure $FeTe_{0.6}Se_{0.4}$ bulk samples with high density, much larger crystal grains and better grain

connectivity. We note that the annealing process at 400℃ only has slight improving effects on the superconducting properties and it does not change the grain morphology, as checked by SEM analysis.

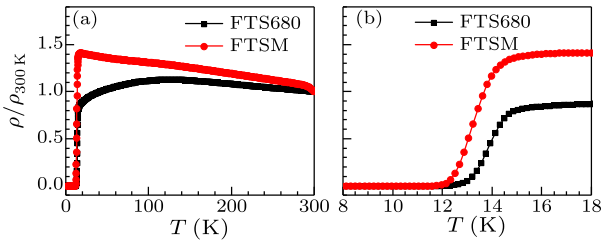

Fig. 2. (a) The temperature dependences of resistivity for the FTS680 and FTSM samples. (b) Expanded plots near the resistivity transitions.

The normalized temperature dependences of resistivity for both the FTS680 and FTSM samples are shown in Fig. 2. The resistivity values at room temperature are 1.6 mΩ·cm for the FTS680 sample, and 1.2 mΩ·cm for the FTSM sample, respectively. The FTSM sample has slightly lower resistivity, which is possibly due to the better connectivity at the grain boundary. All of the samples show semiconducting behavior above superconducting transitions, which is typical for some of the Fe(Te,Se) superconductors and is often observed in previous reports but is not yet clearly understood.[39] The magnified view around the superconducting transition is depicted in Fig. 2(b), which shows sudden superconducting drops in resistivity curves at about 14.6 K for the FTS680 sample and 14.3 K for the FTSM sample. The zero resistivity occurs at 12.6 K for the FTS680 sample and 12.0 K for the FTSM sample. The resistive superconducting transitions show slight differences between the FTS680 and FTSM samples.

The magnetic properties are characterized and shown in Fig. 3. The dc magnetic susceptibility measured under a constant magnetic field of 10 Oe using zero-field-cooling (ZFC) and field-cooling (FC) modes is depicted in Figs. 3(a) and 3(b). The FTS680 sample shows an onset of diamagnetic superconducting transition at around 11.5 K, which is comparable with the previously reported T_c of polycrystalline samples synthesized with the same method, and the lower magnetic T_c than the resistive transition is believed to be caused by the magnetic pair-breaking effect from the existence of interstitial Fe atoms.[34] However, a much higher T_c of 14.3 K was found in the FTSM sample, which is consistent with the resistive transition and very similar to T_c of the high quality single crystals.[33] The FTSM sample also reveals a higher superconducting shielding volume fraction derived from the ZFC data at 2 K, which indicates the higher bulk quality of the FTSM sample. Both the samples show slight magnetic anomaly in the M–T curve with the transition temperatures of 119 K for the FTS680 sample and 127 K for the FTSM sample, respectively. The origin of this anomaly was attributed to the existence of tiny magnetic impurity of iron oxides inside the polycrystalline samples as reported previously.[40,41] The isothermal magnetization (M–H) plots for both the samples at 2 K under a changing magnetic field from −7 T to 7 T are shown in Figs. 3(c) and 3(d). The two kinds of samples show very different hysteresis behaviors in the magnetic loops. The M–H curve of the FTS680 sample shows very narrow hysteresis loops upon a ferromagnetic background signal, which is very typical for the Fe(Te,Se) superconductors obtained by the solid state reaction method. The magnetic background is commonly considered to originate from the interstitial Fe atoms which suppress the critical current density severely. On the other hand, the M–H curve of the FTSM sample indicates a typical type Ⅱ superconductor with high quality and broad hysteresis loops, and no magnetic background can be observed, which is very similar to the annealed single crystal samples without interstitial Fe atoms.[34,42] When the c-axis is smaller, the T_c in magnetic transition will be higher and the M–H loops without magnetic background for the FTSM samples will be better. This gives strong indications that there are no interstitial Fe atoms existing in the crystal lattice of the FTSM sample, although this needs further direct evidence from more characterizations. Although the reaction mechanism is unclear, the elimination of interstitial Fe atoms is possibly due to the very fast microwave-assisted chemical reaction during several minutes and thus it proves an effective route to synthesize the high quality superconducting Fe(Te,Se) bulks by the direct microwave synthesis method.

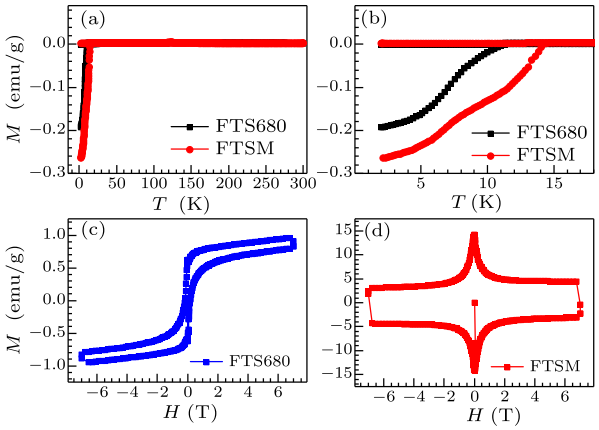

Fig. 3. (a) The temperature dependences of ZFC and FC magnetization curves for the FTS680 and FTSM samples under a field of 10 Oe. (b) Expanded plots near the magnetic transitions. (c) The magnetic hysteresis curves at 2 K for the FTS680 sample. (d) The magnetic hysteresis curves at 2 K for the FTSM sample.

To further characterize the electrical current transport properties for future high field applications of the FTSM sample, the isothermal magnetic hystere-

sis curves for the FTSM sample at different temperatures of 2–6 K were measured under sweeping magnetic fields from −7 T to 7 T, and the critical current density J_c (A/cm^2) was evaluated from the M–H magnetic hysteresis loops using the extended Bean model with the formula $J_c = 20\Delta M/[a(1 - a/3b)]$, where ΔM is the difference of magnetizations when sweeping fields up and down, a and b are the sample widths ($a < b$),[43] as shown in Figs. 4(a) and 4(b), respectively. The magnetic hysteresis curves show symmetric and broad loops at all temperatures, even at the measured highest fields of 7 T. The estimated J_c is above 10^4 A/cm^2 at 2 K in all fields, and it reaches a high value of 1.2×10^4 A/cm^2 even under the magnetic field of 7 T. For comparison, the estimated J_c for the FTS680 sample is only about 4.1×10^2 A/cm^2 at 2 K under 7 T. The critical current density J_c was greatly enhanced by nearly 30 times by the direct microwave synthesis method than the solid-state reaction method. Moreover, J_c for the FTSM sample decreases with the increase of temperature, but it is quite robust with the increase of the magnetic field. Various synthesis techniques have been developed to prepare high quality Fe(Te,Se) polycrystals, which includes low-temperature sintering, infra-red radiation sintering, hot pressing, self-propagating synthesis, elements doping, and high temperature melting etc. However, it is still difficult to achieve higher J_c above 10^4 A/cm^2 stably, especially under high fields.[26–30,44–46] By further improving the sample density and introducing additional flux pinning centers, our microwave synthesized polycrystalline Fe(Te,Se) samples offer promise as raw materials for the non-toxic Fe-based superconducting wires.

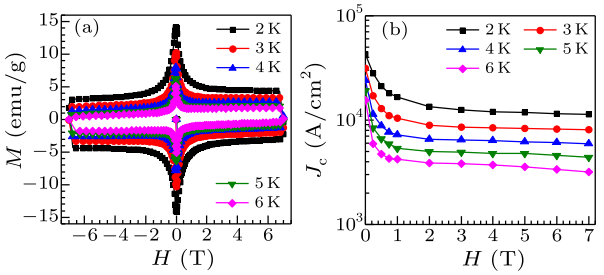

Fig. 4. (a) The magnetic hysteresis curves from 2 K to 6 K for the FTSM sample. (b) The magnetic field dependence of critical current density J_c from 2 K to 6 K for the FTSM sample.

In conclusion, we have successfully prepared high quality polycrystalline $FeTe_{0.6}Se_{0.4}$ samples by a direct microwave synthesis method. Compared with the samples prepared by the common solid-state reaction method, these samples exhibit larger grain size, better grain connectivity, smaller c-axis, higher T_c in magnetic transitions, better M–H loops without magnetic background, which give strong indications that there are possibly no interstitial Fe atoms existing in the crystal lattice. Moreover, the critical current density J_c is greatly enhanced by nearly 30 times to a value about 1.2×10^4 A/cm^2 at 2 K and 7 T in these polycrystalline bulk materials. This may lead to a promising microwave synthesis route by further optimization for fabrication of Fe-based non-toxic superconducting wires for large currents and high field applications.

References

[1] Kamihara Y et al 2008 *J. Am. Chem. Soc.* **130** 3296
[2] Ren Z A et al 2008 *Chin. Phys. Lett.* **25** 2215
[3] Rotter M et al 2008 *Phys. Rev. Lett.* **101** 107006
[4] Chen X H et al 2008 *Nature* **453** 761
[5] Hsu F C et al 2008 *Proc. Natl. Acad. Sci. USA* **105** 14262
[6] Wang X C et al 2008 *Solid State Commun.* **148** 538
[7] Yakita H et al 2014 *J. Am. Chem. Soc.* **136** 846
[8] Chen D Y et al 2016 *Chin. Phys. Lett.* **33** 067402
[9] Lu X F et al 2014 *Phys. Rev. B* **89** 020507
[10] Guo J G et al 2010 *Phys. Rev. B* **82** 180520
[11] Yu J et al 2017 *Sci. Bull.* **62** 218
[12] Wang X C et al 2017 *Chin. Phys. Lett.* **34** 077401
[13] Hosono H et al 2018 *Mater. Today* **21** 278
[14] Pallecchi I et al 2015 *Supercond. Sci. Technol.* **28** 114005
[15] Kida T et al 2009 *J. Phys. Soc. Jpn.* **78** 113701
[16] Katase T et al 2011 *Nat. Commun.* **2** 409
[17] Zhang X P et al 2017 *IEEE Trans. Appl. Supercond.* **27** 7300705
[18] Zhang X P and Ma Y W 2013 *Chin. Sci. Bull.* **58** 986
[19] Pyon S et al 2018 *Supercond. Sci. Technol.* **31** 055016
[20] Wang Q Y et al 2012 *Chin. Phys. Lett.* **29** 037402
[21] He S L et al 2013 *Nat. Mater.* **12** 605
[22] Mizuguchi Y et al 2009 *Appl. Phys. Express* **2** 083004
[23] Jia J F 2015 *Sci. Bull.* **60** 1368
[24] Dong C H et al 2013 *Chin. Phys. B* **22** 087401
[25] Si W D et al 2013 *Nat. Commun.* **4** 1347
[26] Ozaki T et al 2012 *J. Appl. Phys.* **111** 013912
[27] Mizuguchi Y et al 2011 *Supercond. Sci. Technol.* **24** 125003
[28] Li X et al 2016 *J. Supercond. Novel Magn.* **29** 1755
[29] Gao Z S et al 2011 *Supercond. Sci. Technol.* **24** 065022
[30] Feng J Q et al 2016 *Mater. Lett.* **170** 31
[31] Yuan P S et al 2015 *Supercond. Sci. Technol.* **28** 065009
[32] Li X et al 2015 *Physica C* **517** 16
[33] Taen T et al 2009 *Phys. Rev. B* **80** 092502
[34] Sun Y et al 2016 *Sci. Rep.* **6** 32290
[35] Chen J T et al 2016 *J. Phys. Soc. Jpn.* **85** 104714
[36] Vallance S R et al 2009 *Adv. Mater.* **21** 4502
[37] Rybakov K I et al 2013 *J. Am. Ceram. Soc.* **96** 1003
[38] Muir S W et al 2012 *Mater. Res. Bull.* **47** 798
[39] Ding Q P et al 2011 *Supercond. Sci. Technol.* **24** 075025
[40] Lim E H H, Tan K Y, Liew J Y C et al 2015 *J. Supercond. Novel Magn.* **28** 2839
[41] Fedorchenko A V, Grechnev G E, Desnenko V A et al 2011 *Low Temp. Phys.* **37** 83
[42] Sun Y, Tsuchiya Y, Yamada T et al 2014 *Physica C* **504** 12
[43] Bean C P 1964 *Rev. Mod. Phys.* **36** 31
[44] Ahn J H and Oh S 2013 *Curr. Appl. Phys.* **13** 1096
[45] Liu G H, Xia T L, Yuan X Y et al 2016 *Mater. Des.* **106** 349
[46] Li X, Shi X T, Wang J P et al 2015 *J. Alloys Compd.* **644** 523