1-1-2014

The formation of nano-layered grains and their enhanced superconducting transition temperature in Mg-doped FeSe0.9 bulks

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Abstract

To search a proper dopant to further improve superconductivity in 11 type Fe-based superconductors makes sense to both their superconductivity mechanism and possible technological applications. In present work, Mg doped FeSe polycrystalline bulks were obtained by a two-step solid-state reaction method. Even though there are many MgSe and iron impurities existing in the Mg heavy doped FeSe bulks, they exhibit obviously increased T_c compared to undoped FeSe sample. It was found that Mg addition has little effect on the crystal lattice parameters of superconducting beta-FeSe, whereas leads to the formation of nano-layered grain structure consisted of MgSe and beta-FeSe with similar X-ray diffraction characteristics. Lots of nano-structural interfaces between FeSe and MgSe formed in this homogenous layered grain structure have significant effect on the superconducting properties and are responsible for the enhancement of T_c, as like the case of FeSe thin film on some specific substrates. Our work not only demonstrates a powerful way for raising T_c in bulk superconductors, but also provides a well-defined platform for systematic studies of the mechanism of unconventional superconductivity by considering interface effect.

Keywords

9, fese0, doped, mg, temperature, transition, superconducting, bulks, enhanced, formation, their, grains, layered, nano

Disciplines

Engineering | Physical Sciences and Mathematics

Publication Details

Lan, F., Ma, Z., Liu, Y., Chen, N., Cai, Q., Li, H., Barua, S., Patel, D., Hossain, M. Al., Kim, J. & Dou, S. Xue. (2014). The formation of nano-layered grains and their enhanced superconducting transition temperature in Mg-doped $FeSe_{0.9}$ bulks. Scientific Reports, 4 6481-1-6481-5.

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SCIENTIFIC REPORTS

OPEN

CONFERENCE PROCEEDINGS

ACSMS2014

The formation of nano-layered grains and their enhanced superconducting transition temperature in Mg-doped $FeSe_{0.9}$ bulks

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SUBJECT AREAS:

SUPERCONDUCTING PROPERTIES AND MATERIALS

APPLIED PHYSICS

Received
21 July 2014

Accepted
28 August 2014

Published
26 September 2014

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To search a proper dopant to further improve superconductivity in 11 type Fe-based superconductors makes sense to both their superconductivity mechanism and possible technological applications. In present work, Mg doped FeSe polycrystalline bulks were obtained by a two-step solid-state reaction method. Even though there are many MgSe and iron impurities existing in the Mg heavy doped FeSe bulks, they exhibit obviously increased T_c compared to undoped FeSe sample. It was found that Mg addition has little effect on the crystal lattice parameters of superconducting β-FeSe, whereas leads to the formation of nano-layered grain structure consisted of MgSe and β-FeSe with similar X-ray diffraction characteristics. Lots of nano-structural interfaces between FeSe and MgSe formed in this homogenous layered grain structure have significant effect on the superconducting properties and are responsible for the enhancement of T_c, as like the case of FeSe thin film on some specific substrates. Our work not only demonstrates a powerful way for raising T_c in bulk superconductors, but also provides a well-defined platform for systematic studies of the mechanism of unconventional superconductivity by considering interface effect.

The recent discovery of the Fe-based high temperature superconductors with superconducting transition temperatures as high as 55 K[1,2] have attracted world-wide attention despite the magnetism of Fe. Among them, 11 compounds with Tc of 8 K possesses the simplest crystal structure[3], containing a single layer of tetrahedrally coordinated Fe atoms to chalcogen atoms (Se/Te). This simplicity of structure and presence of less toxic Se as compared to As make 11 compounds more attractive to study the superconductivity mechanism in iron based superconductors as well as their possible technological applications.

Even more remarkably, the onset T_c of binary β-$FeSe_{1-x}$ was shown to be as high as 27 K[4] with applied hydrostatic pressure, which suggests a possibility of increasing T_c via the chemical pressure route. Therefore, it is considered that chemical substitutions can be an alternative way to introduce pressure to change parameters and thereby affect superconductivity in the search for novel superconducting materials. Subsequently, several groups focused on different substitutions of ions with varied ionic radius upon either the Fe-site or the Se-site. Until now, the partial substitution of Se by Te and S has been found to significantly increase the T_c, e.g. with a maximum onset T_c of 15 K for $FeSe_{0.5}Te_{0.5}$ or $FeS_{0.2}Te_{0.8}$[5–7].

Meanwhile, the effect of various metals dopants, such as Al, Ti, V, Cr, Mn, Co, Ni, Cu, Ga, In, Ba and Sm on the $FeSe_{1-x}$ superconducting polycrystalline samples obtained by a solid state reaction was investigated in previous study[8,9]. Among them, Co, Ni, Cu, Al, Ga or Sm doped samples consist of mainly the tetragonal phase, and these dopants occupied the Fe-sites and resulted in the changes in the lattice constants. On the other hand, the rest of the studied metal dopants did not incorporate into the host lattice of superconducting $FeSe_{1-x}$ and mainly formed inclusions with elements (Fe or Se) not incorporated into the matrix. However, in either case, the T_c in these doped $FeSe_{1-x}$ samples were generally suppressed, or even no longer emerged according to the resistivity as a function of temperature. Superconducting single crystal of pure $FeTe_{1-x}Se_x$ ($x = 0.3$–0.55) doped with Co, Ni, Cu, Mn, Zn, Mo, Cd, In, Pb, Hg, V, Ga, Mg, Al, Ti, Cr, Sr or Nd were also studied, and the similar results were found in these doped single crystals[10].

Based on these backgrounds, doping of various metals in the FeSe polycrystalline bulks or single crystal samples seems to be a noneffective way to raise T_c. Consequently, lots of research teams around world lost their interest in exploring the doping of various metals and mainly focused on the research of substitution of Se-site by Te and S in recent years. Nevertheless, in present work, Mg doped FeSe polycrystalline bulks were prepared by two-step solid-state reaction method, which exhibits enhanced T_c compared to undopoed FeSe sample. The corresponding enhancement mechanism is also discussed in detail, appearing to be quite different from that of the other metals doped FeSe polycrystalline bulks in previous studies.

Experimental details

Polycrystalline bulk samples $FeSe_{0.9}Mg_x$ (x = 0, 0.2, 0.4 and 1) were prepared by two-step solid-state reaction method. The Fe powder (99.99% purity) and Se powder (99.5% purity) were firstly mixed in a molar ratio of $FeSe_{0.9}$. The mixed powders were cold-pressed into pellets of 5 mm in diameter and 2 mm in thickness under a uniaxial pressure of 5 MPa. All the pressed pellets were placed in an alumina crucible inside a quartz tube furnace and then sintered at 650°C for 24 h under protection of ultra-high purity Ar gas. After slowly cooling down to room temperature, these sintered $FeSe_{0.9}$ bulks were reground into powders. Then these powders was mixed homogeneously with Mg powders (99.99% purity) in a molar ratio of $FeSe_{0.9}Mg_x$ (x = 0, 0.2, 0.4 and 1). The mixed powders were cold-pressed into pellets again. All the pressed pellets were placed in an alumina crucible inside a quartz tube furnace again and then sintered at 750°C for 0.5 h under protection of ultra-high purity Ar gas.

The phase composition of the sintered samples was determined by X-ray diffractometer (XRD) using Rigaku D/max2500 X-ray diffractometer with Cu Kα radiation. The morphologies were examined by field–emission scanning electron microscopes (SEM, S-4800, Hatachi). The sample resistance was measured using the standard four-probe method.

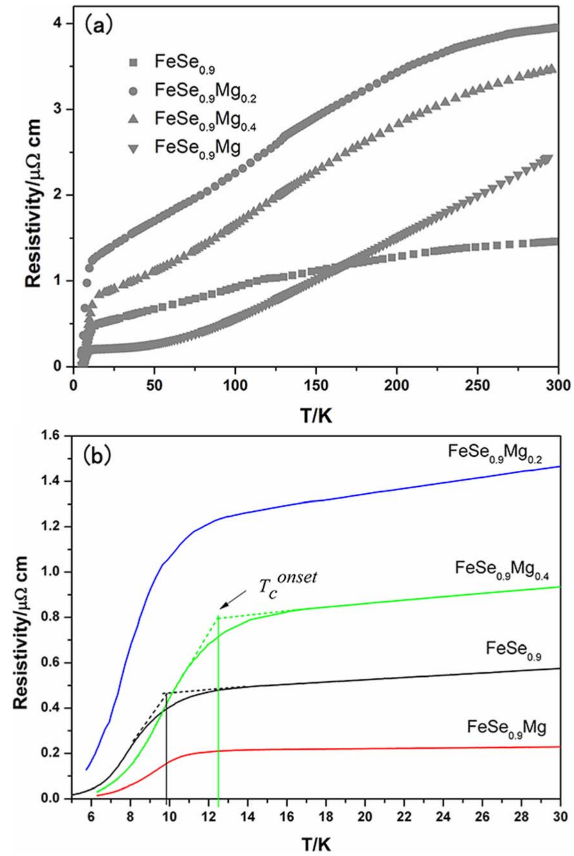

Figure 1 | the temperature dependence of electrical resistivity for the $FeSe_{0.9}Mg_x$ (x = 0, 0.2, 0.4 and 1) samples prepared by two-step sintering, with (a) the whole measured temperature range from 5 K to 300 K and (b) the enlarged range between 5 K and 30 K.

Results and Discussion

Figure 1 shows the temperature dependence of electrical resistivity for the sintered $FeSe_{0.9}Mg_x$ (x = 0, 0.2, 0.4 and 1) samples. The positive slope of ρ(T) indicates that these samples exhibit metallic behavior. It is also found that Mg-doped samples possess higher resistivity than that of undoped samples at normal state, which can be attributed to the electron scattering effect owing to Mg doping. From this point of view, the resistivity of doped samples at normal state ought to increase as the amount of Mg addition increases. But their actual resistivity performance is out of our expectation. In fact, the resistivity of doped samples at normal state gradually decreased as the amount of Mg addition increased from $FeSe_{0.9}Mg_{0.2}$ to $FeSe_{0.9}Mg$. Especially, the resistivity of $FeSe_{0.9}Mg$ is even lower than undoped $FeSe_{0.9}$ sample when the temperature is below 150 K. These unique results are totally different from the case of other metal doped FeSe samples reported in previous study[8,9]. Figure 1b presents the detailed temperature dependence of electrical resistivity for the sintered samples between 5 K and 30 K. It can be found that the onset of the transition temperature (T_c^{onset}) of undoped $FeSe_{0.9}$ is about 9.8 K, consistent with previous report[3]. As for $FeSe_{0.9}Mg_{0.2}$ and $FeSe_{0.9}Mg$ sintered samples, their T_c^{onset} are comparable to the undoped sample. More precisely, their T_c^{onset} are even a bit higher than that of undoped sample. On the other hand, the T_c^{onset} of $FeSe_{0.9}Mg_{0.4}$ is significantly increased to 12.3 K, about 25% higher than that of undoped sample. This result is abnormal considering that most of metal dopants substituting on Fe site generally brought about the depression of T_c[8–10].

The abnormal results of T_c obtained hereby imply that the introduction of proper amount of Mg addition by two-step sintering method seems open possible windows for the enhancement of T_c in FeSe superconductors via metal doping. In order to clarify the enhancement mechanism in the T_c of the prepared sample, the phase composition and microstructure are investigated in detail.

Figure 2a shows the X-ray diffraction patterns of sintered $FeSe_{0.9}Mg_x$ (x = 0, 0.2, 0.4 and 1) samples. One can see that superconducting phase, β-FeSe, is the main phase in all the sintered samples. Some common impurities, Fe_7Se_8 and Fe_3O_4, are also recognized in $FeSe_{0.9}$ sample. As the amount of Mg dopant was added from $FeSe_{0.9}Mg_{0.2}$ to $FeSe_{0.9}Mg$, the intensity of β-FeSe peaks decreased while the peaks corresponding to MgSe and Fe emerge and gradually become stronger. Observing Fig. 2a more carefully, one can also see that all the MgSe main peaks are very close to, and even overlap with β-FeSe peaks in the patterns (for example, MgSe (200) peak and β-FeSe (002) peak, MgSe (220) peak and FeSe (112) peak, MgSe (111) peak and FeSe (101) peak). Besides, it is noticed that the positions of (001) and (101) peaks corresponding to β-FeSe phase almost keep unchanged with the amount of Mg addition increasing, as shown in Fig. 2b and Fig. 2c, suggesting that the lattice parameters (a and c) of β-FeSe almost remain unchanged. Based on the above XRD results, it can be concluded that Mg dopant mainly reacted with FeSe forming MgSe and Fe: Mg + FeSe = MgSe + Fe, and seldom entered into crystal lattice of β-FeSe and substitute of Fe-site.

The SEM images of sintered $FeSe_{0.9}Mg_x$ (x = 0, 0.2, 0.4 and 1) samples are given in Fig. 3. It can be seen that the sintered undoped FeSe sample is dense and consisted of small randomly aligned grains (about 500 nm in size, see Fig. 3a), which is the typical characteristic of FeSe bulks prepared by traditional solid-state sintering[11,12]. On the other hand, regular layered grains are observed in the sintered Mg-doped samples. As the amount of Mg addition increases, the percent

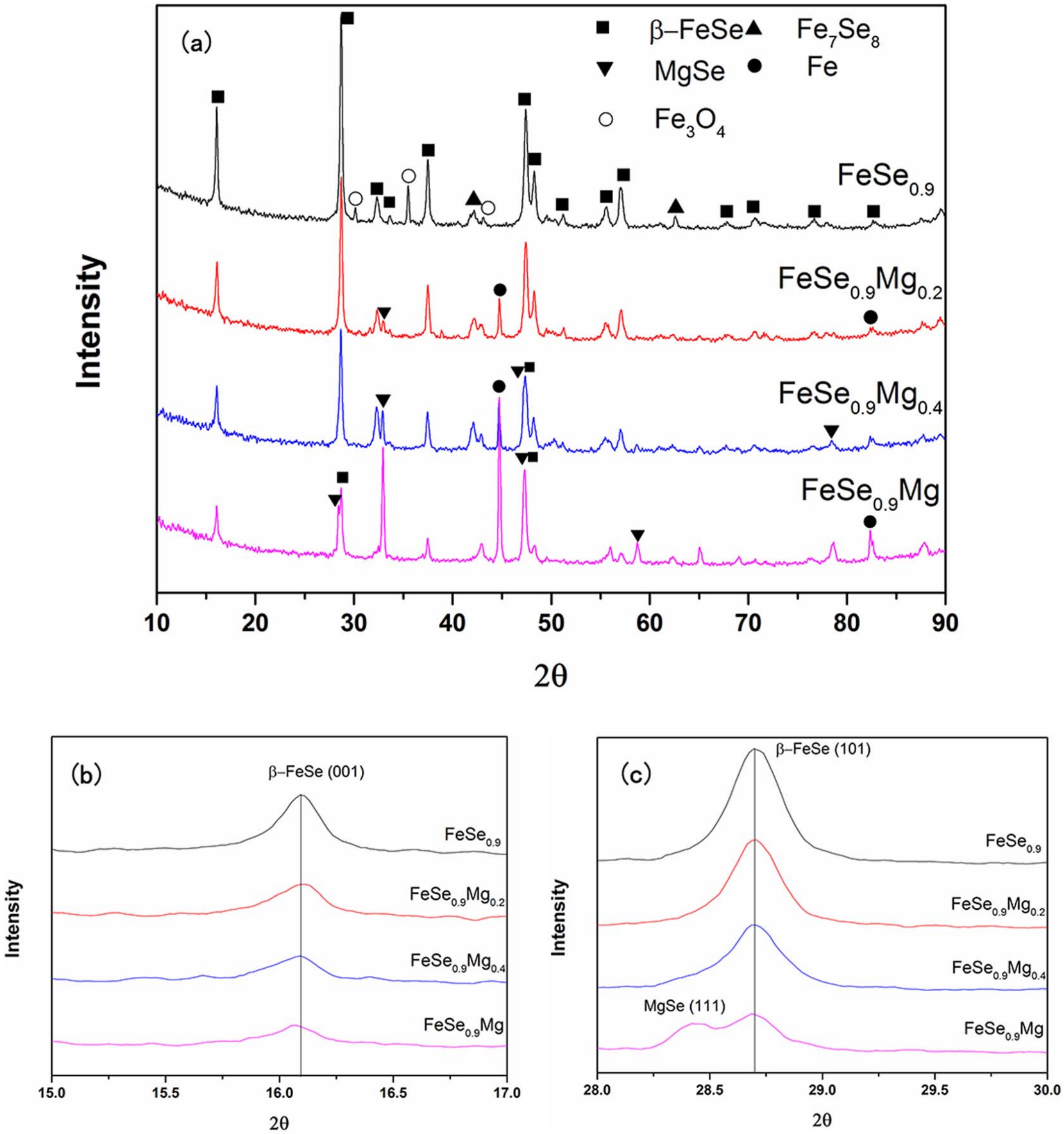

Figure 2 | the X-ray diffraction patterns of $FeSe_{0.9}Mg_x$ (x = 0, 0.2, 0.4 and 1) samples prepared by two-step sintering, with (a) The whole measured view, (b) Magnified view of *β*-FeSe (001) peak and (c) Magnified view of *β*-FeSe (101) peak.

of layered grains increased, and finally the layered grains dominate in the microstructure of sintered $FeSe_{0.9}Mg_{0.4}$ and $FeSe_{0.9}Mg$ samples. Moreover, the size of layered grains also enlarges as Mg addition increases. Interestingly, observing Fig. 3c and Fig. 3d more carefully, one can see that the thickness of each layer in these layered grains is very small (only about 100 nm) and also very homogeneous. This unique microstructure was seldom observed in other-metal doped FeSe samples. Combined with the XRD results, Mg addition mainly reacts with FeSe forming MgSe. The formation of these layered grains is supposed to be closely related with this reaction. Since the produced MgSe shares the similar x-ray diffraction characteristics with *β*-FeSe, it can incorporate into superconducting *β*-FeSe matrix, finally forming these multi-layered grain structure in the sintered Mg-doped sample. This speculation can be further proved by the elemental maps of Se, Fe and Mg for the microstructure of Mg doped smple, as shown in Fig. 4. It can be seen from Fig. 4 that Fe distributes uniformly in the whole SEM image while Mg and Se are relatively concentrated at the region of layered grains, as marked by white squires in Fig. 4. This result suggests that the layered grains are mainly consisted of MgSe and FeSe.

Combined with all the above results of superconducting properties, phase composition and microstructure, As Mg addition has little effect on the crystal lattice parameters of *β*-FeSe, but leads to the formation of unique layered grain structure consisted of MgSe and FeSe, it can be suggested that the enhancement of T_c in the $FeSe_{0.9}Mg_{0.4}$ sample should be attributed to the multi-layered grain structure. Interestingly, Nabeshima et al have just reported that FeSe epitaxial thin film deposited on CaF_2 (100) substrate exhibits significantly enhanced T_c[13]. In fact, the multi-layered grain structure in sintered $FeSe_{0.9}Mg_{0.4}$ samples here is consisted of lots of homogenous and thin MgSe and FeSe layers (as described above, the thickness of each layer is about 100 nm, see Fig. 3c), just like as the FeSe thin films on the MgSe substrates. MgSe is very similar with CaF_2 in the crystal structure and crystal constants (Cubic, a = 5.463 and 5.462 for MgSe and CaF_2, respectively). From this view, our result is coincidently consistent with their research. They attribute the enhancement of T_c to the change of crystal lattice parameters *a/c* ratio. However, the lattice parameters of FeSe bulks almost keep unchanged by Mg doping in our work. There must be other mechanism underlying the enhancement of T_c here.

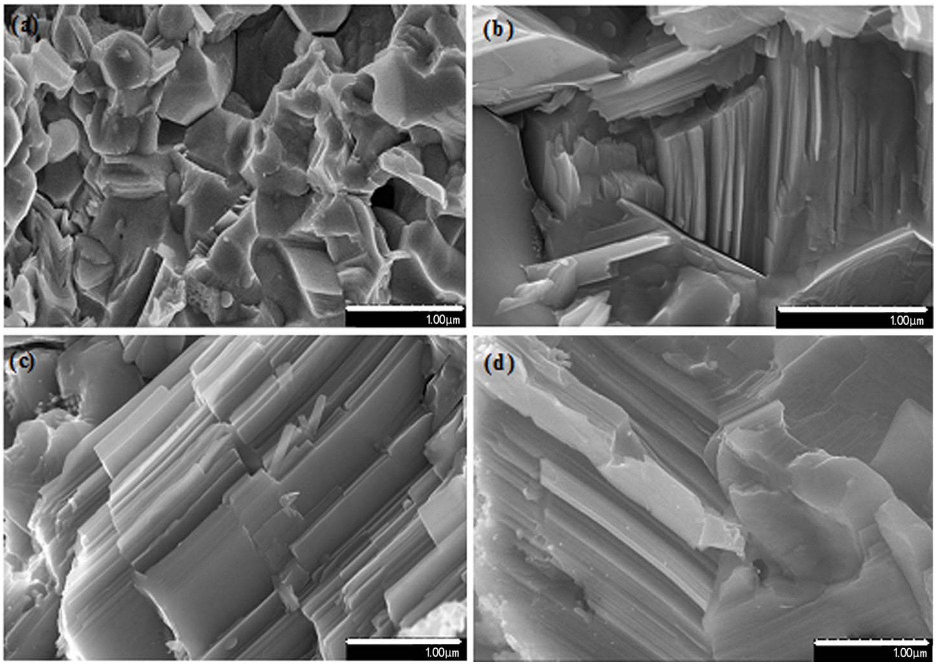

Figure 3 | the typical SEM images of (a) $FeSe_{0.9}$, (b) $FeSe_{0.9}Mg_{0.2}$, (c) $FeSe_{0.9}Mg_{0.4}$ and (d) $FeSe_{0.9}Mg$ samples prepared by two-step sintering.

Besides Nabeshima et al's work, FeSe and $FeSe_xTe_{1-x}$ thin films with much higher T_c than those of bulk superconductors have also been achieved by other groups recently, especially the thin films on the substrate with quite similar lattice constants with them[14–16]. In these films, it was found that the T_c of these films is significantly enhanced, whereas their lattice parameters changed very little, or even remained unchanged. The effect of the change in lattice parameters is too weak to account for the improvement of T_c. It was suggested that the interface effect plays an important role in increasing T_c of these thin films[14,16]. In fact, interface effect has always been an interesting topic in the superconducting field. A lot of previous studies reported some unique superconducting phenomena at the various interfaces[17–19].

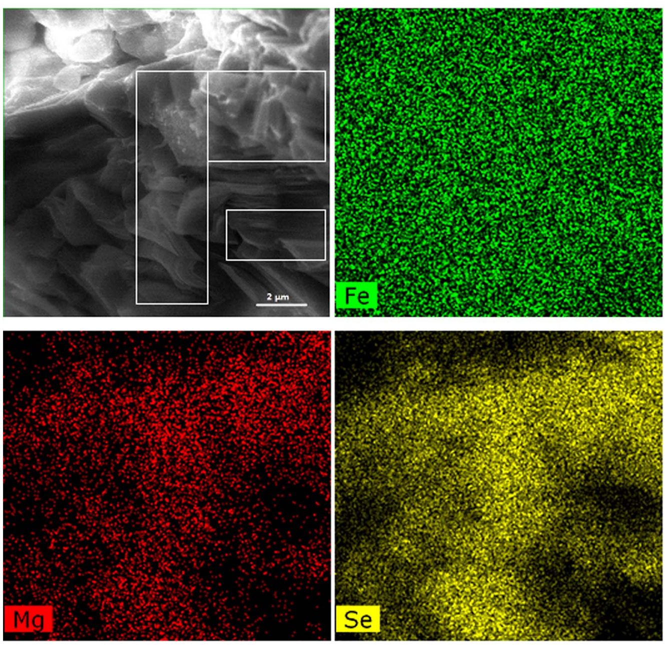

Figure 4 | the elemental maps of Fe, Mg and Se For the microstructure of Mg doped $FeSe_{0.9}$ sample prepared by two-step sintering. The region of some layer grains was marked by white squares.

In the case of $FeSe_{0.9}Mg_{0.4}$ sample prepared in present work, there are a lot of nano-structural interface between FeSe and MgSe formed in the multi-layered grain structure of Mg-doped sample. As we all know, MgSe is wide band gap semiconductor with bandgap energy of about 4.0 ev. One can imagine that the interfaces between MgSe and FeSe forming in present work have an important effect on the superconducting properties of FeSe. These interfaces might enhance electron-phonon coupling, as reported in the interface of atomically uniform films of Ag on Fe substrate[17]. Another possibility is formation of two-dimensional electron gas at these interfaces, which may cause the higher T_c, as demonstrated in Ref. [18]. Further research need to be carried out to elucidate the mechanism underlying the enhancement of T_c observed here.

Based on the interface effect discussed above, it also explains well why the T_c performance in $FeSe_{0.9}Mg_{0.4}$ sample is best among these three Mg doped samples. As for $FeSe_{0.9}Mg_{0.2}$ sample, Mg addition is not enough and the interface between MgSe and FeSe in the layered grains is insufficient to affect the overall T_c of sintered sample. When it comes to the $FeSe_{0.9}Mg$, excess MgSe is formed and the superconducting β-FeSe is decreased too much, which also decrease the interfaces between MgSe and FeSe, and thus affects T_c performance.

Conclusions

Mg doped FeSe polycrystalline bulks were obtained by two-step solid-state reaction method, which exhibits increased T_c compared to undoped FeSe sample. it was found that Mg addition has little effect on the crystal lattice parameters of superconducting β-FeSe, whereas leads to the formation of nano-layered grain structure consisted of MgSe and β-FeSe. Lots of nano-structural interfaces between FeSe and MgSe formed in this homogenous layered grain structure have significant effect on the superconducting properties and are responsible for the enhancement of T_c. Although T_c in the Mg doped FeSe bulks in present work needs to be further enhanced via optimizing both the amount of dopants and the synthesis technique to form better layered structure, our work not only demonstrates a powerful way for raising T_c in bulk superconductors, but also provides a well-defined platform for systematic studies of the mechanism of unconventional superconductivity through considering interface effect. Besides, FeSe thin film on MgSe substrate is also worth being studied in terms of interfacial superconductivity.

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Acknowledgments

The authors are grateful to National Natural Science Foundation of China (Grant No. 51302186), the Natural Science Foundation of Tianjin(Grant No. 13JCZDJC32300 and 14JCQNJC03300), New Teachers' Fund for Doctor Stations, Ministry of Education (Grant No. 20120032120016). This work is also supported by the Australian Research Council (Grant No. DE140101333).

Author contributions

Z.M., Y.L. and H.L. discussed and designed the experimental scheme. F.L., N.C. and S.B. prepared the samples. Q.C. and D.P. did most of the characterizations. Z.M. analysized the data and wrote the paper. M.H., J.H.K. and S.X.D. helped with the experiment and data analysis.

Additional information

Competing financial interests: The authors declare no competing financial interests.

How to cite this article: Lan, F. *et al.* The formation of nano-layered grains and their enhanced superconducting transition temperature in Mg-doped $FeSe_{0.9}$ bulks. *Sci. Rep.* **4**, 6481; DOI:10.1038/srep06481 (2014).