A novel iron-based superconductor synthesized by the ion exchange technique

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Keywords: superconductivity, FeSe-based superconductor, ion exchange, nearly vacancy-free precursor

Abstract
The superconductivity of the FeSe-based superconductor is extremely sensitive to Fe vacancies in the FeSe plane. In order to reduce the formation of Fe vacancies in the FeSe plane, various low-temperature methods are developed. However, it is still complex and time consuming to control the Fe vacancies concentration. Here, a hybrid iron-based superconductor, Li0.21Se0.05(EG)0.26FeSe (EG: ethylene glycol, C2H6O2), is synthesized by a solvothermal ion-exchange technique using a nearly vacancy-free precursor of (TBA)0.3FeSe as the matrix. Bulk superconductivity with transition temperature ($T_c$) of 30 K is confirmed by the characterization with the magnetic susceptibility and resistivity measurements. Compared with the pristine FeSe single crystal, x-ray photoelectron spectroscopy results show a decrease of the Fe valence, indicating that electron doping to FeSe plane accounts for the increase of the $T_c$. Our result suggests that (TBA)0.3FeSe, a nearly vacancy-free precursor with a large distance between the adjacent FeSe planes, is a good template candidate for the synthesis of other hybrid iron-based superconductors using the ion exchange technique.

1. Introduction
Since the discovery of iron-based superconductors [1, 2], FeSe, with the layered anti-PbO structure, has always been the research hotspots of iron-based superconductors. The superconducting transition temperature of FeSe under ambient pressure is only 8.5 K [3], but the $T_c$ of FeSe can be significantly increased by applying hydrostatic pressure, electron doping or ionic-liquid gating methods [4–6]. The $T_c$ of FeSe can be increased from 8.5 K to above 40 K by intercalation of alkali metal ions, small molecules, alkali metals and organic amine, such as $A_x$Fe$_2$Se$_2$ ($A =$ alkali metal) [7], (Li,Fe)OHFeSe [8–10], Li$_4$(NH$_3$)$_2$(NH$_3$)$_2$Fe$_2$Se$_2$ [11], Li$_3$(C$_3$H$_5$N)$_2$Fe$_2$Se$_2$ [12], (TMA)$_3$Fe$_2$Se$_2$ [13], etc. In addition, FeSe-based superconductors have a similar electronic structure with only electron pockets on the Fermi surface, which are quite different from that of iron pnictide [14, 15].

In FeSe-based superconductors, it can be seen from the Fe–Se phase diagram that iron–selenium compounds tend to form Fe vacancies. The formation of Fe vacancies is closely related to the material synthesis method. Formation of Fe vacancies arises from the fact that the valence state of Fe lower than 2+ is unstable. The formation of Fe vacancies needs to cost energy, so that the Fe vacancies in FeSe-based superconductors are easily produced by high temperature synthesis method. For example, the Fe vacancies are formed in the K$_r$Fe$_2$,Se$_2$ superconductor synthesized by the high temperature solid state reaction.
The antiferromagnetic insulating phase K$_2$Fe$_4$Se$_5$ exhibits Fe-vacancy order in a $\sqrt{5} \times \sqrt{5}$ supercell below 580 K [16]. The superconducting phase of K$_{1-x}$Fe$_2$Se$_2$ with $T_c \sim 30$ K is intergrown with the insulating phase of K$_2$Fe$_4$Se$_5$, and can be only obtained by the epitaxial growth on K$_2$Fe$_4$Se$_5$, which leads to a very low superconducting volume [16]. However, the story is different under low temperature synthesis. If the synthesis temperature is low enough, the FeSe layer will remain intact [17].

In order to reduce the Fe vacancies in the FeSe plane, various low-temperature synthesis methods are used to synthesize FeSe-based superconductors, such as: liquid ammonia method, hydrothermal/solvothermal method, and ion exchange method, although limited nonstoichiometry are crucial to enhance superconductivity in FeSe [18]. However, controlling Fe vacancies in the FeSe plane is complicated and time-consuming. For example, (Li,Fe)OHFeSe [19] and [(Fe,Al)(OH)$_2$][FeSe]$_{1.2}$ [20] crystals are usually synthesized by ion exchange technique using insulating K$_{0.8}$Fe$_{1.8}$Se$_2$ single crystal as the matrix. In order to make up for the Fe vacancies in the FeSe layer, we must add a large amount of nano-iron powder as the iron source to the reaction system or use post-processing methods. Recently an FeSe-based superconductor (TBA)$_{0.3}$FeSe was discovered with $T_c \sim 50$ K, which was synthesized by an electrochemical intercalation process [21]. Such a high $T_c$ indicates that the Fe vacancy in the FeSe plane should be as little as possible. Furthermore, in view of the large interlayer distance of 15.5 Å and small interaction between the organic ion and the FeSe plane, we think (TBA)$_{0.3}$FeSe should be a good template candidate to facilitate the ion exchange.

Here, we report a new FeSe-derived superconductor, Li$_{0.21}$Se$_{0.05}$(EG)$_{0.26}$FeSe, synthesized through a solvothermal ion exchange technique using a nearly vacancy-free precursor. Its superconducting transition temperature is confirmed by magnetic susceptibility and electrical resistivity measurements. Without adding additional iron source or using post-processing methods, Li$_{0.21}$Se$_{0.05}$(EG)$_{0.26}$FeSe can achieve 30 K superconductivity. X-ray photoelectron spectroscopy (XPS) results display a decrease of the Fe valence relative to FeSe, indicating that electron doping to the FeSe plane accounts for the increase of the $T_c$.

2. Experiment

The Li$_{0.21}$Se$_{0.05}$(EG)$_{0.26}$FeSe was synthesized by a solvothermal ion exchange technique using (TBA)$_{0.3}$FeSe as a matrix. First, 0.001–0.004 mol of Li$_2$Se, 0.001–0.002 mol of NaBH$_4$ (Sinopharm Chemical Reagent, 98% purity) and several pieces of (TBA)$_{0.3}$FeSe were added to a mixed solvent (2.5 ml ethylene glycol (EG, C$_2$H$_4$O$_2$, Sinopharm Chemical Reagent, 99.5% purity) and 2.5 ml N,N-Dimethylformamide (DMF, C$_5$H$_8$NO, Innochem, 99.9% purity, extra dry with molecular sieves)) and loaded into a stainless steel autoclave of 25 ml capacity with Teflon liner. The detailed synthesis process of Li$_2$Se and (TBA)$_{0.3}$FeSe were described in supplemental material (https://stacks.iop.org/NJP/24/043035/mmedia). Then the autoclave was tightly sealed and heated at 120 °C for 72 h. The ion exchange synthesized Li$_{0.21}$Se$_{0.05}$(EG)$_{0.26}$FeSe was obtained by washing and clearing, then samples were dried under vacuum and stored in an argon-filled glovebox. The atomic ratio of Li:Fe:Se is determined to be 0.21:1:1.05 by inductively coupled plasma-atomic emission spectroscopy (ICP-AES).

Powder x-ray diffraction (PXRD) patterns were collected at room temperature on a powder x-ray diffractometer (SmartLab-9, Rigaku Corp.) with Cu Kα radiation and a fixed graphite monochromator. Phase analysis and lattice parameter refinements were performed using the Le-Bail method for profile fitting and phase identification [22]. The Li$_{0.21}$Se$_{0.05}$(EG)$_{0.26}$FeSe sample is easy to decompose during the grinding process at room temperature. In order to obtain the polycrystalline sample for further structure refinement, the as-synthesized sample was ground in liquid nitrogen in an argon-filled glovebox. Special attention should be paid to the fact that liquid nitrogen is very dangerous. In order to avoid frostbite, low temperature protective gloves should be worn during the grinding process. The resistivity measurement was performed on Elementar vario EL cube to determine the type of intercalated molecules. Thermogravimetry-infrared spectroscopy-mass spectrometry (TG/IR/MS) was performed at a heating rate of 20 °C min$^{-1}$ under He atmosphere at 40 ml min$^{-1}$ using Perkin Elmer Pyris 1, Perkin Elmer Frontier, Perkin Elmer Clarus SQ8T. The sample stayed at 100 °C for 10 min during the heating process. XPS data was obtained using an ESCAlab250. XPS using monochromatized Al Kα x-ray source. The binding energies were calibrated against the C 1s peak (284.6 eV) of the residual carbon absorbed on the surface of the sample. The energy-dispersive x-ray spectroscopy (EDS) measurement was measured by the Hitachi SU8220 field emission scanning electron microscope equipped with energy dispersive x-ray (Oxford instrument X-Max® 150). Electron probe x-ray micro-analyzer (EPMA) measurement was carried out on the EPMA-8050G, Shimadzu.
3. Results and discussions

The shape of the as-synthesized Li_{0.21}Se_{0.05}(EG)_{0.26}FeSe is basically the same as that of its precursor (TBA)$_3$FeSe. The optical images of the (TBA)$_3$FeSe and the as-synthesized Li$_{0.21}$Se$_{0.05}$(EG)$_{0.26}$FeSe are shown in figure S1. Figure 1(a) shows the as-synthesized Li$_{0.21}$Se$_{0.05}$(EG)$_{0.26}$FeSe has a preferred orientation along the c direction, just like its precursor (TBA)$_3$FeSe which is shown in figure S4(a). The lattice parameters of (TBA)$_3$FeSe is about 15.5 Å for the c-axis, as shown in figure S4(a). Figure 1(a) displays the lowest angle Bragg peaks at d-spacing of 13.85 Å, smaller than that of (TBA)$_3$FeSe. This indicates that the TBA$^+$ ions are deintercalated from the precursor (TBA)$_3$FeSe and other smaller unknown species are inserted at the same time. In fact, we also tried insulating K$_{0.8}$Fe$_{1.6}$Se$_2$ single crystal as the precursor or only EG (ethylene glycol, C$_2$H$_4$O$_2$) as the solvent, and the same target product Li$_{0.21}$Se$_{0.05}$(EG)$_{0.26}$Fe$_{1-x}$Se can be obtained. The ICP-AES result shows there are about 14% Fe vacancies in the FeSe plane. The synthesized Li$_{0.21}$Se$_{0.05}$(EG)$_{0.26}$Fe$_{1-x}$Se is non-superconducting due to the large amount of Fe vacancies in the FeSe plane. The detailed experimental process and results are shown in the supplemental material. We summarize that the key points to obtain the target product are the suitable precursor, Li$_2$Se and EG. In figure 1(b), Le Bail method was performed for the ground Li$_{0.21}$Se$_{0.05}$(EG)$_{0.26}$FeSe, the refined structural parameter and agreement factors (conventional Rietveld R-factor for pattern) for tetragonal crystal system and P4/nmm space group were: a = 3.8353(1) Å, c = 13.8554(6) Å, Rp = 7.06%, Rwp = 9.83%, χ$^2$ = 2.576. It is worth noting that the as-synthesized sample is easy to decompose during the grinding process at room temperature. As shown in figure 1(b), part of the as-synthesized sample still decomposes into FeSe, even if ground in liquid nitrogen. Figure S2 shows the electron diffraction pattern along the [001] zone axis of the as-synthesized Li$_{0.21}$Se$_{0.05}$(EG)$_{0.26}$FeSe, which forms a tetragonal pattern. The value a = 3.88(1) Å agrees with the result obtained from the XRD refinement.

We used several different characterization techniques to determine the elemental composition of the new compound. The results are listed in table S1. It can be seen in table S1, the ICP-AES measurement result shows that the atomic ratio of Li:Fe:Se is 0.21:1:1.05. Both EDS and EPMA measurement results show that the atomic ratio of Li:Fe:Se is 0.21:1:1.05. Both EDS and EPMA measurement results show that the atomic ratio of Fe:Se is 1:1.05, which are consistent with the ICP measurement result. In the (TBA)$_3$FeSe precursor, the ICP-AES measurement result shows that the atomic ratio of Fe:Se is 1:1 (exactly 1.0002:1), indicating that the Fe vacancy in the FeSe layer of (TBA)$_3$FeSe is as little as possible within the range of experimental error. The CHN measurement result shows that the atomic ratio of C:H:N is 1:3.17:0.03. Small amount of N atom indicates that the main organic species in the sample is EG. This result is also consistent with our experimental process, because we can obtain the target product Li$_{0.21}$Se$_{0.05}$(EG)$_{0.26}$FeSe using only EG as the solvent. Real-time monitoring of TG/IR/MS technique is an effective approach for in-depth analyzing the thermolysis mechanism of the as-synthesized sample and it can also help us further understand the composition of the as-synthesized sample. It can be seen in figure 2(a) that the as-synthesized sample has obvious mass loss during the heating process, while figure S3 shows that the weight of the FeSe single crystal sample is almost unchanged during the same heating process. This result shows that the mass loss comes from the species inserted into the adjacent FeSe layers, just like the FeSe-derived superconductors obtained through the low temperature ammonia solution routes [11, 23]. Meanwhile, figure S9 shows that the residue of the thermal decomposition experiment is FeSe after the as-synthesized sample is annealed at 530 °C for 30 min. According to the results in table S1, the chemical formula of the as-synthesized sample is determined to be Li$_{0.21}$Se$_{0.05}$(EG)$_{0.26}$FeSe. The more discussion of the composition of Li$_{0.21}$Se$_{0.05}$(EG)$_{0.26}$FeSe is shown in the supplemental material.
Moreover, the TG curve in figure 2(a) shows that the mass loss mainly occurs in two temperature ranges: 150 °C–250 °C and 325 °C–400 °C. During these two temperature ranges, the gas product is collected and measured by an infrared spectrometer, which is shown in figure 2(b). At 225 °C, which is in the first mass loss temperature range, the gas products mainly contain EG and DMF (N,N-Dimethylformamide, C3H7NO). For EG, the characteristic absorption bands shown in figure 2(b) are as follows: −OH (3673 cm⁻¹), −CH1 (2945 cm⁻¹, 1380 cm⁻¹ and 1264 cm⁻¹) and C–O (1052 cm⁻¹). For DMF, the characteristic absorption bands shown in figure 2(b) are as follows: C=O (1723 cm⁻¹), CH1 (1383 cm⁻¹ and 1081 cm⁻¹). Refer to the infrared spectra of H2Se [24] in the previous literature, at 360 °C, which is in the second mass loss temperature range, the gas product mainly contains H2Se and EG. The mass spectrum data also supports the above results. Figure 2(c) depicts ion current intensity-temperature profiles for the gaseous products. As shown in figure 2(c), EG and DMF are the main gaseous species in the first mass loss stage; EG and H2Se are the main gaseous species in the second mass loss stage, consistent to the results of IR data. DMF can provide an alkaline environment, which is beneficial to the synthesis of Li0.21Se0.05(EG)0.26FeSe, but it is difficult to be completely removed, so we can see the existence of DMF in the measurement of TG/IR/MS. Based on the PXRD, ICP-AES, electron diffraction and TG/IR/MS results, the inferred crystal structure of Li0.21Se0.05(EG)0.26FeSe is shown in figure S10. Li⁺ ion, EG molecules and Se²⁻ ion are intercalated between the FeSe layers. The more discussion of the inferred crystal structure of Li0.21Se0.05(EG)0.26FeSe is shown in the supplemental material.

Figure 3(a) shows the temperature dependent resistivity of the as-synthesized Li0.21Se0.05(EG)0.26FeSe. A rapid decrease of resistivity appears around 30 K, and zero resistivity is reached at 28 K (figure 3(a) inset). The temperature dependent magnetic susceptibility of the as-synthesized Li0.21Se0.05(EG)0.26FeSe is shown in figure 3(b) with an external magnetic field of 10 Oe. The as-synthesized sample shows a diamagnetic transition around 30 K (figure 3(b) inset), which is consistent with the resistivity curve. The shielding fraction is about 59% at 2 K in the ZFC curve, which indicates that the superconductivity is a bulk superconductivity. The resistivity measurements at various magnetic fields are shown in figure 3(c). The superconducting transition displays a strong suppression with magnetic fields. The temperature dependence of the upper critical field $H_{c2}(T)$ for the as-synthesized sample is shown in figure 3(d). The upper critical field at $T = 0$ K can be determined by the Werthamer–Helfand–Hohenberg equation [25]

$H_{c2}(0) = 0.693\left(-\frac{dH_{c2}/dT}{T}\right)_{T=0}$. From the figure 3(d), we can have $\left(-\frac{dH_{c2}/dT}{T}\right)_{T=0} = 0.803$ T K⁻¹. Here, the $H_{c2}$ at limited temperatures is obtained by taking a criterion of the field at 50% of the normal-state resistivity. Then the $H_{c2}(0)$ can be estimated to be 15.7 T, which is significantly smaller than that of (Li,Fe)OHFeSe single crystal [19, 26].

XPS was carried out to check the valence state of Fe, which makes it possible to qualitatively estimate charge transfer in the as-synthesized Li0.21Se0.05(EG)0.26FeSe. Figures 4(a) and (b) shows the Fe2p3/2 peaks of pristine FeSe single crystal and the as-synthesized samples, respectively. It is obvious that these peaks are asymmetric. After deduced the background with the Shirley function [27], four peaks can be identified. For the pristine FeSe single crystal, the four peaks are 712.39 eV, 709.30 eV, 707.57 eV and 706.82 eV. Due to the slightly oxidation of the sample surface, the first two peaks at 712.39 eV and 709.30 eV can be attributed to the Fe³⁺ peak from iron oxide and the Fe²⁺ peak from FeO, respectively [28, 29]. The latter two peaks at 707.57 eV and 706.82 eV could be attributed to the Fe²⁺ peak and the metallic phase peak of FeSe, which are consistent with the previous results of FeSe thin film and single crystal [28, 30]. For the as-synthesized sample, the first two peaks remain almost unchanged, at 712.39 eV and 709.30 eV, respectively. However, the latter two peaks are reduced to 707.39 eV and 706.34 eV, respectively, which indicates a decrease in the
Figure 3. (a) The temperature dependent resistivity of the as-synthesized Li$_{0.21}$Se$_{0.05}$(EG)$_{0.26}$FeSe. (b) The temperature dependent magnetic susceptibility of the as-synthesized Li$_{0.21}$Se$_{0.05}$(EG)$_{0.26}$FeSe. (c) The temperature dependence of the resistivity around $T_c$ of Li$_{0.21}$Se$_{0.05}$(EG)$_{0.26}$FeSe under increasing magnetic fields. (d) Temperature dependence of the upper critical field $H_{c2}(T)$ for the as-synthesized Li$_{0.21}$Se$_{0.05}$(EG)$_{0.26}$FeSe.

Figure 4. (a) and (b) The XPS for the Fe2p$_{3/2}$ spectrum taken on pristine FeSe single crystal and the as-synthesized Li$_{0.21}$Se$_{0.05}$(EG)$_{0.26}$FeSe, respectively. The Fe2p$_{3/2}$ peak can be decomposed with four peaks. (c) The superconducting transition temperature ($T_c$) plotted as a function of the central point of the FeSe spectral weight. The valence state of Fe. This result shows that there is charge transfer to the FeSe layer in the Li$_{0.21}$Se$_{0.05}$(EG)$_{0.26}$FeSe sample.

In our previous article, we also investigated the valence state of Fe in (Li,Fe)OHFeSe [31]. Table S2 lists the central point of the FeSe spectral weight taken on the Li$_{0.21}$Se$_{0.05}$(EG)$_{0.26}$FeSe sample and the (Li,Fe)OHFeSe [31]. Here, we use the center of the weight of Fe2p$_{3/2}$ peaks to qualitatively describe the change of Fe valence state. As shown in table S2, the central point of the FeSe spectral weight (Fe2p$_{3/2}$ peaks) gradually decreases from 707.36 eV (pristine FeSe), 706.91 eV (Li$_{0.21}$Se$_{0.05}$(EG)$_{0.26}$FeSe), 706.56 eV (Li$_{0.83}$Fe$_{0.16}$OHFe$_{0.93}$Se) and eventually to 706.34 eV (Li$_{0.70}$Fe$_{0.29}$OHFe$_{0.97}$Se), indicating a qualitative decrease of Fe valence state. With decreasing the valence state of Fe, more charges are transferred to the FeSe layer. Consequently, the superconducting transition temperature is enhanced. In addition, the molecular formulas in table S2 show that the more charge transferred from the blocking layer to the FeSe layer, the higher the superconducting transition temperature ($T_c$), which is consistent with the above results. By the way, compared with the (TBA)$_{0.3}$FeSe precursor, the as-synthesized Li$_{0.21}$Se$_{0.05}$(EG)$_{0.26}$FeSe has less charge transferred to the FeSe layer, so its superconducting transition temperature ($T_c$) becomes lower. Figure 4(c) displays the superconducting transition temperature ($T_c$) plotted as a function of the central point of the FeSe spectral weight. As shown in figure 4(c), the superconducting transition temperature ($T_c$) increases along with the decrease of the central point of the FeSe spectral weight. From the limited XPS data above, it seems that a qualitative relationship can be derived: within a certain doping...
concentration range, the more charges transferred to the FeSe plane, the higher the superconducting transition temperature ($T_c$) will be.

There has been a considerable effort to find the relationship between superconducting transition temperature ($T_c$) and superfluid density, carrier density, and other parameters for a long time for a wide range of superconductors, since the discovery of superconductivity. A linear relation between superconducting transition temperature ($T_c$) and zero-temperature superfluid density is known as Uemura’s law [32], which has been found in many cuprate superconductors [33, 34] and some Fe-based superconductors [11, 35]. In iron-based superconductors, the relationship between superconducting transition temperature ($T_c$) and the anion heights from the Fe layer [36], the bond angles of the Fe-anion tetrahedrons [37] and the carrier density [38] was also investigated. Superconducting transition temperature ($T_c$) exhibits sharp peaks for both of anion height and bond angle variations. In the cuprate superconductors and K-dosed thick FeSe films, firstly superconducting transition temperature ($T_c$) increases with increasing carrier density, whereas in heavily doped samples, superconducting transition temperature ($T_c$) exhibits saturation and suppression with increasing carrier density [32, 38]. Our above result shows that: in bulk FeSe-based superconductors, at a finite doping level, the higher the doping level, the higher the superconducting transition temperature ($T_c$). It indicates that our samples are still in the underdoped range, which is consistent with the result of K-dosed thick FeSe films reported by Wen et al [38]. At higher doping level, the relationship between superconducting transition temperature ($T_c$) and doping level requires further investigation.

4. Conclusions

In summary, we successfully synthesized a hybrid iron-based superconductor Li$_{0.21}$Se$_{0.05}$(EG)$_{0.26}$FeSe via a solvothermal ion exchange technique using (TBA)$_{0.3}$FeSe as a matrix. Without adding additional iron source or using post-processing methods, Li$_{0.21}$Se$_{0.05}$(EG)$_{0.26}$FeSe can directly achieve superconductivity $T_c \sim 30$ K. Compared with the pristine FeSe single crystal, XPS analysis shows a decrease in the valence state of Fe in the as-synthesized Li$_{0.21}$Se$_{0.05}$(EG)$_{0.26}$FeSe, which indicates that enhancement of the $T_c$ is caused by the electron doping effect. We think (TBA)$_{0.3}$FeSe is a good template candidate in the process of synthesizing hybrid iron-based superconductors using ion exchange technique, because the Fe vacancy in the FeSe layer of (TBA)$_{0.3}$FeSe is as little as possible and the unit cell parameter in the c direction are large enough to facilitate ion exchange.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (11888101), the National Key Research and Development Program of the Ministry of Science and Technology of China (2017YFA0303001, 2016YFA0300201 and 2019YFA0704901), the Strategic Priority Research Program of Chinese Academy of Sciences (XDB25000000), Anhui Initiative in Quantum Information Technologies (AHY160000), the Science Challenge Project of China (Grant No. TZ2016004), and the Key Research Program of Frontier Sciences, CAS, China (QYZDYSSW-SLH021).

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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