FeSe-based superconductors with a superconducting transition temperature of 50 K

M Z Shi\(^1\), N Z Wang\(^1\), B Lei\(^1\), JJ Ying\(^1\), C S Zhu\(^1\), Z L Sun\(^1\), J H Cui\(^1\), F B Meng\(^1\), C Shang\(^1\), L K Ma\(^1\) and X H Chen\(^{1,2,3}\)

\(^1\) Hefei National Laboratory for Physical Sciences at the Microscale and Department of Physics, and CAS Key Laboratory of Strongly-coupled Quantum Matter Physics, University of Science and Technology of China, Hefei, Anhui 230026, People’s Republic of China

\(^2\) CAS Center for Excellence in Superconducting Electronics (CENSE), Shanghai 200030, People’s Republic of China

\(^3\) Collaborative Innovation Center of Advanced Microstructures, Nanjing University, Nanjing 210093, People’s Republic of China

E-mail: chenxh@ustc.edu.cn

Keywords: superconductivity, FeSe-based superconductor, intercalation

Abstract

Due to the strong reactivity of alkaline metals and the easy formation of the impurity phase, the superconducting transition temperature (\(T_c\)) of alkaline metals intercalated FeSe is usually limited to 45 K. To avoid the formation of impurity and improve the \(T_c\), we intercalate a more chemically inert organic ion (rather than the chemically reactive alkaline metals) into FeSe single crystal in this report. A new FeSe-based superconductor, namely (TBA)\(_{0.3}\)FeSe, with \(T_c\) of 50 K, is synthesized by intercalating FeSe single crystal with organic ion tetrabutyl ammonium (TBA\(^+\)) via an electrochemical intercalation method, which has the highest \(T_c\) among FeSe-based bulk superconductors. The structure of the organic ion intercalated product consists of the alternate stacking of monolayer FeSe and the organic molecule. The superconductivity of (TBA)\(_{0.3}\)FeSe is confirmed by both the magnetic susceptibility and the transport measurement. It is suggested that the chemically inert organic ion should play a key role in the enhancement of \(T_c\) by avoiding the formation of impurity and disorder in FeSe plane as possible. We also suggest that the TBA\(^+\) intercalated FeSe with well defined shape and higher \(T_c\) offer a good playground for further bulk measurement investigation.

1. Introduction

Simple crystal structure \([1]\), large pressure effect \([2]\), and the highest superconducting transition temperature (\(T_c\)) above 65 K in monolayer FeSe/SrTiO\(_3\) interface \([3]\) make FeSe a fascinating system in iron-based superconductors. Under ambient pressure, the key factor to improve the \(T_c\) of FeSe-based superconductors is to dope electrons to the FeSe plane to form intercalated structure or charge-transfer interface. The former includes the AFe\(_x\)Se\(_2\) (A is alkaline metals) obtained by high temperature solid state reaction \([4]\), \(A\(_x\)(NH\(_3\))\(_2\)Fe\(_2\)Se\(_2\) obtained by liquid-ammonia method \([5–7]\), \(A\(_x\)(Fe)OHFeSe obtained by hydrothermal method \([8–10]\), \(A\(_x\)(M)\(_2\)Fe\(_2\)Se\(_2\) (M is the organic solvent molecule, C\(_6\)H\(_{14}\)N\(_2\) or C\(_2\)H\(_8\)N\(_2\)) obtained by electrochemical intercalation method \([11–13]\) and alkaline metals and organic amine co-intercalated FeSe obtained by sonochemical insertion method \([14]\). The latter includes FeSe/SrTiO\(_3\) interface \([3, 15]\), potassium coating at ultrahigh vacuum \([16, 17]\), and gating method \([18–20]\). In addition, the highest \(T_c\) of the system containing interfaces is usually higher than that of bulk materials \([3, 6, 20, 21]\). How to achieve the similar high \(T_c\) in FeSe-based bulk superconductors as that in the interface system, for example, at 50 K, is a promising and challenging work, which will help us to understand the real role that the interface plays.

Monolayer FeSe/SrTiO\(_3\) interface system has been wildly investigated by STM and ARPES \([22–24]\). However, limited by its intrinsic small size and air sensitivity \([25]\), traditional bulk characterization methods (x-ray diffraction, magnetic susceptibility, transport measurement, nuclear magnetic resonance, specific heat measurement, etc) are very hard to be conducted on these interface systems. In fact, consistent results between
the magnetic susceptibility and transport measurement on monolayer FeSe/SrTiO₃ interface remain to be reported [25, 26]. As a result, synthesizing a high $T_c$ FeSe-based bulk superconductor is of high importance and will offer a new platform for bulk measurement. Our motivation is to find new FeSe-based bulk superconductors with high $T_c$ so as to provide new research opportunity. Therefore, we concentrate our attention on the doped FeSe with intercalated structure rather than the interface system.

There are two ways to synthesize FeSe-based superconductors with intercalated structure. The first is the high temperature solid state reaction method [4]. However, there exists many Fe vacancies in FeSe plane or even phase separation problem in AFe₂Se₃ obtained from high temperature solid state reaction [27, 28]. The above problems lead to a lower $T_c$ of only 32 K and make it a dirty system for physical measurement [4, 27, 28]. The second method using low temperature to synthesize the target compound avoids the above problems. Liquid-ammonia method [5–7], hydrothermal method [8–10], and electrochemical intercalation method [11, 12] are good ways to obtain high $T_c$ sample with intercalated structure. However, it is very hard to be conducted on FeSe single crystal. In fact, although many alkaline metals can be intercalated into the interlayer of FeSe polycrystalline sample by liquid-ammonia method or electrochemical method, only less reactive metal Li rather than Na or K intercalated FeSe single crystal sample is reported [21]. We attribute it to the easier formation of A₂Se₃ (A is the alkaline metals) impurity for Na and K with the increase of reactivity. Recently, the hydrogen intercalated FeSe₉.₃S₀.₇ single crystal is also reported to have an improved $T_c$, although the intercalation is not uniform [29]. The above results inspire us to intercalate new intercalator that is chemically inert in the sequence table of metal activity. For example, the less reactive metal ion or aprotogenic ion.

After the above analysis and consideration, we try to intercalate less reactive metal ion and aprotogenic ion. To our disappointment, the less reactive metal cannot be intercalated into FeSe due to the electrodeposition of the less reactive metal. As for the aprotogenic ion, we do successfully intercalate organic quaternary ammonium ion into FeSe single crystal and obtain exciting results.

Hereafter, we report the successful intercalation of organic ion TBA⁺ into FeSe single crystal. The structure of the intercalated product contains the alternate stacking of monolayer FeSe and the organic molecule, which is evidenced by the x-ray diffraction and TEM. The superconductivity of the intercalated product is confirmed by both the magnetic susceptibility and the transport measurement. Furthermore, by applying external pressure (0–2.46 GPa), the $T_c$ of (TBA)₀.₃FeSe is gradually suppressed to 29.3 K at 2.46 GPa from 50 K at ambient pressure, with a negative pressure effect on superconductivity with $dT_c/dP = -8.4$ K GPa⁻¹. This is the highest $T_c$ among FeSe-based bulk superconductors at ambient pressure.

2. Experiment

KCl (Aladdin, 99.99%) is dried at 200 °C for 10 h in an Argon gas glove box with O₂ and H₂O amount less than 1 ppm to remove the adsorbed water. AlCl₃ (Alfa-Aesar, anhydrous, 99%), Fe powders (Aladdin, AR, 100 mesh), Se powders (Aladdin, 99.999%, 80 mesh), TBAB (Tetrabutyl ammonium bromide, Aladdin, AR, 99.0%), and DMF (N,N-Dimethylformamide, Innochem, 99.9%, extra dry with molecular sieves, Water less than 50 ppm) are used without further purification.

The FeSe single crystal is synthesized using AlCl₃/KCl as the flux according to a reported paper elsewhere [30]. Firstly, KCl (Aladdin, 99.99%) is dried at 200 °C for 10 h in an Argon gas glove box with O₂ and H₂O amount less than 1 ppm to remove the adsorbed water. Secondly, the KCl and AlCl₃ (Alfa-Aesar, anhydrous, 99%) are mixed and fully grounded in the mole ratio of 1:2 in an argon glove box. Thirdly, Fe powders (Aladdin, AR, 100 mesh) and Se powders (Aladdin, 99.999%, 80 mesh) are mixed and grounded at the mole ratio of 1:0.94 and then mixed and grounded with the flux (AlCl₃/KCl) with the mole ratio of Fe₆SeAlCl₃/KCl = 1:0.94:7:3.5. At last, the above mixture is sealed into a silica ampoule and transported from 390 °C to 260 °C for 30 d. Shining crystal can be obtained after the remove of flux (AlCl₃/KCl) by rising products into the deionized water.

The (TBA)₀.₃FeSe is synthesized through an electrochemical intercalation process using FeSe single crystal as the starting materials. Firstly, FeSe single crystal is weighted using a microgram balance (AX 26). Secondly, the weighted FeSe single crystal is fixed onto an indium wire, which is used as the positive electrode. The negative electrode is composed of a silver piece. The electrolyte is obtained by dissolving 6 g TBAB (Aladdin, AR, 99.0%) into 20 ml DMF (Innochem, 99.9%, extra dry with molecular sieves, water less than 50 ppm). At last, the above electrodes are inserted into the electrolyte and a constant current (20–30 μA) is set to pass through the electrolytic cell. During the current passing through the electrolytic cell, the negative electrode loses electrons while the positive electrode obtains electrons. The above electrochemical reaction can be described as the following equations:

$$Br^− \rightarrow e^- + Ag \rightarrow AgBr,$$

(1)
FeSe + xe⁻ + xTBA⁺ → (TBA)ₓFeSe.

The doping amount x in (TBA)ₓFeSe is controlled by adjusting the current passing through the electrolytic cell and the time through the Faraday law. For a fixed doping amount x, the time t needed can be calculated using the following formula

\[ t = \frac{Fnx}{MI}, \]

where \( t \) is the time (s), \( F \) is the Faraday constant (96 485.31 C mol⁻¹), \( m \) is the mass (g) of the FeSe single crystal, \( x \) is the doping amount, \( M \) is the molar mass of FeSe (g mol⁻¹), and \( I \) is the current (A). The \( x \) is set as 0.3 in this report to obtain a fully intercalated product with pure phase and typical discharge curve is shown in figure S1 available online at stacks.iop.org/NJP/20/123007/mmedia. It is necessary to note that the sample is very sensitive to air and moisture.

The x-ray diffraction pattern of the sample is collected on a diffractometer (Rigaku SmartLab 9) equipped with Cu Kα radiation and a fixed graphite monochromator. The Fourier transform infrared (FTIR) spectroscopy is obtained on a Nicolet 8700 infrared spectrometer. The cross-section transmission electron microscopy (TEM) images of FeSe single crystal is captured from a Talos F200X microscope at 200 kV. The TEM images of (TBA)₀.₃FeSe are obtained from a H7700 microscope at 100 kV. The magnetic susceptibility measurement is conducted on a Quantum Design magnetic property measurement system. The resistivity measurement is carried out on a physical properties measurement system with the standard four-terminal method. Resistance measurement under hydrostatic pressure (0–2.46 GPa) is conducted on a Quantum Design high pressure piston-cylinder cell using Daphne 7373 oil as pressure transmitting medium.

3. Results and discussions

Figure 1(a) shows the optical images of the FeSe single crystal and the intercalated product. The morphology of the intercalated FeSe keeps a well defined shape as that of FeSe single crystal. The area of ab plane nearly does not change with only the enlargement in c axis, indicating the intercalation of TBA⁺ ion. We note that such electrochemical intercalation process can be conducted on very big FeSe single crystal with the mass of FeSe larger than 10 mg, which is helpful for bulk measurement. As a demonstration, figure S1 shows the specific discharge curve of a FeSe single crystal with the mass 12.62 mg. The doping amount in (TBA)ₓFeSe is determined by the discharge curve with the integral of current versus time, and \( x \) is 0.3 in our report. We could not intercalate more TBA⁺ ion into the FeSe single crystal by extending discharging time due to the decomposition of the electrolyte. The well defined morphology of the intercalated FeSe is helpful for further physical characterization including resistance measurement. Figure 1(b) shows the FTIR spectroscopy of FeSe, TBAB and (TBA)₀.₃FeSe. There is no obvious absorption band for FeSe, but the FTIR spectroscopy of (TBA)₀.₃FeSe is very similar to that of TBAB, indicating the intercalation of TBA⁺ ion into FeSe. The x-ray diffraction pattern of FeSe and (TBA)₀.₃FeSe is shown in figure 1(c). Before the intercalation of TBA⁺ ion, FeSe single crystal shows a sharp diffraction peak at around 16°, which reflects the distance of the adjacent FeSe layers (0.55 nm) [1]. However, after the intercalation of FeSe with TBA⁺ ion, the diffraction pattern of (TBA)₀.₃FeSe shows series (00l) diffraction peaks and can be indexed with a lattice parameter of 1.55 nm for c axis. In view of the adjacent distance of FeSe layers (0.55 nm) and the size of TBA⁺ ion (0.84–1.19 nm, depending on the orientation of the TBA⁺, more discussion is shown in the supporting information) [31–36], a crystal model with the stacking of monolayer FeSe and TBA⁺ organic molecule is shown in figure 1(d). The structure model of (TBA)₀.₃FeSe will be confirmed using TEM later. At last, it is necessary to note that the (TBA)₀.₃FeSe sample is not stable in the air. More specific data (figure S3) and discussion is shown in the supporting information. More discussion on the structure of the organic ion intercalated FeSe is also shown in the supporting information. The above results indicate that an organic ion intercalated FeSe-based superconductor has been synthesized.

The structure evolution process from FeSe to (TBA)₀.₃FeSe is investigated using TEM, as is shown in figure 2. Before the intercalation of TBA⁺ ion, the distance of the adjacent FeSe layers (figure 2(a)) is measured to be 0.55 nm, which is consistent with the lattice parameter of FeSe crystal in c axis [1]. After the intercalation of TBA⁺, the distance of the adjacent FeSe layers obtained from the TEM image is 1.49 nm (figure 2(b)), which is close to the value 1.55 nm obtained from XRD pattern. The smaller value in TEM image is possible due to the small angle deviation between the e-beam and c axis of (TBA)₀.₃FeSe. We note that the organic ion TBA⁺ is not observed in the TEM image due to the small diffraction contrast and the possible disorder of the organic molecule. These TEM images confirm the structure model shown in figure 1(d).

The magnetic susceptibility and the transport measurement results of (TBA)₀.₃FeSe are shown in figure 3. Figure 3(a) shows the temperature dependent magnetic susceptibility (\( M–T \) curve) under a magnetic field of 5 Oe applied parallel to the crystallographic c axis of (TBA)₀.₃FeSe. There is a sharp transition in \( M–T \) curve at 48 K (figure 3(a) inset), indicating the emergence of superconductivity at 48 K. Furthermore, there is no transition at
Figure 1. Composition and structure characterization of the organic ion TBA$^+$ intercalated FeSe sample. (a) The optical image of FeSe single crystal and (TBA)$_0.3$FeSe; (b) FTIR of FeSe, TBAB and (TBA)$_0.3$FeSe; (c) x-ray diffraction pattern of (TBA)$_0.3$FeSe; (d) the structure model of (TBA)$_0.3$FeSe with hydrogen atom neglected.

Figure 2. The structure evolution process from FeSe to (TBA)$_0.3$FeSe. (a) The TEM image of FeSe; (b) the TEM image of (TBA)$_0.3$FeSe.
around 8.9 K [1], which indicates that the intercalation process is complete and uniform. The difference of the ZFC and FC curves in figure 3(a) is very small, showing nearly no flux pinning effect. Such results indicate that impurities and defects in FeSe plane should be very small and the intercalation process is uniform because a small difference means that the fraction of sample volume where the magnetic flux is pinned due to defects or impurities is small. Figure 3(b) shows the magnetic susceptibility as a function of magnetic field (M–H curve) at 15 K. The M–H curve shows a typical magnetic hysteresis profile of type-II superconductors and the lower critical field \( H_{c1} \) is about 890 Oe. It is necessary to emphasize that the \( T_c \) of pristine FeSe is about 8.9 K [1], which is lower than 15 K. Furthermore, the transport measurement of (TBA)\(_{0.3}\)FeSe is shown in figure 3(c). The resistance of (TBA)\(_{0.3}\)FeSe drops sharply at 50 K, and goes to zero at 42 K. The mid-point superconducting transition temperature \( T_{c\text{mid}} \) obtained from the resistance curve is 48 K, consistent with the \( T_c \) obtained from the magnetic susceptibility curve (figure 3(a)). It is necessary to note that the temperature where the resistance departs from linear is more than 55 K, a little higher than the value observed on the transport measurement result conducted on monolayer FeSe film grown on undoped SrTiO\(_3\) (54.5 K) [37]. The above results suggest that a new FeSe-based superconductor with \( T_{c\text{onset}} \) of 50 K has been synthesized by intercalating FeSe with TBA\(^+\) ion. The transport measurement of (TBA)\(_{0.3}\)FeSe under different magnetic field is also conducted and the result is shown in figure 3(d). Under external magnetic field, the \( T_{c\text{onset}} \) of (TBA)\(_{0.3}\)FeSe nearly does not change but the transition width is enlarged, more systematic measurements are necessary to be conducted in TBA\(^+\) intercalated FeSe.

At last, the resistance measurement under external pressure (0–2.46 GPa) is also conducted and the result is summarized in figure 4. Under external pressure, the \( T_{c\text{onset}} \) of (TBA)\(_{0.3}\)FeSe is gradually suppressed to 29.3 K at 2.46 GPa from 50 K at ambient pressure, with a negative pressure effect with \( \frac{dT_c}{dP} = -8.4 \text{ K GPa}^{-1} \). Such negative pressure effect is frequently observed in the \( T_c \)-pressure phase diagram of the intercalated FeSe-based superconductor. Usually, there are two domes in the intercalated FeSe-based superconductors [38–40]. When the pressure is lower than the critical pressure \( P_c \), the \( T_c \) decreases with the increase of pressure. However, when
the pressure is above $P_c$, the $T_c$ increases as the increase of pressure, going into the SC-II region. The $P_c$ for $\text{Li}_x(\text{NH}_3)_y\text{Fe}_2\text{Se}_2$ and $\text{Li}_{0.8}\text{Fe}_{0.2}\text{OHFeSe}$ is 5 GPa and 2 GPa, respectively [38, 39]. Our negative pressure effect at the pressure range of 0–2.46 GPa indicates that the $P_c$ of $(\text{TBA})_{0.3}\text{FeSe}$ is higher than 2.46 GPa. Measurement under higher pressure needs to be conducted for further investigation.

In the previous work, FeSe-based superconductors obtained from electrochemical intercalation method or liquid-ammonia method shows a smaller $T_c$ in magnetic susceptibility curve [5–7, 11, 12, 41, 42], typically limited to 45 K. Most of the intercalated sample contains lots of grain boundary, which makes it difficult to conduct resistance measurement. Furthermore, compared with the organic ion, the alkaline metals should be very reactive and easier to form the impurity phase $A_2\text{Se}$ ($A$ is alkaline metals) because the smaller ionic radius of the alkaline metals results in a stronger interaction with the FeSe layer. At last, the chemically inert organic ion should avoid the disorder in FeSe plane as possible compared with the alkaline metals intercalated FeSe, which is benefit for the emergence of superconductivity.

We attribute the high $T_c$ in $(\text{TBA})_{0.3}\text{FeSe}$ to the electron doping to FeSe plane and a smaller interaction between the FeSe and organic ion avoiding the formation of impurity phase and disorder in FeSe plane as possible. We note that the FeSe layers show a wave like shape to some extent in the HRTEM image (figure 2(b)), which is possible induced by the disordered distribution and orientation of the TBA$^+$ in the organic layer, such disorder should be against superconductivity. However, such disorder in FeSe plane induced by the disorder in organic layer should be much smaller than that in alkaline metals intercalated case due to the smaller interaction between the organic layer and FeSe than that between alkaline metals and FeSe. It suggests that the TBA$^+$ intercalated FeSe with well defined shape and higher $T_c$ offers a new platform for the investigation of superconducting mechanism and shields new light on the searching for superconductors with higher $T_c$.

At last, we recall that negative ions including small inorganic ion, for example, $\text{AlCl}_4^-$ and $\text{ClO}_4^-$, and large organic ion $\text{TFSI}^-$ have also been reported to be intercalated into the interlayer of 2D layered materials [43–46]. How to dope hole by intercalating such chemically inert negative ion into FeSe will help us to demonstrate a full electronic phase diagram for FeSe-based superconductors, which is very important for the construction of a universal picture for FeSe-based superconductivity.

4. Conclusions

Here, we have shown that the $T_c$ of FeSe could be improved from 8.9 to 50 K by intercalating FeSe with TBA$^+$ ion. The enhanced $T_c$ should be due to the charge transfer of electrons into the FeSe plane [16–20]. The intercalated sample keeps a well defined morphology and makes it possible for bulk measurement to be conducted.

In summary, a new FeSe-based bulk superconductor with $T_c$ of 50 K, is synthesized by intercalating FeSe single crystal with organic ion tetrabutyl ammonium (TBA$^+$) via electrochemical intercalation method, which has the highest $T_c$ among FeSe-based bulk superconductors. The structure of the organic ion intercalated product consists of the alternate stacking of monolayer FeSe and the organic molecule. The chemically inert
organic ion should avoid the formation of impurity and disorder in FeSe plane as possible. Our finding provides a new platform for the understanding of the superconductivity in FeSe-based superconductors.

Acknowledgments

This work is supported by the National Key R&D Program of China (Grant Nos. 2017YFA0303001 and 2016YFA0300201), the Strategic Priority Research Program (B) of the Chinese Academy of Sciences (Grant No. XDB25010100), the National Natural Science Foundation of China (Grant No. 11534010), and Hefei Science Center CAS (2016HSC-IU001).

References

[1] Williams A J, McQueen T M and Cava R J 2009 Solid State Commun. 149 1507–9
[2] Medvedev S A et al 2009 Nat. Mater. 8 630
[3] Wang Q Y et al 2012 Chin. Phys. Lett. 29 037402
[4] Guo J, Jin S, Wang G, Wang S, Zhu K, Zhou T, He M and Chen X 2010 Phys. Rev. B 82 180520
[5] Burzrud M et al 2013 Nat. Mater. 12 15
[6] Ying T P, Chen X L, Wang G, Jin S F, Zhou T T, Lai X F, Zhang H and Wang W Y 2012 Sci. Rep. 2 426
[7] Ying T, Chen X, Wang G, Jin S, Lai X, Zhou T, Zhang H, Shen S and Wang W 2013 J. Am. Chem. Soc. 135 2951–4
[8] Lu X F, Wang N Z, Zhang G H, Luo X G, Ma Z M, Lei B, Huang F Q and Chen X H 2013 Phys. Rev. B 89 020507(R)
[9] Dong X et al 2013 Phys. Rev. B 92 064515
[10] Sun H et al 2015 Inorg. Chem. 54 1958–64
[11] Hatakeda T, Noji T, Kawamata T, Kato M and Koike Y 2013 J. Phys. Soc. Jpn. 82 123705
[12] Hosono S, Noji T, Hatakeda T, Kawamata T, Kato M and Koike Y 2015 J. Phys. Soc. Jpn. 85 031702
[13] Shen S J, Ying T P, Wang G J, Jin S F, Zhang H, Lin Z P and Chen X L 2015 Chin. Phys. B 24 114706
[14] Jin S, Fan X, Wu X, Sun R, Wu H, Huang Q, Shi C, Xi X, Li Z and Chen X 2017 Chem. Commun. 53 9729–32
[15] Tan S et al 2013 Nat. Mater. 12 634
[16] Wen C H et al 2016 Nat. Commun. 7 10840
[17] Miyata Y, Nakayama K, Sugawara K, Sato T and Takahashi T 2015 Nat. Mater. 14 775–9
[18] Lei B, Cui J H, Xiang Z J, Shang C, Wang N Z, Ye G J, Luo X G, Wu T, Sun Z and Chen X H 2016 Phys. Rev. Lett. 116 077002
[19] Shiogai J, Ito Y, Mitushashi T, Nojima T and Tsukazaki A 2016 Nat. Phys. 12 42–6
[20] Miyakawa T et al 2018 Phys. Rev. Mater. 2 031801
[21] Sun S, Wang S, Yu R and Lei H 2017 Phys. Rev. B 96 064512
[22] Zhao L et al 2016 Nat. Commun. 7 10608
[23] He J et al 2014 Proc. Natl Acad. Sci. USA 111 18501–6
[24] Fan Q et al 2015 Nat. Phys. 11 946
[25] Xing Y and Wang J 2015 Chin. Phys. B 24 117404
[26] Zhang Z, Wang Y H, Song Q, Liu C, Peng R, Moler K A, Feng D and Wang Y 2015 Sci. Bull. 60 1301–4
[27] Ksenofontov V, Wortmann G, Medvedev S A, Tsurkan V, Deisenhofer J, Loddfal A and Felser C 2011 Phys. Rev. B 84 180508
[28] Ricci A et al 2011 Phys. Rev. B 84 060511
[29] Cui Y et al 2018 Sci. Bull. 63 11–6
[30] Charreee D, Osadchii E, Kuzmichev T, Lin J Y, Kuzmichev S, Volkova O and Vasiliev A 2013 CrystEngComm 15 1989–93
[31] Gao Q, Giraldo O, Tong W and Subh S L 2001 Chem. Mater. 13 778–86
[32] Omomo Y, Sasaki T, Wang L and Watanabe M 2003 J. Am. Chem. Soc. 125 3568–75
[33] Kim H N, And S W K, Mallouk T E, Schmitt J and Decher G 1997 Chem. Mater. 9 1411–21
[34] Liu Z, Oot K, Kanoh H, Tang W and Tomida T 2000 Langmuir 16 4154–64
[35] Sugimoto W, Iwata H, Yasunaga Y, Murakami Y and Takasu Y 2003 Angew. Chem., Int. Ed. 42 4092–6
[36] Fukuda K, Kato H, Sato J, Sugimoto W and Takasu Y 2009 J. Solid State Chem. 182 2997–3007
[37] Zhang W H et al 2014 Chin. Phys. Lett. 31 017401
[38] Sun J P et al 2018 Nat. Commun. 9 380
[39] Shahi P, Sun J P, Wang S H, Jiao Y Y, Chen K Y, Sun S S, Lei H C, Uwatoko Y, Wang W B and Cheng J G 2018 Phys. Rev. B 97 020508
[40] Sun L et al 2012 Nature 483 67
[41] Alekseeva A M et al 2016 Sci. Rep. 6 25264
[42] Shi M Z, Wang N Z, Lei B, Shang C, Meng F B, Ma I K, Zhang F X, Kuang D Z and Chen X H 2018 Phys. Rev. Mater. 2 074801
[43] Lin M C et al 2015 Nature 520 325–9
[44] Pan C J, Yuan C, Zhu Z, Zhang Q, Huang C J, Lin M C, Angell M, Hwang B J, Kaghazchi P and Dai H 2018 Proc. Natl Acad. Sci. USA 115 5670–5
[45] Beltrop K, Beuker S, Heckmann A, Winter M and Placke T 2017 Energy Environ. Sci. 10 2090–4
[46] Zhang M, Song X, Ou X and Tang Y 2018 Energy Storage Mater. 16 65–84