Single-crystal growth of the iron-based superconductor $\text{La}_{0.34}\text{Na}_{0.66}\text{Fe}_2\text{As}_2$

Yanhong Gu$^{1,2}$, Jia-Ou Wang$^3$, Xiaoyan Ma$^{1,2}$, Huiqian Luo$^1$, Youguo Shi$^1$ and Shiliang Li$^{1,2,4}$

$^1$ Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100190, People’s Republic of China
$^2$ School of Physical Sciences, University of Chinese Academy of Sciences, Beijing 100190, People’s Republic of China
$^3$ Beijing Synchrotron Radiation Facility, Institute of High Energy Physics, Beijing 100049, People’s Republic of China
$^4$ Collaborative Innovation Center of Quantum Matter, Beijing 100190, People’s Republic of China

E-mail: slli@iphy.ac.cn

Received 3 June 2018, revised 14 September 2018
Accepted for publication 25 September 2018
Published 26 October 2018

Abstract
We report single-crystal growth of a $\text{La}_{0.34}\text{Na}_{0.66}\text{Fe}_2\text{As}_2$ iron-based superconductor several millimeters in size. The samples were accidentally obtained in trying to grow $\text{LaFeAsO}_{1−y}\text{F}_y$ ($y \geq 0.8$) single crystals with NaAs and NaF flux. The sample shows both antiferromagnetic and structural transitions at 106 K. The superconducting transition temperature is about 27 K with a superconducting anisotropy of about 1.9. These values and the temperature dependence of the Hall coefficient suggest that $\text{La}_{0.34}\text{Na}_{0.66}\text{Fe}_2\text{As}_2$ belongs to the hole-doped $\text{122}$ families of iron pnictides with the doping level slightly lower than optimal doping. Compared with previous reports on the polycrystalline samples, our results suggest that either the $T_c$ of the this system can be further increased, or the superconducting dome may not be well formed in this system. In either case, the $\text{La}_{0.5−x}\text{Na}_{0.5+x}\text{Fe}_2\text{As}_2$ system provides a new platform to study the antiferromagnetic and superconducting properties of iron-based superconductors.

Supplementary material for this article is available online

Keywords: iron-based superconductors, single-crystal growth, phase diagram

(Some figures may appear in colour only in the online journal)

1. Introduction

Among various families of iron-based superconductors, the so-called ‘122’ iron pnictides have attracted much interest due to the available of high-quality large-sized single crystals [1–4]. The parent compounds of the ‘122’ materials are typically in the form of $\text{A}_n\text{Fe}_2\text{As}_2$ ($\text{A} = \text{alkaline earth metal, e.g. Ca, Sr, Ba}$), showing both antiferromagnetic (AF) and structural transitions [5–7]. Superconductivity can be achieved through either hole or electron doping by substituting $\text{A}_n$ with alkali metal elements (e.g. Na, K) [8–11] and Fe with transition metals (e.g. Co, Ni) [12–14], respectively. The phase diagrams of these materials show very significant electron–hole asymmetry [15–17], i.e. superconductivity is achieved and optimized at different concentrations for electron and hole carriers. While this asymmetry may have underlying physics [15–20], it is hard to rule out the possibility that it may come from the fact that electron and hole doping are obtained by substituting elements at different sites, especially considering that the electron doping involves the change of FeAs layers.

In growing $\text{LaFeAsO}$ single crystals, it has been found that the single crystal of $\text{La}_{0.4}\text{Na}_{0.6}\text{Fe}_2\text{As}_2$ can be accidentally obtained [21]. The latter has the same crystal structure as $\text{A}_n\text{Fe}_2\text{As}_2$ with both La and Na occupying the $\text{A}_n$ site. It shows first-order AF and structural transitions at $T_N = T_s = 125$ K, which is very similar to underdoped hole-doped $\text{Ba}_{1−x}\text{K}_{x}\text{Fe}_2\text{As}_2$ [16]. Filamentary superconductivity is found when the sample is
immersed in water, most likely due to the effect on its surface. It has been thus proposed that the La_{0.5-x}Na_{x}Fe_{2}As_{2} may provide a unique platform to study the electron–hole asymmetry without disturbing the FeAs layer, since both types of carriers may be introduced from the ‘parent’ compound of La$_{0.5}$Na$_{0.5}$Fe$_{2}$As$_{2}$ [21] by changing the ratio of La and Na. Recently, the hole-doped polycrystalline samples for nominal x from 0–0.35 have been successfully synthesized [22]. The phase diagram is similar to those of sodium-doped A$_{x}$Fe$_{2}$As$_{2}$, showing that x for the parent compound of this system is 0, and superconductivity can be achieved for x ≥ 0.15 with the maximum superconducting (SC) transition temperature $T_c$ of about 27 K for x above 0.3. Unfortunately, the electron-doped side, i.e. x < 0, cannot be synthesized. Moreover, the physical properties of this system have not been studied in detail due to the lack of single crystals.

In this paper, we report the single-crystal growth of La$_{0.34}$Na$_{0.66}$Fe$_{2}$As$_{2}$ with $T_c = 27$ K. Both the resistivity and Hall measurements reveal that the AF and structural transitions happen at 106 K, suggesting that the doping level is slightly lower than the optimal doping level [23–26]. The SC anisotropy ratio $\Gamma$ for the upper critical fields is about 1.9, which is similar to those in the hole-doped ‘122’ systems [27–30]. Surprisingly, the $T_c$ of our samples is already the same as the maximum value reported in polycrystalline samples [22], suggesting that either the value of $T_c$ can be further enhanced, or the SC dome may be absent in this system.

2. Experiments

As reported previously, the La$_{0.34}$Na$_{0.66}$Fe$_{2}$As$_{2}$ single crystals were obtained accidentally [21]. Therefore, the following procedure is actually used to grow the LaFeAsO$_{1-x}$F$_x$ single crystals [31, 32]. The starting materials were La (99.7%), As (99.99%), Fe (99.998%), Fe$_2$O$_3$ (99.998%), NaF (99.99%) and FeF$_2$ (98%). LaAs powders were prepared by reacting La chips with As chips at 500°C for 15 h and then 850°C for 15 h. LaAs, Fe$_2$O$_3$, Fe and FeF$_2$ powders were mixed together according to the ratio La: Fe: As: O: F = 1: 1: 1: x with x ranging from 0.8–0.98, and then pressed into pellets. The pellets were put into an Al$_2$O$_3$ crucible and then sealed into an evacuated quartz tube, which was heated at 1150°C for 60 h and then slowly cooled down to room temperature. Flux NaAs was prepared by Na chunk and As chips in an Al$_2$O$_3$ crucible sealed into an evacuated quartz tube, which was heated at 400°C for 20 h and then cooled down to room temperature with intermediate grindings. The nominal LaFeAsO$_{1-x}$F$_x$ pellets, NaAs and NaF were ground together with a molar ratio of 1:17:11 and sealed into a Ta tube under argon atmosphere. To avoid oxidation at high temperature, the Ta tube was sealed into an evacuated quartz tube and heated at 1150°C for 10 h, then slowly cooled down to 700°C at a speed of 2°C/h followed by a fast cooling down to room temperature. Plate-like single crystals were obtained by dissolving the final products of the above procedure in water. The composition and lattice parameters are determined by single-crystal x-ray diffraction (SC-XRD), energy dispersive x-ray (EDX) and inductively coupled plasma (ICP) analysis. The analysis of the EDX spectrum is obtained by averaging the measurements on different areas of several single crystals. The x-ray photoelectron spectroscopy (XPS) was performed on a Beamline 4B9B Photoelectron Spectroscopy Station at the Beijing Synchrotron Radiation Facility. The resistivity and Hall resistivity were measured by the standard four-probe method in a physical property measurement system (Quantum Design). The latter was obtained by averaging the values at the positive and negative fields to avoid the effect of magnetoresistivity. The DC-magnetic susceptibility was measured in a magnetic property measurement system (Quantum Design).

3. Results

The inset of figure 1(a) shows the photo of the as-grown single crystals, which are plate-like with the in-plane size of several millimeters and the thickness of several micrometers. Figure 1 shows the powder XRD result on the in-plane of the crystal, which only shows sharp (0,0,1) peaks similar to those reported in [21]. The magnetic susceptibility measurement shows a clear diamagnetic signal and gives a $T_c$ of 27 ± 0.5 K, as shown in figure 1(b). Both the EDX and ICP measurements suggest that there is neither fluorine nor oxygen elements in the samples and the ratio of (La+Na):Fe:As is close to 1:2:2, suggesting that La$_{0.5-x}$Na$_{x}$Fe$_{2}$As$_{2}$ has been successfully grown. We have also measured the XPS core-level spectra and compared the results with those of LaFeAsO$_{0.74}$F$_{0.26}$ [33], as shown in figures 1(c) and (d). The oxygen peaks between 531 and 532 eV are from the oxygen contamination on the surfaces. The peaks at about 685 and 529 eV are for the fluorine and oxygen core levels, respectively. Apparently, the samples studied here contain neither fluorine nor oxygen.

Figure 2 shows the precession image in (h, k, 0) plane for the SC-XRD measurement. Only well-defined dots are observed, suggesting the high quality of the sample. Table 1 shows the refinement results of the SC-XRD measurement, where the lattice parameters a and c are similar to those of La$_{0.5-x}$Na$_{x}$Fe$_{2}$As$_{2}$ [21, 22]. There are 127 peaks that have been observed with the maximum $(H, K, L) = (5, 5, 16)$. The ratio between La and Na is 0.34:0.66, which is close to that determined by EDX (0.39:0.61) and ICP (0.27:0.73). Considering the uncertainties in the EDX and ICP measurements due to some reasons that have been discussed previously [21], such as the contamination from the flux and the reaction with water, the Na doping level is taken as x = 0.16 according to the SC-XRD, results as done previously for the x = 0.1 single crystal [21]. This doping level is also consistent with results from other measurements, as shown later.

Figure 3(a) shows the temperature dependence of normalized resistance $R_N = R(T)/R(300K)$, which confirms that the $T_c$ is about 27 K. In La$_{0.4}$Na$_{0.6}$Fe$_{2}$As$_{2}$ [21], a small upturn
in $R(T)$ is found at $T_N$, whereas in our case, a broad hump feature can be seen. This is similar to those observed in La$_{0.5-x}$Na$_{0.5+x}$Fe$_2$As$_2$ for $x \geq 0.15$ [22], Ba$_{1-x}$K$_x$Fe$_2$As$_2$ and Ba$_{1-x}$Na$_x$Fe$_2$As$_2$ around optimal doping level [23–25]. The temperature dependence of $dR_N/dT$ shows a small dip at 106 K, which suggests the AF and structural transitions happen at the same temperature as in Ba$_{1-x}$K$_x$Fe$_2$As$_2$ [23].

Figure 3(c) shows the field dependence of the Hall resistivity $\rho_{xy}$ at different temperatures for $H//c$, which all show linear field dependence with positive slopes, confirming that the sample is hole-doped. Accordingly, we derive the temperature dependence of the Hall coefficient $R_H$, as shown in figure 3(d). The quick increase of $R_H$ below 100 K with decreasing temperature is consistent with the establishment of the AF order below $T_N$ [23–26]. The $R_H$ values are also similar to those of the nearly optimally hole-doped ‘122’ materials [23–26].

Figures 4(a) and (b) show the temperature dependence of the resistance for various magnetic fields applied within the ab plane and along the c-axis, respectively. The broadening of the SC transition under the field is not obvious. The suppression of $T_c$ for the field along the c-axis is larger than that for the field within the ab plane. This anisotropy can be further confirmed by checking the angle dependence of the resistance with the field rotating between the ab plane and c-axis, as shown in figure 4(c). Figure 4(d) shows the change of $T_c$ under the field, which gives $dH_{c1}^{ab}(T)/dT \approx 6.8$ T/K and $dH_{c2}^{ab}(T)/dT \approx 3.6$ T/K with $H_{c1}^{ab}$ and $H_{c2}^{ab}$ representing the upper critical fields within the ab plane and along the c-axis, respectively. The value of the zero-temperature upper critical field can be estimated by the Werthamer–Helfand–Hohenberg formula $H_{c2}(0) = -0.693T_c(dH_{c2}/dT)|_{T_c}$. Taking $T_c = 27$ K, the values of the upper critical fields are $H_{c1}^{ab}(0) \approx 128$ T, $H_{c2}^{ab}(0) \approx 67$ T. The SC anisotropy $\gamma = H_{c1}^{ab}/H_{c2}^{ab}$ is about 1.9, which is close to those in the hole-doped ‘122’ materials [27–30].

Figure 5 shows the phase diagram of La$_{0.5-x}$Na$_{0.5+x}$Fe$_2$As$_2$ by summarizing the previous works on both polycrystals and single crystals [21, 22]. We have measured several samples.
from different batches and the values of both $T_N$ and $T_s$ show no change. Therefore, our sample is near the boundary where the AF order disappears and the superconductivity appears. It should be noted that the doping level $x$ in the polycrystalline samples is nominal [22], while those in the single crystals are determined by SC-XRD [21].

4. Discussions

Our results provide the first example of growing SC single crystal of hole-doped La$_{0.5-x}$Na$_{0.5+x}$Fe$_2$As$_2$ with $x = 0.16$. In the previous report [21], the growth of the $x = 0.1$ single crystal is due to the use of the Al$_2$O$_3$ crucible in growing LaFeAsO. While Na is from the NaAs flux, varying its percentage in the mixture does not change $x$ in the final product. It has been suggested that the reaction between the NaAsO$_2$ formed in the growing process [34] and the Al$_2$O$_3$ crucible may consume the oxygen and result in the growth of the La$_{0.4}$Na$_{0.6}$Fe$_2$As$_2$ sample. In our case, the Al$_2$O$_3$ crucible was used in the pretreatment of the LaFeAsO$_{1-y}$F$_y$ pellets, where there is no reaction between these two since the pellets remained the same shape before and after the treatment, and the crucibles remained clear except for a little dark powder left in the contacted areas between the pellets and the crucibles. In the final growing process, the mixture was put into the

**Table 1.** Parameters of La$_{0.34}$Na$_{0.66}$Fe$_2$As$_2$ at room temperature from SC-XRD (see the online supplementary data available at stacks.iop.org/sust/31/125008/mmedia for details)

| Parameter                      | Value               |
|--------------------------------|---------------------|
| Bond precision As-Fe           | 0.001 1 Å           |
| Wavelength                     | 0.710 73 Å          |
| Cell a = 3.867 6(7) Å, c = 12.287(4) Å | α = 90°, β = 90°, γ = 90° |
| Space group                    | I 4/m               |
| Sum formula As4 F0 Fe4 La0.68 Na1.32 O0 Ta0 |  |
| Mu (mm$^{-1}$)                 | 29.431              |
| F000                           | 289.0               |
| h, k, l max                    | 5, 5, 16            |
| Nref                           | 127                 |
| R (reflections)                | 0.042 7(124)        |
| wR2 (reflections)              | 0.130 2(127)        |
| S                              | 1.252               |
| Npar                           | 9                   |

**Figure 2.** Precession image in (h, k, 0) plane for the SC-XRD measurement. All the peaks can be indexed by the I 4/m structure, as shown in table 1.

Supercond. Sci. Technol. 31 (2018) 125008 Y Gu et al
Ta tube without the Al$_2$O$_3$ crucible. Depending on the original fluorine content $y$ in the pellets, LaFeAsO$_{1−y}$F$_y$ and La$_{0.34}$Na$_{0.66}$Fe$_2$As$_2$ single crystals were grown when $x = 0.5$ and $x = 0.8$, respectively [32]. Considering the large amount of NaAs and NaF used, the La$_{0.5−x}$Na$_{0.5+x}$Fe$_2$As$_2$ should be the product from the oxygen-poor or oxygen-free environment. Moreover, it is most likely that the presence of NaF enables more Na doping into the samples. Whether higher Na doping level can be achieved with the change of the ratio between NaAs and NaF needs further study.

The properties of La$_{0.34}$Na$_{0.66}$Fe$_2$As$_2$, such as the coexistence of magnetism and superconductivity, the value and temperature dependence of the Hall coefficient and the SC anisotropy, are similar to those of the nearly optimally hole-doped ‘122’ materials, as shown in the previous section. The coexistence of superconductivity and magnetism is very common in iron-based superconductors. In particular, what we observed in figures 3(b) and (d) are very similar to those in Ba$_{1−x}$K$_x$Fe$_2$As$_2$ [23–26], suggesting that this coexistence in our sample is intrinsic. Near optimal doping level, the effect of magnetic transition on the sample is very weak, so one can only observe it in $dR/dT$, as also shown in Ba$_{1−x}$K$_x$Fe$_2$As$_2$ [23–25]. The dip in figure 3(b) is sharp enough to conclude that the La/Na content should be homogeneous, or one would expect a broad crossover-like feature. In the polycrystal samples [22], the resistivity is an averaged result from different directions and it may not be sensitive enough to see the dip in $dR/dT$.

It is surprising that the value of $T_c$ in our sample ($x = 0.16$) is the same as the maximum value in the polycrystalline samples for $x = 0.3$. This difference may be due to different ways of determining the Na content, but the presence of $T_N$ in the $x = 0.16$ single crystal suggests that it is not the optimally doped sample. Therefore, it is possible that the $T_c$ of the single-crystal samples may be further enhanced, or the La$_{0.5−x}$Na$_{0.5+x}$Fe$_2$As$_2$ system does not have the typical SC dome found in most iron-based superconductors. Moreover, this may also be related to the $C_4$ magnetic phase that has been observed in many hole-doped ‘122’ families [35–39], since if it presents, the $T_c$ in our sample should not be maximum in the La$_{0.5−x}$Na$_{0.5+x}$Fe$_2$As$_2$ system. In any case, the successful growth of SC single-crystal samples provides a new platform to investigate these interesting questions with respect to iron-based superconductors.

5. Conclusions

We have successfully grown the SC La$_{0.34}$Na$_{0.66}$Fe$_2$As$_2$ single crystals by the flux method for the first time, which
were accidentally obtained in growing LaFeAsO$_{1-x}$F$_x$ single crystals. The comparison between previous reports suggests that the ratio of NaAs/NaF may be important in controlling the doping level. The normal-state and SC properties of La$_{0.34}$Na$_{0.66}$Fe$_2$As$_2$ show that its doping level is slightly lower than optimal doping with $T_c$ = 27 K and $T_N$ = 106 K. Our results suggest that the La$_{0.5-x}$Na$_{0.5+x}$Fe$_2$As$_2$ system may be a new platform to study the antiferromagnetism and superconductivity in iron-based superconductors.

**Acknowledgments**

This work is supported by the National Key R&D Program of China (Nos. 2017YFA0302900, 2016YFA0300502, 2017YFA0303103, 2016YFA030604, 2015CB921300), the National Natural Science Foundation of China (Nos. 11674406, 11874401, 11374011, 11774399, 11474330), the Strategic Priority Research Program (B) of the Chinese Academy of Sciences (XDB25000000, XDB07020000, QYZDB-SSW-SLH043) and the China Academy of Engineering Physics (No. 2015AB03). H L is supported by the Youth Innovation Promotion Association of CAS.

**ORCID iDs**

Shiliang Li @ https://orcid.org/0000-0001-7922-3730

---

**Figure 4.** (a) and (b) Suppression of the superconductivity under magnetic fields for $H//ab$ and $H//c$, respectively. (c) Angle dependence of resistance under 9 Tesla from 23.6 to 25.6 K with a 0.2 K step, 26 K and 27 K, for the lines from bottom to top. Zero and ±90 degrees correspond to $H//c$ and $H//ab$, respectively. (d) $T_c$ for the field along $c$-axis (black squares) and within the $ab$ plane (red circles). Straight lines are the linearly fitted results.

**Figure 5.** Phase diagram of La$_{0.5-x}$Na$_{0.5+x}$Fe$_2$As$_2$. AF and SC regimes are from measurements on the polycrystalline samples [22]. Diamond represents $T_N$ of the $x = 0.1$ single crystal [21]. Circle and star represent $T_N$ and $T_c$, respectively, of the $x = 0.16$ single crystal studied here.
References

[1] Hosono H and Kuroki K 2015 Physica C 514 399
[2] Luo X and Chen X 2015 Sci. Chin. Mater. 58 77
[3] Dai P 2015 Rev. Mod. Phys. 87 855
[4] Yi M, Zhang Y, Shen Z X and Liu D 2017 npj Quantum Mater. 2 57
[5] Huang Q, Qiu Y, Bao W, Green M A, Lynn J W, Gasparovic Y C, Wu T, Wu G and Chen X H 2008 Phys. Rev. Lett. 101 257003
[6] Krellner C, Caroca–Canales N, Jesche A, Rosner H, Ormeci A and Geibel C 2008 Phys. Rev. B 78 100504
[7] Ronning F, Klimczuk T, Bauer E D, Volz H and Thompson J D 2008 J. Phys.: Condens. Matter 20 322201
[8] Rotter M, Tegel M and Johrendt D 2008 Phys. Rev. Lett. 101 107006
[9] Goko T et al 2009 Phys. Rev. B 80 024508
[10] Zhao K, Liu Q Q, Wang X C, Deng Z, Lv Y X, Zhu J L, Li F Y and Jin C Q 2011 Phys. Rev. B 84 184534
[11] Shimohara N, Tokiwa K, Fujihisa H, Gotoh Y, Ishida H, Kihou K, Lee C H, Eisaki H, Yoshida Y and Iyo A 2015 Supercond. Sci. Technol. 28 062001
[12] Sefat A S, Jin R, McGuire M A, Sales B C, Singh D J and Mandrus D 2008 Phys. Rev. Lett. 101 117004
[13] Li L J et al 2009 New J. Phys. 11 025008
[14] Ni N, Thaler A, Kracher A, Yan J Q, Bud’ko S L and Canfield P C 2009 Phys. Rev. B 80 024511
[15] Fang L et al 2009 Phys. Rev. B 80 140508
[16] Avci S et al 2012 Phys. Rev. B 85 184507
[17] Neupane M et al 2011 Phys. Rev. B 83 094522
[18] Xu G, Zhang H, Dai X and Fang Z 2008 Europhys. Lett. 84 67015
[19] Dai P, Hu J and Dagotto E 2012 Nat. Phys. 8 709
[20] Gu Y et al 2017 Phys. Rev. Lett. 119 157001
[21] Yan J Q et al 2015 Phys. Rev. B 91 024501
[22] Iyo A, Kawashima K, Ishida S, Fujihisa H, Gotoh Y, Eisaki H and Yoshida Y 2018 J. Am. Chem. Soc. 140 369
[23] Shen B, Yang H, Wang Z S, Han F, Zeng B, Shan L, Ren C and Wen H H 2011 Phys. Rev. B 84 184512
[24] Aswartham S et al 2012 Phys. Rev. B 85 224520
[25] Ohgushi K and Kiuchi Y 2012 Phys. Rev. B 85 064522
[26] Liu Y and Lograsso T A 2014 Phys. Rev. B 90 224508
[27] Ni N, Bud’ko S L, Kreyssig A, Nandi S, Rustan G E, Goldman A I, Gupta S, Corbett J D, Kracher A and Canfield P C 2008 Phys. Rev. B 78 014507
[28] Wang Z S, Luo H Q, Ren C and Wen H H 2008 Phys. Rev. B 78 140501
[29] Sun D L, Liu Y and Lin C T 2009 Phys. Rev. B 80 144515
[30] Haberkorn N, Maiorov B, Jaime M, Usov I, Miura M, Chen G F, Yu W and Civale L 2011 Phys. Rev. B 84 064533
[31] Yan J Q et al 2009 Appl. Phys. Lett. 95 222504
[32] Gu Y et al 2017 Phys. Rev. Lett. 119 157001
[33] Gu Y et al unpublished
[34] Yan J Q, Jensen B, Dennis K W, McCallum R W and Lograsso T A 2011 Appl. Phys. Lett. 98 072504
[35] Avci S et al 2014 Nat. Commun. 5 3845
[36] Böhmmer A E, Hardy F, Wang L, Wolf T, Schweiss P and Meingast C 2015 Nat. Commun. 6 7911
[37] Wang L, Hardy F, Böhmmer A E, Wolf T, Schweiss P and Meingast C 2016 Phys. Rev. B 93 014514
[38] Taddei K M et al 2016 Phys. Rev. B 93 134510
[39] Taddei K M et al 2017 Phys. Rev. B 95 064508