SCIENTIFIC REPORTS

OPEN

Superconductivity in a 122-type Fe-based compound (La,Na,K)Fe₂As₂

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Received: 16 May 2018

Accepted: 11 October 2018

Published online: 14 November 2018

We synthesized a Fe-based superconductor (FeSC), (La,Na,K)Fe₂As₂, and characterized its superconducting properties. It was found that (La,Na,K)Fe₂As₂ has a 122-type (ThCr₂Si₂-type) structure with a space group *I4/mmm* (No. 139), identical to (Ba,K)Fe₂As₂ and (La,Na)Fe₂As₂ but distinct from so-called 1144-type FeSCs such as CaKFe₄As₄ and (La,Na)CsFe₄As₄. The results demonstrate that the formation of the 1144-type phase necessitates the large ionic radius mismatch among the so-called A-site constituent elements of the AFe₂As₂ formula. The lattice constants are $a = 3.850(1)$ Å and $c = 13.21(1)$ Å. The La, Na, and K ions occupy the same atomic site of Wyckoff position 1a. Electrical resistivity and magnetic susceptibility show the superconducting transition at 22.5 K. The transition temperature (T_c) of (La,Na,K)Fe₂As₂ is comparable with that of 122-type (La,Na)Fe₂As₂ and 1144-type (La,Na)AFe₄As₄ (A = Rb, Cs), while being more than 10 K lower than those of typical 122- and 1144-type FeSCs. The results suggest that the random distribution of La³⁺ and Na⁺ ions is the main reason for lower T_c in the AE = (La,Na) 122-type and 1144-type FeSCs.

The discovery of superconductivity in LaFeAs(O,F) in 2008 has triggered the search for new Fe-based superconductors¹. A large number of Fe-based superconductors (FeSCs) with various crystal structures have been reported, such as *Ln*FeAs(O,F) (*Ln* corresponds to rare earth elements) — a 1111-type compound^{1–3}, (AE_{1–x}A_x)Fe₂As₂ (AE = Ca, Sr, Ba, Eu, A = Na, K, Rb) — a 122-type compound^{4,5}, AEAFe₄As₄ (AE = Ca, Sr, Ba, Eu, A = Na, K, Rb) — a 1144-type compound^{6–9}, AFeAs (A = Li, Na) — a 111-type compound¹⁰, (Ca,*Ln*)FeAs₂ — a 112-type compound^{11,12}, and perovskite Fe nictide¹³. The superconducting transition temperature (T_c) reaches as high as ~55 K in bulk materials, and several reports have indicated that T_c is close to 100 K in thin film samples^{14,15}.

Usually, the 122-type and the 1144-type compounds contain divalent (mostly alkali earth) elements. On the other hand, we have recently demonstrated that the combination of monovalent Na and trivalent La successfully substitute the divalent ions and form the 122- and 1144-type superconductors, such as La_{0.5–x}Na_{0.5+x}Fe₂As₂ ((La,Na)Fe₂As₂) and (La,Na)AFe₄As₄ (A = Rb, Cs). For 122-type (La,Na)Fe₂As₂, La_{0.4}Na_{0.6}Fe₂As₂ ($x = 0.1$) is a non-superconductor and exhibits a structural phase transition at 130 K¹⁶. Superconductivity appears between $0.15 \leq x \leq 0.35$ as a consequence of hole carrier doping, with the highest T_c of 27.0 K for $x = 0.3$ ¹⁷. On the other hand, 1144-type (La,Na)AFe₄As₄ exhibit superconductivity by themselves, with T_c around 25 K for (La,Na)RbFe₄As₄ and 24 K for (La,Na)CsFe₄As₄, respectively¹⁸.

The previous results indicate that the combinations of (La,Na) yields the 122-type structure while those of (La,Na,Rb) and (La,Na,Cs) yield the 1144-type structure. From the results, we have pointed out two parameters which possibly determine the preferred crystal structure. The first parameter is the ionic size difference between the AE ions and the A ions, namely, $\Delta r = r_{AE} - r_A$, where r_{AE} and r_A are ionic radii of AE (=Ca, Sr, Ba, Eu, (La,Na)) and A (=Na, K, Rb, Cs) ions. Here large Δr favors the 1144-type structure. The second parameter is the lattice mismatch of the original 122-type compound crystal structure, namely, $\Delta a = |a_{AE122} - a_{A122}|$, where a_{AE122} and a_{A122} are the lattice constants of AEAFe₂As₂ and AFe₂As₂. Here small Δa favors the 1144-type structure. According to the criteria, (La,Na) prefers the 122-type while (La,Na,Rb(Cs)) prefers the 1144-type, respectively.

The combination of (La,Na,K) is interesting in the above regard, since its parameters are close to the border of the above criteria. More specifically, the 122-type structure is expected judging from Δr , while the 1144-type is favored based on Δa . In order to extend the material verify of FeSCs, and more importantly, to determine which parameter indeed governs the crystal structure of real materials, we tried to synthesize (La,Na,K)Fe₂As₂. In this paper, we show that (La,Na,K)Fe₂As₂ forms the 122-type crystal structure. The observed T_c is 22.5 K, which is close to that of 122-type (La,Na)Fe₂As₂ and 1144-type (La,Na)AFe₄As₄ (A = Rb, Cs) FeSCs. We discuss the phase stability of (La,Na,K)Fe₂As₂ and possible reasons for their lower T_c based on the experimental observations.

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Figure 1. Powder X-ray patterns of $(\text{La,Na,K})\text{Fe}_2\text{As}_2$.

Results

Figure 1 shows the powder X-ray diffraction (PXRD) pattern of the synthesized sample. The main phase can be indexed as a tetragonal unit cell with a space group $I4/mmm$ (No. 139), which corresponds to the 122-type (ThCr_2Si_2 -type) structure. Extra reflections, assigned to a minor impurity phase, are identified as LaAs and LaOFeAs (non-superconducting phase)^{1,3,19}. Most importantly, there are no peaks corresponding to $h + k + l = \text{odd}$ number, which are the signature of the 1144-type compounds. La, Na, and K occupy the same atomic position (Wyckoff position $1a$) in its crystal structure. The lattice constants of $(\text{La,Na,K})\text{Fe}_2\text{As}_2$ are $a = 3.850(1)\text{Å}$ and $c = 13.21(1)\text{Å}$. The a and c lattice parameters of $(\text{La,Na,K})\text{Fe}_2\text{As}_2$ are between those of $\text{La}_{0.4}\text{Na}_{0.6}\text{Fe}_2\text{As}_2$ ($a = 3.8669(1)\text{Å}$ and $c = 12.108(1)\text{Å}$) and KFe_2As_2 ($a = 3.8414(1)\text{Å}$ and $c = 13.837(1)\text{Å}$)^{16,17,20}. More specifically, a -axis lengths of these compounds are: $\text{KFe}_2\text{As}_2 < (\text{La,Na,K})\text{Fe}_2\text{As}_2 < (\text{La,Na})\text{Fe}_2\text{As}_2$, while c -axis lengths are $(\text{La,Na})\text{Fe}_2\text{As}_2 < (\text{La,Na,K})\text{Fe}_2\text{As}_2 < \text{KFe}_2\text{As}_2$, respectively.

We synthesized samples with various La/Na ratio and determined their lattice parameters and the chemical compositions (Table S1 and Fig. S1 in Supplementary Information). It turned out that the actual chemical composition does not depend on the initial compositions and yields close to $\text{La}_{0.2}\text{Na}_{0.3}\text{K}_{0.5}\text{Fe}_2\text{As}_2$. Correspondingly, the lattice constants do not depend on the initial composition (Table S1 and Fig. S2). Indeed, the change of the lattice constant is, if any, smaller by one order or more compared with the case of $(\text{La,Na})\text{Fe}_2\text{As}_2$ ¹⁷. The results suggest that the 122-type $(\text{La,Na,K})\text{Fe}_2\text{As}_2$ is stable only under fixed chemical composition. We note that T_c shows no La/Na (nominal) composition dependence, in contrast to the continuous change in T_c for 122-type $(\text{La,Na})\text{Fe}_2\text{As}_2$ ¹⁷.

Figure 2 shows the temperature (T) dependence of the magnetic susceptibility of $(\text{La,Na,K})\text{Fe}_2\text{As}_2$ under an applied magnetic field of $H = 10\text{ Oe}$. The magnetic susceptibility exhibits a marked drop at 22.5 K in both ZFC and FC processes. Since the possible impurity phase LaAs and LaOFeAs do not show superconductivity^{1,3,19}, the superconductivity comes from the main $(\text{La,Na,K})\text{Fe}_2\text{As}_2$ phase. The shielding volume fraction is 102%, a reasonable value as a bulk superconductor²¹.

Figure 3 shows the electrical resistivity of $(\text{La,Na,K})\text{Fe}_2\text{As}_2$ as a function of T . The resistivity data shows the metallic behavior with convex curvature down to low- T . This behavior is also observed in other 122- and 1144-type superconductors^{4–9,17,18}. The residual resistivity ratio, $\text{RRR} = \rho_{300}/\rho_0$, is 5.21, indicating the absence of strong scattering arising from impurities and/or grain boundaries, suitable for investigating their physical properties. As seen in the inset of Fig. 3, the resistivity sharply decreases at 23 K and reaches zero resistivity at 22 K .

Figure 4 shows the electrical resistivity data for $(\text{La,Na,K})\text{Fe}_2\text{As}_2$ under various magnetic fields (H) as functions of T . The onset T_c and the zero resistivity temperature decrease systematically with increasing H . The transition width does not change with H up to the highest H . The superconducting transitions are not completely suppressed under $H \leq 90\text{ kOe}$, indicating that the upper critical field of H_{c2} is very large. A plot of $H_{c2}(T)$ versus $T_c(H)$ is shown in Fig. 5. Here $T_c(H)$ is defined as the midpoint of the superconducting transition for each H , and the horizontal bar indicates the T -range between 10% and 90% of the resistivity transition. $H_{c2}(T)$ shows the linear T -dependence within the measured T - and H -range. The slope, dH_{c2}/dT , is -5.015 T/K . Using the Werthamer-Helfand-Hohenberg (WHH) formula, $H_{c2}(0) = -0.69 (dH_{c2}/dT)|_{T_c}$ for a type-II superconductor²², the upper critical magnetic field at 0 K is estimated to be 80 T . The corresponding coherence length (ξ_0) is calculated to be 20.3 Å , estimated from the relationship between $H_{c2} \sim \Phi_0/2\pi\xi_0^2$, where Φ_0 is quantum flux.

Figure 2. Temperature dependence of the magnetic susceptibility of (La,Na,K)Fe₂As₂.

Figure 3. Temperature dependence of the electrical resistivity of (La,Na,K)Fe₂As₂. Inset shows a magnified view near T_c .

Discussion

The present study demonstrates that (La,Na,K)Fe₂As₂ crystalize into a 122-type crystal structure rather than a 1144-type structure. Figure 6 shows the variation of the 122-type and 1144-type compounds in terms of the ionic size (VIII) difference of $\Delta r = r_{AE} - r_A$ (r_{AE} and r_A are ionic radii of AE and A ions) and the lattice constant difference of the end materials, $\Delta a = |a_{AE122} - a_{A122}|$, (a_{AE122} and a_{A122} are the a -axis lattice constants of AEFe₂As₂ and AFe₂As₂). From previous case studies, we have shown that the 1144-type structure is formed when $\Delta a < 0.07$ Å and $\Delta r < -0.35$ Å. In the case of (La,Na,K)Fe₂As₂, $\Delta a = |a_{(La,Na)122} - a_{K122}|$ is 0.03 Å, which possibly favors the 1144-type structure. On the other hand, $\Delta r = r_{(La,Na)} - r_K = -0.34$ Å, which is at the boundary between the 122-type and the 1144-type phases. Giving that (La,Na,K)Fe₂As₂ forms the 122-type structure, one can conclude that the critical parameter which determines the real crystal structure is Δr , rather than Δa .

In Fig. 7 we summarize $T_c^{\max}$ of 122- and 1144-type superconductors with various alkali metal elements (A = Na, K, Rb, Cs). Clearly T_c with AE = (La,Na) is significantly lower, by nearly 10 K, than other 122- and

Figure 4. Temperature dependence of the electrical resistivity of (La,Na,K)Fe₂As₂ under various magnetic fields up to 90 kOe.

Figure 5. H - T phase diagram of (La,Na,K)Fe₂As₂. Dotted lines show the linear fitting result. Inset shows a magnified view near T_c .

1144-type FeSCs. Furthermore, T_c of (La,Na,K)Fe₂As₂ is 22.5 K, much lower than $T_c = 27$ K for (La,Na)Fe₂As₂. In our previous paper, we pointed out two possible origins for lower T_c in the materials containing AE = (La,Na)¹⁸, namely, the difference in the As-FeAs bond angles, and the random distribution of trivalent La³⁺ and monovalent Na⁺ ions, which possibly causes the strong potential disorder and/or local lattice distortion²³. The local lattice distortion is even larger for (La,Na,K)Fe₂As₂ because of the large contrast in the ionic radii of La³⁺ ($r_{La} = 1.16$ Å), Na⁺ ($r_{Na} = 1.18$ Å) and K⁺ ($r_K = 1.51$ Å)²⁴. The present results suggest that the random distribution of the A/AE ions is responsible for the low T_c in the AE = (La,Na) 122-type and 1144-type FeSCs.

Figure 6. Plot of the difference between the ionic radius (VIII) of AE^{2+} and A^+ ($\Delta r = r_{AE} - r_A$) and the difference (absolute value) between the a -axis lengths of $AEFe_2As_2$ (AE122) and AFe_2As_2 (A122) ($\Delta a = |a_{AE122} - a_{A122}|$) for 122- and 1144-type Fe-based superconductors^{4–9,17,18}. Yellow diamond shows (La,Na,K)Fe₂As₂.

Figure 7. $T_c^{\max}$ of 122-type $AE_{1-x}A_xFe_2As_2$ (circles) and T_c of 1144-type $AEAFe_4As_4$ (squares) ($AE = Ca, Sr, Eu, Ba, (La,Na)$) as a function of alkali metal element ($A = Na, K, Rb, Cs$).

Conclusion

We synthesized (La,Na,K)Fe₂As₂, which has a 122-type structure with $T_c = 22.5$ K. This case study successfully demonstrate that namely, the formation of the 1144-type crystal structure requires sufficient amount of ionic radius difference between the constituent $AE (= Ca, Sr, Eu, (La,Na))$ and $A (= Na, K, Rb, Cs)$ ions. T_c of (La,Na,K)Fe₂As₂ is much lower than that of other 122- and 1144-type FeSCs that do not include trivalent La^{3+} in their composition, and is comparable but slightly lower compared with (La,Na)Fe₂As₂ and (La,Na)AFe₄As₄ ($A = Rb, Cs$), presumably due to the mixture of three elements (La,Na,K) with different valence/ionic radius within a same site.

Methods

Preparation of (La,Na,K)Fe₂As₂ samples. Polycrystalline samples of (La,Na,K)Fe₂As₂ were synthesized using the stainless steel (SS) pipe and cap method^{6,17,18} as we have employed in synthesizing the 122-type and the 1144-type compounds. First, the precursors, LaAs, AAs (A = Na, K), FeAs, and Fe₂As, were prepared via the reaction of La, A, or Fe with As. Then the precursor powders were mixed in a molar ratio of La:Na:K:Fe:As = 0.4:0.6:1:4:4 (nominal composition: La_{0.2}Na_{0.3}K_{0.5}Fe₂As₂, ((La,Na,K)Fe₂As₂) together with 5 at% excess AAs (A = Na, K) to compensate for the evaporation of A and As during the heating process. The mixed powder was pressed into a pellet and put into a SS pipe, which was then sealed using tube-fitting caps. The process was carried out in a nitrogen-filled glove box. The SS pipe was heated to 1143 K for 2 h in a box furnace and quenched to room temperature.

Material characterization. The synthesized sample was characterized by powder X-ray diffraction using a diffractometer with CuK α radiation (Rigaku, Ultima IV) equipped with a high-speed detector system (Rigaku, D/teX Ultra). Intensity data were collected with CuK α radiation over a 2θ range from 5° to 80° at a 0.01° step width. The compositions of the samples were analyzed by an energy dispersive X-ray spectrometry (SwiftED3000) equipped in an electron microscope (TM3000, Hitachi High-Technologies). Magnetic susceptibility measurements were performed using a SQUID magnetometer (Quantum Design, MPMS-XL) at temperatures from 5 to 50 K under an applied magnetic field of $H = 10$ Oe. This measurement was carried out on warming after zero-field cooling (ZFC process) and then on cooling in a field (FC process). The electrical resistivity was measured using a conventional DC four-probe method at temperatures from 5 to 300 K at applied magnetic fields up to 90 kOe, using PPMS (Quantum Design).

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Acknowledgements

We are grateful to Dr. Kunihiro Kihou, Profs. Kohji Kishio, Shin-ichi Uchida, and Hideo Aoki at AIST for fruitful discussions. This work was partially supported by JSPS KAKENHI, Grant Number JP16H06439.

Author Contributions

K.K., A.I. and S.I. performed the sample preparation and their characterization. K.K., A.I., H.O., Y.Y. and E.H. drafted the manuscript. K.K., A.I., H.F. and Y.G. discussed crystal structure of superconductor. All authors reviewed and commented on the manuscript.

Additional Information

Supplementary information accompanies this paper at <https://doi.org/10.1038/s41598-018-34265-2>.

Competing Interests: The authors declare no competing interests.

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