BaTh₂Fe₄As₄(N_{0.7}O_{0.3})₂: An iron-based superconductor stabilized by inter-block-layer charge transfer

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The discovery of superconductivity at $T_c = 26$ K in fluorine-doped LaFeAsO [1] has led to the subsequent findings of dozens of new superconducting materials in the class of Fe-based superconductors (FeSCs) [2,3]. All those FeSCs were found to possess antiferromagnetic-like Fe₂X₂ (X = As, Se) layers which were believed to be the crucial structural motif for the emergence of high-temperature superconductivity. This common feature makes it possible to design a new FeSC with the crystal chemistry [3–5]. For example, with the consideration of the intergrowth of BaFe₂As₂ and BaTi₂As₂O, the new FeSC Ba₂Fe₂Ti₂As₄O ($T_c = 21$ K) was discovered [6]. The block-layer-design approach was also demonstrated to be effective for other class of layered materials, such as Eu₃Bi₂S₄F₄ [7], LaPb-BiS₃O [8], La₅Cu₄As₄O₄Cl₂ [9], Pb₅BiFe₃O₁₀Cl₂ [10], and Bi₄O₄Cu_{1.7}Se_{2.7}Cl_{0.3} [11].

Following the reports of “1144”-type FeSCs, AkAeFe₄As₄ (Ak = K, Rb, Cs; Ae = Ca, Sr, Eu) [12–15], we found the first double-Fe₂As₂-layer FeSC, KCa₂Fe₄As₄F₂ ($T_c = 33$ K) [16]. This finding directly led to the birth of the additional seventeen FeSCs in the “12442”-type family ($T_c = 28$ –37 K) [17–20]. The 12442-type compounds can be viewed as the resultant of intergrowth of non-collapsed ThCr₂Si₂-type (122-type) AkFe₂As₂ and ZrCuSiAs-type (1111-type) CaFeAsF (or, ReFeAsO). Our extensive studies [19,20] demonstrate the importance of lattice match, parametrized by the degree of lattice mismatch, $\mu = 2(a_{1111} - a_{122})/(a_{1111} + a_{122})$, where a_{1111} and a_{122} denote the lattice constants of the constituent 1111-type and 122-type compounds. Impressively, all the target 12442 phases can be synthesized with few exceptions, if

the criterion $\mu < 2\%$ is satisfied [20]. The empirical criterion remains valid for other types of FeSCs with intergrowth structures [4]. Note that the 12442-type FeSCs are all intrinsically hole doped, which means a substantial charge transfer between the two constituent layers. It is not clear whether such a charge transfer is also essential for the formation of the intergrowth phase. A relevant issue is that whether the parent compound (with the Fe formal valence of 2+) and even the electron-doped FeSC of the 12442 type can be realized.

Recently, we succeeded in preparing a new 1111-type superconductor ThFeAsN ($T_c = 30$ K) with fluorite-like Th₂N₂ spacer layers [21]. We also carried out heavy electron doping up to $x = 0.6$ in ThFeAsN_{1-x}O_x, in which a second superconducting region with a maximum $T_c^{\max}$ of 17.5 K at $x = 0.3$ was revealed [22]. The results provide an opportunity to explore an electron-doped 12442-type FeSC. The a axis of ThFeAsN_{1-x}O_x is from 4.037 Å at $x = 0$ to 3.971 Å at $x = 0.6$, all satisfying the criterion $\mu < 2\%$ when BaFe₂As₂ ($a = 3.9625$ Å) [23] is taken as the other component for the target 12442-type compound. The large oxygen solubility limit in ThFeAsN_{1-x}O_x allows a wide range of potential charge transfer between the constituent blocks, which may serve as a glue for the formation of the intergrowth phase [4].

Our trials on the synthesis of BaTh₂Fe₄As₄(N_{1-x}O_x)₂ series samples indicate that the oxygen-free target compound, BaTh₂Fe₄As₄N₂, could not be prepared although $\mu < 2\%$ is satisfied. For samples of $0.1 \leq x \leq 0.7$, the 12442-type phase appears, which strongly suggests the essential role of interlayer charge transfer. The best sample was

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obtained for $x = 0.3$. In this Letter, we focus on the synthesis, crystal structure, and the physical properties of $\text{BaTh}_2\text{Fe}_4\text{As}_4(\text{N}_{0.7}\text{O}_{0.3})_2$. The extended data of the $\text{BaTh}_2\text{Fe}_4\text{As}_4(\text{N}_{1-x}\text{O}_x)_2$ series samples can be seen in the Supplementary information.

Fig. 1 shows the X-ray diffraction (XRD) patterns of $\text{BaTh}_2\text{Fe}_4\text{As}_4(\text{N}_{1-x}\text{O}_x)_2$ with $x = 0$ and 0.3 . The main phases in the $x = 0$ sample are identified to be ThFeAsN and BaFe_2As_2 . The result is confirmed by the electron-probe micro-analysis (see Table S2 in the Supplementary information). In contrast, most of the XRD reflections of the $x = 0.3$ sample can be well indexed with a 12442-type unit cell, $a \approx (a_{1111} + a_{122})/2$ and $c \approx 2c_{1111} + c_{122}$. Small extra reflections at $2\theta = 24.6^\circ$ and 38.3° are probably due to unreacted $\text{ThFeAsN}_{0.7}\text{O}_{0.3}$ [22]. The chemical composition in the crystalline grains of $\text{BaTh}_2\text{Fe}_4\text{As}_4(\text{N}_{0.7}\text{O}_{0.3})_2$ is confirmed by the combined study of wavelength-dispersive X-ray spectroscopy and energy-dispersive X-ray spectroscopy (see Tables S1 and S3 in the Supplementary information). Since the lattice mismatch parameter μ in $\text{BaTh}_2\text{Fe}_4\text{As}_4\text{N}_2$ is 1.8, which satisfies the requirement of lattice match [4,20], the failure of synthesis of $\text{BaTh}_2\text{Fe}_4\text{As}_4\text{N}_2$ conversely suggests the necessity of the charge transfer arising from the oxygen doping. In fact, the 12442-type phase appears in a wide range of the nominal oxygen content ($0.1 \leq x \leq 0.7$, see Fig. S3 in the Supplementary information). The oxygen doping induces extra electrons to each Fe_2As_2 layer, equivalent to a charge transfer of $x/2$ from the $\text{ThFeAsN}_{1-x}\text{O}_x$ block to the BaFe_2As_2 one. This inter-block-layer charge transfer enhances the interlayer Coulomb attractions, which stabilizes the target phase. We conjecture that the stabilization in $\text{Bi}_4\text{O}_4\text{Cu}_{1.7}\text{Se}_{2.7}\text{Cl}_{0.3}$ [11] and $\text{Pr}_4\text{Fe}_2\text{As}_2\text{Te}_{1-x}\text{O}_4$ [25] may also be due to a similar interlayer charge transfer mechanism.

The crystal structure of $\text{BaTh}_2\text{Fe}_4\text{As}_4(\text{N}_{0.7}\text{O}_{0.3})_2$ was determined by the XRD Rietveld refinement using the crystallographic data of $\text{KCa}_2\text{Fe}_4\text{As}_4\text{F}_2$ [16] as the initial input. The refinement is successful (Fig. 2) with the reliable factors R_{wp} , R_p , and R_B all less than 5%, and the result is listed in Table 1. The a axis (3.9886 Å) lies between those of $\text{ThFeAsN}_{0.7}\text{O}_{0.3}$ (3.9955 Å) [22] and BaFe_2As_2 (3.9625 Å) [23], yet it is 0.24% larger than the average of the latter two a axes. Meanwhile, the c axis (29.853 Å) is close to, but 0.33% lower than, the sum of that of BaFe_2As_2 (13.0168 Å) [23] and twice of that of $\text{ThFeAsN}_{0.7}\text{O}_{0.3}$ (2×8.4683 Å) [22]. The shrinkage in c axis confirms stronger interlayer chemical bonding that stabilizes the intergrowth structure. Similar results were seen in other 12442-type compounds [16,19,20]; nevertheless,

Figure 1 XRD patterns of the $\text{BaTh}_2\text{Fe}_4\text{As}_4(\text{N}_{1-x}\text{O}_x)_2$ samples with $x = 0$ (bottom) and 0.3 (top). Shown on the right is the expected crystal structure that is stabilized by the charge transfer from the 1111-type block to the 122-type one.

Figure 2 Rietveld refinement of the powder XRD of $\text{BaTh}_2\text{Fe}_4\text{As}_4(\text{N}_{0.7}\text{O}_{0.3})_2$ from which the crystal structure was determined (shown in the right-hand inset). The middle inset shows the structural parameters of the Fe_2As_2 layer.

the axial ratio ($c/a = 7.485$) of the present compound is remarkably lower than those (7.9–8.2) of all the previous 12442-type materials. The fundamental origin is that, unlike the previous 12442-type FeSCs that are all hole doped, the present 12442-type $\text{BaTh}_2\text{Fe}_4\text{As}_4(\text{N}_{0.7}\text{O}_{0.3})_2$ is actually electron doped (see the Hall measurement below) in relation with the interlayer charge transfer.

In the inset of Fig. 2 we show two structural parameters of the Fe_2As_2 layers, the As heights relative to the Fe plane (h_{As}) and the As–Fe–As bond angle (α). The two parameters were proposed to be associated with T_c [26,27].

Table 1 Crystallographic data for $\text{BaTh}_2\text{Fe}_4\text{As}_4(\text{N}_{0.7}\text{O}_{0.3})_2$ (space group: $I4/mmm$, No. 139) at room temperature. The lattice parameters are $a = 3.9886(4)$ Å and $c = 29.853(3)$ Å

Atom	Site	x	y	z	Occ. ^a	B_{iso} ^b
Ba	2a	0	0	0	1.0	1.7(7)
Th	4e	0.5	0.5	0.20839(4)	1.0	0.12(3)
Fe	8g	0.5	0	0.10757(13)	1.0	0.70(9)
As1	4e	0.5	0.5	0.06399(11)	1.0	0.19(9)
As2	4e	0	0	0.15261(10)	1.0	0.2
N/O	4d	0.5	0	0.25	1.0	1.5

a) The occupancy of each atom was fixed to be 1.0 in the Rietveld refinement. b) The B factors of As2 and N/O were fixed to avoid an unphysical negative value.

The highest T_c tends to appear at $h_{\text{As}} = 1.38$ Å or $\alpha = 109.5^\circ$. Because there are inequivalent sites (As1 and As2) for arsenic atoms in $\text{BaTh}_2\text{Fe}_4\text{As}_4(\text{N}_{0.7}\text{O}_{0.3})_2$, we have two distinct values for h_{As} and α . The values of h_{As1} and h_{As2} are 1.302 and 1.343 Å, respectively, substantially lower than the optimal one [26]. Meanwhile, α_1 and α_2 are 113.7° and 112.1° , obviously larger than the ideal value of 109.5° [27]. The deviations from the optimal values may account for the relatively low T_c value (see the result below). Note that the deviations are the opposite in hole-doped 12442-type FeSCs, the latter of which show larger h_{As} and smaller α values (e.g., $h_{\text{As1}} = 1.405$ Å, $h_{\text{As2}} = 1.436$ Å; $\alpha_1 = 108.0^\circ$, $\alpha_2 = 106.8^\circ$ for $\text{KCa}_2\text{Fe}_4\text{As}_4\text{F}_2$ [16]).

Fig. 3 shows the temperature dependence of electrical resistivity (ρ) for the $\text{BaTh}_2\text{Fe}_4\text{As}_4(\text{N}_{0.7}\text{O}_{0.3})_2$ polycrystalline sample. The $\rho(T)$ data behave as a conventional metal. Unlike the $\rho(T)$ behavior in hole-doped 12442-type FeSCs [16–20], here neither a convex curvature at around 150 K nor a linear temperature dependence below 100 K is seen. The low-temperature ($40 \text{ K} < T < 100 \text{ K}$) normal-state resistivity actually satisfies a power relation, $\rho = \rho_0 + AT^n$. The data fitting yields $\rho_0 = 0.288 \text{ m}\Omega \text{ cm}$, $A = 5.23 \times 10^{-5} \text{ m}\Omega \text{ cm K}^{-1.87}$, and $n = 1.87$, coinciding with a Fermi-liquid behavior. The resistivity starts to drop at 30 K, and zero resistivity is achieved at 20 K. The origin of the broad superconducting transition will be discussed later.

The superconducting resistive transitions shift to lower temperatures under external magnetic fields. Taken the criterions of resistivity drop to 90% and 10%, the upper critical fields were obtained and plotted in the lower inset of Fig. 3. The $\mu_0 H_{c2}(T)$ data are basically linear. The absolute values of the slopes are fitted to be 1.63 and 1.29 T K^{-1} , respectively, both of which are about one order of magnitude smaller than those of the hole-doped 12442-type FeSCs [16,17,28]. The result suggests much longer superconducting coherence length in the electron-

Figure 3 Temperature dependence of resistivity for the $\text{BaTh}_2\text{Fe}_4\text{As}_4(\text{N}_{0.7}\text{O}_{0.3})_2$ polycrystalline sample. The solid pink line represents the data fitting with the formula shown ($n = 1.87$). The upper-left inset shows the superconducting transitions under external magnetic fields, and the lower-right inset plots the upper critical field (H_{c2}) defined in the text.

doped FeSCs. There are no pronounced resistivity tails under magnetic fields, different from the case of hole-doped 12442-type FeSCs [16,17,28]. The phenomenon could be understood by the longer coherence length which leads to more three-dimensional superconductivity in $\text{BaTh}_2\text{Fe}_4\text{As}_4(\text{N}_{0.7}\text{O}_{0.3})_2$.

Fig. 4a shows the superconducting diamagnetic transition in the direct current (DC) magnetic susceptibility (χ). The onset diamagnetic transition temperature at 30 K is seen in the inset, consistent with the resistivity measurement above. The magnetic shielding volume fraction, measured in zero-field-cooling (ZFC) process, is about 100% at temperatures far below T_c , suggesting bulk superconductivity. Nevertheless, the value of $4\pi\chi_{\text{ZFC}}$ becomes very small at temperatures approaching T_c (e.g., -2.4% at 20 K). The possible explanation is that 30-K superconductivity appears at the crystalline-grain surfaces

Figure 4 Temperature dependence of magnetic susceptibility (a) and specific heat (b) for $\text{BaTh}_2\text{Fe}_4\text{As}_4(\text{N}_{0.7}\text{O}_{0.3})_2$. The top inset shows a close-up for the onset superconducting transition. The bottom inset plots the specific-heat difference, from which a bulk superconducting transition at ~ 22 K is revealed.

and/or grain boundaries, and bulk superconductivity seems to emerge at a lower temperature. Indeed, a kink-like anomaly in χ_{FC} can be observed at 23 K, which could be the sign of bulk superconducting transition.

To demonstrate the bulk superconducting transition, we performed the specific-heat (C) measurement. Fig. 4b shows the $C(T)$ data at zero and 9-T fields. No specific-heat anomaly associated with the superconducting transition can be directly seen in the raw data. Nevertheless, the specific-heat difference, $C_{0\text{T}} - C_{9\text{T}}$, clearly shows a peak-like feature at 22 K (the negative background could be due to the contribution from a Schottky anomaly under magnetic fields). The peak height (ΔC) is estimated to be $380 \text{ mJ K}^{-1} \text{ mol}^{-1}$, corresponding to $\Delta C/T_c = 17 \text{ mJ K}^{-2} \text{ mol}^{-1} = 4.3 \text{ mJ K}^{-2} \text{ mol-Fe}^{-1}$. The latter is comparable to the counterpart of $\text{LaFeAsO}_{0.9}\text{F}_{0.1-\delta}$ [29], confirming the bulk superconductivity. One may also see a small anomaly just below 30 K. This seems to be associated with the onset superconducting transitions observed above in $\rho(T)$ and $\chi(T)$.

Fig. 5 shows the Hall resistance as a function of magnetic field for $\text{BaTh}_2\text{Fe}_4\text{As}_4(\text{N}_{0.7}\text{O}_{0.3})_2$. The Hall resistance

Figure 5 Field dependence of Hall resistance of the $\text{BaTh}_2\text{Fe}_4\text{As}_4(\text{N}_{0.7}\text{O}_{0.3})_2$ sample. The inset plots the Hall coefficient (R_H) as a function of temperature.

decreases almost linearly for all the data sets measured at different temperatures. The result indicates dominant electron-type conduction, confirming the electron-doping scenario. The Hall coefficient (R_H) near T_c is $-2.6 \times 10^{-9} \text{ m}^3 \text{ C}^{-1}$, corresponding to a Hall carrier number of 0.14 electrons/Fe within a single-band model (albeit of the multi-band reality). The Hall number coincides with the expected electron concentration of 0.15 electrons/Fe from the nominal composition. The inset of Fig. 5 shows that R_H increases with temperature, probably due to the common multi-band effect in FeSCs. As a comparison, the R_H value of ThFeAsN is $-2.5 \times 10^{-8} \text{ m}^3 \text{ C}^{-1}$ at 50 K [30], an order of magnitude larger, suggesting much fewer electron doping in ThFeAsN than that in $\text{BaTh}_2\text{Fe}_4\text{As}_4(\text{N}_{0.7}\text{O}_{0.3})_2$.

Because the Fe_2As_2 layers in $\text{BaTh}_2\text{Fe}_4\text{As}_4(\text{N}_{0.7}\text{O}_{0.3})_2$ are electron doped, the emergence of superconductivity seems not surprising [2,3]. However, the single- Fe_2As_2 -layer material $\text{ThFeAsN}_{0.85}\text{O}_{0.15}$, which bears the same electron doping level as $\text{BaTh}_2\text{Fe}_4\text{As}_4(\text{N}_{0.7}\text{O}_{0.3})_2$ does, is not superconducting down to 2 K [22]. In fact, the series $\text{BaTh}_2\text{Fe}_4\text{As}_4(\text{N}_{1-x}\text{O}_x)_2$ show similar T_c values (see Figs S5 and S6 in the Supplementary information). These results suggest that the FeSCs with single and double Fe_2As_2 layers can be very different.

To summarize, we have discovered the first electron-doped double- Fe_2As_2 -layer FeSC, $\text{BaTh}_2\text{Fe}_4\text{As}_4(\text{N}_{0.7}\text{O}_{0.3})_2$, whose T_c^{onset} and T_c^{bulk} are 30 and 22 K, respectively. The new FeSC shows contrasting differences in the structural details of the Fe_2As_2 layers and in the normal-state physical properties, compared with the previous hole-doped 12442-type FeSCs. It also exhibits difference with its

single- Fe_2As_2 -layer counterpart, $\text{ThFeAsN}_{0.85}\text{O}_{0.15}$. More importantly, we found that this exceptional 12442-type FeSC was stabilized by the inter-block-layer charge transfer. Such interlayer charge transfer serves as an additionally essential role for the formation of an intergrowth structure. This conclusion could be helpful for the exploration of broader layered materials.

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- Kamihara Y, Watanabe T, Hirano M, *et al.* Iron-based layered superconductor $\text{La}[\text{O}_{1-x}\text{F}_x]\text{FeAs}$ ($x = 0.05\text{--}0.12$) with $T_c = 26$ K. *J Am Chem Soc*, 2008, 130: 3296–3297
- Johnston DC. The puzzle of high temperature superconductivity in layered iron pnictides and chalcogenides. *Adv Phys*, 2010, 59: 803–1061
- Jiang H, Sun YL, Xu ZA, *et al.* Crystal chemistry and structural design of iron-based superconductors. *Chin Phys B*, 2013, 22: 087410
- Wang ZC, Cao GH. Self-doped iron-based superconductors with intergrowth structures. *Acta Phys Sin*, 2018, 67: 207406
- Johrendt D, Hosono H, Hoffmann RD, *et al.* Structural chemistry of superconducting pnictides and pnictide oxides with layered structures. *Z für Kristallographie*, 2011, 226: 435–446
- Sun YL, Jiang H, Zhai HF, *et al.* $\text{Ba}_2\text{Ti}_2\text{Fe}_2\text{As}_4\text{O}$: A new superconductor containing Fe_2As_2 layers and Ti_2O sheets. *J Am Chem Soc*, 2012, 134: 12893–12896
- Zhai HF, Zhang P, Wu SQ, *et al.* Anomalous Eu valence state and superconductivity in undoped $\text{Eu}_3\text{Bi}_2\text{S}_4\text{F}_4$. *J Am Chem Soc*, 2014, 136: 15386–15393
- Sun YL, Ablimit A, Zhai HF, *et al.* Design and synthesis of a new layered thermoelectric material $\text{LaPbBiS}_3\text{O}$. *Inorg Chem*, 2014, 53: 11125–11129
- Eul M, Johrendt D, Pöttgen R. An extension of pnictide oxide chemistry—salt flux synthesis and structure of $\text{La}_3\text{Cu}_4\text{As}_4\text{O}_4\text{Cl}_2$. *Z für Naturforschung B*, 2009, 64: 1353–1359
- Batuk M, Batuk D, Tsirlin AA, *et al.* Layered oxychlorides $[\text{PbBiO}_2]_{A_{n+1}}\text{B}_n\text{O}_{3n-1}\text{Cl}_2$ ($A = \text{Pb/Bi}$, $B = \text{Fe/Ti}$): intergrowth of the hematophanite and sillen phases. *Chem Mater*, 2015, 27: 2946–2956
- Gibson QD, Dyer MS, Whitehead GFS, *et al.* $\text{Bi}_4\text{O}_4\text{Cu}_{1.7}\text{Se}_{2.7}\text{Cl}_{0.3}$: intergrowth of BiO_2CuSe and $\text{Bi}_2\text{O}_2\text{Se}$ stabilized by the addition of a third anion. *J Am Chem Soc*, 2017, 139: 15568–15571
- Iyo A, Kawashima K, Kinjo T, *et al.* New-structure-type Fe-based superconductors: $\text{CaAFe}_4\text{As}_4$ ($A = \text{K, Rb, Cs}$) and $\text{SrAFe}_4\text{As}_4$ ($A = \text{Rb, Cs}$). *J Am Chem Soc*, 2016, 138: 3410–3415
- Kawashima K, Kinjo T, Nishio T, *et al.* Superconductivity in Fe-based compound $\text{EuAFe}_4\text{As}_4$ ($A = \text{Rb and Cs}$). *J Phys Soc Jpn*, 2016, 85: 064710
- Liu Y, Liu YB, Tang ZT, *et al.* Superconductivity and ferromagnetism in hole-doped $\text{RbEuFe}_4\text{As}_4$. *Phys Rev B*, 2016, 93: 214503
- Liu Y, Liu YB, Chen Q, *et al.* A new ferromagnetic superconductor: $\text{CsEuFe}_4\text{As}_4$. *Sci Bull*, 2016, 61: 1213–1220
- Wang ZC, He CY, Wu SQ, *et al.* Superconductivity in $\text{KCa}_2\text{Fe}_4\text{As}_4\text{F}_2$ with separate double Fe_2As_2 layers. *J Am Chem Soc*, 2016, 138: 7856–7859
- Wang Z, He C, Tang Z, *et al.* Crystal structure and superconductivity at about 30 K in $\text{ACa}_2\text{Fe}_4\text{As}_4\text{F}_2$ ($A = \text{Rb, Cs}$). *Sci China Mater*, 2017, 60: 83–89
- Wang ZC, He CY, Wu SQ, *et al.* Superconductivity at 35 K by self doping in $\text{RbGd}_2\text{Fe}_4\text{As}_4\text{O}_2$. *J Phys-Condens Matter*, 2017, 29: 11LT01
- Wang ZC, He CY, Wu SQ, *et al.* Synthesis, crystal structure and superconductivity in $\text{RbLn}_2\text{Fe}_4\text{As}_4\text{O}_2$ ($\text{Ln} = \text{Sm, Tb, Dy, and Ho}$). *Chem Mater*, 2017, 29: 1805–1812
- Wu SQ, Wang ZC, He CY, *et al.* Superconductivity at 33–37 K in $\text{ALn}_2\text{Fe}_4\text{As}_4\text{O}_2$ ($A = \text{K and Cs}$; $\text{Ln} = \text{lanthanides}$). *Phys Rev Mater*, 2017, 1: 044804
- Wang C, Wang ZC, Mei YX, *et al.* A new ZrCuSiAs -type superconductor: ThFeAsN . *J Am Chem Soc*, 2016, 138: 2170–2173
- Li BZ, Wang ZC, Wang JL, *et al.* Peculiar phase diagram with isolated superconducting regions in $\text{ThFeAsN}_{1-x}\text{O}_x$. *J Phys-Condens Matter*, 2018, 30: 255602
- Rotter M, Tegel M, Johrendt D, *et al.* Spin-density-wave anomaly at 140 K in the ternary iron arsenide BaFe_2As_2 . *Phys Rev B*, 2008, 78: 020503
- Izumi F, Momma K. Three-dimensional visualization in powder diffraction. *SSP*, 2007, 130: 15–20
- Katrych S, Rogacki K, Pisoni A, *et al.* $\text{Pr}_4\text{Fe}_2\text{As}_2\text{Te}_{1-x}\text{O}_4$: A layered FeAs-based superconductor. *Phys Rev B*, 2013, 87: 180508
- Mizuguchi Y, Hara Y, Deguchi K, *et al.* Anion height dependence of T_c for the Fe-based superconductor. *Supercond Sci Technol*, 2010, 23: 054013
- Lee CH, Iyo A, Eisaki H, *et al.* Effect of structural parameters on superconductivity in fluorine-free LnFeAsO_{1-y} ($\text{Ln} = \text{La, Nd}$). *J Phys Soc Jpn*, 2008, 77: 083704
- Wang ZC, Liu Y, Wu SQ, *et al.* Giant anisotropy in superconducting single crystals of $\text{CsCa}_2\text{Fe}_4\text{As}_4\text{F}_2$. *Phys Rev B*, 2019, 99: 144501
- Gang M, Xi-Yu Z, Lei F, *et al.* Nodal gap in Fe-based layered superconductor $\text{LaO}_{0.9}\text{F}_{0.1-\delta}\text{FeAs}$ probed by specific heat measurements. *Chin Phys Lett*, 2008, 25: 2221–2224
- Mao H, Wang C, Maynard-Casely HE, *et al.* Neutron powder diffraction study on the iron-based nitride superconductor ThFeAsN . *EPL*, 2017, 117: 57005

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Author contributions Cao GH designed the experiment, discussed the results and wrote the paper. Wang ZC and Wang C also contributed the research idea and discussed the results. Shao YT synthesized the samples, performed the structural characterizations and physical property measurements with assistance from Li BZ, Wu SQ, Wu JF, Ren Z, Qiu SW, and Rao C.

Conflict of interest The authors declare no competing financial interest.

Supplementary information Experimental details and supporting data are available in the online version of the paper.

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BaTh₂Fe₄As₄(N_{0.7}O_{0.3})₂: 块层间电荷转移稳定化铁基超导体

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摘要 本文基于结构设计、采用高温固相反应, 首次合成了电子掺杂“12442”型超导体BaTh₂Fe₄As₄(N_{0.7}O_{0.3})₂. 研究发现, “BaFe₂As₂”和“ThFeAsN_{0.7}O_{0.3}”块层间的电荷转移是稳定该目标化合物的必要条件. 霍尔测量证实该化合物主要为电子型导电. 电阻、直流磁化率和比热测量的综合结果表明, 样品在22 K呈现体超导电性.