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Communication

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$Ba_2Ti_2Fe_2As_4O$: A New Superconductor Containing Fe_2As_2 Layers and Ti_2O Sheets

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Supporting Information

ABSTRACT: We have synthesized a new oxypnictide, $Ba_2Ti_2Fe_2As_4O$, via a solid-state reaction under a vacuum. The compound crystallizes in a body-centered tetragonal lattice, which can be viewed as an intergrowth of $BaFe_2As_2$ and $BaTi_2As_2O$, thus containing Fe_2As_2 layers and Ti_2O sheets. Bulk superconductivity at 21 K is observed after annealing the as-prepared sample at 773 K for 40 h. In addition, an anomaly in resistivity and magnetic susceptibility around 125 K is revealed, suggesting a charge- or spin-density wave transition in the Ti sublattice.

The discovery of Fe-based superconductors (FeSCs)[1] has triggered enormous research activities in recent years.[2] So far, dozens of FeSCs in several crystallographic types have been discovered. The representative systems (with an abbreviation in numbers corresponding to their chemical compositions) are (i) FeSe (11),[3] (ii) LiFeAs (111),[4] (iii) $BaFe_2As_2$ (122),[5] (iv) $K_xFe_{2-y}Se_2$ (122*),[6] and (v) LaFeAsO (1111),[1] which were studied intensively.[2] All these compounds consist of an anti-fluorite-like Fe_2X_2 (X = As, Se) layer; therefore, the Fe_2X_2 layer is considered a crucial structural unit for Fe-based superconductivity. This point is further supported by the fact that some other compounds[7−10] containing the same Fe_2X_2 layers (but with different block layers in between) also show superconductivity or become superconducting upon suitable chemical doping, with relatively high critical temperature (T_c).

To explore new FeSCs with potentially high T_c, therefore, a rational strategy is to build a new structure with the necessary Fe_2X_2 layers by inserting distinct block layers between them. In some oxychalcogenides and oxypnictides,[11−22] layers of "M_2X_2O" (M = Fe, Co or Mn for X = S or Se;[11−15] M = Ti for X = As or Sb[16−22]) are possible candidates for the new building block. The oxypnictides with Ti_2O sheets (a reverse analogue of the CuO_2 sheets in well-known cuprate superconductors) have received considerable interest because of a possible charge-density wave (CDW) or spin-density wave (SDW) transition in the Ti sublattice.[18−21] So, it is appealing to combine Fe_2As_2 layers with Ti_2O sheets. In this Communication, we report our successful adventures in the synthesis and characterization of a new quinary oxypnictide, $Ba_2Ti_2Fe_2As_4O$. The crystal structure is actually an intergrowth of $BaFe_2As_2$ and $BaTi_2As_2O$[22] (see Figure 1), containing both Fe_2As_2 layers and Ti_2O sheets. The new material exhibits bulk superconductivity at 21 K and a possible CDW/SDW transition around 125 K.

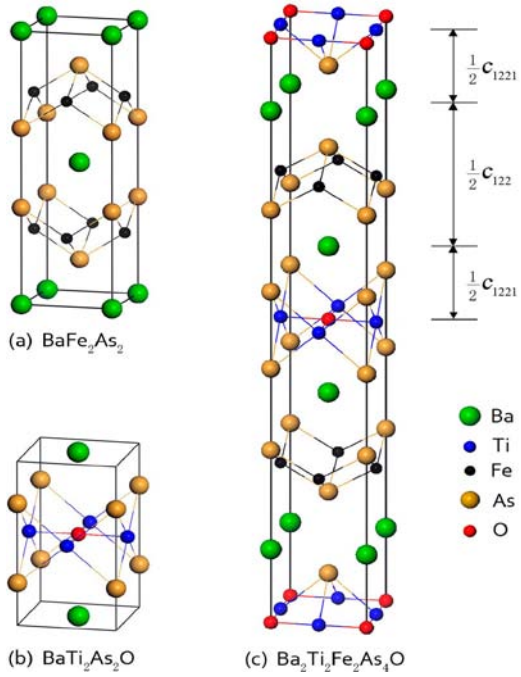

Figure 1. Intergrowth of $BaFe_2As_2$ (a) and $BaTi_2As_2O$ (b) forms a new compound, $Ba_2Ti_2Fe_2As_4O$ (c). The designed "22241" structure has space group *I*4/*mmm*, with an expected *c*-axis of $c_{22241} \approx (c_{122} + 2c_{1221}) \approx 27.57$ Å.

Polycrystalline samples of $Ba_2Ti_2Fe_2As_4O$ were synthesized by solid-state reaction using the starting materials Ba, Ti, Fe, As, and TiO_2 with high-purity (≥99.9%). A stoichiometric mixture of the starting materials was placed into an alumina tube and sealed in an evacuated quartz ampule. The ampule was slowly heated to 1173 K, holding for 24 h. After the first stage of reaction, the product was ground, pelletized, and sintered at 1373 K in a vacuum for 40 h, followed by cooling to room temperature after switching off the furnace. Some of the as-prepared sample was annealed at 773 K for 40 h in a vacuum. Note that all the procedures except for the ampule sealing and heating were performed in a glovebox filled with high-purity argon.

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Powder X-ray diffraction (XRD) was carried out at room temperature using a D/Max-rA diffractometer with Cu Kα radiation and a graphite monochromator. To confirm the structural model, high-resolution transmission electron microscopy (HRTEM) was employed using a FEI Tecnai G^2 F20 scanning transmission electron microscope. The detailed structural parameters were obtained by Rietveld refinement[23] using step-scan (4 s/step) data. The bond-valence sum (BVS)[24] was calculated on the basis of the crystallographic data refined. The electrical resistivity was measured by a standard four-terminal method with silver paste as the contact electrodes. The dc magnetic susceptibility was measured on a Quantum Design Magnetic Property Measurement System (MPMS-5).

The XRD patterns of the sample can be well indexed with a tetragonal unit cell, as shown in Figure 2a, except for several

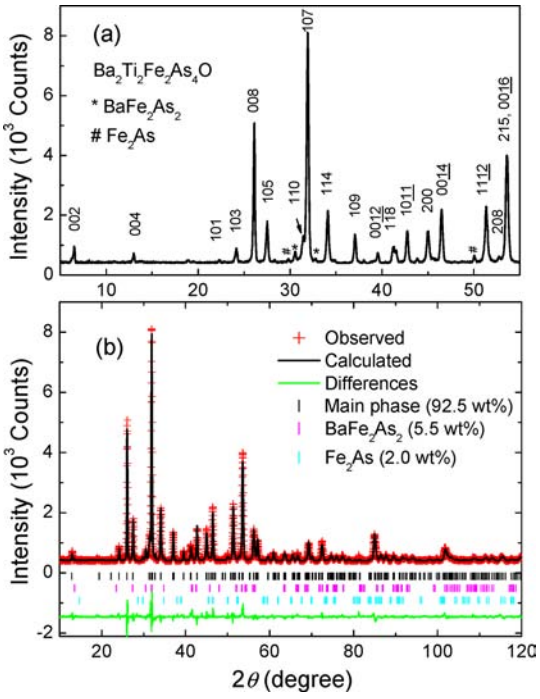

Figure 2. Indexing (a) and Rietveld refinement profile (b) of the powder X-ray diffraction for the as-prepared $Ba_2Ti_2Fe_2As_4O$.

small peaks coming from tiny impurities such as $BaFe_2As_2$, Fe_2As, and $BaTi_2As_2O$. Reflections appear only for the index (h k l) with $h + k + l$ = even numbers, indicating a body-centered lattice. The series of (0 0 l) reflections, especially for those at the lower 2θ region, point to a layered structure with $c \approx 27.3$ Å. Meanwhile, the a-axis value is close to that of $BaTi_2As_2O$.[22] Obviously, the unit cell coincides with the structural model shown in Figure 1c. Furthermore, the HRTEM images shown in Figure 3 directly confirm the crystal structure.

Indeed, Rietveld refinement based on the intergrowth structure shows that the calculated profile well matches the experimental data. The weighted reliable factor R_{wp} and the goodness of fit S are 5.98% and 1.40, respectively, further indicating correctness of the structure.

The refined structural parameters of $Ba_2Ti_2Fe_2As_4O$ are listed in Table 1, for comparison with those of $BaFe_2As_2$ and $BaTi_2As_2O$. The a-axis is 0.48% smaller than that of $BaTi_2As_2O$ and 1.6% larger than that of $BaFe_2As_2$; thus, the Fe_2As_2 layers are more stretched within the basal planes compared with those of $BaFe_2As_2$. On the other hand, the Ti_2O sheets are under

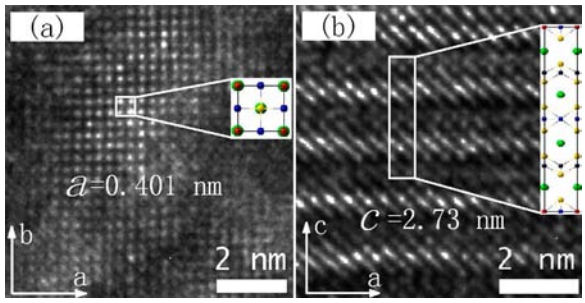

Figure 3. High-resolution transmission electron microscope images of the as-prepared $Ba_2Ti_2Fe_2As_4O$ sample: (a) [001] zone and (b) [010] zone.

Table 1. Crystallographic Data for $Ba_2Ti_2Fe_2As_4O$ at Room Temperature and Comparison of Some Structural Parameters with Those of the Two Related Compounds, $BaFe_2As_2$[5] and $BaTi_2As_2O$[22]

atom	x	y	z	B_{iso} (fixed)
Ba	0	0	0.1321(1)	0.1
Ti	0.5	0	0	0.5
Fe	0.5	0	0.25	0.4
As(1)	0	0	0.2996(1)	0.3
As(2)	0.5	0.5	0.0645(1)	0.3
O	0	0	0	1.0

parameter	$Ba_2Ti_2Fe_2As_4O$	$BaFe_2As_2$	$BaTi_2As_2O$
space group	*I*4/*mmm*	*I*4/*mmm*	*P*4/*mmm*
a (Å)	4.0276(1)	3.9625(1)	4.047(3)
c (Å)	27.3441(4)	13.0168(3)	7.275(4)
V (Å^3)	443.57(2)	204.38(2)	119.2(3)
As height (Å)	1.356(1)	1.360(1)	n/a
As−Fe−As angle (°)	112.1(1)	111.1(1)	n/a
BVS for Ti	3.09	n/a	2.99

compression. It is also noted, for the c-axis direction, that the cell parameter c is 0.81% smaller than the expected value of 27.57 Å for the intergrowth structure. The shrink in c-axis implies enhanced interlayer chemical bonding, which stabilizes the compound.

Figure 4 shows the temperature dependence of electrical resistivity for the $Ba_2Ti_2Fe_2As_4O$ polycrystalline samples. Both the as-prepared and the annealed samples exhibit metallic

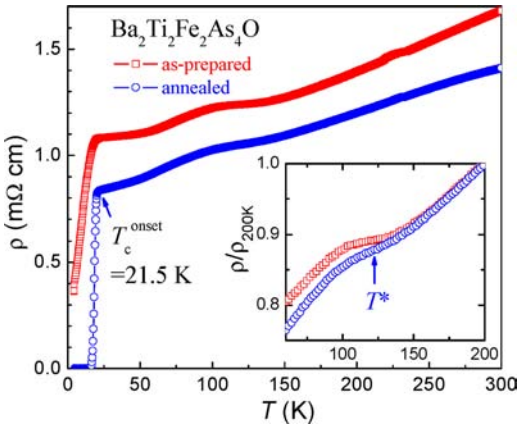

Figure 4. Temperature dependence of electrical resistivity for as-prepared and annealed $Ba_2Ti_2Fe_2As_4O$ samples. The inset displays an expanded plot, showing an anomaly at T^*.

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behavior with resistivity about 1 mΩ·cm, which is comparable to that of $BaFe_2As_2$,[5] but 1 order of magnitude larger than that of $BaTi_2As_2O$.[22] The resistivity exhibits a "shoulder" at $T^* \approx 125$ K. Below $T_c \approx 21$ K, the resistivity decreases rapidly, and it goes to zero at 16 K for the annealed sample, indicating the existence of superconductivity in the system.

The temperature dependence of magnetic susceptibility is shown in Figure 5. Under low magnetic field, signals of magnetic shielding (ZFC curve) and repulsion (FC curve) were observed at low temperature for both samples. The estimated shielding volume fraction at 2 K is 0.7% and 23% for the as-prepared and the annealed samples, respectively. This result corresponds with the broad and sharp transitions in the resistivity measurement. The zero resistance and relatively large shielding fraction in the annealed sample indicate that the new "22241" compound is a superconductor (note that the annealed sample keeps the 22241 phase completely, as confirmed by the XRD measurement). The "loss" of bulk superconductivity in as-prepared samples may be due to the partial occupation of Ti at the Fe site, which could destroy superconductivity.

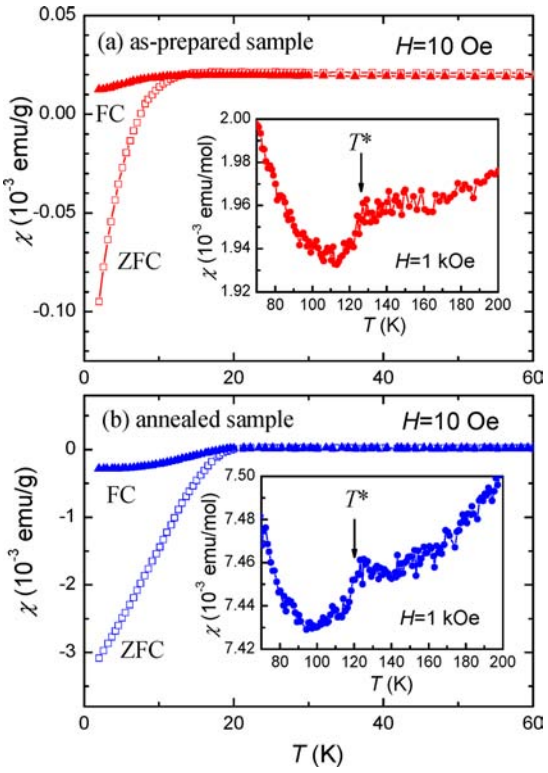

Figure 5. Temperature dependence of magnetic susceptibility for as-prepared (a) and annealed (b) $Ba_2Ti_2Fe_2As_4O$. Both zero-field-cooling (ZFC) and field-cooling (FC) processes were employed. Note that, in the insets, a higher magnetic field (H = 1 kOe) was applied to trace the magnetic anomaly at T^*.

The insets of Figure 5 clearly show a magnetization drop at $T^* \approx 125$ K. This magnetic anomaly is not likely to be associated with the Fe_2As_2 layer which is responsible for superconductivity. Note that a similar drop in magnetic susceptibility was also observed in other compounds with Ti_2X_2O block layers.[17,19−22] In $BaTi_2As_2O$, for example, the transition occurs at a higher temperature of 200 K, which was ascribed to a CDW/SDW ordering.[22] Therefore, the 125 K anomaly in the present system may be due to a suppressed CDW/SDW transition in the Ti_2As_2O block layers. Such a drop in susceptibility suggests a decrease in the density of states at the Fermi level, $N(E_F)$, possibly due to a gap opening.[19] This picture may qualitatively explain the "shoulder" in resistivity shown in Figure 4 because of the loss of $N(E_F)$ for the gap opening.

The appearance of superconductivity without extrinsic doping as well as the suppression of CDW/SDW order (as compared with $BaTi_2As_2O$) in the Ti_2As_2O block layers could be ascribed to the internal compression (from the $BaFe_2As_2$ block) and/or electron transfer from Ti-3d to Fe-3d. Electron transfer is inferred from the variations in the BVS of Ti. Compared with $BaTi_2As_2O$, the BVS value for the 22241 phase increases by 0.10, impling that approximately 10% of Ti-3d electrons transfer to the Fe-3d states. A similar self-doping mechanism was revealed in the $Sr_2VFeAsO_3$ system, where the electrons are transferred from V to Fe.[25]

Some structural parameters, such as the As−Fe−As angle[26] and the As height,[27] were proposed to determine the potential T_c values in the FeSCs. While the two parameters for the present material (see Table 1) are appropriate for producing superconductivity, a higher T_c would be expected by optimizing the As−Fe−As angle and/or the As height through suitable chemical doping and/or applying pressures.

To summarize, a new oxypnictide, $Ba_2Ti_2Fe_2As_4O$, containing both Fe_2As_2 layers and Ti_2O sheets was successfully synthesized. Measurements of resistivity and magnetization indicated bulk superconductivity at 21 K related to the Fe_2As_2 layers, as well as an electronic transition around 125 K possibly associated with a CDW/SDW ordering in the Ti_2O sheets. The coexistence of Fe_2As_2-layer superconductivity and Ti_2O-sheet CDW/SDW ordering is quite rare and deserves further investigation.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

X-ray crystallographic file (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Kamihara, Y.; Hiramatsu, H.; Hirano, M.; Kawamura, R.; Yanagi, H.; Kamiya, T.; Hosono, H. *J. Am. Chem. Soc.* **2006**, *128*, 10012. Kamihara, Y.; Watanabe, T.; Hirano, M.; Hosono, H. *J. Am. Chem. Soc.* **2008**, *130*, 3296.

(2) Johnston, D. C. *Adv. Phys.* **2010**, *59*, 803. Stewart, G. R. *Rev. Mod. Phys.* **2011**, *83*, 1589.

(3) Hsu, F.-C.; Luo, J.-Y.; Yeh, K.-W.; Chen, T.-K.; Huang, T.-W.; Wu, P. M.; Lee, Y.-C.; Huang, Y.-L.; Chu, Y.-Y.; Yan, D.-C.; Wu, M.-K. *Proc. Natl. Acad. Sci. U.S.A.* **2008**, *105*, 14262.

(4) Wang, X. C.; Liu, Q. Q.; Lv, Y. X.; Gao, W. B.; Yang, L. X.; Yu, R. C.; Li, F. Y.; Jin, C. Q. *Solid State Commun.* **2008**, *148*, 538.
(5) Rotter, M.; Tegel, M.; Johrendt, D. *Phys. Rev. Lett.* **2008**, *101*, 107006.
(6) Guo, J.; Jin, S.; Wang, G.; Wang, S.; Zhu, K.; Zhou, T.; He, M.; Chen, X. *Phys. Rev. B* **2010**, *82*, 180520(R).
(7) Zhu, X.; Han, F.; Mu, G.; Zeng, B.; Cheng, P.; Shen, B.; Wen, H. H. *Phys. Rev. B* **2009**, *79*, 024516. Shirage, P. M.; Kihou, K.; Lee, C. H.; Kito, H.; Eisaki, H.; Iyo, A. *J. Am. Chem. Soc.* **2011**, *133*, 9630.
(8) Ogino, H.; Matsumura, Y.; Katsura, Y.; Ushiyama, K.; Horii, S; Kishio, K; Shimoyama, J. *Supercond. Sci. Technol.* **2009**, *22*, 075008. Zhu, X.; Han, F.; Mu, G.; Cheng, P.; Wen, H. H. *Phys. Rev. B* **2009**, *79*, 220512(R).
(9) Kawaguchi, N.; Ogino, H.; Shimizu, Y.; Kishio, K.; Shimoyama, J. *Appl. Phys. Exp.* **2010**, *3*, 063102.
(10) Ni, N.; Allred, J. M.; Chen, B. C.; Cava, R. J. *Proc. Natl. Acad. Sci. U.S.A* **2011**, *108*, E1019.
(11) Mayer, J. M.; Schneemeyer, L. F.; Siegrist, T.; Waszczak, J. V.; Dover, B. V. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1645.
(12) Kabbour, H.; Janod, E.; Corraze, B.; Danot, M.; Lee, C.; Whangbo, M. H.; Cario, L. *J. Am. Chem. Soc.* **2008**, *130*, 8261.
(13) He, J. B.; Wang, D. M.; Shi, H. L.; Yang, H. X.; Li, J. Q.; Chen, G. F. *Phys. Rev. B* **2011**, *84*, 205212.
(14) Wang, C.; Tan, M. Q.; Feng, C. M.; Ma, Z. F.; Jiang, S.; Xu, Z. A.; Cao, G. H.; Matsubayashi, K.; Uwatoko, Y. *J. Am. Chem. Soc.* **2010**, *132*, 7069.
(15) Ni, N.; Climent-Pascual, E.; Jia, S.; Huang, Q.; Cava, R. J. *Phys. Rev. B* **2010**, *82*, 214419.
(16) Adam, A; Schuster, H. -U. *Z. Anorg. Allg. Chem.* **1990**, *584*, 150.
(17) Axtell, E. A., III; Ozawa, T.; Kauzlarich, S. M.; Singh, R. R. P. *J. Solid State Chem.* **1997**, *134*, 423.
(18) Pickett, W. E. *Phys. Rev. B* **1998**, *58*, 4335.
(19) Ozawa, T. C.; Kauzlarich, S. M.; Bieringer, M.; Greedan, J. E. *Chem. Mater.* **2001**, *13*, 1804.
(20) Liu, R. H.; Tan, D.; Song, Y. A.; Li, Q. J.; Yan, Y. J.; Ying, J. J.; Xie, Y. L.; Wang, X. F.; Chen, X. H. *Phys. Rev. B* **2009**, *80*, 144516.
(21) Liu, R. H.; Song, Y. A.; Li, Q. J.; Ying, J. J.; Yan, Y. J.; He, Y.; Chen, X. H. *Chem. Mater.* **2010**, *22*, 1503.
(22) Wang, X. F.; Yan, Y. J.; Ying, J. J.; Li, J. Q.; Zhang, M.; Xu, N.; Chen, X. H. *J. Phys.: Condens. Matter* **2010**, *22*, 075702.
(23) Izumi, F.; Ikeda, T. *Mater. Sci. Forum* **2000**, *321*, 198.
(24) Brown, I. D.; Altermatt, D. *Acta Crystallogr.* **1985**, *B41*, 244. Brese, N. E.; O'Keeffe, M. *Acta Crystallogr.* **1991**, *B47*, 192.
(25) Cao, G. H.; Ma, Z. F.; Wang, C.; Sun, Y. L.; Bao, J. K.; Jiang, S.; Luo, Y. K.; Feng, C. M.; Zhou, Y.; Xie, Z.; Hu, F. C.; Wei, S. Q.; Nowik, I.; Felner, I.; Zhang, L.; Xu, Z. A.; Zhang, F. C. *Phys. Rev. B* **2010**, *82*, 104518.
(26) Lee, C. H.; Iyo, A.; Eisaki, H.; Kito, H.; Fernandez-Diaz, M. T.; Ito, T.; Kihou, K.; Matsuhata, H.; Braden, M.; Yamada, K. *J. Phys. Soc. Jpn.* **2008**, *77*, 083704. Zhao, J.; Huang, Q.; Cruz, C. d. l.; Li, S.; Lynn, J. W.; Chen, Y.; Green, M. A.; Chen, G. F.; Li, G.; Li, Z.; Luo, J. L.; Wang, N. L.; Dai, P. *Nat. Mater.* **2008**, *7*, 953.
(27) Mizuguchi, Y.; Hara, Y.; Deguchi, K.; Tsuda, S.; Yamaguchi, T.; Takeda, K.; Kotegawa, H.; Tou, H.; Takano, Y. *Supercond. Sci. Technol.* **2010**, *23*, 054013.