

Novel Polymorphic Phase of BaCu₂As₂: Impact of Flux for New Phase Formation in Crystal Growth

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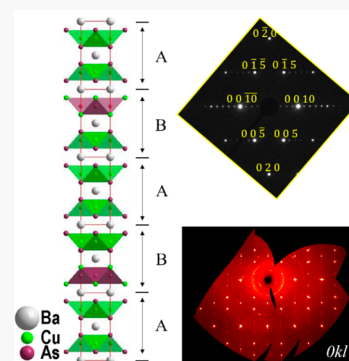


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ABSTRACT: In this work, we have thoroughly studied the effects of flux composition and temperature on the crystal growth of the BaCu₂As₂ compound. While Pb and CuAs self-flux produce the well-known α -phase ThCr₂Si₂-type structure ($Z = 2$), a new polymorphic phase of BaCu₂As₂ (β -phase) with a much larger c lattice parameter ($Z = 10$), which could be considered an intergrowth of the ThCr₂Si₂- and CaBe₂Ge₂-type structures, has been discovered via Sn flux growth. We have characterized this structure through single-crystal X-ray diffraction, transmission electron microscopy (TEM), and scanning transmission electron microscopy (STEM) studies. Furthermore, we compare this new polymorphic intergrowth structure with the α -phase BaCu₂As₂ (ThCr₂Si₂ type with $Z = 2$) and the β -phase BaCu₂Sb₂ (intergrowth of ThCr₂Si₂ and CaBe₂Ge₂ types with $Z = 6$), both with the same space group $I4/mmm$. Electrical transport studies reveal p-type carriers and magnetoresistivity up to 22% at 5 K and under a magnetic field of 7 T. Our work suggests a new route for the discovery of new polymorphic structures through flux and temperature control during material synthesis.



INTRODUCTION

The discovery of Fe-based superconductors¹ has spurred worldwide efforts not only to understand the interplay between magnetism and superconductivity but also to search for new types of superconductors with similar structures. Among them, the so-called 122 family, in which the parent compounds have the composition AFe₂As₂ ($A = \text{Ca, Sr, Ba, Eu, K, Rb, and Cs}$) with the tetragonal ThCr₂Si₂-type structure and space group $I4/mmm$, is probably the most studied and exploited^{2–9} due to the availability of high-quality single crystals allowing a broad range of advanced characterization and the large materials base in this particular crystal-structure family. Many techniques have been developed to grow the crystals, and among them, high-temperature flux growth is widely used for obtaining single crystals of 122-family compounds. Different types of flux, from metal flux, such as Sn¹⁰ and In,^{11,12} to self-flux (*i.e.*, the flux is consumed and is partially incorporated into the resulting crystals), such as FeAs¹³ and KAs,¹⁴ are used. However, single crystals grown by metal flux sometimes show different properties than those obtained from self-flux. For instance, the spin density wave transition is significantly suppressed in the Sn-flux-grown BaFe₂As₂^{10,15} due to the inclusion of small amounts of Sn into the lattice. BaFe₂As₂ crystals grown from In flux^{11,12} even show a superconducting transition with a full drop in resistivity but without diamagnetic screening at various values of T_c (19–23 K). Whether such superconductivity is induced by the incorporation of In into the lattice remains unclear at this moment. Annealing studies indicate that such a

transition is not related to lattice distortion or strain, in contrast to similar superconducting behavior observed in FeAs-flux-grown SrFe₂As₂.¹⁶ X-ray crystallography, when paired with precise chemical analysis, is an effective tool^{15,17–19} for unambiguously determining the quantity and location of Sn in the lattice.

In order to obtain further insight into the physics of Fe pnictides, much research effort has also been devoted to searching for superconductivity in the Fe-free pnictide systems with similar structures, initially in those with ThCr₂Si₂-type structures and later expanding to those with the variant CaBe₂Ge₂- and BaAl₄-type structures.^{20–37} In fact, many new superconductors have been discovered in these families, but with a different Fermi surface topology than the Fe-based superconductors.^{20,21,23,27–31} The Cu-based 122 pnictides are another family of compounds that initially attracted attention since they could possibly serve as a bridge between the cuprate and Fe-based superconductors.^{38–42} Unfortunately, no superconductivity has been discovered in these compounds thus far. Both calculations and angle-resolved photoemission spectroscopy studies of BaCu₂As₂ have shown that its Cu 3d bands are

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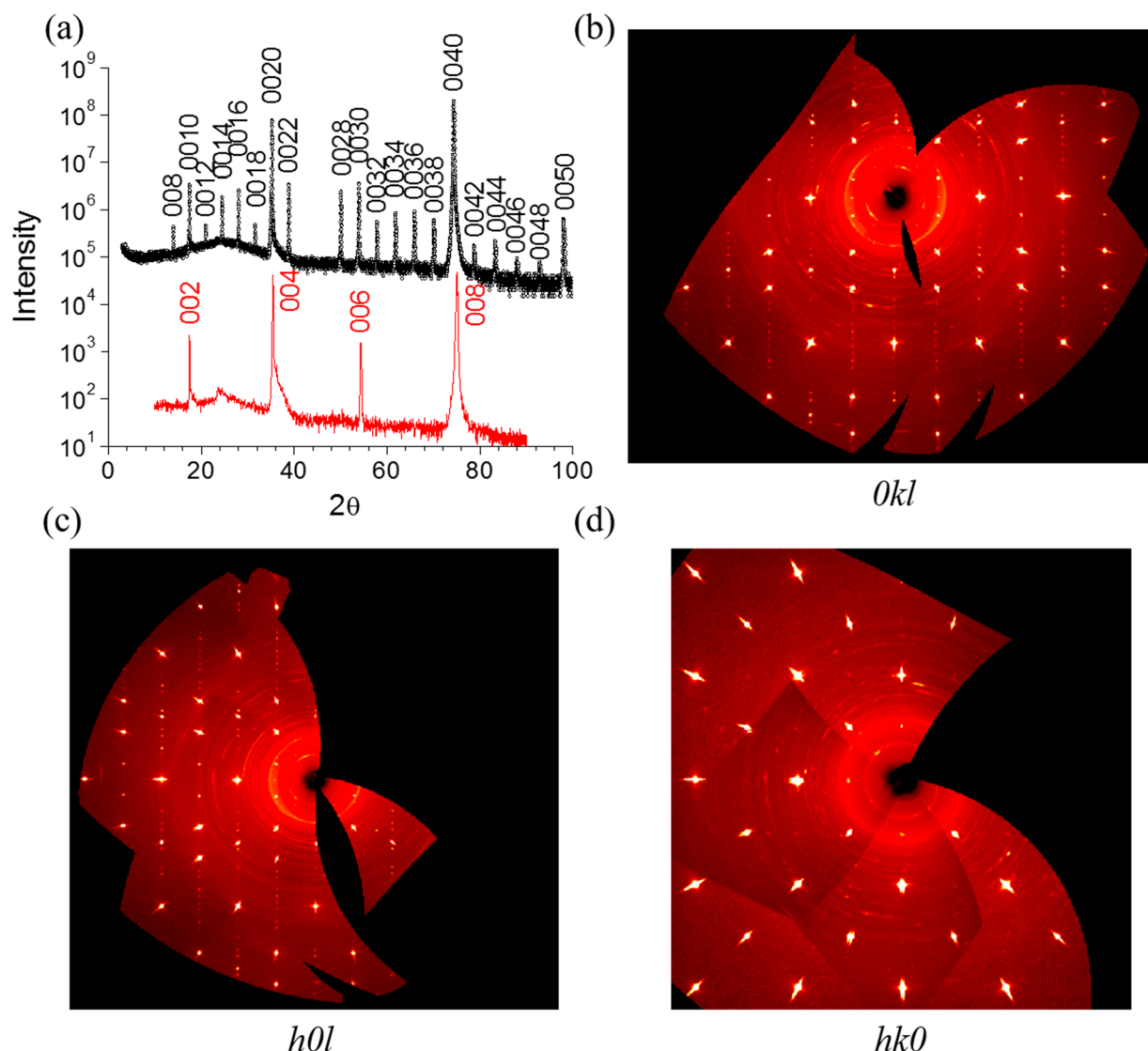


Figure 1. (a) XRD patterns of α -BaCu₂As₂ (red) and β -BaCu₂As₂ (black) along the (00*l*) orientation using the logarithmic scale; the intensity of the β -BaCu₂As₂ pattern is offset along the ordinate axis for better comparison. (b–d) Integrated precession images from the full X-ray single-crystal data collection of β -BaCu₂As₂ along (0*kl*), (*h*0*l*), and (*hk*0), respectively, showing the superstructure along the *c* axis.

far below the Fermi level and thus have a weak electronic correlation.^{43–46} Nevertheless, this family of compounds is rather interesting from a structural perspective. The As-based compounds ACu₂As₂ (A = Ca, Sr, Ba, and Eu) all crystallize with a body-centered tetragonal ThCr₂Si₂ structure, but the Sb-based compounds ACu₂Sb₂ (A = Sr, Ba, and Eu) mainly crystallize in the related primitive-tetragonal CaBe₂Ge₂-type structure.^{47–49} For BaCu₂Sb₂, a very interesting intergrowth structure with ordered ThCr₂Si₂ and CaBe₂Ge₂ types of unit cells has been reported.^{38,39} The formation of such an intergrowth structure appears to be independent of flux (self-flux or Pb flux) but rather depends on the synthetic temperature profile. This finding triggered our interest in exploring the effects of flux and temperature on BaCu₂As₂ crystal growth. Here, we report on a new polymorphic phase of BaCu₂As₂ that is different from the BaCu₂Sb₂ polymorph and has a much larger *c* lattice parameter (51.05 compared to 32.6 Å). This new structure has been unambiguously verified by single-crystal diffraction, TEM, and STEM studies. The effects of starting materials, flux, temperature profiles, and possible

flux inclusion into the lattice were also thoroughly studied. Our results suggest that the discovery of new polymorphic phases is possible through carefully controlled flux conditions. Electrical transport studies of this new phase reveal that it exhibits p-type carriers and magnetoresistivity up to 22% at 5 K and under a magnetic field of 7 T.

EXPERIMENTAL SECTION

Materials Synthesis and Single-Crystal Growth. Ba rods (99.5%), Cu powder (99.99%), As lumps (99.999%), Sn shots (99.99%), and Pb ingots (99.999%) from Alfa Aesar were used as received for our reactions. Three different fluxes were used for our crystal growth: CuAs, Sn, and Pb. The X-ray powder pure CuAs precursor was synthesized through heating a stoichiometric mixture of Cu and As in a sealed quartz tube at 800 °C for 2 days and in two iterations. The ThCr₂Si₂-type α -phase BaCu₂As₂ single crystals were grown by either the self-flux method using CuAs as the flux with Ba:CuAs in a molar ratio of 1:4 or the Pb flux method with a molar ratio of Ba:Cu:As:Pb = 1:2:2:10. In each case, the materials were sealed in an evacuated quartz tube using an alumina crucible as a container and subsequently heated up overnight to a target temperature. For CuAs flux, the assembly was heated up to 1080

Table 1. Crystallographic Data for α -BaCu₂As₂ and β -BaCu₂As₂

	α -BaCu ₂ As ₂ (ThCr ₂ Si ₂ type)	β -BaCu ₂ As ₂
empirical formula	α -BaCu ₂ As ₂ (ThCr ₂ Si ₂ type)	β -BaCu ₂ As ₂
space group	<i>I4/mmm</i> (No.139)	<i>I4/mmm</i> (No.139)
unit-cell dimensions	$a = 4.445(2)$ Å, $c = 10.073(6)$ Å	$a = 4.425(1)$ Å, $c = 51.05(1)$ Å
unit-cell volume	$199.0(2)$ Å ³	$999.7(4)$ Å ³
Z	2	10
absorption coefficient	36.629 mm ⁻¹	36.462 mm ⁻¹
$F(000)$	360	1800
crystal size	$0.11 \times 0.08 \times 0.05$ mm ³	$0.08 \times 0.08 \times 0.01$ mm ³
theta range for data collection	4.05 to 29.18°	1.596 to 28.288°
reflections collected	494	3140
independent reflections	$100 [R_{\text{int}} = 0.0342]$	$445 [R_{\text{int}} = 0.0327]$
max and min transmission	0.746, 0.355	0.746, 0.287
data/restraints/parameters	100/0/9	445/0/35
goodness-of-fit on F^2	1.225	1.136
Final R indices [$I > 2\sigma$]	$R_1 = 0.0308$, $wR_2 = 0.0813$	$R_1 = 0.0378$, $wR_2 = 0.1250$
R indices (all data)	$R_1 = 0.0311$, $wR_2 = 0.0815$	$R_1 = 0.0365$, $wR_2 = 0.1235$
extinction coefficient	$0.016(4)$	$0.0014(2)$
largest diff. peak and hole	$1.68/-1.26$	$2.04/-1.53$

°C for 24 h and then slowly cooled at a rate of 3 °C/h down to 800 °C. For the Pb flux, the assembly was heated up to 1100 °C for 24 h and then slowly cooled at a rate of 3 °C/h down to 600 °C. The new polymorphic β -phase of BaCu₂As₂ was synthesized using Sn flux, in which Ba:CuAs:Sn in a 1:4:30 molar ratio was sealed in an evacuated quartz tube with an alumina crucible, heated up to 1100 °C for 24 h, and then slowly cooled at a rate of 3 °C/h down to 550 °C. Large plate-like crystals with a typical size of $3 \times 3 \times 0.5$ mm³ were obtained by decanting the flux with a centrifuge at high temperature (800 °C for CuAs flux, 600 °C for Pb flux, and 550 or 500 °C for Sn flux) using quartz wool as a filter. It should be noted that needle-like BaCu₁₀As₄ crystals are also produced as byproducts during CuAs-flux growth and can be easily separated from the plate-like α -phase BaCu₂As₂ due to their different morphologies. To fully investigate the growth conditions for the new β -phase BaCu₂As₂, several growth parameters (e.g., precursor materials and their concentrations) and growth temperature profiles have been tested, with results provided below.

Characterization. X-ray Diffraction. Powder X-ray diffraction (XRD) was performed using a Rigaku Smartlab diffractometer with Cu $K\alpha$ radiation. Single-crystal X-ray diffraction was performed using a Bruker SMART diffractometer equipped with an Apex II area detector and an Oxford Cryosystems 700 Series temperature controller at room temperature. A hemisphere of frames was measured using a narrow-frame method with a scan width of 0.30° in ω and an exposure time of 60 s/frame with Mo $K\alpha$ radiation. The collected data set was integrated using the Bruker Apex II program, with the intensities corrected for the Lorentz factor, polarization, air absorption, and absorption due to variation in the path length through the detector faceplate. The data were scaled, and the absorption correction was applied using SADABS.⁵⁰ A starting model was obtained using the intrinsic method in SHELXT,⁵¹ and atomic sites were refined anisotropically using SHELXL2014.

Chemical Analysis. Chemical analyses were performed using both energy-dispersive X-ray spectroscopy (EDS) and wavelength-dispersive spectrometry (WDS) on a JEOL JXA-8600 electron microprobe analyzer. Data were collected at multiple (>5) points for each sample to ensure accuracy. The instrumental error of these results is smaller than 0.5%.

TEM and STEM. Atomic-resolution high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images, high-resolution TEM (HRTEM), and selected area electron diffraction (SAED) were performed using an aberration-corrected JEM-ARM200F (JEOL USA Inc.) operated at 200 kV. SAED simulation was performed by JEMS software. TEM lamellae were prepared using a FEI Nova 200 dual-beam focused-ion-beam system (FIB, FEI Inc.) by the lift-out method.

Electrical Transport and Magnetic Studies. Temperature (T)- and magnetic-field (H)-dependent electrical resistivity $\rho(T, H)$ using a four-probe configuration and Hall resistivity with a five-probe configuration were measured down to 5 K and up to a 7 T magnetic field in a Quantum Design Physical Property Measurement System (PPMS). Gold wires, each with a radius of 20 μ m, were used as the electrical leads for the measurements and were attached to the crystal surfaces using silver paste with a contact resistance normally of ~ 1 – 5 Ω . Temperature-dependent magnetic susceptibility measurement was carried out down to 5 K at a 5 T magnetic field in a Quantum Design Magnetic Property Measurement System (MPMS).

RESULTS AND DISCUSSION

The new β -phase of BaCu₂As₂ was initially identified from XRD scanning of the plate-shaped crystals grown by three different fluxes. The XRD diffraction patterns are highly c -axis-oriented due to the preferred orientation of the crushed single crystals, as expected. We observed a few additional small peaks in the XRD patterns of the Sn-flux-grown crystals and initially attributed them to misalignment of the crystals or possible impurities. However, chemical analysis from both EDS and WDS measurements clearly indicated the existence of only elemental Ba, Cu, and As in the crystals, and neither impurities nor flux inclusions were detected within the instrument detection limits. Furthermore, the (00 l) Miller indices of these additional peaks suggest an ordered crystal lattice, implying the presence of a superstructure in these Sn-flux-grown crystals, as shown in the logarithmic scale in Figure 1a (black pattern). For the CuAs- and Pb-flux-grown crystals, we did not observe these peaks (red pattern in Figure 1a), suggesting that these crystals indeed adopted a conventional ThCr₂Si₂-type structure. We therefore employed X-ray single-crystal diffraction to investigate the superstructure and fully understand the structure of this new phase in detail. A fast omega scan using a narrow-frame algorithm with an exposure time of 30 s/frame initially leads to the assignment of the ThCr₂Si₂-type unit cell. However, under a full set of data collection with a longer exposure time of 50 s/frame, all Sn-flux-grown crystals clearly show a superstructure with a much larger c axis of 51.05(1) Å, while the CuAs- and Pb-flux-grown crystals have the ThCr₂Si₂-type structure with $c = 10.073(6)$ Å. Crystallographic parameters and refinement details are provided in Table 1. Atomic coordinates, anisotropic displace-

Table 2. Atomic Coordinates, Selected Interatomic Distances, and Equivalent Isotropic Displacement Parameters (U_{eq}) of α - BaCu_2As_2 and β - BaCu_2As_2 ^a

type	atom	Wyckoff site	Symm.	x/a	y/b	z/c	occ.	U_{eq} (\AA^2)
α	As	4e	$4mm$	1/2	1/2	0.1277(1)	1	0.0105(5)
	Cu	4d	$-4m2$	0	1/2	1/4	1	0.0177(8)
	Ba	2a	$4/mmm$	0	0	0	1	0.0143(5)
β	As1	4e	$4mm$	1/2	1/2	0.02537(2)	1	0.0111(4)
	As2	4e	$4mm$	0	0	0.07412(2)	1	0.0107(4)
	As3	4e	$4mm$	0	0	0.12441(2)	1	0.0094(4)
	As4	4e	$4mm$	1/2	1/2	0.17481(2)	1	0.0086(4)
	As5	4d	$-4m2$	1/2	1	1/4	1	0.0089(4)
	Ba1	2a	$4/mmm$	0	0	0	1	0.0111(4)
	Ba2	4e	$4mm$	1/2	1/2	0.10086(2)	1	0.0097(4)
	Ba3	4e	$4mm$	0	0	0.19948(2)	1	0.0088(4)
	Cu1	8g	$2mm$	0	1/2	0.05008(2)	1	0.0212(4)
	Cu2	8g	$2mm$	0	1/2	0.14997(2)	1	0.0166(4)
	Cu3	4e	$4mm$	1/2	1/2	0.22486(2)	1	0.0134(4)
	selected interatomic distances (\AA)	α	Cu1–As1	2.541(1)			As1–As1	2.572(3)
		β	Cu1–As1	2.547(1)	Cu2–As4	2.550(1)	As1–As1	2.590(2)
			Cu1–As2	2.530(1)	Cu3–As5	2.557(1)	As2–As3	2.567(1)
			Cu2–As3	2.569(1)				

^a U_{eq} is defined as 1/3 of the trace of the orthogonalized U_{ij} tensor.

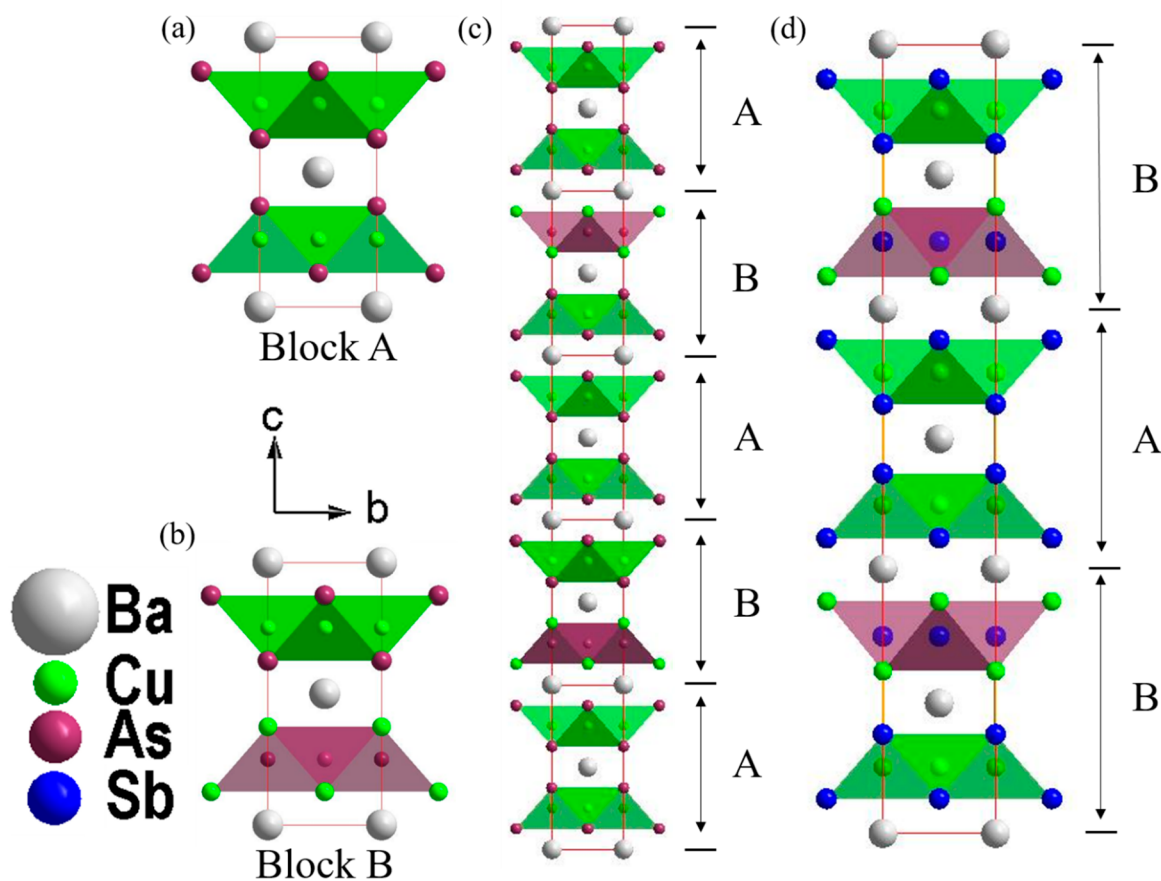


Figure 2. (a) α - BaCu_2As_2 with the ThCr₂Si₂-type (block A motif) structure; (b) α - BaCu_2As_2 with a hypothetical CaBe₂Ge₂-type (block B motif) structure; (c) intergrowth structure of β - BaCu_2As_2 with the ABABA stacking pattern; and (d) intergrowth structure of β - BaCu_2Sb_2 with the BAB stacking pattern.

ment parameters, occupancies, and some selected interatomic distances and angles are provided in Table 2. The integrated precession images of the $(0kl)$, $(h0l)$, and $(hk0)$ layers from the complete set of single-crystal diffraction data, as shown in

Figure 1b–d, provide clear visualization of the existence of the superstructure in our new phase.

The refined crystal structure of the new β -phase BaCu_2As_2 is shown in Figure 2. For purposes of comparison, we also

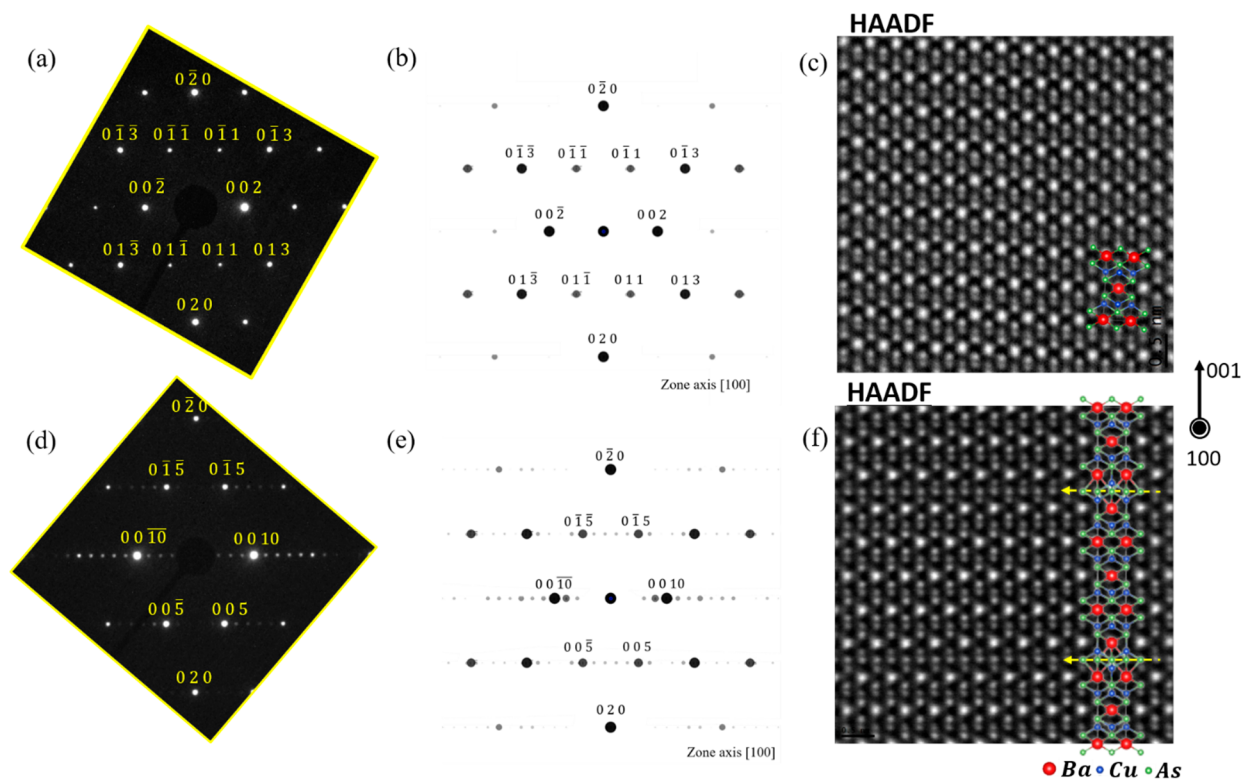


Figure 3. (a) Acquired and (b) simulated SAED patterns and (c) STEM image of α -BaCu₂As₂. (d) Acquired and (e) simulated SAED patterns and (f) STEM image of β -BaCu₂As₂.

plotted the α -phase of BaCu₂As₂ with the ThCr₂Si₂-type structure (Figure 2a) and a hypothetical BaCu₂As₂ with the closely related CaBe₂Ge₂-type structure (Figure 2b). Both structures contain two tetragonally coordinated Cu₂As₂ layers per unit cell sandwiched by the Ba atoms. In the ThCr₂Si₂-type structure, the neighboring Cu₂As₂ layers are equivalent and are related by inversion symmetry, which results in a body-centered lattice. The As–As distances between the two identical Cu₂As₂ layers are relatively short, suggesting significantly strong interactions between the Cu₂As₂ layers, akin to the collapsed tetragonal phases discovered in the Fe pnictide superconductors.^{52–55} CaBe₂Ge₂-type structures are instead made up of alternating Cu₂As₂ and As₂Cu₂ layers and thus break both the mirror and inversion symmetries, resulting in a primitive lattice. The new β -phase of BaCu₂As₂ could be considered an ordered intergrowth of ThCr₂Si₂-type (block A motif) and CaBe₂Ge₂-type (block B motif) structures. The unit cell of our β -phase BaCu₂As₂ consists of five of these unit-cell blocks stacked along the *c* axis, where CaBe₂Ge₂-type blocks are sandwiched between ThCr₂Si₂-type blocks with an ABABA stacking pattern (Figure 2c). Interestingly, this stacking pattern retains the mirror symmetry, resulting in an overall space group symmetry of *I*4/*mmm*, the same as for the ThCr₂Si₂-type structure. The position exchange of Cu (Wyckoff 4d site) and As (Wyckoff 4e site), which swap positions from the α -phase ThCr₂Si₂-type structure to the CaBe₂Ge₂-type structure, and the overall ABABA stacking lead to 11 unique crystallographic sites in our β -phase BaCu₂As₂, in comparison to only 3 unique positions in the α -phase BaCu₂As₂. We have paid close attention to the possibility of Sn flux inclusion in the crystal lattice during our single-crystal studies, as has been seen in Fe-based superconductors grown from Sn flux.¹⁰ The full occupancy at each crystallographic site in our crystal

refinement excludes such a possibility. This observation, together with the chemical analysis results from EDS and WDS measurements, leads us to conclude that flux inclusion during the flux growth of Cu-based 122 compounds is unlikely, which is consistent with other reports.

It is also worth mentioning that a different intergrowth stacking pattern of ThCr₂Si₂-type (block A motif) and CaBe₂Ge₂-type (block B motif) structures has also been reported in the Sb-analogue β -BaCu₂Sb₂.^{39,40} Different from our β -BaCu₂As₂, the β -BaCu₂Sb₂ consists of three unit-cell blocks with the same overall symmetry *I*4/*mmm*, where a ThCr₂Si₂-type block is sandwiched between two CaBe₂Ge₂-type blocks with a BAB stacking pattern, as illustrated in Figure 2d.

To further elaborate the structural difference between the α - and β -phases of BaCu₂As₂ crystals, HRTEM and HAADF-STEM images were obtained. SAED and STEM imaging were carried out along the [100] zone axis. All SAED simulations were conducted using constructed models that were built based on the single-crystal diffraction results. Acquired TEM and SAED patterns are both consistent with the simulated patterns, indicating that the constructed models accurately represent the single crystals. Figure 3a,b shows the acquired and simulated SAED patterns, respectively, of α -BaCu₂As₂, and Figure 3d,e shows these respective SAED patterns for β -BaCu₂As₂. It can be clearly seen in the simulated SAED pattern of β -BaCu₂As₂ shown in Figure 3d that there are not only {001} fundamental spots but also additional 1/5{00*l*} superstructure reflections, which are not observed for α -BaCu₂As₂ (Figure 3b), further supporting the single-crystal diffraction results. Figure 3c shows the HAADF-STEM image taken from an α -BaCu₂As₂ single crystal along the [001] zone axis. The STEM images were filtered to enhance contrast by

removing noise. The existence of each element was confirmed by STEM and EDX analyses, from which we also observed the lack of flux inclusions in our crystals. In Z-contrast HAADF images, each atom can be distinguished easily by brightness and size. Ba atoms are clearly recognized as bright dots, and Cu atoms are dimmer than As atoms. For comparison, STEM images from a β -BaCu₂As₂ single crystal were obtained and are shown in Figure 3f. Each constructed model is overlapped with the STEM images to confirm their consistency. Additional As planes are clearly observed in the BaCu₂As₂ superstructure and are marked yellow in Figure 3f, which also shows the intergrowth superstructure in β -BaCu₂As₂ consisting of two CaBe₂Ge₂-type unit-cell blocks and three ThCr₂Si₂-type unit-cell blocks, which is consistent with our X-ray single-crystal diffraction and SAED pattern results.

To fully understand the effect of flux on the formation of different polymorphic phases, to determine the growth window for this new β -BaCu₂As₂ phase, and to further explore possible new phases using flux growth, we have systematically studied the effects of the precursors, temperature, and materials/flux ratios in a series of controlled experiments with some of the key results summarized in Table 3. We found the following:

Table 3. Growth Conditions for α -BaCu₂As₂ and β -BaCu₂As₂ Single Crystals

[Ba:CuAs (or Cu:As): flux]	flux	temperature (°C) (initial/centrifuge)	products
1:1:10	Sn	950/500	Ba ₃ Sn ₂ As ₄ ⁵⁶
1:2:10	Sn	950/500	Ba ₃ Sn ₂ As ₄ ⁵⁶
1:2:2:10 (Cu:As)	Sn	950/500	Ba ₃ Sn ₂ As ₄ ⁵⁶
1:2:30	Sn	950/550	Ba ₃ Sn ₂ As ₄ ⁵⁶
1:4:30	Sn	950/500	β -BaCu ₂ As ₂ (Z = 10)
1:4:30	Sn	1100/550	β -BaCu ₂ As ₂ (Z = 10)
1:2:10 (CuAs)	Pb	1100/600	α -BaCu ₂ As ₂ (Z = 2)
1:2:2:10 (Cu:As)	Pb	1100/600	α -BaCu ₂ As ₂ (Z = 2)
1:4	CuAs	1080/800	α -BaCu ₂ As ₂ (Z = 2)
1:2:30	Ga	900/500	no crystal

(1) Using a CuAs precursor is preferred to elemental Cu and As for the crystal growth when using Sn flux. Regardless of the starting ratios, using Ba:Cu:As:Sn generally produces the known air-sensitive ternary compound Ba₃Sn₂As₄⁵⁶ rather than the BaCu₂As₂ phase. (2) The starting Ba:CuAs ratio needs to be less than 1:2 to obtain BaCu₂As₂ crystals rather than Ba₃Sn₂As₄ crystals during Sn flux growth. A Ba:CuAs ratio of 1:4 is optimal to consistently obtain a high-quality BaCu₂As₂ phase. (3) β -BaCu₂As₂ phase formation is insensitive to the growth temperature (at least for the temperature range studied here). We found that growth temperatures ranging from 800 to 1100 °C for a Ba:CuAs:Sn ratio of 1:4:30 all result in the β -BaCu₂As₂ phase with the same superstructure features based on X-ray diffraction results. (4) The starting materials are not important for Pb-flux growth. Both elemental Cu/As and CuAs precursors are able to produce the α -phase BaCu₂As₂. On the other hand, attempts to use Ga as flux under similar synthesis conditions did not produce any crystals. Clearly, Sn flux has a compelling advantage over other fluxes for the growth of β -BaCu₂As₂, but the synthetic temperature does not make a difference in the phase formation once the flux is chosen.

These results are different from the observation for BaCu₂Sb₂, where it is the temperature profile rather than the flux that plays an important role in determining α - or β -phase crystal growth. This further suggests that potential new phases, especially the intergrowth of ThCr₂Si₂-type and CaBe₂Ge₂-type structures that we observed here could be further explored in other 122 compounds through careful modification of both different types of flux (or their joint flux) and synthetic temperature profiles.

Both field-dependent transverse Hall resistivity, temperature-dependent in-plane longitudinal resistivity measurement and magnetic susceptibility measurement were carried out on this new polymorphic β -BaCu₂As₂, as shown in Figure 4. The room-temperature Hall resistivity suggests hole-like carriers in this system, and the estimated carrier concentration is about $6.63 \times 10^{21}/\text{cm}^3$ based on a single-band model (Figure 4a). The temperature-dependent in-plane resistivity data show overall metallic behavior, as expected, with a reasonably high residual resistivity ratio (RRR) ≈ 8.3 compared to the other Cu-based 122 crystals^{38,39} and a residual resistivity of 1.8 $\mu\Omega$ cm, relatively low among the 122-type compounds,^{27–29,31,33,34,38,39} further indicating the high quality of our grown crystals.

Surprisingly, with a magnetic field of 7 T applied perpendicular to the *ab* plane, we observed a high in-plane magnetoresistivity up to 22% at 5 K. This is quite unusual, as both theoretical^{43,44} and angle-resolved photoemission spectroscopy studies⁴⁵ have suggested that α -BaCu₂As₂ behaves as a simple sp metal with weak electronic correlations and Cu¹⁺ oxidation states. A Cu¹⁺ oxidation state corresponds to a completely filled 3d¹⁰ configuration, which should not have any net spin moment. A closer look and more careful analysis of the resistivity of our β -BaCu₂As₂ indicates that a fairly weak resistivity anomaly can be deduced by the first derivation of the temperature-dependent resistivity data at 43 K, as shown in inset of Figure 4b. This coincides with the magnetoresistivity data where the magnetoresistance starts to emerge below 50 K, as shown in Figure 4b. Through detailed fitting with a Fermi liquid model in the low-temperature regime using $\rho = \rho_0 + AT^2$ (Figure 4c), we obtained $\rho_0 = 1.70(1) \mu\Omega$ cm and $A = 0.0009(1) \mu\Omega$ cm/K². However, we found the existence of a small deviation from the Fermi liquid fitting at low temperature below 10 K, which suggests the possible existence of spin fluctuation in this system.^{42,57,58} Magnetic susceptibility, shown in Figure 4d, is nearly flat between 50 and 300 K but increases rapidly when temperature is below 50 K. A weak anomaly is also observed at around 40 K by taking the first derivation of susceptibility data (inset, Figure 4d), which further supports the possible existence of spin fluctuations in the system.

α -BaCu₂As₂ has already been demonstrated to be nonmagnetic,⁴⁶ and it is analogous to the nonmagnetic collapsed tetragonal phases in iron pnictide superconductors resulting from a strong interlayer interaction. However, in β -BaCu₂As₂, the incorporation of CaBe₂Ge₂-type blocks into the structure will influence the interlayer As–As bonding, as the interlayer interaction in the CaBe₂Ge₂-type structure is between Cu and As atoms rather than As–As, which we speculate will drive the Cu state away from the filled 3d¹⁰ configuration and cause the spin fluctuation in this new phase. This spin fluctuation might become magnified, or new types of magnetic order could emerge, if one could further chemically dope this phase through either nonmagnetic or magnetic ions to tune the

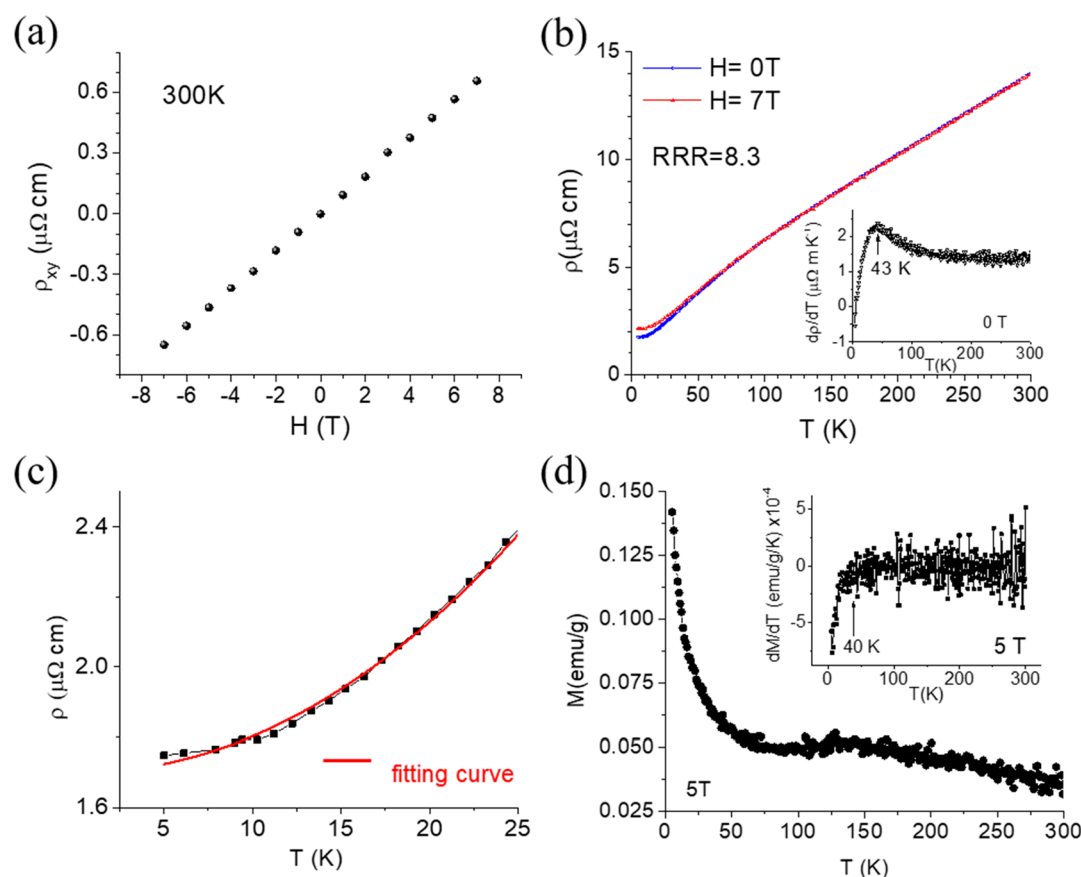


Figure 4. (a) Hall resistivity data at room temperature for β -BaCu₂As₂. (b) Resistivity data of β -BaCu₂As₂ from 5 to 300 K under magnetic fields of 0 and 7 T. The inset shows first derivative of resistivity data under a magnetic field of 0 T. (c) Resistivity data at low-temperature range between 5 and 25 K under a magnetic field of 0 T, together with a fitting curve (solid red line). (d) Magnetic susceptibility data of β -BaCu₂As₂ from 5 to 300 K under a magnetic field of 5 T. The inset is the first derivative of susceptibility data, which shows an anomaly at 40 K.

interlayer As–As interactions, as seen in the other 122 systems.^{59–61} This will be the subject of future studies.

CONCLUSION

In conclusion, we have reported a completely new polymorphic phase of β -BaCu₂As₂ with a much larger c lattice parameter than that of α -BaCu₂As₂. This new phase is an ordered intergrowth structure with CaBe₂Ge₂-type blocks sandwiched between ThCr₂Si₂-type blocks that retain body-centered symmetry ($I4/mmm$), as confirmed by X-ray single-crystal diffraction, TEM and STEM studies, and comparisons between our intergrowth structure and the simpler ThCr₂Si₂-type structure of α -BaCu₂As₂. This new phase displays unusual magnetoresistivity up to 22% at 5 K and under a magnetic field of 7 T, which suggests the existence of spin fluctuation in this system. Our results indicate a route for the discovery of new polymorphic structures through flux and temperature control during material synthesis.

ASSOCIATED CONTENT

Accession Codes

CCDC 1998158 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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