**Supporting Information for:** 

# **Creating binary Cu–Bi compounds via high-pressure synthesis: A combined experimental and theoretical study**

Samantha M. Clarke,<sup>1†</sup> Maximilian Amsler,<sup>2†</sup> James P. S. Walsh,<sup>1</sup> Tony Yu,<sup>3</sup> Yanbin Wang,<sup>3</sup> Yue Meng,<sup>4</sup> Steven D. Jacobsen,<sup>5</sup> Chris Wolverton,<sup>2\*</sup> Danna E. Freedman<sup>1\*</sup>

<sup>1</sup>Department of Chemistry, Northwestern University, Evanston, Illinois 60208, USA

<sup>2</sup>Department of Materials Science and Engineering, Northwestern University, Evanston, Illinois 60202, USA

<sup>3</sup>GeoSoilEnviroCARS, Center for Advanced Radiation Sources, The University of Chicago, Chicago, Illinois 60637, USA

<sup>4</sup>HPCAT, Geophysical Laboratory, Carnegie Institution of Washington, Argonne, Illinois 60439, USA

<sup>5</sup>Department of Earth and Planetary Sciences, Northwestern University, Evanston, Illinois 60208, USA

Chemistry of Materials

# **Table of Contents**

Experimental Synthetic Details	<b>S3</b>
Crystallographic and Other Characterization	<b>S3</b>
Figure S1. Schematic of the modified 14/8 "G2" high-pressure cell assembly.	<b>S5</b>
Figure S2. Schematic of the DAC for <i>in situ</i> reactions.	<b>S6</b>
Figure S3. Structural comparison of NiAs and CuBi.	<b>S7</b>
Figure S4. Rietveld refinement of the synchrotron PXRD pattern.	<b>S8</b>
Figure S5. Differential scanning calorimetry measurement.	<b>S9</b>
Figure S6. SEM image of CuBi.	S10
Figure S7. ELF of CuBi, RhBi <sub>4</sub> and IrBi <sub>4</sub> .	<b>S11</b>
Figure S8. Negative formation free energies of $Cu_{11}Bi_7$ and $CuBi$ .	S12
Figure S9. Low temperature magnetometry data for CuBi.	S13
Table S1. Refinement details for CuBi.	<b>S14</b>
References	<b>S15</b>

#### **Experimental synthetic details**

#### Details of DAC assembly

A short symmetric diamond anvil cell (DAC) with 99° opening was equipped with two 300 µm culet Type Ia (100)-oriented Boehler–Almax diamonds seated on 80° conical tungsten carbide supports. The laser micro-machining system at HPCAT<sup>1</sup>, Advanced Photon Source, Argonne National Laboratory, was used to drill a 150  $\mu$ m diameter sample chamber into a rhenium gasket, pre-indented to ~40  $\mu$ m thickness. We employed thin MgO discs as a thermal insulator, pressure calibrant, and a pressure-transmitting medium. Detailed description of the preparation of these circular discs is discussed in a previous publication.<sup>2</sup> In air, a small amount of a mixture of elemental copper and elemental bismuth was pressed between two diamond anvils into a thin foil of approximately 10 µm thickness. In the DAC, a circular piece of the MgO was placed in the center of the drilled rhenium gasket. A small flake of the sample foil was transferred using an acupuncture needle into the gasket space of the assembled DAC, on top of the MgO piece. A ruby sphere was added as a pressure calibrant. The upper MgO disc (used to insulate the sample from the diamonds) was also added. The cell was then closed and pressurized (Figure S1). Sample pressure was monitored during the initial pressurization using the  $R_1$  fluorescence line of the ruby spheres loaded into the sample space. During the *in situ* experiments, pressure was determined from the lattice parameter of the MgO using the well-known equation of state for MgO.<sup>3</sup> Heating of the sample was performed from both sides of the cell using a microfocused laser (FWHM =  $40 \mu m$ ), while concurrently acquiring *in situ* X-ray diffraction at the heating spot.<sup>4</sup> Since temperatures below ~600 °C are difficult to monitor precisely, we inferred the temperature during the reaction from the various elemental phase changes in Bi.<sup>5</sup> Diffraction images were integrated using the Dioptas software package.<sup>6</sup> Powder X-ray diffraction data were analyzed by the Rietveld method using TOPAS.<sup>7</sup> The background was fit using a Chebyshev polynomial. Pseudo-Voigt line broadening was employed for each phase.

## Crystallographic and other characterization

The structure of CuBi was solved by Rietveld refinement of the synchrotron powder X-ray diffraction (PXRD) pattern from the high-resolution 11-BM diffractometer at the Advanced Photon Source, Argonne National Laboratory, with an incident wavelength of  $\lambda = 0.414203$  Å. The samples were coated on the outside of a Kapton capillary using Dow Corning #4 electrical insulating grease, cooled to 100 K, and spun at ~600 rpm during collection. Powder diffraction data were analyzed by the Rietveld method using the computer program TOPAS.<sup>8</sup> The pattern was fit in the 2 $\theta$  range of 2.5° to 40° and the background was fit using a Chebyshev polynomial with 30 parameters. Pseudo-Voigt line broadening was employed for each phase. The pattern can be indexed to the orthorhombic space group *Pmma* 

with unit cell parameters a = 5.18899(2) Å, b = 4.23081(2) Å, and c = 7.86634(3) Å. A search of the Inorganic Crystal Structure Database (ICSD)<sup>9</sup> listed Mn(Bi<sub>0.85</sub>Sb<sub>0.15</sub>) as having similar symmetry and lattice parameters (*Pmma*, a = 5.70 Å, b = 4.27 Å, and c = 7.40 Å). The structure of Mn(Bi<sub>0.85</sub>Sb<sub>0.15</sub>) was first reported by Göbel et al.<sup>10</sup> and was later revised by Cenzual et al.<sup>11</sup> The structure of Mn(Bi<sub>0.85</sub>Sb<sub>0.15</sub>) contains three Mn sites and two x sites where  $x = Bi_{0.85}Sb_{0.15}$ . The Mn(1) site at (<sup>1</sup>/<sub>4</sub>, 0, 0.285) and Mn(3) site at (0, 0, 0) are partially occupied with occupancies of 0.63 and 0.39, respectively. We were able to use the atomic positions from this structure as a starting point for the refinement of CuBi, using the Mn sites for Cu and the x sites for Bi. Upon refinement of the atomic positions, the Bi atoms move slightly away from their original positison toward the a-b plane. Interestingly, the Cu sites change drastically. The Cu(1) site refines to full occupancy and moves dramatically away from the a-b plane toward the plane of Cu(2) atoms. We hypothesize that this reflects the tendency of the Cu and Bi atoms to phase segregate on the atomic level, even at high pressures. The Cu(3) site refines to zero occupancy, thereby forming the unique layered structure. PXRD indicates near complete conversion of the elements into CuBi (88.71%) with a small amount of residual elemental bismuth (2.90%) and copper (8.39%) (Figure S3). As described in the main text, small copper and bismuth rich areas were also seen in the EDS, supporting the presence of excess Bi.

Differential scanning calorimetry (DSC) data were collected on a Mettler Toledo DSC822e under an  $N_2$  purge at 2 °C min<sup>-1</sup> heating and cooling rates.



**Figure S1** Schematic of the modified 14/8 "G2" high-pressure cell assembly used in the multi-anvil press synthesis of  $Cu_{11}Bi_7$  and CuBi.



**Figure S2** Side-view schematic of the DAC after closing the cell and before the initial pressurization. MgO discs are placed on the center of the upper and lower diamond culets. The MgO acts simultaneously as the pressure medium, the pressure calibrant, and the thermal insulation between the sample and the diamond. The sample, which is a pressed flake of copper and bismuth mixture with a thickness of around 10  $\mu$ m, is placed on top of the lower MgO piece along with a ruby sphere. The top diamond is lowered carefully into place so that it settles into the indentation and delivers the upper MgO disc to the sample chamber. Upon compression, the sample chamber collapses so that the MgO fills the volume, holding the sample flake and ruby in the center of the chamber.



**Figure S3** Structural comparison of NiAs and CuBi. Bonds are exclusively drawn between the transition metal chains and nearest Bi atoms to highlight the similarity between the structures. The structure of CuBi can be generated from the NiAs structure type by an ordered vacancy of Cu chains and interstitial Cu sites that destroy the hexagonal close packing of the Bi atoms.



**Figure S4** Rietveld refinement of the synchrotron powder X-ray diffraction pattern. The experimental data (black circles) was fit (purple) accounting for the majority CuBi phase (88.80%) along with elemental Bi (2.88%) and Cu (8.31%) phases. The difference trace is plotted in grey. Full details of the refinement are given in Table S1.  $\lambda = 0.406626$  Å.  $R_{wp} = 6.26$  GOF = 1.20.



**Figure S5** Differential scanning calorimetry (DSC) measurement of CuBi with a heating and cooling rate of 2 °C/min. The cooling curve has been offset by -0.4 mW for clarity. The first broad exothermic event upon heating centered at 158 °C can be assigned to the decomposition of CuBi and the sharp endothermic peak at 270 °C corresponds to the melting of elemental bismuth. The exothermic events on cooling with an onset of 250 °C are the crystallization of the undercooled bismuth melt. The absence of a peak upon cooling around 158 °C confirms the metastability of CuBi. The decomposition of the sample into elemental Cu and Bi after thermal analysis was confirmed by X-ray diffraction.



**Figure S6** Backscatter electron scanning electron microscopy (SEM) image of the polished top surface of the sample pellet of CuBi from the multi-anvil press synthesis. Very dark regions are holes in the samples and dark grey regions are Cu-rich areas. Integration of the EDS spectrum of the light grey area indicates a composition of  $Cu_{48.9(7)}Bi_{51.1(7)}$  which is in agreement with the composition determined by crystallography.



**Figure S7** Crystal structures of CuBi (a), RhBi<sub>4</sub> (b), and IrBi<sub>4</sub> (c) with isosurfaces of the electron localization function (ELF), highlighting the voids formed by the bismuth atoms in each structure. The ELF isosurface with a value of 0.93 is shown in pink in each structure. The highly localized ELF isosurfaces indicate lone pairs on the Bi atoms that point toward the voids, in the opposite direction of their nearest neighbor bonds.



**Figure S8** Gibbs free formation energies of (a) CuBi and (b)  $Cu_{11}Bi_7$ . The shaded areas indicate the preferred decomposition into Cu and different elemental Bi phases. The red and blue areas show the *PT* regime where the Gibbs free formation energies of CuBi and  $Cu_{11}Bi_7$ , respectively, are negative.



**Figure S9** | Variable temperature molar dc magnetic susceptibility of an as-synthesized pellet of CuBi with  $H_{dc} = 10$  Oe. Filled shapes indicate zero field cooled measurement and outline shapes indicate field cooled measurements. The onset of the superconducting transition occurs at 1.3 K.

			Phase 1: CuBi					
Formula	CuBi	Stephens orthorhombic model			Atomic parameters			
R <sub>B</sub>	1.107	eta	0.4325419	Site	x	У	Ζ	
Space group	Pmma	S400	1318.346	Bi1	0.25	0.5	0.18144(3)	
a (Å)	5.18899(2)	S040	2481.384	Bi2	0.25	0	0.75930(3)	
<b>b</b> (Å)	4.23077(1)	S004	169.4405	Cu1	0.25	0	0.41846(9)	
c (Å)	7.86658(2)	S220	-888.0396	Cu2	0	0.5	0.5	
Cell mass	1090.106	<i>S202</i>	1708.608					
Cell volume (Å <sup>3</sup> )	172.6990(9)	S022	2982.781					
Density (g cm <sup>-3</sup> )	10.48161(5)							
Fraction (%)	88.71(3)							
			Phase 2: Cu					
Formula	Cu	Stephens cubic model			Atomic parameters			
R <sub>B</sub>	2.060	eta	0.4692114	Site	x	у	Z	
Space group	$Fm\overline{3}m$	S400	7780.884	Cu1	0	0	0	
<i>a</i> (Å)	3.60513(2)	S220	631.629					
Cell mass	254.184							
Cell volume (Å <sup>3</sup> )	46.8559(8)							
Density (g cm <sup>-3</sup> )	9.0081(1)							
Fraction (%)	8.39(3)							
			Phase 3: Bi					
Formula	Bi	Stephens hexagonal model			Atomic parameters		s	
R <sub>B</sub>	1.356	eta	0.7203154	Site	x	у	Z	
Space group	$R\overline{3}m$	S400	2638.628	Bi1	0	0	0.23573	
a (Å)	4.53423(6)	S004	84.34906					
b (Å)	11.8195(4)	S202	731.6615					
Cell mass	1253.882							
Cell volume (Å <sup>3</sup> )	210.443(9)							
Density (g cm <sup>-3</sup> )	9.8940(4)							
Fraction (%)	2.89(2)							

 Table S1 | Refinement details for the new CuBi binary compound.

## References

- (1) Hrubiak, R.; Sinogeikin, S.; Rod, E.; Shen, G. The Laser Micro-Machining System for Diamond Anvil Cell Experiments and General Precision Machining Applications at the High Pressure Collaborative Access Team. *Rev. Sci. Instrum.* **2015**, *86*, 72202.
- (2) Walsh, J. P. S.; Clarke, S. M.; Meng, Y.; Jacobsen, S. D.; Freedman, D. E. Discovery of FeBi<sub>2</sub>. *ACS Cent. Sci.* **2016**, 1, 668–669.
- (3) Speziale, S.; Zha, C.-S.; Duffy, T. S.; Hemley, R. J.; Mao, H.-K. Quasi-hydrostatic compression of magnesium oxide to 52 GPa: Implications for the pressure–volume–temperature equation of state. *J. Geophys. Res.: Solid Earth* **2001**, *106*, 515–528.
- (4) Meng, Y.; Hrubiak, R.; Rod, E.; Boehler, R.; Shen, G. New Developments in Laser-Heated Diamond Anvil Cell with in Situ Synchrotron X-Ray Diffraction at High Pressure Collaborative Access Team. *Rev. Sci. Instrum.* 2015, *86*, 72201.
- (5) Klement, W.; Jayaraman, A.; Kennedy, G. C. Phase Diagram of Arsenic, Antimony, and Bismuth at Pressures up to 70 Kbars. *Phys. Rev.* **1963**, *131*, 632–637.
- (6) Prescher, C.; Prakapenka, V. B. DIOPTAS: a program for reduction of two dimensional X-ray diffraction data and data exploration. *High Pressure Research*, **2015**, *35*, 223-230.
- (7) Coelho, A. A. TOPAS Academic: General Profile and Structure Analysis Software for Powder Diffraction Data, Bruker AXS, Karlsruhe, Germany, 2007.
- (8) A. A. Coelho, *TOPAS Academic: General Profile and Structure Analysis Software for Powder Diffraction Data*, Bruker AXS, Karlsruhe, Germany, 2007.
- (9) Inorganic Crystal Structure Database (ICSD) Web, Version 3.5.0, FIZ Karlsruhe, Germany, 2017.
- (10) Göbel, H.; Wolfgang, E.; Harms, H. Properties of MnBi Compounds Partially Substituted with Cu, Zn, Ti, Sb, and Te. I. Formation of Mixed Phases and Crystal Structures. *Phys. Status Solidi* 1976, 34, 553–564.
- (11) Cenzual, K.; Gelato, L. M.; Penzo, M.; Parthe, E.; Parthé, E. Inorganic Structure Types with Revised Space Groups. I. *Acta Crystallogr. Sect. B* 1991, *47*, 433–439.