Discovery of FeBi$_2$

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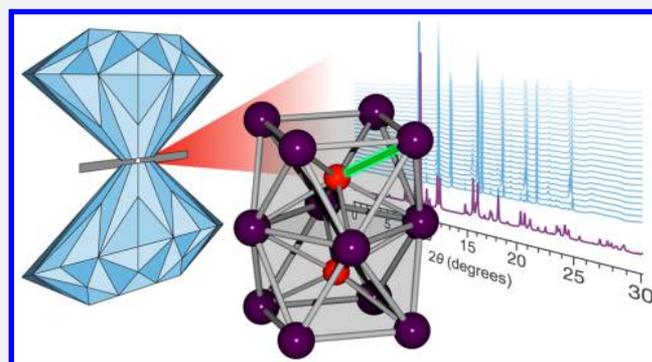
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S *Supporting Information*

ABSTRACT: Recent advances in high-pressure techniques offer chemists access to vast regions of uncharted synthetic phase space, expanding our experimental reach to pressures comparable to the core of the Earth. These newfound capabilities enable us to revisit simple binary systems in search of compounds that for decades have remained elusive. The most tantalizing of these targets are systems in which the two elements in question do not interact even as molten liquids—so-called immiscible systems. As a prominent example, immiscibility between iron and bismuth is so severe that no material containing Fe−Bi bonds is known to exist. The elusiveness of Fe−Bi bonds has a myriad of consequences; crucially, it precludes completing the iron pnictide super-conductor series. Herein we report the first iron−bismuth binary compound, FeBi$_2$, featuring the first Fe−Bi bond in the solid state. We employed geologically relevant pressures, similar to the core of Mars, to access FeBi$_2$, which we synthesized at 30 GPa and 1500 K. The compound crystallizes in the Al$_2$Cu structure type (space group $I4/mcm$) with a = 6.3121(3) Å and c = 5.4211(4) Å. The new binary intermetallic phase persists from its formation pressure of 30 GPa down to 3 GPa. The existence of this phase at low pressures suggests that it might be quenchable to ambient pressure at low temperatures. These results offer a pathway toward the realization of new exotic materials.

INTRODUCTION

Creating and understanding new bonding interactions is central to chemistry; each new bond gives rise to undiscovered electronic structure and provides novel insight into chemical bonding in materials. Thousands of unique chemical inter-actions are known, and yet within the periodic table there remain bonds that are counterintuitively absent. This is particularly enigmatic when the two elements in question exhibit a diverse chemistry with other elements across the periodic table. For chemists, such systems represent unexplored regions of phase space with tremendous potential for discovery; iron−bismuth is a prominent example of such a system. Indeed, the immiscibility of the elements is so severe that there have been no reports of Fe−Bi bonds in the solid-state literature. This is particularly intriguing from a chemical standpoint because there are numerous applications that would benefit from the creation of this interaction, notably magnetism and superconductivity.

Our interest in the intersection of iron and bismuth arises from the potential for transformative magnetic properties. By fusing the paramagnetism of iron with the spin−orbit coupling inherent to bismuth, we envision the creation of a new family of magnetic materials. Creating an iron−bismuth bonding interaction is also of urgent interest to the superconductivity community, where iron−bismuth interactions are a prerequisite

to create the missing members of the iron pnictide family of superconductors.[1] Creating new bismuth superconductors could provide crucial insight into the mechanism of these exotic iron-based materials. Despite over a decade of focused interest within this area, iron−bismuth bonds remain elusive within solid-state materials.

One key challenge in creating an iron−bismuth interaction is the immiscibility of the two elements. Even at the elevated temperature of 1873 K, where both metals are in the liquid state, the solubility of bismuth in iron is only 0.16 wt %.[2] This suggests that extreme conditions may be required to access a binary compound. Toward that end, we considered the application of geologically relevant pressures. Bismuth is unusually well-suited to high-pressure synthesis due to its numerous high-pressure phases and associated structural transformations.[3,4] Indeed, recently, high pressure was employed as a vector to access new binary compounds in bismuth systems that were previously devoid of intermetallic phases, including CoBi$_3$[5] and Cu$_{11}$Bi$_7$.[6] Both of these compounds are the first structurally characterized intermetallic phases in their respective binary systems,[7,8] and both were synthesized by reaction of the elements at high-pressure
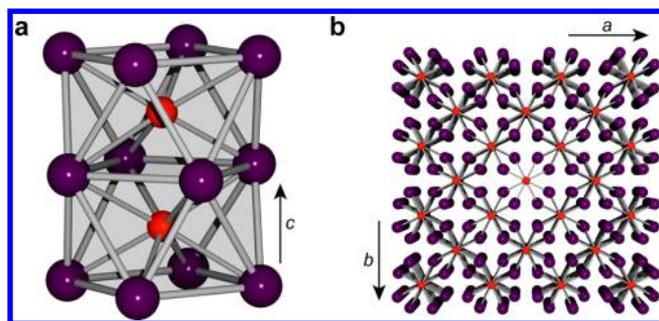
Figure 1. Crystal structure of FeBi$_2$ determined at 29.9(1) GPa. Purple and orange spheres represent Bi and Fe, respectively. (a) View of two face-sharing {FeBi$_8$} square antiprisms stacking along the *c*-direction. (b) View down the *c*-axis showing the edge-sharing linkages formed between the stacked columns.

conditions (4−6 GPa) using a large volume press (LVP). We hypothesized during our research on the Cu$_{11}$Bi$_7$ system that the mutual solubility of the Cu and Bi enabled its facile synthesis at relatively low pressures.

Given the immiscibility of elemental iron and bismuth, even in the molten state (Figure S1),[9] we postulated that we would require access to a significantly higher pressure regime in order to create the first iron−bismuth binary compound. Toward that end, we employed a diamond anvil cell (DAC), which permits *in situ* structural and physical characterization over a much wider range of pressure−temperature space than can be achieved in the LVP. Indeed, DACs are capable of pressures well beyond 250 GPa, which is over an order of magnitude higher than the maximum pressures achievable in LVP reactions. To contextualize this increase in pressure, while our previous synthesis of Cu$_{11}$Bi$_7$ was performed at pressures comparable to the core of the Moon (∼6 GPa), these experiments at ∼30 GPa are performed at pressures comparable to the core of Mars.[10]

Herein we report the synthesis of the first iron−bismuth binary compound, FeBi$_2$ (Figure 1), via pressurization in a DAC at 30 GPa and laser-heating to 1500 K. Decompression studies demonstrate that the material retains the Al$_2$Cu structure type down to at least 2.9(1) GPa, suggesting that it might be possible to quench the phase to ambient pressures at low temperatures.

■ RESULTS AND DISCUSSION

We targeted the synthesis of a novel iron−bismuth binary at pressures between 12−40 GPa using a DAC (see Supporting Information for full details). We performed reactions within this pressure range to ensure that iron would be present as *ε*-Fe (*hcp*), the high-pressure phase of Fe, since our prior reactions at lower pressures—where iron is in the *α*-Fe (*bcc*) phase—were unsuccessful. The experiment was monitored by continuous *in situ* powder X-ray diffraction (PXRD) during laser heating of an iron and bismuth mixture inside a DAC, which allows for the real-time visualization of phase formation as the reaction takes place. This remarkable capability facilitates the exploration of pressure−temperature phase space for a given composition, and also aids in the optimization of the experimental procedure. We employed MgO as a thermal insulator between the sample and the diamond anvils during the laser heating, and also as a pressure-transmitting medium. Fortuitously, its well-defined equation of state also enabled its use as a precise pressure calibrant at the reaction site.[11]

We heated pressurized samples of elemental iron and bismuth using a microfocused infrared laser (fwhm = 40−80 μm) while performing *in situ* PXRD at beamline 16-ID-B, HPCAT, Advanced Photon Source (APS). Between 12 and 30 GPa, we did not observe the formation of any novel phases during heating, even up to 2000 K. However, at pressures above 30 GPa, and upon heating to approximately 1500 K, peaks belonging to a new phase began to appear in the diffraction pattern. These peaks grew in intensity for about 4 min, at which point no further changes were observed. We then switched off the laser heating to thermally quench the reaction. The reaction can be reproduced successfully by pressurizing iron and bismuth in the range of 30−35 GPa and heating at or above ca. 1500 K (see the Supporting Information for details).

Examination of the diffraction patterns acquired at high pressure reveals four phases: MgO (*fcc*), Bi(V) (*bcc*), *ε*-Fe (*hcp*), and a new phase. The observation of a high quality MgO diffraction pattern enables us to employ it as a pressure calibrant by studying the change in lattice parameters at pressure. By placing the compressed MgO lattice parameters into its well-described equation of state, we can determine that the initial pressure before heating was 32.2(1) GPa, and fell to 29.9(1) GPa after thermal quenching.

The *in situ* PXRD experiments at the synchrotron source offered sufficient resolution to enable the simultaneous modeling of all four phases using the TOPAS software package (Figure 2).[12] The gradual appearance of the new phase over a 4 min time window enabled us to easily isolate and index its associated peaks. The relatively small number of peaks in the diffraction pattern was indicative of a high symmetry crystal system, which we indexed to the tetragonal space group, I4/mcm. A search of known binary structure types with this space group yielded the Al$_2$Cu structure type, in which several iron binary compounds crystallize.[13−15] The new phase was well modeled with Rietveld refinement as FeBi$_2$ in the Al$_2$Cu structure type, with lattice parameters of a = 6.3121(3) Å and c = 5.4211(4) Å (at 29.9(1) GPa). The early transition metal−antimonides, TiSb$_2$[16] and VSb$_2$,[17,18] crystallize within the same Al$_2$Cu structure type at ambient pressures, while CrSb$_2$ and
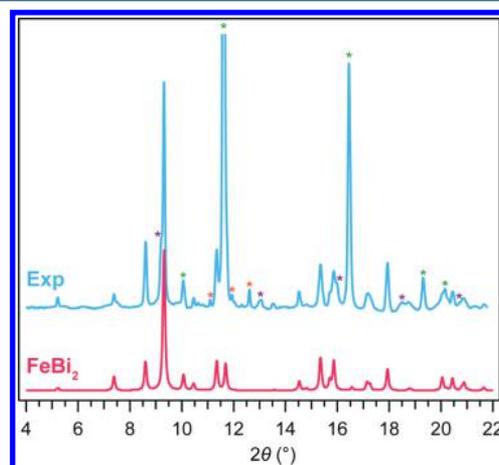

Figure 2. Background-subtracted X-ray diffraction pattern of the reaction site after cooling to room temperature (λ = 0.406626 Å, P = 29.9(1) GPa). The experimental trace is plotted in blue, with asterisks denoting the peaks arising from MgO (green), unreacted Bi(V) (purple), and unreacted *ε*-Fe (orange). The simulated pattern of FeBi$_2$ based on the final fit parameters is plotted in pink.

FeSb$_2$ undergo a pressure-induced transition from the marcasite FeS$_2$ structure type into the Al$_2$Cu structure type at pressures of 5.5 GPa[19] and 14.3 GPa,[13] respectively. FeBi$_2$ can therefore be considered as a structural analogue of the high-pressure phase of FeSb$_2$.

The structure of FeBi$_2$ is composed of iron atoms coordinated by eight bismuth atoms to form square antiprisms with the C_4 axes parallel to the unit cell c-axis (Figure 1a). The square faces are not perfectly staggered, with an angle of 37.5(1)° between them. This structure is reminiscent of the recently isolated ternary cluster anion [Ni$_2$Sn$_7$Bi$_5$]$^{3-}$, which features a 12-atom Sn/Bi cage surrounding two nickel atoms.[20] In FeBi$_2$, the {FeBi$_8$} square antiprisms share both of their square faces with adjacent antiprisms to form columns along the c-direction (Figure 1a), and these columns share edges with neighboring columns throughout the ab-plane (Figure 1b). At 30 GPa, the eight Fe–Bi interactions around each iron atom are equivalent by symmetry, with interatomic distances of 2.719(2) Å. For comparison, molecular Fe–Bi bonds are known to exist in iron carbonyl species, where they possess lengths up to 2.85 Å.[21−23] The sum of the covalent radii of iron and bismuth is 1.25 Å (r_{Fe}) + 1.46 Å (r_{Bi}) = 2.71 Å,[24] which compares very well with the value obtained for Fe–Bi in FeBi$_2$ at the formation pressure. We should note that covalent radii may underestimate bond lengths in intermetallic compounds, due to the increased electron delocalization across the structure coupled with the larger number of interactions common in intermetallic compounds, as compared with the highly directional interactions found in molecules. However, these numbers are still useful as a first approximation of bonding distances in intermetallic compounds. The shortest Fe–Fe distances in FeBi$_2$ are those along the c-axis, 2.7107(3) Å, which is longer than the Fe–Fe distance found in high-pressure FeSb$_2$ (2.536 Å at 28.2 GPa),[13] but shorter than those featured in the Al$_2$Cu-type compound FeZr$_2$, 2.798(2) Å.[15]

There are three unique Bi–Bi interactions within each antiprism: one that forms the edges of the square faces, 3.333(2) Å, and two that form the sides of the triangular faces that connect the upper and lower square faces in each prism, 3.106(3) Å and 3.419(3) Å. An even shorter Bi–Bi interaction exists between bismuth atoms on adjacent antiprism columns (Figure 3), with a distance of 2.948(5) Å. The large range of distances for the Bi–Bi bonds led us to further examine the nature of these interactions. The shortest Bi–Bi distance of 2.948(5) Å is quite short for a Bi–Bi bond, indicating that the interaction is higher order than that of a single Bi–Bi bond. Although high pressure may contribute to the bond contraction, it is worthwhile to note that the single Bi–Bi bond in elemental Bi(V) at 30 GPa is significantly longer (3.1044(3) Å) than the distance seen here. Indeed, the short Bi–Bi bond in FeBi$_2$ is reminiscent of the Bi$_2$ dimer found in the alkali metal–bismuthide binaries, such as Cs$_3$Bi$_2$, 2.976(2) Å, and K$_3$Bi$_2$, 3.014 Å,[25] and in the transition metal–bismuth intermetallic compounds, PtBi$_2$[26] and RhBi$_2$.[27] Within these compounds, a Bi$_2^{2-}$ species, with an extra electron delocalized within the structure, is commonly invoked to understand the electronic structure. The frequently observed Bi–Bi structural motif suggests that this proximal interaction may be important in the formation of this structure. Indeed, there are a number of molecular species featuring a similarly short Bi–Bi bond,[28−33] indicating that this may be a crucial stabilizing factor. As the pressure is released, this Bi–Bi bond distance elongates to
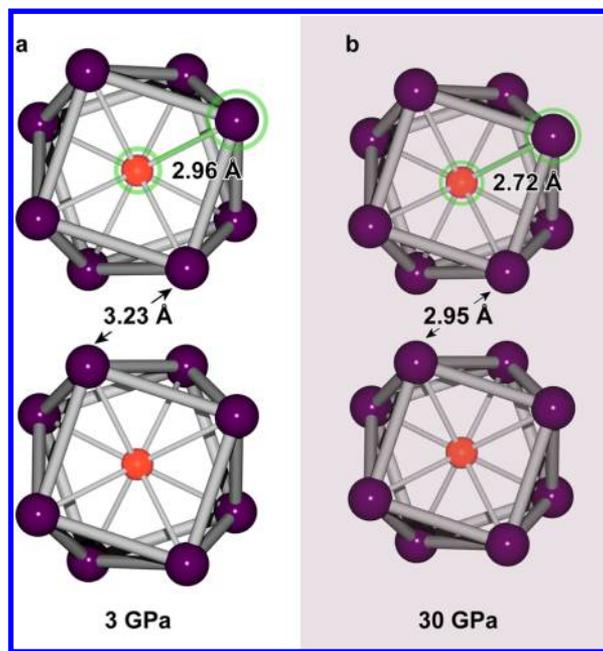

Figure 3. View down the c-axis at 3 GPa (a) and 30 GPa (b), illustrating the effect of increased pressure on the Fe–Bi interaction and the intercolumn Bi–Bi interaction. Purple and orange spheres represent Bi and Fe atoms, respectively.

3.2270(4) Å at 3 GPa, indicating that the stabilizing influence of this dinuclear interaction has diminished (Figure 3).

Compounds displaying long-term stability under ambient conditions after high-pressure synthesis are referred to as quenchable. In order to assess whether the structure could be quenched to ambient pressures, we incrementally decompressed a sample of FeBi$_2$. Rietveld refinement of PXRD patterns collected after each decompression step shows a smooth change in the unit cell parameters of FeBi$_2$ as the pressure is released (Figure 4). Peaks belonging to the FeBi$_2$ phase were evident down to 2.9(1) GPa, but were no longer present upon the final decompression to 0.5(1) GPa, indicating that the compound either decomposed or lost crystallinity.
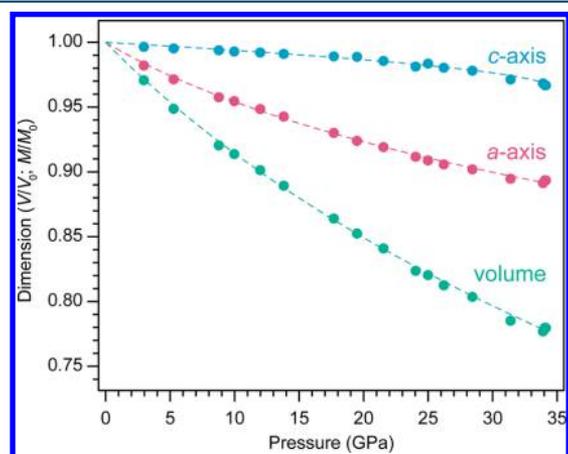

Figure 4. Experimental pressure dependence of the normalized unit cell parameters upon decompression of FeBi$_2$. Dashed lines are fits of the experimental data using the third-order Birch–Murnaghan isothermal equation of state, as described in the Supporting Information.

Completing the iron pnictide series of compounds enables us to gain insight into the structural properties of these materials. First-principles calculations carried out on the known Al_2Cu structure type iron pnictides, FeP_2, $FeAs_2$, and $FeSb_2$, suggest a decrease in compressibility as the reference volume (V_0) increases.[34] Specifically, there is an inverse linear relationship between V_0 (145.2 Å^3, 177.4 Å^3, and 237.0 Å^3, respectively) and the bulk modulus, B_0 (153, 109, and 68 GPa, respectively), for this family of compounds. In order to evaluate the compressibility of $FeBi_2$, we fit the evolution of the $FeBi_2$ lattice parameters (Table S6) as a function of pressure with a third-order Birch–Murnaghan isothermal equation of state (BM3) using the software package EosFit-7c.[35]

For $FeBi_2$, we obtain V_0 = 273(3) Å^3, B_0 = 99(5) GPa, and B_0' = 2.7(2). Using a second-order fit (B_0' = 4 implied), we obtain V_0 = 278(1) Å^3 and B_0 = 75(2) GPa. If we compare the BM3 values to those reported for $FeSb_2$, which is a close structural analogue to $FeBi_2$, we find that $FeBi_2$ is roughly 45% more incompressible than $FeSb_2$. If the trend of increasing compressibility were to continue upon moving down the iron pnictide series, then V_0 = 273(3) Å^3 would lead to an expected value of $B_0 \simeq 49$ GPa for $FeBi_2$. Since we actually observe a decreased compressibility in $FeBi_2$ compared to $FeSb_2$, this trend does not appear to extend to the bismuthides. We hypothesize that this unexpected result could stem from the increased importance of relativistic effects in bismuth,[36] which are known to cause discontinuities in chemical trends going down the pnictogen series. The potential for anomalous behavior arising from relativistic effects provides further motivation for the creation and investigation of new bismuth-based intermetallic compounds.

The extrapolated zero-pressure unit cell lengths obtained from the axial compressibility plots are a_0 = 6.98(2) Å and c_0 = 5.666(4) Å. We can use these values to estimate the structural parameters under ambient conditions, which then allows us to compare structural parameters with other reported solid-state structures. One parameter that we are particularly interested in is the Fe–Bi distance. Fe–Bi bonds are, to the best of our knowledge, completely absent from solid-state materials. The extrapolated zero-pressure Fe–Bi distance in $FeBi_2$ is 2.96 Å. At the elevated pressure of 29.9(1) GPa, the Fe–Bi bond distance in $FeBi_2$ is 2.719(2) Å.

Based on the structural metrics and examination of the pnictide literature, we hypothesize that two driving forces behind the formation of the phase are the pressure-induced stabilization of the Fe–Bi bond and the intercolumn Bi–Bi bonding interaction (Figure 3). The numerous examples of compounds featuring Bi–Bi bonds across the solid-state and molecular literature bolster our supposition that creating stronger bonding interactions between pairs of bismuth atoms is a stabilizing factor. Indeed, this may serve as a design principle for the synthesis of additional bismuth based phases. As the pressure is decreased, the stabilizing influence of these bonds is expected to diminish until eventually phase separation (decomposition) becomes the thermodynamically favored process. Therefore, one possible explanation for the loss of the diffraction pattern of the compound below 2.9(1) GPa at room temperature is that, at this pressure, ambient temperature provides sufficient thermal energy to enable decomposition of the metastable phase. Future work will explore the quench-ability of this phase at low temperatures, and with slow gas membrane decompression, since the rate of pressure release is known to be an important factor in quenching metastable phases.[37−39]

CONCLUSIONS

We synthesized the first compound in the iron–bismuth system, which also features the first Fe–Bi bond in the solid state. This compound persists down to at least 2.9(1) GPa, offering the potential for future quenchability. Ongoing work is focused on the scale-up of this reaction with a unique, highly specialized press capable of reaching the required pressures in order to enable studies of the electronic properties of this fascinating new material.

The results reported here ignite promise for new discoveries within the iron pnictide systems, and demonstrate the value of high pressure as a viable route toward new intermetallic compounds, and indeed toward creating new bonds in the solid state. In particular, the stabilizing effect of the Bi–Bi interaction within this compound offers significant promise for the high-pressure synthesis of iron–bismuth superconductors within the $ThCr_2Si_2$ structure type. Simple visual inspection of the Bi–Bi distances in the known $BaMn_2Bi_2$ structure hints that high pressure could be an appropriate vector to synthesize the iron analogue. Future work will focus on completing the series of pnictide superconductors via high-pressure synthesis.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscentsci.6b00287.

Experimental details, Rietveld refinement parameters, and cell parameters used for BM3 fits (PDF)
Crystallographic information for $FeBi_2$ (CIF)

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Notes
The authors declare no competing financial interest.

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