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## Controlling dimensionality in the Ni–Bi system with pressure

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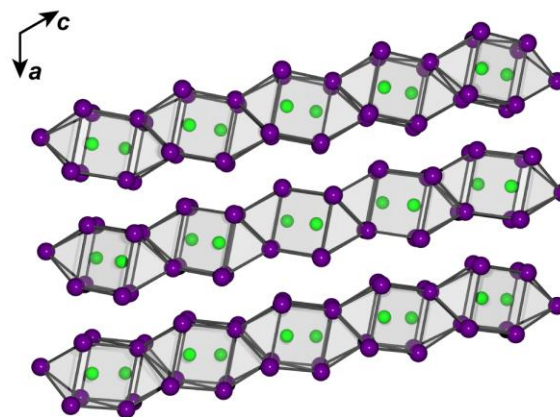
**ABSTRACT:** The discovery of new layered materials is crucial for the development of novel low-dimensional materials. Here, we report *in situ* high-pressure studies of the quasi-1D material NiBi<sub>3</sub>, revealing the formation of a new layered intermetallic phase, NiBi<sub>2</sub>. *In situ* diffraction data enabled us to solve the structure of NiBi<sub>2</sub>, which crystallizes in the same structure type as PdBi<sub>2</sub>, adding to a growing number of examples in which first-row transition-metal binary systems form structures at high pressure comparable to the ambient pressure structures of their second-row congeners. Based upon the diamond anvil cell reactions, we initiated scale up reactions in a multi-anvil press and isolated bulk NiBi<sub>2</sub>. Isolating a bulk sample enabled us to evaluate prior theoretical predictions of phase stability for NiBi<sub>2</sub>. Our findings of metastability within this phase are contrary to previous predictions, recommending continuing research into this phase. The dimensionality of the building units seems to vary as a function of synthesis pressure in the Ni–Bi system, being quasi-1D at ambient pressures (NiBi<sub>3</sub>), quasi-2D at ~14 GPa (NiBi<sub>2</sub>), and 3D at ~39 GPa (β-NiBi). This observation represents the first demonstration of dimensionality control in a binary intermetallic system via application of pressure.

The discovery and characterization of new two-dimensional (2D) materials is at the forefront of contemporary physics and materials science.<sup>1,2</sup> The dimensional reduction from bulk to 2D transforms the electronic structure of these materials, resulting in unexpected physical and electronic properties including unusual magneto-optical effects, superconductivity, and unexpectedly high electron mobilities.<sup>3–5</sup> Discovering new synthetic approaches to create layered structures amenable to exfoliation is the key initial step to accessing novel 2D materials.<sup>6,7</sup> One initially counterintuitive approach is the application of high pressure to increase the dimensionality of one-dimensional (1D) compounds to create layered systems. Our specific target of interest was the Ni–Bi binary system, which contains two thermodynamically stable superconducting intermetallic compounds: α-NiBi ( $T_c = 4.25$  K) and quasi-1D NiBi<sub>3</sub> ( $T_c = 4.06$  K).<sup>8–12</sup> We sought to compress the quasi-1D NiBi<sub>3</sub> to create a new, layered Ni–Bi intermetallic compound. Toward that end we harnessed the transparency of diamond to probe the formation of new phases in the Ni–Bi system within a diamond anvil cell (DAC). We can use powder X-ray diffraction (PXRD) to observe the reaction progression, and thereby establish the reaction conditions required for scale-up.

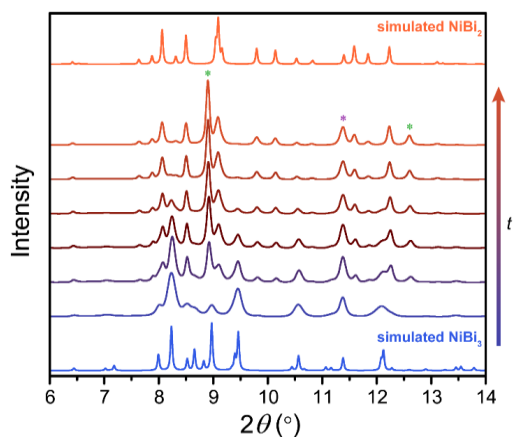
Herein, we report the discovery of the new layered binary intermetallic compound, NiBi<sub>2</sub>, synthesized at ~14 GPa and ~675 °C from a pure sample of NiBi<sub>3</sub>. NiBi<sub>2</sub> is composed of Bi–Ni–Bi layers that stack along the crystallographic *a*-axis (Figure 1). Intriguingly, the basic structural unit comprising the layers is identical to that found in the quasi-1D NiBi<sub>3</sub> compound, as well as the compact high-pressure β-NiBi phase.<sup>13</sup> To the best of our knowledge, this is the first example in a binary intermetallic system where the underlying coordination geometry of

the transition metal is maintained while the dimensionality of the structure is controlled by pressure from quasi-1D to quasi-2D. The new intermetallic is pressure quenchable, and preliminary magnetic measurements suggest a potential superconducting transition at  $T_c \sim 4.2$  K. The discovery of this compound illuminates the layered structures achievable at high pressure.

*In situ* structural and spectroscopic monitoring of reactions during pressurization and heating were performed in a laser-heated diamond anvil cell (LH-DAC).<sup>14</sup> A polycrystalline powder of NiBi<sub>3</sub> was pressed into a flake and placed into the cell



**Figure 1:** Structure of NiBi<sub>2</sub> emphasizing the layered nature of the material. Violet and green spheres represent Bi and Ni, respectively.



**Figure 2:** Background-subtracted *in situ* powder X-ray diffraction patterns taken during heating of NiBi<sub>3</sub> in a LHDAC at 14.8(1) GPa and ~675 °C ( $\lambda = 0.406626$  Å). During heating, NiBi<sub>3</sub> converts to NiBi<sub>2</sub> and elemental Bi (denoted by green asterisks) and the pressure drops slightly to 14.5(1) GPa. MgO is denoted by a violet asterisk. The top and bottom patterns are simulated powder patterns of NiBi<sub>2</sub> and NiBi<sub>3</sub>, respectively.

between two discs of single crystal MgO, which were used as a thermal insulator, pressure-transmitting medium, and *in situ* pressure calibrant.<sup>15</sup> Heating within the cell was achieved using two infrared lasers, each focused to a full width at half maximum (FWHM) of ~40  $\mu\text{m}$ . We acquired *in situ* synchrotron powder X-ray diffraction (PXRD) data continuously during heating, using 30 keV radiation focused to a FWHM of ~10  $\mu\text{m}$ .<sup>14</sup> All *in situ* data were acquired at 16-ID-B, HPCAT at the Advanced Photon Source (APS).

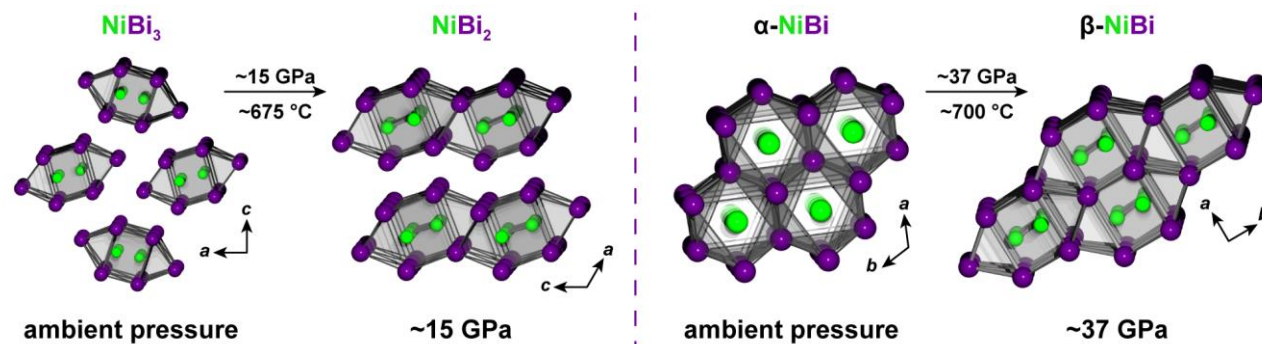
To search for new low dimensional intermetallic compounds we pressurized the sample of NiBi<sub>3</sub> to ~14.8(1) GPa. The PXRD pattern before laser heating consisted of broad peaks corresponding to NiBi<sub>3</sub> and MgO. The broadness of the peaks is due to the microscopic strain induced by non-hydrostatic compression in the solid pressure transmitting medium, MgO. As the temperature was increased, the peaks sharpened due to thermal annealing, which relieves the strain in the NiBi<sub>3</sub> powder. Upon heating to approximately 675 °C, new Bragg peaks began to appear in the PXRD pattern concomitant with a decrease in intensity of the peaks corresponding to NiBi<sub>3</sub>, suggesting the synthesis of a new intermetallic phase (Figure 2). After approximately two minutes at this temperature, the peaks corresponding to NiBi<sub>3</sub> were no longer observable and the pressure within the cell had gradually decreased to 14.5(1) GPa. Since the diffraction pattern remained invariant, we turned off the laser to thermally quench the reaction. After quenching the reaction, three phases were present in the PXRD pattern: the unidentified phase, elemental Bi(V), and MgO. The new Bragg reflections did not correspond to the known structures of  $\alpha$ -NiBi,  $\beta$ -NiBi, *fcc*-Ni, nor any other polymorphs of elemental bismuth, indicating a new compound had been accessed through high-*PT* synthesis. Further, the generation of elemental Bi(V) during heating suggested the new intermetallic phase was formed by a release of bismuth from the NiBi<sub>3</sub> structure.

The high quality of the PXRD data enabled structural identification of the new phase with the aid of a structural model. We initially modeled the known MgO and Bi(V) phases, enabling assignment of the Bragg peaks corresponding to the new phase. These peaks were indexed to the monoclinic space group *C2/m* with lattice parameters  $a = 12.1135(3)$  Å,  $b = 3.83754(9)$  Å,  $c = 5.2749(2)$  Å, and  $\beta = 100.909(3)^\circ$  at a pressure of 14.1(1) GPa

using the TOPAS software package.<sup>16</sup> We searched the Inorganic Crystal Structure Database (ICSD)<sup>17</sup> for known structures with similar chemistry, symmetry, and lattice parameters, and determined the new phase could be modelled in the CeAlCo structure type with Ni residing on the Co site and Bi on both the Ce and Al sites.<sup>18</sup> In the refined structure of NiBi<sub>2</sub> in the CeAlCo structure type, the Ni atoms are coordinated by seven Bi atoms and two Ni atoms, in a tricapped trigonal prismatic geometry (Figure S3). Excluding the Ni atoms, the coordination of the Bi around the central Ni atom is a monocapped trigonal prism (Figure S3). These polyhedra are rectangle-face-sharing to form prism rods and enable Ni–Ni bonding in the form of a zig-zag chain. These prism rods are triangle-face-sharing to form a layered structure (Figure 1). Further inspection of the ICSD revealed that the chemically similar superconducting intermetallic mineral froodite, or PdBi<sub>2</sub> ( $T_c = 1.7$  K), crystallizes in this same structure type.<sup>19</sup> This finding is in accordance with a guideline to predict high-pressure structural changes formulated by Prewitt and Downs: “elements behave at high pressure like the elements below them in the periodic table at lower pressure.”<sup>20</sup> The ambient-pressure stability of PdBi<sub>2</sub> and high-pressure stability of NiBi<sub>2</sub> suggest that this approach can be extended to binary systems. In this case, the first-row transition metal binary compound NiBi<sub>2</sub> behaves at high pressure like the second-row binary intermetallic PdBi<sub>2</sub> behaves at ambient conditions. This type of behavior is also observed for the high-pressure phase CoBi<sub>3</sub>, which crystallizes in the same space group as ambient-stable RhBi<sub>3</sub>.<sup>21,22</sup> The extension of this rule could have important implications for other transition-metal main-group binary systems where the second-row compound exists but no first-row analogue is known. Using this guideline as a predication pathway enables the selection of stoichiometric ratios of elements for high-pressure synthesis and hints at pathways to isolate desired structure types with different elements.

Further consideration of the structure of NiBi<sub>2</sub> reveals it is the quasi-2D analogue of the quasi-1D RhBi<sub>3</sub> structure type that the thermodynamically stable precursor, NiBi<sub>3</sub>, crystallizes in (Figure 3).<sup>11</sup> Both structures are comprised of Ni-centered Bi<sub>7</sub> monocapped trigonal prisms that are rectangle-face-sharing along the *b*-axis to form 1D NiBi<sub>3</sub> prism rods. In NiBi<sub>3</sub>, these rods are spatially separated, connected by weak Bi–Bi bonds (Figure 3, left). In NiBi<sub>2</sub>, the 1D prism rods are triangle-face-sharing perpendicular to their running direction, generating a layered structure. Strikingly, the structural motif of 1D rods is also present in the recently reported high-pressure  $\beta$ -NiBi phase (Figure 3, right).<sup>13</sup> In this structure, the 1D prism rods are triangle-face sharing both perpendicular to their running direction and along the crystallographic *a*-axis, forming a compact 3D structure. In elemental examples, it is common for atoms to increase coordination number and adopt close-packed arrangements under pressure.<sup>20,23</sup> This system is particularly interesting because as pressure is increased, the coordination of Ni remains constant such that the NiBi<sub>3</sub> prism rod motif is maintained. Instead, we observe an overall increase in dimensionality from the quasi-1D NiBi<sub>3</sub>, to quasi-2D NiBi<sub>2</sub>, to compact 3D  $\beta$ -NiBi by a “polymerization” of prism rod building blocks and a corresponding change in stoichiometry associated with a decrease in bismuth content. Note:  $\beta$ -NiBi has only been synthesized from  $\alpha$ -NiBi, indicating that other factors also play an important role in going from one compound to another.

There is precedent for such behavior in the form of chemical pressure as a mechanism to control dimensionality. One example is within the AeNiGe (Ae = Mg, Ca, Sr, Ba) system, where an increase of the cation size led to a reduction of the



**Figure 3:** Polyhedral representation of the crystal structure of four known Ni-Bi intermetallic compounds. Violet and green spheres represent Bi and Ni, respectively. Thermodynamically-stable precursor  $\text{NiBi}_3$  forms layered  $\text{NiBi}_2$  by heating at  $\sim 15$  GPa (left). Thermodynamically-stable  $\alpha\text{-NiBi}$  was previously reported to form  $\beta\text{-NiBi}$  upon heating at  $\sim 37$  GPa (right).<sup>13</sup> The polyhedral representation clearly depicts the identical subunits that form quasi-1D  $\text{NiBi}_3$ , quasi-2D  $\text{NiBi}_2$ , and compact  $\beta\text{-NiBi}$ .

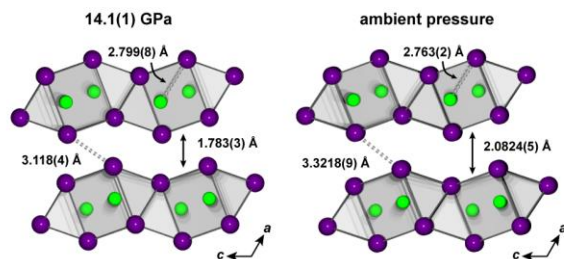
dimensionality of the  $[\text{NiGe}]$  building blocks.<sup>24</sup> Further, the dimensionality of binary compounds comprised of light elements, such as  $\text{SiS}_2$ , can be controlled from 1D to 3D with relatively low physical pressure.<sup>25</sup> To the best of our knowledge, the Ni-Bi system is the only example of a binary intermetallic system where the structural subunits can pack from quasi-1D to quasi-2D and ultimately to 3D depending on the synthesis pressure and precursor stoichiometry. These results recommend the high-pressure exploration of other intermetallic systems that under ambient conditions exhibit low dimensionality, such as  $\text{Ta}_4\text{SiTe}_4$ ,<sup>26</sup>  $\text{ZrTe}_5$ ,<sup>27</sup> and  $\text{CoSn}_3$ .<sup>28</sup>

While the new  $\text{NiBi}_2$  phase forms from  $\text{NiBi}_3$  with the expulsion of Bi at  $\sim 14$  GPa and  $\sim 675$  °C, previous experiments using  $\alpha\text{-NiBi}$  as the precursor do not produce  $\text{NiBi}_2$  at similar pressures and temperatures. When qualitatively determining which materials may be more stable at high pressure, the unit cell volume of the materials may be considered, as increasing pressure tends to favor higher densities in materials. Under temperature and pressure conditions at which  $\text{NiBi}_2$  and  $\text{Bi(V)}$  form from  $\text{NiBi}_3$ ,  $\text{NiBi}_3$  has a unit cell volume of  $85.6(1) \text{ \AA}^3$  per formula unit, while  $\text{NiBi}_2$  and  $\text{Bi(V)}$  have a combined unit cell volume of  $84.54(1) \text{ \AA}^3$ . Therefore, the formation of  $\text{NiBi}_2$  is favorable from a density perspective, as the volume of the system decreases by 1.2% upon conversion from  $\text{NiBi}_3$  to  $\text{NiBi}_2 + \text{Bi(V)}$ . In comparison, at about  $14.1(1)$  GPa,  $\alpha\text{-NiBi}$  has a unit cell volume of  $68.48(1) \text{ \AA}^3$  per two formula units, while  $\text{NiBi}_2 + \text{Ni}$  have a combined volume of  $70.50(8) \text{ \AA}^3$  per formula unit.<sup>29</sup> Thus, forming  $\text{NiBi}_2$  and Ni from  $\alpha\text{-NiBi}$  requires a  $\sim 3\%$  increase in the summed volume of the phases, which is unfavorable from a density standpoint. This may account for why  $\text{NiBi}_2$  forms from  $\text{NiBi}_3$  but not from  $\alpha\text{-NiBi}$  in this pressure range, and reinforces the importance of stoichiometry in determining which products are formed at high-*PT* conditions.

After isolating the new phase at high-pressure conditions within the LH-DAC, we performed a decompression study to assess if the compound remained stable to ambient pressure, *i.e.* to determine whether it was pressure-quenchable (Figure S4). Bragg peaks corresponding to  $\text{NiBi}_2$  persisted upon decompression to ambient pressure, indicating the phase was in fact pressure-quenchable. We scaled up the reaction using a multi-anvil press (MAP) to probe the physical properties of  $\text{NiBi}_2$ . The new binary compound was obtained in  $\sim 75\%$  yield by reaction of the elements at  $\sim 15$  GPa and  $\sim 675$  °C for 1 hour (see SI for details). Scanning electron microscopy and energy dispersive X-ray spectroscopy performed on the decompressed sample confirmed the majority of the sample consisted of  $\text{NiBi}_2$  and indicated the presence of unreacted elemental Ni and Bi, as

well as regions of Ni:Bi 1:1 and 2:1 (Figure S6). Because of the layered structure and the high-pressure synthesis conditions, crystals sufficiently large for single-crystal X-ray diffraction could not be isolated from the reaction product. The structure of  $\text{NiBi}_2$  at ambient pressure was confirmed by Rietveld refinement of the synchrotron PXRD pattern (Figure S9). A comparison of the high-pressure and ambient-pressure structures highlights the layered nature of the structure. The unit cell volume of the new phase upon decompression increases by 16.3%. Notably, the interlayer spacing increases by 16.8% upon decompression, indicating that the interlayer region, likely occupied by the Bi lone pair, is the area of highest compressibility in the structure (Figure 4). The anisotropic compressibility of the sample is further emphasized by the surprising 1.3% *decrease* in the Ni1-Bi1 distance compared to the 6.5% *increase* in the Bi1-Bi1 interaction distance (Figure 4). The ambient pressure Bi1-Bi1 distance ( $3.3218(9) \text{ \AA}$ ) is slightly greater than twice the atomic radius of bismuth ( $2r_a = 3.2 \text{ \AA}$ ),<sup>30</sup> suggesting the possibility for a Bi-Bi bonding interaction between layers. Electronic structure calculations and detailed bonding analyses are necessary to evaluate the nature of this Bi-Bi interaction. The overall change in atomic distances from high pressure to ambient pressure, and the persistence of the network of strong Ni-Bi interactions, verifies the layered nature of the structure.

To purify the sample for physical properties measurements, we ground the as-synthesized sample from the high-pressure MAP reaction and magnetically separated the ferromagnetic elemental Ni component. Synchrotron PXRD indicate that unreacted elemental Ni is absent from the sample after magnetic separation and demonstrate that the sample consists of 74.4 wt%  $\text{NiBi}_2$ , 20.73 wt% Bi, and 4.8 wt%  $\text{NiBi}_3$  (Figure S9). Preliminary variable-temperature dc magnetic susceptibility measurement of this sample acquired at  $H_{dc} = 5$  Oe show a broad and continuous downturn in susceptibility with an onset of  $T_c \sim 4.2$  K (Figure S8). This behavior is indicative of a superconducting transition, however the broad nature of the transition, which is potentially due to strain in the 2D lattice or ferromagnetic amorphous Ni, prevent us from a definitive assignment of bulk superconductivity arising from this phase. It should be noted that the  $\text{NiBi}_3$  impurity in the sample may be the source of the superconducting signal, as  $\text{NiBi}_3$  is a superconductor. Our attribution of the superconductivity to a new phase arises largely from the higher  $T_c$  in the pellet described above ( $T_c \sim 4.2$  for our sample;  $T_c = 4.06$  for  $\text{NiBi}_3$ ). This implies but does not confirm that superconductivity arises from a different phase than  $\text{NiBi}_3$ .



**Figure 4:** Comparison of the 14.1(1) GPa and ambient-pressure crystal structures of NiBi<sub>2</sub>. Notably, the interlayer spacing increases by ~16% and the Ni–Bi bond decreases by ~1.3%. Violet and green spheres represent Bi and Ni, respectively.

Future measurements will focus on elucidating the physical properties of this material in higher purity samples, and using additional techniques such as heat capacity and resistivity.

Calculations performed by Wehrigh and coworkers in 2013, and in 2018 by Wolverton and coworkers, suggest that the monoclinic layered phase of NiBi<sub>2</sub> experimentally realized here should be stable with respect to decomposition at ambient pressure, and should be synthetically accessible using traditional solid-state methods.<sup>31,32</sup> To assess the metastability of the high-pressure phase, we performed differential scanning calorimetry (Figure S7). Upon heating the sample, we observe an exothermic event at 262 °C immediately followed by the endothermic melting of elemental Bi at 271 °C. A corresponding crystallization event is not observed upon cooling, suggesting that NiBi<sub>2</sub> is in fact metastable. If the compound is metastable at ambient pressure, methods that promote atomic mixing at low or ambient temperature, such as molecular beam epitaxy or co-sputtering, may be able to successfully isolate this phase. This could further prove useful in generating thin film samples for properties measurements. Importantly, it could have far-reaching implications for the discovery of low-temperature thermodynamically stable phases in simple binary systems.

The foregoing results illustrate the high-*PT* synthesis of the new binary compound NiBi<sub>2</sub>. This quasi-2D material exhibits the same basic structural unit present in the thermodynamically stable quasi-1D NiBi<sub>3</sub> and the metastable high-pressure phase β-NiBi. This structural continuity is suggestive of control of dimensionality via pressure, and highlights the structural diversity that can be achieved at high pressures. Crucially, the newly isolated binary phase comprises a potentially exfoliable layered material bearing a heavy main group element. Future studies will focus on increasing yield and exfoliating this material.

## ASSOCIATED CONTENT

### Supporting Information

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The Supporting Information is available free of charge on the ACS Publications website. Details of experimental procedure and characterization (PDF) High-pressure and ambient-pressure crystal structures (CIF).

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### Notes

The authors declare no competing financial interests.

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