ABSTRACT: Alloys between Mg₃Sb₂ and Mg₃Bi₂ have recently been shown to be exceptional thermoelectric materials due in part to their anomalously low thermal conductivity. In the present study, in situ high-pressure synchrotron X-ray diffraction was used to investigate the structure and bonding in Mg₃Sb₂ and Mg₃Bi₂ at pressures up to 50 GPa. Our results confirm prior predictions of isotropic in-plane and out-of-plane compressibility but reveal large disparities between the bond strength of the two distinct Mg sites. Using single-crystal diffraction, we show that the octahedral Mg−Sb bonds are significantly more compressible than the tetrahedral Mg−Sb bonds in Mg₃Sb₂, which lends support to prior arguments that the weaker octahedral Mg bonds are responsible for the anomalous thermal properties of Mg₃Sb₂ and Mg₃Bi₂. Further, we report the discovery of a displacive and reversible phase transition in both Mg₃Sb₂ and Mg₃Bi₂ above 7.8 and 4.0 GPa, respectively. The transition to the high-pressure structure involves a highly anisotropic volume collapse, in which the out-of-plane axis compresses significantly more than the in-plane axes.

INTRODUCTION

The compound Mg₃Sb₂ was discovered by Edward Zintl in 1933 before falling into almost complete obscurity for more than 70 years.¹ In the past five years, however, alloys between Mg₃Sb₂ and Mg₃Bi₂ have emerged as exceptional room-temperature thermoelectric materials, threatening to overthrow the decades-long reign of Bi₂Te₃.²−⁷ Mg₃Sb₂ and Mg₃Bi₂ are binary members of the CaAl₂Si₂ structure type (P3̅m1) shown in Figure 2a, making them part of a broader family of AM₂X₂ Zintl compounds that are traditionally considered to be layered materials.⁸−¹⁰ Many compounds in this family are well-described as consisting of covalent [MₓX₂]²⁻ slabs with the ionically bonded interlayer A²⁺ cations providing charge neutrality.¹¹ However, this picture is not suitable in the case of Mg₃Sb₂ and Mg₃Bi₂; in these binary compounds, Mg resides in both the octahedrally coordinated Mg₁ site (i.e., the cation site) and the tetrahedrally coordinated Mg₂ site (typically occupied by a more electronegative post-transition metal).¹² First-principles chemical bonding analysis has suggested that the Mg₁−Sb and Mg₂−Sb bonds in Mg₃Sb₂ are quite similar with respect to the degree of charge transfer from Mg to Sb.¹³ This prediction of quasi-isotropic bonding in Mg₃Sb₂ was accompanied by first-principles calculations of nearly isotropic compressibility in the in-plane (a−b plane) and out-of-plane (c-axis) directions under pressure.¹⁴ An improved understanding of chemical bonding is particularly germane to Mg₃Sb₂ and Mg₃Bi₂, since the low thermal conductivity of these materials is thought to arise from soft and anharmonic bonding between the octahedrally coordinated Mg₁ atoms and pnictogen species.¹⁵

In the present study, we investigate these questions experimentally using in situ diffraction of Mg₃Sb₂ and Mg₃Bi₂ at pressures up to ~50 GPa. The application of high pressure allows investigation of bonding environments without varying chemical composition or introducing the complications associated with high temperature (i.e., large entropy, phase separation, thermal excitations, etc.).¹⁶ In particular, the compressibility of individual bonds can be directly measured, shedding light on structural instabilities that can lead to desirable phonon behavior. Despite intense interest in these compounds in recent years, no experimental high-pressure...
investigation exists to date. In fact, there have been only a handful of high-pressure studies of compounds in the CaAl2Si2 structure type,17–21 despite their long history and potential technological importance. Here, we report on the discovery of a previously unrecognized high-pressure phase transition in Mg3Pn2 (Pn = Sb, Bi) using in situ high-pressure synchrotron X-ray diffraction (XRD) combined with first-principles calculations. Through high-pressure single-crystal X-ray diffraction, we extract the pressure-dependent volume change of the polyhedra of the ambient structure and solve the structure of the high-pressure phase, revealing large disparities between the bond strength of the two distinct Mg sites.

### EXPERIMENTAL SECTION

**Synthesis.** Polycrystalline Mg3Sb2 and Mg3Bi2 samples were synthesized by direct ball-milling of the elements followed by spark plasma sintering. Stoichiometric quantities of Mg (granules, Alfa Aesar 99.8%), Bi (shot, 99.99% RotoMetal), and Sb (shot, 99.99% Alfa Aesar) were cut into small pieces in an argon-atmosphere glove box, loaded into stainless steel vials with two 10 mm diameter stainless steel balls, and milled under an argon atmosphere for 1 h using a SPEX mill. The powder was then loaded into graphite dies and sintered at 213 MPa using a Dr. Sinter SPS-211LX. The Mg3Sb2 and Mg3Bi2 powders were heated to 850 and 650 °C in 5 min and then holding at the target temperature for 10 min. The pressure was removed immediately after cooling was completed. The samples were ground into fine powders, the phase purity of which was confirmed using a Rigaku SmartLab X-ray diffractometer (XRD) with Cu Kα radiation. Based on relative peak intensities, Mg3Sb2 and Mg3Bi2 powders contain less than 1% of Sb and less than 3% of Bi as impurity phases, respectively.

Small Mg3Sb2 single crystals (∼100 μm) grown via chemical vapor transport were also used in this study. These were obtained as a byproduct of an attempt to grow larger Mg3Sb2 crystals from a flux. Elemental Mg (granules, Alfa Aesar 99.8%) and Sb (shots, 99.99% Alfa Aesar) were mixed in a molar ratio of 2:3 Mg/Sb, loaded into an Al2O3 crucible with a second Al2O3 crucible on top serving as a cap. These were sealed in a quartz ampule under vacuum (∼10−3 torr). The ampule was heated to 800 °C in a tube furnace during an 8 h period and then moved upward through the furnace at a rate of 1.8 mm h−1. Upon inspection, small Mg3Sb2 single crystals were found to be deposited on the top crucible. Selected crystals, not bigger than ∼100 μm in their longest dimension, were broken under liquid N and screened by single-crystal XRD using a Bruker AXS Diffractometer at ambient pressure.

**High-Pressure X-ray Diffraction.** In situ high-pressure X-ray diffraction experiments were conducted at the Advanced Photon Source (APS), beamlines 13-BM-C (GSECARS) and 16-BM-D (HPCAT) at Argonne National Laboratory. The distance and orientation of the detector was calibrated using a CeO2 standard. The beam size was 12 μm (horizontal) × 18 μm (vertical) FWHM at GSECARS and 4 μm × 4 μm FWHM at HPCAT. The detector was an online Pilatus 1M at GSECARS and a Mar345 image plate at HPCAT. Diamond anvils with culets of diameter 300 and 800 μm were used, with rhenium gaskets from H-Cross preindented to thicknesses of ∼45 μm (see Figure 1c). To form the sample chamber, the gaskets were drilled using the laser micromachining system at HPCAT.22 The polycrystalline samples were ground into powder and then pressed into flakes before loading into the DACs. A ∼40 μm × 40 μm Mg3Sb2 single crystal was screened for crystallinity at APS before loading into a diamond anvil cell (DAC), as shown in Figure 1d. Ruby was placed next to each sample for pressure readings. Neon was loaded as the hydrostatic pressure medium using the COMPRES/GSECARS gas loading system for all samples. For powder measurements, a gas membrane setup was used to remotely increase or decrease pressure as needed and the pressure was read via the in situ ruby fluorescence system before and after each data collection.23 All experiments were carried out at ambient temperature. Further experimental details specific to beamline 13-BM-C can be found in ref 24.

Raw single-crystal and powder diffraction patterns were preprocessed in Bruker APEX3 software suite25 and Dioptras,26 respectively. The high-pressure structure was solved with the OLEX2 software27 using the high-pressure Mg3Sb2 single-crystal data. The crystallographic details can be found in Supporting Information (Tables S1
Vienna Ab initio Simulation Package (VASP). 31 functional theory (DFT) simulations were performed using the and con indicating the nonquenchability of the high-pressure phase

$P_3m$1 structure at higher pressures. The $P3m1$ structure was completely recovered when the pressure was reduced (see Supporting Information, Figure S3), indicating the nonquenchability of the high-pressure phase and confirming that the new peaks at high-pressure are not a result of decomposition.

To solve the high-pressure structure and to obtain atomic positions as a function of pressure, we turned to single-crystal diffraction, using the Mg$_6$Sb$_2$ crystal shown in Figure 1c. Single-crystal diffraction patterns collected at pressures below and above the phase transition show a crystal-to-crystal transformation, with no signs of specimen fracture (Figure 1d). A structure solution for Mg$_6$Sb$_2$ at 7.8 GPa was reached in the monoclinic C2/m space group (see Supporting Information (Tables S1 and S2) for detailed crystallographic data from the single-crystal experiments). The same C2/m structure solution provides a satisfactory fit for Mg$_6$Sb$_2$ and Mg$_6$Bi$_2$ powder data at high pressure (as shown in Supporting Information, Figures S4 and S5), suggesting that both phases undergo the same high-pressure phase transition. Below, however, we will focus our discussion of structure to the Sb-analogue.

The high-pressure (HP) monoclinic structure of Mg$_6$Sb$_2$, shown in Figure 2b, is a highly distorted variant of the ambient-pressure (AP) trigonal CaAl$_2$Si$_2$ structure type (Figure 2a). The tetrahedrally coordinated (Mg$_2$)$_2$Sb$_2$ slab in AP-Mg$_6$Sb$_2$ (shown in blue/cyan) transforms at high pressure into a layer with alternating tetrahedral and square pyramidal coordination environments. In this respect, HP-Mg$_6$Sb$_2$ has structural similarities to previously reported HP-CaMn$_2$Bi$_2$ (space group P2$_1/m$), which exhibits a highly similar Mn$_6$Bi$_2$ slab at pressures above 2 GPa. However, HP-Mg$_6$Sb$_2$ shows key differences with HP-CaMn$_2$Bi$_2$ with respect to the octahedral Mg$_1$ layer shown in red; in HP-Mg$_6$Sb$_2$, every other octahedron distorts to form a square-planar environment, accompanied by the breaking of two opposing Mg(1)–Sb bonds. This bond breaking allows the remaining Mg$_1$ atoms to achieve a near ideal octahedral environment. In contrast, the Ca-centered octahedra in the HP-CaMn$_2$Bi$_2$ structure do not undergo bond breaking. Instead, they simply distort such that one of the Ca–Bi bonds in each octahedron is elongated (see Supporting Information, Figure S10).

Density functional theory calculations confirm that the monoclinic C2/m structure of Mg$_6$Sb$_2$ is indeed more stable than the trigonal P3m1 structure at higher pressures. The calculated energy–volume curves shown in Figure 3 for the ambient- and high-pressure phases of Mg$_6$Sb$_2$ indicate a critical volume per formula unit of 116 Å$^3$, which corresponds to a pressure of approximately 5.6 GPa. Above this pressure, the monoclinic structure is more stable. This prediction agrees reasonably well with our experimental transition pressure, which was found to be approximately 7.8 GPa for Mg$_6$Sb$_2$ powder. In addition, we calculated the energy of Mg$_6$Sb$_2$ with the P2$_1/m$ space group and found that it was significantly higher than that of either P3m1 or C2/m, which supports the current findings.

Compressibility of Mg$_6$Sb$_2$ and Mg$_6$Bi$_2$. The pressure response of the ambient- and high-pressure structures of

![Figure 2. Comparison of the (a) ambient- ($P3m1$) and (b) high-pressure (C2/m) structure of Mg$_6$Sb$_2$. (c) Depiction of the four Mg coordination environments in the high-pressure structure. The tetrahedral and octahedral layers of the ambient-pressure structure are shown in cyan and red, respectively. These layers, though highly distorted, can still be recognized in the high-pressure structure. The black box in both images illustrates the distortion of the original trigonal unit cell.](https://dx.doi.org/10.1021/acs.chemmater.0c03678)
Mg3Sb2 and Mg3Bi2 can be used to provide a deeper understanding of the chemical bonding and in turn thermal transport. The pressure dependence of the unit cell volume for Mg3Bi2 and Mg3Sb2 is shown in Figure 4. The Mg3Sb2 single-
crystal data collected as a function of pressure (shown as the asterisk symbols in Figure 4) agree well with the powder data (circle symbols). The unit cell volume obtained from the powder data decreases abruptly above approximately 7.8 and 4.0 GPa for Mg3Sb2 and Mg3Bi2, respectively. Note that the data collected at 7.8 GPa, which can be seen in Figure 1, is not included here, as the lattice parameters could not be accurately refined, possibly because the phase transition was already in progress. The bulk modulus, \( K_0 \), at \( P = 0 \) GPa of the ambient- and high-pressure phases was obtained from a second-order Birch–Murnaghan equation of state, represented by the solid lines.

Figure 3. Energy–volume relation for Mg3Sb2 calculated by DFT. The solid curve corresponds to the high-pressure structure (\( C2/m \)), and the dashed line corresponds to the ambient structure (\( P3m1 \)). The curves indicate a critical transition at approximately 5.6 GPa, which is slightly lower than the experiment. Note that the unit cell volume is per formula unit (1/4 of the high-pressure unit cell).

Figure 4. Pressure dependence of the volume per formula unit for Mg3Sb2 and Mg3Bi2 from powder (circles) or single-crystal (asterisks) samples. The zero-pressure bulk modulus, \( K_0 \), of both the ambient- and high-pressure phases was obtained from a second-order Birch–Murnaghan equation of state, fit using the single-crystal data collected in the present study to investigate bond length as a function of pressure (see Supporting Information, Figures S6). The fits are displayed as the solid curves. In the case of the high-pressure phases, the zero-pressure volume, \( V_0 \), was treated as a fitting parameter. The uncertainties of the pressure and lattice parameters are shown in Supporting Information (Tables S3–S6), and the parameters of the second- and third-order Birch–Murnaghan fit can be found in Supporting Information (Table S7). The zero-pressure bulk modulus of AP- and HP-Mg3Sb2 is 38 and 46 GPa, respectively, while the zero-pressure bulk modulus of AP- and HP-Mg3Bi2 is 37 GPa and 49 GPa, respectively. The HP structures of both compounds are slightly stiffer than the AP structures, similar to the behavior reported for CaMn2Bi2.21 The zero-pressure bulk moduli of AP-Mg3Sb2 and AP-Mg3Bi2 obtained in this study are comparable to the results of resonant ultrasound spectroscopy (36 and 38 GPa, respectively)14 and DFT (42 and 37 GPa, respectively).37

The question of whether or not Mg3Pn2 (Pn = Sb, Bi) are layered structures has been under debate.38 Anisotropic compressibility is a key feature of layered structures, in particular those characterized by weak interlayer van der Waals bonding. In such materials, the out-of-plane axis is significantly more compressible than the in-plane axis.39–41 In contrast, the in-plane (Mg2–Pn) and out-of-plane (Mg1–Pn) bonding in Mg3Pn2 has been shown to be chemically similar, in the sense that both bonds can be described as primary ionic bonds. A prior computational study of the pressure dependence of AP-Mg3Sb2 by Zhang et al.13 predicted nearly isotropic compressibility of the \( a \)- and \( c \)-axes. As shown in Figure 5a, our experimental powder diffraction data (circle and square symbols) is consistent with Zhang’s predictions (dashed lines) up to 8 GPa. Further, powder data for Mg3Bi2 up to 4 GPa (Figure 5b) reveals that the \( a \)-axis and \( c \)-axis of AP-Mg3Bi2 compress at nearly identical rates, suggesting that its compressibility is even more isotropic than AP-Mg3Sb2. The compressibility along each direction, defined as \( K_0(a) \) and \( K_0(c) \) here, was fitted with the second-order Birch–Murnaghan equation using \( a^0 \) and \( c^0 \) vs pressure. For AP-Mg3Sb2, \( K_0(a) \) and \( K_0(c) \) are 43 and 38 GPa, respectively, and for AP-Mg3Bi2, \( K_0(a) \) and \( K_0(c) \) are 40 and 37 GPa, respectively. The exact values and uncertainties of each data point in Figure 5 can be found in Supporting Information (Tables S3–S6).

It is important to emphasize that the nearly isotropic in-plane and out-of-plane compressibility in ambient-pressure \( P3m1 \) Mg3Pn2 (Pn = Sb, Bi) does not mean that the octahedral Mg1–Pn bonds are equal in strength to the tetrahedral Mg2–Pn bonds. Previous \( \text{ab initio} \) calculations of the partial phonon density of states of Mg3Sb2 predict significantly lower frequency phonon modes associated with the octahedral Mg1 compared with the tetrahedrally bonded Mg2, indicating that the former has weaker bonding.14 To test that prediction, we used the single-crystal data collected in the present study to investigate bond length as a function of pressure (see Supporting Information, Figures S12–S14), revealing that the octahedral bonds compress more rapidly than the tetrahedral bonds. As shown in Figure 6, the total volume of the octahedral Mg1 environment decreases more rapidly than the tetrahedral Mg2 volume. Here, we show polyhedral volume instead of individual bond length to minimize the influence of significant uncertainty in the Mg2 z position. This is the first direct experimental evidence that the Mg1–Pn bonds are softer than the Mg2–Pn bonds. We note that the octahedral Mg1–Sb bonds are significantly longer than the tetrahedral Mg2–Sb bonds, which likely explain much of the disparity in their compressibility. The relatively weak octahedral Mg1–Pn bonds help to explain the anomalously weak shear modulus and soft transverse phonon modes reported in Mg3Pn2 compounds. These instabilities are
in turn responsible for the low thermal conductivity and excellent thermoelectric performance of Mg$_3$P$_n$$_2$ compounds.\textsuperscript{14}

Figure 5. (a, b) Comparison of the unit cell of the $P\overline{3}m1$ (ambient) and $C2/m$ (high-pressure) structures. The blue and gray lines are used to outline the ambient-pressure cell in both structure types, while the cyan lines represent the interatomic distance, $x$, which is equal to $a$ and $b$ in the $P\overline{3}m1$ symmetry. Here, we define $a' = b'$ and $c'$, $a'$ and $y'$ to represent the primitive unit cell after it has lost its trigonal symmetry. Note that these parameters do not correspond to the true $a$, $b$, and $c$-axes of the monoclinic $C2/m$ unit cell. (c, d) Comparison of the lattice constants and interatomic distance, $x$, of powder Mg$_3$Sb$_2$ and Mg$_3$Bi$_2$, normalized to their respective values at $P = 0$ GPa. The dashed lines in panel (c) show the results of a prior computational study by Zhang et al.\textsuperscript{13}

As can be seen in Figure 5c,d, the $c$-axes (gray square symbols) of Mg$_3$Sb$_2$ and Mg$_3$Bi$_2$ exhibit a sudden collapse at the phase transition pressure, while the $a = b$ axes (blue circle/triangle symbols) remain largely unaffected and show no discontinuity. The drastic collapse of the out-of-plane $c$-axis can be attributed to the distortion of the half of the [Mg–Sb$_5$] octahedra to a square-planar coordination environment (see Figure 2a–c). In the high-pressure $C2/m$ structure, the $c'$ direction is tilted slightly relative to the $a' = b'$ plane (i.e., $\alpha = 90^\circ$ becomes $\alpha' \sim 92.5^\circ$). Meanwhile, the in-plane angle $\gamma = 120^\circ$ increases to $\gamma' \sim 122.5^\circ$ at the phase transition, leading to the sudden collapse of the distance defined by $x'$ to (cyan circle symbols).

\section*{CONCLUSIONS}

The present work resulted in the discovery of a new high-pressure phase above 7.8 and 4 GPa for Mg$_3$Sb$_2$ and Mg$_3$Bi$_2$, respectively, and confirmed the reversibility of the phase transition in the case of Mg$_3$Bi$_2$. The transition to the high-pressure structure was shown to involve a highly anisotropic collapse of the lattice parameters. Single-crystal diffraction at high pressure was used to solve the monoclinic high-pressure structure ($C2/m$), which is a distorted variant of the ambient-pressure structure containing four unique Mg coordination environments. The high-pressure structure of Mg$_3$Sb$_2$ and Mg$_3$Bi$_2$ has some similarities with the previously reported HP-CaMn$_2$Bi$_2$ but differs in symmetry and the coordination of the cation layer. Although the ambient-pressure structures of Mg$_3$Sb$_2$ and Mg$_3$Bi$_2$ exhibit isotropic compressibility, analysis of the single-crystal data shows that the octahedral Mg–Pn
bonds are more compressible than the tetrahedral Mg–Pn bonds, a conclusion that was supported by DFT calculations as a function of pressure. The results obtained here serve as a means for a deeper understanding of chemical bonding and thermal properties of this class of thermoelectric materials.

**ASSOCIATED CONTENT**

1. **Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.chemmater.0c03678.

Crystallographic details (CIF)

Optical microscopy of as-grown mass of Mg3Sb2 crystals; parameters from the second- and third-order Birch–Murnaghan EOS; octahedra in Mg3Sb2 and CaMg3Bi2; at ambient pressure; pressure dependence of individual and octahedral bond lengths; summary of uncertainties for polyhedral volume (PDF)

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