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High-pressure synthesis of the BiVO₃ perovskite

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We report the high-pressure, high-temperature synthesis of BiVO₃, a cubic perovskite that thus far remained inaccessible under ambient pressure conditions. We created this new material at ~25 GPa and 1500 K in a laser heated diamond anvil cell and recovered it to ambient pressure and temperature. Our synthetic approach circumvents the oxidative chemistry that, at ambient pressures, previously rendered the cubic BiVO₃ perovskite inaccessible. We find through density functional theory calculations that this material is a unique metallic and antiferromagnetic transition metal oxide.

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Perovskites are ubiquitous in our planet and society. They are one of the primary mineral phases in the Earth's mantle [1–3], the structural foundation for cuprate superconductors [4–6], and platforms for a new class of photovoltaics [7,8]. This extremely broad range of applications stems from the vast chemical and structural variation possible in the simple ABX₃ formula. The A, B, and X sites are all easily chemically substituted. As such, perovskites are ideal platforms for the rational design of materials with specific, tailored magnetic and electronic functionality via chemical substitution. The ability to design perovskites has led to the realization of materials that are extremely promising candidate photovoltaics [9,10], photocatalysts [11,12], and multiferroics [13,14].

The family of bismuth–first-row transition metal oxide perovskites, BiMO₃, exhibits particularly intriguing behavior ($M = \text{Sc, Cr, Mn, Fe, Co, Ni}$) [15–20]. For example, in BiMnO₃, the stereochemically active lone pair of electrons belonging to Bi is argued to give rise to (anti)ferroelectric behavior. Simultaneously, the electronic spins on the Mn ions couple ferromagnetically, making BiMnO₃ a magneto-electric multiferroic [21–23].

The family of BiMO₃ perovskites is almost complete. To date, only the perovskites with $M = \text{Ti}^{3+}$ and V^{3+} remain undiscovered. Targeting BiVO₃ is particularly promising due to previous theoretical studies which suggest it may exhibit multiferroic behavior and that it may be an efficient, visible light-driven photocatalyst for water oxidation due to its bandgap and optical absorption properties [24,25]. While a thin film of BiVO₃ was recently reported [26], bulk, crystalline BiVO₃ remains synthetically inaccessible at ambient pressure because the Bi³⁺ ions preferentially oxidize the V³⁺ ions to form V⁵⁺ species and Bi⁰ metal [17,27,28].

High-pressure synthesis is a powerful technique ideal for isolating metastable phases of matter [29–34]. High applied pressures transform potential energy landscapes

and allow for the isolation of phases that, under ambient pressures, are inaccessible metastable products [35,36]. Indeed, the application of high pressures enabled the discovery of several new perovskites [37–43]. Therefore, we hypothesized that high applied pressure may shift the thermodynamic landscape in the Bi–V–O system to favor the formation of BiVO₃.

Herein, we utilize *in situ* powder x-ray diffraction (PXRD) coupled with high-pressure and -temperature conditions in a laser heated diamond anvil cell (LHDAC) to synthesize the elusive BiVO₃ perovskite at ~25 GPa and 1500 K. This study demonstrates that the perovskite forms in the cubic $Pm\bar{3}m$ space group and that it is recoverable to ambient conditions after decompression and thermal quenching. We perform density functional theory (DFT) calculations and show that the perovskite is simultaneously antiferromagnetic and metallic, and we briefly discuss this rare magnetic and electronic structure predicted for BiVO₃.

For the synthesis, we pressed the Bi⁰ and V₂O₅ reagents into a flake and loaded the flake in a DAC [44]. We pressurized the sample to 25.1(5) GPa and then laser heated to ~1550 K at beamline 16-ID-B (HPCAT, Advanced Photon Source, Argonne National Laboratory) using infrared lasers [45]. We utilized *in situ* PXRD, which is an especially effective technique when paired with high-pressure synthesis as it provides time-resolved characterization of crystalline solid-state products. The use of a 2D detector enabled phase analysis via the polycrystalline texture of the diffraction rings. Uniform rings of intensity indicate randomly oriented powders while rings of individual spots indicate a collection of randomly oriented sub-micron size single crystals, with a higher degree of polycrystalline texture. An analysis of the polycrystalline texture allowed different materials that contribute to a single pattern to be distinguished.

As we heated beyond ~1200 K, new Bragg peaks formed in the integrated diffraction patterns, corresponding

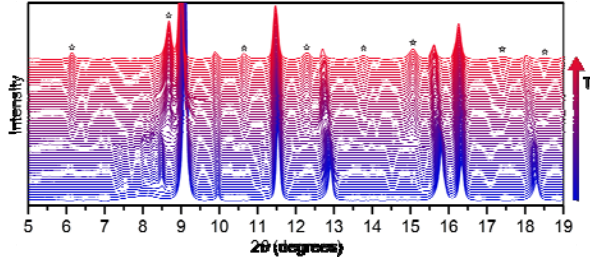


FIG. 1. Bragg peaks from the new phase appear in the PXRD patterns after heating the Bi-V-O sample at high pressure ($\lambda = 0.40663 \text{ \AA}$). The temperature increases as indicated by the color of the patterns and by the colored arrow (red is high temperature). Stars mark the position of the new peaks. During the heating process, the recrystallization of Bi leads to unphysical saturation features in select patterns.

to rings of individual spots in the 2D detector images. We held the temperature between 1200 K and 1250 K for ~ 3.5 min, during which time the peaks grew in intensity (Fig. S7, discussed in the supplemental material). Once the peaks were no longer increasing in intensity, we rapidly increased the temperature to ~ 1450 K. At 1400 K, the first set of new peaks promptly disappeared and, simultaneously, a second set of new peaks grew in. These peaks manifested in the 2D detector images as smooth rings of intensity evenly distributed across the azimuth. The second set of new peaks then grew in intensity in the patterns as we slowly increased the temperature between 1450 and 1550 K over ~ 6.5 min, after which time the peaks no longer changed intensity. We then thermally quenched the reaction. The second set of new peaks retained their intensity after the thermal quench. By the end of the heating experiment, the pressure had dropped to 21.4(5) GPa.

We sought to establish which peaks in the powder pattern originated from a new phase, and indeed whether a single new phase or multiple new phases were created. Here, the time-resolved, *in situ* nature of the experiment was crucial. The fact that we observed a set of new peaks appearing concurrently at a specific time (and therefore a specific temperature and pressure) allowed us to attribute these peaks to the same phase. The observation that these peaks subsequently grew in intensity at the same rate, along with the shared morphology of their Bragg peaks as observed in the plot of azimuthal intensity in 2θ -space (Fig. S1, top), further supported this interpretation. These observations together suggested that the first set of new peaks (between 1200 K and 1400 K) corresponded to one distinct phase while the second new set of peaks (above 1400 K) belonged to a second new phase.

We attempted to index both new phases. Unfortunately, we were unable to index the first new set of peaks we observed between 1200 and 1400 K, perhaps in part due to the weak diffraction from this phase coupled with the highly non-uniform polycrystalline texture in the 2D detector images. However, we successfully indexed the higher-temperature phase using the TOPAS software package [46]. At high pressure, the peaks indexed to the cubic $Pm\bar{3}m$

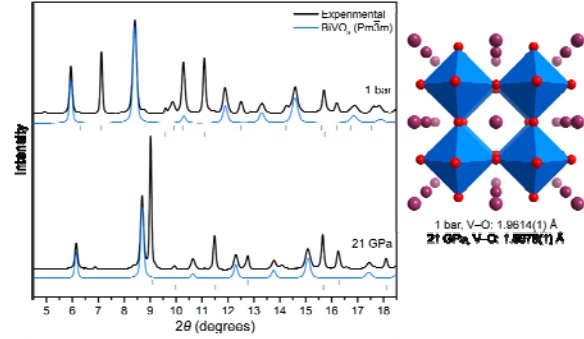


FIG. 2. Rietveld refinements at ~ 21.1 GPa and at ambient pressure (left, $\lambda = 0.40663 \text{ \AA}$) yield the structure of the new phase to be the cubic BiVO_3 perovskite (right). Beneath the patterns, magenta tick marks denote peaks from the crystalline MgO , green marks denote peaks from the Bi(V) phase at 21.1 GPa, and blue marks denote peaks from the Bi(I) phase. The structure comprises Bi atoms, O atoms, and VO_6 moieties (represented as purple and red spheres and as blue octahedra, respectively).

space group, the aristotype space group for perovskites [47–49]. To test whether the observed phase was the targeted BiVO_3 perovskite, we performed a Rietveld refinement on the patterns between 2θ values of 3° and 22° (Fig. 2) [50]. In the refinements, we included the appropriate bismuth polymorph [51], MgO , and the $Pm\bar{3}m$ phase. The $Pm\bar{3}m$ phase comprised 13 distinct peaks in this 2θ range with a powdery polycrystalline texture. In addition, we also observed a set of weak peaks – only observed after thermal quenching and removal of the heating apparatus – that were not modelled by our Rietveld analysis. We hypothesize they may arise from a minority oxide phase formed in the cooler tail of the laser heating spot during the heating reaction. These peaks are distinct from the $Pm\bar{3}m$ phase both temporally and in terms of the crystalline morphology in the 2D detector images. Unfortunately, the weak nature of these peaks precluded indexing. The Rietveld refinement using the cubic BiVO_3 phase reproduced the observed intensities well.

Once synthesized, we sought to determine if the BiVO_3 perovskite was stable at ambient pressure and temperature conditions. Towards that end, we obtained PXRD patterns as we slowly decompressed the sample while at ambient temperature [52]. In the diffraction patterns, all of the peaks from the BiVO_3 phase persist across the entire range of pressures, and all of the Bragg peaks consistently shift with pressure without significant changes in relative intensity. In addition, we fit these data and obtained the 2nd order Birch-Murnaghan equation of state for BiVO_3 (Fig. S4, S5, Tables S8, S9). The bulk modulus of BiVO_3 is 165(4) GPa, consistent with the calculated parameters for similar perovskites [53–55].

The perovskite exhibits vertex-sharing VO_6 octahedra spaced by Bi^{3+} ions in the A cation position. In general, the crystal symmetry for $\text{A}^{3+}\text{B}^{3+}\text{O}_3$ perovskites may be pre-

dicted based on the ionic radii of A and B [56–58]. The ionic radii of the ions are related by the Goldschmidt tolerance factor, t , such that the perovskite is expected to be cubic when $0.9 < t < 1.0$ [58]. For BiVO_3 , $t = 0.895$ based on the ambient pressure ionic radii for $\text{V}_{\text{VI}}^{3+}$, $\text{Bi}_{\text{VII}}^{3+}$, and $\text{O}_{\text{II}}^{2-}$ (the subscript roman numeral indicates the ion's coordination number) [56]. We were not able to find detailed ionic radius information for $\text{Bi}_{\text{XII}}^{3+}$ in the literature. Additionally, the ions' ionic radii decrease with increasing pressure at different rates [35]. The ionic radius of Bi^{3+} decreases more rapidly with increasing pressure than does the V^{3+} radius. This manifests in the pressure-induced changes in the V–O bond distance and the Bi–O contact distance (Fig. S6). The V–O bond distance decreases by $\sim 6.4(1)$ pm as pressure increases from ambient pressure to 21.1(5) GPa, and the Bi–O contact distance decreases by $\sim 9.0(1)$ pm over the same pressure interval. While these distances are affected by the nature of the cation-oxygen bonding, the cations' radii still change size significantly over this pressure interval [35]. Therefore, as pressure increases, we hypothesize that t increases and satisfies the requirement for cubic symmetry. And, although the ambient pressure value is right on the verge of a non-cubic t value, we hypothesize that the metastable cubic phase is kinetically trapped at ambient pressure.

Using density functional theory calculations, we investigated the magnetic and electronic properties of BiVO_3 . We used the Vienna Ab initio Software Package (VASP) with the projected augmented wave method potentials [59,60], and the newly developed meta-GGA SCAN functional [61]. Our calculations suggest that the A-type antiferromagnetically ordered structure (A-AFM), with $q=(0,0,1) \pi/a$, is the lowest in energy when compared to all other magnetic orderings, with the paramagnetic phase being ~ 16 meV per formula unit higher in energy (Table S14). We found a local magnetic moment of $1.51 \mu_B$ on the V atom. The relaxed lattice parameter differs by only $\sim 1.01\%$ with respect to the experimental value ($3.88 \text{ \AA}$). There have been reports that suggest that the accuracy of the SCAN functional suffers when describing magnetism in the transition metals [62,63]. To assess the accuracy of the SCAN functional in our calculations, we also conducted calculations using the PBEsol (+ U) method. We found that both functionals predict a metallic antiferromagnetic ground state. The notable difference between the results is that the value of U stabilizes either the C-type or A-type AFM ordering (Fig. S20) while maintaining the metallic character.

Our calculations show that cubic BiVO_3 is antiferromagnetic and metallic (Fig. 3) with strongly dispersive bands (Fig. S2). This is a highly unusual combination, and suggests this compound is worthy of further investigation. Usually, undoped, magnetic transition metal oxides fall into two categories: semiconducting antiferromagnets and metallic ferromagnets [64,65]. To the best of our knowledge, there are only a handful of reported metallic antiferromagnetic transition metal oxides: SrCrO_3 [37–39], CaCrO_3 [40,41], $\text{Ca}_3\text{Ru}_2\text{O}_7$ [66], LaNiO_3 [42], $\text{LaCu}_3\text{Cr}_4\text{O}_{12}$ [43],

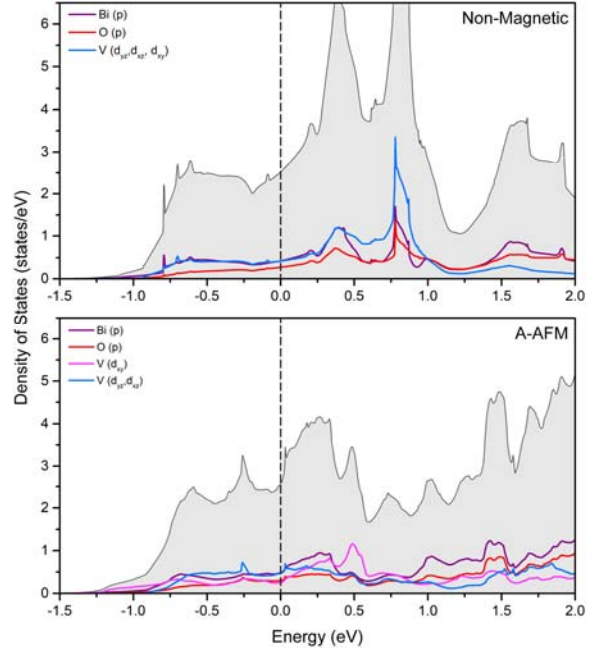


FIG. 3 | The DOS per formula unit for cubic BiVO_3 for the non-magnetic case (top) and for the A-type antiferromagnetic ordering case (bottom) both show a non-zero DOS at the Fermi energy. Several van Hove singularities are present in the non-magnetic DOS diagram above the Fermi energy. In the A-AFM DOS, the bands derived from the d_{xy} orbital are no longer degenerate with those of d_{yz}, d_{xz} symmetry owing to the spin order. The legend indicates the underlying orbital contributions to the total (gray) DOS. The dashed vertical line denotes the Fermi energy.

RuO_2 [67,68], and $(\text{La},\text{Sr})_3\text{Mn}_2\text{O}_7$ [69]. In LaCrO_3 and SrCrO_3 , it is proposed that the antiferromagnetism is stabilized by orbital ordering, which lowers the symmetry of the system and lifts the degeneracy of the Cr t_{2g} manifold. Yet, the mechanism for the anomalous antiferromagnetism in these metallic systems remains incompletely understood, and in some cases, the electronic transport properties remain controversial [70–72].

Our DFT calculations using the SCAN functional show that A-type AFM ordering, with planes of ferromagnetic spins coupled antiferromagnetically, is the ground state spin structure for cubic BiVO_3 . The anti-aligned 2D ferromagnetic planes in the structure requires that the magnetic unit cell exhibits a lower symmetry than the cubic crystal structure. To understand the stability of the coexisting metallicity and A-type antiferromagnetism in cubic BiVO_3 perovskite, we examined in more detail the electronic density of states (DOS) for two spin configurations: the nonmagnetic (NM) and the ground state A-AFM. Near the Fermi level of the NM DOS, we find the presence of several van Hove singularities with a high DOS indicative of a magnetic instability. In contrast, the A-AFM DOS shows that the t_{2g} states split such that the d_{xy} orbital has a lower occupancy than the degenerate d_{xz}, d_{yz} doublet leading to orbital polarization (Table S12). In combination with the metallicity of the system, the kinetic energy gain when describing the system using the Stoner model should stabi-

lize itinerant ferromagnetism. However, superexchange originating from the electron localization (well defined moments exist on the V sublattice) leads to the FM order on {110} planes with adjacent planes exhibiting anti-aligned spin orientations. Therefore, we attribute the stability of the A-type AFM ordering to the competition between superexchange and the itinerant Stoner mechanism [73]. Another factor that might influence the magnetic ordering is the presence of the Bi p-states at the Fermi level, since hybridization of these states with the V 3d orbitals will affect the superexchange pathways. Lastly, the A-type and C-type ordering are in competition depending on the value of U in the PBEsol (+ U) calculations. We acknowledge that it is difficult to unambiguously differentiate between these two similar spin structures.

To assess the importance of spin-orbit coupling on the magnetic and electronic structure of BiVO_3 , we conducted a DFT calculation incorporating spin-orbit coupling at the Bi ions using the SCAN functional. We noticed a small decrease in magnetization at the V ions from 1.51 to 1.12 μ_B , however the A-AFM ordering remains stable and the DOS (Fig. S23) shows that the metallicity is retained. We therefore hypothesize that the effects of spin-orbit coupling are minor in this system and that they do not have a significant effect on the magnetic or the electronic properties of BiVO_3 .

In conclusion, we reported the synthesis of the bismuth vanadium oxide perovskite, BiVO_3 . We employed a non-traditional synthetic approach, LHDAC-enabled heating at high- PT conditions coupled with *in situ* PXRD analysis, to realize this previously inaccessible perovskite. The BiVO_3 perovskite forms in the cubic $Pm\bar{3}m$ space group when synthesized at high pressures and is recoverable to ambient conditions. The BiVO_3 perovskite expands the known family of bismuth-first-row transition metal perovskites. We performed density functional theory calculations and determined that competition between electron delocalization and superexchange favors the A-type or C-type AFM ordering, which might be further enhanced by the anomalous Bi p-states. We are working to scale up the synthesis of the BiVO_3 perovskite using multi-anvil press techniques to validate the theoretical prediction of the metallicity concomitant with intrinsic antiferromagnetism in BiVO_3 . We anticipate that a deeper understanding of the origins of these properties in BiVO_3 will help illuminate the underlying physics in the other antiferromagnetic and metallic transition metal oxides.

Lastly, the need for developing non-traditional synthetic techniques scales with the ever growing societal and environmental demands for efficient catalytic, photovoltaic, and multiferroic materials. Our work illustrates the utility of high applied pressures for isolating metastable phases which, at ambient pressure, remain thermodynamically unstable and synthetically inaccessible.

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