Electronic Structure of the Bond Disproportionated Bismuthate $\text{Ag}_2\text{BiO}_3$

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We present a comprehensive study on the silver bismuthate $\text{Ag}_2\text{BiO}_3$, synthesized under high-pressure high-temperature conditions, which has been the subject of recent theoretical work on topologically complex electronic states. We present X-ray photoelectron spectroscopy results showing two different bismuth states, and X-ray absorption spectroscopy results on the oxygen $K$-edge showing holes in the oxygen bands. These results support a bond disproportionated state with holes on the oxygen atoms for $\text{Ag}_2\text{BiO}_3$. We estimate a band gap of $\sim 1.25$ eV for $\text{Ag}_2\text{BiO}_3$ from optical conductivity measurements, which matches the band gap in density functional calculations of the electronic band structure in the non-symmetric space group $\text{Pnn}2$, which supports two inequivalent Bi sites. In our band structure calculations the disproportionated $\text{Ag}_2\text{BiO}_3$ is expected to host Weyl nodal chains, one of which is located $\sim 0.5$ eV below the Fermi level. Furthermore, we highlight similarities between $\text{Ag}_2\text{BiO}_3$ and the well-known disproportionated bismuthate $\text{BaBiO}_3$, including breathing phonon modes with similar energy. In both compounds hybridization of Bi-6$p$ and O-2$p$ atomic orbitals is important in shaping the band structure, but in contrast to the Ba-5$p$ in BaBiO$_3$, the Ag-$4d$ bands in $\text{Ag}_2\text{BiO}_3$ extend up to the Fermi level.

I. INTRODUCTION

Transition-metal oxides include many novel classes of materials that host a wide range of structures and electronic properties. The field of condensed matter physics had made a great leap forward with the discovery of high transition temperature superconductivity ($T_c$) in the layered copper oxides [1] and in the hole-doped cubic bismuthate (Ba,K)BiO$_3$ [2]. The undoped BaBiO$_3$ is a disproportionated insulator. Also, oxide materials have shown promise for exploring topological properties [3–5]. We identified the silver bismuthates as a promising set of materials for studying highly correlated electron systems and for finding topologically non-trivial oxides. $\text{Ag}_2\text{BiO}_3$ was recently highlighted in theoretical work with various predictions of topologically protected states [6–8].

The previous work on $\text{Ag}_2\text{BiO}_3$ has resulted in a number of crystal structures reported in the Inorganic Crystal Structure Database (ICSD), which fall into the space groups $\text{Pnna}$, $\text{Pnn}2$, and $\text{Pn}$ [9, 10]. $\text{Pnna}$ is the oldest structure reported, which has a single bismuth site implying a uniform 4+ state for bismuth and as a result equal Bi-O distances. A Bi$^{4+}$ state is unusual, however, and typically a compound with nominal charge of 4+ on bismuth disproportionates. The disproportionation in BaBiO$_3$ is reflected in the existence of two distinct sites for Bi, but the nature of this disproportionation is debated. It was emphasized in a following neutron diffraction study that $\text{Ag}_2\text{BiO}_3$ has two distinct bismuth sites and crystallizes in the $\text{Pnn}2$ space group [10], and the two sites were explained with the disproportionation of Bi$^{4+}$ into Bi$^{3+}$ and Bi$^{5+}$ states. The existence of two distinct bismuth sites in $\text{Ag}_2\text{BiO}_3$ ($\text{Pnn}2$) is similar to BaBiO$_3$, but these compounds crystallize in different crystal structures, with a combination of corner- and edge-sharing BiO$_6$ octahedra in $\text{Ag}_2\text{BiO}_3$ and only corner-sharing BiO$_6$ octahedra in the perovskite BaBiO$_3$. By thoroughly characterizing the disproportionated state in $\text{Ag}_2\text{BiO}_3$ and comparison to BaBiO$_3$, we establish ($M^{1+}$)$_2\text{BiO}_3$ as a new class of disproportionated bismuthates beyond those forming in the perovskite structure.

The disproportionation of the Bi site and resulting $\text{Pnn}2$ symmetry also have important ramifications for the topological nature of $\text{Ag}_2\text{BiO}_3$. Theoretical predictions of topological phases in $\text{Ag}_2\text{BiO}_3$ include an hourglass nodal net semimetal [7], a Dirac semimetal [6], and an hourglass Dirac semimetal [8]. All of these topological predictions were made on $\text{Ag}_2\text{BiO}_3$ in the $\text{Pnna}$ phase with a single bismuth site, where breaking Bi charge order to attain the $\text{Pnna}$ symmetry is important to realizing these topologically nontrivial phases. However, we will show that $\text{Ag}_2\text{BiO}_3$ crystallizes in the $\text{Pnn}2$ space group with two crystallographically distinct bismuth sites even when synthesized under high-pressure and high-temperature conditions. The topological predictions made for the $\text{Pnna}$ phase therefore do not apply to Ag$_2$BiO$_3$ crystallizing in the $\text{Pnn}2$ phase. Rather, we predict Weyl states in the $\text{Pnn}2$ phase.

In this paper, we characterize $\text{Ag}_2\text{BiO}_3$ samples synthesized at 6 GPa using powder X-ray diffraction (XRD) and various spectroscopic techniques. We present evi-
II. EXPERIMENTAL DETAILS

Ag$_2$BiO$_3$ samples were synthesized with a high-pressure, high-temperature method utilizing a belt-press. Bi$_2$O$_3$ and AgO powders were well mixed in a mortar and pestle, then loaded into a gold capsule with a drop of KOH to speed up the reaction. The capsule was then pressed to 6 GPa and heated at 730 K for 1 hour before quenching and retrieving the polycrystalline product. A finely ground sample was loaded into a 0.3 mm capillary, and powder XRD patterns of Ag$_2$BiO$_3$ were collected while rotating the capillary using Ag radiation (0.5594 Å). The samples were cooled down to ∼200 K for low temperature XRD.

X-ray absorption spectra of the oxygen K-edges were recorded in partial fluorescence yield (PFY) mode at the Spherical Grating Monochromator (SGM) beamline at the Canadian Light Source. Spectra in PFY mode are collected using energy resolving silicon drift detectors, which allow selection of only the oxygen K-edge fluorescence. The average of data from four separate silicon drift detectors was used for the PFY spectra. Spectra are calibrated in energy by using a TiO$_2$ reference sample [12]. Spectra were then normalized by the incident beam inten-
FIG. 2: X-ray photoelectron spectra of O, Ag, and Bi in Ag$_2$BiO$_3$ are shown in (a), (b), and (c). In (a) the three peaks A, B, and C are needed to fit the measured spectra for the O-1s states. In (b) the splitting between peaks D1 and D2 is consistent with that expected due to spin-orbit-coupling (SOC) for Ag-3d states. In (c) the splitting between F1 and F2 is consistent with that expected due to SOC for Bi-4f states, and the same can be said for the split between G1 and G2. Due to the asymmetry of the measured spectra, four curves are needed to fit the Bi-4f states. This leads us to conclude the existence of two different Bi states in Ag$_2$BiO$_3$, both close in energy to Bi$^{3+}$ [11].

sity, and normalized according to post-edge intensity after subtracting a linear background. The Ag$_2$BiO$_3$ spectra were collected under ultrahigh vacuum at room temperature from a pressed pellet attached to carbon tape, with the pellet surface at an angle of 45° to the incident beam. The XPS data were collected using a commercial Kratos AXIS Ultra spectrometer and a monochromatized Al K$_\alpha$ source (photon energy: 1486.6 eV). The base pressure during XPS was in the low 10$^{-10}$ mbar range. The spectra were collected using an analyzer pass energy of 20 eV. XPS spectra were analyzed using the CasaXPS software. The charge-neutralizer was used and the C 1s was set to 284.8 eV for binding energy calibration [13, 14]. To fit the peaks, a combination of multiple Gaussian-Lorentzian mixture functions and a Shirley background was used. The binding energy separation and the area ratio of the doublets were not constrained but the results are within experimental error of the tabulated values [15]. The sum of all the fitted functions to XPS peaks is shown with a black curve in Fig. 2.

Optical spectroscopic ellipsometry measurements were performed using a variable-angle spectroscopic ellipsometer (VASE, Woollam) with photon energy in the range of 0.7—6.5 eV at incident angles of 70°. The real and imaginary parts of the dielectric function can be obtained accurately from the ellipsometric angles $\psi(\omega)$ and $\Delta(\omega)$ extracted from the optical spectra, without the need of a Kramers-Kronig analysis.

The Raman data were collected in backscattering geometry using a Dilor XY-triple grating Raman spectrometer equipped with a charge coupled device camera as detector. With power of 0.2 mW at 632 nm it was possible to measure Raman spectra on polished surfaces of the Ag$_2$BiO$_3$ samples. Low temperature Raman measurements were performed between 10-300 K. The resolution of our spectrometers for this experiment was about 3 cm$^{-1}$.

III. COMPUTATIONAL DETAILS

The band structure calculations for Ag$_2$BiO$_3$ presented in Fig. 3 (d) were obtained using the Vienna ab initio Simulation Package (VASP 5.4) with the generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE) type exchange-correlation potential [16]. The cutoff energy of plane wave basis set was set to be the ENMAX value in the pseudo-potential plus 30%. A-centered \(3 \times 3 \times 2\) Monkhorst-Pack grid was used for the self-consistent field (SCF) calculations.

The electronic structure calculations shown in Figs. 4 (a)-(d) were performed using density functional theory (DFT) with the full-potential linearized-augmented-plane-wave code WIEN2k [17]. Exchange and correlation effects were treated within the local density approximation (LDA) [18]. For Ag$_2$BiO$_3$, we use the \(Pnn2\) unit cell with the lattice constants \(a = 5.983\ \text{Å}, b = 6.324\ \text{Å}, \) and \(c = 9.576\ \text{Å},\) as determined in Ref. [10]. For BaBiO$_3$, we use the \(P2_1/n\) unit cell with the lattice constants \(a = 6.174\ \text{Å}, b = 6.125\ \text{Å},\) and \(c = 8.652\ \text{Å},\) as determined in Ref. [19]. For both bismuthates, a \(6 \times 6 \times 4\) \(k\)-point grid was used for the Brillouin-zone integration. Projections onto oxygen molecular orbitals were performed with a modified version of WIEN2k, following the procedure outlined in Ref. [20].
IV. RESULTS AND DISCUSSION

A. Analysis of XRD, XPS, and XAS

We used XRD, XPS and XAS measurements to demonstrate that Ag$_2$BiO$_3$ in the Pnn2 phase is a bond-disproportionated bismuthate. As it is difficult to distinguish the Pnna structure from the Pnn2 structure with only PXRD data, as demonstrated in Fig. 1, we will start by accepting the reported Pnn2 phase reported and assess the consistency of various properties we measure with this structure. The lower scattering power of oxygen in X-ray diffraction and natural twinning of Ag$_2$BiO$_3$ crystals makes it difficult to discern the Pnna from the Pnn2 structure. A previous powder neutron diffraction study, which is more sensitive to diffraction from oxygen than X-rays, on Ag$_2$BiO$_3$ resulted in a precise refinement of O atomic positions and a structure where Bi has two distinct sites [10]. We compare the simulated powder XRD and neutron diffraction patterns in Sup. Fig. 1 to demonstrate how the Pnn2 phase can be identified in neutron diffraction [21].

In the Pnn2 phase, Ag$_2$BiO$_3$ has two distinct bismuth sites resulting in two BiO$_6$ octahedra with shorter and longer Bi-O bonds. It should be emphasized that the Bi-O distances vary within each of the two types of octahedra in Ag$_2$BiO$_3$. These Bi-O$_6$ octahedra are edge-sharing along the a direction, but only share corners along the b and c directions. The O-O distances at the shared edges of these octahedra are shorter than the distances between the other oxygen atoms, which may correspond to oxygen dimerization at the shared edges. The Ag atoms are sitting between the BiO$_6$ octahedra channels and are bonded to 3 oxygen atoms each. The shortest Ag-O distances for both Ag sites are 2.1464 and 2.2065 Å, which are expected for Ag$^{1+}$ typically seen in oxides.

The X-ray photoelectron spectra for Ag, Bi, and O in Ag$_2$BiO$_3$ are presented in Figs. 2(a)-(c). As expected, only one state is observed for Ag, with peak centers at 373.8 eV (peak D1 in Fig. 2(b)) and 367.8 eV (peak D2 in Fig. 2(b)) which match the transition seen in Ag$^{1+}$ in other oxides and chalcogenides [15]. The splitting here is expected for the d-states due to spin-orbit-coupling (SOC). The XPS of O shows three peaks at 529.1 eV (C), 530.8 eV (B), and 532.6 eV (A). As for the minor peak at 532.6 eV (peak A in Fig. 2(a)), it was attributed to surface contaminants in other bismuthates [22], and such contaminants may be present on the surface of our samples. The binding energy of the main peak for O 1s at 529.1 eV (peak C in Fig. 2(a)) is comparable to the binding energy of O 1s in BaBiO$_3$ [22]. XPS shows evidence for KOH on the surface of the sample as evidenced by an observed K peak (shown in Sup. Fig. 2(a)); we cannot rule out that some of the intensity at 350.8 eV originates from KOH [23](peak B in Fig. 2(a)). Furthermore, contamination like carbonates, which were also observed in the C 1s spectrum (see Sup. Fig. 2(a)) might also contribute the peak B. However, analyzing the relative amount of potassium and carbonate contaminations peak B cannot be purely due to those contaminations, see Sup. Table I. Considering, that the area of the fitted curve at 530.8 eV is comparable to the area of the main peak at 529.1 eV (Table I in SI), we expect the signal to originate from a similar amount of oxygen atoms on the surface of the Ag$_2$BiO$_3$ samples. Looking at the different O-O and Bi-O distance for oxygen atoms at the shared edges and corners of the BiO$_6$ octahedra, we propose that the peaks at 530.8 eV and 529.1 eV may originate from different states in the oxygen atoms at the shared corners and the shared edges of the BiO$_6$ octahedra.

Assigning distinct oxygen atoms as the origin for the different XPS peaks, the peak at 529.1 eV may originate from the dimerized oxygen at the shared edges of the octahedra with a bond length of 2,658 Å, while the contribution to the peak at 530.8 eV from Ag$_2$BiO$_3$ likely comes from the corner shared oxygens. Another possibility is that the different oxygen states at 529.1 and 530.8 eV arise from the interaction of the oxygen atoms with silver atoms at different distances, where the oxygen atoms at the shared corners of the octahedra are further away from the nearest silver atoms, while the oxygen atoms at the shared edges are closer to silver atoms. If all oxygen atoms in Ag$_2$BiO$_3$ have equivalent Bi-O interaction, then the electronic origin for the split peaks at 529.1 and 530.8 eV depends on the extent of the O 1s core-hole potential and the Bi 6s/O 2p hybridization [22].

The Bi 4f spectra, shown in Fig. 2(c), support the presence of two Bi states in this compound, and these states have similar binding energy (158.0 eV for peak G2 and 158.5 eV for peak F2). The ratio of the areas of the two peaks is nearly 1:1, suggesting that the two different Bi states are due to the two distinct Bi atoms in the unit cell. It might be possible that one of the Bi states is due to surface contaminations like hydroxides or carbonates. However, this would imply that the Bi 4f binding energies are similar to those for Bi$_5^+$ like in NaBiO$_3$ [24] and Bi$_3^+$ like in Bi$_2$O$_3$ [11] we realize that both are close to the value for Bi$^{3+}$. This might hint that the system is bond disproportionated rather than charge disproportionated. Please note that the Bi 4f binding energies are similar to the one observed in BaBiO$_3$ [25] but the Bi 4f spectrum for Ag$_2$BiO$_3$ shows a clearer asymmetry.

The XPS spectra thus indicate two different Bi sites, consistent with a disproportionated state, and optical conductivity evidence for a band gap (Section IV B) support this interpretation. However, whether Ag$_2$BiO$_3$ is charge or bond disproportionated remains unclear without examining the XAS data. XAS results at the oxygen K-edge, presented in Fig. 3(a), show a sharp pre-peak at 529 eV, which originates from a high hole density in
FIG. 3: (a) The X-ray absorption spectra at the Oxygen K-edge of Ag$_2$BiO$_3$ and a reference sample of BaBiO$_3$. (b) Optical spectroscopy data on Ag$_2$BiO$_3$ extracted from ellipsometry measurement. (c) Brillouin zone of Ag$_2$BiO$_3$ with the high-symmetry points indicated by black dots. The nodal chains are schematically illustrated by the blue and red lines. At the Z and S points (yellow) there are fourfold degeneracies, formed by two Weyl points with opposite chirality. (d) Band structure of Ag$_2$BiO$_3$ in the Pnm2 phase using DFT calculation with hybrid functionals.

the oxygen $p$ orbitals. This is similar to the results on BaBiO$_3$ [22]. The higher energy region at the K-edge is clearly different from the BaBiO$_3$ spectrum, reflecting the different oxygen environment in Ag$_2$BiO$_3$. A second peak is seen in the XAS results of Ag$_2$BiO$_3$, and the two XAS peaks (marked with yellow and blue circles in Fig. 3(a)) are $\sim$2 eV apart. This energy difference is similar to peaks B and C in the oxygen XPS spectra.

The combination of corner and edge sharing octahedra in Ag$_2$BiO$_3$ can contribute to the different XAS spectra above 530 eV. Another peak at 531 eV is seen for Ag$_2$BiO$_3$, and the origin of this peak is the higher energy states of O in Ag$_2$BiO$_3$. If we compare Figs. 4(c) and (d), we see a peak in the oxygen partial density of states at 2 eV in Ag$_2$BiO$_3$ that is much less intense than in BaBiO$_3$. In the ionic-limit, we have Ag$^{1+}$–4d$^{10}$, Bi$^{3+}$–6s$^2$, and O$^{2–}$–2p$^6$ ions making up Ag$_2$BiO$_3$, where the BiO$_6$ octahedron are either made up of Bi$^{3+}$ (6s$^2$)–O bonds with longer bonds or Bi$^{3+}$ (6s$^2$L$^2$)–O with shorter bonds. The ligand hole pairs (L$^2$) condense on these smaller octahedra, where the O atoms have equal charge on them. The disproportionation leading to the small and large octahedra in this case is described as bond-disproportionation.

One is tempted to conclude a similar origin for both of these sets of peaks, such as the difference between oxygen atoms at the shared edges and corners of the BiO$_6$ octahedra. However, the area under the curve for the XPS peaks is equivalent for B and C. Reconciling the XAS and XPS results, if the oxygen atoms are equivalent in terms of interaction with Bi and the split in the O 1s XPS is electronic in nature, then an oxygen ligand hole will be distributed over 6 oxygen atoms in the BiO$_6$ octahedron. In the case of O 1s, the XPS peak splitting originates from oxygen atoms at different distances to bismuth, which suggests an oxygen hole may be distributed over 4 oxygen atoms at the shared edges of the BiO$_6$ octahedra. The oxygen hole ligand distribution in the octahedra of Ag$_2$BiO$_3$ is discussed below in section IV C.
B. Band Gap and Topology in Disproportionated \( \text{Ag}_2\text{BiO}_3 \)

The band structure of \( \text{Ag}_2\text{BiO}_3 \) in the \( Pmn2 \) phase resulting from DFT calculations is presented in Fig. 3(d), where we have a band gap of \( \sim 1.25 \) eV resulting from hybridization of O 2p bands and Bi 6s band, with antibonding character. The second set of bands above the Fermi level (\( E_F \)) is located \( \sim 3 \) eV above \( E_F \) and corresponds to the unfilled Bi 6p bands. The band gap from optical conductivity measurement is around \( \sim 1.25 \) eV (Fig. 3(b)), transition between bands marked with an orange arrow, which corresponds well with transitions expected in our calculated band structure, marked with an orange arrow in Fig. 3(d). The real and imaginary parts of the dielectric constant of \( \text{Ag}_2\text{BiO}_3 \) are shown in Sup. Fig. 3. The upturn starting at \( \sim 2.5 \) eV in the optical conductivity corresponds to transitions from bands below \( E_F \) to the empty Bi 6p bands in \( \text{Ag}_2\text{BiO}_3 \), which are marked with green arrows in Figs. 3(b) and (d). The consistency between the features seen in our optical conductivity measurement and the expected transitions in our calculated band structure provide further evidence for \( \text{Ag}_2\text{BiO}_3 \) being in the disproportionated \( Pmn2 \) phase. In the \( Pnma \) phase \( \text{Ag}_2\text{BiO}_3 \) is a semimetal and expected to have a nonzero density of state at the Fermi level [6], so no gap in the optical conductivity.

We emphasize that the non-symmorphic space group \( Pmn2 \) (Space Group 34) of \( \text{Ag}_2\text{BiO}_3 \) leads to symmetry-enforced nodal loops in all bands, i.e., twofold Weyl crossings along 1D loops. These nodal loops are protected by the glide mirror symmetries \( \{m_{010}|\frac{1}{2}\frac{1}{2}\frac{1}{2}\} \) and \( \{m_{100}|\frac{1}{2}\frac{1}{2}\frac{1}{2}\} \) and touch each other on the intersection lines of the mirror planes, thereby forming “nodal chains” [26–28], see Fig. 3(c). These Weyl nodal lines carry a nontrivial \( \pi \)-Berry phase, leading to drumhead surface states.

To access the anomalous magnetotransport properties of the nodal chains [26], we may be tempted to use chemical doping to shift the Fermi level and approach these band crossings. However, if the chemical doping changes the \( Pmn2 \) symmetry, then these topological features may be annihilated. In addition, we note that at the S and Z points the bands form fourfold degeneracies, composed of two Weyl points with opposite chirality (yellow dots in Fig. 3(c)).

Including hybrid functionals in our calculations results in an increase in the band gap for \( \text{Ag}_2\text{BiO}_3 \) in comparison with calculations in the literature [6] with a direct gap of \( \sim 1.0 \) eV at the \( R \) point in the band structure. However, this value remains slightly lower than the experimentally estimated value of \( \sim 1.25 \) eV from our optical conductivity measurement. This may be limited by the optically active transitions in \( \text{Ag}_2\text{BiO}_3 \) that do not correspond to the lowest band gap in our band structure, or the in-
adequacy of the band calculations in providing accurate band gap values even with hybrid functionals. Ag$_2$BiO$_3$ in the Pnn2 is predicted to be a good photovoltaic material [29], and our results clarifying the band gap experimentally are an important step forward. The $\sim 1.25$ eV band gap in Ag$_2$BiO$_3$ falls within 1.1-1.45 eV range where maximum efficiency is expected for single junction solar cells [30]. XPS results, shown in Sup. Fig. 2(b), suggest the valence band is $\sim 0.9$ eV below the Fermi level, and this shows promise for introducing in-gap-states in Ag$_2$BiO$_3$. In future studies, we will need to examine the stability of Ag$_2$BiO$_3$ when exposed to different radiation to assess its potential in photovoltaic applications.

C. Comparing Ag$_2$BiO$_3$ and BaBiO$_3$

Next, we would like to highlight the extent of similarity and some of the differences between Ag$_2$BiO$_3$ and BaBiO$_3$. Both materials have a bulk band gap due to disproportionation of “Bi$^{4+}$”, but the octahedra are only corner sharing in BaBiO$_3$ while the octahedra are sharing edges and corners in Ag$_2$BiO$_3$. The nominal Bi$^{4+}$ oxidation state that leads to the disproportionated charge/bonds in these compounds is achieved through a different number of atoms. While having one Bi atom and three oxygen atoms, it takes two monovalent Ag$^{+}$ ions or one divalent Ba$^{2+}$ ion to achieve the same average formal charge of 4+ for Bi. Thus, (Ag$^{+}$)$_2$(Bi$^{4+}$)(O$^{2-}$)$_3$ and (Ba$^{2+}$)(Bi$^{4+}$)(O$^{2-}$)$_3$ have the same unstable average formal charge for Bi in different crystal structures, and lead to disproportionation in both Ag$_2$BiO$_3$ and BaBiO$_3$. However, similar to BaBiO$_3$, there is a significant amount of oxygen character in the empty conduction states of Ag$_2$BiO$_3$ above the Fermi level. To be more specific, these states are formed by oxygen molecular orbitals with $a_{1g}$ symmetry centered on the small BiO$_6$ octahedra. In Fig. 4 (a), they are highlighted as purple fat bands for Ag$_2$BiO$_3$, while in Fig. 4 (b), they are highlighted as red fat bands for BaBiO$_3$. In the previous theoretical studies on BaBiO$_3$[31, 32], this situation was referred to as a bi-polaronic condensation of oxygen holes. For Ag$_2$BiO$_3$ we show in Sup. Fig. 4 the orbital contribution from Bi-$s$ and $p$ in the small and large O$_6$ octahedral cages, as well as the O-$2p$. The significant contribution of O-$2p$ above the Fermi level is consistent with high density of oxygen holes as evidenced by the pre-peak in XAS (Fig. 3(a)).

As one can also see in Fig. 4, the valence state within $\sim 1$ eV range below the Fermi level has, in turn, a strong character of O-$a_{1g}$ molecular orbitals centered on the large BiO$_6$ octahedra (brown fat bands for Ag$_2$BiO$_3$ and blue fat bands for BaBiO$_3$). Together, these two sets of oxygen molecular orbital states around the Fermi level constitute the anti-bonding manifold resulting from the strong hybridization between the Bi-$6s$ and O-$a_{1g}$ orbitals. The latter appears to be as strong in Ag$_2$BiO$_3$ as it was found to be in BaBiO$_3$, which is evident from both systems the banding combination is pushed down as far as -10 eV. A new feature of the Ag$_2$BiO$_3$ band-structure is the presence of Ag–4$d$ bands in the same energy region where the non-bonding oxygen bands are located, from $\sim 7$ eV up to the Fermi level (Shown in Sup. Fig. 4(a)). It was demonstrated in BaBiO$_3$ that the octahedral angle between Bi-O$_6$ octahedra effects the Bi-O hybridization [32]. Band calculations in BaBiO$_3$ with a 6$^\circ$ and 16$^\circ$ octahedral tilting show bands with narrower energy dispersion with increased tilt angle. The conduction band in Ag$_2$BiO$_3$ is considerably narrower compared to that in BaBiO$_3$, which is probably a result of weaker Bi-O hybridization due to the geometrical arrangement of the BiO$_6$ octahedra in Ag$_2$BiO$_3$. In Ag$_2$BiO$_3$, the edge-sharing Bi-O$_6$ octahedra along the $a$ direction, and the high angle of 36$^\circ$ between the Bi-O-Bi at the shared corners along the $b$ and $c$ directions contribute to reduced hybridization. This qualitative statement about the hybridization should be confirmed with DFT calculations in future studies. The Ag might play a role in reducing the band gap in Ag$_2$BiO$_3$, as seen in the Ag-containing pyrochlore oxides [33]. This narrowing effect is not clear when we compare Ag$_2$BiO$_3$ with BaBiO$_3$ due to the different crystal structure, but replacing the Ag with another monovalent atom, such as Na$_2$BiO$_3$, can help us to study the effect of Ag. The contribution from Ag bands near the Fermi level is shown in the partial density of states (PDOS) of Ag$_2$BiO$_3$ presented in Fig. 4(c). In comparison, the PDOS of BaBiO$_3$, shown in Fig. 4(d), has significant contribution from only Bi and O near the Fermi level and no significant contribution from the Ba.

While in BaBiO$_3$ we have an indirect band gap as shown in Fig. 4 (b), in Ag$_2$BiO$_3$ the band gap is direct as shown in Fig 3(d) and Fig. 4 (a). The role of the Ag–4$d$ bands that extend over a wide energy range below the Fermi level is not clear for now. Identifying the effect of edge sharing BiO$_6$ octahedra, crystal symmetry, and Ag bands on the band structure of Ag$_2$BiO$_3$ will be an important part of future studies. Future work should include replacing Ag with other monovalent metal $M^{4+}$ atoms, varying tilting angle of Bi-O$_6$ octahedra, and studying the lower symmetry $Pn$ phase.

The Raman spectra of Ag$_2$BiO$_3$ have a strong phonon mode at 520 cm$^{-1}$, shown in Fig. 5, which is similar to the phonon mode observed in pristine BaBiO$_3$ at 570 cm$^{-1}$ [34]. In the case of BaBiO$_3$, the phonon is attributed to the breathing mode originating from local distortion in the bond disproportionated BaBiO$_3$, so it is likely that a similar energy phonon originates from a similar breathing mode accompanying the disproportionation in Ag$_2$BiO$_3$. The slight difference in energies between the phonon modes in Ag$_2$BiO$_3$ and BaBiO$_3$ is due to the different arrangement of the BiO$_6$ octahedra in the two compounds and the slightly different Bi-O distances. A higher energy phonon mode originating from higher harmonic phonon modes can be seen in the Raman spectra of Ag$_2$BiO$_3$ at 1100 cm$^{-1}$, which is similar in value to phonons in the spectra of pristine BaBiO$_3$ [34].
FIG. 5: (a) Raman spectra of Ag$_2$BiO$_3$ at different $T$, between 290–10 K. (b) The same Raman spectra in (a), emphasizing the peak at 520 cm$^{-1}$, characteristic of the breathing mode in disproportionated bismuthates. (c) Powder-XRD of Ag$_2$BiO$_3$ collected at different $T$, between 293–203 K. The calculated XRD pattern for Ag$_2$BiO$_3$ in the $Pm\bar{n}m2$ phase is plotted at the bottom.

D. Transition to $Pn$ Phase in Ag$_2$BiO$_3$

We have closely measured the phonon mode at 520 cm$^{-1}$ as a function of temperature between 290 K and 10 K, and have observed a shift in the phonon peak position cooling down from 290 K to 250 K, but no further shift in the phonon mode cooling down to 10 K. We have performed powder XRD measurements on Ag$_2$BiO$_3$ at low $T$ and observe a splitting in some peaks at 240 K that corresponds to the monoclinic distortion previously reported [10]. This distortion leads to reduction of symmetry of Ag$_2$BiO$_3$ from $Pm\bar{n}m2$ to $Pn$.

As explained in Sec. IV A, it is difficult to distinguish whether Ag$_2$BiO$_3$ crystallizes in the $Pm\bar{n}m2$ or the $Pnma$ phase from XRD alone, and neutron diffraction studies were required to clarify the $Pm\bar{n}m2$ phase at room temperature [10]. The band gap and splitting in the Bi XPS states measured on our samples suggest that Ag$_2$BiO$_3$ is indeed in the $Pm\bar{n}m2$ phase. However, the $Pn$ phase of Ag$_2$BiO$_3$ is distinct from the higher symmetry phases and can be identified with XRD. The splitting of the (202) peak at $\sim 12.6^\circ$ for temperatures $< 243$ K is highlighted with a blue circle in Fig. 5(c), which results from the reduced symmetry of Ag$_2$BiO$_3$ $Pm\bar{n}m2$ to $Pn$.

It is likely that the shift in the phonon mode observed in Raman measurements at 250 K is related to the phase transition observed in powder XRD. The transition observed in our samples is consistent with the previously reported phase transition in neutron diffraction measurements on Ag$_2$BiO$_3$ [10]. In future studies, we hope to investigate the effect of different synthesis conditions on the oxygen content in Ag$_2$BiO$_3$, and whether this influences the distortion in these samples at low $T$.

Measurements that can be used to probe the band structure of Ag$_2$BiO$_3$ such as scanning tunneling spectroscopy or angle-resolved photoemission spectroscopy are typically performed at low temperature. Any properties measured on Ag$_2$BiO$_3$ below $\sim 250$ K are representative of the material in the $Pn$ phase, and the band structure of this phase will be the relevant one for those measurements. Luckily, the $Pn$ (Space Group 7) symmetry falls into the non-symmorphic space groups where a single glide mirror symmetry is expected to lead to symmetry-enforced Weyl nodal lines [26–28], albeit not a nodal chain as in the $Pm\bar{n}m2$ phase.

The disproportionation of Ag$_2$BiO$_3$ is still prevalent in the $Pn$ phase, which would lead to a band gap much like the $Pm\bar{n}m2$ phase. Repeating the XPS and XAS measurements at temperatures where Ag$_2$BiO$_3$ is in the $Pn$ phase will help reveal whether this transition affects the Bi states or the oxygen holes.

V. CONCLUSIONS

We have demonstrated that despite the use of a high pressure of 6 GPa, Ag$_2$BiO$_3$ samples crystallize in a structure consistent with the $Pm\bar{n}m2$ phase as evidenced by the XPS data for Bi and the measured band gap. The band gap observed in our study is consistent with our band calculations, and we demonstrate that Ag$_2$BiO$_3$ even in the $Pm\bar{n}m2$ phase is topologically non-trivial and contains Weyl-nodal chains in its band structure ($\sim 0.5$ eV below the Fermi level). We observe a phase transition in Ag$_2$BiO$_3$ at low temperatures associated with distortion from the $Pm\bar{n}m2$ phase to the $Pn$ phase from our XRD pattern and Raman spectra. Even in the $Pn$ phase Ag$_2$BiO$_3$ falls into a non-symmorphic space group and Weyl nodal-line features are expected.

The XAS spectra of Ag$_2$BiO$_3$ suggests the presence of oxygen holes much like BaBiO$_3$, which is consistent with Ag$_2$BiO$_3$ being a bond disproportionated bismuthate. Despite the different arrangement of BiO$_6$ octahedra in BaBiO$_3$ and Ag$_2$BiO$_3$, we observe a phonon mode in the Raman spectra of Ag$_2$BiO$_3$ at similar energy associated...
with breathing mode of the disproportionated BaBiO₃. Our results push forward the group of monovalent bismuthates \((M^+1)_2\)BiO₃ as a new class of bismuthates with novel topological properties. Doping of divalent atoms on the Ag-site and performing in-situ high-pressure experiments may allow us to destabilize the disproportionation in Ag₂BiO₃, and achieve a metallic state and perhaps even superconductivity in this class of materials in analogy to BaBiO₃. We envision that this work will open up the field of disproportionated oxides beyond those in the perovskite structure.

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Supplementary Figure 1: Powder X-ray diffraction (PXRD) and powder neutron diffraction (PND) simulation Ag\textsubscript{2}BiO\textsubscript{3} in the *Pnn*\textsubscript{2} phase shown in (a) and (b), respectively. PXRD and PND simulation of Ag\textsubscript{2}BiO\textsubscript{3} in the *Pnna* phase shown in (c) and (d), respectively. Diffraction patterns are plotted as a function of the reciprocal lattice vector (Q). Black circles in the figures highlight one of the peaks only observable in the PND for the *Pnn*\textsubscript{2} phase.
Supplementary Figure 2: X-ray photoelectron spectra of K 2p and C 1s (a) and of the valence band of Ag₂BiO₃ (b). In (b) the valence band edge is approx. 0.9 eV below the Fermi level.

Supplementary Table I: Binding energy, assignment, full width at half-maximum (FWHM) and amount of the species observed via XPS. Please note that due to surface contaminations, error in the detector function and atomic sensitivity the amount might have an error in the range of 10-15%.

| element    | Assignment                          | Binding energy [eV] | FWHM [eV] | Amount in [%] |
|------------|-------------------------------------|---------------------|-----------|---------------|
| O 1s       | Ag₂BiO₃ edge shared (peak C)        | 529.1               | 1.1       | 11.9          |
| O 1s       | Ag₂BiO₃ corner shared (peak B)      | 530.8               | 1.7       | 11.8          |
|            | (small amounts of OH, carbonate contaminations) |                     |           |               |
| O 1s       | Water, hydroxides (peak A)         | 532.6               | 1.7       | 1.9           |
| C 1s       | C-C, C-H contaminations             | 284.8               | 1.5       | 8.4           |
| C 1s       | C-OH contaminations                 | 285.7               | 2.2       | 6.0           |
| C 1s       | carbonate                            | 288.5               | 1.7       | 4.0           |
| K 2p₃/₂    | KOH                                 | 292.6               | 1.5       | 2.5           |
| Ag 3d₅/₂   | Ag₂BiO₃ (peak D2)                   | 367.8               | 1.2       | 16.1          |
| Bi 4f₇/₂   | Ag₂BiO₃ (peak G2)                   | 158.0               | 0.9       | 4.4           |
| Bi 4f₇/₂   | Ag₂BiO₃ (peak F2)                   | 158.5               | 1.4       | 5.2           |
Supplementary Figure 3: Imaginary ($\varepsilon_2$, top figure) and real ($\varepsilon_1$, bottom figure) parts of the dielectric constant of $\text{Ag}_2\text{BiO}_3$ extracted from ellipsometry measurement.
Supplementary Figure 4: (a) The DFT (LDA) band structures of Ag$_2$BiO$_3$ in the $P$mn2 phase with fat band representation of atomic orbital contributions. (a) The atomic orbital of the Ag-4$d$ shown in grey fat bands. (b) The fat bands of Bi-$s$ (green) and Bi-$p$ (purple) contribution in the small O$_6$ octahedral cage. (c) The fat bands of Bi-$s$ (green) and Bi-$p$ (brown) contribution in the large O$_6$ octahedral cage. (d) The atomic orbital of the O-2$p$ shown in pink fat bands.