Spectroscopy of Ag-Bi-O Phases Synthesized Under High Pressure

Mohamed Oudah,[a, b] *M. Kim,*[a] *G. McNally,*[a] *K. Rabinovich,*[a] *B. Kilic,*[a] *A. Schnyder,*[a] *S. Borris,*[a] *D. Bonn,*[b] *B. Keimer,*[a] *and H. Takagi,*[a, c]

[a] Max Planck Institute for Solid State Research, Stuttgart, Germany

[b] Stewart Blusson Quantum Matter Institute, University of British Columbia, Canada

[c] Department of Physics, University of Tokyo, Japan

Mohamed.Oudah@UBC.ca

Introduction

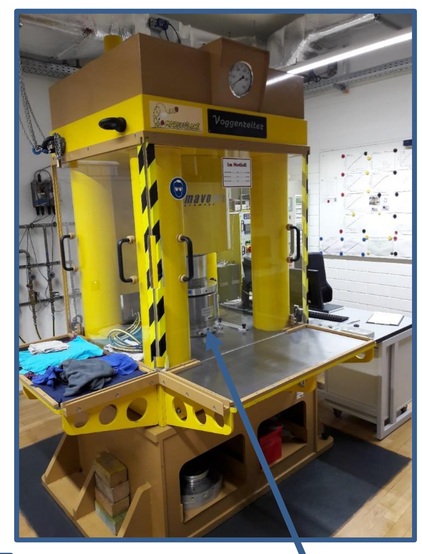
The stoichiometric silver bismuthate **Ag_2BiO_3** typically contains equal amounts of bismuth in the Bi^{+3} and Bi^{+5} states, and this charge ordering renders Ag_2BiO_3 insulating [1]. Recent theoretical predictions of a metal-insulator transition and Weyl semimetal state in Ag_2BiO_3 have revived the interest in this material [2]. However, such novel properties are expected in the absence of charge ordering.

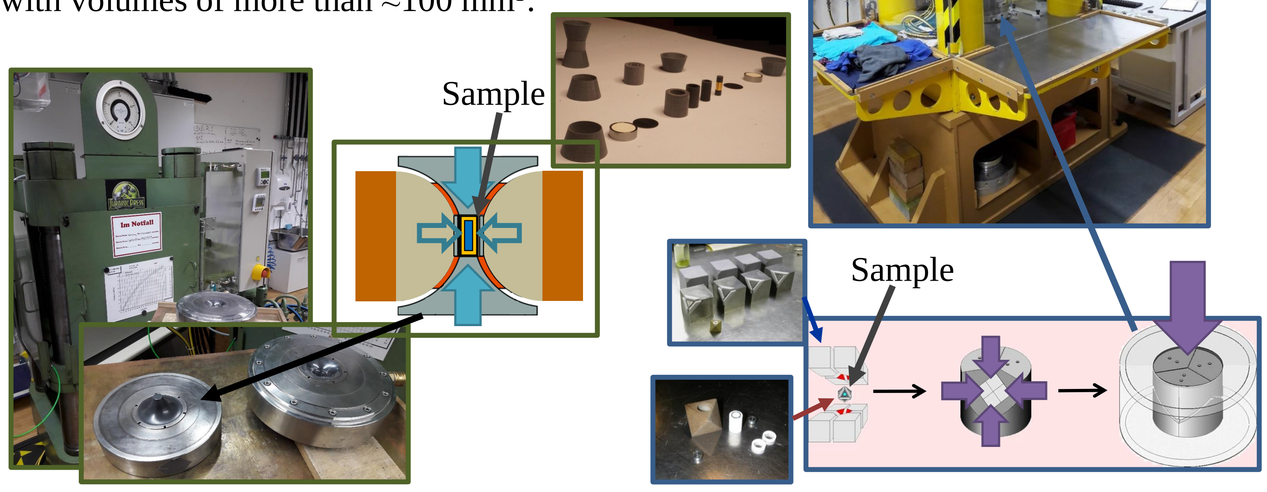
Here, we utilize spectroscopic tools to examine the possibility of suppressing the charge ordering in Ag_2BiO_3 via chemical substitution/doping, and achieving the topologically nontrivial phase predicted. We present a new high-pressure synthesis route for Ag_2BiO_3, which we utilize for substituting/doping at the Ag site.

Furthermore, predictions of a topological insulating state were made in the ilmenite structure of **$AgBiO_3$**. We have investigated the effect of pressure on $AgBiO_3$ and identified a new polymorph at 6 GPa. Optical conductivity results reveal a comparable gap of ~1.0 eV in $AgBiO_3$ and Ag_2BiO_3, while Raman spectroscopy shows a peak at ~515 cm^{-1},characteristic of local distortion in bismuthates.

High Pressure Synthesis

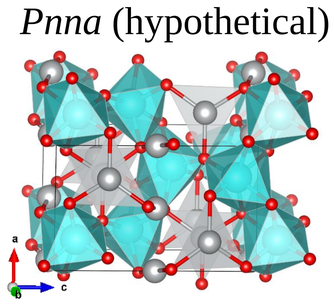
Solid state syntheses of materials in the Ag-Bi-O system have been carried out at about **6-12 GPa** and **460-900 °C**. An *octahedron*-within-*cubes* assembly in a Walker-type multi-anvil press (**right**) and a Belt-type press (**bottom**) allow the synthesis of samples with volumes of more than ≈100 mm^3.



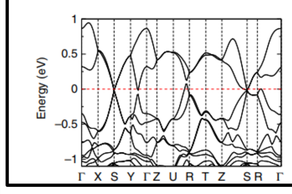


Ag_2BiO_3 Phase

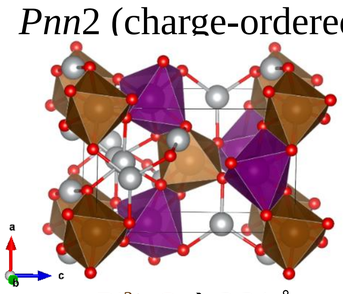
$(Ag^{1+})_2(Bi^{4+})(O^{2-})_3$
Pnna (hypothetical)



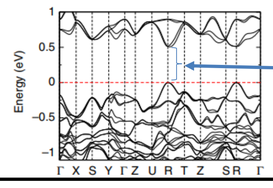
Bi^{4+}–O → 2.16-2.23 Å



$(Ag^{1+})_4(Bi^{3+}Bi^{5+})(O^{2-})_6$
*Pnn*2 (charge-ordered)

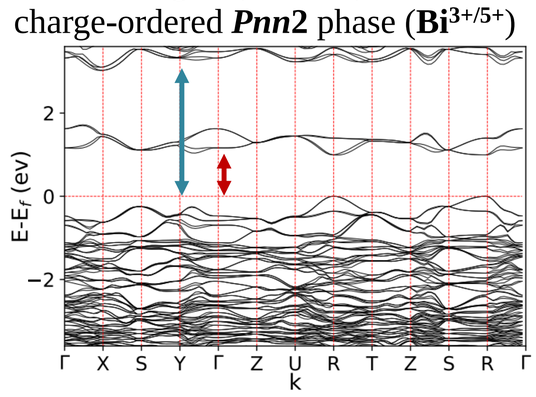


Bi^{3+}–O → 2.34 Å
Bi^{5+}–O → 2.13 Å

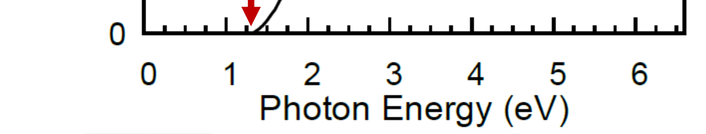


Gap calculated in **VASP** is underestimated.

Optical spectroscopy measurement of Ag_2BiO_3 suggests a **band gap (~1.3 eV)**, consistent with charge-ordered ***Pnn*2** phase (**$Bi^{3+/5+}$**)

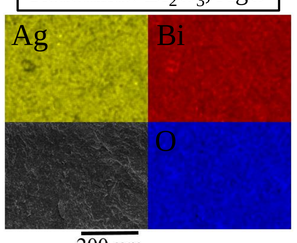


Local-density approximation (LDA) with **Heyd-Scuseria-Ernzerhof (HSE) hybrid functional**.

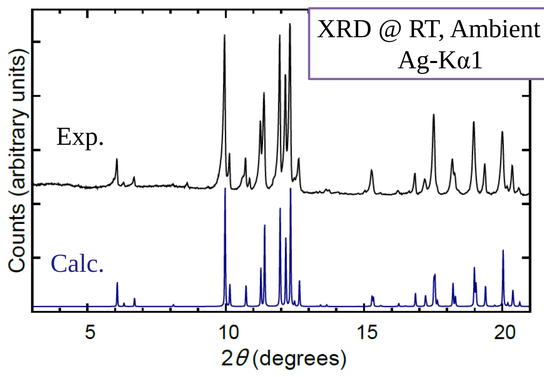


The band calculations of Ag_2BiO_3 reveal a Dirac crossing in the *Pnna* crystal structure and an insulating state in *Pnn*2 structure[2].

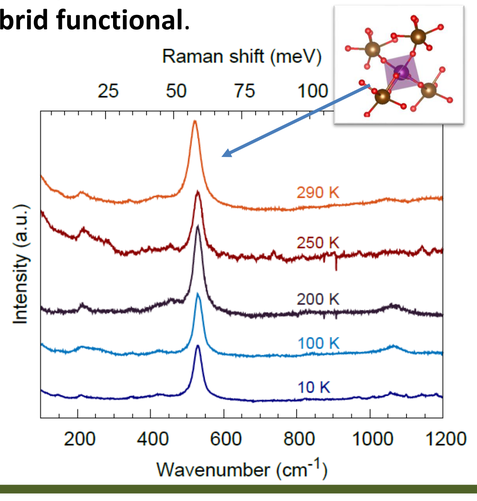
Belt Press Synthesis at:
P = 6 GPa , *T* = 460 ºC
Reactants: Bi_2O_3, AgO



SEM



Breathing phonon peak at **~520 cm^{-1}** similar to $BaBiO_3$, $(Ag^{1+})_4(Bi^{3+}Bi^{5+})(O^{2-})_6$ also locally distorted [4].

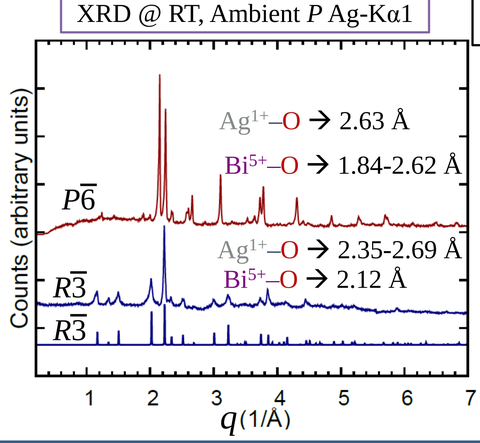


$Ag_{2-x}Ca_xBiO_3$

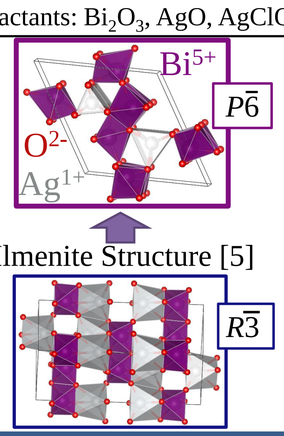
Now, we are using optical conductivity and Raman spectroscopy to investigate the effect of **electron doping** on the **band gap** and the phonon modes.

$AgBiO_3$ Phases

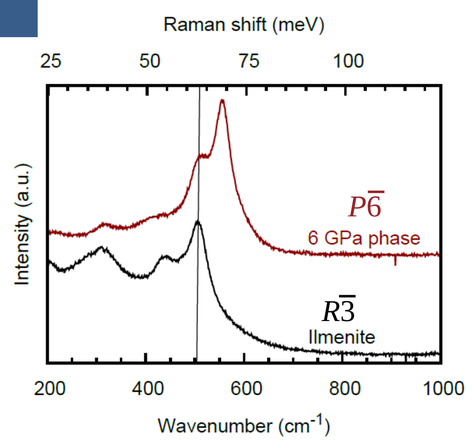
XRD @ RT, Ambient *P* Ag-Kα1

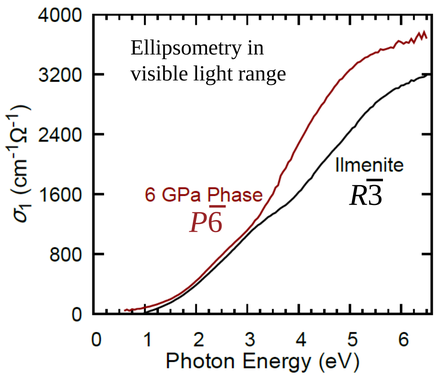


Cubic-Anvil Press Synthesis at:
P = 6 GPa , *T* = 460 ºC
Reactants: Bi_2O_3, AgO, $AgClO_4$



- **Ilmenite (*R*$\bar{3}$)** phase has gap of **~1 eV**.
- Finite optical conductivity of high pressure phase *P*$\bar{6}$ even at **0.6 eV**.
- Breathing phonon at **~510 cm^{-1}** suggests $(Ag^{1+})(Bi^{5+})(O^{2-})_3$ locally distorted.
- Breathing phonon at **~550 cm^{-1} in 6 GPa phase**, may come from shorter Bi-O bonds.





Conclusion

- Our study reveals that **Ag_2BiO_3** is a **charge ordered insulator** with a **band gap of ~1.0 eV**, contradictory to the theoretical prediction of Dirac-semimetal phase!
- We found a **band gap in two $AgBiO_3$ phases** (*R*$\bar{3}$ and *P*$\bar{6}$), again inconsistent with DFT.
- The **breathing phonon at ~520 cm^{-1}** is observed in these silver bismuthates.
- Our band structure calculations (**HSE**) match the features in optical spectroscopy results!
- Our results give guidance to **design of new topological insulating materials**.
- **X-ray absorption spectroscopy** will be performed to confirm the bismuth oxidation state.

References

[1] C. B. M. Oberndorfer et al., *Solid State Sci.* **8**, 267 (2006).

[2] J. He et al., *Nat. Commun.*, **9**, 492 (2018).

[3] T. Zhang et al., *arXiv:1807.08756* (2018).

[4] S. Tajima et al., *Phy. Rev. B*, **46**, 1232 (1992).

[5] N. Kumada et al., *Mater. Res. Bull.* **35**, 2397 (2000).