

# Discovery of Novel Braunite Related Structure $\text{Cu}_4\text{MnSb}_2\text{SiO}_{12}$ and Dimorphism

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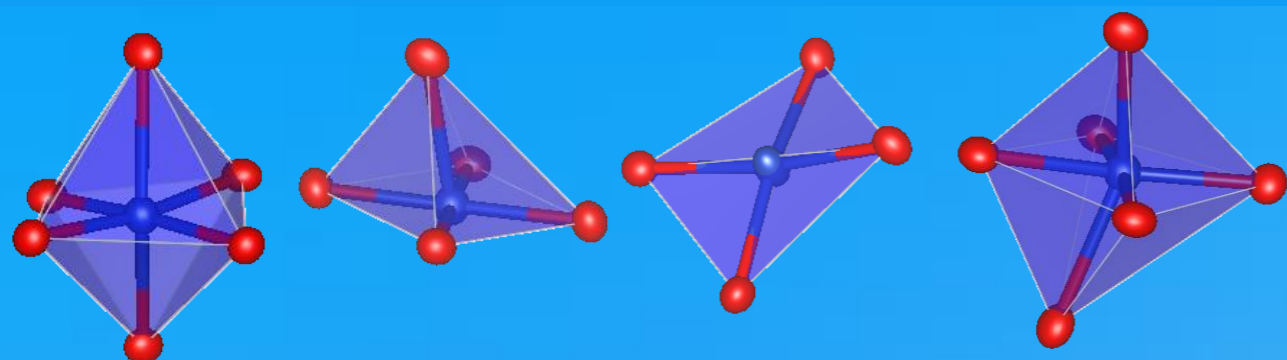
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## Introduction

Single crystals of the only copper antimony silicate  $\text{Cu}_5\text{Sb}_2\text{SiO}_{12}$  have been grown.[1] Single crystal X-ray diffraction (XRD) was used to confirm a parwelite related structure. The parwelite structure has been described as the most complex anion deficient fluorite related crystal structures[2].

Cu occupies 7 unique crystallographic sites with varying local coordination spheres. This wealth in complexity makes  $\text{Cu}_5\text{Sb}_2\text{SiO}_{12}$  an excellent candidate to study for its electronic and magnetic properties.

The magnetic structure of  $\text{Cu}^{2+}$  ( $3d^9$ ) compounds is often difficult to solve due to poor scattering of the single unpaired electron (per Cu) with neutrons. In our attempts to resolve the magnetic structure we synthesised the solid solution  $\text{Cu}_{5-x}\text{Mn}_x\text{Sb}_2\text{SiO}_{12}$  ( $x = 0 - 2$ ) and discovered a new braunite related crystal structure with the composition  $\text{Cu}_4\text{MnSb}_2\text{SiO}_{12}$  (space group  $I4_1/acd$ ), which is the first discovered copper manganese antimony silicate.



Examples of different coordination environments for Cu (blue) in  $\text{Cu}_5\text{Sb}_2\text{SiO}_{12}$ . From left to right; apically elongated octahedron, distorted square pyramid, distorted square planar, distorted (2+2+2) octahedron.

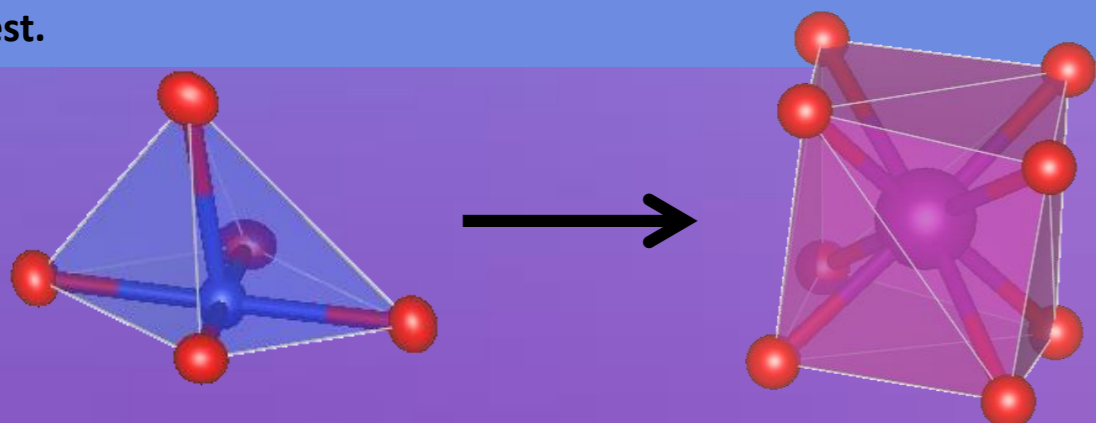
## Synthesis

- Single crystals of  $\text{Cu}_5\text{Sb}_2\text{SiO}_{12}$  can be grown through chemical vapour transport (CVT) or direct solid-state reaction of the bixbyite  $\text{Cu}_3\text{Sb}_{1+x}\text{O}_{5.5+3x/2}$  with  $\text{SiO}_2$ .
- Single crystals of  $\text{Cu}_4\text{MnSb}_2\text{SiO}_{12}$  with the new braunite related phase can be grown through CVT or recrystallisation from  $\text{Cu}_2\text{MnSbO}_6 + \text{SiO}_2$  at  $p\text{O}_2 > 1$  bar,  $T \geq 1270$  K and a strongly reducing transport agent.
- Synthesis of  $\text{Cu}_{5-x}\text{Mn}_x\text{Sb}_2\text{SiO}_{12}$  in air at  $T \geq 1170$  °C always yields a combination of both the parwelite and braunite related phases for  $x > 0.75$ .
- Using  $\text{Mn}^{2+}$  containing precursors, higher temperatures and higher pressures all increase the relative braunite related phase content.

## X-ray Absorption Spectroscopy

X-ray absorption spectroscopy (XAS) experiments were conducted in transmission mode at the Cu and Mn K-edge.

- The major Cu species is  $\text{Cu}^{2+}$ .
- $\text{Cu}^{1+}$  is present in  $\text{Cu}_5\text{Sb}_2\text{SiO}_{12}$ , as Mn content is increased with doping the  $\text{Cu}^{1+}$  content is consistently reduced suggesting that Mn is preferentially displacing  $\text{Cu}^{1+}$  from within the parwelite related phase.
- The major Mn species is  $\text{Mn}^{3+}$  with some  $\text{Mn}^{2+}$ .
- The  $\text{Mn}^{2+}$  content is greatest for the precise composition of  $\text{Cu}_4\text{MnSb}_2\text{SiO}_{12}$  which is where the composition of the new braunite related phase is greatest.



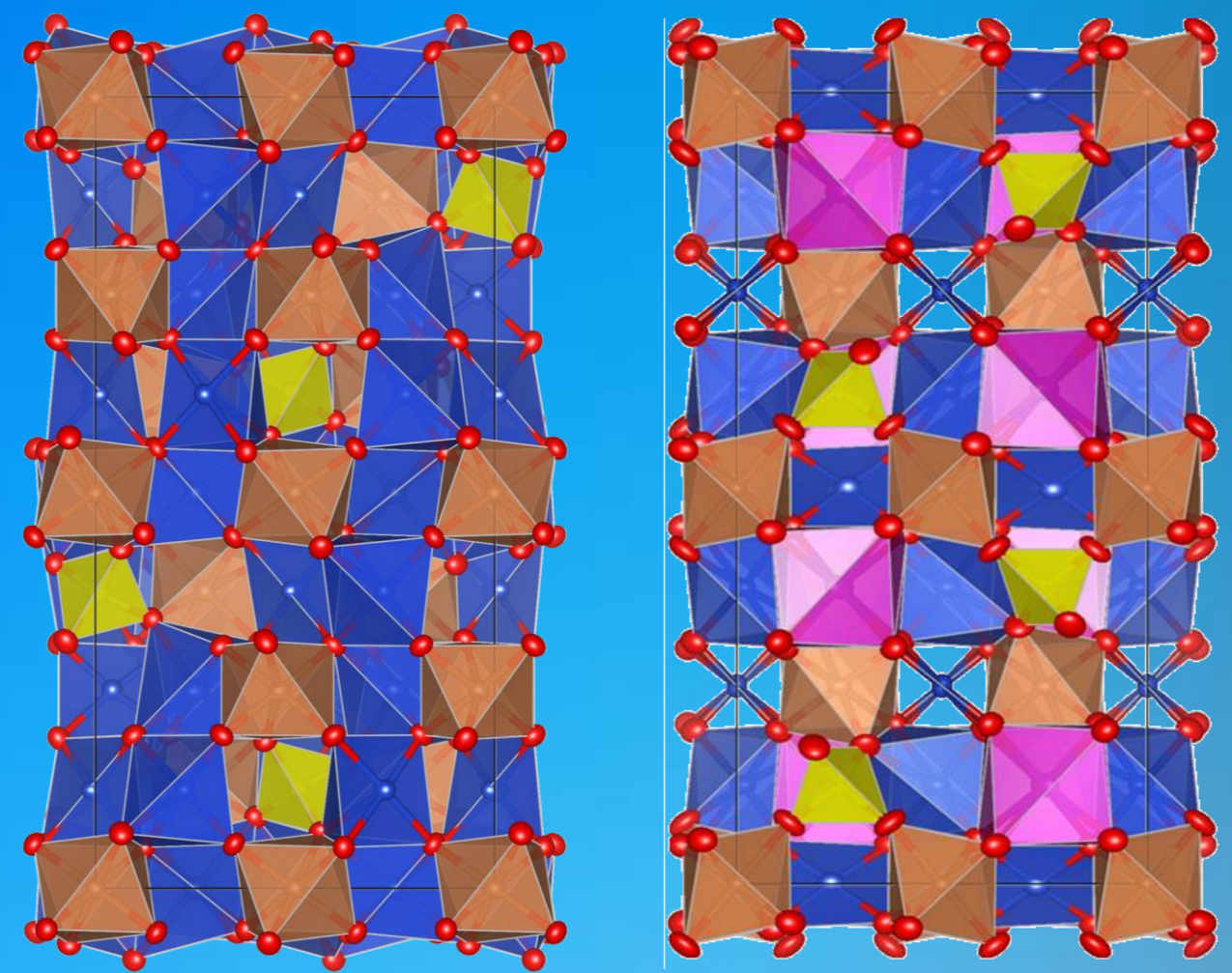
## Summary

A new braunite related crystal structure with the composition  $\text{Cu}_4\text{MnSb}_2\text{SiO}_{12}$  was solved. The composition is a polymorph of the parwelite/ $\text{Cu}_5\text{Sb}_2\text{SiO}_{12}$  related structure which depending on the selective occupation of Mn stabilises either one or the other structure.

## References

- Moore, P. B., & Araki, T. (1977). Parwelite,  $\text{Mn}_{10}\text{Sb}_2\text{V}_2\text{As}_2\text{Si}_2\text{O}_{24}$ , a complex anion-deficient fluorite derivative structure. *Inorganic Chemistry*, 16(8), 1839–1847.
- M. Fakhfakh, A. Seguatni, P. Molinier and N. Jouini, *Mater. Res. Bull.* 42, 1539 (2007).

## Acknowledgements

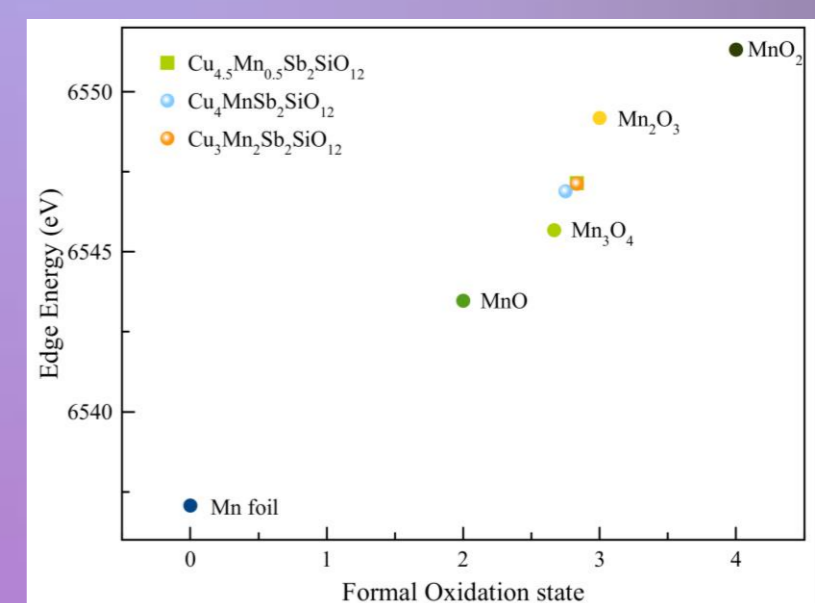
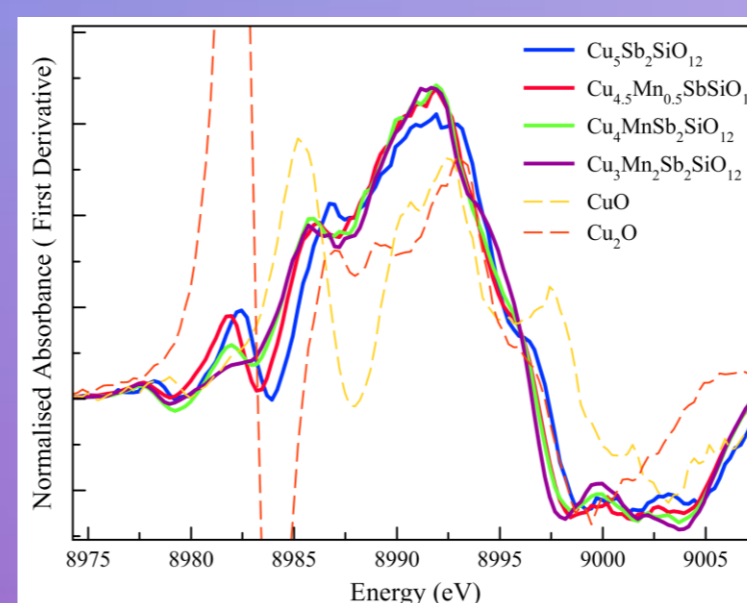


Crystal structure of  $\text{Cu}_5\text{Sb}_2\text{SiO}_{12}$  (left) and the novel braunite related structure and polymorph  $\text{Cu}_4\text{MnSb}_2\text{SiO}_{12}$  (right) from single crystal XRD ( $\text{Ag K}\alpha$ ,  $\lambda = 0.56$  Å).  $\text{MnO}_8$  = magenta,  $\text{SbO}_6$  = brown,  $\text{SiO}_4$  = yellow,  $\text{CuO}_4$ ,  $\text{CuO}_5$  and  $\text{CuO}_6$  = blue.

## Neutron Powder Diffraction

Ambient and low temperature neutron powder diffraction experiments were conducted.

- With Mn doping, Mn preferential occupied the distorted trigonal pyramidal site followed by the distorted square planar site.
- This trigonal pyramidal site forms the distorted cubic site typically hosting a divalent cation in the braunite structure.
- $\text{Mn}^{3+}$  is a  $3d^4$  system preferencing a high spin configuration, this exhibits strong Jahn-Teller effect (JTE) similar to  $\text{Cu}^{2+}$ .
- Synthesis conditions where  $\text{Mn}^{2+}$  is more likely to be preferred over  $\text{Mn}^{3+}$  produces a larger % of the braunite related phase. Whereas  $\text{Mn}^{3+}$  is less likely to force a change in symmetry
- Long-range antiferromagnetic (AFM) ordering below 28 K.
- Propagation vector relating the magnetic cell  $\mathbf{k} = (0,0,0)$
- Magnetic structure of the parwelite related phase is likely closely related to the  $\text{Mn}_7\text{SiO}_{12}$  magnetic structure space group  $P2_1$  but this is still work in progress



First derivative of the Cu K-edge of select samples and standards (left), Mn K-edge energy in relation to formal oxidation state of a number of standards and synthesised samples (right).