

Synthesis of New Cuprate's through High Pressure Chemical Vapour Transport

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Chemical vapour transport (CVT) reactions has allowed for the growth of many inorganic single crystals which would be difficult or completely impossible to grow using alternative methods like flux related methods or from congruent melt. Most CVT reactions are done in evacuated and sealed quartz tubes where the internal pressure is typically in the range from 1 to 10^{-3} bar where diffusion is the dominant contributor to transport kinetics.[1] Diffusion limited transport is preferred over convective transport because it minimises nucleation, favouring the growth of larger single crystals with fewer defects.

Many metal oxides are simply not thermodynamically stable under these conditions making it difficult to transport and crystallise the desired phase or composition. We have found this to be the case for many cuprates with the braunite, parwelite and various Cu_3TeO_6 related structures. To circumvent this limitation we have explored the unconventional high pressure CVT (HPCVT) method. As a result of these experiments we have been able to successfully grow and solve the structures of single crystals of new polymorphs and structures, this includes $\text{Cu}_5\text{Sb}_2\text{SiO}_{12}$, $\text{Cu}_4\text{MnSb}_2\text{SiO}_{12}$, $\text{Cu}_2\text{GaSbO}_6$ and $\text{Cu}_3\text{Ga}_3\text{SbSiO}_{12}$. Samples have been characterised by X-ray and neutron diffraction and magnetic susceptibility measurements. These structures exhibit exotic gallium and copper coordination environments making them suitable candidates for studying various magnetic phenomena.

HPCVT is a useful method not only for the growth of new inorganic compounds but also as an alternative, environmentally friendly method for growing known structures. Under pressure, water seems to be a major contributor to the transport reaction making it possible to grow samples without a reliance on halogens or commonly used salts like HgBr or TeCl_4 . Since the transport rates are high as a result of greater convective currents, a significantly smaller temperature gradient is necessary to conduct the experiments making much simpler experimental designs possible and accessible without the need for multi-zone furnaces.

[1] Binnewies, M.; Glaum, R.; Schmidt, M.; Schmidt, P. Chemical Vapor Transport Reactions. 2012.

Speakers Gender

Level of Expertise

Student

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No

Primary author(s) : SPASOVSKI, Martin (University of Auckland); AVDEEV, Max (Australian Nuclear Science and Technology Organisation, Australian Centre for Neutron Scattering); SOEHNEL, Tilo (The University of Auckland)

Presenter(s) : SPASOVSKI, Martin (University of Auckland)

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