Hydroflux Synthesis of Copper Tellurates : Discovery of Three New Phases & Competing Cu:Te Solubility Trends Through A-Cu-Te-O(H) [A = Cs, K, CS+K]

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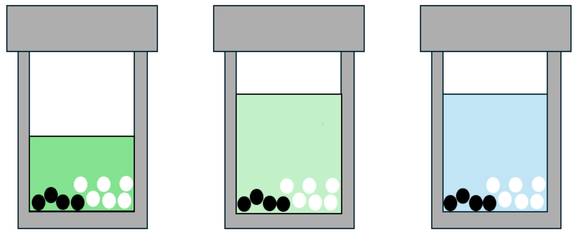
AN NSF MATERIALS INNOVATION PLATFORM

Motivation

- Generation of materials depend on innovations in synthesis techniques to explore new regions of phase space. → *We need to try new things to get interesting results.*
- Hydroflux synthesis combines the techniques [3]:

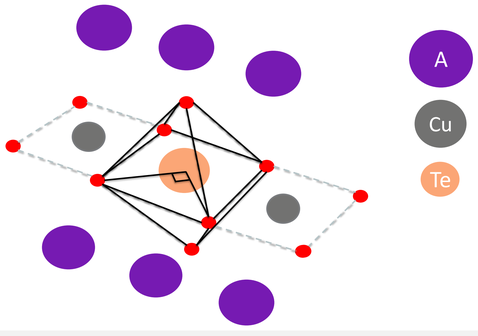
1. **Hydrothermal:** reagents react with supercritical H_2O
2. **Flux:** reagents react with fluxes, such as hydroxide.



- Hydroxide is highly basic while H_2O has low-melt temp.
- Combining both environments allow for unique formation reactions → ***However there is a need to better understand their nature for rational synthesis.***

Why an Alkali, Cu, and Te?

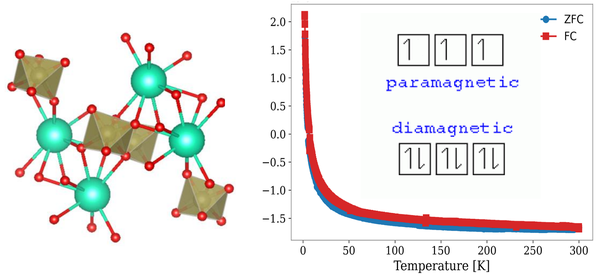
- Potential for new magnetic oxide phases!
- Fully oxidized Cu^{2+} has a d^9 configuration. Can act as a model spin 1/2 ions → Cu^{2+} ions can magnetically order based on their distances and geometries.
- Fully oxidized Te^{6+} has a full d^{10} shell and octahedrally coordinates to oxygen, facilitating Cu-Cu magnetic interactions via superexchange [2].
- Partially oxidized Te^{4+} exhibits the lone pair effect due to its s_2 electron pair and has anisotropic coordination. Expected to affect the magnetism in these systems as magnetic pathways may be disrupted or impeded [2].



Previous work showed that K-Cu-Te-O(H) generates 2D magnetic layers with alkali spacers. [1]
Perhaps Cs could increase interlayer distance due to its large ionic radius!

Discovery of Three New Magnetic Oxides

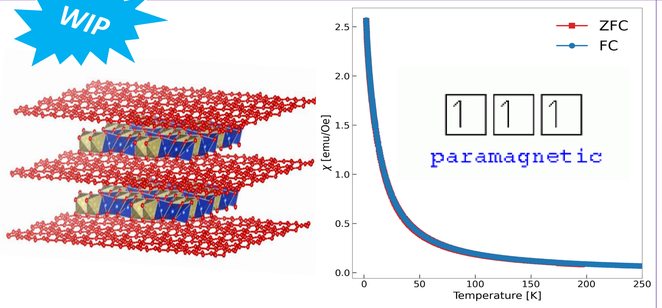
$CsTeO_3(OH)$



- Forms as white needles or clusters.
- Two Cs environments both coordinated to 9 O atoms.
- Generates large and distorted unit-cell, reflected in its lower symmetry (P -1 vs P 21).
- Two TeO_6 environments with distorted octahedra.
- Diamagnetic with paramagnetic impurities confirmed in isothermal magnetization [not depicted] and temperature-dependent magnetic susceptibility (above) measurements.

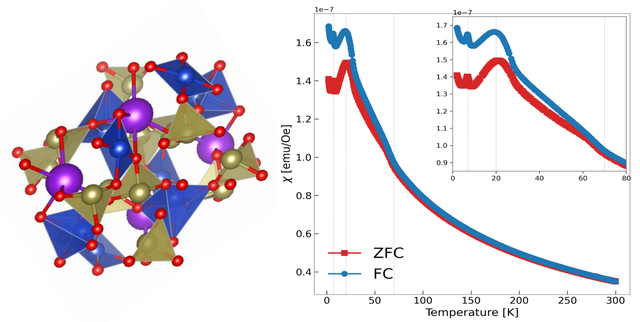
Layered Cs-Cu-Te

WIP



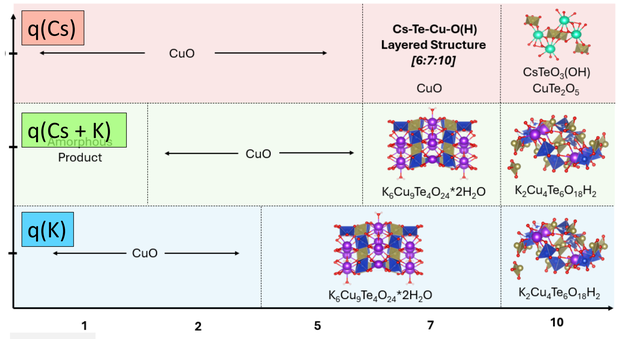
- Three CuO_4 square planar plaquettes & two TeO_6 octahedra.
- Confirmed to have Cs through EDS from SEM.
- Approximate stoichiometry determined, currently problem-solving locations of Cs atoms within disordered layer and if H_2O is present and its placement.
- Paramagnetic but is likely to order antiferromagnetically at low temperature as deduced from Curie-Weiss fitting.

$K_2Cu_4Te_6O_{18}H_2$



- Two Cu coordinations, CuO_4 square plaquette and CuO_5 square pyramid. Te^{+4} in neither an octahedron or tetrahedron, forming highly distorted environment.
- High coordination results in many possible different magnetic pathways. → Three magnetic transitions can be seen: two short range antiferromagnetic correlations at T = ~70K, ~20K, and an antiferromagnetic transition at T= ~7K.

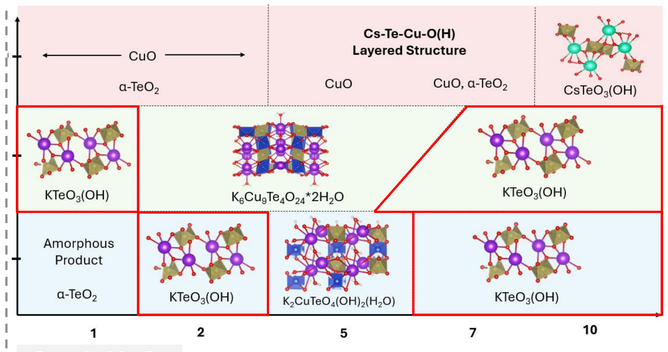
Comparison of Cu-Te Phase Spaces



3mL H_2O

q(A) [H_2O mols : AOH mols]

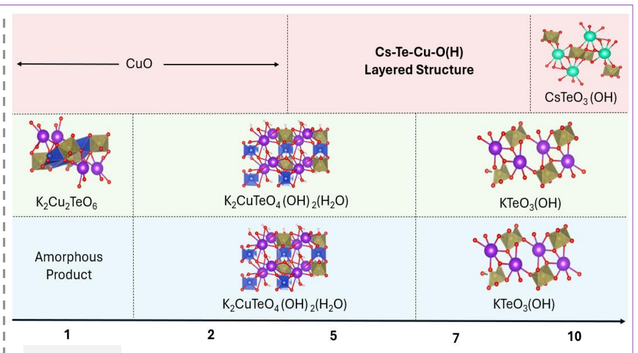
Cu:Te Ratio Increases in Diluted AOH



2 mL H_2O, 1 mL H_2O_2

q(A) [H_2O mols : AOH mols]

$KTeO_3(OH)$ Reentrance Phenomena



3mL H_2O_2

q(A) [H_2O mols : AOH mols]

Larger O_2 Population Yields More Layered Structures.

"Why These Systems? Why This Approach?"

- Investigated K- and Cs+K- to better understand Cs- behavior, the least studied alkali hydroxide in hydroflux, and mixed hydroxide dynamics.
- Systematic study of alkali ionic size, a comparative approach rarely (if ever) done in exploratory synthesis. *Analysis will assist rational design efforts!*
- Study focused on a phase space region where Cu:Te was 1:10 as higher Cu concentrations yielded primarily CuO products in preliminary studies on the Cs- system.

Alkali Hydroxide Dependence and Oxidization Observations:

- H_2O_2 and AOH generate additional oxidizing agents within the hydroflux solution → Allows for tuning of in-solution reactions and provides limited control on the solid formed and Te oxidization.
- K- and Cs+K- phase space changed depending on 0%, 10%, 30% H_2O_2 while Cs- system was largely independent indicating Cs prefers to remain in-solution.
- Te was always fully oxidized in the presence of H_2O_2, while without it was positively correlated with hydroxide concentration.

Cu/Te Solubility Modeling

- Intermediates within the highly basic solution were determined and yielded these dissolution reactions:

$$CuO\ (s) + H_2O + 2[OH]^- \rightarrow [Cu(OH)_4]^{2-}$$
$$2TeO_2\ (s) + O_2 + 4[OH]^- \rightarrow 2[TeO_4]^{2-} + 2H_2O$$
$$2TeO2\ (s) + 4[OH]^- \rightarrow 2H_2O + 2[TeO3]2-$$

- Reactions involving $[Cu(OH)_4]^{2-}$, $[TeO_4]^{2-}$, and $[TeO_3]^{2-}$ and forming the products observed within the phase diagrams were determined and compared.
- Relative amounts of these intermediates, with the observation of re-entrance, correctly modeled the competing Cu:Te solubilities observed.

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Conclusion

- Cs- system has vastly different solid formation dynamics than K- and K+Cs- despite having the similar inverse Cu:Te solubilities and in-solution reactions.

References

[1] Allana G. Iwanick *et al.* Hydroflux-Controlled Growth of Magnetic L-Cu-Te-O(H) Phases, 27 Mar 2024
[2] Eder, F. (2023). *Crystal engineering of Oxidotellurates* [Dissertation, Technische Universität Wien].
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