Solubility and Phase Selection of Copper Tellurates in Alkali Hydroflux

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I. Introduction

Hydroflux synthesis merges two well-established methods of crystal growth: high-temperature fluxes and hydrothermal synthesis [20]. To understand why hydroflux reactions offer unique opportunities within the exploratory synthesis, both hydrothermal and flux systems must be understood. The primary solvent in hydrothermal reactions is H2O which autodissociates into OH- and H+ [20]. These ions assist in the dissolution of regents which generate in-solution complexes that can undergo precipitation reactions that may generate crystals. On the opposite end of the spectrum, flux reactions are highly ionic species that easily generate A+ ions and [OH]- cations that may further dissociate into H2O and O2- depending on the identity (A) of the hydroxide [5]. By incorporating a roughly equimolar solution of water and (often alkali or alkaline earth) hydroxide heated in a sealed reaction vessel, hydroflux mixtures are basic, oxidizing, low melting reaction environments which can enable formation of distinct products unattainable by either flux or hydrothermal conditions alone. Currently hydroflux synthesis remains relatively underexplored with modern research primarily focused on generating new phases while characterizing their fundamental thermal, magnetic, or optical properties. There is a notable lack of studies addressing the dynamics of H2O-AOH interactions with regents in solution and their influence on solid-state formation mechanisms. Understanding these interactions through exploratory synthesis is crucial for the systematic design of materials and their syntheses. Additionally such studies can provide valuable insights on the connections between structure-property and structure-formation relationships, enhancing the construction of materials through rational design.

In this study, we simultaneously investigated and compared two analogous Cu-Te containing phase spaces, Cs-Cu-Te-O(H) and K-Cu-Te-O(H), to explore the synthesis of novel magnetic materials and elucidate the impact of alkali ionic radius and alkali hydroxide dissociation on the hydroflux environment, solubilities of starting reagents, and resulting solid-state incorporation. Additionally, we explored a 1:1 mixed hydroxide phase space, Cs+K-Cu-Te-O(H), to examine how the presence of multiple alkali ions affects product outcome. The K- system was selected due to previous studies that successfully established design trends involving the relative ratios between Cu:Te and H2O:AOH, which informed the methodology for the Cs- system which is a less extensively studied alkali element. Growth techniques and starting reagents remained constant throughout all reactions and consistent with those performed by A. G. Iwanicki et al [8]. This study focused on a region of phase space where Cu:Te was 1:10 as higher Cu concentrations yielded primarily CuO products in preliminary studies on the Cs- system.

These phase spaces were also selected because of their potential to produce new magnetic oxide phases. Fully oxidized Cu2+ has a d9 electronic configuration and can act as a model spin 1/2 ion. When ordered in a crystalline lattice, the Cu2+ ions can interact and magnetically order based on their relative distances and geometries [8]. Fully oxidized Te6+ has a full d10 outer shell and octahedrally coordinates to oxygen, facilitating Cu-Cu magnetic interactions in copper tellurates via superexchange. Partially oxidized Te4+ exhibits the lone pair effect due to its s2 electron pair and has anisotropic coordination which is expected to affect the magnetism in these systems as magnetic pathways may be disrupted or impeded. Furthermore, these phase spaces were evaluated under three distinct levels of reaction environment oxidation, controlled by varying the concentration of H2O2 reagent. This allowed for exploration into different regions of phase space across the three systems which were then compared. This allowed us to conclude whether or not the presence of additional oxidizing agents O2- altered the reactions that occurred within the solution environment. More specifically, since hydroflux synthesis is conducted in a closed vessel, this allowed for the incorporation of superoxide and hydroxyl

radicals within the hydroflux reactions. This H2O2 study analyzed how the strength of the alkali hydroxide compared to addition of the oxidizing agent, allowing for comparative claims about how CsOH and KOH affected in-solution dynamics

Unique solubility dynamics are present within the Alkali-Cu-Te hydroflux system compared to CuO or TeO2 in neutral or alkaline environments. Previous research conducted by McDowell et al. and Muller at room temperature have found that the solubility of CuO increases as the [OH]- population increases in alkaline environments using NaOH and KOH, opposite of what is observed in the hydroflux system [9][10]. More modern studies conducted by Navarro M. et al also agree that the population of Cu2+ ions with solution scales with [OH]- for LiOH and NaOH highly concentrated alkaline solutions for temperatures up to 60 C but disagree with the magnitude of values reported by McDowell et. al [11]. It has also been determined that CuO is less soluble in neutral solutions than highly basic and acidic solutions in temperatures ranging from 25 to 450 C, implying the presence of H2O is reducing the solubility of CuO [12][13]. While the solubility of CuO in solutions with varying pH and [OH]- populations has been studied intensively, TeO2 has not and needs to be in order to better understand the formation of these systems. One study stated that the solubility of TeO2 is pH dependent and that it is relatively high in academic or basic solutions whilst minimal in neutral solutions [14]. It was also found that its solubility sharply increases as the temperature increases past 40 C [14].

II. Results

Alkali Ion Dependence For Hydroflux Mixture

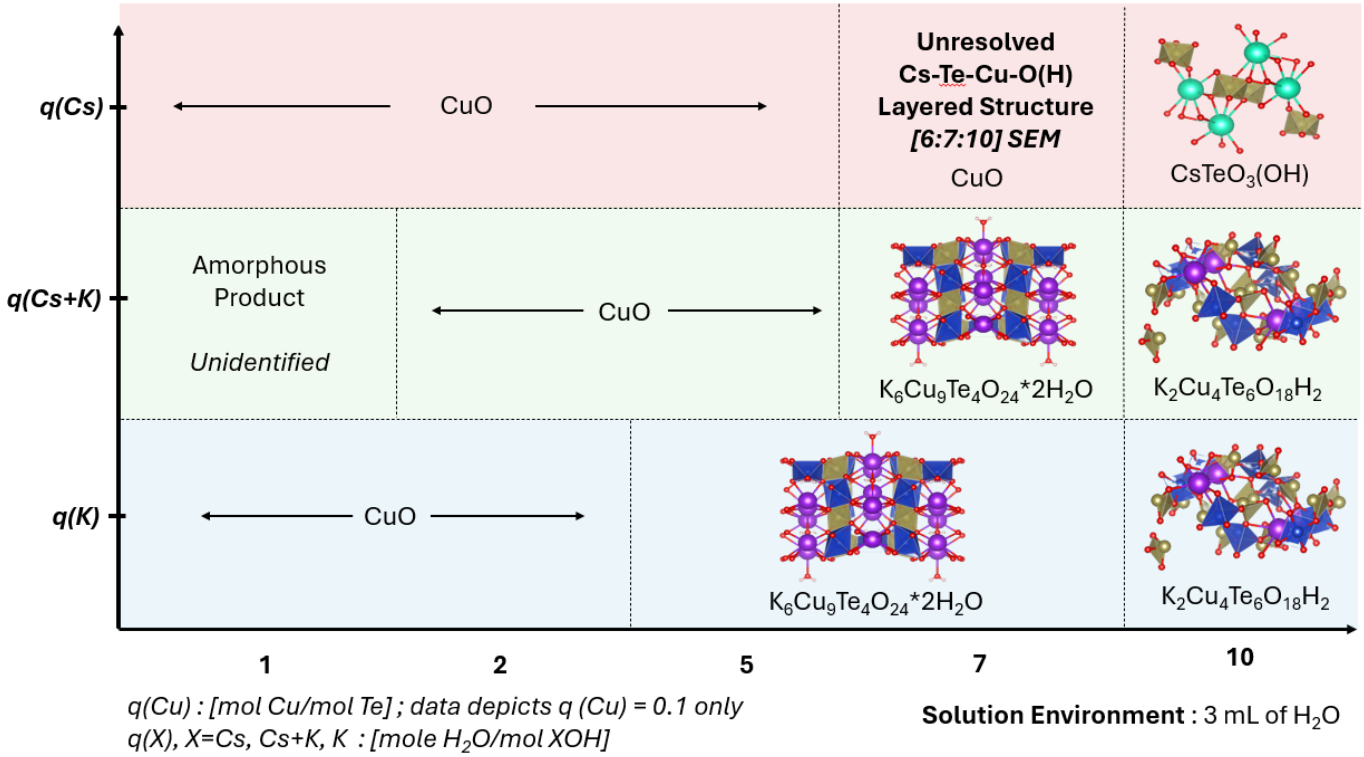

FIG 1: Cs-Te-Cu-O(H), K-Te-Cu-O(H), and 1:1 mixed (Cs+K)-Te-Cu-O(H) phase spaces in the hydroflux environment with no additional oxidizing agents (3 mL H2O).

The purpose of this work was to investigate the dependence of alkali ionic radius and concentration on the hydroflux properties by characterizing the solid products which precipitate out of three AOH-Cu-Te-O(H) phase spaces, where A = K, Cs, and K+Cs. Since flux behavior of wet hydroxides may depend strongly on available O2, O2 present in solution was

varied by testing 0%, 10%, and 30% H2O2 aqueous solutions at a range of hydroflux strengths. We then analyzed each product through a reaction equilibrium involving rational intermediate ions in solution as follows.

Reactions which form Te4+ and Te6+ products likely involve the distinct intermediates [TeO3]2- and [TeO4]2- respectively, with some equilibrium between these two intermediates in each reaction.[cite] To form [TeO4]2- from TeO2 reagent, a redox reaction must occur, so the equilibrium between the two intermediates depends on the concentration of accessible oxidizing species. Since all Cu-containing products contain Cu2+ in square planar or similar coordination, [Cu(OH)4]2- is likely the intermediate Cu ion in solution. Simple formation reactions for these solution intermediates can be seen below in EQ 1 - 3.

$$CuO\ (s) + H2O + 2[OH]- \rightarrow [Cu(OH)4]2-\ (1)$$
$$2TeO2\ (s) + O2 + 4[OH]- \rightarrow 2[TeO4]2- + 2H2O\ (2)$$
$$2TeO2\ (s) + 4[OH]- \rightarrow 2H2O + 2[TeO3]2-\ (3)$$

From these equations, it can be seen that the solvation of CuO requires both constituents of the mixed H2O-[AOH] flux, while TeO2 may be dissolved in the presence of only [AOH], hinting at solubility trends in this system. However, the solubility of CuO in CsOH in this study and in KOH in a previous study vary, suggesting either that these compounds dissociate differently under the reaction conditions, or that a more complicated mechanism of solubilizing CuO occurs, involving the alkali cation.

For all alkali systems in this phase space, the correlation between hydroxide concentration and ratios of Cu and Te in the precipitates suggests that Cu and Te have different solubility trends as a function of hydroxide concentration. At high hydroxide concentration, TeO2 dissolves fully into solution while CuO reagent can be seen as the majority product; no mixed Cu-Te phases are formed in this region. As the hydroxide concentration decreases, products are formed with Cu:Te = 9:4 for the Cs+K and K spaces and 7:10 in the Cs space, suggesting that Cu and Te complexes are interacting in solution. In the most dilute hydroxide concentrations tested, Cu:Te decreases to 9:4 in the Cs+K and K spaces while the Cs space predominantly yields species with exclusively Te or Cu:Te = 1:2 (resulting from a minority phase CuTe2O5). There is an additional correlation between hydroxide concentration, alkali identity, and Te oxidation state in the product. For K-containing systems, intermediate hydroxide concentrations yield Te6+, while the most dilute hydroxide concentrations yield Te4+. However, the Cs system yielded Te6+ even at the most dilute hydroxide concentration, and the mixed system yielded Te6+ at a more dilute hydroxide concentration than the pure K system. There are two possibilities to consider: that there is less Te4+ than Te6+ in solution at higher hydroxide concentration, or alternatively, that the ratios of these intermediates do not change with hydroxide concentration but instead Te4+ becomes less reactive than Te6+ towards the Cu intermediate at higher hydroxide concentration.

K- and Cs-K systems may generate similar results while different from Cs- system for several reasons. First, the large ionic radius of Cs+ (say number and cite shannons ionic radius table) may prevent it from stably incorporating into the lattice like its smaller analogue K+, instead remaining complexes in solution. This may explain a difference between K-containing and non K- containing systems with the same OH- concentration. However, this does not account for the differences within the K and Cs+K phase spaces. This explanation implies that the K ions have more influence on the precipitation reactions within the hydroflux solution and that the Cs ions are likely forming complexes that remain in solution. By itself, this explanation fails to account for the differences between the Cs+K)-Te-Cu-O(H) and K-Te-Cu-O(H). A potential explanation for these dynamics may be caused by the difference in K ion population within the environment as bystander ion concentrations can influence product formation which is further detailed later in results. Additionally, in experiments conducted in open vessels CsOH formed more peroxide and superoxide species than KOH, suggesting a greater oxygen affinity which may actually hinder free O2 mobility and thus oxidation of Cu and Te in our closed vessel syntheses [5]. Further testing should be performed with a variety of mixed hydroxide phase spaces to reach a more definitive conclusion.

Hydroflux Solution Oxidation Dependence

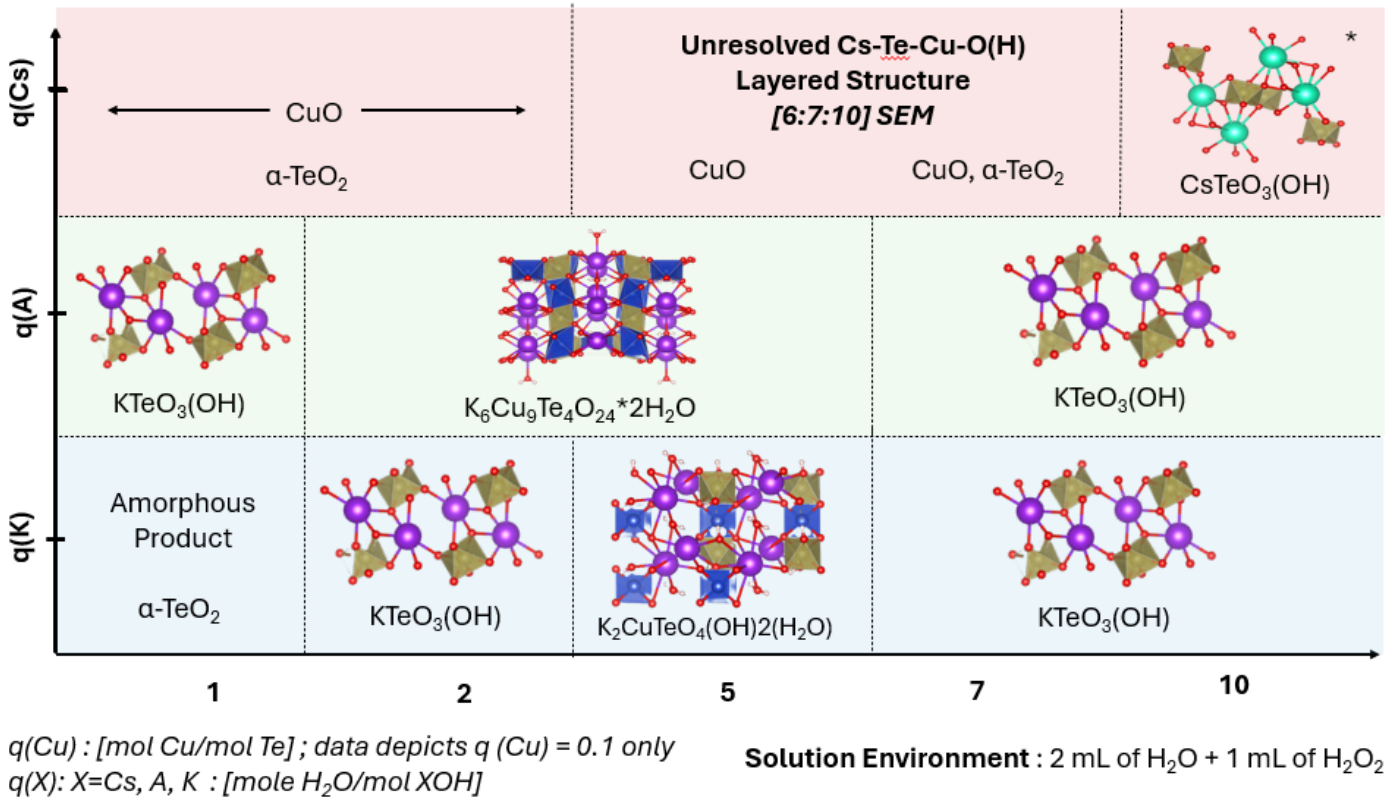

FIG 2: Cs-Te-Cu-O(H), K-Te-Cu-O(H), and 1:1 mixed (Cs+K)-Te-Cu-O(H) phase spaces in the hydroflux environment with no additional oxidizing agents (1 mL and 2 mL H2O).

To investigate the the dynamics of oxidation potential on the hydroflux solution and the products formed within the Cu-Te-O(H) phase spaces, Cs-, K-, and (Cs+K)- phases spaces at q(Cu)= 0.1 were recreated but with the 3 mL H2O environment changed to 2 mL of H2O and 1 mL of H2O2, which can dissociate into H2O and O2 groups and act as an oxidizing agent. The results of which can be seen in FIG 8. The addition of H2O2 had varying effects on the Cs-Te-Cu-O(H), K-Te-Cu-O(H), and 1:1 mixed (Cs+K)-Te-Cu-O(H) phases spaces. The Cs system was minimally affected with primarily differences resulting from the expansion of Layered Cs-Te-Cu into the q(Cs) of 5 region of phase space, the precipitation of alpha-TeO2 throughout the high and mildly hydroxide concentrated regions, and the removal of CuTe2O5 from q(Cs) of 10 region. CuTe2O5 is removed from the H2O and H2O2 phase spaces due to the additional O2 groups reacting to form fully oxidized Te, increasing the population of 2[TeO4]2- and decreasing 2[TeO3]2-. This is also reflected in how all products formed, independent of alkali identity, have Te+6.

The K and Cs+K systems were heavily altered by the presence of H2O2 and seemed to change the phase space entirely, showing that increasing the concentration of lone O2 groups in the hydroflux solution has an immense impact compared to altering the concentration of hydroxide for medium sized alkali. A new product is observed within this region, KTeO3(OH), which follows the same series of reactions (EQ 12 - 15) as its Cs analogue. Both systems showed that KTeO3(OH) renters the phase space, showing that the phase has a boundary at both a high and low concentration of hydroxide which is referred to as reentrance and is indicative of complex competing solubility trends [18][19]. As seen in the H2O only phase space, CuO and TeO2 have inverse stabilities in the hydroflux environment that depends on the

concentration of the hydroxide species and thus the solution's oxidizing potential which heavily implies competing solubility trends which the reentrance of KTeO3(OH) confirms. This also shows that KTeO3(OH) is the dominant product at two extreme regions, which implies that the increased population of [OH]- at highly concentrated hydroxide regions primarily reacts with [TeO4]2- as with the increased population of H2O at low concentrations of hydroxide. In the mildly concentrated region, we instead get intermixing between the Te and Cu intermediates mediated through the near equal population of [OH]- and H2O which appears crucial for the formation of the K products that separate KTeO3(OH) regions.

An additional difference between K and Cs+K space is that, unlike in the H2O only system, the K product formation and its stability depends on the relative amount of K ions in the hydroflux mixture. The Cs+K system was able to produce K6Cu9Te4O24*2H2O with reactions q(Cs + K) of 2 and 5 while the K system created K2CuTeO4(OH)2(H2O) only with the reaction q(K) of 5. The formation of K2CuTeO4(OH)2(H2O) requires more K ions than K6Cu9Te4O24*2H2O as seen in EQ. An additional difference is that the K only system yielded an amorphous product while the Cs+K phase did not, the inverse of what was observed in the H2O only system.

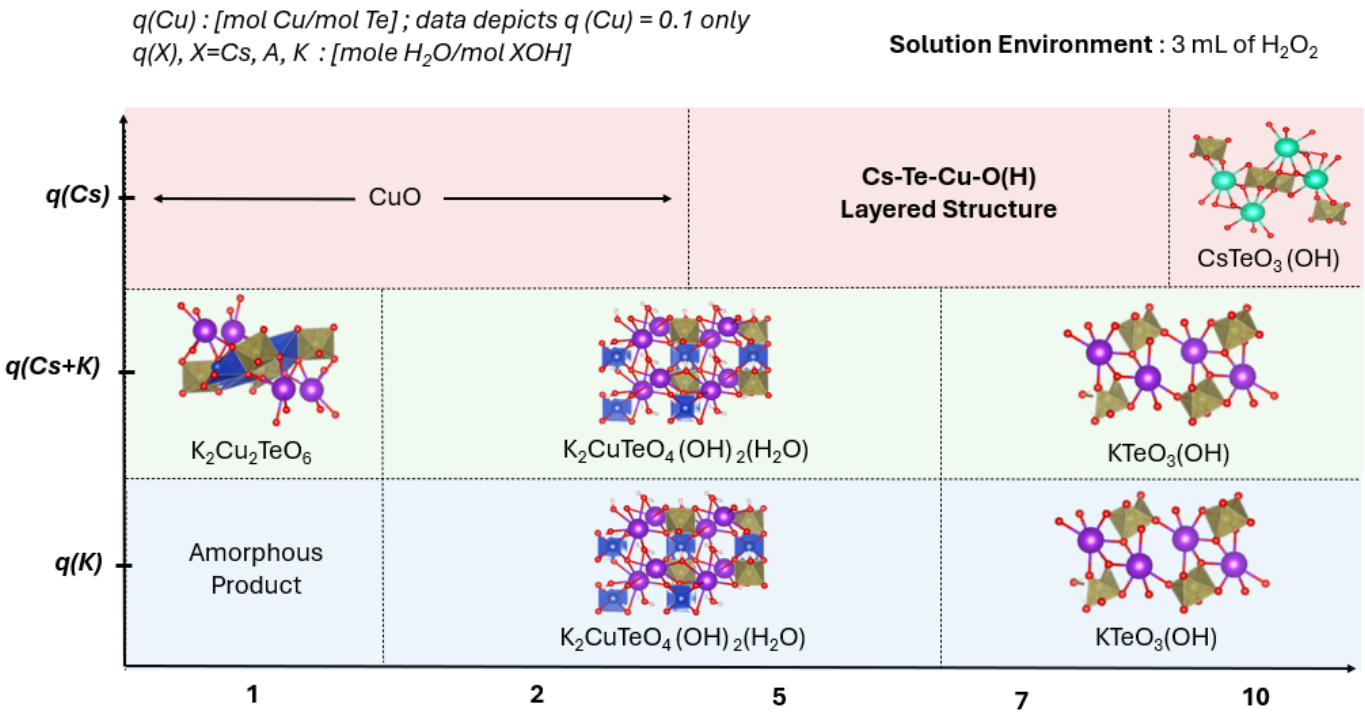

FIG 3: Cs-Te-Cu-O(H), K-Te-Cu-O(H), and 1:1 mixed (Cs+K)-Te-Cu-O(H) phase spaces in the hydroflux environment with no additional oxidizing agents (3 mL H2O2).

In order to further quantify the role of the oxidizing agent in these Cu-Te-O(H) systems and the products they form, the phase spaces were recreated with a liquid regent of 3 mL of H2O2 and no H2O to create a highly oxidizing hydroflux mixture - the results for which is depicted in FIG 9. Again, the Cs-Cu-Te-O(H) system changed minimally from the additional oxidizing agents. The only differences that occurred are that as we move away from the Cu:Te equilibrium is that the formation of alpha-TeO2 ceases, as observed in the H2O only system, while the expansion of Layered Cs-Cu-Te remains. However, the formation of CuTe2O5 does not occur, further confirming that the presence of H2O2 in the hydroflux mixture eliminates the formation of phases with partially oxidized Te in Cu-Te-O(H) systems. K-Cu-Te-O(H) and Cs+K-Cu-Te-O(H) phase spaces are similar, as seen in the H2O and H2O & H2O2 systems. The only major difference between the two is that at the highest hydroxide concentration, q(X) of 1, the product K2Cu2TeO6 is formed in the Cs+K system and a slightly crystalline but mostly amorphous product is formed in the K system. The products found

within the mild and dilute hydroxide concentrations are the same in the two systems, K2CuTeO4(OH)2(H2O) and KTeO3(OH) respectively. K2Cu2TeO6 can be formed using the intermediates [Cu(OH)4]2- and 2[TeO4]2-.

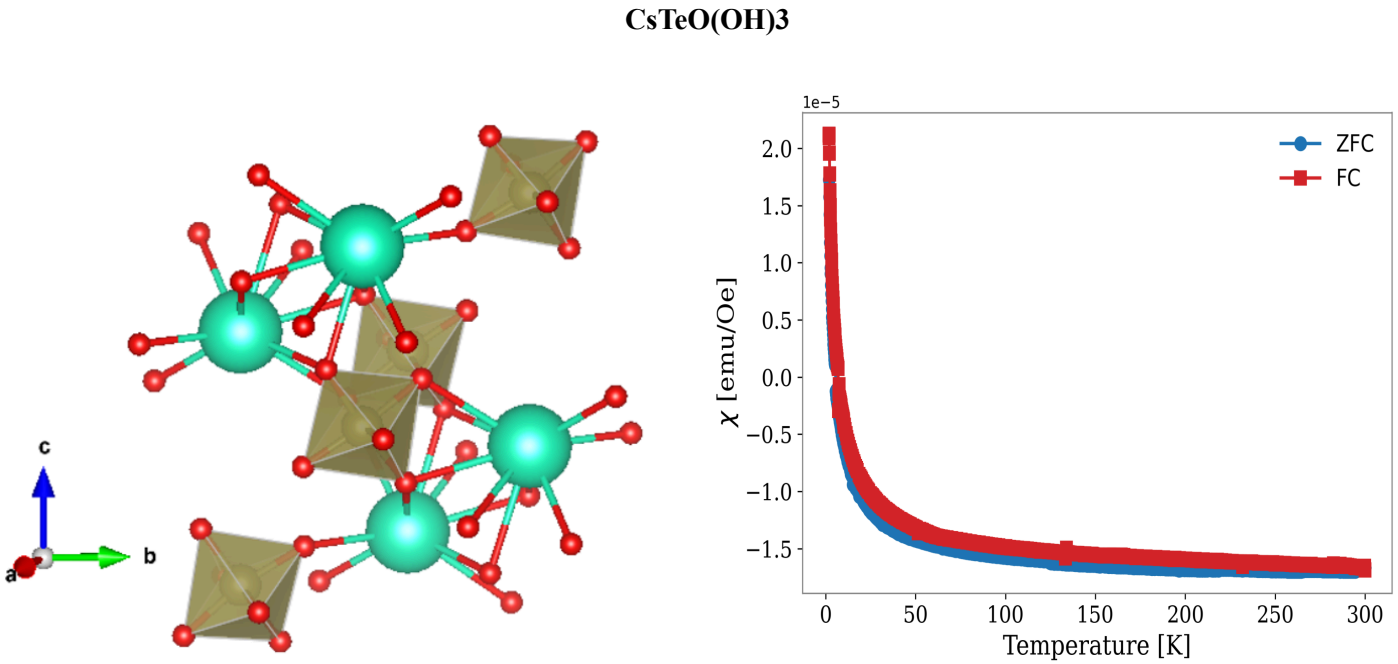

FIG 4: (a) Structure of CsTeO3(OH). Outermost TeO6 octahedra are edge sharing and connect to Cs atoms while the innermost connect to each other. (b) Magnetic susceptibility of CsTeO3(OH) measured using ZFC and FC protocols with an external field of H =10000 Oe showing a strong paramagnetic response with insignificant field splitting.

CsTeO3(OH) was produced in several reactions, from lowest to highest yield, q(Cs) 0f 10 with 3 mL of H2O, 2 mL of H2O with 1 mL of H2O2, and 3 mL of H2O2. Additionally, CsTeO3(OH) was produced using q(Cs) of 7 in the 2 mL of H2O and 1 mL of H2O2 phase space but as a minority phase. CsTeO3(OH) formed small, needle-like crystals that were grown either independently or in ball-like clusters. All products of the reactions were mixed-phase, however as the reaction environment became more oxidizing the products became increasingly more pure phase and the yield of CsTeO3(OH) increased. For more information regarding what phases were co-produced with CsTeO3(OH), please refer to SI. A phase with the same stoichiometry was briefly mentioned in [1] but no structural information was included. Here, we present the synthesis, structure, and magnetic properties of this phase. CsTeO3(OH) has two distinct Cs coordinations with minimal structural differences. In both environments, the Cs atoms are coordinated to 9 O atoms. As expected from the large ionic radius of Cs, the overall unit cell volume and alkali-oxygen coordination both are increased relative to other alkali analogues of this phase [2-4]. CsTeO3(OH) crystallizes in the space group P -1, in contrast to the P21/c space group observed in KTeO3(OH) and NaTeO3(OH). On the opposite extreme of the alkali column, LiTeO3(OH) has a space group of P21 which shows that CsTeO3(OH) has the lowest symmetry of the alkali tellurites. This lower symmetry is reflected in its unit cell parameters, where CsTeO3(OH) displays 89°-89°-X angles, diverging from the 90°-90°-X angles seen in other ATeO3(OH) structures [A=Li, Na, K]. CsTeO3(OH) also has two distinct TeO6 coordination environments that generate distorted octahedra. One TeO6 site is edge-sharing while the other is not and heavily deviates from the ideal 90-90 O-Te-O structure.

The fully oxidized states of Te and Cs lead to a lack of strong magnetic ordering due to an absence of lone spins. The only expected magnetic ordering was from weak responses from paired spins in closed orbitals, generating diamagnetic interactions. Despite this, paramagnetic responses were recorded from isolated lone spins as seen in both ZFC and FC χ vs

T measurements in FIG 4. The source of these interactions are either impurities created from generating multiple phases within the reaction's products, such as CuTeO5, or broken bonds within a small population of CsTeO3(OH) crystals. The expected diamagnetic response was confirmed in isothermal magnetization measurements, also in FIG 2, where at low temperatures the magnetic moments within CsTeO3(OH) generate diamagnetic ordering with the applied magnetic field, but paramagnetic interactions at higher temperatures. This also confirms that, despite being a minority phase, the ordering of the impurities is stronger than that of CsTeO3(OH) and that the material is weakly magnetic.

K2Cu4Te6O18H2

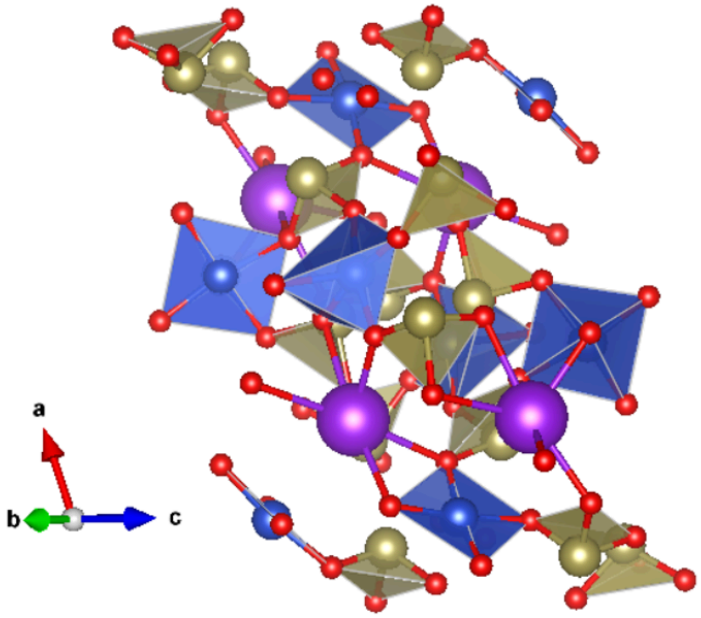

FIG 5: Crystal structure of K2Cu4Te6O18H2 (left). CuO4 square planar plaquettes and CuO5 square pyramids are linked by Te4+ in a distorted coordination due to its lone pair.

K2Cu4Te6018H2, FIG 3, was generated as the majority phase at q(K) = 10, H2O only, and q(Cs+K) = 10, H2O only. Unlike other new phases identified in this work, this reaction product was phase pure and has no other alkali analogues. The three distinct Te 4+ sites all exhibit the lone pair effect; the lone pairs tend to point towards interstitial sites but bond lengths and angles vary. There are two Cu2+ sites, with square planar CuO4 plaquettes or CuO5 square pyramids.

Due to the complexity of the Te and Cu coordination environments, magnetic pathways are difficult to fully determine and require DFT modeling or neutron diffraction studies [6-8]. However, ZFC & FC χ vs T and MvH measurements can be used to determine what magnetic ordering and transitions are occurring and their relative strength. As depicted in FIG 4, three magnetic transitions are present, one sharp antiferromagnetic transition at 7 K, where the ZFC/FC splitting is largest, and two possible short range correlations at ~22 and ~70 K. Isothermal magnetization data depicts possible metamagnetic transitions at ~2T at 2K and 10K.

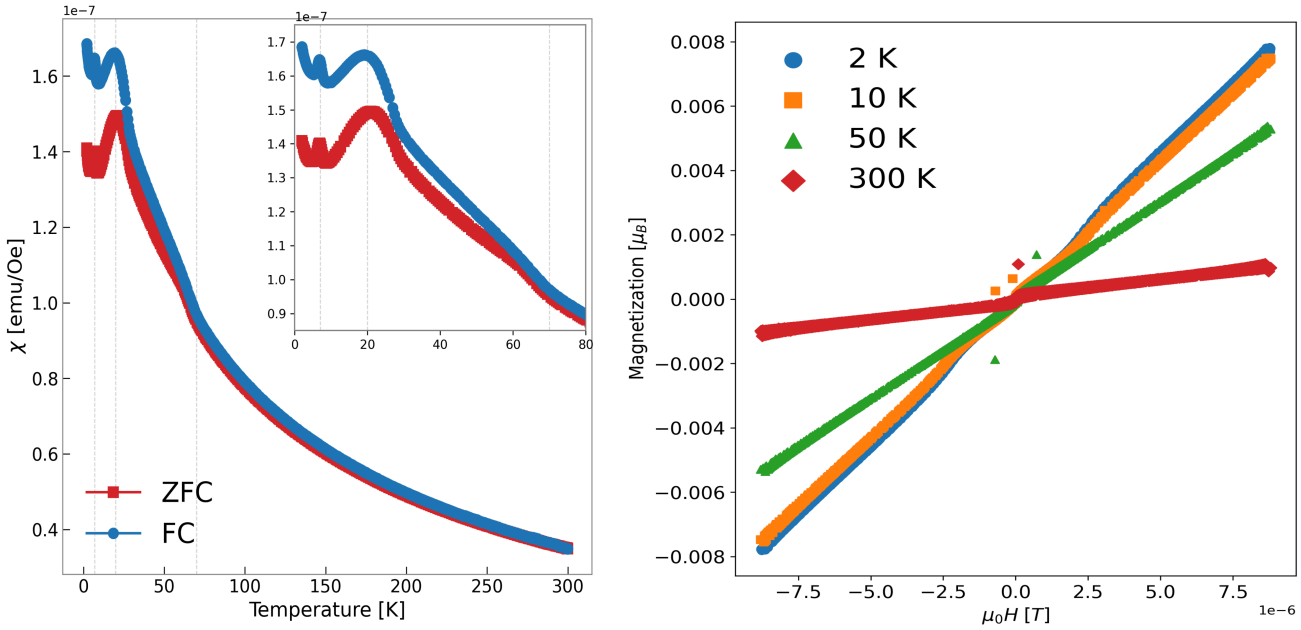

FIG 6: (a) Magnetic susceptibility of K2Cu4Te6O18H2 measured under ZFC and FC conditions with an external field of H = 10000 Oe. Three transitions can be seen: two short range antiferromagnetic correlations at T = ~70 K and T= ~20 K, and an antiferromagnetic transition at T= ~7 K. (b) Isothermal magnetization of K2Cu4Te6O18H2 measured at T = 2, 10, 150 and 300 K in the range of μ0H = ± 7 T applied external field. The T = 2K and 10K curves show possible metamagnetic transitions at ~2T. Outlier points at low fields are due to instrumental noise.

III. Experimental Methods

Samples were synthesized via hydroflux reactions as follows: powder reagents CuO (Thermo Scientific, 99.995%) and TeO2 (Acros Organics, 99+%) were combined in the ratio 1:10 with a total quantity of 11mmol. Alkali hydroxides KOH*H2O (Fisher Chemical 86.6%) and CsOH*H2O (SIGMA-ALDRICH 90.0%) were combined with DI H2O and/or H2O2 (Fisher Chemical 30%) to achieve molar ratios defined as q(K) = (moles H2O)/(moles KOH) = 1, 2, 5, 7, 10, q(Cs) = (moles H2O)/(moles CsOH) = 1, 2, 5, 7, 10, and, with equimolar KOH and CsOH, q(Cs+K) = (moles H2O)/(moles KOH + CsOH) = 1, 2, 5, 7, 10. q(K), q(Cs), and q(Cs+K) were calculated assuming anhydrous alkali hydroxide for simplicity. H2O2 concentration in aqueous solution was varied at 0%, 10%, and 30% for all systems studied. Reagents were loaded into a 22 mL capacity teflon-lined autoclave with H2O2 added last and dropwise to minimize sudden O2 gas formation. The autoclaves were heated at 200 ◦C for 2 days in a low temperature oven and quenched to room temperature. Samples were rinsed with DI H2O and filtered using a vacuum funnel. Single crystal X-ray diffraction (SCXRD) measurements were performed using a SuperNova diffractometer (equipped with Atlas detector) with Mo Kα radiation (λ = 0.71073 ˚A) under the program CrysAlisPro (Version 1.171.42.49, Rigaku OD, 2020 - 2022). The same program was used to refine the cell dimensions and for data reduction. All reflection intensities were measured at T = 213(2) K. The structure was solved with the program SHELXS-2018/3 and was refined on F 2 with SHELXL-2018/3.[13] Analytical numeric absorption corrections using a multifaceted 3 crystal model were performed using CrysAlisPro. The temperature of the data collection was controlled using the Cryojet system (Oxford Instruments).

Phase purity was determined using powder X-ray diffraction (pXRD) on a Bruker D8 Focus diffractometer equipped with a LynxEye detector using Cu Kα radiation (λ = 1.5406 ˚A). Data was collected in the range 2θ = 5-120◦ with a step size of

0.01715◦ and a step time of 2 seconds. pXRD Rietveld refinements were performed using Topas5 using the refined single crystal structure as the starting point refinement for each compound. Subsequently, only lattice parameters, peak shape, and instrumental zero error were refined and changed from the single crystal solution. Temperature-dependent magnetic susceptibility data was collected on a Quantum Design Magnetic Property Measurement System (MPMS3) from T = 2 - 300 K under an applied field of H = 1000 Oe or μ0H = 1 T with and without field cooling. Isothermal magnetization measurements were collected at various temperatures with a field range of ±7 T. All magnetic data were collected on powderized samples. All crystal structure visualizations were done using VESTA.

IV. Conclusions

The results of these studies include the synthesis and magnetic characterization of three novel phases: CsTeO3(OH), K2Cu4Te6O18H2, and a Cs-Cu-Te-O layered structure. These products were formed throughout multiple areas within phase space with varying crystal morphologies which is further explained in Results. This study also found that Cs ions in hydroflux reaction environments, independent of solution oxidation, are not likely to incorporate into solid structure and instead remain within solution compared to K ions. This was seen in the lack of variety in product formation for the Cs system and due to K-Te-Cu-O(H) and Cs+K-Te-Cu-O(H) phase spaces producing similar products, implying that the influence of Cs ions was little. Studies generating partitioned, layered materials with 2D magnetism in K-Te-Cu-O(H) show little trend with the Cs- system which only generated one layered structure with weak magnetic ordering. Lastly, this study found evidence supporting that inverse Cu and Te trends exist within these Alkali-Cu-Te-O(H) phase spaces, facilitated through the intermediate products 2[TeO3]2-, 2[TeO4]2-, and [Cu(OH)4]2-. Together, exploratory synthesis and in-solution ration dynamics elucidated Cu-Te solubility trends not previously reported and allowed for the systematic study of the alkali identity within hydroxide and the effect of additional oxidizers on the hydroflux environment while revealing three new phases.

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