Flux-Mediated Syntheses, Structural Characterization and Low-Temperature Polymorphism of the *p*-Type Semiconductor Cu₂Ta₄O₁₁

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ABSTRACT

A new low-temperature polymorph of the copper(I)-tantalate, α -Cu₂Ta₄O₁₁, has been synthesized in a molten CuCl-flux reaction at 665 °C for 1 h and characterized by powder X-ray diffraction Rietveld refinements (space group *Cc* (#9), $a = 10.734(1)$ Å, $b = 6.2506(3)$ Å, $c = 12.887(1)$ Å, $\beta = 106.070(4)^\circ$). The α -Cu₂Ta₄O₁₁ phase is a lower-symmetry monoclinic polymorph of the rhombohedral Cu₂Ta₄O₁₁ structure (i.e., β -Cu₂Ta₄O₁₁ space group $R\bar{3}c$ (#167), $a = 6.2190(2)$ Å, $c = 37.107(1)$ Å), and related crystallographically by $a_{\text{hex}} = a_{\text{mono}}/\sqrt{3}$, $b_{\text{hex}} = b_{\text{mono}}$, and $c_{\text{hex}} = 3c_{\text{mono}}\sin\beta_{\text{mono}}$. Its structure is similar to the rhombohedral β -Cu₂Ta₄O₁₁ and is composed of single layers of highly-distorted and edge-shared TaO₇ and TaO₆ polyhedra alternating with layers of nearly linearly-coordinated Cu(I) cations and isolated TaO₆ octahedra. Temperature dependent powder X-ray diffraction data show the α -Cu₂Ta₄O₁₁ phase is relatively stable under vacuum at 223 K and 298 K, but reversibly transforms to β -Cu₂Ta₄O₁₁ by at least 523 K and higher temperatures. The symmetry-lowering distortions from β -Cu₂Ta₄O₁₁ to α -Cu₂Ta₄O₁₁ arise from the out-of-center displacements of the Ta $5d^0$ cations in the TaO₇ pentagonal bipyramids. The UV-Vis diffuse reflectance spectrum of the monoclinic α -Cu₂Ta₄O₁₁ shows an indirect bandgap transition of ~2.6 eV, with the higher-energy direct

transitions starting at ~2.7 eV. Photoelectrochemical measurements on polycrystalline films of α -Cu₂Ta₄O₁₁ show strong cathodic photocurrents of ~1.5 mA/cm² under AM 1.5G solar irradiation.

Keywords: Flux synthesis; semiconductor; copper(I) tantalate

INTRODUCTION

The synthetic preparation of complex metal-oxide semiconductors is a shared and timely challenge within a number of different chemical systems [1-5]. Towards this broad objective, a diverse set of synthetic techniques has been utilized, such as hydrothermal methods, solid-state methods, and molten-salt synthetic methods [6-10]. The flux synthesis method is a versatile and advantageous technique for the modification of chemical composition, structure, and particle morphologies and sizes, as highlighted in recent reviews [7, 11]. Reactions within molten-salt fluxes have been shown to yield faster reaction rates at relatively lower temperatures, highly-faceted particles with more homogeneous particle distributions, and decreased activation barriers for the growth of solid-state compounds with limited thermal stability [12-14]. Changes in chemical composition and single-crystal particle morphologies of metal-oxides have been found to impact their physical properties, including their optical, electronic and photocatalytic properties. For example, the Na₂Ta₄O₁₁, AgNbO₃ and PbTiO₃ phases can be prepared in shortened reaction times of down to ~1 hr [9,15,16], resulting in highly-faceted particles that exhibit significantly enhanced photocatalytic rates. In related examples, both Cu₂Nb₈O₂₁ and PbTa₄O₁₁ show limited thermal stability [17,18], but can be prepared in high purity at lower temperatures using flux synthesis methods.

In order to target the discovery of new *p*-type metal-oxide semiconductors, the Maggard research group has investigated new high-purity syntheses within several Cu(I)-M(V) (M = V, Nb, Ta) oxide systems using both solid state and molten-salt flux methods, such as for Cu₃VO₄ [19], CuNb₃O₈ [20], Cu₂Nb₈O₂₁ [17], Cu₃Ta₇O₁₉ [21], and β-Cu₂Ta₄O₁₁ [22,23]. The use of a CuCl molten salt (melting point ~426 °C) within these systems significantly shortens their reaction times down to ~15-30 min, with nanoparticle reactants rapidly growing to micron-sized single-crystal particles, e.g., as reported for Cu₂Nb₈O₂₁, CuNb₃O₈ and β-Cu₂Ta₄O₁₁. When these phases are heated in the absence of the CuCl flux they are highly susceptible to oxidation or disproportionation of the Cu(I) cations at their surfaces in air or under vacuum, respectively, resulting in the formation of Cu(s) and/or Cu(II)-containing oxides. Thus, the flux reactions within CuCl are critical to overcoming their limited thermal stability and in preparing high-purity products. Conversely, the formation of small amounts of CuO nanoparticles on their surfaces, i.e., by heating them to low temperatures in air, yields Cu-deficient polycrystalline films with relatively high cathodic photocurrents (~1 to 2 mA/cm²) when irradiated by visible light. Recent examples include Cu_{1-x}Nb₃O₈, Cu_{5-x}Ta₁₁O₃₀, and Cu_{3-x}VO₄, wherein the CuO surface nanoparticles have been shown to form a charge rectification barrier that helps to drive charge separation of the electron-hole pairs [19,20,24]. Flux synthesis of these phases as highly-faceted single-crystal particles has been critical for elucidating the role of the surface CuO nanoparticles.

The Cu₂Ta₄O₁₁ phase was first discovered in very small quantities in a high-resolution electron microscopy investigation of the solid-state products in the Cu₂O-Ta₂O₅ system in the temperature range of 700 °C to 1100 °C [25,26]. More recently, the Cu₂Ta₄O₁₁ phase was prepared in high purity with the use of a CuCl flux and a reaction temperature between 625 °C to

700 °C [23]. Its structure has been previously reported to be a member of a family of polysomatic structures with the general composition $A^{m+}_{(n+1)/m}M_{3n+1}O_{(8n+3)}$ (e.g., A = Ag, Na, Cu, Pb, Bi; M = Ta, Nb), that contains single ($n = 1$), double ($n = 2$), or a combination ($1 < n < 2$) of layers of MO_7 polyhedra that alternate with a layer of isolated MO_6 polyhedra [27-29]. Interestingly, the $Cu_2Ta_4O_{11}$ phase was found to undergo a phase transition to a lower-symmetry structure (previously unknown) when stored at room temperature in air for several weeks [23]. Described herein is the flux synthesis and structural characterization of this low-temperature monoclinic polymorph of $Cu_2Ta_4O_{11}$, and measurements of its thermal stability, and optical and photoelectrochemical properties in the form of polycrystalline films.

EXPERIMENTAL

A. Materials and Synthesis. The nanoparticle Cu_2O and Ta_2O_5 reactants were prepared according to previously reported procedures [30,31]. The $CuCl$ (Alfa Aesar, 99.999%) reagent was used as received. Reactions targeting the monoclinic α - $Cu_2Ta_4O_{11}$ phase were performed by combining Cu_2O and Ta_2O_5 nanoparticles in a 2:1 molar ratio, respectively, and mixed with a $CuCl$ flux in a 10:1 flux-to-reactant molar ratio. The reactants and flux were well-ground together inside a nitrogen-filled glovebox, sealed within an evacuated fused-silica tube, and heated at 665 °C for 1 h. The reaction vessel was then quenched in air immediately upon completion of the heating cycle. The products were repeatedly washed with concentrated ammonium hydroxide and deionized water in order to remove the $CuCl$ flux. Minor impurities of starting reagent Ta_2O_5 (≤ 5 %) were sometimes observed in the powder X-ray diffraction patterns of the obtained product.

B. Bulk Characterization Techniques. Temperature-dependent powder X-ray diffraction data were collected at 223K, 298K, 523K, 623K, and 723K on a Bruker D8 Advanced powder diffractometer configured in Bragg Brentano geometry with a LYNXEYE XE detector using Cu K α radiation ($\lambda = 1.54056 \text{ \AA}$). The temperature was controlled via an MTC temperature stage with a precision of $\sim 3 \text{ K}$. Data were collected in a 2θ range of $10\text{-}80^\circ$ in 0.01 steps with a dwell time of 4 s at each step. A small amount of Ta $_2$ O $_5$ impurity was masked in the region from $\sim 25.9^\circ$ to $\sim 27.6^\circ$, as indicated by the purple lines in the refinement profile in Figure 1. The refinements were performed within the GSAS-II software package [32] using the following strategy. The scale factor, background (Chebyshev function with 4 terms), sample displacement and transparency, and unit cell were independently refined. The starting atomic models for the Rietveld refinements of the Cu $_2$ Ta $_4$ O $_{11}$ phase were obtained from single crystal data on a Bruker-Nonius X8 Apex2 diffractometer within both monoclinic and hexagonal crystal systems. Refinements were attempted within the $R\bar{3}c$, $R3c$, $R3$, $C2/c$ and Cc space groups starting from the atomic positions as known within the layered $A^{m+}_{(n+1)/m}B_{(3n+1)}O_{(8n+3)}$ family, such as previously reported for Ag $_2$ Nb $_4$ O $_{11}$ and Na $_2$ Nb $_4$ O $_{11}$ [33-35]. Ultimately, the noncentrosymmetric structural model with space group Cc (No. 9) gave the statistically best goodness-of-fit ($\chi^2 = 2.5$) and R-values ($wR = 0.096$, $wR_{\text{exp}} = 0.0545$). The atomic positions were refined in order of decreasing scattering length, followed by the refinement of isotropic temperature factors (U_{iso}). The U_{iso} values were fixed for O atoms, and the peak shape profiles (Gaussian and Lorentzian terms) were refined. The occupancy factors of the Cu-sites were independently refined and found to not show a statistically significant deviation from the ideal $\sim 66.7\%$ occupancy for the charge-balanced chemical composition of Cu $_2$ Ta $_4$ O $_{11}$. Subsequently, the occupancy factors were fixed at 66.7% . Lattice constant refinements were performed on the powder X-ray diffraction

data in the monoclinic unit cell at 223 K and 298 K, and in the hexagonal unit cell appropriate for the β -Cu₂Ta₄O₁₁ structure at temperatures from 523 K to 723 K [23]. Selected data collection and refinement parameters for the monoclinic α -Cu₂Ta₄O₁₁ at 298 K are listed in Table 1. Nearest-neighbor interatomic distances are given in Table 2. Results of the lattice constants refinements as well as a more complete listing of the refined structural and atomic parameters are included in the Supplementary Material (Tables S1 and S2).

UV-Vis diffuse reflectance spectra of α -Cu₂Ta₄O₁₁ were collected on a Shimadzu UV-Vis-NIR Spectrophotometer (UV-3600) equipped with an integrating sphere. A pressed tablet of barium sulfate was used as the reference. The data were plotted as the remission function $F(R_\infty) = (1-R_\infty)^2/(2R_\infty)$, where R is the diffuse reflectance based on the Kubelka-Munk theory [36,37]. The reflectance data were analyzed in the form of Tauc plots as $[F(R) \times h\nu]^n$ versus $h\nu$, where $n = 2$ for direct allowed transitions and $n = 1/2$ for indirect allowed transitions [38,39]. The optical bandgap sizes were estimated from the onset of absorption, as extrapolated from the linear section of the curve that intersects with the baseline.

C. Photoelectrochemical Measurements. Polycrystalline films of α -Cu₂Ta₄O₁₁ were prepared on TEC-15 fluorine-doped tin oxide (FTO) slides (Hartford Glass Inc.). First, FTO slides are sonicated in de-ionized water, followed by ethanol and acetone for 30 min each, and then dried in air in an oven set at 80 °C. A ~1 cm² area was taped off using Scotch tape on the conducting side of the FTO slide, and a slurry of Cu₂Ta₄O₁₁ in a water/tert-butanol solution was deposited using the doctor blade method. Each film was annealed under dynamic vacuum ($P < 50$ mTorr) at 500 °C for 3 h to sinter the particles together and to the FTO slide. After sintering, the films were heated in air to temperatures of 250 °C or 350 °C for 3 h each. The linear sweep

voltammetry (LSV) measurements were taken on a CH-Instruments CH620a potentiostat under chopped AM 1.5 G irradiation at $\sim 100 \text{ mW/cm}^2$ (Oriel) using a scan rate of $0.0250 \text{ V}\cdot\text{s}^{-1}$. Chronoamperometric measurements were taken in the short-circuit condition (applied bias of $V = 0$) for 1,000 s each. The polycrystalline films served as the working electrodes, Pt foil as the counter electrode and an SCE (sat. KCl) electrode served as the reference electrode during the measurements. Each photoelectrochemical measurement was performed in a 0.5 M Na_2SO_4 aqueous solution that had been adjusted to a pH = 6.5 using dilute aqueous H_2SO_4 . This solution was purged with N_2 gas for 30 min both prior to and continuously during the photoelectrochemical measurements in order to remove any dissolved O_2 in the electrolyte solution.

D. Electronic Structure Calculations. Electronic structure calculations were performed on the geometry-optimized $\alpha\text{-Cu}_2\text{Ta}_4\text{O}_{11}$ monoclinic crystal structure using plane-wave density functional theory (DFT) within the *Vienna Ab initio Simulation Package* (VASP; ver. 4.6) [40-43]. The band-structure diagram and the densities-of-states calculations were performed using the Perdew-Burke-Ernzerhof functional in the generalized gradient approximation, using the projector augmented wave method. Automatic sampling of the Brillouin-zone was performed using a $2 \times 2 \times 1$ Monkhorst-Pack grid [44]. The Cu deficiencies were modeled as a random distribution of vacancies throughout the unit cell. The band structure calculation followed the standard k -path of special k -points through the Brillouin group for a monoclinic unit cell [45].

RESULTS AND DISCUSSION

A. Synthesis and Structural Characterization. High-surface-area Cu_2O and Ta_2O_5 nanoparticle reactants are required for the flux synthesis of both polymorphs of the $\text{Cu}_2\text{Ta}_4\text{O}_{11}$

phase. The rhombohedral structure of $\text{Cu}_2\text{Ta}_4\text{O}_{11}$, hereafter referred to as $\beta\text{-Cu}_2\text{Ta}_4\text{O}_{11}$, was previously reported to be formed in reactions between 625 °C to 700 °C [23]. However, experimental evidence of a second lower-symmetry polymorph was found in the splitting of several of its powder X-ray diffraction (PXRD) peaks (e.g., (113), (116), and (119)) after storage in air at room temperature for several weeks. This phase is hereafter referred to as $\alpha\text{-Cu}_2\text{Ta}_4\text{O}_{11}$. The present results show that this lower-symmetry polymorph can be directly synthesized in high purity by reaction of the nanoparticle reagents in a 2:1 ($\text{Cu}_2\text{O}:\text{Ta}_2\text{O}_5$) molar ratio at 665 °C for 1 h in a molten CuCl flux, followed by immediate quenching in air. With the use of commercial bulk-scale reagents, i.e., without nanoparticle reactants, a significantly higher amount of unreacted Ta_2O_5 (~20%) is found together with $\alpha\text{-Cu}_2\text{Ta}_4\text{O}_{11}$. Further reaction of $\alpha\text{-Cu}_2\text{Ta}_4\text{O}_{11}$ with excess Cu_2O in a CuCl flux at 665 °C for an additional 1 h results in its complete conversion to the $\beta\text{-Cu}_2\text{Ta}_4\text{O}_{11}$ phase.

The structure of $\alpha\text{-Cu}_2\text{Ta}_4\text{O}_{11}$ was determined by Rietveld refinements on powder X-ray diffraction data collected at 223 K and 298 K. Both refinements yielded similar monoclinic structures, with the results plotted in Figure 1 for the data collected at 298 K. As shown in Figure 2, the structure consists of single layers of distorted, edge-shared TaO_7 polyhedra that are bridged via their apical oxygen atoms to interlayer, octahedrally-coordinated Ta and linearly-coordinated Cu atoms. This is generally similar to the structure as found for the rhombohedral $\beta\text{-Cu}_2\text{Ta}_4\text{O}_{11}$ phase, with a tripling of the *c*-axis dimension and a re-orientation of the TaO_7 layers in the *ab* plane within both structures. The monoclinic $\alpha\text{-Cu}_2\text{Ta}_4\text{O}_{11}$ structure consists of three symmetry-unique Ta sites (Ta1, Ta2, Ta3) with nearest neighbor interatomic Ta – O distances in the range of 1.92(8) Å to 2.45(8) Å, generally consistent with the bond distances observed for the rhombohedral $\beta\text{-Cu}_2\text{Ta}_4\text{O}_{11}$, as shown in Figure 3. However, the monoclinic $\alpha\text{-Cu}_2\text{Ta}_4\text{O}_{11}$

structure results in three symmetrically-inequivalent Cu-sites in the unit cell (Cu1, Cu2, Cu3) with interatomic Cu – O distances in the range of 1.71(8) Å to 2.01(9) Å. The TaO₆ octahedra are formed by the apical oxygen atoms of the TaO₇ pentagonal bipyramids, with Ta – O distances of 1.92(7) Å to 2.20(4) Å. A structural view of the layer of isolated TaO₆ octahedra bridged to the linearly-coordinated Cu(I) cations is provided in the Supplementary Material, Figure S3.

The Cu₂Ta₄O₁₁ structure is an $n = 1$ member of the family of previously reported Cu(I)-tantalates that are constructed from α -U₃O₈ type layers. These structures contain single ($n = 1$), double ($n = 2$), or a combination ($1 < n < 2$) of layers of edge-shared TaO₇ pentagonal bipyramids that alternate with layers of isolated TaO₆ octahedra surrounded by the A-site cations. The occupancy of the Cu-site is 66.7% for the rhombohedral β -Cu₂Ta₄O₁₁, in order to satisfy the charge-balancing requirements. Full occupation of this site would result in the non-charge-balanced Cu₃Ta₄O₁₁ composition. Higher Cu-site occupancies are found in the related copper(I)-tantalate structures of Cu₅Ta₁₁O₃₀ (83%; $n = 1.5$) and Cu₃Ta₇O₁₉ (100%; $n = 2$). The symmetry-lowering distortion of the rhombohedral β -Cu₂Ta₄O₁₁ to the monoclinic α -Cu₂Ta₄O₁₁ has not previously been observed in these related copper(I)-tantalate structures. However, similar symmetry-lowering distortions have been found for Na₂Nb₄O₁₁ and Ag₂Nb₄O₁₁ ($n=1$) [33-35], as described below.

B. Symmetry-Lowering Distortions in the A₂M₄O₁₁ Phases. The relationship of the structural transformation between the monoclinic and hexagonal-rhombohedral unit cells has been reported previously [33], as illustrated in Figure S4 in the Supplementary Material. The layered niobates Ag₂Nb₄O₁₁ and Na₂Nb₄O₁₁ are the only previously reported structures to exhibit a phase transition within this family of related structures [33-35]. Generally, it has been noted

that niobates, as compared to tantalates, more commonly exhibit symmetry-lowering phase transitions owing to the differences in their atomic sizes and interatomic distances. For example, the c lattice parameter, unit cell volume, and Ta-O interatomic distances of $\text{Ag}_2\text{Ta}_4\text{O}_{11}$ are relatively shorter in comparison to $\text{Ag}_2\text{Nb}_4\text{O}_{11}$. The $\text{Ag}_2\text{Nb}_4\text{O}_{11}$ phase displays a polar phase transition between the rhombohedral space groups $R\bar{3}c$ and $R3c$ upon cooling at temperatures below $\sim 127^\circ\text{C}$. The driving force for the symmetry-lowering polar distortion observed in $\text{Ag}_2\text{Nb}_4\text{O}_{11}$ can be attributed to atomic displacements of the Nb cations in the NbO_7 pentagonal bipyramids towards the apical O atoms, and the displacement of Ag cations in the AgO_6 octahedra toward their octahedral faces along the c -axis direction. By comparison, $\text{Na}_2\text{Nb}_4\text{O}_{11}$ exhibits a centrosymmetric distortion from the $R\bar{3}c$ to the $C2/c$ space group upon cooling below $\sim 107^\circ\text{C}$. The latter compound has smaller unit-cell dimensions and shorter Na-O1 interatomic distances, i.e., $\sim 2.51\text{ \AA}$ within a NaO_7 polyhedron, versus the Ag-O distances in $\text{Ag}_2\text{Nb}_4\text{O}_{11}$ of $\sim 2.65\text{ \AA}$. A comparison of the c lattice parameter, unit cell volumes and Nb/Ta-O interatomic distances of the rhombohedral structures of $\text{Na}_2\text{Nb}_4\text{O}_{11}$, $\text{Ag}_2\text{Nb}_4\text{O}_{11}$, $\text{Ag}_2\text{Ta}_4\text{O}_{11}$, and $\text{Cu}_2\text{Ta}_4\text{O}_{11}$ show striking similarities. In $\text{Cu}_2\text{Ta}_4\text{O}_{11}$, the Cu(I) cations adopt a nearly linear coordination with significantly shorter Cu-O interatomic distances i.e., $1.71(8)\text{ \AA}$ to $2.01(9)\text{ \AA}$. The rhombohedral $\beta\text{-Cu}_2\text{Ta}_4\text{O}_{11}$ structure displays an out-of-center displacement of the Ta $5d^0$ cation in the edge-shared TaO_7 pentagonal bipyramid layer, as illustrated in Figure 4.

Symmetry-lowering transitions driven by d^0 cations in an octahedral coordination are known to occur as a result of a second-order Jahn-Teller effects [46]. The driving force for a second-order Jahn-Teller distortion is expected to increase as the energy separation between the metal-based t_{2g} d -orbitals and the non-bonding O $2p$ states decrease [47]. The second order Jahn-Teller distortions have typically been reported and observed for octahedral d^0 cations with

high valency, with the magnitude of the distortion increasing in the following order: $\text{Zr}^{4+} < \text{Ta}^{5+} < \text{Nb}^{5+} < \text{W}^{6+} < \text{V}^{5+} < \text{Mo}^{6+}$ [47]. There are few to no known prior examples (to our knowledge) of a second-order Jahn-Teller distortion of Ta $5d^0$ cations in pentagonal bipyramidal coordination environments. A possible explanation for the phase transition observed in $\text{Cu}_2\text{Ta}_4\text{O}_{11}$ can be suggested based on the Ta-O bond lengths. The Ta-O bond distances in the TaO_6 octahedron are relatively larger, in the range of 1.92(7) to 2.20(6) Å, as compared to those in $\text{Ag}_2\text{Ta}_4\text{O}_{11}$ at ~1.9845(5). Also, the interatomic distances in the equatorial plane of edge-shared pentagonal bipyramids are slightly larger for Ta1-O3 in $\text{Cu}_2\text{Ta}_4\text{O}_{11}$ as compared to those in $\text{Ag}_2\text{Ta}_4\text{O}_{11}$, at 2.45(8) Å and 2.398(2) Å, respectively. The longer Ta-O interatomic distances observed in the TaO_6 and TaO_7 polyhedra in $\text{Cu}_2\text{Ta}_4\text{O}_{11}$ are comparable to the Nb-O distances in $\text{Na}_2\text{Nb}_4\text{O}_{11}$ and $\text{Ag}_2\text{Nb}_4\text{O}_{11}$. Thus, by comparison, a distorted environment is more likely to occur owing to the out-of-center displacement of the Ta/Nb cations. Kunz and Brown have reported that the directions of the displacements of the d^0 cations are not primarily determined from the electronic second-order Jahn-Teller effect [48]. Using bond-valence arguments, the conclusion was that the preferential direction of the cation displacement is influenced by bond network stresses (e.g., asymmetry in the bond network from the nearest neighbors) as well as cation-cation repulsions from near-neighbor cations that share edges or faces. For example, the tendency of V(V) to favor a distorted environment is observed in the ZnV_2O_6 structure which contains an asymmetrical bond network, leading to the displacement of the V d^0 cations. In the rhombohedral $\beta\text{-Cu}_2\text{Ta}_4\text{O}_{11}$ structure, effects from cation-cation repulsion likely cause the nearest neighbor Ta $5d^0$ cations within three edge-shared TaO_7 polyhedra to move out of the center of the polyhedra, as shown in Figure 4B. Furthermore, the preferential directions of the out-of-center displacement of the Ta cations are towards the vertices of the polyhedra not shared

by neighboring Ta cations. Thus, the repulsion from nearest neighbor cations appears to direct the out-of-center displacement of Ta d^0 cations towards an edge of the polyhedron that is not shared by a neighboring Ta cation within the structure.

As a result of these out-of-center displacements, the rhombohedral β -Cu₂Ta₄O₁₁ structure transforms into the monoclinic α -Cu₂Ta₄O₁₁ structure. The TaO₇ pentagonal bipyramid layer distorts into a layer containing TaO₆ and TaO₇ polyhedra, where Ta3 and Ta1 maintain the TaO₇ pentagonal bipyramid coordination environment and Ta2 centers a highly-distorted TaO₆ octahedron. The monoclinic α -Cu₂Ta₄O₁₁ structure contains fewer edges that are shared as the Ta2-O2 interatomic distance lengthens to 2.55(3) Å, an increase of ~0.13 Å as compared to the rhombohedral β -Cu₂Ta₄O₁₁ structures, as shown in Figures 3 and 4, respectively. The changes in all interatomic distances are listed in Table 2.

C. Thermal Decomposition of α -Cu₂Ta₄O₁₁. The phase transformation between the monoclinic α -Cu₂Ta₄O₁₁ and the rhombohedral phase β -Cu₂Ta₄O₁₁ was investigated in the temperature range of 223 K to 723 K in an inert atmosphere. Powder XRD data of the phase transformation are shown in Figure 6, and indicate the monoclinic α -Cu₂Ta₄O₁₁ transforms into the rhombohedral β -Cu₂Ta₄O₁₁ phase by at least 523 K. At higher temperatures, the powder XRD data indicate the rhombohedral β -Cu₂Ta₄O₁₁ structure is stable. The lattice constants of the monoclinic α -Cu₂Ta₄O₁₁ and rhombohedral β -Cu₂Ta₄O₁₁ phases are listed as a function of temperature in the Supplementary Material, Table S2. The monoclinic a , b , c , and β lattice constants and unit cell volume all decrease as the temperature increases from 223 K to 298 K. This trend is further observed for the lattice constants and unit cell volumes of the rhombohedral β -Cu₂Ta₄O₁₁ as the temperature increases from 523 K to 723 K. Upon heating α -Cu₂Ta₄O₁₁ from 523 K to 623 K, a change from a yellowish to a tannish color is observed. This observation is

similar to the change in color observed after heating $\text{Cu}_5\text{Ta}_{11}\text{O}_{30}$ in air, and resulting in the formation of Cu-deficient structure, $\text{Cu}_{5-x}\text{Ta}_{11}\text{O}_{30}$ [24]. Previous investigations of the thermal instability of $\text{Cu}_5\text{Ta}_{11}\text{O}_{30}$ and CuNb_3O_8 have found the extrusion of Cu(I) and the formation of CuO nanoparticles on the surfaces of the crystallites after heating at temperatures of 450 °C and 550 °C for 3 h [20,24]. The highest amounts of Cu(I) extrusion at the temperature of 550 °C leads to increased Cu-site vacancies in $\text{Cu}_{1-x}\text{Nb}_3\text{O}_8$ and the emergence of ‘O–’ species at the surfaces. Ongoing research is aimed at determining if small changes in the Cu-deficiency occur during the transition between $\alpha\text{-Cu}_2\text{Ta}_4\text{O}_{11}$ and $\beta\text{-Cu}_2\text{Ta}_4\text{O}_{11}$.

D. Optical and Photoelectrochemical Properties. The optical band gap and photoelectrochemical properties of the $\alpha\text{-Cu}_2\text{Ta}_4\text{O}_{11}$ compound were examined in order to compare to the previously known members of the Cu(I)-tantarate family, i.e., $\text{Cu}_5\text{Ta}_{11}\text{O}_{30}$ and $\text{Cu}_3\text{Ta}_7\text{O}_{19}$. The $\text{Cu}_5\text{Ta}_{11}\text{O}_{30}$ and $\text{Cu}_3\text{Ta}_7\text{O}_{19}$ compounds are *p*-type semiconductors with bandgap energies of ~2.6 eV and ~2.5 eV, respectively. The UV-visible diffuse reflectance data for the monoclinic $\alpha\text{-Cu}_2\text{Ta}_4\text{O}_{11}$ were calculated and analyzed as Tauc plots of $(F(R)h\nu)^n$ versus $h\nu$ ($h\nu$ = photon energy), as shown in Figure 6. Onset of the direct transition of ~2.71 eV and a lower-energy indirect bandgap transition of ~2.61 eV were observed, and are comparable to the previously reported the rhombohedral $\beta\text{-Cu}_2\text{Ta}_4\text{O}_{11}$ phase [23].

The photoelectrochemical properties of polycrystalline films of $\text{Cu}_2\text{Ta}_4\text{O}_{11}$ were investigated under simulated AM 1.5G solar irradiation as a function of the applied potential. The polycrystalline films were annealed under vacuum at 500 °C for 3 h and heated in air at temperatures of 250 °C and 350 °C. After the annealing process, the $(\bar{3}13)$ and (022) peaks are shifted to higher and lower 2θ values, respectively, merging into the (116) of the $\beta\text{-Cu}_2\text{Ta}_4\text{O}_{11}$ phase, as shown in the Supplementary Material, Figure S6. Current data indicate that this phase

transition is highly sensitive to the external conditions, such as under flowing nitrogen or vacuum. The post-annealing heat treatments of copper(I)-tantalates $\text{Cu}_5\text{Ta}_{11}\text{O}_{30}$ and $\text{Cu}_3\text{Ta}_7\text{O}_{19}$ have been shown to increase the *p*-type dopant concentration of the semiconductors, thus enhancing their cathodic photocurrents. Linear sweep voltammetry and chronoamperometric measurements of the $\text{Cu}_2\text{Ta}_4\text{O}_{11}$ films before heating and after heating at 250 °C and 350 °C for 3 h are shown in Figure 7. The cathodic photocurrent increased from -0.25 mA/cm^2 to -1.5 mA/cm^2 before and after heating in air, respectively. For $\text{Cu}_5\text{Ta}_{11}\text{O}_{30}$ polycrystalline films, this increase with heating in air has been attributed to CuO formation at its surfaces. Chronoamperometric measurements were taken to investigate the photocurrents produced over time. Shown in Figure 9 are the chronoamperometric data for $\alpha\text{-Cu}_2\text{Ta}_4\text{O}_{11}$ films annealed under vacuum at 500 °C, followed by heating in air to 250 °C and 350 °C for 3 h each. As seen previously in the LSV data, higher cathodic photocurrents are achieved with an increase in heating temperature. To determine whether the enhanced photocurrents occur from the phase change of monoclinic $\alpha\text{-Cu}_2\text{Ta}_4\text{O}_{11}$ into rhombohedral $\beta\text{-Cu}_2\text{Ta}_4\text{O}_{11}$, or an increase in the *p*-type defects, or a combination of both, CuO nanoparticles were deposited onto the surfaces of a polycrystalline $\alpha\text{-Cu}_2\text{Ta}_4\text{O}_{11}$ film. As reported previously [24], this was performed by soaking the film in an ethanolic solution of $\text{Cu}(\text{NO}_3)_2$ and heating to 250 °C for 20 min. A control experiment was also performed by heating a film under the same conditions without the addition of CuO to the surface. Increased photocurrents were observed as CuO is added to the surface, as shown in Figure 8. However, the photocurrent densities were not as significant as observed for films heated to 350 °C. Powder X-ray diffraction data confirm the films remain $\alpha\text{-Cu}_2\text{Ta}_4\text{O}_{11}$ after phototesting, given in the Supplementary Material.

E. Electronic Structure Calculations. Electronic structure calculations were performed using density-functional-theory methods for the α -Cu₂Ta₄O₁₁ structure refined at 298 K. The band structure diagram and densities-of-states, with the Fermi level (E_f) indicated by a dashed line, were calculated as given in the Supplementary Material, Figures S7 and S8. The band structure diagram indicates a direct bandgap transition along the Γ point and lower-energy indirect bandgap transitions from the Γ point to the E, X, and M points. The densities-of-states diagram shows the upper-most valence band states and the lower-most conduction band states arise from the filled Cu $3d^{10}$ and empty Ta $5d^0$ orbitals, respectively. Shown in Figure 10, the electron densities are plotted within a range of 0.75 eV of the uppermost region the valence band and 0.1 eV the lowermost region of the conduction band. The electron density at the upper-most valence band energies indicate a delocalization of the electron density over the Cu atoms with some contributions of electron density from the O $2p$ orbitals within the layer. The electron density within the lower-most energy states of the conduction band are composed of orbital contributions from the Ta $5d$ orbitals found in the two layers containing isolated TaO₆ octahedra and TaO₇ pentagonal bipyramid layers, as well as small contributions from the O $2p$ orbitals located on TaO₆ octahedra. These results are the generally the same as found previously for the β -Cu₂Ta₄O₁₁ phase [23].

CONCLUSIONS

A low-temperature α -Cu₂Ta₄O₁₁ polymorph was synthesized from a reaction of Cu₂O and Ta₂O₅ nanoparticles within a CuCl flux at 665 °C for 1 h. Its structure was characterized by Rietveld refinements to be comprised of alternating layers of distorted edge-shared TaO₆ and TaO₇ polyhedra coordinated to layers of linearly coordinated Cu(I) atoms and isolated TaO₆

octahedra. The $\text{Cu}_2\text{Ta}_4\text{O}_{11}$ structure is found to transform from a rhombohedral $R\bar{3}c$ space group to the noncentrosymmetric monoclinic Cc space group. The structural distortions arise from out-of-center displacements of the nearest-neighbor Ta cations in the layer of edge-shared TaO_7 polyhedra. The $\alpha\text{-Cu}_2\text{Ta}_4\text{O}_{11}$ phase is thermally unstable by at least 523 K and transforms into the rhombohedral $\beta\text{-Cu}_2\text{Ta}_4\text{O}_{11}$. The UV-vis diffuse reflectance spectra of $\alpha\text{-Cu}_2\text{Ta}_4\text{O}_{11}$ exhibits a direct transition of ~ 2.7 eV and a lower-energy indirect transitions beginning at ~ 2.6 eV. The visible light absorbing semiconductor is p -type and produces cathodic photocurrents of up to $\sim 1.5 \text{ mA/cm}^2$ under AM 1.5G irradiation. Thus, this investigation has provided new insights into the stabilization of metastable Cu(I)-containing compositions and a new example of asymmetry-lowering structural distortion in this family.

ACKNOWLEDGEMENTS. The authors would like to thank Dr. Roger D. Sommer at North Carolina State University for the single crystal data collection of the monoclinic $\alpha\text{-Cu}_2\text{Ta}_4\text{O}_{11}$.

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Table 1. Selected Rietveld Refinement Data for α -Cu₂Ta₄O₁₁.

Refined Formula	Cu ₂ Ta ₄ O ₁₁
Formula Weight (g/mol)	1030.69
Space Group, <i>Z</i>	<i>Cc</i> (9), 4
Crystal System	Monoclinic
Temperature (K)	298
Unit Cell (Å), <i>a</i>	10.734 (1)
<i>b</i>	6.2506(3)
<i>c</i>	12.887(1)
β	106.070(4)
<i>V</i> (Å) ³	830.8(1)
No. of unique data collected	7005
No. of variables residuals ^a	R ₁ , [F _o >4 σ (F _o)], 0.0431
	<i>wR</i> = 0.0965
	<i>wR</i> _{exp} = 0.0545
Goodness-of-Fit	2.5
$R1 = [\sum F_o - F_c / \sum F_o] \quad wR2 = [\sum [w(F_o - F_c)^2] / \sum wF_o^4]^{1/2}$ $w^{-1} = [\sigma(F_o^2) + (Ap)^2 + Bp] \quad p = [\max(F_o^2, 0) + 2F_c^2] / 3$	

Table 2. Selected Interatomic Distances for the Symmetry-Inequivalent Metal Sites in α - $\text{Cu}_2\text{Ta}_4\text{O}_{11}$ from the powder Rietveld refinement at 298 K.

Atom	Atom pair	Distance (Å)	Δ_{dist}^a (Å)	Atom	Atom pair	Distance (Å)	Δ_{dist}^a (Å)
Ta1, pentagonal bipyramid				Ta4, octahedron			
	Ta1-O1	2.10(8)	+0.106		Ta4-O4	2.20(4)	+0.21
	Ta1-O2	2.07(8)	+0.077		Ta4-O5	1.98(7)	-0.01
	Ta1-O3	2.12(6)	+0.092		Ta4-O7	1.99(8)	0.0
	Ta1-O4	1.98(7)	+0.006		Ta4-O8	2.08(10)	+0.09
	Ta1-O5	2.08(9)	+0.086		Ta4-O9	1.92(7)	-0.07
	Ta1-O6	2.19(5)	+0.169		Ta4-O10	2.16(7)	+0.17
	Ta1-O11	1.96(8)	-0.48			$\Sigma s_{ij} =$	4.32
		$\Sigma s_{ij} =$	4.74				
Ta2, octahedron				Cu1, linear			
	Ta2-O1	2.08 (7)	+0.059				
	Ta2-O2	1.92(8)	-0.074		Cu1-O5	1.96(9)	+0.055
	Ta2-O6	2.15(8)	+0.156		Cu1-O9	1.77(7)	-0.19
	Ta2-O9	2.11(8)	+0.138			$\Sigma s_{ij} =$	0.99
	Ta2-O10	1.91(7)	+0.068				
	Ta2-O11	2.06(8)	+0.034	Cu2, linear			
		$\Sigma s_{ij} =$	4.68		Cu2-O7	1.88(7)	-0.025
					Cu2-O8	1.78(9)	-0.125
Ta3, pentagonal bipyramid						$\Sigma s_{ij} =$	1.06
				Cu3, linear			
	Ta3-O1	2.12(7)	+0.099		Cu3-O4	1.71(8)	-0.195
	Ta3-O2	2.45(4)	+0.01		Cu3-O10	2.01(9)	+0.105
	Ta3-O3	2.07(5)	+0.077			$\Sigma s_{ij} =$	1.05
	Ta3-O6	1.98(7)	-0.013				
	Ta3-O7	1.95(8)	-0.22				
	Ta3-O8	2.07(10)	+0.108				
	Ta3-O11	1.99(8)	-0.031				
		$\Sigma s_{ij} =$	4.76				

^a Δ_{dist} (Å) is the difference between the interatomic distance as compared to the α - $\text{Cu}_2\text{Ta}_4\text{O}_{11}$ structure from the single crystal XRD structure refinement at 298 K for the rhombohedral $R\bar{3}c$.

Figure 1. The Rietveld refinement pattern of the monoclinic α - $\text{Cu}_2\text{Ta}_4\text{O}_{11}$ at 298 K. The observed intensities are indicated in blue (+), calculated intensities in green, the difference pattern line is light blue, and the peak positions indicated by the blue tick marks. Impurities of Ta_2O_5 were masked, as indicated by the purple lines.

Figure 2. Polyhedral view of the α - $\text{Cu}_2\text{Ta}_4\text{O}_{11}$ structure determined at 298 K in the monoclinic Cc space group, with the unit cell outlined in blue. The Cu and O atoms are in blue and red, respectively. The Ta cations and polyhedra are shown in tan.

Figure 3. Structural views of the layer of edge-sharing TaO_7 pentagonal bipyramids in $\alpha\text{-Cu}_2\text{Ta}_4\text{O}_{11}$; a) the edge sharing layer of Ta cations along the ab plane with the unit cell outline as a blue dashed line, the black line indicates the distortion of Ta2 into an octahedra in the edge-shared tantalate layer, b-d) the local coordination environment of Ta3, Ta1 and Ta2.

Figure 4. Structural views of the layer of edge-sharing TaO₇ pentagonal bipyramids in β -Cu₂Ta₄O₁₁; a) the edge sharing layer of Ta cations along the *ab* plane with the unit cell outline as a blue dashed line, b) a smaller segment from the uppermost three Ta cations, with grey arrows indicating the out-of-center displacement of the Ta cations and c-e) local views of the Ta cation coordination environments.

Figure 5. Powder X-ray diffraction patterns of α - $\text{Cu}_2\text{Ta}_4\text{O}_{11}$ in an inert atmosphere with i) the simulated XRD of α - $\text{Cu}_2\text{Ta}_4\text{O}_{11}$ from the Rietveld refinement, ii-vi) the experimental powder XRD patterns when heated at 223 K, 273 K, 523 K, 623 K, and 723 K, and vii) the simulated XRD pattern of β - $\text{Cu}_2\text{Ta}_4\text{O}_{11}$.

Figure 6. Tauc plots of the UV-vis diffuse reflectance data for the monoclinic $\alpha\text{-Cu}_2\text{Ta}_4\text{O}_{11}$ showing the onset of the indirect ($n = 1/2$; orange) and direct ($n = 2$; green) band gap transitions.

Figure 7. Linear sweep voltammetry scans of the polycrystalline $\alpha\text{-Cu}_2\text{Ta}_4\text{O}_{11}$ films annealed under vacuum at 773 K for 3 h (red) and heated in air at 523 K (blue) and at 623 K (green) for 3 h each.

Figure 8. Linear sweep voltammetry scans of the polycrystalline α - $\text{Cu}_2\text{Ta}_4\text{O}_{11}$ films heated in air to 523 K for 3 h (red), 523 K for 20 min with CuO on surface (blue), and 623 K for 3 h (green) with no added CuO.

Figure 9. Chronoamperometric scans of α -Cu₂Ta₄O₁₁ polycrystalline films annealed under vacuum at 500 °C for 3 h not heated (red), heated to 250 °C for 3 h (blue) and heated to 350 °C for 3 h (green).

Figure 10. Plots of the electron density for the α -Cu₂Ta₄O₁₁ phase with the orbital contributions in the A) valence band with electron density contributions in blue shading and in the B) conduction band with electron density contributions in tan shading.

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