Flux-Mediated Syntheses, Structural Characterization and Low-Temperature Polymorphism of the $p$-Type Semiconductor Cu$_2$Ta$_4$O$_{11}$

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ABSTRACT

A new low-temperature polymorph of the copper(I)-tantalate, $\alpha$-Cu$_2$Ta$_4$O$_{11}$, 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 $\alpha$-Cu$_2$Ta$_4$O$_{11}$ phase is a lower-symmetry monoclinic polymorph of the rhombohedral Cu$_2$Ta$_4$O$_{11}$ structure (i.e., $\beta$-Cu$_2$Ta$_4$O$_{11}$ 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 $\beta$-Cu$_2$Ta$_4$O$_{11}$ and is composed of single layers of highly-distorted and edge-shared TaO$_7$ and TaO$_6$ polyhedra alternating with layers of nearly linearly-coordinated Cu(I) cations and isolated TaO$_6$ octahedra. Temperature dependent powder X-ray diffraction data show the $\alpha$-Cu$_2$Ta$_4$O$_{11}$ phase is relatively stable under vacuum at 223 K and 298 K, but reversibly transforms to $\beta$-Cu$_2$Ta$_4$O$_{11}$ by at least 523 K and higher temperatures. The symmetry-lowering distortions from $\beta$-Cu$_2$Ta$_4$O$_{11}$ to $\alpha$-Cu$_2$Ta$_4$O$_{11}$ arise from the out-of-center displacements of the Ta $5d^0$ cations in the TaO$_7$ pentagonal bipyramids. The UV-Vis diffuse reflectance spectrum of the monoclinic $\alpha$-Cu$_2$Ta$_4$O$_{11}$ shows an indirect bandgap transition of ~2.6 eV, with the higher-energy direct
transitions starting at \(\sim 2.7\) eV. Photoelectrochemical measurements on polycrystalline films of \(\alpha\)-Cu\(_2\)Ta\(_4\)O\(_{11}\) show strong cathodic photocurrents of \(\sim 1.5\) mA/cm\(^2\) 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 Na\(_2\)Ta\(_4\)O\(_{11}\), AgNbO\(_3\) and PbTiO\(_3\) phases can be prepared in shortened reaction times of down to \(\sim 1\) hr [9,15,16], resulting in highly-faceted particles that exhibit significantly enhanced photocatalytic rates. In related examples, both Cu\(_2\)Nb\(_8\)O\(_{21}\) and PbTa\(_4\)O\(_{11}\) 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 Cu$_3$VO$_4$ [19], CuNb$_3$O$_8$ [20], Cu$_2$Nb$_8$O$_{21}$ [17], Cu$_3$Ta$_2$O$_{19}$ [21], and $\beta$-Cu$_2$Ta$_4$O$_{11}$ [22,23]. The use of a CuCl molten salt (melting point $\sim$426 °C) within these systems significantly shortens their reaction times down to $\sim$15-30 min, with nanoparticle reactants rapidly growing to micron-sized single-crystal particles, e.g., as reported for Cu$_2$Ta$_4$O$_{21}$, CuNb$_3$O$_8$ and $\beta$-Cu$_2$Ta$_4$O$_{11}$. 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 ($\sim$1 to 2 mA/cm$^2$) when irradiated by visible light. Recent examples include Cu$_{1-x}$Nb$_3$O$_8$, Cu$_{5-x}$Ta$_{11}$O$_{30}$, and Cu$_{3-x}$VO$_4$, 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 Cu$_2$Ta$_4$O$_{11}$ phase was first discovered in very small quantities in a high-resolution electron microscopy investigation of the solid-state products in the Cu$_2$O-Ta$_2$O$_5$ system in the temperature range of 700 °C to 1100 °C [25,26]. More recently, the Cu$_2$Ta$_4$O$_{11}$ 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., $A = \text{Ag, Na, Cu, Pb, Bi}; \ M = \text{Ta, Nb}$), that contains single ($n = 1$), double ($n = 2$), or a combination ($1 < n < 2$) of layers of $\text{MO}_7$ polyhedra that alternate with a layer of isolated $\text{MO}_6$ polyhedra [27-29]. Interestingly, the $\text{Cu}_2\text{Ta}_4\text{O}_{11}$ 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 $\text{Cu}_2\text{Ta}_4\text{O}_{11}$, 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$_2$O and Ta$_2$O$_5$ 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 $\alpha$-$\text{Cu}_2\text{Ta}_4\text{O}_{11}$ phase were performed by combining Cu$_2$O and Ta$_2$O$_5$ 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$_2$O$_5$ (≤ 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 Kα radiation (λ = 1.54056 Å). The temperature was controlled via an MTC temperature stage with a precision of ~3 K. Data were collected in a 2θ range of 10-80° in 0.01 steps with a dwell time of 4 s at each step. A small amount of Ta₂O₅ impurity was masked in the region from ~25.9° to ~27.6°, 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 Cu₂Ta₄O₁₁ 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 R3c, 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 Ag₂Nb₄O₁₁ and Na₂Nb₄O₁₁ [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 (\(wR = 0.096, \ wR_{exp} = 0.0545\)). 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 ~66.7% occupancy for the charge-balanced chemical composition of Cu₂Ta₄O₁₁. 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 \(n = \frac{1}{2}\) 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 ~100 mW/cm² (Oriel) using a scan rate of 0.0250 V·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 Na₂SO₄ aqueous solution that had been adjusted to a pH = 6.5 using dilute aqueous H₂SO₄. This solution was purged with N₂ gas for 30 min both prior to and continuously during the photoelectrochemical measurements in order to remove any dissolved O₂ in the electrolyte solution.

D. Electronic Structure Calculations. Electronic structure calculations were performed on the geometry-optimized α-Cu₂Ta₄O₁₁ 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 × 2 × 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 Cu₂O and Ta₂O₅ nanoparticle reactants are required for the flux synthesis of both polymorphs of the Cu₂Ta₄O₁₁
phase. The rhombohedral structure of Cu$_2$Ta$_4$O$_{11}$, hereafter referred to as β-Cu$_2$Ta$_4$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 α-Cu$_2$Ta$_4$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 (Cu$_2$O:Ta$_2$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$_2$O$_5$ (~20%) is found together with α-Cu$_2$Ta$_4$O$_{11}$. Further reaction of α-Cu$_2$Ta$_4$O$_{11}$ with excess Cu$_2$O in a CuCl flux at 665 °C for an additional 1 h results in its complete conversion to the β-Cu$_2$Ta$_4$O$_{11}$ phase.

The structure of α-Cu$_2$Ta$_4$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 β-Cu$_2$Ta$_4$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 α-Cu$_2$Ta$_4$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 β-Cu$_2$Ta$_4$O$_{11}$, as shown in Figure 3. However, the monoclinic α-Cu$_2$Ta$_4$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 \( \alpha\text{-U3O8} \) 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 \( \beta\text{-Cu2Ta4O11} \), 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 \( \beta\text{-Cu2Ta4O11} \) to the monoclinic \( \alpha\text{-Cu2Ta4O11} \) 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 \( A_2M_4O_{11} \) 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 \( R\bar{3}c \) 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 NbO7 pentagonal bipyramids towards the apical O atoms, and the displacement of Ag cations in the AgO6 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., \( \sim 2.51 \, \text{Å} \) within a NaO7 polyhedron, versus the Ag-O distances in \( \text{Ag}_2\text{Nb}_4\text{O}_{11} \) of \( \sim 2.65 \, \text{Å} \). 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., \( 1.71(8) \, \text{Å} \) to \( 2.01(9) \, \text{Å} \). 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 TaO7 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 5\(d^0\) 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 \(\sim 1.9845(5)\). 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 \(\text{ZnV}_2\text{O}_6\) 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 5\(d^0\) 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 $d^9$ 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 $\beta$-Cu$_2$Ta$_4$O$_{11}$ structure transforms into the monoclinic $\alpha$-Cu$_2$Ta$_4$O$_{11}$ structure. The TaO$_7$ pentagonal bipyramid layer distorts into a layer containing TaO$_6$ and TaO$_7$ polyhedra, where Ta3 and Ta1 maintain the TaO$_7$ pentagonal bipyramid coordination environment and Ta2 centers a highly-distorted TaO$_6$ octahedron. The monoclinic $\alpha$-Cu$_2$Ta$_4$O$_{11}$ 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 $\beta$-Cu$_2$Ta$_4$O$_{11}$ structures, as shown in Figures 3 and 4, respectively. The changes in all interatomic distances are listed in Table 2.

C. Thermal Decomposition of $\alpha$-Cu$_2$Ta$_4$O$_{11}$. The phase transformation between the monoclinic $\alpha$-Cu$_2$Ta$_4$O$_{11}$ and the rhombohedral phase $\beta$-Cu$_2$Ta$_4$O$_{11}$ 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 $\alpha$-Cu$_2$Ta$_4$O$_{11}$ transforms into the rhombohedral $\beta$-Cu$_2$Ta$_4$O$_{11}$ phase by at least 523 K. At higher temperatures, the powder XRD data indicate the rhombohedral $\beta$-Cu$_2$Ta$_4$O$_{11}$ structure is stable. The lattice constants of the monoclinic $\alpha$-Cu$_2$Ta$_4$O$_{11}$ and rhombohedral $\beta$-Cu$_2$Ta$_4$O$_{11}$ phases are listed as a function of temperature in the Supplementary Material, Table S2. The monoclinic $a$, $b$, $c$, and $\beta$ 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 $\beta$-Cu$_2$Ta$_4$O$_{11}$ as the temperature increases from 523 K to 723 K. Upon heating $\alpha$-Cu$_2$Ta$_4$O$_{11}$ 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 Cu$_5$Ta$_{11}$O$_{30}$ in air, and resulting in the formation of Cu-deficient structure, Cu$_{5-x}$Ta$_{11}$O$_{30}$ [24]. Previous investigations of the thermal instability of Cu$_5$Ta$_{11}$O$_{30}$ and CuNb$_3$O$_8$ 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 Cu$_{1-x}$Nb$_3$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 α-Cu$_2$Ta$_4$O$_{11}$ and β-Cu$_2$Ta$_4$O$_{11}$.

D. Optical and Photoelectrochemical Properties. The optical band gap and photoelectrochemical properties of the α-Cu$_2$Ta$_4$O$_{11}$ compound were examined in order to compare to the previously known members of the Cu(I)-tantalate family, i.e., Cu$_5$Ta$_{11}$O$_{30}$ and Cu$_5$Ta$_7$O$_{19}$. The Cu$_5$Ta$_{11}$O$_{30}$ and Cu$_5$Ta$_7$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 α-Cu$_2$Ta$_4$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 β-Cu$_2$Ta$_4$O$_{11}$ phase [23].

The photoelectrochemical properties of polycrystalline films of Cu$_2$Ta$_4$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 (313) and (022) peaks are shifted to higher and lower 2θ values, respectively, merging into the (116) of the β–Cu$_2$Ta$_4$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 under flowing nitrogen or vacuum. The post-annealing heat treatments of copper(I)-tantalates Cu$_5$Ta$_{11}$O$_{30}$ and Cu$_3$Ta$_7$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 Cu$_2$Ta$_4$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 Cu$_5$Ta$_{11}$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 $\alpha$-Cu$_2$Ta$_4$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 $\alpha$-Cu$_2$Ta$_4$O$_{11}$ into rhombohedral $\beta$-Cu$_2$Ta$_4$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 $\alpha$-Cu$_2$Ta$_4$O$_{11}$ film. As reported previously [24], this was performed by soaking the film in an ethanolic solution of Cu(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 $\alpha$-Cu$_2$Ta$_4$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 \( \alpha-\text{Cu}_2\text{Ta}_4\text{O}_{11} \) 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 \( \Gamma \) point and lower-energy indirect bandgap transitions from the \( \Gamma \) 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 3\( d^{10} \) and empty Ta 5\( d^0 \) 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 2\( p \) 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 5\( d \) orbitals found in the two layers containing isolated TaO\(_6\) octahedra and TaO\(_7\) pentagonal bipyramid layers, as well as small contributions from the O 2\( p \) orbitals located on TaO\(_6\) octahedra. These results are the generally the same as found previously for the \( \beta-\text{Cu}_2\text{Ta}_4\text{O}_{11} \) phase [23].

CONCLUSIONS

A low-temperature \( \alpha-\text{Cu}_2\text{Ta}_4\text{O}_{11} \) polymorph was synthesized from a reaction of Cu\(_2\)O and Ta\(_2\)O\(_5\) 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 TaO\(_6\) and TaO\(_7\) polyhedra coordinated to layers of linearly coordinated Cu(I) atoms and isolated TaO\(_6\)
octahedra. The Cu$_2$Ta$_4$O$_{11}$ structure is found to transform from a rhombohedral R$3c$ 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 $\alpha$-Cu$_2$Ta$_4$O$_{11}$ phase is thermally unstable by at least 523 K and transforms into the rhombohedral $\beta$-Cu$_2$Ta$_4$O$_{11}$. The UV-vis diffuse reflectance spectra of $\alpha$-Cu$_2$Ta$_4$O$_{11}$ exhibits a direct transition of $\sim$2.7 eV and a lower-energy indirect transitions beginning at $\sim$2.6 eV. The visible light absorbing semiconductor is $p$-type and produces cathodic photocurrents of up to $\sim$1.5 mA/cm$^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 $\alpha$-Cu$_2$Ta$_4$O$_{11}$. 
REFERENCES


Table 1. Selected Rietveld Refinement Data for $\alpha$-Cu$_2$Ta$_4$O$_{11}$.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
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</thead>
<tbody>
<tr>
<td>Refined Formula</td>
<td>Cu$_2$Ta$<em>4$O$</em>{11}$</td>
</tr>
<tr>
<td>Formula Weight (g/mol)</td>
<td>1030.69</td>
</tr>
<tr>
<td>Space Group, Z</td>
<td>Cc (9), 4</td>
</tr>
<tr>
<td>Crystal System</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>Temperature (K)</td>
<td>298</td>
</tr>
<tr>
<td>Unit Cell (Å), a</td>
<td>10.734 (1)</td>
</tr>
<tr>
<td></td>
<td>6.2506 (3)</td>
</tr>
<tr>
<td></td>
<td>12.887 (1)</td>
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<tr>
<td></td>
<td>106.070 (4)</td>
</tr>
<tr>
<td>$V$ (Å$^3$)</td>
<td>830.8 (1)</td>
</tr>
<tr>
<td>No. of unique data collected</td>
<td>7005</td>
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<tr>
<td>No. of variables residuals$^a$</td>
<td>$R_1$, $[F_o&gt;4\alpha(F_o)]$, 0.0431</td>
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<tr>
<td></td>
<td>$wR = 0.0965$</td>
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<tr>
<td></td>
<td>$wR_{exp} = 0.0545$</td>
</tr>
<tr>
<td>Goodness-of-Fit</td>
<td>2.5</td>
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</table>

$R_1 = \frac{\sum |F_o| - |F_c|}{\sum |F_o|}$

$wR = \frac{\sum w(F_o - F_c)^2}{\sum wF_o^2}^{1/2}$

$w^{-1} = [\sigma(F_o^2) + (Ap)^2 + Bp]$

$p = [\max(F_o^2), 0] + 2F_c^2 / 3$
Table 2. Selected Interatomic Distances for the Symmetry-Inequivalent Metal Sites in α-Cu$_2$Ta$_4$O$_{11}$ from the powder Rietveld refinement at 298 K.

<table>
<thead>
<tr>
<th>Atom pair</th>
<th>Distance (Å)</th>
<th>$\Delta_{\text{dist}}$ (Å)</th>
<th>Atom pair</th>
<th>Distance (Å)</th>
<th>$\Delta_{\text{dist}}$ (Å)</th>
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<tbody>
<tr>
<td>Ta1-O1</td>
<td>2.10(8)</td>
<td>+0.106</td>
<td>Ta4-O4</td>
<td>2.20(4)</td>
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<tr>
<td>Ta1-O2</td>
<td>2.07(8)</td>
<td>+0.077</td>
<td>Ta4-O5</td>
<td>1.98(7)</td>
<td>-0.01</td>
</tr>
<tr>
<td>Ta1-O3</td>
<td>2.12(6)</td>
<td>+0.092</td>
<td>Ta4-O7</td>
<td>1.99(8)</td>
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</tr>
<tr>
<td>Ta1-O4</td>
<td>1.98(7)</td>
<td>+0.006</td>
<td>Ta4-O8</td>
<td>2.08(10)</td>
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<tr>
<td>Ta1-O5</td>
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<tr>
<td>Ta1-O6</td>
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<td>Ta4-O10</td>
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<tr>
<td>Ta1-O11</td>
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<td>Ta2-O9</td>
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<tr>
<td>Ta2-O10</td>
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<tr>
<td>Ta2-O11</td>
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<tr>
<td>Ta3-O1</td>
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<td>Cu3-O4</td>
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<tr>
<td>Ta3-O2</td>
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<td>+0.01</td>
<td>Cu3-O10</td>
<td>2.01(9)</td>
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<tr>
<td>Ta3-O3</td>
<td>2.07(5)</td>
<td>+0.077</td>
<td>$\Sigma s_{ij} = 1.05$</td>
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<tr>
<td>Ta3-O6</td>
<td>1.98(7)</td>
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<td>Ta3-O7</td>
<td>1.95(8)</td>
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<td>Ta3-O8</td>
<td>2.07(10)</td>
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<td>1.99(8)</td>
<td>-0.031</td>
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<tr>
<td>$\Sigma s_{ij} = 4.76$</td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

$\Delta_{\text{dist}}$ (Å) is the difference between the interatomic distance as compared to the α-Cu$_2$Ta$_4$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-Cu$_2$Ta$_4$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$_2$O$_5$ were masked, as indicated by the purple lines.
Figure 2. Polyhedral view of the $\alpha$-$\text{Cu}_2\text{Ta}_4\text{O}_{11}$ 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 $\alpha$-Cu$_2$Ta$_4$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 TaO$_7$ pentagonal bipyramids in β-Cu$_2$Ta$_4$O$_{11}$; 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 $\alpha$-Cu$_2$Ta$_4$O$_{11}$ in an inert atmosphere with i) the simulated XRD of $\alpha$-Cu$_2$Ta$_4$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 $\beta$-Cu$_2$Ta$_4$O$_{11}$. 
Figure 6. Tauc plots of the UV-vis diffuse reflectance data for the monoclinic $\alpha$-Cu$_2$Ta$_4$O$_{11}$ showing the onset of the indirect ($n = \frac{1}{2}$; orange) and direct ($n = 2$; green) band gap transitions.
Figure 7. Linear sweep voltammetry scans of the polycrystalline $\alpha$-Cu$_5$Ta$_4$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 $\alpha$-Cu$_2$Ta$_4$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 $\alpha$-Cu$_2$Ta$_4$O$_{11}$ 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 \( \alpha\text{-Cu}_2\text{Ta}_4\text{O}_{11} \) 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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