Selective Crystal Growth and Structural, Optical, and Electronic Studies of \( \text{Mn}_3\text{Ta}_2\text{O}_8 \)

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ABSTRACT: \( \text{Mn}_3\text{Ta}_2\text{O}_8 \) is a stable targeted material with an unusual and complex cation topology in the complicated Mn-Ta-O phase space, has been grown as a ≈3-cm-long single crystal via the optical floating-zone technique. Single-crystal absorbance studies determine the band gap as 1.89 eV, which agrees with the value obtained from density functional theory electronic-band-structure calculations. The valence band consists of the hybridized Mn d–O p states, whereas the bottom of the conduction band is formed by the Ta d states. Furthermore, out of the three crystallographically distinct Mn atoms that are four-, seven-, or eight-coordinate, only the former two contribute their states near the top of the valence band and hence govern the electronic transitions across the band gap.

1. INTRODUCTION

Complex cationic topological networks (CCTNs), with multiple coordination sites for identical atomic species, have been investigated for important applications, including transparent electrodes and laser materials. Of particular interest are archetypal CCTNs that can accommodate a range of compositions and oxidation states while retaining the parent structure. Such networks offer the possibility of correlating desirable properties with dopants and substitutes because local alterations have far-reaching repercussions to the cation order in the crystalline lattice. As a result of the complexity that defines these materials, however, the structure solution of a CCTN is difficult without a single crystal. Furthermore, these complex systems are rife with secondary phases, and obtaining a pure polycrystalline phase presents its own challenges.

One example of a structure with such a complex network is the unusual and rare, anion-deficient, fluorite-related phase that is only exhibited, to the authors' knowledge, by Ga\text{3-x}In\text{x}Se\text{2+x} (\( 0.3 \leq x \leq 1.6 \)), Na\text{2-Ln}(WO\text{4})\text{4} (where Ln = Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, or Lu), and Mn\text{3-Ta}\text{2-O}\text{8}. This CCTN maintains four distinct cation environments, four-, six-, seven-, and eight-coordinate, and a wide array of oxidation states, ranging from 1+ to 6+. In particular, Mn\text{3-Ta}\text{2-O}\text{8} provides a challenge for single-crystal growth, owing to the similarities in the stoichiometry and the differences in the structure of the ternaries in the Mn–Ta–O phase space, as shown in Figure 1.5,7,9–21 Most of the known phases have only been characterized via powder X-ray diffraction (XRD), often in the presence of secondary phases, and vary widely in structure, including fluorite-related compositions such as Mn\text{3-Ta}\text{2-O}\text{8}, as well as the η-carbide, columbite, corundum, corundum/rock salt, CoSn, rutile, tantalite, trirutile, wodginitc, and wolframite structure types.5,9,11,12,16 Single-crystal growth of ternaries in this system has been most successful in producing what are reported to be metastable structures, which are polymorphs of the reported stable structures of identical stoichiometry (Mn\text{Ta}\text{2-O\text{6}}, Mn\text{3-Ta}\text{2-O\text{8}} and Mn\text{11-Ta}\text{4-O\text{21}}) obtained via solid-state syntheses.16 To date, only a single instance of a ternary manganese tantalate crystal that is classified as thermodynamically favored has been grown, to the authors' knowledge: the anion-deficient fluorite Mn\text{3.35-Ta}\text{2.24-O\text{1.4}}.14 Thus far, the crystal growth methods reported for phases in the Mn–Ta–O system have been arc-melt and oven-melt methods, and the limits of these methods have likely been reached. There are no reported single crystals of Mn\text{3-Ta}\text{2-O\text{8}}, but such crystals would be desirable for precise property characterization, such as determination of the optical band gap.22 Additionally, Mn\text{3-Ta}\text{2-O\text{8}} combines a high density of six-coordinate sites, which appears to be related to good conductivity, with Mn\text{2+} ions with d⁵ electronic configurations, which are appealing from a band-engineering point of view.23–26 Moving beyond p-block elements has already been accomplished in p-type materials, which can include d⁴ or d¹⁰ metals.27–29

The difficulty inherent in growing a single crystal of a targeted composition in the Mn–Ta–O phase space can be reduced by employing the optical floating-zone furnace method. This method maintains a smaller amount of molten sample than most other crystal growth procedures while

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feeding in material of the desired stoichiometry, which inhibits the formation of a heterogeneous molten zone by enabling precise control over the stoichiometry of the final crystal. Additionally, the oxidation state of manganese can be controlled by varying the atmosphere. Herein, the first growth of a large single crystal of Mn₃Ta₂O₈ is reported along with the full-matrix least-squares method. 

2. EXPERIMENTAL AND THEORETICAL METHODS

Crystal Growth. Feed material of manganese(II) oxide (Alfa Aesar, 99%) and tantalum(V) oxide (Alfa Aesar, 99%) with a 3:1 molar ratio (3MnO/Ta₂O₅) was prepared via thorough mixing with a Fritsch planetary ball mill using agate media at 600 rpm for 8 cycles of 15 min, with pauses of 5 min between cycles. The feedstock was then packed into cylindrical molds of 6 mm diameter and 130 mm length, which were pressed at 60 MPa for 5 min. These rods were then removed from the mold and densified by firing in an argon atmosphere. The firing heated the samples to 1200 °C at a rate of 5 °C/min and held the samples at 1200 °C for 28 h. The resulting rods’ densities were 92% of the single-crystal density of 7.078 g/cm³ (≈92% of the single-crystal density of 7.078 g/cm³ determined in the structural characterization).

A feed rod was suspended from the upper shaft of a Crystal Systems Inc. FZ-T-10000-H-VI-VP optical image furnace with a platinum wire. A seed rod was firmly affixed to an alumina chuck with nickel wire, and the chuck was attached to the furnace’s bottom shaft. Growth was carried out in the optical image furnace with four 300 W tungsten halide lamps. Each lamp was centered in an elliptical mirror, which focused the light onto the sample. The growth chamber was enclosed in a fused silica tube through which purified argon was flowed at 1.0 L/min during the growth. Mn₃Ta₂O₈ was grown at a rate of 3.00 mm/h using 78.5% of the lamps’ power, and the feed and seed rods had counterrotations of 13.0 rpm. The end result of this procedure was a 5-cm-long deposition of reddish-brown solidified material on the seed rod. Of this, ≈3 cm was determined to be a single crystal based upon the lack of grain boundaries and its uniform extinction of polarized light. The rods are pictured in Figure 2 at each stage of this procedure.

Structural Characterization. A portion of the single-crystal section was removed via cleavage. This portion was then carefully

Table 1. Crystallographic and Acquisition Parameters of the Single-Crystal X-ray Data for Mn₃Ta₂O₈, Powder X-ray Data, and Powder Neutron Data

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Mn₃Ta₂O₈</th>
<th>Powder X-ray</th>
<th>Powder neutron</th>
</tr>
</thead>
<tbody>
<tr>
<td>fw (g/mol)</td>
<td>654.72</td>
<td>654.72</td>
<td>654.72</td>
</tr>
<tr>
<td>temperature (K)</td>
<td>100</td>
<td>room</td>
<td>room</td>
</tr>
<tr>
<td>lam (Å)</td>
<td>0.71073</td>
<td>0.65</td>
<td>1.47</td>
</tr>
<tr>
<td>space group</td>
<td>H₄/a</td>
<td>tetragonal</td>
<td>tetragonal</td>
</tr>
<tr>
<td>a (Å)</td>
<td>11.2133(4)</td>
<td>11.2782(2)</td>
<td>11.2728(2)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>9.7723(3)</td>
<td>9.8030(3)</td>
<td>9.8030(3)</td>
</tr>
<tr>
<td>Z</td>
<td>8</td>
<td>8</td>
<td>8</td>
</tr>
<tr>
<td>ρ_{calc} (g/cm³)</td>
<td>7.078</td>
<td>room</td>
<td>room</td>
</tr>
<tr>
<td>F(000)</td>
<td>22800</td>
<td></td>
<td></td>
</tr>
<tr>
<td>crystal size (mm³)</td>
<td>0.47 × 0.304 × 0.413</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ρ_{ew} (g/cm³)</td>
<td>6.98</td>
<td></td>
<td>6.98</td>
</tr>
<tr>
<td>ρ_{pow} (g/cm³)</td>
<td>6.98</td>
<td></td>
<td></td>
</tr>
<tr>
<td>R (all)</td>
<td>0.1133</td>
<td></td>
<td></td>
</tr>
<tr>
<td>extinction coefficient (Å²)</td>
<td>0.0080(5)</td>
<td></td>
<td></td>
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<tr>
<td>reported T_{min}, T_{max}</td>
<td>0.004, 0.035</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 2. Seed (left) and feed (right) rods used in the crystal growth of Mn₃Ta₂O₈: (a) presintering; (b) post-sintering; (c) post-growth. Scale marks are millimeters. Approximately 7/16 of the growth (≈3 cm) in part c is a single crystal. The remainder transitions from highly polycrystalline to single crystal along the direction of the growth.
The collection path to selectively examine a circular region of diameter was placed on a glass coverslip at the focus of a 20× Pow

cromatic Mo Kα fractometer. The detector-to-sample distance was 50 mm with mono-

ced over the range 0.70–2.92 eV (703–424 nm) at 298 K using a Mo target. For determination of the

temperature. The detector-to-sample distance was 3 cm with polychromatic radiation from a Mo target. For determination of the
crystal orientation, the Cologne Laue indexation program was used.

Orientation Determination. Following the absorbance measurements, the same slice was mounted on a steel cylinder with clay. A
back-reflection Laue diffraction pattern was obtained at room temperature. The detector-to-sample distance was 3 cm with polychromatic radiation from a Mo target. For determination of the crystal orientation, the Cologne Laue indexation program was used.

Band-Structure Calculations. The electronic band structure of Mn3Ta2O8 was investigated using a first-principles density functional theory approach, as implemented in the Vienna ab initio simulation package (VASP). The PBE functional within the projector augmented-wave method was used.

Brillouin-zone sampling was done with a Γ-centered Monkhorst pack with k-point meshes 3 × 3 × 3; a cutoff energy of 500 eV was used. The internal atomic positions were optimized using the force and total energy minimization. To describe correctly the d5 states of Mn3+, the exchange correlation functional in the generalized gradient approximation (GGA) with an on-site Coulomb term (GGA+U) was employed. We used LDAUTYPE=2,
Table 4. Anisotropic Thermal Displacement Parameters (Å² x 10⁸), Defined by 2π²(h²a⁰²U₁₁ + ... + 2hkbU₁₂), for Mn₃Ta₂O₈ from Single-Crystal XRD Data

<table>
<thead>
<tr>
<th>atom</th>
<th>U₁₁</th>
<th>U₁₂</th>
<th>U₁₃</th>
<th>U₂₂</th>
<th>U₂₃</th>
<th>U₃₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ta1</td>
<td>8.9(3)</td>
<td>8.7(3)</td>
<td>7.4(3)</td>
<td>0.26(9)</td>
<td>-0.11(10)</td>
<td>0.25(9)</td>
</tr>
<tr>
<td>Mn1</td>
<td>13.1(7)</td>
<td>11.7(7)</td>
<td>13.8(6)</td>
<td>2.8(5)</td>
<td>-5.2(5)</td>
<td>-2.1(5)</td>
</tr>
<tr>
<td>Mn2</td>
<td>12.3(8)</td>
<td>12.3(8)</td>
<td>9.7(13)</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Mn3</td>
<td>10.3(8)</td>
<td>10.3(8)</td>
<td>8.6(13)</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>O₁</td>
<td>8(2)</td>
<td>15(3)</td>
<td>9(3)</td>
<td>1(2)</td>
<td>1(2)</td>
<td>0(2)</td>
</tr>
<tr>
<td>O₂</td>
<td>13(3)</td>
<td>6(2)</td>
<td>14(3)</td>
<td>2(2)</td>
<td>-2(2)</td>
<td>-1(2)</td>
</tr>
<tr>
<td>O₃</td>
<td>7(3)</td>
<td>11(3)</td>
<td>14(3)</td>
<td>2(2)</td>
<td>1(2)</td>
<td>-0.1(19)</td>
</tr>
<tr>
<td>O₄</td>
<td>7(2)</td>
<td>14(3)</td>
<td>8(3)</td>
<td>0(2)</td>
<td>-2(2)</td>
<td>-3(2)</td>
</tr>
</tbody>
</table>

as implemented in VASP, with U = 2 or 3 eV for the Mn d states.²⁴,⁴³ In addition, the electronic-band-structure calculations with U = 0, 1.5, or 3 eV for the Ta d states were performed to verify the nature of the conduction band. Finally, to study the optical properties of the oxide, the complex dielectric function, ε(ω) = ε₁(ω) + iε₂(ω), was calculated based on the electronic band structure and polarization and momentum operators.⁴⁴ The imaginary part, ε₂(ω), is related to the optical absorption at a given frequency ω.

3. RESULTS AND DISCUSSION

Structure Comparison. The crystallographic and acquisition parameters of a single-crystal of Mn₃Ta₂O₈ are provided in Table 1, with the previously reported structure solutions determined via powder neutron diffraction (ND) and synchrotron powder XRD.⁵,⁷ In the first report of the Mn₃Ta₂O₈ structure, electron diffraction data suggested both a primitive space group and a larger c axis (multiplied by 3 or 6).⁵ Neither of these were evident in the single-crystal structure solution. In precession images of the collected data (see the Supporting Information, SI), the structure solution reported herein accounts for all major reflections. There are some background-level reflections that could be a result of a superstructure, but primitive tetragonal lattices and/or larger c axes produce inferior fitting of the major reflections.

The major difference between these structure solutions is the contraction of the single-crystal lattice parameters, and a experiences a greater change than c. This contraction can be attributed to the lower temperature at which the single-crystal data were collected. A second consequence of this contraction is a reduction in the interatomic distances of the single-crystal sample, provided in Table 2. The atomic positions, provided in Table 3, are very similar. Anisotropic thermal displacement parameters for the single-crystal structure are provided in Table 4.

The anion-deficient, fluorite-related Mn₃Ta₂O₈ structure’s cation topology is an approximate cubic-close-packed cation lattice (the distorted, face-centered-cubic motif is shown in Figure 3) and maintains four distinct cation coordination environments: four-coordinate (Mn₃), six-coordinate (Ta), seven-coordinate (Mn₁), and eight-coordinate (Mn₂). Each coordination polyhedron can be compared to the ideal cube of fluoride if the cube is distorted and missing anions.⁷ This results in a complex cation network, as shown in Figure 4, which has two compositionally unique layers on unusual angles with inversion operations that produce the ABC motif of the cubic-close-packed system. The odd angles arise from the tetragonal cell because the close-packed layers in fluoride can be viewed in the [1 0 1] direction, which is the face diagonal of the cubic cell. With a tetragonal cell, however, the same diagonal becomes distorted, making layer designation difficult. This complexity, however, can be simplified by extracting a single close-packed layer, as given in Figure 5.⁴⁴ Inside each layer, there is a repeating rectangular unit of 20 atoms (12 Mn and 8 Ta) that can be used to generate the entire cation occupancy. Each adjoining unit, in all directions, is translated by a single row of atoms. Furthermore, all of the close-packed layers in Mn₃Ta₂O₈ share this repeating unit; that is, the layers are identical. The differences in the unit cell layers are the result of shifts and inversions, but this overall pattern is maintained in each layer.

Optical Band Gap. The optical band gap of Mn₃Ta₂O₈ was characterized through analysis of the fundamental absorption...
edge in collected absorbance spectra. The band gap was approximated as the intersection between a linear extrapolation of the band edge and the background in the plot of the absorption coefficient, \( \alpha \), versus incident photon energy, \( h\nu \), as depicted in Figure 6. This method does not assume that the band gap is direct or indirect and yields a transition energy of 1.89 eV, which is consistent with the reddish brown color of the crystal. Absorbance spectra collected at other locations on the crystal confirm this result. Results from Laue diffraction show that the [001] crystal axis was oriented roughly collinear with the illumination direction. For reference, the plots and band gaps obtained with \( \alpha^2 \) and \( \alpha^{1/2} \) versus \( h\nu \) are provided in the SI (with transition energies of 1.97 and 1.83 eV, respectively).

Although the electronic band structure in Figure 7 does show an indirect band gap, the energy difference between the direct and indirect gaps is minute. As the nature of the optical band gap is unclear, we instead report an approximate transition energy derived from the absorption coefficient spectrum.

**Electronic Band Structure.** According to the previously reported magnetic characterization of Mn\(_3\)Ta\(_2\)O\(_8\), it has a complex antiferromagnetic (AFM) structure, which is assigned to a strong exchange coupling along the helical strings of Mn\(_1\) atoms connected via short bonds with O3 atoms (cf. Table 2). The electronic band structure of AFM Mn\(_3\)Ta\(_2\)O\(_8\) as obtained from GGA+U calculations with \( U = 2 \) eV for the Mn d states (left) and the corresponding total (middle) and partial (right) DOS. The partial DOS is spin-resolved. The Fermi level is at 0 eV.

This agrees with our spin-polarized GGA+U calculations, which show that the total energy of the AFM configuration is 0.344 eV lower than the total energy of the ferromagnetic (FM) state. The calculated magnetic moments on Mn atoms are 4.54, 4.58, and 4.44 \( \mu_B \) in the FM configuration and \( \pm4.52 \), \( \pm4.57 \), and \( \pm4.42 \mu_B \) in the AFM configuration for Mn\(_1\), Mn\(_2\), and Mn\(_3\), respectively. These values are in accordance with the reported magnetic moment of 4.0 \( \mu_B \). The calculated band gaps, 1.7 eV for the FM case and 2.1 eV for the AFM case, are nearly equally close to the experimentally determined value of 1.89 eV.

The electronic band structure of AFM Mn\(_3\)Ta\(_2\)O\(_8\) calculated within GGA+U with \( U = 2 \) eV for the Mn d states is shown in Figure 7. Both the top of the valence band and the bottom of the conduction band show low-energy dispersion for the bands calculated along the high-symmetry directions of the Brillouin zone. The bottom of the conduction band consists of a single band that is split from the rest of the bands. From the total and projected density of states (DOS), the valence band consists of the hybridized Mn d–O p states, whereas the Ta s (the single band at the bottom) and d states are the major contributors to the conduction band bottom. The structure of Mn\(_3\)Ta\(_2\)O\(_8\) contains three crystallographically nonequivalent types of Mn atoms, Mn\(_1\), Mn\(_2\), and Mn\(_3\), which are seven-, eight-, and
four-coordinate with O atoms, respectively (cf. Table 2). The projected DOS (cf. Figure 7) reveals that only the states of Mn1 and Mn3 contribute near the top of the valence band. Therefore, the Mn1 and Mn3 states are expected to control the electronic transitions across the band gap.

To verify the nature of the conduction band, additional calculations with \( U = 0, 1.5, \) and 3 eV for the Ta d states were performed. Apart from the slight increase of the band gap by 0.3 eV as the on-site Coulomb value increased from 0 to 3 eV, the unoccupied Ta d states governed the bottom of the conduction band independent of the U value. Similarly, an increased value of Coulomb \( U \) for the Mn d states, namely, from 2 to 3 eV, resulted in a larger band-gap value of 2.4 eV in the AFM case, whereas the nature of the valence and conduction bands remained unchanged. We note here that the peculiar electronic band structure of Mn3Ta2O8 with Mn or Ta states governing the valence or conduction bands, respectively, suggests a possibility for controlled carrier generation via targeted substitutional doping, as has been performed for other Mn2+ materials.25

Finally, the real and imaginary parts of the dielectric constant were calculated to understand the optical properties of Mn3Ta2O8. The results, given in Figure 8, verify the onset of the electronic dielectric function for Mn3Ta2O8.

\[ \text{Figure 8. Calculated imaginary (solid line) and real (dotted line) parts of the complex dielectric function for Mn}_3\text{Ta}_2\text{O}_8. \]

4. CONCLUSION

Mn3Ta2O8, a specific composition in the complex Mn−Ta−O system, was targeted for crystal growth, and large crystals were successfully obtained via the optical floating-zone method. The crystal structure of this material agrees well with prior powder X-ray diffraction studies, with a slight lattice contraction as a result of differing collection temperatures. This structure is an example of a rare fluorite-related tetragonal phase that contains different cation coordination environments and a complex cation topology with repeating units of 20 cations. Absorbance spectroscopy determined the approximate band gap as 1.89 eV, which agrees with the calculated electronic band structure and optical properties. The validity of the electronic structure is corroborated by its agreement with the previously reported magnetic characterization of Mn3Ta2O8. The electronic structure also shows that the absorption edge is governed by the four- and seven-coordinate Mn sites.

ASSOCIATED CONTENT

Supporting Information

X-ray crystallographic data in CIF format, coordinate transformations, precession X-ray images, orientation determination, alternative band-gap calculations, AFM configuration, and GGA (no U) DOS plots. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.5b00853.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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