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Discovery of a Ternary Pseudobrookite Phase in the Earth-Abundant Ti-Zn-O System

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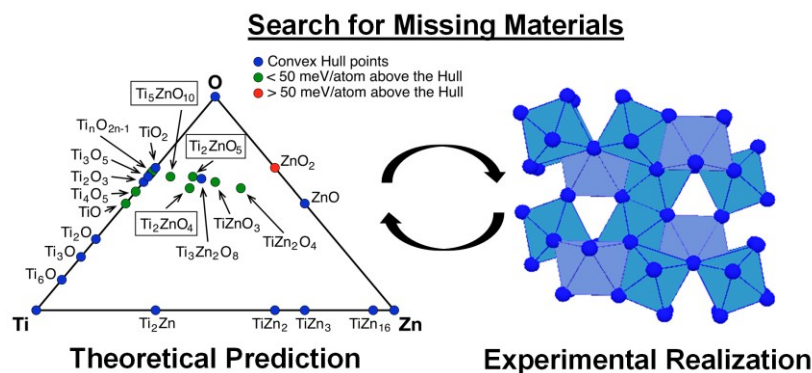
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Abstract

We combine theory with experiment in searching for “missing,” stable materials within the Zn-Ti-O chemical system, leading to the discovery of a new pseudobrookite phase, $Zn_xTi_{3-x}O_{5-\delta}$. This ternary system was chosen for 1) technological relevance, 2) earth abundance, and 3) the fact that many compounds in this system are predicted from enthalpies of formation to be borderline stable, suggesting an important role of entropic contributions in their stabilization and making this

chemical system a perfect test bed for exploring the limits of theoretical predictions. The initial set of exploratory experimental syntheses, via sintering in evacuated ampoules and quenching, resulted in a single phase $\text{Zn}_x\text{Ti}_{3-x}\text{O}_{5-\delta}$ composition with $x \approx 0.6$ and an almost stoichiometric oxygen content, as evaluated by X-ray fluorescence, energy dispersive spectroscopy, thermogravimetric analysis, and X-ray photoelectron spectroscopy. The theoretically calculated lowest energy crystal structure for the closest stoichiometric $\text{ZnTi}_5\text{O}_{10}$ composition matched that measured experimentally by synchrotron X-ray diffraction (allowing for differences attributable to cation disorder). The measured broad optical absorption, n-type electrical conductivity, and stability in acidic media are comparable to those of other ternary pseudobrookites and Ti-O Magnéli phases, suggesting comparable applicability as a robust electrode or catalyst support in electrochemical devices or water remediation. However, the new phase decomposes upon heating in air as it oxidizes. The success of the present approach to identify a “missing material” in an earth-abundant and applications-rich system suggests that future efforts to experimentally realize and theoretically confirm missing materials in this and similar systems are warranted, both scientifically and technologically.

1. Introduction

The prediction and realization of “missing materials” – compounds that have previously not been reported and are absent from databases such as the Inorganic Crystal Structure Database (ICSD)¹ – represents a new approach to discovery of scientifically and technologically important materials, with potential impact across a wide range of applications. This discovery process is accelerated by leveraging high-throughput theoretical calculations in combination with targeted experimental synthesis and characterization. In recent demonstrations of this approach^{2,3,4,5} new compounds, including previously unknown ABX compositions^{2,3} and new sodium carbonophosphates^{4,5}, were predicted to be stable using theory and high-throughput computations,

then successfully synthesized based purely on theoretical predictions of their existence. In the present work we apply a similar approach, iterating between theory and experiment, to oxide materials, and in particular, to the Zn-Ti-O ternary phase space.

The Zn-Ti-O system is both relatively earth-abundant⁶ and technologically significant. In air, the compounds ZnO (typically wurtzite), Zn₂TiO₄ (inverse cubic spinel), ZnTiO₃ (rhombohedral ilmenite), Zn₂Ti₃O₈ (cubic defect spinel), and TiO₂ (rutile/anatase/brookite) have already been identified^{7,8,9,10} and applied as wide bandgap semiconductors in photovoltaic cells and transparent electronics^{11,12}, photocatalysts for water splitting and water remediation^{13,14,15,16,17}, sensors¹⁸, microwave dielectrics¹⁹, pigments^{20,21}, and sunscreens²². At lower oxygen partial pressures, the Magnéli phases (Ti_nO_{2n-1}) are known stable compounds in the Ti-O binary system²³; selected compositions have been applied as robust electrodes for electrochemical cells and as catalyst substrates²⁴. Table 1 provides further information about the structures of these known compounds. In contrast to the binary Ti-O system, the ternary Zn-Ti-O system has not been extensively studied at low oxygen partial pressures/ chemical potentials, to the authors' knowledge. This region of the phase space represents uncharted territory, where as-yet-undiscovered, stable materials may exist.

Table 1: List of the phases considered in the theoretical part of the work. We list the compound chemical formula, international space group number and the ICSD number (in parentheses), distance to the convex hull and the enthalpy of formation calculated using the FERE approach (experimental ΔH_f [27] are given in parentheses) in both eV/atom and kJ/mol.

Compound formula	chem.	Intl. Space Group No. (ICSD No.)	Distance to Convex Hull [eV/atom]	ΔH_f^{FERE} ($\Delta H_f^{\text{exp.}}$)	
				[eV/atom]	[kJ/mol]
Ti-O binaries					
TiO ₂		136 (009161)	0.000	-3.24 (-3.26)	-941.60 (-944.7)
Ti ₉ O ₁₇		2 (009042)	0.008	-3.22	-8084.44
Ti ₈ O ₁₅		2 (035123)	0.008	-3.22	-7148.29
Ti ₇ O ₁₃		2 (009040)	0.009	-3.22	-6210.10
Ti ₆ O ₁₁		2 (035121)	0.011	-3.21	-5269.62
Ti ₅ O ₉		2 (009038)	0.014	-3.20	-4330.58
Ti ₄ O ₇		2 (010148)	0.011	-3.20	-3399.68
Ti ₃ O ₅		63 (020361)	0.000	-3.20 (-3.18)	-2472.75 (-2459.4)
Ti ₂ O ₃		167 (006095)	0.000	-3.13 (-3.15)	-1511.58 (-1520.9)
Ti ₄ O ₅		87 (077697)	0.008	-2.92	-2532.72
TiO		12 (015327)	0.008	-2.65 (-2.69)	-512.41 (-519.7)

Ti ₂ O	164 (023574)	0.000	-1.88	-543.94
Ti ₃ O	163 (024082)	0.000	-1.46	-565.24
Ti ₆ O	159 (017009)	0.000	-0.88	-594.03
Zn-O binaries				
ZnO	186(167690)	0.000	-1.77 (-1.80)	-341.70 (-348.28)
ZnO ₂	205(60763)	0.174	-1.01	-291.51
Ti-Zn binaries				
TiZn ₂	194 (106184)	0.000	-0.26	-76.34
TiZn ₃	221 (106185)	0.000	-0.20	-76.52
TiZn ₁₆	63 (106186)	0.000	-0.05	-78.30
Ti ₂ Zn	139 (653304)	0.000	-0.21	-60.41
Ti-Zn-O ternaries				
TiZnO ₃	148 (022382)	0.034	-2.63 (-2.70)	-1268.38 (-1302.5)
TiZn ₂ O ₄	91 (109093)	0.022	-2.38 (-2.44)	-1611.44 (-1647.7)
Ti ₃ Zn ₂ O ₈	212 (083525)	0.000	-2.80	-3511.67
Ti ₂ ZnO ₄ *	227	0.002	-2.78	-1878.42
Ti ₂ ZnO ₅ *	63	0.023	-2.86	-2207.63
Ti ₅ ZnO ₁₀ *	63	0.018	-3.02	-4670.31

* Previously unknown (unreported) Ti-Zn-O phases

Recent theoretical work²⁵ suggested the possible existence of an unreported ternary Ti₂ZnO₄ phase under highly reducing conditions (high temperatures and low oxygen partial pressures). The authors predicted 100 new metal-chalcogenides with A₂BX₄ stoichiometry, to be stable with respect to decomposition. The stability of the Ti₂ZnO₄ phase, on the other hand, lay within the error bars of the theoretical enthalpies of formation, ~50 meV/atom ≈ 1 kcal/(mol atom) ≈ 5 kJ/(mol atom)²⁶. In addition to the relative abundance of its constituent elements and its wide-ranging utility, the Ti-Zn-O system is particularly interesting as a case study for exploring the existence of new compounds and exploring the limits of the current theoretical approaches, because the stability of all *known* ternary phases also lies within this narrow range. For example, using measured enthalpies of formation (see Table 1 and Ref. ²⁷), the enthalpy of the decomposition reaction TiZnO₃ → TiO₂ + ZnO is only ΔH = 20 meV/atom = 1.93 kJ/(mol atom); similarly, the reaction TiZn₂O₄ → TiO₂ + 2ZnO has a positive enthalpy of only ΔH = 10 meV/atom = 0.92 kJ/(mol atom). Therefore, finite temperature effects such as configurational and/or vibrational entropy

could be of importance in deciding the stability of phases, and potentially many new stable phases remain to be synthesized in this phase space.

In this paper we report the synthesis and experimental characterization of a new, pseudobrookite-structured compound, $Zn_xTi_{3-x}O_5$ ($x \approx 0.6$ in the present work) along with a more in-depth theoretical study of its stability.

2. Experimental Approach

2a. Synthesis

Owing to the volatility of ZnO in reducing conditions, synthesis in flowing gas in a tube furnace was avoided. Instead, stoichiometric amounts of dried ZnO (99.99%, Alfa Aesar, Ward Hill, MA) and Ti_2O_3 (99.9%, Sigma-Aldrich, St. Louis, MO) in a Zn:Ti:O atomic ratio of 1:2:4 were ground together with an agate mortar and pestle, pressed into pellets at ~ 120 MPa, and individually sealed under vacuum in quartz ampoules. (This ratio was chosen to initially target the missing compound Ti_2ZnO_4 .) Pellets were sintered in the evacuated ampoules at 750-1100°C, with heating at 5°C/min and cooling by quenching to room temperature. Table 2 lists synthesis conditions and outcomes in terms of phase composition. Certain pellets contained intentional excess ZnO in an attempt to compensate for the slight loss of Zn/ZnO onto ampoule walls during high temperature processing.

Table 2: Synthesis conditions and phase outcomes of pellets sintered and quenched in evacuated ampoules.

Zn:Ti:O in pressed pellet (atomic ratio)	Sintering Temp. (°C); Time (h)	Phase(s) by XRD
1 : 2 : 4	1100; 60	Magneli phase, Ti_nO_{2n-1} (n=7,8) + pseudobrookite*
1.32 : 2 : 4.32	1100; 60	Pseudobrookite*
1.32 : 2 : 4.32	1100; 401	Pseudobrookite*
1 : 2 : 4	750; 168	Spinel(s) + rutile
1 : 2 : 4	800; 336	Spinel(s) + rutile*

* evaporation of Zn or ZnO onto ampoule observed

2b. Characterization

Structure: The phase composition of quenched samples was identified by room temperature powder X-ray diffraction, using an XDS2000 diffractometer (Scintag Inc., Cupertino, CA) or a DMAX diffractometer (Rigaku, The Woodlands, TX), with a step size of 0.02° over the 2θ range $25-80^\circ$ (using Cu $K\alpha$ radiation), and a dwell time of 1s. Selected samples were also measured with high resolution synchrotron powder diffraction using the rapid access program at beamline 11-BM of Argonne National Laboratory's Advanced Photon Source, with an average wavelength of 0.413076\AA . The diffracted intensities were measured by twelve discrete detectors covering an angular range from -6 to $16^\circ 2\theta$, which were scanned over a $34^\circ 2\theta$ range, with data points collected every $0.001^\circ 2\theta$ at a scan speed of $0.01^\circ/\text{s}$. The 11-BM diffractometer was calibrated using NIST standard reference materials, and the data were corrected for 2θ offset, source intensity fluctuations, detector sensitivity, and small ($\sim 1\text{eV}$) differences in wavelength between detectors. Rietveld analysis, using JADE 9 (Materials Data, Inc.) and GSAS²⁸ (with the EXPGUI interface) programs, was employed to examine phase purity, structure, and lattice parameters.

Composition: Bulk chemical composition (cation ratio) was analyzed quantitatively using X-ray fluorescence (XRF), with a Maxxi5/PIN instrument (Roentgenanalytik Messtechnik GmbH, Taunusstein, Germany), XMASTER data acquisition software (Roentgenanalytik Messtechnik GmbH, Taunusstein, Germany), and MTFPP data analysis software (Matrix Metrologies, Ronkonkoma, USA). Cation content was also mapped semi-quantitatively on a fracture surface with energy dispersive spectroscopy (EDS) in a S4800 FE-SEM (Hitachi High- Technologies, Schaumburg, IL). Surface chemical composition and oxidation states were evaluated with X-ray photoelectron spectroscopy (XPS) using an Omicron ESCA (Electron Spectroscopy for Chemical Analysis) probe with Al $K\alpha$ excitation. Multiple spectra taken from three different locations on the sample, after manually grinding off the as-sintered surface, were fit using the program XPSPEAK²⁹ to determine the location and integrated intensity of each peak after background subtraction. During the fitting process, the splitting between Ti $2p_{3/2}$ and $2p_{1/2}$ energies was constrained to 5.7 eV for Ti^{4+} and 5.2

eV for Ti^{3+} peaks³⁰. The intensity ratio for Ti $2p_{3/2}$: $2p_{1/2}$ was constrained as 2 : 1. Energies were calibrated using the adventitious C 1s signal. Atomic concentrations (C) of Zn and Ti were determined from Ti and Zn $2p_{3/2}$ peak intensities (I) and calibrated sensitivity factors (S) for these peaks, using the equation:

$$C_i = \frac{I_i/S_i}{\sum_i I_i/S_i}$$

where i refers to the cation species (C_i in this case is a cation ratio, e.g., $\text{Zn}/(\text{Zn}+\text{Ti})$ or $\text{Ti}^{3+}/(\text{Ti}^{3+}+\text{Ti}^{4+})$).

The oxygen content in the pseudobrookite phase was determined using thermogravimetric analysis (TA Instruments 2950, New Castle, DE) by measuring the mass increase of the sample as it oxidized to known phases in air during heating at 2 °C/min from 26 to 800 °C. The final mass after cooling to room temperature at the same rate was identical to the mass at 800 °C. Decomposition into other phases occurred during the process, as noted by a post-measurement X-ray diffraction pattern (see results section). Subsequent TGA measurements of fresh samples to 1000 °C in N_2/O_2 mixtures confirmed that there was no significant further mass change above 800 °C.

Electrical and Optical Properties: Room temperature electrical conductivity was measured (after grinding off the pellet surfaces) with a spring-loaded, collinear four-point probe (Cascade Microtech, Beaverton, OR, model C4S-44-1S); current was applied via the outer probes using a Keithley current source (model 224, Keithley Inc., Cleveland, OH), and voltage was measured between the inner probes with a digital multimeter (model 195A, Keithley Inc.). Ohmic behavior was confirmed, and sample resistivities were determined from the average slopes of 3 current-voltage plots using the following equation; there was no correction for porosity:

$$\rho = \frac{\pi}{\ln(2)} t \left(\frac{V}{I} \right) f_1 f_2$$

where t is sample thickness, V is voltage, I is current, and f_1 and f_2 are correction factors for finite thickness and finite diameter^{31,32}. Thermopower close to room temperature ($T_{\text{ave}} = 32.5^\circ\text{C}$) was measured in a custom-built setup, which clamps the sample between a heat source and heat sink, each attached to type S thermocouples. Voltage and temperature differences across the pellet were measured every 3 seconds while the temperature difference decreased from $\Delta T=20$ to 0°C . Thermopower, $\lim_{\Delta T \rightarrow 0} (-\Delta V/\Delta T)$, was calculated from the slope of the $-\Delta V$ vs. ΔT plot, with a correction for the reference junction temperature. Diffuse reflectance spectroscopy, using a Lambda 1050 UV/Vis/NIR spectrophotometer with an integrating sphere attachment (PerkinElmer, Oak Brook, IL), was used to examine the optical properties. The 100% reflectance baseline spectrum was measured using a pressed polytetrafluoroethylene powder compact.

3. Theoretical Approach

Theoretical predictions of the existence of new compounds require solving two rather complex problems, as explained in more detail in Ref. 25. The first problem is the prediction of the structure of an unknown phase, and the second, given the structure, is the determination of whether the hypothetical new compound is thermodynamically stable with respect to decomposition into competing phases (combinations of pure elements and other binary and/or ternary phases). The approach used to answer these two questions is based on the knowledge of the total energies of solid-state systems, which are calculated using Density Functional Theory (DFT) with an additional Hubbard term (DFT+U) within the generalized gradient approximation (GGA). Parameterization of the GGA exchange-correlation functional proposed by Perdew, Burke and Ernzerhof³³ is used in this work as implemented in VASP computer code³⁴. Only the valence electrons are treated explicitly and the valence-core interactions are modeled within the projector augmented wave method³⁵. A rotationally invariant DFT+U approach was employed³⁶ with a constant $U = 3$ eV value for all transition metals except Cu and Ag, for which we used $U = 5$ eV. For

all non-transition metal elements as well as for Zn, Cd, and Hg, the Hubbard U parameter was set to zero. A Monkhorst-Pack k-point sampling³⁷ was applied with all total energies converged within 3 meV/atom with respect to the number of k points. The plane wave cutoff was set to the value 30% higher than the highest suggested value by the employed pseudopotentials (e.g., 520 eV for oxygen). Further details about the theoretical/numerical approach (type of the pseudopotentials, cutoffs, k-point sampling, etc.) are given in refs. 25 and 26.

Structures of all known phases considered in this work have been taken from the ICSD¹. We restrict this study to only fully stoichiometric compounds within the Ti-Zn-O chemical system. This includes 14 different Ti-O binary phases, 2 different Zn-O binary phases, 4 different Ti-Zn intermetallic compounds, and three known Ti-Zn-O ternary systems which are all given in Figure 4 and Table 1 together with their structures (more precisely the international space group number) and the ICSD number. In cases where multiple inequivalent entries exist in the ICSD, we calculate total energies of all such entries and report here only the lowest energy structure. In addition, we include in this study three heretofore unknown/unreported ternary phases: (i) Ti_2ZnO_4 in the normal spinel structure as reported in ref. 25, (ii) Ti_2ZnO_5 , assumed to have the ICSD-reported structure of the known, chemically similar, Ti_2MgO_5 compound, and (iii) $\text{Ti}_5\text{ZnO}_{10}$ phase, fully stoichiometric, with the composition close to the phase synthesized for the first time and reported in this work, assumed to have the lowest-energy pseudobrookite structure of the known Ti_3O_5 binary phase (space group #63) in which one out of six Ti atoms (two formula units) is replaced by one Zn atom. Inclusion of this structure in our study was motivated by the knowledge of the chemical composition resulting from the initial experimental efforts.

Stability at zero temperature of different phases with respect to decomposition can be analyzed by plotting the convex hull in the 4-dimensional, composition-enthalpy of formation space. The convex hull of any set of points encloses the smallest possible volume of this space in such a

way that all lines connecting any two points lie within the same volume. In the present case, points consist of three coordinates (n,l,m) defining the composition $(\text{Ti}_n\text{Zn}_m\text{O}_l)$ and the fourth being the enthalpy of formation (ΔH_f) . The compounds represented by the points that lie on the convex hull are predicted to be stable, whereas those that are located inside the convex hull are predicted to be unstable with respect to decomposition. The distance of the compound from the convex hull, i.e., the shift of its ΔH_f value that, for a given fixed composition, brings the compound to the convex hull, can be used to estimate how “unstable” the compound actually is.

To perform this kind of stability analysis we used the recently developed FERE approach²⁶ to calculate ΔH_f values of compounds. FERE stands for Fitted Elemental-phase Reference Energies, which are actually semi-empirically determined total energies of pure elements in their conventional phases, constructed to provide accurate ΔH_f values when combined with GGA total energies of compounds. It has been demonstrated in Ref. 26 that this approach overcomes the problems that standard approximations to DFT, e.g. pure GGA, have in reproducing measured enthalpies of formation, and it is currently the most accurate way of computing ΔH_f of compounds, achieving an accuracy of ~ 50 meV/atom ≈ 1 kcal/(mol atom) ≈ 5 kJ/(mol atom). In Table 1, calculated enthalpies of formation are given for all phases considered. Existing experimental ΔH_f values from Ref. 27 are also provided (both in eV/atom and in kJ/mol). The largest relative deviation of the FERE values compared to the measured ones is 2.6 % (TiZnO_3), while the average relative deviation, i.e. the expected relative error, amounts to ~ 1.4 %. Alternatively, in cases where main decomposition reactions do not include pure elemental phases, it has been shown that an equally accurate stability analysis can be performed from pure density functional theory (or DFT+U)³⁸ as evidenced by similar distances from the convex hull reported by the Materials Project³⁹ for the Ti-Zn-O compounds from ICSD.

The Ti-Zn intermetallic compounds are special cases. As noted in Ref. 26, the FERE method is constructed for application to metal-nonmetal compounds for which the DFT based methods are known to make severe errors. FERE is not supposed to work as well when applied to intermetallics, because of the different nature and magnitude of the DFT error when computing enthalpies of formation. Namely, as discussed in greater detail in Ref. 26 in metal-nonmetal compounds the DFT error is dominated by the insufficient error cancelation between the compound (ionic system) and its elemental constituents (pure metals and/or molecules). In case of intermetallic systems both the compound and the elements are physically and chemically more similar (metallic) and pure DFT is expected to provide more accurate enthalpies of formation. The FERE method is constructed to deal with the errors in ionic systems and cannot be expected to perform well for intermetallic systems. Therefore, the ΔH_f values of Ti-Zn compounds presented in Table 1 are calculated using pure GGA for both compound total energies and the total energies of pure solid Ti and solid Zn.

4. Results: Experimental

Structure: A synchrotron powder X-ray diffraction pattern for the phase is shown in figure 1. Apart from trace (intensity < 200) unidentified peaks at $2\theta = 3.40, 5.88, 8.35, 8.99, 9.34, 10.22,$ and 10.50° , the peak locations and intensities are consistent with an orthorhombic pseudobrookite phase (space group Cmcm, #63) and match quite well with PDF 01-080-1213 for FeTi_2O_5 , a known pseudobrookite-structured compound. The pattern does not match quite as well with PDF 01-089-4733 for unsubstituted Ti_3O_5 with the pseudobrookite structure, which may result from the difference in lattice parameters, suggesting Zn incorporation. The pattern also exhibits significant differences vs. lower-symmetry Ti_3O_5 (e.g., PDF 01-082-1138, space group C2/m), which may result from both the high processing temperature and the incorporation of Zn into the lattice. While pure Ti_3O_5 transitions from a distorted monoclinic pseudobrookite to an orthorhombic pseudobrookite only above $\sim 500\text{K}$ ⁴⁰, it has been reported that impurities and intentional substitution for Ti in Ti_3O_5

improve the symmetry and stabilize the orthorhombic structure to lower temperatures^{40,41}. In fact the symmetric structure of pure Ti_3O_5 is reportedly not maintained even upon quenching to room temperature⁴², so the higher symmetry in the present case is possible evidence of Zn substituting on Ti sites. As calculated from integrated peak intensities, the sample appears to be 99.9 wt% phase-pure.

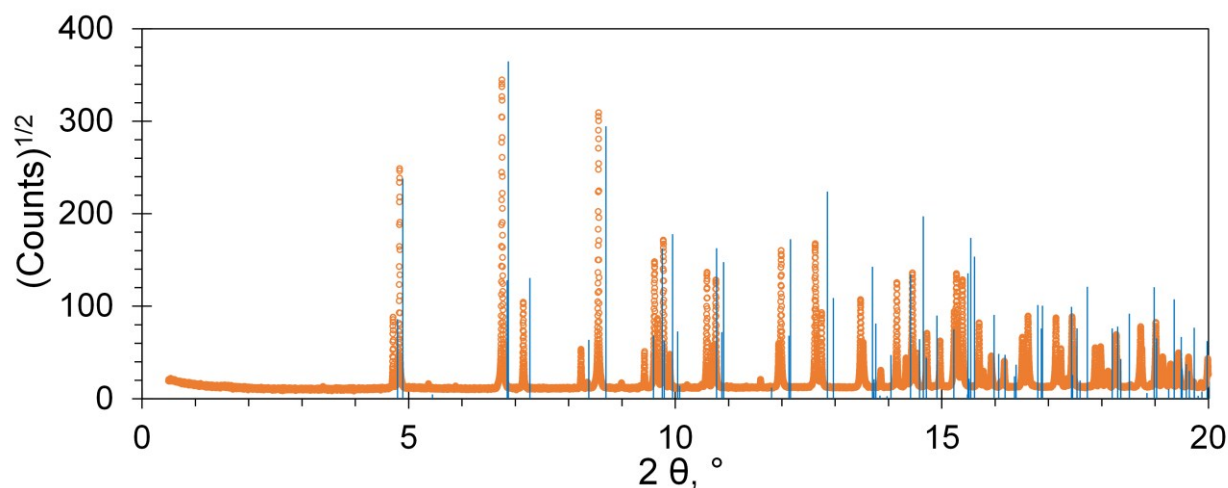


Figure 1: Synchrotron ($\lambda=0.413076 \text{ \AA}$) powder X-ray diffraction pattern for pseudobrookite phase (circles), cropped to first 20° of 50° measured and refined, compared to the pattern simulated from the theoretically predicted lowest energy structure (lines). The offset between patterns at higher angles is due to slightly different lattice parameters, as discussed in the text.

During Rietveld refinement, varying types of peak asymmetry and broadening were observed in different families of peaks, such that the profile function could not be adequately modeled. Peaks in the $\{010\}$ family, such as (020), are symmetric, while peaks outside of this family, such as (022), are asymmetric in different directions. The observed lack of asymmetry for peaks in the $\{010\}$ family may be attributed to stacking faults in the $[010]$ direction. The shifting of planes in the $[100]$ and/or $[001]$ directions causes broadening of peaks that are not in the $\{010\}$ family. Such shifts may be related to the structural changes that occur in the transformation between lower and

higher symmetry pseudobrookite phases; it is known that the transition from low temperature α to high temperature β (and β') Ti_3O_5 structures is accomplished primarily by displacement of atoms in the a-c plane^{40,42}. Steiner *et al.*⁴⁰ also noted the possibility of twinning during the gradual transition between the intermediate-temperature distorted monoclinic pseudobrookite (β) and the high-temperature, orthorhombic pseudobrookite (β') phases. Grains in the present sample were observed to be relatively large (2-3 μm) and equiaxed, so anisotropic microstrain and/or size effects originating in acicular particles are not thought to be responsible for the peak profile effects. Experimental lattice parameters are $a=3.756$, $b=9.800$, $c=10.056$; these values are quite close to those reported for FeTi_2O_5 ⁴³.

Composition: The bulk cation ratios analyzed by X-ray fluorescence for the as-prepared pseudobrookite, the up-oxidized sample, and the pseudobrookite synthesized with an extended sintering time were $\text{Zn}/(\text{Zn}+\text{Ti})=0.202$, 0.203 , and 0.215 , respectively. Uncertainty in $\text{Zn}/(\text{Zn}+\text{Ti})$ was 0.0013 and in $\text{Ti}/(\text{Zn}+\text{Ti})$ was 0.008 . The EDS mapping showed that Zn was incorporated uniformly in the grains and did not appear to form a second phase or segregate exclusively to grain boundaries; the average cation ratio from EDS was $\text{Zn}/(\text{Zn}+\text{Ti})=0.19\pm 0.03$ (4 measurements). Sample XPS peaks of Ti and Zn 2p, with fitting, are shown in figure 2. The Ti^{3+} $2p_{3/2}$ peak was identified as a low energy shoulder on the Ti^{4+} $2p_{3/2}$ peak at 456.8 eV, while Ti^{4+} was ascribed to the main Ti $2p_{3/2}$ peak at 458.6 eV. The Zn $2p_{3/2}$ peak was at 1021.6 eV. These binding energies are consistent with reported values^{30,44}. By XPS the average, semi-quantitative, cation ratio on the surface was $\text{Zn}/(\text{Zn}+\text{Ti})=0.144\pm 0.006$ (3 measurements). The ratio of Ti^{3+} to Ti^{4+} at a freshly exposed surface was also studied; results suggested that a relatively small amount of the Ti was in the 3+ state at the surface (4-9%).

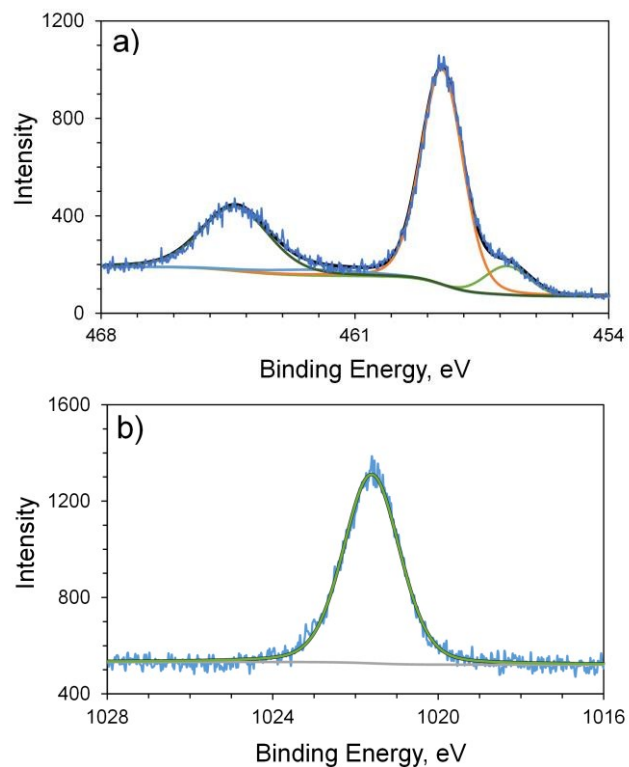


Figure 2: X-ray photoelectron spectra of Ti 2p_{3/2} and 2p_{1/2} (a) and Zn 2p_{3/2} (b) peaks, with fits shown. Data in these scans are the average of 3 sweeps at this location without smoothing.

The mass change that was measured by TGA, upon heating of the pseudobrookite sample in air, is shown in figure 3. It can be seen that most of the mass change occurred between 250 and 450 °C, and the overall increase in mass (measured after cooling to room temperature) was 3.1%. This increase of mass is attributed to the uptake of oxygen from the air atmosphere, since the Zn:Ti ratio, measured by XRF before and after the TGA run, did not change (within error). The absence of further mass change upon cooling suggests that the sample was fully oxidized at 800 °C. Subsequent measurements on fresh samples confirmed no significant additional mass gain upon heating above 800 °C and additionally demonstrated comparable mass gains in 20% O₂ / 80% N₂ vs. 100% N₂, the only difference being a more gradual mass uptake up to 750 °C in pure N₂. After the TGA measurement, room temperature X-ray diffraction (and a color change from dark grey to pale tan/orange) of the sample indicated that it had decomposed into rutile TiO₂ with small amounts of

$\text{Zn}_2\text{Ti}_3\text{O}_8$ and ZnTiO_3 present. The composition of the initial pseudobrookite phase was calculated by two approaches. By the first method, assuming 3 cations per formula unit and complete up-oxidation of the Ti ions by the end of the TGA measurement, and using the cation ratio determined from XRF, the initial composition of the pseudobrookite sample can be calculated from the weight gain as $\text{Zn}_{0.61}\text{Ti}_{2.39}\text{O}_{4.94}$. By the second method, Rietveld refinement on the X-ray diffraction pattern of the post-TGA products was performed using the JADE 9 software. The initial cation ratio, $\text{Zn}/(\text{Zn}+\text{Ti})$, determined from the quantitative phase results, was 0.2134, in good agreement with the measured value by XRF. Then the relative amounts of each constituent phase were adjusted within the error bars from the initial analysis to satisfy the constraint that $\text{Zn}/(\text{Zn}+\text{Ti}) = 0.2025$ from XRF analysis. Using the resulting final phase composition and the mass gain, the composition of the as-prepared pseudobrookite was again determined to be $\text{Zn}_{0.61}\text{Ti}_{2.39}\text{O}_{4.94}$. Within uncertainty both methods agree that the Zn-Ti-O pseudobrookite composition is close to the nominal formula, M_3O_5 .

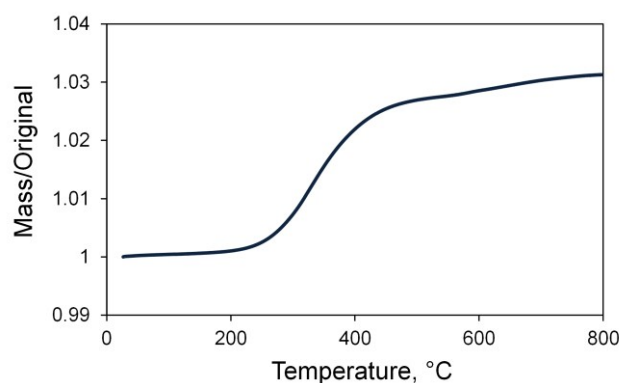


Figure 3: Thermogravimetric analysis (TGA) of pseudobrookite phase upon heating in air at 2 °C/min. Subsequent TGA showed that there was no significant further mass gain above 800 °C.

Electrical and Optical Characterization: The room temperature conductivity and thermopower of the pseudobrookite sample were 1.88 ± 0.06 S/cm (3 measurements) and -133 $\mu\text{V}/\text{K}$, respectively. The sign of the thermopower indicates n-type conductivity. The

conductivity reported is uncorrected for porosity. Diffuse reflectance spectra did not reveal an optical absorption onset in the wavelength range measured (300-1200 nm); rather, the dark grey sample absorbed relatively uniformly over all wavelengths studied.

5. Results: Theoretical

Theoretical (computational) results are summarized in Figure 4 and Table 1. In Figure 4 all Ti-Zn-O phases included in our study, both known and unknown, are plotted on a ternary phase diagram as a function of composition. Each blue circle represents a compound that is predicted to be stable, i.e., its enthalpy of formation lies on the convex hull. Green circles represent all compounds that are predicted to be unstable, but whose values fall above the convex hull by an amount smaller than the estimated accuracy of the theoretical FERE approach of ~ 50 meV/atom ≈ 1 kcal/(mol atom) ≈ 5 kJ/(mol atom), whereas red circles stand for those compounds which are unstable beyond any doubt. In Table 1 all these phases are listed together with their structures, actual distance from the convex hull (the positive deviation of the computed enthalpy of formation from the convex hull) and their enthalpies of formation. It is apparent that many of the phases that are predicted to be unstable at absolute zero (only ΔH_f used for predictions), have been synthesized. This subset includes all the Ti_nO_{2n-1} Magnéli phases, Ti_4O_5 , TiO , ZnO_2 , as well as known ternary phases $TiZnO_3$ and $TiZn_2O_4$. This result implies that 1) the accuracy of the theory is insufficient to describe this chemical system, which has many phases that are only weakly stable with respect to decomposition, 2) the experimental realization of binary and ternary phases predicted to be unstable may be attributable to finite temperature effects such as configurational and/or vibrational entropies, or 3) the phases obtained may be metastable, i.e., favored by a particular growth method and/or kinetically trapped. Whichever the correct explanation may be, it is evident that in chemical systems such as Ti-Zn-O with all phases only weakly stable or weakly unstable at

zero temperature (within 1 kcal/(mol atom)) there is significant opportunity to find new phases despite the fact that this system is earth-abundant and well-studied.

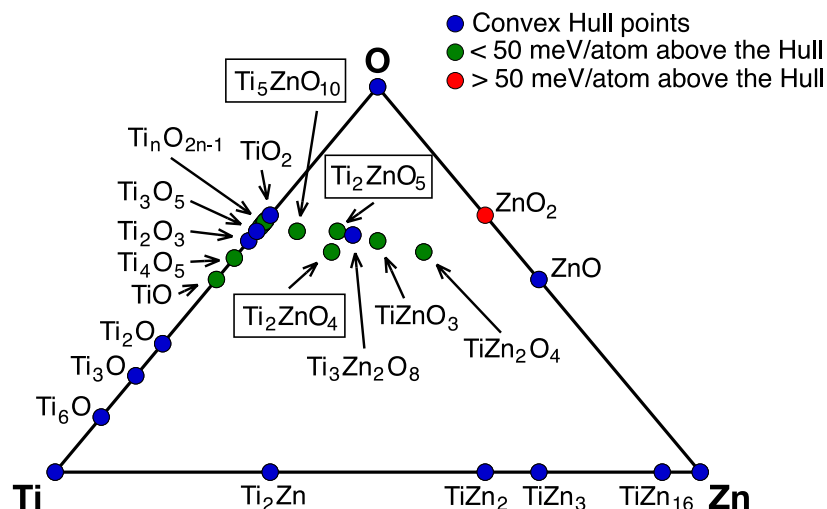


Figure 4: Graphical representation of the Ti-Zn-O phase map including all phases considered in this work and listed in Table 1. Phases that are previously unreported are shown in rectangular boxes. Ti_nO_{2n-1} stands for 6 stoichiometric Magnéli phases. Blue circles denote phases that lie on the convex hull, i.e., that are predicted to be stable with respect to decomposition; green circles stand for those which are predicted to be unstable, but lie within the error bars of the theoretical approach (50 meV/atom \approx 1 kcal/(mol atom) \approx 5 kJ/(mol atom)), and red circles denote phases that are predicted to be unstable.

In particular, all unknown ternary phases considered here are also only weakly unstable, with their distances to the convex hull comparable to those of the known (reported) compounds in this system. All three previously unreported phases - Ti_2ZnO_4 in the normal spinel structure, Ti_2ZnO_5 in the structure borrowed from the chemically similar Ti_2MgO_5 compound, and Ti_5ZnO_{10} in the high-symmetry Ti_3O_5 structure (pseudobrookite) with every other Ti^{4+} ion substituted for one Zn - lie within 30 meV/atom of the convex hull. Therefore, from the point of view of the applied theory, they all are just as likely to be synthesized in actual experiments as those that have already been reported, provided that the needed chemical potentials are accessible experimentally. Support for this statement can be found in the successful experimental synthesis of the $Zn_xTi_{3-x}O_5$ phase in the present work which is close in composition and adopts essentially the same structure as the

Ti₅ZnO₁₀ compound studied theoretically. Since at finite temperatures the entropy contributions are expected to play an important role in this system, significant off-stoichiometry and/or site occupancy disorder may be expected. Experimentally, endothermic formation enthalpies and the corresponding role of entropy from cation disorder in stabilizing various pseudobrookite phases have been previously shown⁴⁵.

We find that in the Ti₅ZnO₁₀ compound the lowest energy structure is when one Zn ion substitutes for one of the Ti ions within the unit cell of the parent Ti₃O₅ compound. Namely, there are two formula units in a single primitive unit cell of Ti₃O₅, and there are two types of Ti atoms, four nominally three-valent Ti atoms and two nominally four-valent Ti ions occupying *f* and *c* Wyckoff positions, respectively, at zero temperature. The lowest energy Ti₅ZnO₁₀ structure, with the fixed primitive unit cell (16 atoms), is obtained by replacing one out of two Ti cations occupying the *c* Wyckoff site with one Zn ion. The possibility of Zn ions ordering on one half of the *c*-sublattice and the further lowering of energy due to ordering has not been addressed here. However, if a random distribution of Zn ions is assumed, then the theoretically predicted Ti₅ZnO₁₀ structure, which keeps the symmetry of the parent Ti₃O₅ (with different lattice parameters), agrees reasonably well with the experimentally observed phase as shown in Figure 1.

6. Discussion

Stability: Experimentally, the pseudobrookite phase appears to be a stable phase within the chemical potential conditions of the ampoule, at least at high temperatures, because it remains present as a single phase even after extended sintering times (at 1100 °C for over 2 weeks; see table 2). At lower synthesis temperatures (750-800 °C) it was not observed (table 2), and it decomposes to other phases when heated in N₂ / O₂. Determination of the exact bounds of stability in terms of temperature, oxygen partial pressure, and cation ratio remains an exercise for future studies. Theoretically the pseudobrookite phase was demonstrated to exhibit similar stability, relative to

decomposition into competing phases, as all other known or unknown ternary Ti-Zn-O phases, including the previously calculated Ti_2ZnO_4 . This result suggests that the pseudobrookite phase could form provided the appropriate chemical potential conditions. The theoretically-predicted ground state structure for the $\text{ZnTi}_5\text{O}_{10}$ composition matches the experimentally observed crystal structure, lending support to the predictions and stability of the synthesized phase. From a comparison of theoretically predicted and experimentally observed X-ray diffraction patterns in Figure 1, only slight differences in structure are observed. The differences in peak positions at high angles (differences in lattice parameters) and in peak intensities in the experimental vs. theoretical patterns are thought to be caused by differences in cation disorder and possibly in average Ti valence state between the experimental and theoretical structures. For example, it has been suggested⁴⁰ that disordering of Ti^{3+} site occupancy is primarily responsible for the elongation of the c-axis observed in substituted vs. pure, and high temperature vs. low temperature, Ti_3O_5 . Additionally, significant changes in lattice parameters in the related compound MgTi_2O_5 were attributed to changes in cation disorder, controlled by temperature⁴⁶; at higher temperatures, some of the larger Mg cations occupy the more distorted $8f$ site, while some of the smaller Ti cations occupy the more regular $4c$ site. Considering the similar ionic radii of Mg and Zn⁴⁷, some cation disorder may be present in the $\text{Zn}_x\text{Ti}_{3-x}\text{O}_5$ case also, assisting the entropic stabilization of this phase at high temperatures. Similarly, in discussing a variety of related ternary pseudobrookites, Navrotsky has highlighted both the low temperature instability (in many cases) and the positive formation enthalpies as being consistent with temperature-dependent cation anti-site disorder and entropic stabilization⁴⁵. As already noted, the present work shows the potential for finding new phases within chemical systems such as Zn-Ti-O, for which the stability of ternary phases, i.e., the enthalpies of all decomposition reactions, appear on a scale of ~ 50 meV/atom.

Properties in Comparison to Similar Phases: The electrical and optical properties of this pseudobrookite phase are comparable to known, related phases. Reported conductivities of other

pseudobrookites (Ti_3O_5 , $\text{Mg}_x\text{Ti}_{3-x}\text{O}_5$, $\text{Li}_x\text{Ti}_{3-x}\text{O}_5$, and CrTi_2O_5) lie in the range of 0.4-70 S/cm at room temperature⁴⁰, while those for Magnéli phases ($\text{Ti}_n\text{O}_{2n-1}$) are in the range of 0.2-2000 S/cm, depending on factors such as microstructure and the value of n ^{24,48}. Conductivity was also reported as n-type for $\text{Mg}_x\text{Ti}_{3-x}\text{O}_5$ ⁴⁹, and the conduction mechanism of various ternary pseudobrookites has been described as small polaron hopping at moderate temperatures^{40,49}. This behavior differs from pure Ti_3O_5 , which exhibits metallic behavior in the orthorhombic pseudobrookite phase⁵⁰, and from the high temperature behavior of ternary titanates. In contrast to the more oxidized TiO_2 and ZnTi_2O_4 compounds with band gaps over 3 eV^{17,51}, the new pseudobrookite in this work absorbed light over the visible and near IR ranges, similar to Magnéli phases⁴⁸. This new phase also exhibited resistance to being dissolved in acid and was not fully soluble even in hot, concentrated sulfuric acid. Such chemically robust behavior has also been observed in the Magnéli phases²⁴.

Potential Applications: Owing to their good electrical conductivity at high temperatures, stability under reducing conditions, and catalytic activity, ternary titanates including $\text{Mg}_x\text{Ti}_{3-x}\text{O}_5$ and $\text{Li}_x\text{Ti}_{3-x}\text{O}_5$ pseudobrookites have been investigated as anode materials for solid oxide fuel cells⁴⁰. In the present case, however, the limited stability range for the Zn-Ti-O pseudobrookite and the volatility of Zn might preclude its application in devices operating over large temperature or oxygen partial pressure ranges. On the other hand, the new compound may be promising for use in lower temperature applications within harsh environments, given its stability in acid coupled with its reasonable electronic conductivity. The similar Magnéli phases have been used as electrodes and catalyst supports in both acidic and alkaline environments (e.g., polymer electrolyte fuel cells, water remediation)²⁴.

7. Summary and Conclusions

Following high-throughput theoretical predictions indicating the stability of new, “missing materials,” (at zero temperature), we applied theoretically-guided experimental synthesis,

experimental characterization, and further in-depth computational theory to the earth-abundant and applications-rich Zn-Ti-O ternary system, wherein a new pseudobrookite phase was discovered, having the composition, $Zn_xTi_{3-x}O_5$ (with $x \approx 0.6$). The crystal structure measured by XRD confirmed the theoretically-predicted lowest energy space group/ symmetry. The composition, determined by XRF and TGA, with support from XPS and EDS, was shown theoretically to be no less stable than other ternary Zn-Ti-O phases considered. Exhibiting modest n-type electrical conductivity, broad optical absorption, and resistance to degradation in acid, the compound may be promising for similar applications as the known Ti-O Magnéli phases or other compounds with the pseudobrookite structure. This discovery, together with our computational results showing formation enthalpies comparable to those of as-yet-unknown ternary Zn-Ti-O phases, suggests that future explorations of this and other M-Ti-O phase spaces are warranted. Given the calculated borderline stability of these phases at zero temperature, however, entropic contributions under the experimental synthesis conditions may be necessary for stabilization of these new “missing” compounds. A combined theoretical-experimental approach to such work enables 1) rational guidance regarding targeted synthesis attempts (i.e., which regions of phase space to explore) and 2) greater insight into the stability of new products, including the relative importance of entropy vs. enthalpy.

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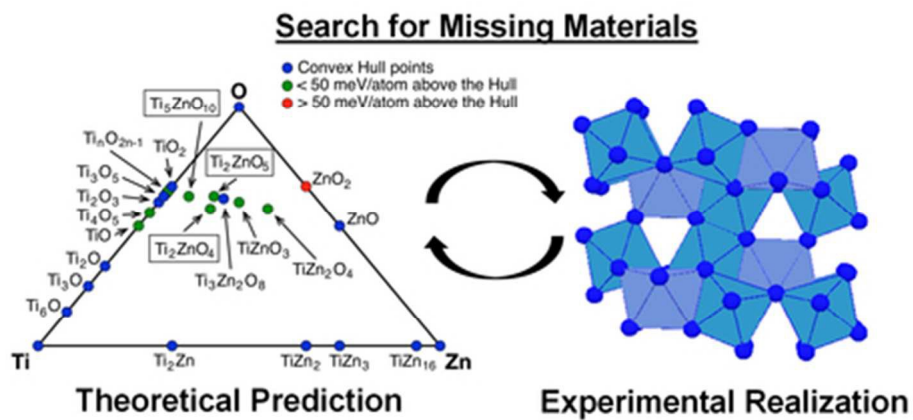
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We apply a combined theoretical and experimental approach to the search for “missing,” stable materials within the ternary Zn-Ti-O chemical system, leading to the discovery of a new pseudobrookite phase, $Zn_xTi_{3-x}O_{5-\delta}$.

38x17mm (300 x 300 DPI)