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Original Article

Sub-solidus phase equilibria in the $YO_{1.5}$-$TaO_{2.5}$ system

Abel N. Fernandez[1], Chandra A. Macauley*,[2], Daesung Park, Carlos G. Levi

Materials Department, University of California, Santa Barbara, CA, USA

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ABSTRACT

The phase equilibria in the $YO_{1.5}$-$TaO_{2.5}$ binary system were studied in air from 1250 °C to 1700 °C across the entire composition range, clarifying discrepancies in previous investigations. Materials were synthesized by precursor routes and phases identified by X-ray diffraction and Raman spectroscopy. Solubility limits were determined using TEM/EDS and EPMA. The fluorite phase field was shown to extend down to at least 1250 °C. Ordering phenomena in two closely related phases near Y_3TaO_7 were investigated, suggesting a second-order ordering relationship between them. The order-disorder transformation to fluorite was observed to occur through formation of a superstructure. The homogeneity range for YTa_7O_{19} was expanded based on chemical analysis, while YTa_3O_9 was shown to be a line compound. The emerging understanding provides valuable insight into related ternary systems as well as inputs for thermodynamic assessments.

1. Introduction

The $YO_{1.5}$-$TaO_{2.5}$ system contains multiple phases of technological interest in addition to playing an important role in relevant higher order systems such as ZrO_2-$YO_{1.5}$-$TaO_{2.5}$ [1–3] and $(Zr,Ti)O_2$-$(Y/Yb/Gd)O_{1.5}$-$TaO_{2.5}$ [4]. The Y-rich portion of the binary phase diagram contains oxygen-deficient phases of interest for ionic conductors in fuel cells, gas sensors, and catalysts [5]. The equimolar compound, $YTaO_4$, has been studied extensively as an x-ray phosphor material, both alone and doped with rare earths [6–8]. On the Ta-rich side, Ta_2O_5, has been studied for its catalytic [9], dielectric [10] and luminescent [11] properties, while YTa_7O_{19} is of interest in phosphor and laser applications [12,13].

The binary system is also of interest in novel thermal barrier coatings (TBCs) based on the ternary ZrO_2-$YO_{1.5}$-$TaO_{2.5}$ system [2,14]. The equimolar compound, $YTaO_4$, shows potential for adequate fracture toughness ascribed to a ferroelastic toughening mechanism similar to that operating in the state of the art ZrO_2-8 ± 0.5 mol%$YO_{1.5}$ (8YSZ) [15,16]. In general, the thermal conductivities of $YO_{1.5}$-$TaO_{2.5}$ oxides have been shown to be within the range attractive for use as TBCs [17] and $YO_{1.5}$ exhibits potential benefits for mitigation of molten silicate attack [18].

Despite the technological interest in $YO_{1.5}$-$TaO_{2.5}$ compositions, there is a paucity of understanding of the phase equilibria and transformations in this system. The purpose of the present study is to elucidate equilibrium relationships in the $YO_{1.5}$-$TaO_{2.5}$ system by investigating binary compositions heat treated at temperatures between 1250 °C and 1700 °C. Compositional and crystallographic analyses were used to construct a complete binary phase diagram from 0 to 100 mol% $TaO_{2.5}$, which clarifies discrepancies in previous studies and can aid in future efforts for thermodynamic modeling of the binary and related ternaries.

2. Background on the $YO_{1.5}$-$TaO_{2.5}$ binary

The available literature is reviewed first to provide context for the present study. The relevant phases and their shorthand notation are listed in Table 1. Two experimental phase diagrams have been published, one covering the entire composition range from 1600 °C to the liquid-solid range [19] and another above 1350 °C to melting, but only for the yttria-rich side, $YO_{1.5}$-$YTaO_4$ [20,21]. A third study reporting sub-solidus equilibria at 1250 °C and 1410 °C provides additional background [22]. The reported phase equilibria are compiled and compared in Fig. 1(a). A thermodynamic assessment of this binary has not been systematically conducted, except for a simplified version in the context of the ZrO_2-$YO_{1.5}$-$TaO_{2.5}$ system which excluded all intermediate phases except for $YTaO_4$, modeled as a line compound with unspecified structure [23].

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* Corresponding author at: Department of Materials Science and Engineering, Friedrich-Alexander Universität Erlangen-Nürnberg, Institute I, Erlangen 91058, Germany.
E-mail address: chandra.macauley@fau.de (C.A. Macauley).

[1] Presently Graduate Student in the Department of Materials Science and Engineering at University of California, Berkeley, California 94720, USA.

[2] Presently post-doctoral researcher in the Department of Material Science and Engineering at Friedrich-Alexander-Universität (FAU) Erlangen-Nürnberg, Institute I, Erlangen, 91058, Germany.

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Table 1
Phase identification references.

Compound	Structure	*Group*	Abbr.	PDF number
$YO_{1.5}$	bixbyite (cubic)	$Ia\bar{3}$	*C*	00-041-1105
	hexagonal	$P\bar{3}m1$	*H*	
$TaO_{2.5}$	tetragonal	$I4_1/amd$	α	01-075-9704
	orthorhombic	*Pmm2*	β	00-025-0922
$YTaO_4$	scheelite (tetragonal)	$I4_1/a$	*T*	
	met. fergusonite (monoclinic)	*I2*	*M*	00-024-1415
	fergusonite (monoclinic)	*P2/a*	*M'*	00-024-1425
Y_3TaO_7	weberite (orthorhombic)	*Ccmm*	*W*	
	orthorhombic	*Cmmm*	*o*	
	defect-fluorite (cubic)	$Fm\bar{3}m$	*F*	
YTa_3O_9	perovskite (orthorhombic)	*Cmmm*	*P*	01-072-2030
	tetragonal	*P4/mmm*	τ	
YTa_7O_{19}	hexagonal	$P\bar{6}c2$	*h*	00-030-1465

2.1. Terminal phases

The structure and phase transformations in $YO_{1.5}$ are well understood. Across the entire temperature range of interest for technological applications $YO_{1.5}$ adopts the C-type rare-earth oxide structure known as bixbyite (*C*, $Ia\bar{3}$), a defect-fluorite with 25% of the anion sites vacant and ordered. The ordering leads to a doubling of the lattice parameter relative to fluorite [24]. Above 2325 °C $YO_{1.5}$ transforms to a hexagonal form (*H*, $Pm\bar{3}1$) which is stable until melting at 2430 °C [24] as noted in Fig. 1(a).

The $TaO_{2.5}$ structures and their relationships have been a subject of study for decades [25]. It is generally acknowledged that $TaO_{2.5}$ undergoes a sluggish first-order phase transformation near 1360 °C [26], but the nature of the higher and lower temperature forms[3] remains under debate. The lower temperature form, *β*, is generally described as one of various orthorhombic superstructures based on a common subcell [27] with different multiplicities along [010] [25,28–30]. Proposed space groups for *β* include *Pn2a* [31], *Pmm2* [32], *Pccm* [33], *Pmmm* [34] or *Pncm* [25]. Alternate monoclinic structures have also been proposed for *β*, e.g. one with space group *C112/m* [35]. The most common metastable form is *δ*-Ta_2O_5 (hexagonal, *P6/mmm*) [32,36], which transforms irreversibly to *β* on heating [32,37]. Above ~1360 °C Ta_2O_5 exhibits a tetragonal structure (*α*, $I4_1/amd$) [38], originally reported as monoclinic (*C2*) [39], which melts congruently at 1872 °C [26]. Alternate descriptions for *α* include orthorhombic (*Imma*) and monoclinic (*A12/m1*) variants [38]. It is well established that *α* transforms upon cooling to a metastable triclinic structure, with an intermediate monoclinic stage [40,41]. For the purposes of this study the relevant structures are *β* and the triclinic product of the transformation of *α*.

It has been reported that the terminal phases have only marginal mutual solubility. Based on a study at 1410 °C, somewhat more TaO2.5 is soluble in YO1.5 (~5%)[4] than the amount of YO1.5 soluble in TaO2.5 (< 1%) [22].

2.2. Intermediate compounds

There are three different structures in the $YO_{1.5}$-rich portion of the phase diagram in Fig. 1(a). Two related orthorhombic structures are reported to be stable below 1500 °C between 25–30 %$TaO_{2.5}$, namely Y_3TaO_7 (*W*, $C222_1$) at ~25%$TaO_{2.5}$ and $Y_7Ta_3O_{18}$ (*o*, *Cmmm*) at 28–30 %$TaO_{2.5}$ [21,42–44]. *W* is proposed to decompose to *o* and a defect-fluorite type structure (*F*, $Fm\bar{3}m$) above 1600 °C [5,21,45], and *o* to decompose to *F* and *T-YT* above 1870 °C [21]. A more recent study of RE_3TaO_7 (RE = lanthanide or Y) argued the space group $C222_1$ results in unrealistic Ta—O bond distances and proposed *Ccmm* as a more accurate space group for Y_3TaO_7 [46].

The equimolar composition $YTaO_4$ (*YT*) has a monoclinic fergusonite structure, designated *M'* (*P2/a*), from room temperature to 1425 °C, above which it undergoes a reconstructive transformation to a scheelite-type, tetragonal structure, designated *T* ($I4_1/a$) [47–49], which melts congruently at 2044 °C [21]. On cooling *T* does not transform back to *M'*, which is considered to be the true equilibrium structure at room temperature, but instead undergoes a displacive transformation to a metastable monoclinic fergusonite phase, *M* (*I/2a*), which resists transformation back to *M'* [7].

The $TaO_{2.5}$-rich portion of the system has two distinct phases, YTa_3O_9 (YT_3, also written $Y_{1/3}TaO_3$) and YTa_7O_{19} (YT_7). YT_3 has an orthorhombic defect perovskite structure (*P, Cmmm*) with two-thirds of the A (Y)-sites vacant relative to the aristotype ABO_3 perovskite [50]. It is stable from 1500 °C until melting congruently at 1800 °C [19]. There is some discrepancy in the homogeneity range of this phase, which is reported as negligible [19] or up to 2 mol percent [22] although the latter treatments may not have achieved full equilibration. YT_7 is reported to have a hexagonal structure (*h*, $P\bar{6}c2$) from 1250 °C to 1590 °C where it decomposes into YT_3 and α-$TaO_{2.5}$ [12,13,22,51].

3. Experimental methods

Binary $YO_{1.5}$-$TaO_{2.5}$ compositions synthesized from precursors were equilibrated at temperatures from 1250 °C–1600 °C for times from 48 to 400 h, as detailed in Tables 2–6.[5] These compositions were chosen with the goal of probing the two-phase regions, with the exception of compositions 75Y25Ta and 72Y28Ta, which were chosen to yield single-phase samples in order to examine the difference between the *W* and *o* structures suggested by Yokogawa [21]. Samples of pure $YO_{1.5}$ and $TaO_{2.5}$ were synthesized in order to verify the structures of the terminal phases of the system as well as to serve as standards for compositional analysis.

3.1. Powder synthesis and thermal treatment

Powders were synthesized via reverse co-precipitation as described elsewhere [2,52]. Yttria-rich powders (≥50%$YO_{1.5}$) were pyrolyzed in air at 650 °C while those rich in tantala required pyrolysis at 900 °C to ensure full conversion of the Ta-rich hydroxides to oxides. Selected samples in the vicinity of Y_3TaO_7 were heat treated in air at 900 °C and 1000 °C for relatively short times (18 h) to explore the evolution from the initial metastable fluorite resulting from the low temperature pyrolysis into the stable phases. Powders intended for BSE-SEM and TEM analysis were pressed into 10 mm pellets by uniaxial compression at 500 MPa, then sintered in air at 1250–1600 °C with heating/cooling rates of 10 °C/min. Sample 73.5Y26.5Ta was prepared via solid-state reaction of an equal mixture of pyrolyzed 72Y28Ta and 75Y25Ta powders ground together in an alumina mortar and pestle. 72Y28Ta and 75Y25Ta were "quenched" from 1250 °C, 1500 °C, 1600 °C and 1700 °C by rapid removal from the furnace in an effort to minimize transformations to lower temperature phases. Samples of $YO_{1.5}$ and $TaO_{2.5}$ were heat treated for 48 h at each temperature. For all heat treatments the pellets were placed on a platinum foil in a covered alumina crucible.

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[3] These are often designated H and L but to avoid confusion in this study where H and L refer to the hexagonal form of yttria and the liquid, respectively, the phases are labeled as α and β, respectively.

[4] Unless specified otherwise all compositions given in mole percent of oxide based on a single cation formula, i.e. $YO_{1.5}$, $TaO_{2.5}$, etc.

[5] For reference the nominal sample compositions in these tables are abbreviated by their cation percentages, excluding oxygen. For example, 75Y25Ta stands for 75%$YO_{1.5}$-25%$TaO_{2.5}$.