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A new class of entropy stabilized oxides: Commensurately modulated $A_6B_2O_{17}$ (A = Zr, Hf; B = Nb, Ta) structures



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ARTICLE INFO

Article history: Received 8 June 2021 Accepted 5 July 2021 Available online 13 July 2021

Keywords: Entropy stabilized oxides High entropy oxides Cation disorder Calorimetry A₆B₂O₁₇

ABSTRACT

High entropy oxides (HEOs) have experienced a meteoric rise in the past decade. Here, we report a new class of entropy stabilized $A_6B_2O_{17}$ (A = Zr, Hf; B = Nb, Ta) oxides whose enthalpies of formation have been determined by high temperature oxide melt solution calorimetry. All four compounds have endothermic enthalpies of formation from binary oxides (AO_2 and B_2O_5), indicating that these modulated phases are entropy stabilized. The unfavorable energetics of formation are counterbalanced by large configurational entropy arising from cation disorder. The calculated configurational entropy per formula unit for $A_6B_2O_{17}$ is 4.50R J/mol·K, which is ~2.8 times higher than the maximum configurational entropy value of 1.61R for an equimolar five cation containing "high entropy oxide". Based on X-ray and neutron diffraction data, measured enthalpies of formation and calculated configurational entropies, one can infer that all four compounds have a high degree of disorder.

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Disorder and its possible tuning in crystal structures opened unprecedented opportunities to stabilize materials at standard conditions. The concept of "high entropy oxides" (HEOs) derived from "high entropy alloys" (HEAs) has been in vogue and led to the fabrication of advanced materials with unique multifunctional properties for innovative applications [1-10]. As an orthodoxy, the singlephase, high entropy solid solution should be composed of at least five principal components in approximately equi-atomic proportions to reach the maximum configurational entropy (S_{conf}) of mixing [2,11–13]. While this is attainable for HEA with near ideal mixing of metal constituents, the interaction of cations in multicomponent oxides is substantially more intricate due to the larger contribution of ionic and covalent bonding (non-ideal mixing i.e. the cocktail effect) [14]. The thermodynamic stability of HEOs may not depend on the number of constituents in the system as such, but on their chemical composition and mutual interaction. As a result, certain binary or ternary oxides can be even more entropically stabilized or possess "higher entropy" than five component oxide phases. Particularly, the entropy stabilization of two component oxides was noted by Navrotsky and Kleppa fifty years ago

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in energetically unstable copper-containing spinels with disordered cation distributions [15,16]. Recently, Voskanyan et al. observed entropy stabilization in pseudobinary $TiO_2-Nb_2O_5$ crystallographic shear (CS) phases, in which positive enthalpies of formation are offset by large positive entropies arising from cation disorder at high temperatures and not from the shear planes per se [17,18]. These results demonstrate that the entropy stabilization of energetically unfavorable materials is possible through the disorder of even two cations instead of five or more. Therefore, the thermodynamic stabilization via configurational entropy is more prevalent than was formerly realized and discoveries of numerous entropically stabilized binary/ternary compounds are pending.

The (Zr,Hf)O₂–(Nb,Ta)₂O₅ pseudobinary system forms a fascinating class of materials with wide compositional range [19–29]. Among different possible compositions, the single-phase compounds with $A_6B_2O_{17}$ (A = Zr, Hf; B = Nb, Ta) stoichiometry and orthorhombic crystal structures (space group: Ima2, #46) were the first-born in this family [19,22]. The $Zr_xNb_2O_{2x+5}$ and $Zr_xTa_2O_{2x+5}$ phases ($5 \le x \le 8$) with α -PbO₂ related superstructures have been described as a (A,B)_mO_{2m+1} (A and B are metal and m is multiplicity) homologous series [22]. Subsequently, Thompson et al. showed that at intermediate multiplicities, where molar ratios are no longer rational numbers, a series of incommensurately modulated solid solutions of closely related phases ($5.1 \le x \le 10$) form [23]. Although the structure of single crystal Zr₆Nb₂O₁₇



solved by Galy and Roth in 1973 [22], the structures of the other three analogs have only been recently solved by McCormack and Kriven [28]. In addition, commensurately modulated $Hf_3Ta_2O_{11}$, $Zr_5Nb_2O_{15}$, $Hf_5Ta_2O_{15}$, and $Hf_7Ta_2O_{19}$ structures have been also synthesized and successfully refined [27,29,30].

Although the structural complexity, compositional diversity, and thermodynamic stability of these compounds are far from being understood completely, the doped hafnium tantalum and niobium zirconium oxides have been extensively utilized in the electronics industry, particularly in metal oxide-semiconductor field-effect transistors (MOSFET) [31–33]. In addition, several materials derived from this system have been employed in high-temperature environments as thermal barrier coatings and dielectric films [34,35].

This work reports experimentally measured formation enthalpies of $A_6B_2O_{17}$ (A = Zr or Hf; B = Nb or Ta) phases from their corresponding binary oxides by employing high temperature oxide melt solution calorimetry (HTOMSC). We found that these pseudobinary modulated structures are entropy stabilized, stable only above a critical temperature, when large positive entropies generated from cation disorder compensate for their positive enthalpies of formation from parent oxides.

Syntheses of Zr₆Ta₂O₁₇, Hf₆Nb₂O₁₇ and Hf₆Ta₂O₁₇ and other experimental details are described in McCormack and Kriven [28]. Phase pure Zr₆Nb₂O₁₇ was synthesized by the organic steric entrapment of cations [36]. The zirconium source was zirconium (IV) chloride 99.9% (metal basis) (Alfa Aesar) and the niobium source was niobium(V) chloride, 99.99% (metal basis) (Alfa Aesar). The zirconium (IV) chloride was dissolved in deionized water and the niobium(V) chloride was dissolved in isopropanol. The two solutions were mixed in ratios of Zr:Nb = 6:2 and stirred for one hour. Ethylene glycol (Aldrich) was added in the proportion to maintain a cation valence charge to monomer ratio of four to one. The solution was then heated on a hot plate at 300 °C until water and isopropanol were evaporated to allow for gelation. The gel was subsequently dried at 100 °C in a box furnace producing a porous mass. It was ground using a zirconia mortar and pestle and calcined at 1050 °C for 3 h in a zirconia crucible, at a heating and cooling rate of 10 °C min⁻¹. Then, the powders were pressed into pellets and annealed at 1300 °C in a platinum crucible for 10 h. The obtained pellet was crushed, ground and sieved to $< 45 \,\mu m$.

X-ray powder diffraction (XRPD) data were collected for $Zr_6Ta_2O_{17}$, $Hf_6Nb_2O_{17}$ and $Hf_6Ta_2O_{17}$ at the Synchrotron 11-BM beamline ($\lambda = 0.041$ nm) at the Advanced Photon Source (Argonne National Laboratory, Argonne, IL, USA). Neutron diffraction (ND) data with a flight path of 63.2m were collected at the POWGEN beamline at the Spallation Neutron Source (Oak Ridge National Laboratory, Oak Ridge, TN, USA). Lab source Bruker D5000 diffractometer ($\lambda = 0.154$ nm) was used to analyze the phase purity of $Zr_6Nb_2O_{17}$. The PXRD patterns were acquired from 10 to 65° at 1° min⁻¹ and step size of 0.02°.

To obtain the thermodynamic properties of $A_6B_2O_{17}$ compounds, high temperature oxide melt solution calorimetry (HTOMSC) experiments have been performed. Each sample (4–7 mg) was hand-pressed into pellets which were dropped from room temperature (298 K) into 20 g of molten sodium molybdate solvent (3Na₂O·4MoO₃) equilibrated at 1073 K inside a Tian Calvet twin calorimeter (AlexSYS, Setaram, France). Oxygen gas was continuously bubbled through the solvent at 10 mL/min and flushed over the solvent to ensure thorough mixing, complete dissolution, and minimize local saturation in the solvent, as well as to maintain oxidizing conditions. The calibration factor was obtained by dropping corundum (α -Al₂O₃) pellets. The experimental setup and fundamental details are described elsewhere [37].

The $Zr_6Ta_2O_{17}$, $Hf_6Nb_2O_{17}$ and $Hf_6Ta_2O_{17}$ compounds used in this study were from the same batch used by McCormack and Kriven [28] to solve their crystal structure using 11BM synchrotron

X-ray and POWGEN neutron diffraction. These diffractograms have been reproduced to highlight the purity of samples for calorimetric studies (Fig. 1). The phase purity of $Zr_6Nb_2O_{17}$ was only confirmed by powder X-ray diffraction. From Fig. 1, it is clear that these compounds are isomorphous, have Ima2 symmetry, and are phase pure.

The crystal structure of commensurately modulated A₆B₂O₁₇ is schematically illustrated in Fig. 2. Unlike CS structures in which reduction of anion content, as required by stoichiometry, is accompanied by condensation of octahedra and formation of shear planes (stacking faults) at different periodicities, the increase in anion content (with respect to parent structure) in A₆B₂O₁₇ is accommodated by distortion of the anionic array, generating new coordination polyhedra. The accommodation of excess anions can also be represented as the transformation of periodic square nets (Schläfli symbol 4⁴) of anions into denser triangular nets (Schläfli symbol 3⁶). In the A₆B₂O₁₇ structure, six-coordinated distorted octahedra (Fig. 2 (E), label 1), seven-coordinated distorted capped trigonal prisms (Fig. 2 (E), label 2), and eight-coordinated distorted bicapped trigonal prisms (Fig. 2 (E), label 3) form blocks of equidistant cations that are arranged along the c axis. The six-coordinated octahedra are connected to the capped trigonal prisms via cornersharing and the latter are linked to the eight-coordinated polyhedra via edge-sharing. The distorted bicapped trigonal prisms are connected by both corner and edge sharing. The layers of two substructures with one-atom thickness are assembled alternately along the b direction, generating the commensurately modulated A₆B₂O₁₇ phases with a very long periodic structure. The cation coordination is midway between that in monoclinic H-Nb₂O₅ and YF₃. There is a gradual transformation from octahedral coordination to the YF₃-type (eight-coordinated polyhedra). The sevencoordinated polyhedra (baddeleyite type) possess an intermediate configuration linking the neighboring slabs.

The average enthalpies of drop solution (ΔH_{ds}) of $(Zr \text{ orHf})O_2-(Nb \text{ orTa})_2O_5$ compounds and two standard deviations of the mean obtained via HTOMSC are summarized in Table 2. Using the measured values, along with previously reported ΔH_{ds} values for constituent oxides ZrO_2 , Ta_2O_5 , HfO_2 and Nb_2O_5 , the molar enthalpies of formation $(\Delta H_{f,ox})$ per formula unit of each tantalate and niobate from binary oxides, as well as from elements $(\Delta H_{f,el})$, were calculated via the thermochemical cycles shown in Table 1. The calorimetric data demonstrate that the ΔH_{ds} and corresponding $\Delta H_{f,ox}$ for $A_6B_2O_{17}$ phases from (Nb or Ta)_2O_5 + 6(Zr or Hf)O_2 are endothermic for all four compositions Eqs. (1)–((4)) with similar values of $\Delta H_{f,ox}$ within experimental limits of error.

$$6HfO_2 + Ta_2O_5 = Hf_6Ta_2O_5(\Delta H_{f,ox} = 42.94 \pm 7.03kJ/mol)$$
(1)

$$6HfO_2 + Nb_2O_5 = Hf_6Nb_2O_5(\Delta H_{f,ox} = 38.44 \pm 6.75 kJ/mol)$$
(2)

$$6ZrO_2 + Nb_2O_5 = Zr_6Nb_2O_5(\Delta H_{f,ox} = 35.52 \pm 6.45 kJ/mol)$$
(3)

$$6ZrO_2 + Ta_2O_5 = Zr_6Ta_2O_5(\Delta H_{f,ox} = 33.64 \pm 5.42kJ/mol)$$
(4)

These calorimetric data indicate that the $A_6B_2O_{17}$ structures, and perhaps the other modulated structures as well, are energetically unstable but apparently stabilized by their entropy and represent a new class of "entropy stabilized oxides." Like CS plane formation in ReO₃-derived block structures, the structural modulation in $A_6B_2O_{17}$ is the best option for the system at a given stoichiometry to overcome otherwise unfavorable energetics. To get a negative Gibbs free energy of formation (ΔG_f) from oxides at a synthesis temperature of (1573 K), the entropy of formation (ΔS_f) for $A_6B_2O_{17}$ phases must be significantly positive. However, the



Fig. 1. Synchrotron (11BM) powder X-ray diffraction patterns and neutron (POWGEN) powder diffraction patterns, and Rietveld refinement verifying single phase for Zr₆Ta₂O₁₇ (A and D), Hf₆Nb₂O₁₇ (B and E) and Hf₆Ta₂O₁₇ (C and F).

differences in vibrational entropies among solid phases are relatively small and thus it is anticipated that they will have a minor contribution to the ΔS_f from oxides. As a result, it can be deduced that these modulated structures are thermodynamically stabilized mainly through the configurational entropy, S_{conf_i} arising from cation disorder, making these compounds stable only above some minimum temperature. The similar ionic radii of cations in $A_6B_2O_{17}$ phases and corresponding small bond-length mismatches facilitate near ideal mixing of components. As a rule, the small differences in valence, size, and coordination between two cations located at the same crystallographic site lead to the stabilization of a more disordered structure. We calculated the maximum configurational entropies originating from complete A(Zr,Hf)-B(Ta,Nb) disorder in crystal structures. The statistical mixing of six A atoms

Table 1

Thermochemical cycles used for calculating enthalpies of $A_6B_2O_{17}$ (A = Zr, Hf; B = Nb, Ta) formation at 298 K from corresponding binary oxides and elements (based on drop solution calorimetry in molten $3Na_2O\cdot4MoO_3$ solvent at 1073 K)

$\Delta H_1 = \Delta H_{ds} \ \Delta H_2 \ \Delta H_3$
$\Delta H_{f,ox} = 6\Delta H_2 + \Delta H_3 - \Delta H_1$
$\Delta H_1 = \Delta H_f^o (AO_2) \Delta H_2 = \Delta H_f^o (B_2O_5)$
$\Delta H_3 = \Delta H_{f,ox}$
$\Delta H_{f,el}=6\Delta H_1+\Delta H_2+\Delta H_3$

Table 2

Enthalpies of drop solution in molten sodium molybdate solvent at 1073 K, enthalpies of formation from binary oxides and elements at 298 K, entropies and calculated lower temperatures of stability of $A_6B_2O_{17}$ (A = Zr, Hf; B = Nb, Ta).

Compound	$\Delta H_{ds}(kJ/mol)$	$\Delta H_{f.ox}(kJ/mol)$	$\Delta H_{f.el}(kJ/mol)$	$\Delta S_{conf}{}^{a}(J/mol \!\cdot\! K)$	T _{decmp} ^b (K)	T _{decmp} ^c (K)
Hf ₆ Ta ₂ O ₁₇ Hf ₆ Nb ₂ O ₁₇ Zr ₆ Ta ₂ O ₁₇ Zr ₆ Nb ₂ O ₁₇	$\begin{array}{c} 211.01 \pm 4.28 \\ 232.46 \pm 1.15 \\ 252.57 \pm 1.56 \\ 267.01 \pm 3.88 \end{array}$	$\begin{array}{c} 42.94 \pm 7.03 \\ 38.44 \pm 6.75 \\ 33.64 \pm 5.42 \\ 35.52 \pm 6.45 \end{array}$	$\begin{array}{r} -8871.48 \pm 13.40 \\ -8729.54 \pm 7.22 \\ -8615.70 \pm 12.13 \\ -8467.38 \pm 12.63 \end{array}$	37.402 37.402 37.402 37.402 37.402	$\begin{array}{c} 1148 \pm 188 \\ 1028 \pm 180 \\ 899 \pm 145 \\ 950 \pm 172 \end{array}$	$\begin{array}{c} 2296 \pm 376 \\ 2055 \pm 360 \\ 1798 \pm 290 \\ 1899 \pm 344 \end{array}$

^{*a*}Configurational entropy change calculated assuming full cation disorder in all $A_6B_2O_{17}$ phases. ^{*b*}Temperature for decomposition to the binary oxides assuming that $A_6B_2O_{17}$ phases are fully disordered. ^{*c*}Temperature for decomposition to the binary oxides if $A_6B_2O_{17}$ phases are 50 % disordered.



Fig. 2. A depiction of the $A_6B_2O_{17}$ disordered structure looking down the c-axis (A) along with a key for A (Zr, Hf), B (Nb, Ta) and oxygen atoms (B). A depiction of the polyhedra in the $A_6B_2O_{17}$ structure looking down the a-axis (C), and the c-axis (D) along with a key for the different types of polyhedron present (E): 1 - a six-coordinated distorted octahedron, 2 - a seven coordinated capped trigonal prism and 3 - an eight-coordinated distorted bicapped trigonal prism. If ordered, the A (Zr or Hf) atoms will occupy the brown polyhedra while the B (Nb or Ta) atoms will occupy the green polyhedra (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.).

with two B atoms results in 37.40 J/mol·K (4.50R J/mol·K) configurational entropy per formula unit, which is 4.68 J/mol·K (0.56R J/mol·K) per cation. This configurational entropy per formula unit is ~2.8 times higher than the maximum configurational entropy value of 1.61R for the random mixing of equimolar amounts of five cations in a conventional "high entropy oxide" system. The calculated maximum of S_{conf} can be approximated to the maximum entropy of formation $S_{conf} = \Delta S_{conf}$ because constituent binary oxides are not disordered (Table 2). Therefore, the decomposition temperatures for $A_6B_2O_{17}$ to binary oxides can be calculated using the ΔS_{conf} and measured $\Delta H_{f,ox}$ values and the results are listed in Table 2. The obtained low temperature stability limits calculated using $\Delta H_{f,ox}/\Delta S_{conf}$ are below the synthesis temperature, indicating that these compounds as synthesized, should have substantial cation disorder, but not necessarily random distribution. Based on this, we also calculated the low temperature stability limits assuming that the $A_6B_2O_{17}$ was 50 % disordered. The calculated values listed in Table 2 are now higher than the actual synthesis temperature, which immediately implies that these modulated phases must be at least 50 % disordered to be synthesizable at 1573 K. Therefore, one can infer that the energetically metastable $A_6B_2O_{17}$ (A = Zr, Hf; B = Nb, Ta) phases possess very substantial disorder when synthesized. Once disordering of cations takes place at high temperatures and the compound forms, that disordered configuration gets "frozen -in" kinetically and persists on cooling.

Pronounced cation disorder was observed in Zr₆Ta₂O₁₇ and Hf₆Nb₂O₁₇ by McCormack and Kriven via XRD measurements [28]. Since Zr,Ta and Hf,Nb atomic pairs have different X-ray scattering factors, the ordered and disordered structures were distinguishable by the presence of additional peaks in the difference patterns. It was found that Zr₆Ta₂O₁₇ and Hf₆Nb₂O₁₇ were clearly disordered, as additional high intensity Bragg peaks required for the ordered structure were not present. Thus, successful refinement of the structure was only achieved with a disordered cation sublattice. For Zr₆Nb₂O₁₇ and Hf₆Ta₂O₁₇, the ordered and disordered structures were indiscernible through XRD analysis because of their almost identical scattering factors. However, based on their isomorphous crystal structures, it was concluded that the Zr₆Nb₂O₁₇ and Hf₆Ta₂O₁₇ are most probably also disordered. Furthermore, the absence of long-range metal ordering in Zr₆Nb₂O₁₇ and Zr₁₀Nb₂O₂₅ was demonstrated using synchrotron radiation data [25,26]. Moreover, the lack of cation ordering was also observed in Hf₃Ta₂O₁₁ via neutron diffraction experiments [27].

The homologous series of compounds with a similar cation sublattice is formed by altering the concentration of seven-coordinated polyhedral units in the parent $A_6B_2O_{17}$ structure as shown in Fig. 3. The removal of one set of symmetrically equivalent seven-coordinated planar units from $A_6B_2O_{17}$ leads to the formation of compounds with $A_4B_2O_{13}$ general formula (Fig. 3A), while the addition of one set of symmetrically equivalent planar units to the $A_6B_2O_{17}$ structure results in $A_8B_2O_{21}$ stoichiometry (Fig. 3C). In other words, by adding or removing a seven-coordinated slab, the series of homologs with different AO_2 mole fractions can be gener-



Fig. 3. Different homologs of the $(A,B)_mO_{2m+1}$ series are related to each other through the addition or removal of one set of symmetrically equivalent seven-coordinated slabs. (A) is the disordered $A_4B_2O_{13}$ (m = 6) which is generated by removing one set of seven-coordinated slabs. (B) is the disordered $A_6B_2O_{17}$ (m = 8) structure. (C) is the disordered $A_8B_2O_{21}$ (m = 10) which is generated by adding one set of seven-coordinated slabs.

ated. Although these homologs have different molecular formulae, they have the same configurational entropy per cation. Our thermodynamic results show that embedding B₂O₅ into the AO₂ structure is energetically unfavorable and therefore $A_4B_2O_{13}$ (0.25B₂O₅: AO_2) should be thermodynamically less stable than the $A_6B_2O_{17}$ (0.17B₂O₅: AO₂) counterpart, even assuming its full configurational entropy arising from the random cation distribution. To the best of our knowledge, compounds with $A_4B_2O_{13}$ (A = Zr, Hf; B = Nb, Ta) stoichiometry have not been synthesized. Only highly metastable Hf₃Ta₂O₁₁, which has a slightly different crystal structure, has been produced via a sol-gel method and claimed not to be attainable through high temperature solid state reaction from oxides [26]. On the other hand, AO₂-rich A₈B₂O₂₁ (0.125B₂O₅: AO₂) should possess similar or marginally higher stability than the A₆B₂O₁₇ family due to its large AO_2/B_2O_5 molar ratio. Indeed, the modulated Zr₈Ta₂O₂₁, Zr₈Nb₂O₂₁, and even Zr₁₀Nb₂O₂₅ phases have been successfully synthesized [21,24,25]. Hence, our results not only provide thermodynamic properties of individual compositions but can also predict the energetic stability of other homologs in this family. Thus, the logical question arises as to whether there is a class of compounds with $A_{12}B_2O_{29}$ stoichiometry waiting to be discovered. While this question remains open, it is apparent that all these different homologs should have positive enthalpies of formation, and as a result, all of them must be entropy stabilized.

We have investigated the enthalpies of formation of A₆B₂O₁₇ (A = Zr or Hf; B = Nb or Ta) commensurately modulated phases via high temperature oxide melt solution calorimetry. We found that all four compounds of this family have endothermic enthalpies of formation from their constituent binary oxides which are neutralized by configurational entropies arising from cation disorder. The configurational entropy per formula unit of A₆B₂O₁₇ is almost 3 times higher than the maximum configurational entropy which can be achieved for an equimolar, five cation containing "high entropy oxide". Therefore, pseudobinary A₆B₂O₁₇ modulated phases, and most likely the other modulated phases of (A,B)_mO_{2m+1} homologous series as well, can be considered as new examples of entropy stabilized oxides. These compounds contain an extensive degree of disorder, they are metastable at room temperature, and only stable at elevated temperatures. The generalization is that, although the formation of such homologous series, with commensurate or incommensurate modulation of structure, is presumably energetically more stable than the formation of completely random structures, such stabilization is not enough to make enthalpies of formation from binary oxides negative, and residual cation disorder, outside the ordered regions, with ensuing large configurational entropy, is essential to stabilizing these structures at high temperatures. Thus, the structures exist through a competition of order and disorder. This work demonstrates that entropy stabilized oxides are not rare, and it opens new horizons for design and discovery of other entropy stabilized oxide systems.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

The work at Arizona State University was supported by the Department of Energy Office of Basic Energy Sciences, Grant DE-FG02-03ER46053 and by staff support from the Navrotsky Eyring Center for Materials of the Universe. The work at the University of Illinois at Urbana Champaign was supported by the National Science Foundation, Division of Materials Research (Award No. 1411032) and support for travel for experiments was supported by the National Science Foundation graduate INTERN supplemental funding. The authors are grateful to Shuhao Yang for fruitful discussions.

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