

Extended Cation Solubility in the $A_6B_2O_{17}$ ($A = \text{Zr, Hf}; B = \text{Nb, Ta}$) Family of Phases

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The potential for improved, tunable functionality enabled by entropy-driven extended solubility in multicomponent materials provides the impetus for exploring previously unmapped thermodynamic phase spaces in complex systems [1,2]. Commercially relevant properties, such as high dielectric permittivity or ferroelectricity, are frequently associated with phase instability and structural disorder [3], making these compositional regions particularly ripe for experimentation. In this report, we investigate extended cation solubility in the $A_6B_2O_{17}$ ($A = \text{Zr, Hf}; B = \text{Nb, Ta}$) family of disordered oxides as the basis for ongoing electrical property studies of these phases.




The $A_6B_2O_{17}$ -type oxides have recently attracted substantial attention due to their cation-disordered structure and strong entropic contribution to phase stability [4–6]. Notably, this structure possesses multiple unique cation sites (6-, 7-, and 8-fold oxygen coordinations) [7] on which cations are disordered. The chemical diversity and structural disorder tolerated by this material may, in turn, result in a unique combination of properties which support composition-based tunability. Given that the full structure solution for $A_6B_2O_{17}$ -type oxides has only been recently completed, relatively few reports have dealt with exploration of extended (multicomponent) solubility or property exploration in this system. Here, we focus on the bulk solubility of three additional cation species in the $A_6B_2O_{17}$ phase: Ti^{4+} , Sn^{4+} , and Ce^{4+} .

This series of cations was curated to sample a range of radii mismatches relative to “typical” $A_6B_2O_{17}$ cations (i.e. Zr^{4+} , Hf^{4+} , Nb^{5+} , Ta^{5+}). Figure 1 highlights the distribution of ionic radii of solute species relative to the “typical” $A_6B_2O_{17}$ cations. In keeping with

expectations based on preservation of charge neutrality, we anticipate preference for 4+ valence states for A species cations; therefore, we measure the concentration of solute cation relative to substitution with A species cations (e.g. Zr^{4+}).

Bulk ceramics are synthesized via single-step reactive sintering at high temperatures (≥ 1300 °C) in air from uniaxial-pressed green bodies (1 g, 0.5-in. stainless steel die) of stoichiometric ball-milled powders (30-hr ball-mill, methanol). For this report, we focus on cation solubility in the $\text{Zr}_6\text{Nb}_2\text{O}_{17}$ ternary permutation, but ongoing work is exploring extended solubility in other ternary phases as well as the high-entropy quaternary phase. Characterization is conducted via X-ray diffraction (Panalytical Empyrean, $\text{Cu K}\alpha \lambda = 1.54$ Å) and scanning electron microscopy (Phenom ProX) to assess phase segregation and solid solubility.

Secondary phase peaks are visible in X-ray diffraction for 5 atomic percent A-species Ce, indicating insolubility of Ce in $\text{Zr}_6\text{Nb}_2\text{O}_{17}$ at this concentration. This is confirmed by scanning electron microscopy and energy dispersive spectroscopy, which show high Z-contrasted Ce_xO_y precipitates from the $\text{Zr}_6\text{Nb}_2\text{O}_{17}$ matrix. However, when Ti and Sn are substituted at the same concentration to form $(\text{Zr}_{5.7}\text{A}'_{0.3})\text{Nb}_2\text{O}_{17}$, neither X-ray diffraction nor backscattered electron micrographs indicate secondary phase precipitation under the same thermal budget. This suggests that while Ce has a solubility limit below 5 at% A-species, Ti and Sn are both soluble to at least this limit.

These rough solubility ranges highlight the tolerance limits of the $\text{A}_6\text{B}_2\text{O}_{17}$ structure with respect to solute cationic radii. Generally, we find that species with smaller or equivalent radii (i.e. Ti, Sn) are more soluble in $\text{Zr}_6\text{Nb}_2\text{O}_{17}$ than cations with larger radii (i.e. Ce). Ongoing work focuses on bulk studies of solubility in other permutations of the $\text{A}_6\text{B}_2\text{O}_{17}$ phase as well as solubility in the thin film regime. We are also exploring the impact of solute cation species on electronic properties of $\text{A}_6\text{B}_2\text{O}_{17}$ phases, namely dielectric permittivity and loss [9].

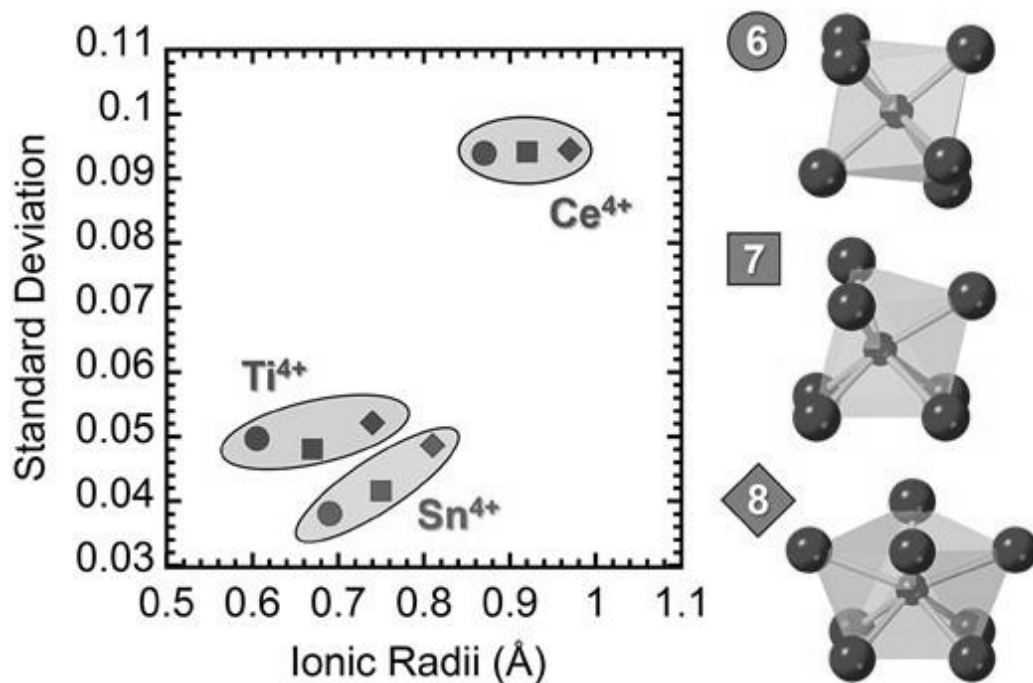


Fig. 1: Standard deviation of ionic radii [8] calculated for the set of cations including all “typical” $\text{A}_6\text{B}_2\text{O}_{17}$ cations (Zr, Hf, Nb, and Ta) plus an additional solute cation (either Ti^{4+} , Sn^{4+} , or Ce^{4+}) plotted as a function of the solute cationic radii for each species in 6-, 7-, and 8-fold coordinations.

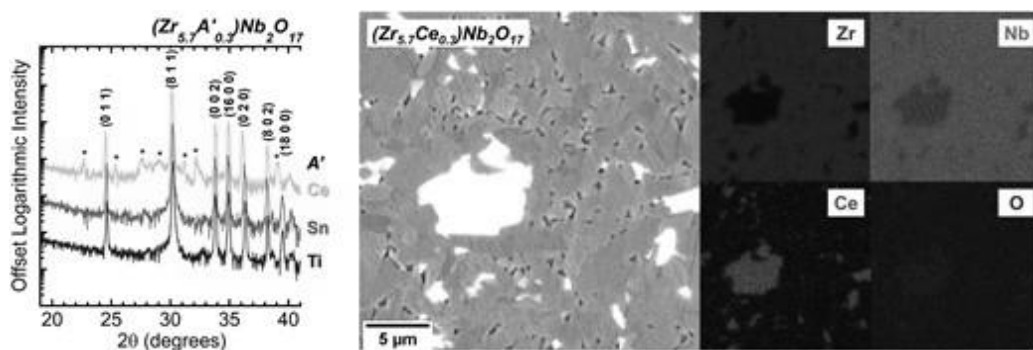


Fig. 2: X-ray diffraction scans (left) show phase segregation of Ce_xO_y at 5 at% A'-species Ce, while Sn and Ti appear soluble up to this limit in $\text{Zr}_6\text{Nb}_2\text{O}_{17}$. Scanning electron microscopy and accompanying energy dispersive spectroscopy of the $(\text{Zr}_{5.7}\text{Ce}_{0.3})\text{Nb}_2\text{O}_{17}$ sample (right) show Ce_xO_y phase precipitation in a $\text{Zr}_6\text{Nb}_2\text{O}_{17}$ matrix.

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