Compositional control of radionuclide retention in hollandite-structured ceramic waste forms for Cs-immobilization

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Hollandite materials are represented by the general formula $A_2B_8O_{16}$ where the A site is either a mono or divalent element and B site is either a di, tri or tetravalent element. In this study, three Ga-doped titanate hollandites, $Ba_{1.33}Ga_{2.67}Ti_{5.33}O_{16}$, $Ba_{0.667}Cs_{0.667}Ga_2Ti6O_{16}$, and $Cs_{1.33}Ga_{1.33}Ti_{6.67}O_{16}$ were synthesized by a solid-state reaction method. All samples exhibited a single phase tetragonal structure as determined by powder X-ray diffraction. Elemental analysis confirmed the measured stoichiometries were close to the targeted compositions. The enthalpies of formation of all three hollandite phases measured using high temperature oxide melt solution calorimetry were found to be negative, indicating these hollandites are thermodynamically stable with respect to their constituent oxides. Furthermore, the formation enthalpies were more negative and hence more favorable with increased Cs content. In addition to formation energy measurements, the stability with respect to competing phase assemblages including ternary oxides was assessed. Finally, aqueous leaching tests indicated that the hollandite phase with higher Cs-loading exhibited the greatest Cs retention. This work links the capacity for radionuclide retention to atomistic level structural features and bulk thermodynamic properties of materials.