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Synthesis and Leaching Behavior of Novel Multi-element Hollandite Ceramic for Immobilizing Radioactive Cesium

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1. Introduction

The structural formula $A_x(B^{3+},B'^{4+})_8O_{16}$, defining hollandite, exhibits a distinctive BO_6 octahedral framework. This unique structure is characterized by its ability to form square-shaped tunnels and cubic-like cavities, known as A sites. These sites are adept at housing large ions, for instance, Cs^+ and Ba^{2+}. In the realm of nuclear waste management, titanium-based hollandite ceramics have emerged as a focal point for the encapsulation of the radioactive isotope ^{137}Cs, thanks to their inherent structural robustness, thermodynamic consistency, resilience to chemical decay in various environments, and capacity to manage the significant heat output from cesium isotopes. Furthermore, Ti4+ ions are essential for capturing electrons during the β-decay transition of Cs ($^{137}Cs \rightarrow {}^{137}Ba + \beta(e\text{-})$ and $Ti^{4+} + \beta(e\text{-}) \rightarrow Ti^{3+}$) [1 - 4].

Considering the β-decay of ^{137}Cs to ^{137}Ba over a 30-year period, the capability of hollandite structures to securely encase both Cs^+ and Ba^{2+} for extended timeframes is a crucial research topic. Studies have thus been directed towards the $(Ba^{2+},Cs^+)_x(B^{3+},Ti^{4+})_8O_{16}$ variant of hollandite, investigating its creation, structural properties, resilience against radiation-induced damage, chemical robustness, and thermodynamic reliability [4 - 7]. However, there is a lack of research on $Cs_x(B^{3+},Ti^{4+})_8O_{16}$ hollandite, in terms of its thermodynamic stability when altering the cesium ratio and incorporating diverse dopants at the B-site such as Al^{3+}, Cr^{3+}, Fe^{3+}, Ga^{3+}, Mn^{3+}, and Ti^{4+}.

We intend to enhance phase stability through the incorporation of five or more elements in roughly equal amounts inspired by the concept of high-entropy alloys. This method is known for generating a high level of configurational entropy, inducing lattice distortion, and producing a synergistic "cocktail effect," which allows certain high-entropy alloys to display outstanding properties such as enhanced mechanical strength, corrosion resistance, stability at elevated temperatures, and resistance to radiation, unlike conventional alloys. Although the B-site sublattice of hollandite does not fully satisfy the criteria for a high-entropy alloy (requiring an entropy above 1.61R), applying high-entropy concepts to the design of hollandite could offer significant benefits, including improved thermal stability, resistance to corrosion, and tolerance to radiation. Up until now, there has been a lack of research into hollandite materials that incorporate multiple elements, underscoring the innovative aspect of our study in the development of multi-element hollandite materials.

Designing multi-element hollandite materials through experimental methods alone presents a formidable challenge due to the vast array of possible component combinations and configurations. This complexity means that the traditional trial-and-error approach would necessitate a prohibitive amount of time and resources. As a solution to this obstacle, advancements in computational technology have enabled researchers to employ high-throughput screening techniques and machine learning. In the present study, the composition of multi-element hollandite with high thermodynamic stability and high Cs content was predicted through active learning using Bayesian optimization. The designed multi-element hollandites were produced experimentally via the sol-gel method.

During long-term disposal, radioactive nuclides may dissolve from the waste form into groundwater. Accordingly, analysis of the leaching behavior of radioactive nuclides in waste form is necessary. The Product Conductivity Test (PCT) method is a standard test method of ASTM for determining chemical durability of glass waste form but it is also widely used for evaluating the leaching property of the ceramic waste form [8]. Therefore, in the present study, leaching behavior of designed multi-element hollandites were measured by the PCT method.

2. Methods and Results

2.1 Computational details

All first-principles calculations of the total energy for the hollandites were performed using the Vienna Ab initio Simulation Package (VASP), which is an implementation of DFT within the framework of the projector augmented wave (PAW) method. The Perdew, Burke, and Emzerhof (PBE) generalized gradient approximation (GGA) was adopted as the exchange-correlation energy functional. A plane-wave basis set with a 520 eV cut-off energy was employed. The gamma-centered Monkhorst–Pack method was adopted for sampling the Brillouin zone, and the *k*-points density was set to within 0.15 Å^{-1}. The values of the cut-off energy and *k*-points density ensured energy convergence to within 1 meV/atom. The Hubbard *U* correction is used to describe strongly correlated electrons in the 3d orbital of metal atoms such as Cr, Fe, and Mn.

We trained Gaussian process regressor (GPR) models to predict the Gibbs energy of hollandite from the molar fraction of composition. Assuming that the Gibbs energy is continuously determined from the mole fraction, the models were based on the radial basis function (RBF) kernel. To incorporate the statistical noise in the measurements and avoid overfitting to the training data, the kernel was augmented with white noise term setting the noise variance as a learnable parameter. Input to the models was formulated as an 8-dimensional vector of the mole fraction of the hollandite except oxygen, x = [f_{Cs}, f_{Al}, f_{Cr}, f_{Fe}, f_{Ga}, f_{Mn}, f_{Ti}]. To find the kernel parameters that minimize the negative log-marginal likelihood of the estimator, optimizers were allowed with 5 chances to restart the optimization process. Expected improvement strategy is selected for acquisition function [Fig. 1].

Active learning was performed using the calculated initial data set, and the stopping criterion (6.14 kJ/mol) was satisfied through a total of 6 iterative learnings. In other words, 235 learning data were generated, and through learning, a total of 51,128 compositions could be evaluated within an error range of approximately 5.83 kj/mol [Fig. 2].

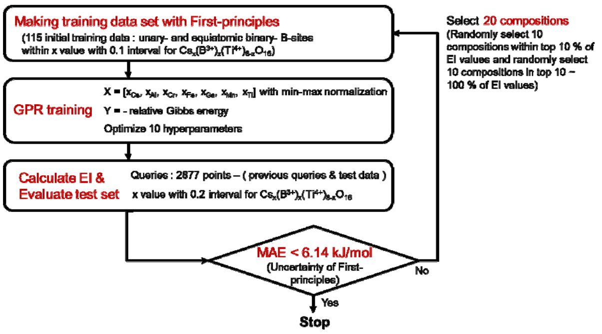

Fig. 1. Schematic of active learning

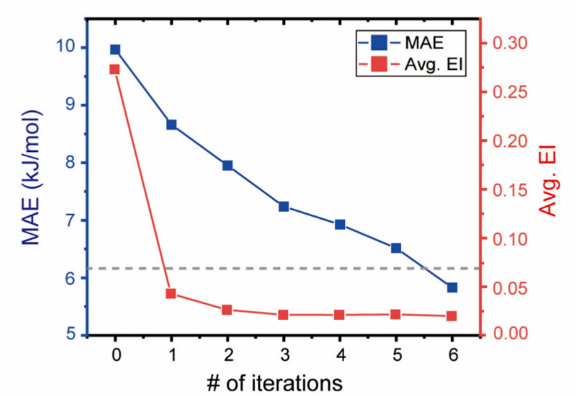

Fig. 2. Result of active learning

2.2 Synthesis of Multi-element Hollandite

Four multi-element hollandite samples with the compositions $Cs_{1.2}Al_{0.2}Fe_{0.3}Ga_{0.4}Mn_{0.3}Ti_{6.8}O_{16}$, $Cs_{1.4}Al_{0.1}Fe_{0.5}Ga_{0.4}Mn_{0.4}Ti_{6.6}O_{16}$, $Cs_{1.5}Fe_{0.8}Ga_{0.4}Mn_{0.3}Ti_{6.5}O_{16}$, $Cs_{1.6}Fe_{0.9}Ga_{0.3}Mn_{0.4}Ti_{6.4}O_{16}$ were synthesized using a sol-gel route. $CsNO_3$, $Al(NO_3)_3$, $Fe(NO_3)_3$, $Ga(NO_3)_3$, $Mn(NO_3)_2$, and titanium ethoxide were used as starting chemicals. The Ti reagents, in the desired stoichiometric proportions, were initially dissolved in anhydrous ethanol within a dry beaker, while the Cs, Al, Fe, Ga, and Mn reagents were separately dissolved in pure water in another beaker. Once the solid powders were completely dissolved, the aqueous solution was gradually introduced into the ethanol-based solution. The resulting mixture was continuously stirred and heated at approximately 120°C for six hours. During this period, the solvent evaporated, leading to the formation of a gel. The gel was subsequently subjected to calcination at 1273 K for two hours to eliminate any remaining organic components [Fig. 3]. The final samples were found to be crystalline, as confirmed by powder X-ray diffraction (XRD) and scanning electron microscopy (SEM) analyses as shown in Fig. 4.

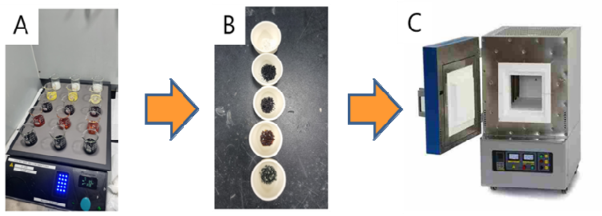

Fig. 3. Synthesis process of multi-element hollandite

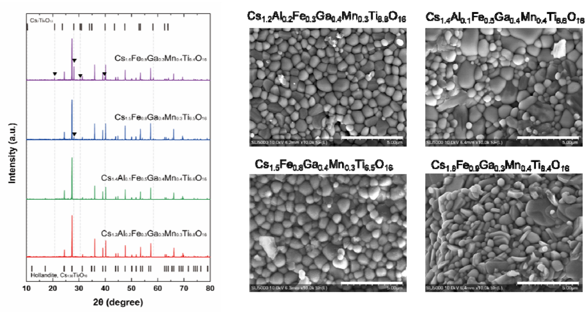

Fig. 4. XRD data and SEM images of multi-element hollandites

2.3 Leaching Test of Multi-element Hollandite

For the PCT procedure, the test specimens were initially ground using an agate mortar, and the resulting powders were passed through 100 to 200 mesh sieves to obtain particles of the desired size. The selected particles were then transferred into the test vessel, which was subsequently filled with fresh ultrapure water. The vessel was securely capped and sealed before being placed in a convection oven preheated to

90°C. After a period of 7 days, the leachate was filtered using a 0.45 μm syringe filter and analyzed with an inductively coupled plasma mass spectrometer (ICP-MS).

The normalized elemental mass loss (g/m2) based on the relase of element i, NL_i can be calculated using Eq 1, where NC_i is normalized concentration (g/L) of element i, SA is surface area (m2) of specimen and V is the leachate volume (L).

$$NL_i = \frac{NC_i}{SA / V} \quad (1)$$

3. Conclusions

The composition of multi-element hollandite with high thermodynamic stability and elevated Cs content, aimed at immobilizing radioactive cesium, was predicted using active learning through Bayesian optimization. Training and test datasets were obtained via first-principle calculations, making this model effective for optimizing Cs content in hollandite for nuclear waste disposal applications. The designed multi-element hollandites were successfully synthesized experimentally using the sol-gel method. Additionally, the leaching behavior of the produced samples was evaluated through the PCT method.

Acknowledgements

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