Development of Multi-element Hollandite Ceramic for Immobilizing Radioactive Cesium Using Active Learning Based on Bayesian Optimization

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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 ($^{137}Cs \rightarrow {}^{137}Ba + \beta(e-)$ and $Ti^{4+} + \beta(e-) \rightarrow Ti^{3+}$) [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. Each data was obtained through first-principle calculations.

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].

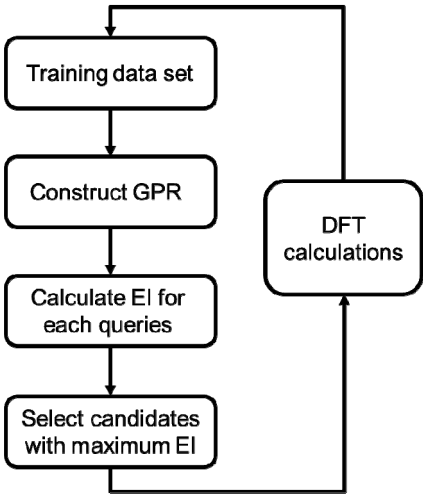

Fig. 1. Schematic of active learning

2.2 Active learning based on Bayesian optimization

GPR model was trained through a total of 5 iterations until uncertainty converged. The final GPR model was evaluated for prediction on a new test set that was not included in the training set, and it was predicted well [Fig 2].

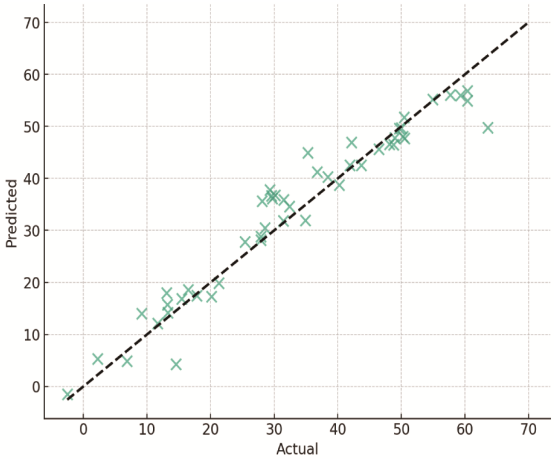

Fig. 2. Comparison of predicted and actual values using test set

3. Conclusions

Composition of multi-element hollandite with high thermodynamic stability and high Cs content for immobilize radioactive cesium was predicted through active learning using Bayesian optimization. Training data and test data set was obtained through first-principle calculations. This model is useful for optimizing Cs content in hollandite for application to nuclear waste disposal.

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