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Unraveling Cs substitution-induced evolution in Fe-hollandite: Linking crystal chemistry to leaching resistance

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Abstract

This study systematically explored the crystal chemistry of Fe-substituted hollandite (Fe-hollandite) solid solutions $(Ba_xCs_y)(Fe_{2x+y}Ti_{8-2x-y})O_{16}$ (x + y = 1.33) yielding reliable results through meticulous Rietveld analysis of XRD data. Continuous Cs substitution triggered a monoclinic-tetragonal (M-T) phase transition, enhancing structural stability, as evidenced by increased tolerance factor $(t_{\rm H})$. The transition boundary, controlled by $t_{\rm H} = .985$, determines the symmetry of the hollandite phase. Unit cell parameters and the local bonding environment were refined, indicating enlarged tunnel sizes/cavities with higher Cs content, attributed to a larger ionic radius (Cs⁺ vs. Ba²⁺). Comparison between Cs/Ba-O bond distances and tunnel cross-section sizes confirmed effective A-site cation immobilization, hindered by oxygen bottlenecks. Additionally, a refined model was proposed and validated to predict lattice constants of Fe-hollandite precisely. Beyond crystal chemistry evolution with Cs substitution, leaching resistance in the same sample suites was assessed. As Cs content increased, normalized elemental release of A-site cations initially decreased until reaching a minimum at intermediate Cs substitution, then rose again. Ba_{0.33}Cs_{1.0}Fe_{1.66}Ti_{6.34}O₁₆ (i.e., HF5) displayed optimal leaching resistance. Variations in leaching resistance might be influenced by the distortion in [BO₆] octahedra and the bonding environment of tunnel cations. This comprehensive analysis highlights intricate correlations between crystal chemistry and leaching resistance, offering insights to guide the design of advanced crystalline nuclear waste forms with enhanced corrosion resistance.

KEYWORDS

crystal chemistry, Cs immobilization, hollandite, leaching resistance, Rietveld analysis

1 | INTRODUCTION

Effective immobilization of radioactive components from nuclear waste is critical for long-term storage and environmental safety. High-level radioactive waste (HLW) contains a variety of radionuclides and nonradioactive species, including Cs, Ba, Sr, actinides, and lanthanides. Both glass and ceramic waste forms, such as borosilicate glass and Synroc ceramics, are designed to sequester these elements effectively.^{1–3}

Hollandite, a key constituent phase in Synroc ceramics, serves as a highly effective nuclear waste form, showcasing exceptional capacity to immobilize radioactive Cs isotopes (e.g., Cs-134, Cs-135, Cs-137) and their decay product Ba cations (e.g., Ba-134, Ba-135, Ba-137). When compared to borosilicate glasses, hollandite demonstrates superior performance, particularly in high Cs loading scenarios.^{1–6} Experimental studies highlight hollandite's exceptional structural stability under self-irradiation, with minimal crystalline-to-amorphous transitions observed at moderate Cs loading. This robustness, combined with its ability to maintain chemical durability and structural integrity under irradiation, meets the stringent demands of long-term radioactive waste immobilization.^{7,8}

The typical chemical formula for a hollandite phase is expressed as $A_x B_8 O_{16}$, where Cs and Ba cations occupy the A-sites. The B-sites can accommodate a diverse range of cations with various charges, such as Co²⁺, Ni²⁺, Zn²⁺, Mg²⁺, Al³⁺, Cr³⁺, Ga³⁺, Mn³⁺, Fe³⁺, Ti³⁺, Ti⁴⁺, etc.^{8–19} Typically adopting the ideal tetragonal symmetry (space group: *I*4/*m*), a titanate-based hollandite exhibits an approximately square-shaped tunnel structure, as illustrated in Figure 1 (left).⁹ Comprising four pairs of edge-linked [BO₆] octahedra, the unit cell forms a rigid framework that creates a tunnel. Cs/Ba cations within the tunnels (purple spheres) and M/Ti⁴⁺ cations on the B-sites (cyan spheres) contribute to its unique structural configuration. Two types of oxygen anions (O1 and O2) positioned at distinct locations play a pivotal role in forming bottlenecks, restricting the mobility of A-site cations and ensuring their immobilization.²⁰ However, a hollandite may also adopt monoclinic symmetry (space group: *I2/m*) that is shown in Figure 1 (right), leading to a rhombusshaped tunnel cross-section and distinct distortions of the [BO₆] octahedral framework.^{9,21–27}

Crystal chemistry significantly influences the properties of complex oxides, impacting polyhedral distortion, symmetries, lattice constants, local ordering/disordering, and more. Perovskites, known for their compositional flexibility, exemplify the role of crystal chemistry in optimizing ferroelectric properties, proton conduction, and structural stability.^{28–30} In olivine-structured materials, the relaxation of structural distortion through cation substitution enhances Li ion mobility in battery applications.^{31–34} Pyrochlore-type materials demonstrate the impact of local ordering/disordering on radiation stability, disordering temperature, and ionic conductivity.³⁵

Hollandite, with diverse applications, underscores the significance of crystal chemistry. Examples include hollandite-type VO_{1.52}(OH)_{0.77} as electronic materials,³⁶ K_{1.54}Mg_{0.77}Ti_{7.23}O₁₆ as promising superionic conductors,^{37–40} and K_xMn₈O₁₆ as cathode materials of Li-ion batteries.⁴¹ The introduction of structural distortion and symmetry reduction, as seen in K-OMS-2 materials, can enhance catalytic activity.⁴² Catalysts like K_{x≈2}Ir₈O₁₆, characterized by distorted [IrO₆] octahedra, significantly influence the electronic structure and oxygen evolution reaction activity.⁴³ In Ag_xMn₈O_{16-δ} nanorods, the distortion of [MnO₆] octahedra facilitates Li-ion diffusion for battery applications.⁴⁴



FIGURE 1 Projection of the crystal structure of the hollandite $(Ba,Cs)_x(M,Ti^{4+})_8O_{16}$ transitioning from an ideal tetragonal form (Left) to a distorted monoclinic form (Right). Cs/Ba cations are denoted by purple spheres, while M/Ti⁴⁺ cations are represented by cyan and blue spheres. The oxygen anions are illustrated as red spheres. Please be aware that the depicted sphere sizes do not correspond to actual ionic radii and are solely for illustrative purposes. The figures were drawn by using the VESTA software.²⁷

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In the realm of nuclear waste forms, the impact of crystal chemistry on hollandite is particularly pronounced. Investigations of $(Ba,Cs)_x(Ti^{3+},Ti^{4+})_8O_{16}$ reveal that increasing Cs content leads to the lateral expansion of tunnels, affecting lattice constant a and tunnel cross-section size.^{45,46} Higher Ba cations occupancy in $Ba_xMg_xTi_{8-x}O_{16}$ induces substantial [BO₆] octahedra distortion and a slight contraction in tunnel cavity size.²⁶ Conversely, Ba_xGa_{2x}Ti_{8-2x}O₁₆ exhibits larger tunnel cavities than $Ba_xAl_{2x}Ti_{8-2x}O_{16}$.⁴⁷ Structural analyses suggest that disordering in tunnels imposes activation-energy barriers, decelerating the transport of the A-site cations.⁴⁸ In the case of (Ba,Cs)_{1,33}(Ga,Ti)₈O₁₆, increased Cs substitution for Ba enlarges the tunnel cross-section, potentially facilitating the A-site cation transport.²⁰ Recent investigations into the effects of crystal chemistry on hollandite's thermodynamic stability reveal a decreasing trend with smaller tunnel cations, attributed to increased structural distortion of the [BO₆] octahedra.⁴⁹ Besides, the composition with higher Cs content has a more disordered local structure around Ga dopants, which enhances thermodynamic stability and further suppresses the release of the A-site cations.¹⁴

While the relationship between structure and properties in hollandite nuclear waste forms has been extensively studied, a notable gap exists in understanding the correlation between crystal chemistry and leaching resistance. This study aims to bridge this gap by examining the Fesubstituted hollandite solid solution (Ba,Cs)_{1.33}(Fe,Ti)₈O₁₆ across a broad compositional range. Rietveld analysis of X-ray diffraction (XRD) data is utilized to extract crystal chemistry information, including symmetries, unit cell parameters, tunnel size, local bonding environment, and structural distortion, as a function of Cs content. Leaching resistance is assessed through various testing and characterization techniques, such as aqueous leaching tests, XRD, scanning electron microscopy (SEM), energy-dispersive spectroscopy (EDS), inductively coupled plasma-optical emission spectroscopy (ICP-OES), among others. This study aims to provide a comprehensive understanding of the effects of crystal chemistry, including distortion of $[BO_6]$ octahedra evaluated by distortion indices, symmetries, and tunnel size, on the normalized elemental release of A-site cations, establishing correlations between crystal chemistry and leaching resistance.

2 | EXPERIMENTAL

2.1 | Material synthesis

A series of $(Ba_xCs_y)(Fe_{2x+y}Ti_{8-2x-y})O_{16}$ (x = 0, .2, .667, .83, 1.0, 1.165 and 1.33; x + y = 1.33) hollandite samples were

Short name	Nominal formula
HF1	$Ba_{1.33}Fe_{2.66}Ti_{5.34}O_{16}$
HF2	$Ba_{1.13}Cs_{0.2}Fe_{2.46}Ti_{5.54}O_{16}$
HF3	$Ba_{0.667}Cs_{0.667}Fe_{2}Ti_{6}O_{16}$
HF4	$Ba_{0.5}Cs_{0.83}Fe_{1.83}Ti_{6.17}O_{16}$
HF5	$Ba_{0.33}Cs_{1.0}Fe_{1.66}Ti_{6.34}O_{16}$
HF6	$Ba_{0.165}Cs_{1.165}Fe_{1.495}Ti_{6.505}O_{16}$
HF7	$Cs_{1.33}Fe_{1.33}Ti_{6.67}O_{16}$

synthesized through a conventional solid-state reaction method. Table 1 displays their respective short names and nominal formulas. Details of sample preparation have been demonstrated in prior studies,¹⁶ so a similar synthesis route adopted in this work is simply described as follows. Starting materials, including barium carbonate, BaCO₃ (Aladdin Scientific Corp., 99.95%), cesium carbonate, Cs₂CO₃ (Aladdin Scientific Corp., 99.99%), iron (III) oxide, Fe₂O₃ (Aladdin Scientific Corp., 99.9%) and titanium oxide (anatase), TiO₂ (Aladdin Scientific Corp., 99.8%) powders, were employed without additional processing. Stoichiometric amounts of the raw powders were mixed for 2 h with yttria-stabilized zirconia grinding balls in a 100 mL zirconia milling jar. To enhance homogeneity, 20 mL of ethanol was added as a dispersive agent. The resultant slurry from post-ball milling was subjected to drying at 80°C in an oven until completely dried powders were obtained. The as-dried powders were then transferred to a covered alumina crucible and heated to 1000°C for 5 h to facilitate the decomposition of carbonates. Following calcination, the powder samples underwent wet ball milling using ethanol solvent, followed by another drying process. Subsequently, the dried samples were ground and mixed with an appropriate amount of 5 wt.% polyvinyl alcohol (PVA) binder to improve sintering performance. The powder mixtures were cold-pressed into green pellets under a pressure of approximately 200 MPa for 2 min. The pressed pellets were then placed in a box muffle furnace for sintering. The sintering process was conducted in air at 1200°C for 5 h to avoid serious Cs volatilization at higher temperatures, with controlled heating and cooling rates of 5°C/min. Finally, a fraction of the as-sintered pellets were crushed and ground into powders to be utilized in further experiments.

2.2 | Characterization

Powder X-ray diffraction (XRD) analyses were performed using a Rigaku SmartLab SE diffractometer equipped with monochromatic Cu K α radiation ($\lambda = 1.54$ Å, 40 kV, and 40 mA) to examine the crystal structure of hollandite samples HF1-HF7. Data acquisition spanned the 10 to 90° 2 θ range with a .01° step size. The microstructure and chemical composition of the samples were investigated using a Hitachi TM4000 SEM coupled with energy-dispersive X-ray spectroscopy (EDS) analysis. Chemical composition and distribution were elucidated through EDS mapping. Sample surface were coated with platinum without polishing. Additionally, the concentration of Cs and Ba in the leachate was determined using inductively coupled plasma-optical emission spectroscopy (ICP-OES, Thermo Fisher iCAP 7400).

2.3 | Rietveld refinement methodology

To elucidate the intricate features of crystal chemistry, Rietveld refinement of XRD data was performed using the General Structure Analysis System-II (GSAS-II) program.⁵⁰ Some standard crystallographic information files, representing monoclinic and tetragonal symmetries, were chosen as the initial models for refining HF1 and HF2-HF7, respectively. As depicted in Figure 1, a standard tetragonal hollandite unit cell comprises one tunnel site for Ba^{2+}/Cs^+ (A-site), one octahedral site for Fe^{3+}/Ti^{4+} (B-site), and two oxygen sites (O1 and O2). In contrast, a standard monoclinic hollandite unit cell features one tunnel site for Ba^{2+}/Cs^+ (A-site), two distinct octahedral sites for Fe³⁺/Ti⁴⁺ (B-site), and four distinct oxygen sites (O1, O2, O3, and O4). The A-site cations exhibit coordination with eight oxygen anions, while the B-site cations have sixfold oxygen coordination.

The refinement procedure followed a systematic approach. Initially, a Chebyshev-1 function was employed to describe the background. Instrument parameters and unit cell parameters were refined, and subsequently, the positions and occupancies of the A-site and B-site cations, as well as oxygen anions, were optimized. The sum of occupancies of Fe^{3+} and Ti^{4+} on the B-sites was constrained to one. Finally, isotropic displacement parameters (U_{iso}) were refined for all sites.

2.4 | Leaching tests procedures

The as-synthesized single-phase hollandite samples were prepared for accelerated leaching measurements following the guidelines in the ASTM C1285-14 product consistency test (PCT).⁵¹ Before testing, the sintered pellets were crushed and ground, and the resulting powder samples, within a specific sieve fraction (i.e., -100/+200), were collected to ensure uniform particle sizes across all leaching

tests. The sieved powder samples were rinsed multiple times with reagent-grade ethanol (\geq 99.5%) to remove finer particles adhering to the surface. It is worth noting that the removal of potential soluble phases containing Cs during the rinsing process should not become a serious concern, because single-phase Fe-substituted hollandites could be readily synthesized based on our previous studies.¹⁶ For each leaching test, approximately 1 g of the sample and 10 mL of deionized (DI) water were placed into a polytetrafluoroethylene (PTFE) vessel. The vessel was sealed with threaded enclosures and placed in an oven at 90 ± 2°C. The samples were maintained at this temperature for seven days. After cooling, the leaching solutions were filtered, acidified, and analyzed. The normalized elemental release (*NL_i*) was calculated using the following equation:

$$NL_i = \frac{C_i}{f_i \times \frac{SA}{V}},\tag{1}$$

where NL_i represents the normalized elemental release of element "*i*" (g/m²), C_i is the concentration of element "*i*" (e.g., Cs) in the leachate solution (g/L), f_i is the fraction of element "*i*" in the unleached waste form (unitless), *SA* is the surface area of the final waste form (m²), and *V* is the volume of leachate solution (L). The surface area of each sample was determined using Brunauer–Emmett–Teller (BET) analysis.

3 | RESULTS

3.1 | Phase formation, microstructure, and chemical compositions

The powder XRD patterns of the synthesized hollandite samples HF1-HF7 are presented in Figure 2A. All samples exhibit a single-phase hollandite structure with high crystallinity, evident from distinct and narrow Bragg's diffraction peaks. HF1 displays a monoclinic structure, as evidenced by peak splitting in the 2-theta (2θ) range of 22° -34°, as depicted in Figure 2B. On the other hand, HF2-HF7 samples exhibit a tetragonal structure. This monoclinictetragonal (M-T) phase transition, induced by increased Cs content in the tunnel sites, aligns well with our previous study.¹⁶ Additionally, Figure 2B reveals a significant peak shift toward a lower 2θ angle for the two families of lattice planes {130} and {220}, indicating that unit cell expansion with continuous Cs substitution for Ba. It is noteworthy that the hollandite samples with the same nominal compositions as shown in HF1-HF3 and HF7 were previously reported in the authors' prior work, and only minor differences in the XRD patterns were observed.¹⁶



FIGURE 2 (A) XRD patterns covering the entire 2θ range for the hollandite samples HF1-HF7; (B) XRD patterns focusing on a partial 2θ range for the hollandite samples HF1-HF7; (C) SEM image of HF6 accompanied by corresponding elemental distribution maps derived from EDS measurements. The scale bar represents 20 μ m.

SEM images of the cross-sections of HF1-HF7 were conducted to observe their microstructures. An SEM image of HF6 is presented in Figure 2C as an illustrative example. In Figure 2C, rod-like grains with a typical hollanditetype morphology are visible, consistent with previous observations.^{14,18,20,52} Beyond morphology, Figure 2C also shows the homogenous elemental distribution in HF6 as a representative sample. No distinguishable segregation or absence of metal elements was observed. Consequently, the successful synthesis of hollandite phases for HF1-HF7, without the presence of secondary phases, is confirmed.

3.2 | Insights from Rietveld analysis: crystal chemistry

The XRD patterns of HF1-HF7 were subjected to further analysis using the Rietveld method with the GSAS II program to extract detailed information related to crystal chemistry, including unit cell parameters, bond distances, bond angles, tunnel cavity volume, $[BO_6]$ octahedral distortion. Monoclinic (*I2/m*: ICSD-60792) and tetragonal (*I4/m*: ICSD-68730, ICSD-71080, ICSD-71069) models were selected to refine the XRD data of HF1 and HF2-HF7, respectively. Representative fitted patterns of HF1 and HF3 with different symmetries are depicted in Figure 3A and 3B. The obtained theoretical density and unit cell parameters for HF1-HF7 are listed in Table 2. Furthermore, Tables 3 and 4 provide the refined atomic positions, site occupancies, multiplicity, U_{iso}, and selected bond distances for a representative sample (e.g., HF2).

In Figure 4A, the lattice constant *a* in HF2-HF7 exhibits a linear increase with increasing Cs content, whereas the abnormal value of the constant a in HF1 has resulted from the different space groups. The maximum percentage change in constant *a* can reach as high as $\sim 1.6\%$. Figure 4B demonstrates that the lattice constant c shows an almost linear decrease with increasing Cs content, though the trend is less pronounced, especially when the Cs content $v \ge 1$. The maximum percentage change in constant *c* is approximately .4% (Note: the values of constant a and c in HF2 are used as references). These minimal changes might be resulted from the less amount of the larger Fe³⁺ substituted for Ti⁴⁺ as increased Cs content. In Figure 4C, the unit cell volume (V_{cell}) significantly expands linearly, primarily due to the increased constant a. Consequently, as shown in Figure 4D, the theoretical density (ρ_{the}) is lower in the sample with higher Cs content, reflecting the expansion of V_{cell} . Additionally, as previously mentioned, the unit cell parameters of the hollandite samples synthesized in prior studies by the authors, with identical nominal compositions as depicted in HF1-HF3 and HF7, were also included.¹⁶ Figure S1 reveals minimal discrepancies in their lattice constants a, c, V_{cell} , and β , suggesting that they are essentially identical materials from a crystallographic perspective.

Additional dimensional information describing the tunnel size of HF1-HF7 is detailed in Table 5, encompassing parameters such as the average diagonal length of the tunnel cross-section (*d*), the volume of the tunnel cavity (V_{cavity}), the average bond distance between the A-sites cations and the nearest eight coordinated oxygen anions



FIGURE 3 XRD refinement patterns of (A) HF1 exhibiting monoclinic symmetry and (B) HF3 with tetragonal symmetry.

TABLE 2 Space groups, unit cell parameters (e.g., lattice constant: *a*, *b*, *c*, distorted angle β , V_{cell}), ρ_{the} , and fitted parameters (e.g., weighted refinement residual R_{wp} and good of fitness χ^2) for HF1-HF7.

Sample	Space group	a (Å)	b (Å)	c (Å)	β(°)	V_{cell} (Å ³)	$\rho_{\rm the}~({\rm g/cm^3})$	R _{wp} (%)	χ^2
HF1	I 2/m	10.2428(3)	2.9787(1)	9.9060(3)	91.10(1)	302.17(2)	4.639	6.545	2.05
HF2	I 4/m	10.1101(6)	-	2.9769(1)	90	304.28(3)	4.616	10.753	1.98
HF3	I 4/m	10.1717(4)	-	2.9705(1)	90	307.33(3)	4.515	9.212	1.25
HF4	I 4/m	10.2015(3)	-	2.9693(1)	90	309.01(2)	4.462	6.077	1.65
HF5	I 4/m	10.2219(3)	-	2.9674(1)	90	310.06(2)	4.454	7.717	1.23
HF6	I 4/m	10.2506(2)	-	2.9676(1)	90	311.82(2)	4.405	6.548	1.76
HF7	I 4/m	10.2737(1)	-	2.9671(3)	90	313.18(1)	4.390	8.053	2.06

 $\label{eq:constraint} \textbf{TABLE 3} \quad \text{Refined atomic positions, site occupancies, multiplicity, and } U_{iso} \text{ for HF2.}$

Element	x	У	z	Occupancy	Multiplicity	$\mathbf{U}_{\mathrm{iso}}$
Ва	0	0	.3556(15)	.2843(14)	4	.0761(20)
Cs	0	0	.2408(17)	.0519(14)	4	.055(9)
Ti/Fe	.3523(3)	.1657(3)	0	1	8	.0205(7)
01	.1567(4)	.2016(4)	0	1.038(10)	8	.0145(31)
02	.5299(5)	.1707(5)	0	1.000(3)	8	.0160(50)

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FIGURE 4 Changes in (A) lattice constant *a*, (B) *c*, (C) V_{cell} , and (D) ρ_{the} of HF1-HF7 with varying Cs content. The blue lines indicate the best fit to the experimental data in the plots.

Sample	d (Å)	V_{cavity} (Å ³)	A-O (Å)	Cs-O* (Å)	Ba-O* (Å)
HF1	5.096 (1)	38.73 (1)	2.983 (1)	_	2.983 (1)
HF2	5.162 (1)	39.67 (2)	3.011 (1)	3.055 (1)	3.003 (1)
HF3	5.239 (1)	40.76 (1)	3.033 (1)	3.050 (1)	3.017 (1)
HF4	5.298 (12)	41.67 (3)	3.059 (1)	3.071 (2)	3.040 (2)
HF5	5.383 (11)	43.01 (2)	3.095 (2)	3.101 (2)	3.074 (2)
HF6	5.388 (9)	43.08 (2)	3.096 (1)	3.099 (1)	3.076 (1)
HF7	5.460 (1)	44.23 (1)	3.127 (1)	3.127 (1)	-

TABLE 5 The values of d, V_{cavity}, A-O, Cs-O bond distance, and Ba-O bond distance for HF1-HF7.

*The average bond distance of Cs/Ba-O is also referred to as the channel size in some literature.53

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Variation of (A) V_{cavity} , channel size, d and (B) various bond distances as a function of Cs content.⁴⁹ FIGURE 5

(A-O), and the average bond distance of Cs-O and Ba-O. Figure 5A illustrates consistent trends in the variations of V_{cavity} , channel size (also referred to as the average Cs/Ba-O bond distance in some literature),⁵³ and d as a function of Cs content. In general, the tunnel size of the Ba-end member is the smallest, confirmed by the smallest V_{cavity} , d, and channel size. As Cs cations substitute Ba cations, the tunnel size gradually increases, reaching the largest V_{cavity} for the Cs-end member. In Figure 5B, the average bond distances of A-O, Cs-O, and Ba-O in HF1-HF7, as a function of Cs content, also align well with the tunnel size trends shown in Figure 5A. Furthermore, as depicted in Figure 5B, the A-O bond distance in Fe-substituted hollandite is larger than that in its Ga-substituted counterpart, indicating that the presence of the larger Fe³⁺ cations on the B-sites contributes to an enlargement of the tunnel size, consistent with previous studies.^{13,49}

The distortion of the polyhedral framework can exert profound effects on the properties and performance of hollandite-structured materials.36,44,49 Nevertheless, quantification of [BO₆] octahedra distortion in the Fesubstituted hollandites across a broad compositional range has not been done before this work. The distortion of $[BO_6]$ octahedra in hollandites can be accessed through two factors: Distortion Indices of Distances (DI_D) and Distortion Indices of Angles (DI_A).⁵⁴ For DI_D , it is defined as follows:

$$\mathrm{DI}_{\mathrm{D}} = \frac{\left(\sum_{i=1}^{6} |l_{i} - l_{0}|\right)}{6l_{0}},$$
(2)

where l_i represents the individual distance from the octahedral cation to the oxygen anion in a [BO₆] octahedron, and l_0 is the mean value of bond distance B-O in the same [BO₆] octahedron.

The other factor DI_A describing distortion, is defined as follows:

$$\mathrm{DI}_{\mathrm{A}} = \frac{\left(\sum_{i=1}^{12} |\theta_i - \theta_0|\right)}{12\theta_0},\tag{3}$$

where θ_i is the bond angle O-B-O in a distorted octahedron, and θ_0 is the mean value of the bond angle O-B-O in the same $[BO_6]$ octahedron.

Based on the definitions of DI_D and DI_A , their values are equal to 0 for a regular [BO₆] octahedron, while the values are positive if a [BO₆] octahedron is distorted. The values of DI_D and DI_A are calculated and provided in Figure 6.

As shown in Figure 6A, when Cs was substituted for Ba, even with a small amount (y = .2), the DI_D increased by ~67%, indicating significant distortion was induced in HF2 compared to HF1. As the Cs content was further increased to the intermediate level (y = .667-1.0), the distortion recovered more than 38% compared to HF1. Among HF3-HF5, DI_D values fluctuated slightly, with HF3 and HF5 having the smaller values and HF4 having the larger value (DI_D: .012 vs. .013). In the high Cs content range $(1.0 < y \le 1.33)$, DI_D values gradually increased, reaching the largest value ($DI_D = .017$) in the Cs-end member HF7, closely resembling the value of the sample ($DI_D = .025$) with identical nominal stoichiometry previously reported by the authors.¹² Nevertheless, the DI value of HF7 is still much smaller than that of HF2. Regarding DIA values, Figure 6B illustrates their gradual increase with some fluctuation as Cs content increases. In summary, the intermediate Cs-containing samples exhibit the smallest DI_D values, although the DIA values rise with continuous Cs substitution.

Xu et al.⁴⁹ investigated the octahedral distortion of Gasubstituted hollandite samples and observed a monotonic

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FIGURE 6 Variation of (A) DI_D and (B) DI_A of [BO₆] octahedra as a function of Cs content for HF1-HF7.

decrease in the DI_D values with increasing Cs content. This finding contrasts with the trend observed for the Fe-substituted analogs discussed in this work. Several factors may contribute to this disparity. For instance, the presence of unpaired electrons in the *d* orbital of Fe³⁺ ions could introduce degeneracy effects, whereas the *d* orbital of Ga³⁺ ions is fully occupied by electrons, potentially mitigating this phenomenon.⁴⁹ Furthermore, the Ga-substituted hollandite series only comprised measurements for three compositions, suggesting that smaller DI_D values might be attainable in other compositions, such as $(Ba_xCs_y)(Ga_{2x+y}Ti_{8-2x-y})O_{16}$ (.667 < *y* ≤ 1.33), which aligns with the trend observed in this work.

3.3 | Leaching resistance variations

The leaching resistance of Cs and Ba in the series of Fesubstituted hollandite was evaluated by aqueous leaching tests. The values of the normalized Cs and Ba release $(NL_{Cs} \text{ and } NL_{Ba})$ are illustrated in Figure 7A showing that the NL_{Cs} values experienced a significant decrease for compositions with intermediate Cs levels (e.g., HF3-HF5) compared to the low Cs-containing sample HF2. Notably, HF5 (y = 1.0) exhibited the minimum NL_{Cs} among the sample series, suggesting superior leaching resistance. However, the NL_{Cs} values increased as the Cs content was further enhanced. The trend of the NL_{Ba} values as a function of Cs content is depicted in Figure 7B. Similarly, NL_{Ba} was substantially improved with increased Cs content, and the lowest values were observed in HF5; NL_{Ba} increased again with higher Cs content substitution. Additionally, the values of NL_{Ba} are three orders of magnitude lower than the NL_{Cs} values, indicating that Ba cations are more easily immobilized in tunnel sites compared to Cs cations.

The SEM images of the sieved and cleaned sample particles, prepared for leaching tests (e.g., HF4-HF6), are presented in Figure 8A. Generally, these particles exhibit

uniform size and possess an identical microstructure with the typical hollandite-type morphology. The chemical compositions were analyzed for the entire sample series. Figure 8B illustrates the elemental distribution of HF5 as an example. It is evident that these elements are evenly distributed across the particle surface. Figure 9A displays SEM images of particles from selected samples after leaching (e.g., HF4-HF6). Upon comparing the microstructure of particles before and after leaching, Figure 8A versus Figure 9A, no structural degradation or significant corrosion features were observed. Figure 9B and 9C presents the EDS mapping of HF5 and a comparison of atomic ratios of the elements in HF5 before and after leaching, respectively. The post-leaching particles of HF5 maintained good elemental homogeneity, and the chemical stoichiometry was conserved. Although the EDS measurements on sample particles are semi-quantitative providing relatively large errors, the analytical results of ICP-OES and ICP-MS rendering higher accuracy have been acquired in this work and prior studies which also confirmed the EDS results. Figure 9D depicts a comparison between the XRD patterns of HF5 before and after leaching, indicating that the hollandite phase remained, and no secondary phases were formed. Therefore, the abovementioned results suggest that the sample series exhibits good structural stability as well as leaching resistance.

4 | DISCUSSION

4.1 | Mechanisms of the M-T phase transition induced by Cs substitution

It is widely recognized that the M-T phase transition is primarily driven by the relative sizes of the average ionic radii of cations on the A-sites (r_A) and B-sites (r_B), along with considerations of structural stability.^{16,22,23} Prior studies.²³ have highlighted that the size effect of ionic radius can



FIGURE 7 Variation of (A) $\rm NL_{Cs}$ and (B) $\rm NL_{Ba}$ as a function of Cs content for HF1-HF7.



FIGURE 8 (A) SEM images depicting the sieved particles of HF4-HF6 before leaching. (B) SEM image capturing the particle surface of HF5 before leaching, along with corresponding elemental distribution maps obtained from EDS measurements.



FIGURE 9 (A) SEM images illustrating the particles of HF4-HF6 after leaching. (B) SEM image displaying the particle surface of HF5 after leaching, along with (C) the corresponding elemental distribution maps. (D) A comparison between the XRD patterns of HF5 before and after leaching.

be appraised through the ratio of $r_{\rm B}/r_{\rm A}$, along with an additional critical parameter $r_{\rm C}$, which is defined as the radius of a tunnel cation that fits perfectly into the tetragonal prism cavity. The value of $r_{\rm C}$ is calculated using the following equation²³:

$$r_{\rm C} = \sqrt{2}(r_{\rm O} + r_{\rm B}) - r_{\rm O},$$
 (4)

where $r_{\rm O}$ represents the ionic radius of an oxygen anion (O^{2–}). Structural stability can be evaluated through the tolerance factor ($t_{\rm H}$), defined as follows⁵⁵:

$$t_{\rm H} = \frac{\left[\left(r_{\rm A} + r_{\rm O} \right)^2 - \frac{1}{2} \left(r_{\rm B} + r_{\rm O} \right)^2 \right]^{\frac{1}{2}}}{\sqrt{\frac{3}{2}} \left(r_{\rm B} + r_{\rm O} \right)}.$$
 (5)

The ratios of $r_{\rm B}/r_{\rm A}$, along with the values of $r_{\rm C}$ and $t_{\rm H}$ for HF1-HF7, were calculated using Shannon's effective ionic radii: Ba²⁺ = 1.42 Å, Cs⁺ = 1.74 Å, Fe³⁺ = .645 Å, and Ti⁴⁺ = .605 Å.⁵⁶ The calculated values are presented in Table 6 and illustrated in Figure 10.

In Figure 10A, the M-T phase transition boundary aligns more closely with the model proposed by Zhang and Burnham²³ than with the critical value ($r_{\rm B}/r_{\rm A}$ = .48) summarized by Post et al.²² Figure 10B illustrates the lin-

TABLE 6 The values of r_A and r_B , r_B/r_A ratios, and values of r_C and t_H for HF1-HF7.

Sample	r _A	r _B	$r_{ m B}/r_{ m A}$	r _C	$t_{ m H}$
HF1	1.420	.618	.435	1.454	.984
HF2	1.468	.617	.421	1.453	1.007
HF3	1.585	.615	.388	1.450	1.063
HF4	1.620	.614	.379	1.448	1.079
HF5	1.661	.613	.369	1.447	1.099
HF6	1.700	.612	.360	1.446	1.118
HF7	1.740	.612	.352	1.445	1.136

ear decrease in $r_{\rm C}$ with increasing Cs content, indicating reduced space for A-site cations to move within the tunnels. Typically, a hollandite exhibits tetragonal symmetry when $r_{\rm A} \ge r_{\rm C}$ and monoclinic symmetry when $r_{\rm A} < r_{\rm C}$. As depicted in Figure 10C, $r_{\rm A}$ is smaller than $r_{\rm C}$ for HF1, indicating a monoclinic structure, while for HF2-HF7, $r_{\rm A}$ is larger than $r_{\rm C}$, suggesting tetragonal structures. Figure 10D shows the variation of $t_{\rm H}$ as a function of Cs content. According to Equations (4) and (5), $r_{\rm A} = r_{\rm C}$ when $t_{\rm H} = 1$. Figure 10D shows the linear increase of $t_{\rm H}$ with higher Cs content, indicating enhanced structural stability due to Cs substitution. Notably, $t_{\rm H}$ in HF1 with monoclinic symmetry is smaller than 1, whereas the $t_{\rm H}$ values in HF2-HF7 with tetragonal symmetry are larger than 1, suggesting that



FIGURE 10 (A) Plot of $r_{\rm A}$ - $r_{\rm B}$ and symmetry prediction models proposed by Zhang and Burnham and Post et al.^{22,23} (B) Variation of $r_{\rm C}$ with Cs content; (C) Plot of $r_{\rm C}$ - $r_{\rm A}$; (D) Variation of $t_{\rm H}$ with Cs content.

 $t_{\rm H} = 1$ might be another criterion for predicting the symmetry of Fe-substituted hollandites. Figure 11A presents the $t_{\rm H}$ and $r_{\rm B}/r_{\rm A}$ values of all known Fe-substituted hollandites. In Figure 11B, a magnified plot of a selected region from Figure 11A reveals that the M-T phase transition occurs when $t_{\rm H} > .985$, slightly smaller than 1. This discrepancy may be due to the hollandite structure's capacity to withstand mild distortion while maintaining higher symmetry. Nevertheless, $t_{\rm H}$ = .985 serves as an effective criterion for predicting the symmetry of Fe-substituted hollandites.

4.2 | Unit cell parameter predictions and refinements

Lattice constants a and c can be predicted using the following equations proposed by Zhang and Burnham²³:

$$a(A) = 5.130(r_{O} + r_{B}) + tZ_{B} + u\delta_{A},$$
 (6)

$$c\left(\mathrm{\AA}\right) = \sqrt{2}\left(r_{\mathrm{O}} + r_{\mathrm{B}}\right) + vZ_{\mathrm{B}} + w\delta_{\mathrm{B}},\tag{7}$$

where r_0 is the ionic radius of an oxygen anion (O^{2-}), r_B is the average ionic radius of the B-site cations, $Z_{\rm B}$ is the valence of the B-site cations, δ_A is the excess size of the A-site cations relative to the BO₆ octahedral framework, $\delta_{\rm B}$ is the excess size of the B-site cations relative to the octahedral cavity, and t, u, v, w are coefficients. Specifically, t = -.0291, u = .411, v = .0366, and w = .552 were fitted by least-squares analysis in the paper of Zhang and Burnham.²³

The predicted unit cell parameters (e.g., lattice constants a and c) of HF2-HF7 were reported in Figure 12A and 12B to assess the precision of this model. However, it is evident that both observed constants a and c are somewhat smaller than the values predicted from the model proposed by Zhang and Burnham.²³ Therefore, refinement of Equations (6) and (7) is necessary. The coefficients t,

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FIGURE 11 (A) The plot of $t_{\rm H}$ – $r_{\rm B}/r_{\rm A}$ in all known Fe-substituted hollandites.^{11,13,15,16,25,57–60} (B) A magnified view of a selected region from A. Black squares indicate samples with tetragonal symmetry, while red squares represent those with monoclinic symmetry.



FIGURE 12 Comparison between predicted and observed values of lattice constants (A) *a* and (B) *c* of HF2-HF7. Predicted values, denoted by circles and triangles, were calculated using the coefficients obtained from Zhang and Burnham²³ and the coefficients refined in this work, respectively. Purple solid lines depict the best fit to the observed data, while blue dashed lines indicate cases where predicted values are equal to the observed values. Similarly, comparison constants (C) *a* and (D) *c* of Fe-substituted hollandites are compared. Predicted values, represented by squares and circles, were calculated using the coefficients obtained from Zhang and Burnham²³ and the coefficients refined in this work, respectively. Blue symbols denote previously reported samples, while red symbols represent HF2-HF7.^{11,13,15,16,25,57-60} Grey dashed lines indicate cases where predicted values are equal to the observed values.



FIGURE 13 (A) An illustration depicting the reduction in octahedral wall thickness in an ideal hollandite structure upon Cs substitution. The purple dashed line represents the ideal wall thickness without Cs content, and the red dashed line indicates the new wall thickness after Cs substitution. (B) Changes in wall thickness as a function of Cs content. Please note that the structural modifications of the octahedral wall in the figures are for qualitative demonstration purposes and do not reflect actual cases.

u, *v*, and *w* underwent refinement through least-squares analysis, yielding the newly fitted values t = -.0682, u = .7272, v = .0238, and w = .9278. The predicted values of a and c using the refined coefficients are depicted in Figure 12A and 12B. The predicted constants closely align with the observed values, confirming the validity of the newly refined equations. Moreover, the new coefficients derived in this work, along with the original coefficients proposed by Zhang and Burnham, were utilized to predict a and c values for Fe-substituted hollandites reported previously.^{11,13,15,16,25,57-60} As illustrated in Figure 12C and 12D, the refined coefficients accurately predicted both a and c values, closely matching the prior experimental results, whereas the predicted values obtained using the original coefficients were consistently overestimated. Therefore, confidence is warranted in utilizing this refined model to predict unknown Fe-substituted hollandites in future studies.

While the refined coefficients differ from the previous ones, the deviations between them are not substantial. More importantly, the newly refined value of u = .7272remains considerably smaller than the expected value of $4\cos 30^\circ = 3.4641$. This suggests that the anticipated expansion of lattice constant a, resulting from the substitution of larger Cs cations for smaller Ba cations, was counteracted to some extent by the reduction in octahedral wall thickness, as illustrated in Figure 13A. The wall thickness can be defined as the apex-to-base distance of the tetrahedral interstice in the double octahedral chain.²³ To validate this hypothesis, the wall thickness of HF1-HF7 was calculated based on the results from the Rietveld analysis of the XRD data. Figure 13B demonstrates that the wall thickness continuously decreased with an increase in Cs content, aligning with previous studies and supporting the aforementioned hypothesis.23,46

4.3 | Exploring the intricate correlations: crystal chemistry versus leaching resistance

An essential consideration in nuclear waste management is the potential migration of the A-site cations (e.g., Ba²⁺ and Cs⁺) along the tunnels. As shown in Figure 14A and 14B, the bottlenecks formed by the eight O1 anions surrounding the tunnel cations play a crucial role in determining their potential mobility. The average diagonal distance O-O (parameter *d* reported in Table 5) compared to the sum of the Ba/Cs and O ionic diameters ($d_{Ba^{2+}} + d_{O^{2-}} = 5.64$ Å; $d_{Cs^+} + d_{O^{2-}} = 6.28$ Å) suggests that these local bonding characteristics may act as diffusion barriers, reducing cation mobility and release.

The normalized elemental release of A-site cations may be influenced by the distortion of the $[BO_6]$ octahedral framework. In Figure 15A, two [BO₆] octahedra are presented-the left one with an ideal structure devoid of distortion and the right one exhibiting distortion. An ideal [BO₆] octahedron comprises six B-O bond distances with equal lengths and twelve O-B-O bond angles set at 90°. Conversely, a distorted $[BO_6]$ octahedron typically features varying B-O bond distances and O-B-O bond angles. Figure 15B and 15C illustrates the variation of DI_D and normalized elemental release (NL_{Cs} and NL_{Ba}) as a function of Cs content. In general, the hollandite samples with smaller DI_D values generally show reduced elemental release. As shown in Table S1, a similar trend could also be observed when the hollandites with different substitutions were compared. However, leaching behavior is complex and may not be solely determined by structural distortion.

The bonding environment of A-site cations might also contribute to the release. For example, the compositions



FIGURE 14 (A) Schematic illustrating the local bonding environments of Cs in the structure of $(Ba,Cs)_{1,33}$ (Fe,Ti)₈O₁₆ hollandite solid solutions with tetragonal symmetry. (B) Variation of the average diagonal distance O-O as a function of Cs content. The top projection of a hollandite structure demonstrates the scenario where Cs cations exhibit limited movement within the tunnels (i.e., $d = d_{CS^+} + d_{O^{2-}} = 6.28$ Å; represented by the purple solid line); the middle projection of a hollandite structure illustrates the case where Ba cations experience restricted movement within the tunnels (i.e., $d = d_{Ba^{2+}} + d_{O^{2-}} = 5.64$ Å; represented by the orange solid line); the lower projection of a hollandite structure demonstrates the situation where neither Cs cations nor Ba cations can freely move in the tunnels, aligning with the sample series in this work. Note: For clarity, the spheres representing Ba cations and the B-site cations have been omitted.



FIGURE 15 (A) Depiction of a distorted $[BO_6]$ octahedron in hollandites, deviating from an ideal, undistorted $[BO_6]$ octahedron; Variation of (B) DI_D and NL_{Cs} , and (C) DI_D and NL_{Ba} as a function of Cs content. The illustrations of $[BO_6]$ octahedra visually capture distinct levels of distortion observed in hollandite samples within this study.

with intermediate Cs contents (HF3-HF6) exhibiting lower normalized elemental release might result from the balance of the bonding interactions and thermodynamic stability. In contrast, the most thermodynamically stable composition (i.e., HF7) with the highest Cs content does not exhibit the lowest Cs release.^{14,16} This may be attributed to the longer Cs-O bond distances, which weaken their interaction and subsequently accelerate Cs dissolution. Additionally, the arrangement of Ba and Cs cations creates varying diffusion barriers, and might also influence elemental release.

While crystal chemistry provides useful insights, its correlation with leaching resistance should be interpreted within the broader context of thermodynamic, chemical, and kinetic influences. Further studies on the synergistic effect of these controlling factors on leaching behaviors will be planned.

5 | CONCLUSIONS

This investigation delves deeply into the complex crystal chemistry of a series of Fe-substituted hollandite solid solutions, synthesized through solid-state reactions. The results, obtained via meticulous Rietveld analysis of XRD data, provide a reliable and comprehensive understanding of the structural intricacies. The observed induction of the M-T phase transition with continuous Cs substitution highlights an improvement in structural stability, evidenced by the increased $t_{\rm H}$. Moreover, $t_{\rm H} = .985$ was validated as the M-T phase transition boundary for Fesubstituted hollandites.

Key unit cell parameters, including V_{cell} and V_{cavity} , demonstrated consistent linear trends with higher Cs content, attributing the behaviors to the larger ionic radius of Cs⁺. The refinement of coefficients in the model proposed by Zhang and Burnham²³ ensured accurate estimations of lattice constants *a* and *c*, with the predominant expansion attributed to an increase in *a*. The analysis of [BO₆] octahedral framework dimensions bolstered the hypothesis that the expansion of *a* was accommodated by a reduction in wall thickness.

Leaching assessed through resistance, NL_{Cs} and NL_{Ba}, showcased optimal performance in $Ba_{0.33}Cs_{1.0}Fe_{1.66}Ti_{6.34}O_{16}$ (i.e., HF5), exemplifying the sample's robust resistance to leaching. The reduced release might be attributed to the improved features of crystal chemistry such as the distortion of the $[BO_6]$ octahedra and the tunnel cation's local environment.

Fundamentally, this study establishes a crucial foundation for comprehending the intricate correlations between crystal chemistry and leaching resistance. As we unravel these relationships, it becomes evident that future materials designed for robust crystalline nuclear waste forms can benefit from a nuanced comprehension of the structural intricacies influencing leaching behavior. This knowledge represents a key advancement in developing highly corrosion-resistant materials for the safe containment of nuclear waste.

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SUPPORTING INFORMATION

Additional supporting information can be found online in the Supporting Information section at the end of this article.

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