

Predicting from first principles the chemical evolution of crystalline compounds due to radioactive decay: The case of the transformation of CsCl to BaCl

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In this Brief Report, we use density functional theory to predict the existence of a heretofore unobserved crystalline compound, BaCl, and additionally predict it to be isostructural with NaCl (rocksalt). Due to the chemistry of Ba, which strongly prefers a 2+ charge state, compounds where Ba nominally exhibits a +1 charge (e.g., BaCl) are unlikely to be synthesized via conventional solid-state approaches. However, in considering the chemical evolution of ¹³⁷Cs to ¹³⁷Ba via β^- radioactive decay in a model nuclear waste form CsCl, we find that BaCl may be indeed relevant. The mechanical stability of this surprising structure is confirmed through examination of its elastic constants and phonon-dispersion relations. We have also analyzed the chemical bonding of rocksalt BaCl and found it to exhibit a complex mixture of ionic, metallic, and covalent characters. From our results, we demonstrate that the chemical evolution of crystalline structures due to radioactive decay may be a viable synthesis route for unforeseen materials with interesting properties.

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Although a nuclear renaissance appears imminent, driven by both the demand for new energy sources and the desire to reduce green-house gas production, the problem of nuclear waste management remains an outstanding and significant challenge. Reprocessing spent nuclear fuel (as opposed to the so-called “burn and bury” option) is currently being investigated as a method to minimize nuclear waste. Separation of radiotoxic actinides for inclusion in transmutation fuel and removal of the short-lived isotopes of Cs and Sr will significantly reduce the load on a geologic repository.¹ This approach not only allows for the recycling of useable nuclear material, but also provides an opportunity to consider the encapsulation of individual fission products in crystalline hosts.

Any consideration of a candidate waste form composition must address durability over very long periods. Previous studies have primarily focused on issues such as radiation tolerance, aqueous durability, and phase separation.^{2–5} However, there is an additional aspect to waste form durability that has been mostly ignored, namely, that the chemical composition of the waste form changes as constituent fission products decay. If the fission product concentration in a waste form is high (as is desired), then this chemical evolution may significantly degrade the structural stability of the material. Therefore, in order to predict the long-term durability of a waste form, it is imperative that we improve our understanding of how these chemical changes modify the stability of the waste form.

In this Brief Report, we consider the encapsulation of a short-lived fission product of interest, ¹³⁷Cs, in a representative crystalline waste form CsCl. This material was chosen as a model system rather than for its potential as an actual waste form, though CsCl pellets containing ¹³⁷Cs have been fabricated in the past.^{6,7} The aim of this study is to investigate, using first-principles calculations based on density functional theory (DFT),⁸ the structural stability and materials property variation of CsCl as a function of Cs decay. Since ¹³⁷Cs beta decays to ¹³⁷Ba with a half life of 30 years, the actual mate-

rial system of interest is Cs_{1-x}Ba_xCl, where x is varied between 0 and 1 to represent different extents of Cs decay. Although the focus of this Brief Report is CsCl, the general concept applies to other compounds containing radioisotopes.

First-principles calculations are performed using the all-electron projector augmented wave method⁹ within the local density approximation (LDA), as implemented in the Vienna *ab initio* simulation package (VASP).¹⁰ The semi-core 5s and 5p electrons of Cs and Ba are explicitly treated as valence electrons. The electronic wave functions are expanded using a plane-wave basis set with a cutoff energy of 350 eV. Convergence tests have been performed to ensure that k -point sampling is sufficient to give fully converged results. All structures are fully relaxed, including both atomic positions and lattice parameters, using a conjugate-gradient scheme.

While it is straightforward to apply DFT calculations to predict material properties of perfectly ordered structures, the situation becomes complicated when treating compositional disorder. Intuitively, one would model disordered A_{1-x}B_x structures by randomly putting A and B atoms on the host lattice. However, this brute-force approach requires very large supercells to adequately reproduce the statistics of random structures and is therefore computationally prohibitive for DFT calculations. In order to adequately mimic the statistics of a random structure in a relatively small (and thus computationally feasible) supercell, we adopt the special quasirandom structure (SQS) approach.^{11–14} In this study, we have developed generalized 32-atom SQSs for substitutionally random pseudobinary A_{1-x}B_xC ($x=0.25, 0.5, 0.75$) compounds in the B1 (rocksalt) and B3 (zinc-blende) crystal structures, respectively. SQSs for B2 (cesium chloride) structure have been developed previously.¹⁴ Table I compares the pair and three-body correlation functions of our generated SQSs to those of the random alloys. In all cases, the SQSs accurately reproduce the pair-correlation functions of the corresponding random compound at least up to the third-nearest neighbor.

TABLE I. Pair and multisite correlation functions of SQSs for representing random $A_{1-x}B_xC$ alloys with $B1$ and $B2$ crystal structures, respectively. SQSs for $B3$ structure are identical to those for $B1$, except in the positions of the C atoms. $\bar{\Pi}_{k,m}$ denotes the correlation function of figure that has k vertices and spans a maximum distance of m ($m=1, 2$, and 3 are the first, second, and third-nearest neighbors, etc.). For the perfectly random $A_{1-x}B_xC$ alloy, $\bar{\Pi}_{k,m}=(2x-1)^k$ since there is no correlation in the occupation between various sites.

Figure	$B1-A_{0.5}B_{0.5}C$		$B1-A_{0.25}B_{0.75}C$		$B2-A_{0.5}B_{0.5}C$		$B2-A_{0.25}B_{0.75}C$	
	Random	SQS-32	Random	SQS-32	Random	SQS-8	Random	SQS-32
$\bar{\Pi}_{2,1}$	0	0	0.25	0.25	0	0	0.25	0.25
$\bar{\Pi}_{2,2}$	0	0	0.25	0.25	0	0	0.25	0.25
$\bar{\Pi}_{2,3}$	0	0	0.25	0.25	0	0	0.25	0.25
$\bar{\Pi}_{2,4}$	0	0	0.25	0.125	0	-1	0.25	0
$\bar{\Pi}_{2,5}$	0	0	0.25	0.25	0	0	0.25	0.25
$\bar{\Pi}_{2,6}$	0	0	0.25	0.25	0	0	0.25	0.25
$\bar{\Pi}_{3,1}$	0	0	0.125	0.125				
$\bar{\Pi}_{3,2}$	0	0	0.25	0.1667	0	0	0.125	0.125

The development of the SQSs allows us to directly examine the phase stability of $Cs_{1-x}Ba_xCl$ compounds as a function of Ba concentration. Since Cs and Ba prefer different charge states (+1 and +2, respectively), Ba would normally not reside on the Cs site without the corresponding creation of charge compensating defects such as a Cl interstitial or a Cs vacancy. However, in the case of ^{137}Cs in a CsCl crystal, the formation of extrinsic charge-compensating defects is forbidden since the decay of ^{137}Cs to ^{137}Ba is an intrinsic process (i.e., without exchange of matter with the environment). In this case, Ba would effectively act as an n -type dopant, increasing the free-electron concentration in the crystal. Note that we have not considered damage due to the decay event¹⁵ itself, as we expect this to be negligible.¹⁶

Figure 1 shows the calculated cohesive energies of $Cs_{1-x}Ba_xCl$ compounds in three competing crystal structures:

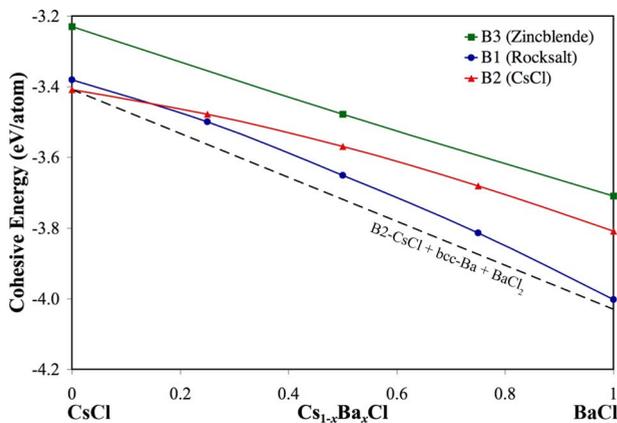


FIG. 1. (Color online) Calculated cohesive energies of $Cs_{1-x}Ba_xCl$ compounds in various competing crystal structures. The dashed line denotes the ground-state energy, i.e., the energy of a mechanical mixture of $B2$ CsCl, bcc Ba, and orthorhombic $BaCl_2$ with the same composition.

$B1$ /rocksalt, $B2$ /cesium chloride, and $B3$ /zincblende. Here the cohesive energy is defined as the energy difference between isolated atoms and the given reference compound. For the binary CsCl compound, our calculations show that the $B2$ structure is more stable than both the $B1$ and $B3$ structures. This result agrees with previous first-principles calculations of alkali halides by Florez *et al.*¹⁷ and is also consistent with the experimental observations that $B2$ CsCl is the low-temperature stable structure in the equilibrium Cs-Cl phase diagram.¹⁸ As the Ba concentration increases, the rocksalt structure is predicted to be energetically more stable than the $B2$ structure for $x > \sim 0.125$. Just like in pure CsCl,¹⁹ the $B2$ - $B1$ phase transformation for these intermediate compositions is likely diffusionless. Surprisingly, when all Cs has been replaced by Ba, we find only a very small (~ 0.03 eV/atom) driving force for the rocksalt $BaCl$ structure to phase separate into a mixture of the orthorhombic-structured $BaCl_2$ [$PbCl_2$ type, space-group $Pnma$ (Ref. 20)] and bcc Ba phases, the two ground-state structures in the Ba-Cl binary system.^{18,21} This suggests that the rocksalt $BaCl$ compound formed via nonequilibrium methods such as radioactive decay is a relatively low-energy metastable structure despite the fact that Ba normally has a +2 charge state instead of +1.²² Similar to the metastable Fe_3C compound widely used for strengthening steels, the rocksalt $BaCl$ compound may well exist at reasonably low temperatures since its decomposition into $BaCl_2$ and Ba metal would require significant mass transport and may therefore be kinetically prohibited due to sluggish atomic diffusion.

The volume of both the $B1$ and $B2$ structures decreases as Cs is replaced by Ba. The volume of the $B1$ structure decreases monotonically from 38.4 to 29.2 $\text{\AA}^3/\text{atom}$ going from CsCl to BaCl, while that of the $B2$ structure decreases from 31.3 to 26.3 $\text{\AA}^3/\text{atom}$. There is also clearly an increase in volume associated with any $B2$ - $B1$ phase transformation of between 7.1 and 2.9 $\text{\AA}^3/\text{atom}$. These volume changes will have implications for cracking of the material as transmuta-

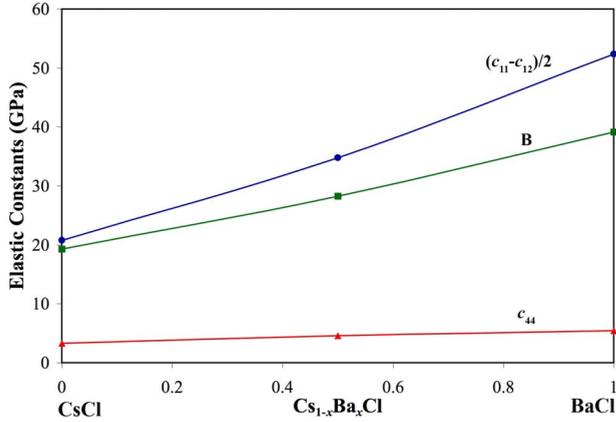


FIG. 2. (Color online) Calculated tetragonal shear modulus $(c_{11}-c_{12})/2$, trigonal shear modulus c_{44} , and bulk modulus $B=(c_{11}+2c_{12})/3$ of rocksalt $\text{Cs}_{1-x}\text{Ba}_x\text{Cl}$ compounds.

tion occurs. It is interesting to note that the volume of CsCl in the $B2$ phase is very similar to that of BaCl in the $B1$ phase.

For a structure to be mechanically stable, its strain energy must be positive against any homogeneous elastic deformation.²³ This criterion imposes the following elastic constant constraints for cubic crystals: $c_{11}-c_{12}>0$, $c_{44}>0$, and $c_{11}+2c_{12}>0$. We obtain the three independent single-crystal elastic constants of rocksalt $\text{Cs}_{1-x}\text{Ba}_x\text{Cl}$ compounds using a stress-strain approach,²⁴ i.e., we determine c_{ij} through a linear least-square fit of the calculated stresses as a function of applied strain. At each given strain, we fully relax all internal atomic positions according to strain-induced forces while holding the distorted lattice vectors fixed. As shown in Fig. 2, rocksalt $\text{Cs}_{1-x}\text{Ba}_x\text{Cl}$ compounds are elastically stable over the entire composition range since their elastic constants obey the above criteria. It can also be seen that those compounds are elastically anisotropic since the Zener ratio $A=2c_{44}/(c_{11}-c_{12})$ is much smaller than unity. Furthermore, the Cauchy relation, $c_{12}=c_{44}$, is approximately satisfied over the whole composition range, suggesting a predominance of central interatomic forces typical of ionic bonding in those compounds.

In addition to the elastic stability criterion, dynamical stability further requires that the phonon spectrum of the structure exhibit no imaginary phonon frequencies.^{25,26} An imaginary phonon mode indicates instability with respect to a particular type of atomic movement, signaling a barrier-less structural phase transition. We use the direct approach^{25,27,28} to calculate the phonon spectrum of rocksalt BaCl. In this approach, the 3×3 interatomic force-constant matrices are fitted to Hellmann-Feynman forces on all atoms in perturbed supercells. Using the fitted force constants, we construct the dynamical matrix for arbitrary wave vectors in the Brillouin zone and obtain the phonon frequencies by solving the eigenvalue equation. In our phonon calculations, we employ large 128-atom supercells to allow for the inclusion of long-range (up to 8.7 Å) force constants in the fit. Our calculated phonon-dispersion relations for rocksalt BaCl along various high-symmetry directions in the Brillouin zone are shown in Fig. 3. There are six phonon branches (three acoustic and

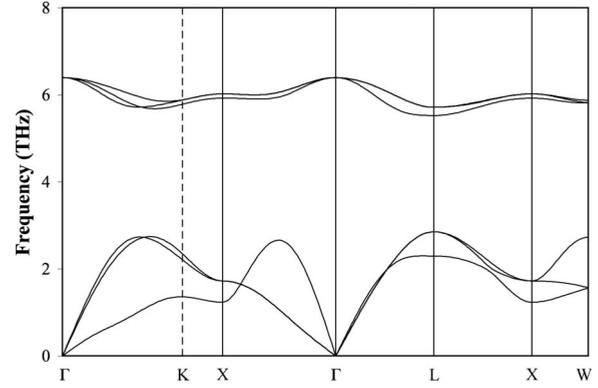


FIG. 3. Phonon dispersion relations for rocksalt BaCl along various high-symmetry directions in the Brillouin zone.

three optical) since the rocksalt primitive unit cell contains two atoms. It is evident that rocksalt BaCl is dynamically stable since all phonon frequencies are positive throughout the Brillouin zone.

To gain insight into the nature of the bonding in BaCl, we have also calculated its electronic density of states (DOS). As shown in Fig. 4(a), rocksalt CsCl is an insulator with a large-band gap, which is consistent with it being a typical ionic compound. Indeed, a Bader charge-density analysis²⁹ indicates that there is significant ($-0.75e$) charge transfer from Cs to Cl atoms. In contrast, we see from the finite DOS at the Fermi level that rocksalt BaCl is metallic [see Fig. 4(b)]. Interestingly, this metallic behavior seems to be consistent with experimental observations that the electric conductivity of CsCl increases upon doping with Ba.³⁰ Indeed, this behavior is what might be expected from a doping perspective as Ba, relative to Cs, has an extra valence electron and would act as an n -type dopant. Since Cl normally takes a -1 charge state, only one electron from Ba will be transferred to Cl to make it fully reduced. The extra $6s$ electron from Ba will then occupy the conduction band, leading to the metallic nature of rocksalt BaCl. Figure 5 further shows the charge-density distribution in the (001) plane of rocksalt BaCl of only those electrons residing in the conduction band. It can be seen that the extra electron from Ba indeed becomes somewhat delocalized, typical of metallic bonding. However,

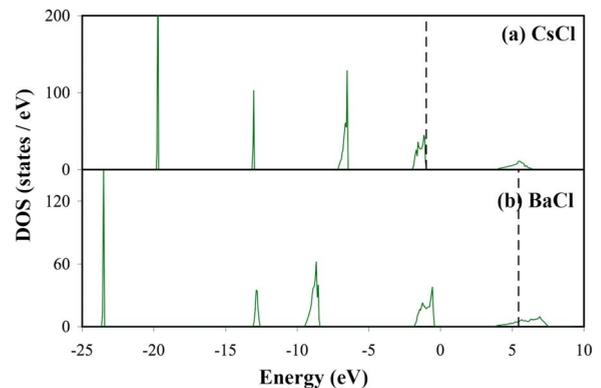


FIG. 4. (Color online) Total electronic density of states of (a) CsCl and (b) BaCl in the rocksalt crystal structure. The vertical lines denote the Fermi level.

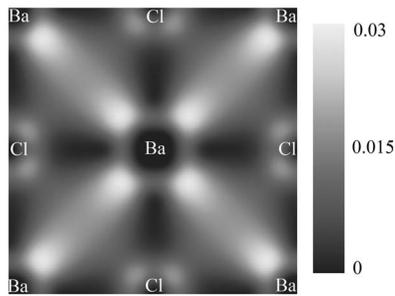


FIG. 5. Conduction band-charge density (in $e/\text{\AA}^3$) on the (001) plane of rocksalt BaCl.

it can also be seen that the bonding between nearest-neighbor Ba atoms does exhibit some directionality, indicative of covalent bonding. Furthermore, it is evident that this extra electron has a stronger association with the Ba ions rather than the Cl ions. This is consistent with a Bader analysis of the BaCl charge density, which finds that the partitioning of the extra electron is about 60% with Ba and 40% with Cl. We thus conclude that the chemical bonding in rocksalt BaCl exhibits a complex mixture of ionic, metallic, and covalent character.

To summarize, using first-principles calculations, we predict the existence of yet unobserved crystalline BaCl in the rocksalt structure. Since there exists a thermodynamic driving force for BaCl to phase separate into BaCl_2 and Ba

metal, it has never been synthesized as a consequence of the difficulty in controlling the Ba/Cl ratio during the synthesis process: given a route to form BaCl_2 , the system would prefer to do so. However, we have identified one clear fabrication route (transmutation of ^{137}Cs atoms in a CsCl host matrix) that can lead to such an unexpected compound. Our calculations indicate that this structure is mechanically stable under ambient conditions and the thermodynamic driving force for phase separation is small. The prediction of metastable BaCl indicates that transmutation may be a potentially powerful fabrication route allowing access to crystalline compounds unable to be synthesized via conventional approaches. This route would be possible for any compound in which one species transmutes into another. For example, unforeseen compounds may arise when SrTiO_3 is fabricated with radioactive ^{90}Sr , which decays first to ^{90}Y and then ^{90}Zr . Due to the complex bonding nature of these compounds, they may exhibit interesting materials properties. It might also be possible to devise clever experiments to fabricate such compounds in more efficient ways.

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