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First principles methods for elpasolite halide crystal structure prediction at finite temperatures

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ABSTRACT

Computational methods able to identify elpasolite halides that crystallize with cubic symmetry are desirable since the isotropic properties of these materials have attractive manufacturing and optical properties. We compare the performance of three levels of theory for four elpasolite halides, $Cs_2NaGdBr_6$, $Cs_2NaLaBr_6$, Cs_2LiLaI_6, and Cs_2LiScI_6, in order to determine the minimum level of theory required to accurately predict the equilibrium crystal structures at finite temperatures. We evaluate ground state, simple harmonic, and quasiharmonic free energies for each material in the common cubic, tetragonal, and trigonal symmetries using Density Functional Theory (DFT) and phonon calculations. The highest level of theory based on a quasiharmonic model accounting for thermal expansion reproduces available experimental phase information for the studied materials and outperforms the simple harmonic model. As expected, ground state energies alone do not provide unambiguous information regarding expected finite temperature crystal structures and fail to identify interesting materials that crystallize with cubic symmetry. The methods we demonstrate will be useful for considering the large number of elpasolite halides that exist to identify desirable crystal structures.

1. Introduction

Scintillators with improved performance that can be produced cost effectively at industrial scales are needed in fields such as national defense, nuclear activity monitoring, and particle physics research [1–3]. Cerium-doped lanthanum halides exhibit excellent room temperature radiation detection properties, but efforts to replace the size-limited Bridgman single crystal growth process with methods that produce high quality polycrystalline ceramics have been unsuccessful [1,3]. Anisotropic crystal structures, mechanical instability, and temperature sensitivity of these materials present manufacturing difficulties. Elpasolite-type scintillator materials such as Cs_2LiYCl_6, conversely, are attractive for large scale production because some of these compounds crystallize in the face-centered cubic (fcc) double perovskite structure associated with desirable isotropic optical and mechanical properties [4]. The cubic structure minimizes lattice strain during single crystal growth and reduces light scattering at grain boundaries [1,2].

Elpasolite halides possess the chemical formula $A_2^+B^+B'^{3+}X_6^-$ where A^+ and B^+ are typically alkali metal cations, B'^{3+} is a trivalent cation such as a rare-earth or transition metal, and X^- is a halogen anion. While the majority of known elpasolite halides crystallize in the Fm-3 m cubic structure, lower symmetry variations occur with changes in composition, temperature, and pressure [5]. Commonly, elpasolites transition reversibly from a low temperature tetragonal phase to a high temperature cubic symmetry. For instance, $Cs_2NaPrCl_6$ and $Rb_2NaTmCl_6$ undergo tetragonal to cubic phase transitions at 158 K and 441 K, respectively [5]. Elpasolites have also been observed in trigonal and orthorhombic symmetries [5].

In this paper, we determine the minimum level of theory needed to identify the temperature-dependent stable crystal structure of four elpasolite halides using Density Functional Theory (DFT). Such modeling capabilities will be useful for identifying cubic elpasolite halide scintillators and for providing phase stability information to guide experiments. Specifically, we use DFT to study the relative thermodynamic stabilities of common cubic, tetragonal, and trigonal phases for $Cs_2NaGdBr_6$, $Cs_2NaLaBr_6$, Cs_2LiLaI_6, and Cs_2LiScI_6. The bromo-elpasolites are known experimentally to undergo phase transitions from tetragonal to cubic structures at 173 K and 316 K for $Cs_2NaGdBr_6$ and $Cs_2NaLaBr_6$, respectively [6]. Cs_2LiScI_6 crystallizes in the trigonal P-3 ml crystal structure, presumably at low temperature [5], and no experimental data on the crystal structure of Cs_2LiLaI_6 is available. Useful thermodynamic models should be able to reproduce the known phase behavior and make an informed prediction for the stable structure of Cs_2LiLaI_6 at finite temperatures. We compare phase predictions based on three levels of theory. In order of increasing computational complexity, these levels include DFT total energies at 0 K that ignore vibrational contributions, a simple harmonic model at

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ground state volumes, and a quasiharmonic model that accounts for thermal expansion.

Methods that have been previously applied to predict phase stability of scintillator materials include both semi-empirical and atomistic approaches. The semi-empirical Goldschmidt tolerance factor has been successful in predicting low temperature crystal structures of perovskite materials [5]. This quantity is based on ideal fcc packing of hard-core spheres with volumes referenced from the ionic radii of constituent atoms. Tolerance factors much greater or less than one indicate distortions of the ideal cubic structure are likely. Babel et al. adapted the tolerance factor for double perovskite elpasolites as

$$t' = \frac{r(A) + r(X)}{\sqrt{2}\left[\frac{r(B)+r(B')}{2} + r(X)\right]}, \tag{1}$$

where r indicates the ionic radius [7]. Use of this criterion, however, does not take into account environmental considerations such as charge transfer and polarizability of ions, and it breaks down for materials such as chloro-elpasolites [5]. Moving beyond the Goldschmidt criterion, a Molecular Dynamics approach based on an embedded ion method that accounts for charge transfer has recently been developed that accepts various properties such as bond lengths, electronegativities, and bond energies. It has been used to predict the crystal structures of alkali halides through simulated annealing and to probe mechanical properties of $LaBr_3$ [4].

While simulated annealing methods are useful for predicting crystal structures for materials with no information available regarding phase stability, DFT-based methods that probe relative stabilities of phases directly may be more computationally efficient for elpasolite halides since the observed crystal structures tend to fall within a small set of likely structures. DFT-based methods are routinely used for geometry optimization, electronic property determination, and ground state crystal structure prediction [8–14]. Several large scale efforts have been made to determine the stable phases of alloys based on DFT total energies at 0 K [15–19]. Higher level methods that evaluate the thermodynamic properties of solids at finite temperature are also commonplace. For example, calculations of the free energy within the simple harmonic level of theory have been used to construct phase diagrams and compute free energies of reaction [20,21]. Quasiharmonic and even explicit anharmonic correction methods have been applied to compute thermodynamic properties of solids, particularly of minerals at elevated pressures [22–27].

2. Levels of theory

At a given temperature, the thermodynamically-preferred phase is that with the lowest Gibbs free energy as given by

$$G = U - TS + PV = F + PV, \tag{2}$$

where U, S, and F are the internal energy, entropy, and Helmholtz free energy contributions, respectively [21]. In our calculations the external pressure P was zero so the quantity calculated was $G = F$, henceforth referred to as the free energy. Three approximations to F with varying computational complexities were utilized. The simplest ground state model is described by

$$F(V_0) = E_0(V_0), \tag{3}$$

with $E_0(V_0)$ as the DFT electronic total energy at 0 K computed at the ground state volume V_0. This model ignores vibrational contributions to the free energy and cannot explicitly predict temperature-dependent phase transitions. The next level of theory, the simple harmonic model, is given by

$$F(V_0, T) = E_0(V_0) + F^{\mathrm{vib}}(V_0, T), \tag{4}$$

and introduces temperature-dependencies through the vibrational free energy F^{vib} evaluated at V_0. $F^{\mathrm{vib}}(T)$ for a given volume was calculated via an integral over the vibrational density of states (VDOS) [21]. The direct method as implemented by Parlinski based on small displacements of non-equivalent atoms in the computational supercell was used to determine and integrate the VDOS, hereafter referred to as a phonon calculation [28]. The computational cost of a simple harmonic model depends greatly on the degree of symmetry of the crystal structure, in particular the number of ion displacements required to compute the VDOS. The cubic, tetragonal, and trigonal symmetries studied in this work required 5, 11, and 21 displacements, respectively.

The third and highest level of theory applied is based on a quasiharmonic model in which the volume dependence of vibrational frequencies is taken into account:

$$F(V, T) = E_0(V) + F^{\mathrm{vib}}(V, T). \tag{5}$$

In contrast to the simple harmonic model, which requires a single phonon calculation at V_0, the quasiharmonic model requires phonon calculations at multiple volumes to determine the free energy surface. At a given temperature, the volume that minimizes $F(V)$ is taken to be the equilibrium volume. Thus, thermal expansion of the solid is implicitly included. In this study, quasiharmonic calculations required an order of magnitude more computational effort than simple harmonic models.

3. Computational details

Plane wave DFT calculations were performed using the Vienna *ab initio* Simulation Package (VASP) [29–33] with the projector augmented wave PW91 GGA exchange–correlation functional [29,34,35]. A cutoff energy of 500 eV was used for the plane wave basis set. Monkhorst–Pack k-point meshes were chosen to give approximately 0.028 Å^{-1} spacing along the reciprocal lattice vectors. First, geometry optimizations were performed on $1 \times 1 \times 1$ unit cells of $Cs_2NaGdBr_6$, $Cs_2NaLaBr_6$, Cs_2LiLaI_6, and Cs_2LiScI_6 in the cubic (Fm-3 m), tetragonal (I4-m), and trigonal (R-3 m) orientations depicted in Fig. 1. Volumes and ion positions were simultaneously relaxed until the Hellman–Feynman forces on each atom were less than 10^{-3} eV Å^{-1}. Crystal structure stabilities based on computed DFT 0 K energies were then compared to remove high energy structures from further consideration for computational efficiency.

For each structure maintained for higher level consideration, volume-only stress minimization (static) quasiharmonic computations were completed, and final values for the ground state and simple harmonic models, Eqs. (3) and (4), were derived from Eq. (5). Static quasiharmonic methods involve performing phonon calculations at each volume in a range of volumes for which the cell shape and ion positions have been simultaneously relaxed, i.e., the potential energy has been minimized. Between 8 and 15 volumes were used to parameterize $F(V,T)$ for $T \leqslant 500$ K for all materials with the exception of Cs_2LiScI_6, which was studied for $T \leqslant 1000$ K. Volume spacing ranged between 10 and 20 Å^3 with the exception of Cs_2LiScI_6, which employed a grid spacing of 5 Å^3 close to the ground state volume and 20 Å^3 at higher volumes to account for volume expansion at high temperatures. For each volume, cell shape and ion positions were relaxed until residual forces on each atom were less than 10^{-3} eV Å^{-1}. Displacement magnitudes were chosen to yield significant maximum forces per atom in the range 0.5–0.8 eV Å^{-1} [28]. For the direct method ion displacement force calculations, trigonal structures were transformed from the hexagonal setting used for initial geometry optimization to a rhombohedral orientation to best approximate a spherical supercell shape. Where soft modes were observed, manifest as