High-throughput Computational Workflows for Screening Fluoride Perovskites for use in Piezoelectrics.

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The search for good piezoelectric materials without toxic elements such as lead is an active area of research. The high-performance piezoelectric lead zirconate titanate relies on the presence of a morphotropic phase boundary (MPB) in the composition-temperature phase diagram where the macroscopic polarization vector quasi-continuously changes direction and/or magnitude, often coupled to a distinct softening of the corresponding elastic constants. A method to design materials that facilitate an MPB is to create a solid solution of two systems with different distorted perovskite structures in their respective ground states. The combination of the systems may then exhibit a desired MPB at some composition ratio between the two endpoints. The approach is to first screen for viable endpoint systems, and then investigate promising solid solutions using an interpolation scheme to screen for combinations with favorable energetics for an MPB. This step is followed by a more in-depth investigation using special quasirandom structures (SQS) for increased precision of the MPB composition.

This research presents a computational investigation that applies automated workflows on a large scale. The workflow is implemented using *httk* [1] and makes use of the automatic error correction and on-the-fly diagnostic that is implemented in the toolkit. The calculations are exclusively done using VASP and the workflow is depicted in Figure 1. The workflow takes a perovskite structure and calculates the ground state energy for the perfect crystal structure and three different distortions via two consecutive relaxation steps. It is then applied to the chemical space of all fluoride perovskites in the form of ABF_3 where the A and B site atoms are all possible permutations of atoms ranging from Li to Bi, excluding the lanthanides, Ne, Ar, and Kr. This gives 3969 fluoride perovskites to screen for candidate systems that can accommodate an MPB.

The first screening step eliminates all the candidates that have a band gap of less than 0.25 eV. Reducing the initial 3969 perovskites to 304 candidates. The second step investigates the energy difference between the cubic phase and three other distortions of the structure; rhombohedral, tetragonal, and rotational. Where the rotational is defined in the scope of this work as a rotation of the octahedra along the 1,1,1 plane. We require a maximum difference between the ground state energy of the phases to be less than 0.5 eV/atom to accommodate an MPB when taken as an endpoint in a solid solution as represented by the second decision romb of Figure 1. The final step in the workflow investigates the stability of the remaining candidates and the results of this step are shown in Figure 3 where out of 131 fluoride perovskites we have found 62 to be stable when compared to Materials project [2] using locally calculated formation energy $E_{form}=E_{ABF3}-E_A-E_B-3E_F$ to compare to the database. From the 62 candidates we construct 192 alloys and using the interpolation schema outlined in [4] we find 27 lead-free fluoride perovskite alloys that have all the prerequisites for accommodating an MPB. The implemented workflows follow closely the work by Armiento et. al. [3] for the chemical space of oxide perovskites, ABO_3.

References

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[3] R. Armiento, B. Kozinsky, M. Fornari, and G. Ceder, Phys. Rev. B, 84:014103, Jul 2011, Screening for high-performance piezoelectrics using high-throughput density functional theory.
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Figures

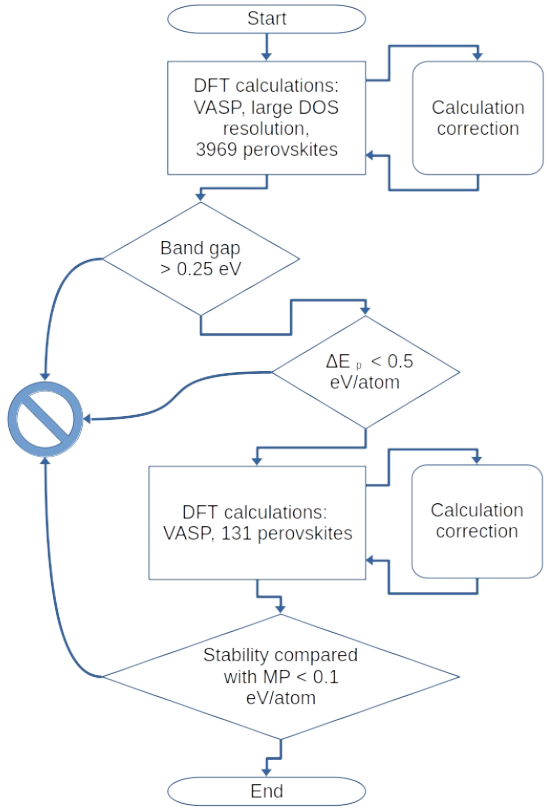

Figure 1. A flowchart over the workflow implemented using *httk*.

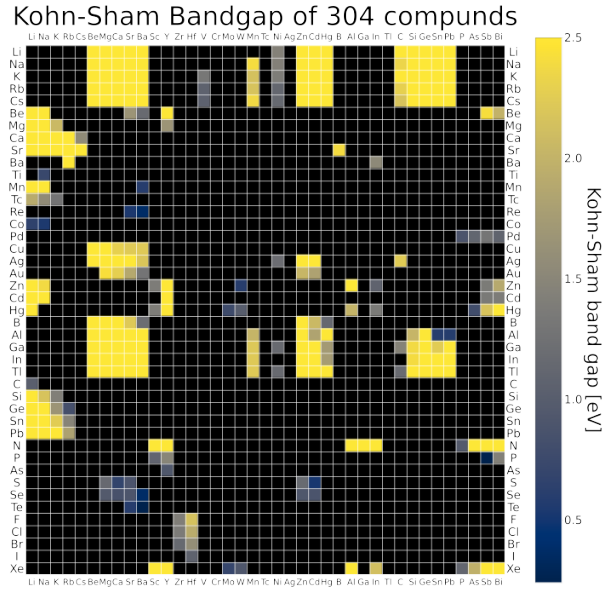

Figure 2. A heat map displaying each of the 304 compounds and their band gap. The color signifies the size of the band gap where bright yellow stands for large and dark blue for small band gap. The largest values are capped at 2.5 eV for readability of the heat map. Every compound with a black color does not meet the criteria and have been excluded. The vertical axis labels represent the A-site atom species, and the horizontal axis labels the B-site atoms species. Columns and rows that would contain only black squares have been excluded from the plot.

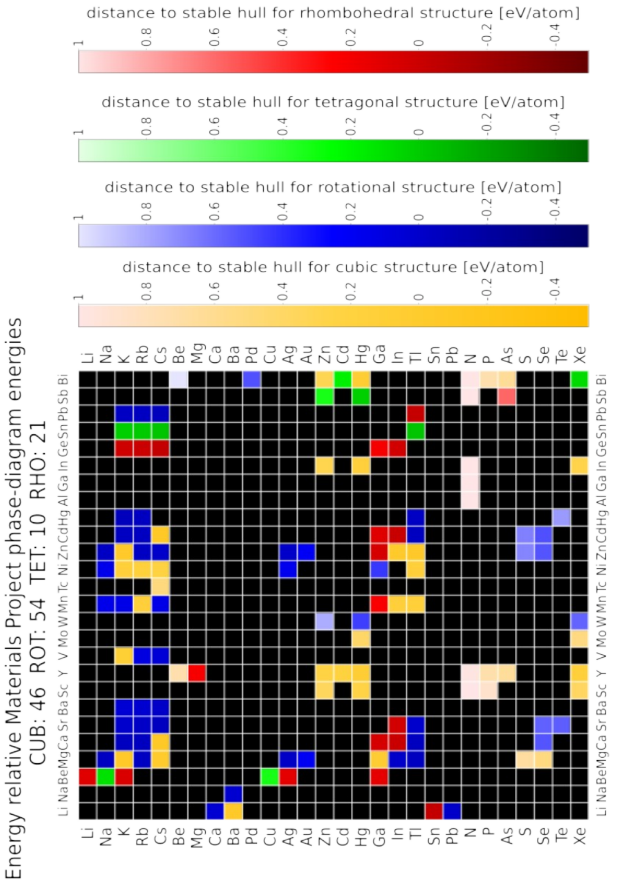

Figure 3. A heat map displaying each of the 131 compounds and there distance from the convex hull of stability as compared to materials project. The color signifies the most stable distortion of the perovskite out of Cubic (yellow), tetragonal (green), rhombohedral (red) and rotation of the octahedra around the 1,1,1 plane (blue). Every compound with a black color does not meet the criteria or have been excluded in a previous step. The vertical axis labels represent the A-site atom species, and the horizontal axis labels the B-site atoms species. Columns and rows that would contain only black squares have been excluded from the plot. The darker the color the more stable the perovskite is found to be.