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**First principles simulations of structural phase transformations in the solid electrolyte $LiBH_4$ with chemical substitutions** NOAM BERNSTEIN, Naval Research Laboratory, KHANG HOANG, North Dakota State University, MICHELLE JOHANNES, Naval Research Laboratory — The proposed hydrogen storage material $LiBH_4$ has been shown to have possible applications as a Li-ion battery solid electrolyte, due to its high Li-ion conductivity over $10^{-3}$ $S/cm^{-1}$ [1], comparable to polymer gel electrolytes. The high conductivity is only observed above a phase transition temperature that is outside of the useful operating range, but doping the material with various substitutions for the Li or $BH_4$ units can bring the phase transition below room temperature. Both smaller and larger substituting species can stabilize the high T structure, indicating that it is not a simple volume effect. We show that variable-cell-shape molecular-dynamics simulations using density functional theory forces and stresses reproduce the structural phase transition. Using umbrella integration to compute the free energy differences between the two structures, we calculate the phase transition temperature and its dependence on substitutional I, Cl, and Na concentrations, and show that they are in very good agreement with experiment. We calculate the effect of K substitution, and predict that it will be even more effective at stabilizing the high T structure. Decomposing the free energy difference changes into enthalpy and entropy contributions shows that the mechanis

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