



FIG. 1. (Color online) Polarization enhancement of PTO/STO configurations with respect to the concentration weighted average of bulk PTO and STO, P_{CE} (), predicted by the cluster expansion approach. The two configurations at breaking points of the convex hull represent the optimal configurations with the largest polarization (LP) at PTO concentrations of 0.25 and 0.5 (named LP0.25 and LP0.5), respectively.

where J_{ij}, J_{ijk}, \dots represent the effective-cluster interactions (ECIs) for pair, three-body, ..., interactions in the chemical system, and the s_i, s_j, s_k, \dots are the multisite cluster functions that form a complete basis set in the configuration space. The ECIs can be obtained by fitting the first-principles calculated results E of a set of ordered configurations to Eq. (1). The CE approach has been applied to total energy [1], Curie temperature [1], elastic modulus [2], thermoconductivity [13], and so on. It is applied here to ferroelectric polarization.

Using the data from DFT calculations, an iterative training process was used to fit the ECIs in Eq. (1). A good convergence was achieved with only 48 DFT inputs. The obtained P_{CE} () includes 15 pairs, one triplet, three quadruplet, and one quintuplet clusters. The cross-validation score [15], representing the prediction error σ_{CE} (), is less than 0.011 C/m^2 .

Searching 3 000 000 configurations for identifying the one with the largest polarization Figure 1 and Fig. S1 [16] show the polarization enhancement P_{CE} () of the $O(3 \times 10^6)$ ordered configurations with respect to the concentration weighted average of the bulk PTO and STO. The two breaking points of the convex hull (PTO concentrations of 0.25 and 0.5) represent the configurations of the largest polarization (LP) that exhibit the mostly enhanced values. Their crystal



