Local structural distortions in the boron sublattice of mixed alkaline earth hexaborides evidenced through reverse Monte Carlo modeling of X-ray pair distribution functions

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Ternary alkaline-earth hexaborides ($Sr_{0.5}Ca_{0.5}B_6$, $Ba_{0.5}Ca_{0.5}B_6$, and $Ba_{0.5}Sr_{0.5}B_6$) synthesized by combustion reactions form metastable nanophase-segregated compounds with large microstrains. X-ray total scattering, analyzed with both symmetry-constrained single unit-cell periodic models and supercell reverse Monte Carlo (RMC) models, is employed to probe the source of this microstrain. Symmetry-constrained single unit-cell models consistently underestimate the B-B length in the pair distribution function (PDF), but provide a good description of medium-to-long range correlations. Through symmetry-breaking deformation of the boron sub-lattice, RMC models successfully account for this elongated B-B correlation distance and reproduce local structure as represented in the PDF. Analysis of RMC refined configurations allows for quantification of this deformation. The greatest deformation occurs with the largest difference between cation radii ($Ba_{0.5}Ca_{0.5}B_6$), and the least deformation occurs with the smallest difference between cation radii ($Sr_{0.5}Ca_{0.5}B_6$). Cubic symmetry breaking has been previously suggested in other alkaline-earth containing hexaborides which show forbidden modes in the Raman spectra. These cubic-forbidden modes are also found in the Raman spectra of the ternary alkaline-earth hexaborides studied here, further supporting the total scattering results.