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Strain analysis of phase transitions in (Ca,Sr)TiO_3 perovskites

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ABSTRACT

A single Landau free energy expansion is used to describe phase transitions in perovskites, from a cubic parent structure to tetragonal and orthorhombic structures with space groups related to the M_3 and R_{25} points of the $Pm\bar{3}m$ reciprocal lattice. This expansion permits relationships between symmetry-adapted forms of the spontaneous strain and individual order parameter components to be predicted. Data from the literature for (Ca,Sr)TiO_3 perovskites are analyzed in the light of these predictions. Shear strains for *I*4/*mcm*, *Pnma*, and *Cmcm* structures tend to conform to the predicted pattern. The $Pm\bar{3}m \leftrightarrow I4/mcm$ transition has nearly tricritical character as a function of temperature in $CaTiO_3$ and more nearly second-order character as a function of composition at the Sr-rich end of the solid solution. Coupling with the volume strain appears to be both temperature and composition dependent, which may be a general feature of phase transitions in perovskites. Renormalization of fourth-order terms by changing the volume coupling coefficients could be responsible for the unusual order parameter evolution shown by $CaTiO_3$ and for changes in thermodynamic character of the phase transitions as a function of composition. The pattern of strain variations also correlates closely with patterns of variations in heat capacity from the literature, suggesting revisions to the subsolidus phase diagram for the (Ca,Sr)TiO_3 solid solution above room temperature.