Elastic anomalies accompanying phase transitions in (Ca,Sr)TiO$_3$ perovskites:  
Part II. Calibration for the effects of composition and pressure

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ABSTRACT

A Landau free energy expansion has been developed in a first attempt to describe the $Pm\overline{3}m \leftrightarrow I4/mcm$ octahedral tilting transition in perovskite across a complete binary solid solution, CaTiO$_3$-SrTiO$_3$ (CST). Only two parameters, the critical temperature and the coefficient, $\lambda_4$, for coupling between the order parameter and the tetragonal strain are given a composition-dependence. The best match between observed and calculated variations of the tetragonal strain as a function of temperature in CaTiO$_3$ (CST0) and as a function of composition at room temperature is found for a model of the solid solution in which the transition is close to tricritical for the composition range CST0 to ~CST90. The change in transition character from second order (246 potential) to tricritical is accounted for by an increase in $|\lambda_4|$ between SrTiO$_3$ (CST100) and ~CST90. The Landau potential is used to calculate the variations of single-crystal and bulk elastic constants through the $Pm\overline{3}m \leftrightarrow I4/mcm$ transition as functions of both pressure and composition. This model for the CST solid solution permits the classical softening effects of strain/order parameter coupling to be separated quantitatively from the much larger superelastic softening observed for twinned crystals of tetragonal SrTiO$_3$ and CST. Data from the literature for relative changes of elastic properties measured at low frequencies have been rescaled to absolute values for comparison with calculated values of Young’s modulus. These appear to show that, below the temperature for domain wall pinning, some 5–10% of softening of the isotropic Young’s modulus could still be due to the effects of twin wall movements.

Keywords: Landau theory, elastic constants, phase transitions, CaTiO$_3$-SrTiO$_3$ solid solution

INTRODUCTION

The CaTiO$_3$-SrTiO$_3$ (CST) solid solution contains perovskites with $Pm\overline{3}m$, $I4/mcm$, and $Pnma$ symmetry, which appear to be closely analogous to the possible structural states of (Mg,Fe)SiO$_3$ and CaSiO$_3$ perovskites. Phase transitions in this system are also easily accessible to in-situ experimental investigation, making them particularly suitable for examining elastic anomalies that accompany changes in structure due to variations in temperature, composition or pressure. It is not necessarily the case that phase transitions occur between the equivalent structural states of silicate perovskites at pressure/temperature conditions within the Earth’s mantle, but studies of elastic anomalies accompanying displacive phase transitions in CST perovskites should provide constraints on the style and magnitude of elastic anomalies that accompany transitions in many perovskite solid solutions as well as in other oxide or silicate phases with ferroelastic instabilities. The present paper is the second in a series of three on this topic. In the first paper (Carpenter 2007), a fully parameterized Landau expansion for the $Pm\overline{3}m \leftrightarrow I4/mcm$ transition in SrTiO$_3$ was tested against diverse experimental data from the literature. The same Landau expansion is used here in a first attempt to produce a quantitative model for the same transition across the entire CST solid solution. In the third paper (Carpenter et al. 2007), new experimental data for bulk and shear moduli obtained as a function of composition and as a function of pressure are used to test the model.

Changes in elastic properties accompanying structural phase transitions can generally be attributed to two basic mechanisms. An intrinsic softening occurs as a consequence of coupling between spontaneous strains, $e$, and the driving order parameter, $Q$. In essence, application of stress causes an elastic deformation, following Hooke’s law, plus an additional relaxation as the order parameter adjusts to the new strain state. The effect is well understood and conforms to standard solutions of Landau free energy expansions (Slonczewski and Thomas 1970, and many subsequent studies). For a relatively recent review of the overall approach to analyzing this elastic behavior, see Carpenter and Salje (1998). In principle, it should be possible to devise a single Landau free energy expansion to describe the strain and elastic behavior of a system in which the symmetry change can be driven by changes in temperature, pressure, and composition. The second important softening mechanism involves movement of twin walls that arise at ferroelastic phase transitions. The amount of softening can be substantially greater than the intrinsic softening due to strain/order parameter coupling, leading to the concept of “superelastic” behavior (Schranz et al. 1999; Kityk et al. 2000a, 2000b; Binder and Knorr 2001; Lemanov et al. 2002; Harrison and Redfern 2002; Harrison et al. 2003, 2004a, 2004b, 2004c). Externally applied stresses cause the twin walls to move, resulting in a strain that can be much greater than the strain due to deforming regions of the crystal between the twin...