Elastic anomalies accompanying phase transitions in (Ca,Sr)TiO₃ perovskites: Part I. Landau theory and a calibration for SrTiO₃

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ABSTRACT

Landau theory has been used to develop expressions for the elastic anomalies that accompany octahedral tilting transitions in perovskites that are associated with the M and R points of the Brillouin zone. The master equation is a 246 Landau potential with saturation terms that provides phenomenological descriptions of transition sequences from a parent cubic structure through tetragonal or rhombohedral intermediates to orthorhombic or monoclinic product structures. Data from the literature have been used to determine values for all the coefficients required to generate a quantitative description of the $Pm\bar{3}m \leftrightarrow I4/mcm$ transition in SrTiO₃, which is taken as a model system. Solutions to the Landau expansion have been adapted to include the general influence of hydrostatic pressure and non-hydrostatic stress on transition temperature and the evolution of the order parameter. Critical examination of elastic constant data from the literature reveals inconsistencies between the results of measurements on tetragonal samples using ultrasonic rather than Brillouin scattering methods. An internally consistent data set has, nevertheless, been assembled. Good qualitative agreement was obtained between the general pattern of calculated and observed variations of all the single crystal elastic constants, and semi-quantitative agreement was obtained for $C_{11}$, $C_{12}$, and $C_{13}$. Some inconsistencies remain in relation to the temperature dependence of the square of the soft mode frequencies in the tetragonal phase, which follow the square of the order parameter rather than its inverse susceptibility, but the 246 potential seems to provide a good description of the structural evolution of SrTiO₃ over a wide temperature interval up to the cubic-tetragonal transition point.

Keywords: Phase transitions, Landau theory, perovskite, SrTiO₃

INTRODUCTION

There has been some debate in the literature as to whether the structure of silicate perovskites is cubic, tetragonal, or orthorhombic at the pressure-temperature conditions of the Earth’s mantle. Current consensus appears to be that the orthorhombic ($Pnma$) structure is most likely to be the stable form of (Mg,Fe)SiO₃ (Wentzovitch et al. 1993; Stixrude and Cohen 1993; Fiquet et al. 1998; Ono et al. 2004a; and references therein). For CaSiO₃, the most recent experimental and computational results appear to be favoring a view that the cubic ($Pm\bar{3}m$) structure may be stable at mantle conditions and that the tetragonal ($I4/mcm$) structure is the stable state at ambient conditions (Ono et al. 2004b; Kurashina et al. 2004; Caracas et al. 2005; Jung and Oganov 2005). Addition of Al stabilizes the orthorhombic structure (Kurashina et al. 2004). It is well known that substantial anomalies in the elastic properties of perovskites occur if they undergo structural phase transitions, and the influence of an individual transition might extend to pressures and temperatures which are well away from the transition point itself (e.g., Carpenter and Salje 1998). Since our understanding of the mantle depends in large part on seismic velocity data which, in turn, depend on the bulk modulus and shear modulus of each of the constituent minerals, considerable efforts have been expended in trying to produce quantitative data for the elastic properties of silicate perovskites. Working directly on the silicate perovskites themselves has been problematic because of the necessity of maintaining high confining pressures to prevent breakdown to other mineral assemblages. Bulk moduli can be obtained from static X-ray diffraction experiments (e.g., Ono et al. 2004a, and references therein), but measuring the shear modulus in-situ at high $P$ and $T$ is much more difficult. The tendency has therefore been to turn to analog systems, which are expected to show similar properties and patterns of structural evolution but have phase transitions in $P$-$T$ ranges that are more amenable to investigation using currently available in-situ methods. One such analog system is the CaTiO₃-SrTiO₃ solid solution. It contains cubic ($Pm\bar{3}m$), tetragonal ($I4/mcm$), and orthorhombic ($Pnma$) forms, with structures that are believed to be exactly analogous to those of the silicate perovskites. Phase transitions between these forms can be induced by changing composition, temperature, or pressure under laboratory conditions (e.g., Mitsui and Westphal 1961; Guyot et al. 1993; Bianchi et al. 1994; Redfern 1996; Grzechnik et al. 1997; Ball et al. 1998; Kennedy et al. 1999; Qin et al. 2000, 2002; Carpenter et al. 2001; Ranjan et al. 2001; Ranjan and Pandey 2001a, 2001b; Yamanaka et al. 2002; Harrison et al. 2003; Ranson et al. 2005; Mishra et al. 2005, 2006a, 2006b). Thus the issue of elasticity as a function of structure type and as a function of transition mechanism can be addressed, with the expectation that the phenomenology will be the same for...