Structural evolution, strain and elasticity of perovskites at high pressures and temperatures

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Octahedral tilting transitions in perovskites are usually identified by the significant lattice distortions which accompany them. The underlying mechanism of coupling between the tilts and the macroscopic strain also gives rise to large anomalies in single crystal and bulk elastic moduli. Landau theory provides an effective framework for describing these different changes in properties and relating them, quantitatively, to the evolution of the driving order parameter for the transition. This approach has been used to analyse the overall elastic behaviour of perovskites belonging to the CaTiO_3 – SrTiO_3 (CST) solid solution, which is expected to be closely analogous to the behaviour of silicate perovskites at higher pressures and temperatures. $Pm\bar{3}m \leftrightarrow I4/mcm$ and $I4/mcm \leftrightarrow Pnma$ transitions in CST perovskites are marked by changes in the shear modulus of ~ 10 – 30% . The evolution of the order parameter and, hence, of the octahedral tilt angles through these can be followed through the variations of spontaneous strains extracted from high resolution lattice parameter data. Contributions to the elastic softening which are due to strain/octahedral tilt coupling have been calculated using a fully parameterised Landau model of the $Pm\bar{3}m \leftrightarrow I4/mcm$ transition as a function of temperature, pressure and composition. Differences between calculated elastic constants and experimental data from Dynamical Mechanical Analysis, pulse-echo ultrasonics and Resonant Ultrasound Spectroscopy suggest that a proportion of the total softening in tetragonal samples may be due to anelastic effects. The anelastic contributions are observed at frequencies of both a few Hz and 10's of MHz, and can be understood in terms of strain contributions arising from movements of transformation twin walls in response to an externally applied shear stress. Similar transitions in other perovskites are likely to display small anomalies in the bulk modulus, due to weak coupling between octahedral tilts and volume strain, but much larger anomalies in the shear modulus. The elastic properties of tetragonal and orthorhombic structures are likely to be quite different due to different anelastic contributions from twin wall displacements.

Keywords: Phase transitions, Elastic constants, Landau theory, Anelasticity, CaTiO_3 – SrTiO_3 solid solution

INTRODUCTION

Of all the physical properties of minerals which are investigated in an earth sciences context, probably those which have the most widespread and pervasive influence are the elastic constants. The importance of seismics in geophysics is self-evident, but many geochemical processes are also directly or indirectly dependent on elastic properties. For example, partitioning of trace elements between crystals and liquids appears to depend systematically on the

effective elastic properties of the crystals (e.g., Van Westrenen et al., 1999), the excess thermodynamic properties of silicate solid solutions can be understood in terms of purely elastic effects (e.g., Carpenter and Boffa Ballaran, 2001; Boffa Ballaran and Carpenter, 2003; Taranino et al., 2003), and the surfaces of crystals differ from their interiors substantially as a consequence of elastic relaxations (Conti and Salje, 2001). For the most part, the elastic properties of minerals vary smoothly with changing pressure, temperature and composition, permitting more or less safe extrapolations or interpolations beyond or between sets of experimental data. If, on the other

Figure 1. Changes in elastic properties through the $\alpha \leftrightarrow \beta$ transition as a function of temperature in quartz (after Carpenter et al., 1998b; Carpenter, 2006). (a) Single crystal elastic constants from the literature (individual symbols) are described by solutions to a Landau free energy expansion for α -quartz and by an expression for the effects of fluctuations in β -quartz. (b) Variations of the bulk (K) and shear (G) moduli for a polycrystalline sample based on the calculated variations of individual elastic constants shown in (a). Solid lines are averages of the Voigt and Reuss limits, which are shown as dotted lines. Solid circles are bulk and shear moduli obtained for a polycrystalline quartz sample by Resonant Ultrasound Spectroscopy at ambient conditions (M.A. Carpenter and T.W. Darling, unpublished data). (c) Variation of P- and S-wave velocities, V_p and V_s , calculated using the Voigt/Reuss averages shown in (b).

hand, a mineral undergoes a displacive phase transition, its elastic constants can change abruptly by 10's of percent. The softening or stiffening can also extend to many hundreds of $^{\circ}\text{C}$ or tens of GPa away from a transition point, as illustrated in Figures 1–3 for transitions in quartz, stishovite and spodumene. The main objective of

the present paper is to give an overview of recent work on the variations in strain and elasticity that accompany octahedral tilting transitions in perovskites. This includes references to new theory and experimental results which will be published in full, elsewhere. The system CaTiO_3 – SrTiO_3 was chosen as an analogue for silicate perovskites, and an overall approach based on Landau theory is used to describe anomalies observed by a variety of experimental methods. It is worth noting that interest in the geophysical or geochemical properties of silicate perovskites represents only a small fraction of the total scientific interest in the solid state properties of man-made perovskites, such as are used in ferroic devices, for example.

Investigations of the layered structure of the earth tend to be focused on discontinuities in elastic behaviour because these are usually more revealing of temperature (T) and composition (X) conditions than the smooth variations with increasing pressure (P) of apparently homogeneous regions. In the case of the reconstructive transition from olivine to wadsleyite, changes in density and seismic velocities across a narrow temperature interval are correlated with PTX information from experimental phase diagrams to provide constraints on T and X at a given depth (e.g., Agee, 1998). Similar information could be provided by discontinuities in the elastic properties of individual minerals, though these may have a distinct advantage in depending on relatively simple phase diagrams. For example, if the transformation from β -quartz (hexagonal) to α -quartz (trigonal) occurred in some silica-rich portion of the crust, it should be marked by a highly distinctive pattern of P- and S-wave velocities – namely a large change in V_p and almost no change in V_s (Fig. 1; Kern 1979, 1982; Carpenter, 2006). The PT trajectory of this transition is well constrained and Mechie et al. (2004) have used it to determine temperature at a depth of 18 km in the Tibetan crust. Marini and Manzella (2005) interpreted a reflecting layer within the lithosphere of Southern Tuscany on a similar basis. The $P4_2/mnm \leftrightarrow Pnnm$ transition at high pressures in stishovite, SiO_2 , is also expected to cause large changes in elastic properties, though the total softening will be spread out over a wider interval owing to the pseudo-proper ferroelastic character. A large anomaly in the shear modulus would be identified through anomalies in both V_p and V_s (Fig. 2; Carpenter et al., 2000; Hemley et al., 2000). Hirose et al. (2005) have explained seismic features with similar attributes in terms of this transition occurring in stishovite at ~ 1500 km depth in subducted MORB crust, northeast of the Mariana subduction zone. A phase transition in monoclinic pyroxene analogous to the $C2/c \leftrightarrow P2_1/c$ transition in spodumene, $\text{LiAlSi}_2\text{O}_6$, would produce yet another distinctive pattern and potential geophysical marker. In spod-

Figure 2. Elastic properties of stishovite as a function of pressure through the tetragonal $\leftrightarrow$ orthorhombic transition at ~ 50 GPa (after Carpenter et al., 2000; Hemley et al., 2000; Carpenter, 2006). (a) Single crystal elastic constants calculated using a Landau model. The superscript $^\circ$ identifies elastic constants of the tetragonal structure without the influence of the phase transition. (b) Bulk and shear moduli calculated as the average of Voigt and Reuss limits for a polycrystalline sample. Dotted lines represent the Voigt and Reuss limits. (c) P- and S-wave velocities through a polycrystalline sample, calculated using the Voigt/Reuss averages shown in (b). Filled circles are experimental values obtained by Li et al. (1996) at room pressure and in-situ at 3 GPa.

umene this transition has first order character and gives sharp discontinuities in compressional wave velocities for selected single crystal orientations (Sondergeld et al., 2006). A semi-quantitative Landau model predicts discontinuities in both the bulk modulus, K , and the shear modulus, G , and, hence, in both V_p and V_s for polycrystalline samples (Fig. 3). The effects of such phase transitions need not be restricted solely to variations of the elastic

Figure 3. Variations of the elastic properties of spodumene, as calculated using a Landau solution for the first order $C2/c \leftrightarrow P2_1/c$ transition at ~ 3.2 GPa (after Sondergeld et al., 2006). The $P2_1/c$ structure is stable above the transition point. (a) Individual elastic constants. For the benefit of clarity, labels for C_{11} , C_{22} , C_{12} , etc. are not shown. Note that a sharp jump is expected in all elastic constants at the transition point and that this pattern is quite different from the patterns of elastic constant variations expected for quartz (Fig. 1) and stishovite (Fig. 2). (b) Bulk and shear moduli calculated for a polycrystalline sample using the single crystal elastic constants shown in (a). Solid lines are averages of the Voigt and Reuss limits, which are shown as dotted lines. (c) Variations of P- and S-wave velocities calculated using the Voigt/Reuss average values of bulk and shear moduli shown in (b).

constants themselves. For example, Cordier et al. (2004) have shown that elastic anisotropy caused by the phase transition in stishovite would contribute to the development of preferred orientations in polycrystalline samples subjected to non-hydrostatic stress. Texturing of this type would give rise to a strongly anisotropic seismic signa-

ture.

Perovskites show a greater diversity of phase transitions than any other man-made or natural materials. The orthorhombic ($Pnma$) structure of $(Mg,Fe)SiO_3$ and the tetragonal ($I4/mcm$) structure of $CaSiO_3$ could both develop by octahedral tilting transitions from their holosymmetric ($Pm\bar{3}m$) forms, for example. If $Pm\bar{3}m \leftrightarrow I4/mcm$ or $I4/mcm \leftrightarrow Pnma$ transitions occurred in these within the mantle, significant elastic anomalies, analogous to those shown in Figures 1–3, would arise. The origin of this anomalous softening need not be restricted to the direct influence of the transitions themselves, however. It was recognised from the early days of elastic constant measurements on $SrTiO_3$ that the displacement of transformation twin walls in response to an applied shear stress can give rise to additional softening and attenuation effects (Rehwald, 1971; Fossheim and Berre, 1972). These can be large in magnitude, giving rise to so-called superelasticity (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). Equivalent behaviour in silicate perovskites cannot be investigated directly because of the high confining pressure required to stabilise them, but a useful analogue system is the binary solid solution $CaTiO_3$ – $SrTiO_3$ (CST). This system displays all the relevant strain, transformation and elasticity phenomena at pressures and temperatures which are readily accessible to in-situ measurements.

PHASE TRANSITIONS IN $(Ca,Sr)TiO_3$ PEROVSKITES

Transition temperatures for the $Pm\bar{3}m \leftrightarrow I4/mcm$ and $I4/mcm \leftrightarrow Pnma$ transitions in CST perovskites vary systematically with composition (Fig. 4a). These are quite well constrained for temperatures above room temperature. Structural behaviour at lower temperatures in samples with compositions at the Sr-rich end of the solid solution is more controversial, but is not relevant in the present context. Transition pressures are less well constrained, but a possible PX phase diagram for room temperature is shown in Figure 4b. The transitions occur by cooperative tilting of the TiO_6 octahedra, and are associated with M and R special points of the Brillouin zone. All such tilting transitions can be described formally using a Landau free energy expansion in which there are three order parameter components, q_1 – q_3 and q_4 – q_6 , associated with each special point (Howard and Stokes, 1998; Carpenter et al., 2001):

Figure 4. T - X and P - X phase diagrams for CST perovskites (M.A. Carpenter, unpublished data). (a) Summary of data from the literature for transition temperatures in the binary solid solution $CaTiO_3$ – $SrTiO_3$, including a stability field for the $Pbcm$ structure (Lemanov, 1997; Ranjan and Pandey, 2001; Qin et al., 2000; Harrison et al., 2003). The horizontal broken line represents room temperature. (Low temperature transitions at Sr-rich compositions are not included). (b) Transition pressures as a function of composition at room temperature. Approximate composition limits for the $Pbcm$ structure at ambient conditions are from Mishra et al. (2006). Data for the $Pm\bar{3}m \leftrightarrow I4/mcm$ transition in $SrTiO_3$ are from Ishidate and Isonuma (1992), Bonello et al. (1989a, 1989b) and Grzechnik et al. (1997). The solid curve is the calculated transition pressure based on Equation 14 and the variation of T_c shown in (a). The data point for CST95 is from M.A. Carpenter (unpublished data). The possible tetragonal $\leftrightarrow$ orthorhombic transition reported by Grzechnik et al. (1997) to be between ~ 12 and ~ 15 GPa is shown arbitrarily at 14 GPa. Broken lines are arbitrary guesses at the trends for $I4/mcm \leftrightarrow Pbcm$ and $Pbcm \leftrightarrow Pnma$ transitions. [Yamanaka et al. (2002) reported that CST65 has $Pnma$ symmetry at 3.5 GPa].

$$G = \frac{1}{2} a_1 \Theta_{s1} \left(\coth \left(\frac{\Theta_{s1}}{T} \right) - \coth \left(\frac{\Theta_{s1}}{T_{c1}} \right) \right) (q_1^2 + q_2^2 + q_3^2) \\ + \frac{1}{2} a_2 \Theta_{s2} \left(\coth \left(\frac{\Theta_{s2}}{T} \right) - \coth \left(\frac{\Theta_{s2}}{T_{c2}} \right) \right) (q_4^2 + q_5^2 + q_6^2)$$

$$\begin{aligned}
& + \frac{1}{4} b_1 (q_1^2 + q_2^2 + q_3^2)^2 + \frac{1}{4} b_1' (q_1^4 + q_2^4 + q_3^4) \\
& + \frac{1}{4} b_2 (q_4^2 + q_5^2 + q_6^2)^2 + \frac{1}{4} b_2' (q_4^4 + q_5^4 + q_6^4) \\
& + \frac{1}{6} c_1 (q_1^2 + q_2^2 + q_3^2)^3 + \frac{1}{6} c_1' (q_1 q_2 q_3)^2 \\
& + \frac{1}{6} c_1'' (q_1^2 + q_2^2 + q_3^2) (q_1^4 + q_2^4 + q_3^4) + \frac{1}{6} c_2 (q_4^2 + q_5^2 + q_6^2)^3 \\
& + \frac{1}{6} c_2' (q_4 q_5 q_6)^2 + \frac{1}{6} c_2'' (q_4^2 + q_5^2 + q_6^2) (q_4^4 + q_5^4 + q_6^4) \\
& + \lambda_q (q_1^2 + q_2^2 + q_3^2) (q_4^2 + q_5^2 + q_6^2) \\
& + \lambda_q' (q_1^2 q_4^2 + q_2^2 q_5^2 + q_3^2 q_6^2) + \lambda_e (q_1^2 + q_2^2 + q_3^2) \\
& + \lambda_2 e_a (q_4^2 + q_5^2 + q_6^2) \\
& + \lambda_3 \left[\sqrt{3} e_o (q_2^2 - q_3^2) + e_t (2q_1^2 - q_2^2 - q_3^2) \right] \\
& + \lambda_4 \left[\sqrt{3} e_o (q_5^2 - q_6^2) + e_t (2q_4^2 - q_5^2 - q_6^2) \right] \\
& + \lambda_5 (e_4 q_4 q_6 + e_5 q_4 q_5 + e_6 q_5 q_6) \\
& + \lambda_6 (q_1^2 + q_2^2 + q_3^2) (e_4^2 + e_5^2 + e_6^2) + \lambda_7 (q_1^2 e_6^2 + q_2^2 e_4^2 + q_3^2 e_5^2) \\
& + \frac{1}{4} (C_{11}^o - C_{12}^o) (e_o^2 + e_t^2) \\
& + \frac{1}{6} (C_{11}^o + 2C_{12}^o) e_a^2 + \frac{1}{2} C_{44}^o (e_4^2 + e_5^2 + e_6^2). \tag{1}
\end{aligned}$$

Note that, here, the symbol G refers to the excess free energy due to a phase transition, rather than the shear modulus. The $I4/mcm$ structure has $q_4 \neq 0$, $q_1 = q_2 = q_3 = q_5 = q_6 = 0$, and the $Pnma$ structure has $q_2 \neq 0$, $q_4 = q_6 \neq 0$, $q_1 = q_3 = q_5 = 0$. T_{c1} and T_{c2} are critical temperatures for the M and R point instabilities, $a_1, a_2, b_1, b_2, \dots$ are standard Landau coefficients, Θ_{s1} and Θ_{s2} are saturation temperatures, $\lambda_1, \lambda_2, \dots$ are coupling coefficients, e_a, e_o, e_t are symmetry-adapted strains and C_{ik}^o are elastic constants of the parent cubic structure. In most cases of tilting transitions in perovskites the structural parameter which should effectively behave as the order parameter is the rotation angle, ϕ , of the octahedra (Glazer, 1972, 1975; Woodward, 1997; Howard and Stokes, 1998). This is zero in the cubic phase and non-zero in the derivative structures. Each of $q_1, q_2, \dots$ can then be related to angles of rotation about different tilt axes. Details of Landau theory applied to minerals have been described in many reviews, including, for example, Salje (1991, 1992), Carpenter (1988, 1992, 2000, 2002), Carpenter et al. (1998a), Carpenter and Salje (1998), Redfern (2000) and Salje et al. (2005). Selected results for perovskites are given below without further

Figure 5. Octahedral tilt angle, ϕ (in degrees), and spontaneous strains through the $Pm\bar{3}m \leftrightarrow I4/mcm$ transition in CST70. (a) The tilt angle for CST70 varies as $\phi^4 \propto (T_c - T)$, implying that the transition is tricritical (after Howard et al., 2005). (b) The tetragonal strain (e_t , filled circles), calculated from lattice parameter data of Howard et al. (2005), varies linearly with ϕ^2 . The volume strain (e_a , open circles) is subject to larger uncertainty than e_t , but varies linearly with ϕ^2 only over a limited range.

explanation.

STRUCTURAL EVOLUTION, OCTAHEDRAL TILTING AND SPONTANEOUS STRAIN

Simple rotation of TiO_6 octahedra about the [001] axis in CST perovskites, with alternate layers parallel to the (001) plane having rotations of opposite sign, leads to the $I4/mcm$ structure. For $(\text{Ca}_{0.3}\text{Sr}_{0.7})\text{TiO}_3$ (CST70), the tilt angle varies with temperature as $\phi^4 \propto (T_c - T)$, where $T_c = 652$ K (Fig. 5a, after Howard et al., 2005). For $q_4 \propto \phi$, this implies that the transition is tricritical in character and, hence, that the order parameter should follow a solution to Equation 1 which has

$$q_4^4 = \frac{a_2 \Theta_{s2}}{(c_2 + c_2'')} \left(\coth \left(\frac{\Theta_{s2}}{T_{c2}} \right) - \coth \left(\frac{\Theta_{s2}}{T} \right) \right). \tag{2}$$

Accompanying the tilting is a tetragonal distortion of the unit cell, e_t , and a volume strain, e_a . In terms of linear strains e_1, e_2, e_3 , these symmetry-adapted strains are given by

$$e_t = \frac{1}{\sqrt{3}}(2e_3 - e_1 - e_2) \quad (3)$$

$$e_a = (e_1 + e_2 + e_3) \quad (4)$$

where $e_1 = (a - a_0)/a_0$, $e_2 = (b - a_0)/a_0$, $e_3 = (c - a_0)/a_0$; a , b , c are lattice parameters of the tetragonal structure at a given temperature and a_0 is the lattice parameter of the cubic structure extrapolated to the same temperature. Setting the equilibrium condition $\partial G/\partial e = 0$ leads to the relationships

$$e_t = -\frac{2\lambda_4 q_4^2}{\frac{1}{2}(C_{11}^0 - C_{12}^0)} \quad (5)$$

$$e_a = -\frac{\lambda_2 q_4^2}{\frac{1}{3}(C_{11}^0 + 2C_{12}^0)} \quad (6)$$

and the prediction that the tetragonal and volume strains should vary linearly with ϕ^2 . Wherever data are available for perovskites, this appears to be true for shear strains such as e_t , and the lattice parameter data of Howard et al. (2005) indeed yield the expected linear dependence (Fig. 5b). Experimental uncertainties introduced in the extrapolation of a_0 from high temperatures tend to result in much greater scatter for the volume strain, e_a , but the non-linear behaviour for CST shown in Figure 5b is not atypical of perovskites; the same type of pattern is seen as a function of temperature in CaTiO_3 and as a function of composition across the CST solid solution at room temperature (Carpenter et al., 2001). Volume strains accompanying the tilting transitions can be positive (increasing pressure favours the high symmetry form) or negative (increasing pressure favours the low symmetry form), showing that the octahedra do not behave as rigid units (Angel et al., 2005). Spontaneous strain data for the cubic $\leftrightarrow$ tetragonal transition show that it is also close to tricritical in pure CaTiO_3 (Carpenter et al., 2001), but more nearly second order in SrTiO_3 (Salje et al., 1998; Hayward and Salje, 1999).

ELASTIC ANOMALIES AS A FUNCTION OF TEMPERATURE

Structural phase transitions lead to elastic softening because of the coupling between spontaneous strains and the order parameter. If the order parameter relates to a particular octahedral tilt, the restoring force opposing this tilt becomes small as the transition point is approached. Because the tilts are linked to macroscopic strains via

strain/order parameter coupling terms such as $\lambda e q^2$, a mechanism is available for the strain response to be modified by the tilting behaviour when an external shear stress is applied. Once the restoring force on the octahedra is small the crystal becomes elastically softer than it would be if the tilting instability did not exist. The important parameters are clearly the strength of coupling between the order parameter and strain, i.e. the magnitude of λ , and the shape of the energy potential which controls the tilting, i.e. $\partial^2 G/\partial q^2$. Expressions for the individual elastic constants are given formally by applying

$$C_{ik} = C_{ik}^0 - \sum_m \frac{\partial^2 G}{\partial e_i \partial q_m} \left(\frac{\partial^2 G}{\partial q_m^2} \right)^{-1} \cdot \frac{\partial^2 G}{\partial e_k \partial q_m} \quad (7)$$

to Equation 1 (Slonczewski and Thomas, 1970). This has been widely used in relation to Landau expansions out to fourth order in q (second order transitions), but only recently extended to the full sixth order potential given above (see, also, Kityk et al., 2000a). For the $Pm\bar{3}m \leftrightarrow I4/mcm$ transition, individual elastic constants, such as C_{11} and C_{44} , are expected to follow

$$C_{11} = C_{22} = C_{11}^0 - \left(2\lambda_2 - \frac{4}{\sqrt{3}}\lambda_4 \right)^2 \chi_4 q_4^2 \quad (8)$$

$$C_{44} = C_{55} = C_{44}^0 - \lambda_5^2 \chi_6 q_4^2, \quad (9)$$

where

$$\chi_4^{-1} = \partial^2 G / \partial q_4^2 = 2(b_2 + b_2')q_4^2 + 4(c_2 + c_2'')q_4^4 \quad (10)$$

$$\chi_6^{-1} = \partial^2 G / \partial q_6^2 = \left[\frac{12\lambda_4^2}{\frac{1}{2}(C_{11}^0 - C_{12}^0)} - b_2' \right] q_4^2 - \frac{2}{3}c_2'' q_4^4. \quad (11)$$

Bulk (K) and shear (G) moduli can be calculated from the individual elastic constants in the usual way by taking the average of Voigt and Reuss limits (Hill, 1952) or by using Hashin-Shtrikman bounds (Watt, 1979; Watt and Peselnik, 1980). Expressions for the Voigt limits have a form which most readily illustrates the relative importance of different parameters in determining how much softening of the bulk properties occurs. For the cubic $\leftrightarrow$ tetragonal transition these are

$$K_V = \frac{1}{3}(C_{11}^0 + 2C_{12}^0) - 4\lambda_2^2 \chi_4 q_4^2 \quad (12)$$

$$G_V = \frac{1}{5}(C_{11}^0 - C_{12}^0 + 3C_{44}^0) - \frac{2}{5}(8\lambda_4^2 \chi_4 + \lambda_5^2 \chi_6) q_4^2. \quad (13)$$

Figure 6. Comparison of calculated variations of single crystal elastic constants for SrTiO_3 with a compilation of experimental data assembled from the literature (M.A. Carpenter, unpublished data). Filled symbols represent ultrasonic data; open symbols represent Brillouin data. Data for C_{12} from Rehwal (1970) are shown as a continuous line (dot-dash line), as in the original paper. Calculated variations of C_{11} , C_{33} , C_{12} , C_{13} and C_{44} are from the Landau parameterisation. Scatter in the data for C_{44} below ~ 30 K, as obtained from conversion of reported data for split acoustic modes directly to elastic constants, is due to additional structural changes which occur in ^{18}O -enriched samples.

Calibration of all the coefficients has been completed for the $Pm\bar{3}m \leftrightarrow I4/mcm$ transition in SrTiO_3 using experimental data for heat capacity, spontaneous strain, phase relations under applied stress, etc. (M.A. Carpenter, unpublished data). This was based on the solution for the evolution of q_4 as a function of temperature obtained by Hayward and Salje (1999), in which both fourth and sixth order terms are significant (246 solution). Calculated variations of the single crystal elastic constants determined with this set of parameters are compared with a compilation of experimental data from the literature in Figure 6.

Figure 7. Elastic properties of polycrystalline SrTiO_3 as a function of temperature. (a) Bulk and shear moduli calculated from single crystal elastic constants (M.A. Carpenter, unpublished data). Solid lines (cubic) and broken lines (tetragonal) are Voigt/Reuss averages based on the Landau solutions shown in Figure 6. The Voigt and Reuss limits are shown as dotted lines. Pseudocubic experimental data (i.e. from twinned crystals) of Rehwal (1970) were used to calculate values of K and G (average of Voigt/Reuss limits) and are shown as by open circles. Experimental data of Lei (1991) are shown as crosses. Experimental data for the bulk modulus are consistent with calculated values for tetragonal SrTiO_3 , but values for the shear modulus are smaller than values calculated assuming that the only softening is due to strain/order parameter coupling. (b) Variations of P-wave and S-wave velocities calculated using the values of K and G shown in (a).

Two features are immediately apparent from the comparison for C_{11} and C_{33} . Firstly, there is close agreement between the model values for the tetragonal structure and Brillouin scattering data collected from within individual twin domains. This represents an independent test of the internal consistency of the Landau model. Secondly, pulse-echo ultrasonic data for single crystals with multiple twin domains show both a higher degree of scatter and a higher degree of softening. This supports the argument that transformation twin walls are important in causing softening which is additional to the effects of strain/order parameter coupling. Overlap of Brillouin and ultrasonic data for C_{44} implies that the presence of transformation

twins does not influence this component of the elastic constant tensor. The experimental data were themselves used to extract values for some of the Landau coefficients, however, so that agreement between the observed and calculated values is a measure of the quality of fit rather than a true test of the model. Variations of K and G are compared in Figure 7a, while the variations of V_p and V_s calculated from these are shown in Figure 7b. The phase transition would be expected to cause only a small deviation in K (λ_2 in Equation 12 is small), but a softening of $\sim 20\%$ is expected in G . The added influence of transformation twins applies only to G and a further $\sim 10\%$ softening is obtained in measurements at frequencies of 10's of MHz.

Softening of the elastic constants of cubic SrTiO_3 ahead of the phase transition (Fig. 6) occurs by a different mechanism that is not discussed here. This type of softening is characteristic of cubic perovskites ahead of cubic $\leftrightarrow$ tetragonal or cubic $\leftrightarrow$ rhombohedral transitions (see Carpenter and Salje, 1998a, and many original references therein). A similar mechanism is responsible for softening in β -quartz ahead of the $\alpha \leftrightarrow \beta$ transition (Fig. 1).

ELASTIC ANOMALIES AS A FUNCTION OF COMPOSITION

A convenient feature of Landau theory is the ease with which variations in composition and pressure can be included simply by allowing selected parameters to become composition and pressure dependent. It is apparent from Figure 4a that the predominant consequence of changing Ca:Sr ratio across the CST solid solution is a systematic change in the transition temperatures. The thermodynamic character of the $Pm\bar{3}m \leftrightarrow I4/mcm$ transition also changes, however, from 246 in SrTiO_3 (Salje et al., 1998; Hayward and Salje, 1999) to tricritical in CST70 (Howard et al., 2005; M.A. Carpenter, unpublished data) and CST0 (Carpenter et al., 2001). The strength of coupling to the tetragonal strain also changes, and the simplest model of the transition which accounts for these effects is one in which only two parameters are adjusted. Firstly, the transition temperature, T_{c2} , is allowed to vary with composition according to the experimental data. Secondly, the coupling coefficient, λ_4 , is set at -0.131 GPa for the composition range CST0–CST92 but allowed to vary linearly between -0.131 GPa at CST92 and -0.075 GPa at CST100. All the other coefficients are assumed to remain constant. Once again, lattice parameter data can be used to test the evolution of the order parameter. At room temperature, e_t is zero in cubic CST92–CST100 but it then increases with increasing Ca-content from CST92. The evolution of q_4^2 at $T = 295$ K is given by Equation 2, with

Figure 8. Strain and elasticity of CST perovskites at room temperature (from M.A. Carpenter, unpublished data). (a) Variations of the tetragonal strain, e_t , and volume strains, e_a , in cubic and tetragonal samples of CST, as extracted by Carpenter et al. (2001) from published lattice parameters. Open circles are experimental values from Ranjan et al. (2001) for the splitting, $\Delta 2\theta$, between 004 and 400/040 reflections in powder X-ray diffraction patterns. These refer to the right hand axis and have been scaled so as to overlap with data for e_t . Solid lines are calculated variations of e_t and e_a at 295 K for a tricritical model of the cubic $\leftrightarrow$ tetragonal transition in the range CST0–CST92. Broken lines refer to a model (246 solution) in which the transition is tricritical in CST0, but becomes progressively more nearly second order with increasing Sr-content (M.A. Carpenter, unpublished data). (b) Predicted variations of single crystal elastic constants due to the $Pm\bar{3}m \leftrightarrow I4/mcm$ transition as a function of composition across the CST solid solution at 295 K (M.A. Carpenter, unpublished data). The value of λ_4 was set at -0.131 GPa for CST0–CST92 (tricritical model). (c) Comparison of observed (filled circles) and calculated (solid lines) bulk and shear moduli. The observed variations are from pulse-echo ultrasonic measurements on polycrystalline pellets (M.A. Carpenter, unpublished data). Calculated variations are averages of the Reuss and Voigt limits from the single crystal elastic constants shown in (b). Approximate composition limits for the $Pbcm$ structure at room temperature are from Mishra et al. (2006). Data for CaTiO_3 and SrTiO_3 (open circles) are values taken from the literature (Bell and Rupprecht, 1963; Liebermann et al., 1977; Ishidate et al., 1988; Ledbetter et al., 1990; Fischer et al., 1993; Sinelnikov et al., 1998; Kung and Rigden, 1999; Lheureux et al., 1999; Webb et al., 1999).

T_{c2} replaced by T_{c2x} to represent the values of T_{c2} at each composition. Values of the strains are then given by Equations 5 and 6, and these are compared with experimental data from the literature in Figure 8a. Close agreement between the experimental data and the calculated strain variations suggests that the tricritical model might also yield robust predictions of single crystal elastic constants and bulk moduli. The latter are shown in Figures 8b and 8c, respectively.

Experimental data for individual elastic constants of intermediate members of the solid solution do not exist, but values of K and G have recently been determined from pulse-echo ultrasonic measurements on polycrystalline pellets of synthetic samples with 16 different compositions (M.A. Carpenter, unpublished data). These have been added to Figure 8c for comparison with the predicted variations. As with data for SrTiO_3 as a function of temperature (Fig. 7a), scatter in the experimental data for K is greater than the small anomaly which is predicted at the transition point. Also as for SrTiO_3 , the experimentally determined values of G for tetragonal samples are significantly softer than the predicted values. This additional softening is at present believed to be due to anelastic effects associated with twin wall motion. The shear modulus of samples with the $Pnma$ structure is significantly stiffer than it is for samples with the $I4/mcm$ structure (Fig. 8c).

ELASTIC ANOMALIES AS A FUNCTION OF PRESSURE

The effect of pressure is introduced into Equation 1 by adding a term Pe_a , where e_a is the volume strain (Eqn. 4). For a thermodynamically continuous $Pm\bar{3}m \leftrightarrow I4/mcm$ transition (second order, 246 or tricritical), the transition pressure, P_c , at a given temperature, T , is then given by M.A. Carpenter (unpublished data) as

$$P_c = \frac{a_2 \Theta_{s2} \frac{1}{3} (C_{11}^0 + 2C_{12}^0)}{2\lambda_2} \left(\coth\left(\frac{\Theta_{s2}}{T}\right) - \coth\left(\frac{\Theta_{s2}}{T_{c2x}}\right) \right). \quad (14)$$

From the known variation of T_{c2} with composition, i.e., T_{c2x} , it is straightforward to predict P_c at room temperature for Sr-rich compositions (Fig. 4b). A general expression for the evolution of q_4 becomes, for the case of a tricritical transition,

$$q_4^4 = \frac{2\lambda_2}{\frac{1}{3}(C_{11}^0 + 2C_{12}^0)(c_2 + c_2'')} (P - P_c). \quad (15)$$

Variations of individual elastic constants and bulk moduli due to the transition can then be calculated as before.

Figure 9. Elastic properties of CST perovskites at high pressures (from M.A. Carpenter, unpublished data). (a) Calculated variations (curves) and observed variations (data points, from Ishidate et al., 1988) of single crystal elastic constants for SrTiO_3 as a function of pressure at room temperature. Straight lines are fits to C_{11} , C_{12} and C_{44} for cubic SrTiO_3 given by Ishidate et al. (b) Comparison of observed (pulse-echo ultrasonic data, filled circles) and calculated variations of bulk and shear moduli as a function of pressure for CST95 at room temperature. Straight lines are fits to the data at low pressures for cubic states, while broken lines are the calculated variations of K and G for tetragonal CST95 ($\lambda_4 = -0.11$ GPa, $P_c = 2.11$ GPa), relative to the extrapolation of the fits to data for the cubic structure. Dotted lines represent trends of data from the literature for SrTiO_3 (Beattie and Samara, 1971; Ishidate et al., 1988; Fischer et al., 1989, 1993; Lheureux et al., 1999).

A comparison of calculated and observed single crystal elastic constants for SrTiO_3 is shown in Figure 9a. The single crystal data given by Ishidate et al. (1988) were collected using Brillouin spectroscopy. At pressures above 6.4 GPa they were from within a single twin domain of the tetragonal structure (Ishidate et al., 1988). Neither of C_{66} and $\frac{1}{2}(C_{11} - C_{12})$ show any deflection through the transition point, as predicted by applying Equation 7 to Equation 1, while the data for C_{11} agree closely with the calculated variations. A comparison of observed and calculated variations of the bulk and shear moduli for CST95 is given in Figure 9b. In this case, the data were obtained in-situ at high pressures using pulse-echo ultrasonics and a polycrystalline sample. The calcu-

lated variations are based on a solution for q_4 and e_1 which is somewhat speculative in assuming that the thermodynamic character is intermediate between tricritical for CST92 and 246 for SrTiO_3 , however, ($\lambda_4 = -0.11$ GPa). The true evolution of q_4 at this composition remains to be determined. (Heat capacity measurements of Gallardo et al. (2003) are consistent with second order character for the transition as a function of temperature in CST96, though their data for the intensities of superlattice reflections are not inconsistent with a 246 solution). Once again, there is little or no deflection of the bulk modulus at the transition point, due to only weak coupling between the order parameter and the volume strain. As with other ultrasonic measurements on twinned tetragonal crystals, the observed softening of the shear modulus differs significantly from the variation calculated on the basis of a standard strain/order parameter coupling model for the transition.

ANELASTICITY AND THE INFLUENCE OF TRANSFORMATION TWIN WALLS

Cubic $\leftrightarrow$ tetragonal transitions characteristically give rise to a microstructure of transformation twins. The spontaneous strain orientation for one twin is different from that of an adjacent twin, so movement of the wall separating them can change the total macroscopic strain of the crystal. If the twin wall moves in response to an applied shear stress, the total resulting strain can become substantially greater than would occur by simple lattice bending and the crystal will be anomalously soft (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). This mechanism of softening involves some dissipation of energy and is anelastic in character. At high temperatures in tetragonal CST perovskites, the dissipation and softening is large, but below a temperature interval centered on ~ 410 K, both effects are substantially reduced (Harrison et al., 2003). Harrison et al. attributed this change to pinning of the twin walls by defects which are mobile at high temperatures but become immobile during cooling. Some anelastic softening occurs in SrTiO_3 below the freezing temperature, however, as seen in published ultrasonic data obtained at MHz measuring frequencies (Figs. 6 and 7) and in Dynamical Mechanical Analysis (DMA) data collected at 1–350 Hz (Schranz et al., 1999; Kityk et al., 2000a, 2000b). Softening of the shear modulus of tetragonal CST beyond what is expected as a consequence of strain/order parameter coupling alone is also seen at room temperature in the pulse-echo ultrasonic data shown in Figure 8c. Evidence that this softening could be due to

Figure 10. Attenuation in CST perovskites from Resonant Ultrasound Spectroscopy (J.W. Walsh, unpublished data). (a) Variation of the quality factor, Q , for polycrystalline samples of CST at room temperature. Tetragonal samples have significantly lower values of Q than cubic or orthorhombic samples, consistent with the view that transformation twins are responsible for a degree of anelastic softening, even at room temperature and frequencies of hundreds of kHz. (b) Variation of Q as a function of temperature for CST50. Transition temperatures delimiting the $4/m\text{cm}$ stability field were taken from Figure 4a. Q has been assigned a value of zero for temperatures at which resonance peaks disappeared from the RUS spectra. The resonance peaks reappeared on heating into the stability field of the cubic structure and on cooling into the stability field of the orthorhombic structure. A high mobility of transformation twin walls at high temperatures is probably responsible for complete attenuation of the signal in tetragonal samples.

anelastic effects is provided by the marked attenuation observed in CST70 and CST80 by Resonant Ultrasound Spectroscopy (RUS) at room temperature (Fig. 10a). Figure 10 shows the variation of the quality factor, Q , as a function of composition from RUS measurements on polycrystalline samples with $\sim 5\%$ porosity (J.W. Walsh, unpublished data). The quality factor is defined as $Q = (\nu/\Delta\nu)$, where ν is the frequency of a strong resonance peak within the frequency range 0.4–1.4 MHz and $\Delta\nu$ is the peak width at half height, and is related to the inverse of

Figure 11. Change in shear modulus, ΔG , as a function of composition and pressure at room temperature for CST perovskites, due to the change from cubic to tetragonal or orthorhombic symmetry (M.A. Carpenter, unpublished data). (a) ΔG was taken as the difference between the observed shear modulus values shown in Figure 8c and a constant value for cubic CST. In the compositional range of tetragonal CST, ΔG scales approximately with q_4 for the tricritical Landau model (broken line, right axis). (b) The difference in shear modulus between cubic (straight line in Fig. 9b) and tetragonal CST95 (filled circles in Fig. 9b) as a function of pressure also scales approximately with q_4 from a Landau model (broken line, right axis).

the attenuation parameter, $\tan\delta$, from DMA experiments (Lee et al., 2000). Details of the dissipation mechanism at MHz frequencies are not known, but twin wall movements could be a more localised bulging between pinning points rather than the macroscopic displacements observed by Harrison et al. (2004a, 2004b, 2004c). At high temperatures resonance peaks in RUS spectra from polycrystalline tetragonal CST samples disappear, implying complete attenuation ($Q \approx 0$). They reappear when the structure becomes cubic at higher temperature or orthorhombic at lower temperatures (Fig. 10b), and the influence of high twin wall mobilities in tetragonal CST is again believed to be involved.

Elastic compliances for different contributions to the elastic properties of a crystal are additive. Thus the compliance, S , of a twinned tetragonal crystal is expected to be given by

$$S = S_{\text{para}} + \Delta S_L + \Delta S_W, \quad (16)$$

where S_{para} is the compliance of the high symmetry form, ΔS_L is the change in compliance described by Landau theory and ΔS_W is the change in compliance due to movements of the twin walls (Schranz et al., 1999; Kityk et al., 2000a, 2000b). Given that the total strain accompanying twin wall movement scales with e_t and, hence, with q_4^2 , the simplest model has $\Delta S_W \propto q_4^2$. This provides an effective description of softening in single crystals of SrTiO_3 (Schranz et al., 1999; Kityk et al., 2000a, 2000b). A different empirical relationship appears to provide a better description of the softening of G for polycrystalline samples of tetragonal CST, however. This has the change in shear modulus, ΔG , due to the cubic $\leftrightarrow$ tetragonal transition varying according to $\Delta G \propto q_4$ as a function of composition at room temperature and as a function of pressure at room temperature for CST95 (Fig. 11). Such an unexpected approximation must arise, at least in part, as a consequence of averaging over all twin wall orientations in a polycrystalline material. Some of the walls will be oriented with respect to an applied shear stress so as to experience the maximum possible displacement. Some will be oriented in such a way that they are not subject to any resolved stress, while most will have orientations intermediate between these limits and therefore be responsible for a range of intermediate strains, as shown in Figure 9 of Harrison et al. (2003).

THE $I4/mcm \leftrightarrow Pnma$ TRANSITION

It has not yet been possible to extend the parameterisation of Equation 1 to all the terms which describe tilting transitions of CST that are associated with the M point of the Brillouin zone (T_{c1} , a_1 , b_1 , ..., λ_1 , λ_3 , ..., etc.). Even without the quantitative information that such a parameterisation would provide, however, it is possible to predict the form of elastic anomalies which might accompany the $I4/mcm \leftrightarrow Pnma$ transition. From expressions for the Voigt limits for changes in K and G due to a $Pm\bar{3}m \leftrightarrow Pnma$ transition (M.A. Carpenter, unpublished data),

$$K_V = \frac{1}{3} (C_{11}^0 + 2C_{12}^0) - 4\lambda_1^2 \chi_2 q_2^2 - 8\lambda_2^2 \chi_4 q_4^2 \quad (17)$$

$$G_V = \frac{1}{5} (C_{11}^0 - C_{12}^0 + 3C_{44}^0) - \frac{2}{5} (8\lambda_3^2 \chi_2 + 3\lambda_6 + 2\lambda_7) q_2^2 - \frac{2}{5} (16\lambda_4^2 \chi_4 + \lambda_5^2 \chi_4 + \lambda_5^2 \chi_5) q_4^2, \quad (18)$$

the $Pnma$ structure in a sequence $Pm\bar{3}m \leftrightarrow I4/mcm \leftrightarrow Pnma$ would be expected to be elastically softer than the

Figure 12. Schematic representation of relative changes in bulk modulus and shear modulus through the sequence of transitions $Pm\bar{3}m \leftrightarrow I4/mcm \leftrightarrow Pnma$ in perovskites. On the basis of Landau expansions for CST (M.A. Carpenter, unpublished data) and excluding the effects of microstructure, each transition is expected to give rise to discontinuous softening of both K and G with falling symmetry (see Equations 12, 13, 17, 18). The amount of curvature just below the transition point depends on how close the evolution of the equilibrium order parameter is to tricritical. Decreasing temperature and increasing pressure should give a sequence which is analogous to increasing CaTiO_3 content.

$I4/mcm$ structure (compare Equations 12 and 13 with Equations 17 and 18). This is because, in the absence of unusual direct coupling effects between q_2 and q_4 , the value of q_4^2 in the $Pnma$ structure will be close to half its value in the $I4/mcm$ structure. If the M point instability is also close to tricritical and the coupling coefficients λ_6 and λ_7 are small, the bulk and shear moduli would be expected to evolve in the manner illustrated in Figure 12 for pressure, temperature or composition as the external variable. That this pattern is not observed (e.g., see Fig. 8c) might be understood in terms of the twin wall related anelasticity of $I4/mcm$ samples. Harrison et al. (2003) found that anelastic contributions to the overall elastic behaviour of CST effectively disappear as soon as $I4/mcm$ symmetry is broken. This is confirmed for frequencies of hundreds of kHz by the increase of Q observed by RUS for $Pnma$ samples, relative to $I4/mcm$ samples (Fig. 10). The reason for such an abrupt change in properties of the twin walls is not understood, but they could simply become immobile (Harrison et al., 2003). Alternatively, the change in tetragonal strain which accompanies the $I4/mcm \leftrightarrow Pnma$ transition could have a bearing. In the $Pnma$ structure the tetragonal strain defined with respect to the crystallographic y -axis, e_{tx} , varies with the R point and M point order parameter components according to (Carpenter et al., 2001)

$$e_{tx} = -\frac{(2\lambda_3 q_2^2 - \lambda_4 q_4^2)}{\frac{1}{2}(C_{11}^o - C_{12}^o)}. \quad (19)$$

This is close to zero at intermediate compositions in the

CST solid solution (Carpenter et al., 2001), implying that λ_3 and λ_4 have the same sign. The net change in strain due to displacement of a twin wall will also be close to zero, therefore, and the elasticity of the bulk crystal will not be affected. Whatever the mechanism might be, the result is that $Pnma$ structures are stiffer than twinned $I4/mcm$ structures (Harrison et al., 2003; M.A. Carpenter, unpublished data; Fig. 8c).

IMPLICATIONS FOR THE ELASTIC BEHAVIOUR OF SILICATE PEROVSKITES

There seems to be a current consensus that $(\text{Mg,Fe})\text{SiO}_3$ perovskite has $Pnma$ symmetry at all pressures and temperatures where it is present in the mantle (Wentzcovitch et al., 1993; Stixrude and Cohen, 1993; Fiquet et al., 1998; Ono et al., 2004a; and references therein). So long as these conditions are substantially away from the tetragonal $\leftrightarrow$ orthorhombic transition point, the amount of softening due to the transition itself is expected to be more or less independent of q_2 and q_4 . In other words, changes in octahedral tilting with changing P , T or composition in the $Pnma$ field will not contribute any additional softening through strain/order parameter coupling effects. If the twin walls are immobile, additional anelastic softening associated with a transformation twin microstructure can be ruled out.

For CaSiO_3 , the most recent experimental and computational results appear to be favouring a view that the tetragonal ($I4/mcm$) structure is stable at ambient conditions and that the cubic ($Pm\bar{3}m$) structure could be stable at mantle conditions (Ono et al., 2004b; Kurashina et al., 2004; Caracas et al., 2005; Jung and Oganov, 2005). Addition of Al substantially stabilises the orthorhombic structure, however (Kurashina et al., 2004). If a cubic $\leftrightarrow$ tetragonal transition occurred in CaSiO_3 within the mantle, it should give rise to a marked anomaly in the shear modulus, as would a tetragonal $\leftrightarrow$ orthorhombic transition. Almost inevitably, tetragonal CaSiO_3 would retain some twinning microstructure, with the implication that the shear modulus would be significantly softer than for either of the cubic or orthorhombic phases and that substantial attenuation of seismic waves would also occur. For pressures and temperatures above the domain wall freezing interval, the amount of softening and attenuation would be expected to be more or less independent of temperature (Harrison and Redfern, 2002; Harrison et al., 2003). For pressures and temperatures below this interval similar effects might be expected, though to a lesser extent and with a strong correlation with the degree of octahedral tilting. If coupling between octahedral tilting and the volume strain is as weak in silicate perovskites as it is

in CST perovskite, any anomalies in the bulk modulus due to tilting phase transitions will be small.

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