The effect of transformation twins on the seismic-frequency mechanical properties of polycrystalline Ca$_{1-x}$Sr$_x$TiO$_3$ perovskite

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ABSTRACT

The low-frequency mechanical properties of polycrystalline Ca$_{1-x}$Sr$_x$TiO$_3$ (0.5 ≤ x ≤ 0.9) have been investigated as a function of temperature and bulk composition using the technique of dynamical mechanical analysis in three-point bend geometry. Ca$_{1-x}$Sr$_x$TiO$_3$ forms a cubic solid solution at high temperatures. At lower temperatures it undergoes successive displacive transitions to tetragonal and orthorhombic phases on cooling and increasing CaTiO$_3$ content. The low-frequency mechanical response of the tetragonal phase is dominated by thermally activated displacements of transformation twin domain walls, causing almost a twofold decrease in storage modulus relative to the twin-free cubic phase on cooling through the phase transition (superelastic softening). Below 140 °C the mobility of domain walls decreases and the storage modulus returns to a value close to that of the cubic phase. For x > 0.85, the cubic to tetragonal transition temperature is below 140 °C and domain walls are immobile immediately on formation, greatly reducing the magnitude of mechanical softening. The frequency dependence of the storage modulus is accurately described by a modified Burgers model of anelastic relaxation. Activation energies of 103 and 96 kJ/mol were obtained for samples with x = 0.7 and 0.74, respectively, suggesting that domain walls are strongly pinned by vacancies at the O positions. Superelastic softening is not observed below $T_c$ for the tetragonal to orthorhombic phase transition in samples with x = 0.5, 0.55, and 0.6. This is explained by the small value of the spontaneous strain in orthorhombic samples with intermediate compositions, which are distorted from cubic symmetry by less than 1%.$^*$ With such small strain contrast between differently oriented twin domains, the effective force on the domain walls due to the external stress is less than the critical unpinning force, preventing displacement of the walls and suppressing superelastic softening.

INTRODUCTION

The attenuation of seismic waves is caused by the dissipation of strain energy as they propagate through an anelastic medium (anelasticity refers to a time-dependent but recoverable strain in response to an applied stress; Nowick and Berry 1972). By combining observations of seismic attenuation with a knowledge of the anelastic properties of minerals, the rheology of the inner Earth may be ascertained. However, the microscopic mechanisms responsible for anelasticity in the Earth’s mantle remain controversial. The two currently favored theories attribute anelasticity in the upper mantle to either the movement of dislocations (e.g., anelastic unpinning) or grain-boundary processes (e.g., grain-boundary sliding) (Karato and Spetzler 1990; Jackson et al. 2003). Recently, however, an alternative mechanism has been proposed as a possible cause of seismic attenuation in the lower mantle from perovskite (Harrison and Redfern 2002). Measurements of the low-frequency mechanical properties of single-crystal LaAlO$_3$ revealed a tenfold decrease in modulus and a large increase in attenuation on cooling through the cubic to rhombohedral phase transition. This was explained by presence of transformation twins in the rhombohedral phase, and their dynamical response to applied force.

Thermally activated displacement of domain walls provides a low-energy mechanism for developing macroscopic strain in response to an applied stress (Fig. 1). In the case of Ca$_{1-x}$Sr$_x$TiO$_3$, the cubic to tetragonal phase transition is accompanied by expansion of the structure along the crystallographic c axis and contraction along the a and b axes. The spontaneous strain is oriented differently in each twin domain. Those domains that are oriented favorably with respect to an applied stress have a lower free energy than those that are oriented unfavorably (e.g., a compressive stress applied along the length of the crystal in Figure 1 would lower the free energy of domain 2 with respect to domain 1, since the axis of contraction in domain 2 is parallel to the axis of compression). This produces an effective force on the domain wall, causing the favorably oriented domains to expand and the material as a whole to change length. The resulting macroscopic strain is determined by the spontaneous strain in each domain, the number of domain walls per unit length, and the distance moved by each wall (Harrison and Redfern 2002). The result is a dramatic reduction in modulus relative to that of the twin-free paraelastic phase, and an increase in energy dissipated due to the interaction between domain walls and lattice defects. This phenomenon, whereby