

Thermoelastic Behaviour of Silicate Perovskites: Insights from New High-Temperature Ultrasonic Data for ScAlO_3

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(Mg,Fe,Al)(Si,Al) O_3 perovskite, the dominant mineral of the Earth's lower mantle, exerts a controlling influence on its elastic properties. In this study, insight into the thermoelastic behaviour of this important high-pressure mineral is enhanced by high-temperature ultrasonic measurements of the elastic wave speeds for a fine-grained polycrystal of its close structural analogue ScAlO_3 assimilated into a thermodynamically consistent model.

1. Introduction

Knowledge of the elastic properties of the dominant (Mg,Fe,Al)(Si,Al) O_3 perovskite phase of the Earth's lower mantle, including the pressure and temperature dependence of the bulk and shear moduli, is critical for analyses of the chemical composition and thermal regime of this remote part of the Earth's interior (at depths of 650 - 2900 km). Substantial progress has recently been made in understanding the equation of state and elasticity of this important high-pressure mineral. However, because measurements undertaken near ambient pressure may be compromised by the marginal metastability of the silicate perovskite phase, and the specimens synthesised under pressures greater than 20 GPa are necessarily very small (linear dimensions < 1 mm), significant uncertainties remain.

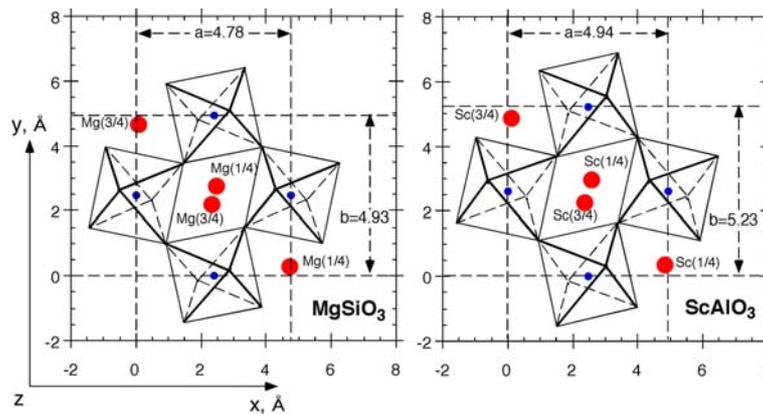


Figure 1. A comparison of the crystal structures of two ABO_3 perovskites: MgSiO_3 (Space group Pbnm with $c = 6.90 \text{ \AA}$ [1]) and ScAlO_3 (Pbnm with $c = 7.20 \text{ \AA}$ [2]). The B (Al or Si) atoms in the layer of BO_6 octahedra are represented by the small filled circles, the A atoms (Mg or Sc) by the large filled circles, and the O atoms by the corners of the octahedra.

For this reason, there is value in the study of close structural analogues such as ScAlO_3 for which specimens of larger volume can be synthesised at lower pressures and tested over a wider range of temperature without risk of retrogressive transformation. Studies of ScAlO_3 ,

the closest structural analogue for magnesium silicate perovskite (Fig. 1), therefore provide potentially important guidance concerning the thermoelastic behaviour of its silicate cousin.

2. Experimental method

A dense fine-grained polycrystalline specimen of ~ 3 mm diameter and 2 mm length, hot-pressed from a gel-derived precursor for previous work in our laboratory was available for the present study. Here we revisit the high-temperature elasticity of ScAlO_3 [3], exploiting enhanced capability for high-temperature ultrasonic interferometry involving the use of a compound steel-alumina acoustic buffer rod within an internally-heated gas-charged pressure vessel [4] and a dual-mode transducer providing for simultaneous measurement of the compressional (V_P) and shear (V_S) wave speeds.

Measurements were performed with a previously described phase-comparison method of ultrasonic interferometry, the essence of which is the creation of conditions for interference between packets of elastic waves reflected back to the transducer from the near and far ends of the specimen. At each interference maximum (minimum) encountered as the carrier frequency f is varied, the two-way path through the specimen contains an integral (half-integral) number p of acoustic wavelengths, or equivalently, the two-way acoustic traveltime t contains p carrier periods, so that $t = p/f$. Measurement of the carrier frequencies of consecutive interference extrema therefore provides precise determinations of traveltime with a high degree of redundancy. A small correction is applied for the effects of the Au foil responsible for mechanical coupling between buffer-rod and specimen.

Mean traveltimes have been determined within a precision of 0.1% at approximately 25°C intervals during cooling from $\sim 700^\circ\text{C}$ to room temperature for common populations of consecutive interference minima for carrier frequencies of 39 - 52 MHz for P waves and 25 - 39 MHz for S waves. The elastic wave speeds V_P and V_S , along with the shear modulus ($G = \rho V_S^2$), compressional modulus ($L = \rho V_P^2$), and adiabatic bulk modulus ($K_S = L - (4/3)G$), have been calculated at each temperature from the mean traveltimes along with the specimen length and X-ray density ρ suitably adjusted for thermal expansion [5].

3. Results and discussion

The elastic moduli vary essentially linearly with temperature as seen in Fig. 2b and c. The derivatives associated with linear fits to the temperature dependence of the bulk and shear moduli are $(\partial K_S/\partial T)_P = -21.3(3)$ MPa K^{-1} and $(\partial G/\partial T)_P = -19.0(1)$ MPa K^{-1} .

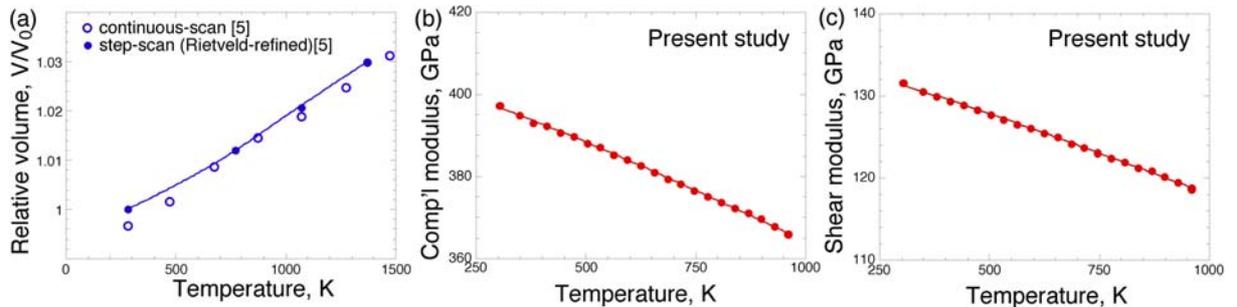


Figure 2. Comparison of the optimal model of Table 1 (curves) with selected thermoelastic data for ScAlO_3 perovskite: (a) The more precise step-scan (Rietveld-refined) data are used to constrain γ_0 and to a lesser degree θ_0 . (b) and (c) Simultaneous fitting of the temperature dependence of the compressional and shear moduli measured in the present study constrains the values of K_{T0} , G_0 , q_0 and η_{s0} .

However, the new data are better assessed within a thermodynamically consistent framework as follows. The Helmholtz free energy $F(V,T)$ is expressed as the sum of static and vibrational contributions, the latter being modelled within the quasi-harmonic approximation by the Debye model with an effective, volume-dependent Debye temperature related to the Debye cut-off frequency ν_D by $\theta(V) = h\nu_D(V)/kT$. Both static and vibrational parts are expanded as Taylor series in the Eulerian finite strain $f = (1/2)[(V/V_0)^{-2/3} - 1]$. Appropriate differentiation with respect to volume, shear strain and temperature then provides an internally consistent framework for the evaluation of all thermoelastic properties including the shear modulus and its pressure and temperature dependence [6].

Table 1. Thermodynamically consistent finite-strain models for the thermoelasticity of ScAlO₃ and MgSiO₃ perovskites.

	ScAlO ₃ ^b	MgSiO ₃ ^c
Parameter ^a		
V_0 , cm ³ mol ⁻¹	27.99	24.45
K_{T0} , GPa	220.3(2)	251(3)
G_0 , GPa	131.4(1)	175(2)
K'_T	3.89(28)	4.1(1)
G'_0	1.90(5)	1.7(2)
θ_0 , K	680(120)	1070(100)
γ_0	1.28(3)	1.48(5)
q_0	2.26(8)	1.4(5)
η_{S0}	2.07(3)	2.6(6)

^a K_T is the isothermal bulk modulus with subscript '0' here and elsewhere denoting ambient conditions ($P = 0.1$ MPa, $T = 300$ K). M' (with $M = K_T, G$) denotes $(\partial M/\partial P)_T$. $\gamma = -d \ln \nu_D / d \ln V$ is the Grüneisen parameter, q and η_S are respectively the logarithmic volume and shear-strain derivatives of γ .

^b This study: see text for details.

^c Parameter values from [6].

Such a model for ScAlO₃ (Table 1) has been optimised by iterative least-squares fitting of $G(f)$ and $L(f)$ from a previous high-pressure study [7], Rietveld-refined $V(T)$ data that are broadly consistent with continuous-scan data of lower precision [5] (Fig. 2a), and simultaneously, $G(T)$ and $L(T)$ from the present study (Fig. 2b and c).

Emerging data for MgSiO₃ perovskite have been similarly fitted to an interim model (Table 1) – although there are substantial residual uncertainties, being addressed by ongoing experimental studies and *ab initio* modelling within the international mineral physics research community. Meanwhile, the robust and comprehensive understanding of the thermoelastic behaviour of the ScAlO₃ analogue may serve as a guide to the properties of its silicate cousin. For example, for both ScAlO₃ and MgSiO₃ perovskites, the isobaric temperature derivative $(\partial G/\partial T)_P$ consists of comparable intrinsic $[(\partial G/\partial T)_V]$ and extrinsic $[-\alpha K_T G']$ contributions. For $(\partial K_S/\partial T)_P$ the intrinsic contribution is negligible for ScAlO₃, whereas the interim model for MgSiO₃ suggests a substantial (~30%) intrinsic contribution. Another parameter of importance in projection of laboratory data to the extreme P - T conditions of the Earth's lower mantle is $(\partial M_S/\partial P)_S$ ($M = K, G$) and its temperature dependence. Evaluation of the new model for ScAlO₃ at high temperature and ambient pressure indicates upward adjustment of $(\partial K_S/\partial P)_S$ by 0.25 between 300 and 1600 K, a plausible potential temperature for the

convecting mantle, compared with 0.11 for the interim model for MgSiO₃. The corresponding adjustments to $(\partial G/\partial P)_S$ are 0.01 and 0.04 for the ScAlO₃ and MgSiO₃ models.

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