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Elasticity of (Mg, Fe)(Si, Al)O_3-perovskite at high pressure

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Abstract

The most abundant mineral on Earth has a perovskite crystal structure and a chemistry that is dominated by $MgSiO_3$ with the next most abundant cations probably being aluminum and ferric iron. The dearth of experimental elasticity data for this chemically complex mineral limits our ability to calculate model seismic velocities for the lower mantle. We have calculated the single crystal elastic moduli (c_{ij}) for (Mg, Fe^{3+})(Si, Al)O_3 perovskite using density functional theory in order to investigate the effect of chemical variations and spin state transitions of the Fe^{3+} ions. Considering the favored coupled substitution of Mg^{2+}–Si^{4+} by Fe^{3+}–Al^{3+}, we find that the effect of ferric iron on seismic properties is comparable with the same amount of ferrous iron. Ferric iron lowers the elastic moduli relative to the Al charge-coupled substitution. Substitution of Fe^{3+} for Al^{3+}, giving rise to an Fe/Mg ratio of 6%, causes 1.8% lower longitudinal velocity and 2.5% lower shear velocity at ambient pressure and 1.1% lower longitudinal velocity and 1.8% lower shear velocity at 142 GPa. The spin state of the iron for this composition has a relatively small effect (<0.5% variation) on both bulk modulus and shear modulus.

Keywords: elasticity; perovskite; ferric iron; density functional theory

1. Introduction

Magnesium-silicate perovskite, the major component of the Earth's lower mantle, is a carrier of iron and the major carrier of Al. From high pressure experimental data, about 5 mol% of Al, proposed as the composition for the Earth's mantle, has been reported to lower the bulk modulus by 10% [1], and cause a decrease in shear modulus only of 5.6% [2]. Theoretical calculations [3] have predicted that adding 25 mol% of $FeSiO_3$ to $MgSiO_3$ perovskite results in a decrease in shear modulus of up to 8% at core–mantle boundary pressure. Even though a number of experimental and theoretical studies have reported the elastic properties of $MgSiO_3$ perovskite [4–8], iron-bearing $MgSiO_3$ perovskite [3,9–13], and Al-bearing $MgSiO_3$ perovskite [1,2,14–21], there is still uncertainty regarding the single crystal elastic properties for (Mg, Fe)(Si, Al)SiO_3 perovskite, which is a composition much closer to that of the Earth's lower mantle than iron-bearing or Al-bearing perovskite alone. Recent studies [22 23] have shown that with the presence of Al, more Fe partition into perovskite compared with

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Al-free system in which Fe partitions preferentially into magnesiowustite at lower mantle conditions. Moreover, in Al-bearing perovskite, Fe^{3+}/total Fe is at least 60%; high level of Fe^{3+} content exists even with the presence of metallic iron. The amount of Fe^{3+}/total Fe in natural (Mg, Fe)O inclusions has been reported as less than 7% [24]. Therefore, Fe^{3+} is expected to be more abundant than its divalent form in the lower mantle.

Complexity resides in the incorporation of trivalent cations into perovskite. In the charge-coupled substitution ($2M^{3+} \rightarrow Mg^{2+}$ and Si^{4+}), two trivalent cations charge balance each other; in the oxygen vacancy forming substitution ($2M^{3+} \rightarrow 2M_{Si} + V_O$), point defects are introduced. Extensive studies on the substitution mechanism in $MgSiO_3$ perovskite in recent years [14,21,25–27] agree that the charge coupled substitution is favoured especially at high pressure. When both Fe^{3+} and Al^{3+} are introduced, the substitution ($Fe^{3+} + Al^{3+} \rightarrow Fe_{Mg} + Al_{Si}$) is energetically favorable [26]. Moreover, the pressure dependence of the spin transition in ferric iron bearing perovskite has been reported by a number of diamond cell experiments [28–30]. The observed transition pressure was further predicted by theoretical calculation [31] on (Mg, Fe)(Si, Al)O_3 with Fe^{3+} occupying the Mg site and Al^{3+} occupying the Si site. We have, therefore, focused on the elastic properties of (Mg, Fe)(Si, Al)O_3, and report here the calculated elastic properties of (Mg, Fe)(Si, Al)O_3 perovskite containing 6.25 mol% of ferric iron (substituting for Mg) and 6.25 mol% of Al^{3+} (substituting for Si). This Al content in this perovskite is close to that expected in a pyrolite composition.

2. Calculation method

Computations are performed using the density functional theory (DFT) based VASP code with the projector augmented wave implementation [32,33] and a plane wave basis set with kinetic energy cut-off of 800 eV. The electron exchange and correlation is described within the generalized gradient approximation (GGA-PW91) [34,35]. The Γ-point is used for Brillouin zone sampling. We used a $2 \times 2 \times 1$ super-cell with *Pbnm* symmetry containing 80 atoms, allowing lattice parameters as well as ionic positions to relax at 0 K, using the conjugate-gradient technique. Calculations were performed with the spin state on the Fe^{3+} ions fixed in high, intermediate, and low spin states at pressures between 0 and 150 GPa. To obtain accurate elastic moduli in the limit of zero strain, positive and negative strain of magnitude 1% were applied and corresponding stress were deduced. Expanding the plane-wave cut-off energy to 1000 eV and the Monkhorst-Pack grids [36] by two *k*-points in each direction varies the enthalpy by less than 1.5 meV/atom and varies the stress and elastic constants by less than 1%. The calculations were considered converged with cut-off energy of 800 eV.

Substitution of iron and aluminum causes a disordered atom arrangement. Even though the space group for a disordered structure remains unaffected for the bulk, each unit cell in a real crystal will not satisfy the space group conditions having distortions from precisely equal and orthogonal lattice parameters [37]. The effect of disorder can be minimized by averaging over the equivalent positions of Fe and Al atom, which are four symmetrically equivalent 4c sites [3]. The listed elastic constants include this average. Table 1 lists five different perovskite models with $Fe^{3+} + Al^{3+} \rightarrow Fe_{Mg} + Al_{Si}$ substitution. In the following, we use the notation used previously [21,31] for the charge-couple model (CCM) with the specific sites for the substitution indicated by 1–5. Elastic moduli for pure perovskite and one iron-free model CCM1 ($Al^{3+} + Al^{3+} \rightarrow Al_{Mg} + Al'_{Si}$) were also calculated for comparison. Based on the calculated elastic moduli, we determine the acoustic velocities as a function of crystallographic direction using the Christoffel equation [38]. The measure of elastic azimuthal anisotropy reported is the ratio of the fastest acoustic velocity to the slowest one.

Despite the fact that iron-bearing minerals such as the B1-structure of FeO [39, 40] and fayalite Fe_2SiO_4 [41] were falsely predicted by DFT as metallic, ferric iron (d^5-ion) is in general better described in DFT than ferrous iron (d^6-ion), and both the geometrical and electronic properties of Fe_2O_3 have been reproduced within the LDA method [42].

Table 1
Initial fractional atom positions of substituted ions for (Mg, Fe)(Si, Al)O_3 perovskite and Fe–Al atom distance for high spin at 0 GPa; the sites for the charge-coupled models (CCM) follow previous notations [21]

	Al^{3+}	Fe^{3+}	*d*(Fe–Al), Å
CCM1	(0.500, 0.248, 0.497)	(0.508, 0.467, 0.747)	2.80
CCM2	(0.496, 0.250, 0.500)	(0.738, 0.219, 0.747)	2.92
CCM3	(0.500, 0.249, 0.500)	(0.491, 0.529, 0.253)	3.29
CCM4	(0.499, 0.250, 0.500)	(0.241, 0.720, 0.750)	5.59
CCM5	(0.499, 0.250, 0.500)	(0.008, 0.790, 0.753)	5.77