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Single-crystal elasticity of (Al,Fe)-bearing bridgmanite and seismic shear wave radial anisotropy at the topmost lower mantle

Suyu Fu^{a,1}, Jing Yang^{a,1,2}, Noriyoshi Tsujino^b, Takuo Okuchi^b, Narangoo Purevjav^b, Jung-Fu Lin^{a,*}

^a Department of Geological Sciences, Jackson School of Geosciences, The University of Texas at Austin, Austin, TX 78712, USA ^b Institute for Planetary Materials, Okayama University, Misasa, Japan

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ABSTRACT

In this study, we investigated the single-crystal elasticity of (Al,Fe)-bearing bridgmanite (Bgm) with chemical compositions of $Mg_{0.95}Fe_{0.033}^{2+}Fe_{0.027}^{3+}Al_{0.04}Si_{0.96}O_3$ (Fe6-Al4-Bgm) and $Mg_{0.89}Fe_{0.024}^{2+}Fe_{0.096}^{3+}Al_{0.11}$ Si_{0.89}O₃ (Fe12-Al11-Bgm) using combined experimental results from Brillouin light scattering (BLS), impulsive stimulated light scattering (ISLS), and X-ray diffraction (XRD) measurements in diamond anvil cells at 25 and 35 GPa. Based on experimentally measured compressional and shear wave velocities (V_P , V_S) as a function of azimuthal angles within selected crystal platelets that are sensitive to derivation of nine elastic constants for each composition, we reliably derived the full elastic constants of Fe6-Al4-Bgm and Fe12-Al11-Bgm at the two experimental pressures. Our results show that the combined Fe and Al substitution results in a reduction of both V_S and V_P in Fe12-Al11-Bgm up to 2.6(±0.5)% and 1.5(±0.3)%, respectively, compared with those in Fe6-Al4-Bgm at the experimental pressures. In particular, we observed strong combined Fe and Al effects on V_S splitting anisotropy of (Al,Fe)-bearing Bgm at the two experimental pressures: Fe6-Al4-Bgm exhibits the highest $V_{\rm S}$ splitting anisotropy of ~8.23-9.0% along the [001] direction, while the direction shifts to the midway between [100] and [001] directions for Fe12-Al11-Bgm with V_S splitting anisotropy of ~7.68-11.06%. Combining the single-crystal elasticity data of Fe6-Al4-Bgm and Fe12-Al11-Bgm with the crystallographic preferred orientation (CPO) results of deformed Bgm at relevant lower-mantle pressure-temperature (P-T) conditions from literature, we modeled the seismic V_S radial anisotropy of deformed (Al,Fe)-bearing Bgm near a subducting slab at conditions relevant to the topmost lower mantle. Taking into account the Fe and Al contents in (Al,Fe)-bearing Bgm with depth in the Earth's topmost lower mantle, the results of our model show that the deformation of Fe6-Al4-Bgm and Fe12-Al11-Bgm crystals would produce \sim 0.9% and \sim 0.8% V $_{S}$ radial anisotropy at depths of \sim 670 and \sim 920 km, respectively. These findings provide mineral physics explanations to the distinct seismically-detected V_{S} radial anisotropies at the topmost lower mantle near subducted slabs, especially in the Tonga-Kermadec subduction region.

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1. Introduction

Seismic shear wave radial anisotropy $(\xi = (V_{SH}/V_{SV})^2$, where V_{SH} and V_{SV} are horizontally and vertically polarized shear waves, respectively) is typically observed in the boundary layers of the Earth's deep interior, including the upper mantle, topmost lower mantle, and the lowermost mantle in the D'' regions (e.g., Montagner and Guillot, 2002; Panning and Romanowicz, 2006;

Corresponding author.

Wookey and Kendall, 2004). These seismic observations appear to be geographically related to subduction zones on a global scale. It has been commonly proposed that the observed seismic anisotropy is caused by mantle convection flow that results in the deformation-induced CPO of the elastically anisotropic minerals in the deep Earth (e.g., Mainprice, 2010). For instance, the deformation with [100]{0kl} slip in olivine, the most abundant mineral in the upper mantle, has been used to explain seismicallyobserved V_S radial anisotropy (<2%) in this region (e.g., Ismail and Mainprice, 1998), while the CPO in silicate post-perovskite is invoked to explain seismically-observed ξ of 1-3% with $V_{SH} > V_{SV}$ in the lowermost mantle near subducted slabs of oceanic lithosphere (e.g., Wu et al., 2017). In particular, while the lower mantle

E-mail address: afu@jsg.utexas.edu (J.-F. Lin).

¹ These authors contributed equally to this work.

 $^{^{2}\,}$ Now at Geophysical Laboratory, Carnegie Institution of Washington, DC, USA.

is believed to be mostly isotropic, a weak shear wave anisotropy (1-2%) has been observed at the topmost lower mantle with depths of ~670-1000 km, in the vicinity of subducting slabs such as the Tonga-Kermadec slab (e.g., Panning and Romanowicz, 2006; Wookey et al., 2002; Wookey and Kendall, 2004). To better understand the seismic anisotropy at the topmost lower mantle, comprehensive knowledge of single-crystal elasticity and CPO of candidate minerals at relevant high P-T is critically needed.

Based on geochemical and geophysical evidence, Earth's lower mantle is believed to consist of a pyrolitic composition with \sim 75 vol% (Al,Fe)-bearing Bgm, \sim 20 vol% ferropericlase (Fp) and \sim 5 vol% calcium silicate perovskite (Ca-Pv) (e.g., Irifune et al., 2010). Bgm, the most abundant mineral in the lower mantle, crystallizes with an orthorhombic structure and exhibits anisotropic properties with nine elastic constants (C_{ii} , contracted in Voigt form in this study) under lower-mantle P-T conditions (e.g., Yeganeh-Haeri, 1994). Early studies indicate that Bgm could accommodate abundant Al and Fe, as much as 10 mol% and 11 mol%, respectively, in its structure via charge-coupled substitution: $Mg_A^{2+} + Si_B^{4+} \leftrightarrow Fe_A^{3+} + Al_B^{3+}$, where Fe^{3+} and Al^{3+} replace dodecahedral-site (A-site) Mg^{2+} and octahedral-site (B-site) Si⁴⁺, respectively (Lin et al., 2016, 2013). The occurrence of extensive Fe^{3+} in Bgm could be further explained by the disproportionation reaction (e.g., Frost et al., 2004; McCammon, 1997). However, studies on the single-crystal elasticity of MgSiO₃ endmember and (Al,Fe)-bearing Bgm are limited to either ab initio calculations for high P or P-T conditions (Karki et al., 1997; Li et al., 2005; Oganov et al., 2001a; Wentzcovitch et al., 2004) or relatively low experimental pressures below 40 GPa due to technical limitations (Fukui et al., 2016: Kurnosov et al., 2017; Yeganeh-Haeri, 1994). In particular, the C_{ii} data from ab initio calculations, even for pure endmember MgSiO₃ Bgm, are not reasonably consistent with each other at high P or *P*-*T* conditions. This is probably due to different approximations used in different studies, such as the static (0 K) computation with local density approximation (LDA) by Karki et al. (1997), combined LDA and quasi-harmonic approximation (QHA) for high P-T elasticity calculations by Wentzcovitch et al. (2004), and combined static calculation and generalized gradient approximation (GGA) with molecular dynamics theory by Oganov et al. (2001a). Furthermore, due to the complexity in the structural and electronic properties of Fe and Al in (Al,Fe)-bearing Bgm system, the substitution of Fe and Al in Bgm would further complicate the ab *initio* simulations. On the other hand, the V_P signal of Bgm can be blocked by the diamond V_S peak at high pressures approximately above 20 GPa when using BLS method, which limits experimental velocity data to reliably derive its full elastic constants at lower-mantle pressures (Lin et al., 2018). A recent experimental study on the single-crystal elasticity of (Al,Fe)-bearing Bgm with a composition of Mg_{0.9}Fe_{0.1}Al_{0.1}Si_{0.9}O₃, denoted as Fe10-Al10-Bgm, with $Fe^{3+}/\Sigma Fe = \sim 0.66$ up to 40 GPa at room temperature using BLS method suggests an Fe³⁺-rich pyrolitic lower mantle at depths of \sim 670-1200 km (Kurnosov et al., 2017). However, Lin et al. (2018) reanalyzed the velocity data of Kurnosov et al. (2017) using Christoffel's equations and finite-strain theory and the analysis showed large uncertainties on the derived C_{ii} values. Lin et al. (2018) further pointed out that Kurnosov et al. (2017) used crystallographic orientations of Bgm that are not sensitive for the derivation of all nine C_{ij} . Additionally, reliable derivation of the full elastic constants of Bgm requires extensive measurements of both V_P and V_S from crystal platelets sensitive to all C_{ij} at lowermantle pressures, instead of limited velocity data using only BLS (Lin et al., 2018).

To overcome the experimental technical challenges, in recent years, ISLS method has been employed to measure V_P of lower mantle minerals at high pressures, together with BLS method to measure V_S (Fu et al., 2017, 2018; Yang et al., 2015). The elastic-

ity of polycrystalline Fe-bearing Bgm measured by both BLS and ISLS showed abnormal V_P softening and slightly increased V_S at 42.6-58 GPa as a result of the spin transition of B-site Fe^{3+} (Fu et al., 2018). This finding challenges our current understanding of the chemical effects of Fe on the elasticity of lower-mantle Bgm (Fu et al., 2018). Furthermore, seismic tomography and mineral physics experiments indicate that the Earth's lower mantle could be laterally and radially heterogeneous (e.g., Garnero and McNamara, 2008: Irifune et al., 2010: Xu et al., 2017). For instance, early studies suggested that under mid-lower mantle conditions, the Fe partitioning coefficient between Bgm and Fp in a pyrolitic composition $(K_D^{Bgm-Fp}, \text{ given by } [Fe^{2+}+Fe^{3+}]_{Bgm}/[Mg^{2+}]_{Bgm})/[Fe^{2+}]_{Fp}/[Mg^{2+}]_{Fp})$ increases from \sim 0.5 at 24 GPa to almost 0.9 at approximately 28 GPa due to charge-coupled substitution. This coefficient is then reduced to ~ 0.5 at approximately 40-50 GPa due to the spin transition of Fe in Fp (e.g., Irifune et al., 2010; Lin et al., 2013; Xu et al., 2017). Together with the changes of Fe content in (Al,Fe)-bearing Bgm, Al content in Bgm will subsequently vary with depth via charge-coupled substitution (Irifune et al., 2010). Early ab initio calculations also showed that the substitution of Fe and Al into Bgm would greatly affect its V_P and V_S , as well as anisotropic properties at high pressure: substitution of Mg^{2+} and Si^{4+} with Fe^{3+} and Al^{3+} in Bgm with an Fe/Mg ratio of 6% reduces V_S by \sim 2-3% and V_P by \sim 1.5% towards the core-mantle-boundary (CMB) conditions (Li et al., 2005). Therefore, the chemical variations of Al and Fe contents in (Al,Fe)-bearing Bgm can play a relevant role in the single-crystal elasticity of (Al,Fe)-bearing Bgm, and thus, seismic anisotropy at the topmost lower mantle.

In this study, we have investigated the single-crystal elasticity of (Al,Fe)-bearing Bgm with two compositions, $Mg_{0.95}Fe_{0.033}^{2+}Fe_{0.027}^{3+}$ $Al_{0.04}Si_{0.96}O_3$ and $Mg_{0.89}Fe_{0.024}^{2+}Fe_{0.096}^{3+}Al_{0.11}Si_{0.89}O_3$, at 25 and 35 GPa in diamond anvil cells (DACs). These compositions, Fe6-Al4-Bgm and Fe12-Al11-Bgm, are selected to represent realistic Fe and Al contents in (Al,Fe)-bearing Bgm in a pyrolite compositional model at depths of approximately 670 and 900-1000 km, respectively. To prepare for high-pressure experiments, we conducted sensitivity tests for Bgm platelet orientations such that the measured V_P and V_S of the platelets with desired orientations can be used to reliably derive their C_{ij} at high pressure. For each composition, we used BLS to measure V_S and ISLS to measure V_P of the selected crystal platelets as a function of azimuthal angles. Together with complementary XRD, we derived full elastic constants of Fe6-Al4-Bgm and Fe12-Al11-Bgm and evaluated Fe and Al substitution effects on the single-crystal elasticity and $V_{\rm S}$ splitting anisotropy of (Al,Fe)-bearing Bgm at the experimental pressures. The single-crystal elasticity data of Fe6-Al4-Bgm and Fe12-Al11-Bgm are used, with earlier literature reports on the CPO of deformed Bgm, to model the V_S radial anisotropy of deformed polycrystalline (Al,Fe)-bearing Bgm at P-T conditions relevant to the topmost lower mantle. These results are applied to understand and explain seismically-observed V_S radial anisotropy at the topmost lower mantle, especially in the Tonga-Kermadec subduction region.

2. Experimental details

Single-crystal (Al,Fe)-bearing Bgm were synthesized using the 5000-ton Kawai-type multi-anvil apparatus at Okayama University at Misasa, Japan (Lin et al., 2016; Mao et al., 2017; Okuchi et al., 2015). Mixtures of powder starting materials including MgSiO₃, Mg(OH)₂, Al₂O₃, and ⁵⁷FeO with desired wt% proportion for each run were packed into a Pt capsule and compressed to 24 GPa. The sample assemblage was then heated to 1750 °C for 7 hours for run number 5K2179 and 1670 °C for 12 hours for run number 5K2417 to permit sufficient growth of large single crystals

(Mao et al., 2017; Okuchi et al., 2015). (Al,Fe)-bearing Bgm crystals were retrieved from the recovered capsules and then analyzed for compositions using wavelength dispersive spectroscopy in a JEOL JXA-8200 electron microprobe in the Department of Geological Sciences, The University of Texas at Austin. These analyses show compositions of Mg_{0.95}Fe_{0.06}Al_{0.04}Si_{0.96}O₃ (Fe6-Al4-Bgm) for run number 5K2417 and Mg_{0.89}Fe_{0.12}Al_{0.11}Si_{0.89}O₃ (Fe12-Al11-Bgm) for run number 5K2179. Further scanning electron microscope analyses, together with energy dispersive spectroscopy chemical mapping, confirmed the chemical homogeneity across each crystal used in this study (Fig. S1). The spin and valance states of Fe in Fe12-Al11-Bgm have been well-documented in an earlier study using Mössbauer spectroscopy (Mao et al., 2017), indicating that Fe12-Al11-Bgm contains 80% Fe^{3+} and 20% Fe^{2+} in the A site, and no B site Fe³⁺. No spin transition or disproportionation of Fe are observed in Fe12-Al11-Bgm up to 120 GPa (Mao et al., 2017). Conventional Mössbauer spectroscopy was also conducted on Fe6-Al4-Bgm at ambient conditions to determine its relative Fe³⁺ and Fe²⁺ abundance. Analysis of the Mössbauer spectra indicates that Fe6-Al4-Bgm contains both Fe^{3+} (45%) and Fe^{2+} (55%) in the A site. Combining the electron microprobe and Mössbauer results, the chemical formula for Fe6-Al4-Bgm and Fe12-Al11-Bgm can thus be written as $Mg_{0.95}Fe_{0.033}^{2+}Fe_{0.027}^{3+}Al_{0.04}Si_{0.96}O_3$ and $Mg_{0.89}Fe_{0.024}^{2+}Fe_{0.096}^{3+}Al_{0.11}Si_{0.89}O_3$, respectively (Mao et al., 2017). We should note that these formulae are calculated using chargebalanced model on three oxygen atoms basis and are written within experimental uncertainties of the analyses. Single-crystal XRD experiments were further performed on the crystals to evaluate lattice parameters, crystal structure, as well as the crystallographic orientations of the samples at ambient conditions at 13IDD or 13BMD beamlines of GeoSoilEnviroCARS (GSECARS) of the Advanced Photon Source (APS), Argonne National Laboratory (ANL) using an incident X-ray with a wavelength of 0.3344 Å. With $\pm 15^{\circ}$ rotation of the crystal about the vertical axis of the sample stage, the collected XRD patterns show that the refined unit cell parameters in the *Pbnm* structure are a = 4.7657(3) Å, b =4.9340(2) Å, c = 6.9032(6) Å for Fe6-Al4-Bgm and a = 4.7867(2)Å, b = 4.9569(2) Å, c = 6.9141(4) Å for Fe12-Al11-Bgm at ambient conditions. Integrated peaks of the diffracted spots show an averaged full-width at half maximum (FWHM) of $\sim 0.043^{\circ}$ (Fig. S2), indicating that the synthesized (Al,Fe)-bearing Bgm are highquality single crystals. Further observations with a polarized light microscope on the (Al,Fe)-bearing Bgm samples show no apparent inclusions or twinning, further confirming the high quality of single crystals used in this study (Fig. S3).

To reliably determine the full elastic constants of orthorhombicstructured Bgm within acceptable uncertainties, it's critical to select multiple crystal platelets with appropriate orientations for velocity measurements (Every, 1980; Lin et al., 2018). In this study, before the selection of a crystal platelet for high-pressure experiments, we determined crystallographic orientations of the doubleside polished platelets from collected single-crystal XRD patterns using the GSE-ADA/RSV software (Dera et al., 2013) and analyzed sensitivities of wave velocities to each C_{ij} in a specific orientation of the platelet (Figs. 1 and S4). The sensitivity (*S*) of wave velocity to variations of C_{ij} is defined as:

$$S = \frac{dV_{P,S1,S2}}{dC_{ii}} \tag{1}$$

where $V_{P,S1,S2}$ are compressional and shear wave velocities (Lin et al., 2018). *S* has a unit of km/s/GPa according to its definition. For instance, the sensitivity of V_P propagating within the (100) plane to variation of C_{11} can be calculated as $\Delta V_P / \Delta C_{11}$ by giving a perturbation of 0.1 GPa to C_{11} with all the other C_{ij} fixed (Lin et al., 2018). The sensitivity test shows that the C_{ij}



Fig. 1. Sensitivity of C_{ij} to experimentally measured compressional and shear wave velocities and phonon directions of single-crystal Fe12-Al11-Bgm in two crystallographic orientations. The C_{ij} of Bgm are chosen from literature theoretical calculations of MgSiO₃ Bgm at 35 GPa as a representative sensitivity test (Wentzcovitch et al., 2004). Intensity of sensitivity with respect to each C_{ij} for the orientations is calculated using Christoffel's equations for the orthorhombic crystal system (Every, 1980; Lin et al., 2018). The intensities are normalized to the highest sensitivity values and are expressed in percentages. (a)-(b) show calculated normalized sensitivities using two platelets of Fe12-Al11-Bgm with crystallographic orientations of (6.1, -0.4, 1.4) and (0.1, -3.2, 3.6), shown as triplets in parentheses in (a) and (b). The use of these two crystallographic orientations of Fe12-Al11-Bgm provides high sensitivities to reliably derive all nine C_{ii} . Furthermore, the C_{ii} are used to produce synthetic V_P and V_S data on the selected orientations of Fe12-Al11-Bgm to guide experimental velocity measurements and eventual derivations of C_{ij} from the measurements. By fitting the synthetic data, (c)-(e) show derived C_{ij} with corresponding uncertainties $(\pm 1\sigma)$ as a function of the number of measured phonon directions with 10° azimuthal angle separation.

with large sensitivities generally have small uncertainties, and vice versa. Thus the calculated sensitivity can be used as a criterion to select crystal platelets with orientations that can provide the best velocity constraints to the full elastic constants (Lin et al., 2018). Based on the sensitivity test, the use of combined single-crystal platelets with orientations (4.5, 0.9, 1.9), (2.0, 4.2, -2.1) and (3.4, -3.5, 0.3) for Fe6-Al4-Bgm, and (6.1, -0.4, 1.4) and (0.1, -3.2, 3.6) for Fe12-Al11-Bgm have sufficiently high sensitivities to reliably derive all C_{ij} from experimental V_P and V_S data as a function of azimuthal angles. Therefore, these crystals were selected for high-pressure velocity measurements (Figs. 1 and S4).

The three selected platelets of Fe6-Al4-Bgm were double-side polished using 3M diamond film to \sim 15-µm thick and loaded separately into three sample chambers of DACs, together with He as the pressure medium and a ruby sphere as the pressure calibrant. The use of each platelet in each DAC allows maximum sample size for velocity measurements and avoids possible BLS and ISLS signal contamination from another concurrently loaded adjacent platelet. Each DAC with a pair of 300 µm culets was equipped with a preindented Re gasket that was 35-µm thick. The pre-indented area was drilled with a 190-µm diameter hole to be used as a sample chamber. The selected platelets with (4.5, 0.9, 1.9) and (3.4, -3.5, -3.5)0.3) orientations were prepared using a focused ion beam (FIB) to cut them into round disks of approximately 70 µm in diameter, while platelet with (2.0, 4.2, -2.1) orientation has a diameter of approximately 80 µm ready for loading without any further cutting (Fig. 2c insert). We should note that ruby spheres in each DAC were placed adjacent to the sample to minimize the pressure uncertainty in the sample chamber and to ensure pressure consistency among the three loaded DACs (Fig. 2c insert). On the other hand, both platelets of Fe12-Al11-Bgm of approximately 60 µm in



Fig. 2. Representative experimental Brillouin light scattering, impulsive stimulated light scattering, and X-ray diffraction spectra of single-crystal (Al,Fe)-bearing Bgm at 25 GPa. (a)-(c) Fe6-Al4-Bgm; (d)-(f) Fe12-Al11-Bgm. (a) and (d) BLS spectra of the samples showing V_{S1} and V_{S2} ; (b) and (e) ISLS spectra; (c) and (f) Fourier-transformed power spectra for V_P . Velocity of pressure medium, helium or neon, is also derived in the modeled power spectrum. We note that although two polarized V_S peaks are expected to exist in BLS spectra for each crystal platelet, only one V_S peak is observed for most crystal platelets in this study. This is a result of interaction between the polarization of the V_S in the used crystallographic orientations and the incident laser with polarization. Insert triplets in parentheses in (a) and (d) represent orientation matrices determined by synchrotron XRD at GSECARS, APS. Inserts in (c) show photos of two Fe6-Al4-Bgm crystals loaded in sample chambers with helium medium at 25 GPa. Representative X-ray diffraction images for Bgm-1 and Bgm-2 platelets are shown in (a) as inserts.

diameter each were loaded simultaneously into a DAC, with Ne as the pressure medium and a ruby sphere as the pressure calibrant. The loaded Bgm samples were compressed to 25 and 35 GPa for velocity measurements. We also note that before BLS and ISLS experiments were conducted, each loaded DAC was held at a given pressure of 25 and 35 GPa for 2-3 days until equilibrium had been achieved and the pressure remained constant at the target pressure.

Both BLS and ISLS experiments were performed at 25 and 35 GPa for the loaded crystals at the Mineral Physics Laboratory of The University of Texas at Austin. A solid-state green laser with 532-nm wavelength (Coherent Verdi V2) was used for the BLS measurements. Brillouin spectra were collected in a symmetric forward scattering geometry with an external scattering angle of 48.1° using a JRS six-pass tandem Fabry-Perot interferometer (Fu et al., 2017, 2018; Yang et al., 2015). The focused beam size at the sample position is approximately 30-40 µm in diameter. A typical power of 0.6 W for the laser was used for BLS measurements with an estimated laser power of \sim 0.3 W shining onto the DACs. To minimize potential geometrical errors of BLS measurements, the normal direction of diamond tables is precisely aligned to be perpendicular to the sample platelet using a series of reference spots and iris diaphragms in the BLS system so that the momentum transfer direction precisely bisects the incident laser and diffracted Brillouin signals. The BLS system was calibrated using standard distilled water and glass monthly. The acoustic wave velocity can be calculated based on the geometry among the incident laser, measured signal and the Brillouin frequency shift:

$$V_{P,S} = \frac{\Delta \upsilon_B \lambda_0}{2 \sin(\theta/2)} \tag{2}$$

where $V_{P,S}$ are the measured compressional and/or shear wave velocities, Δv_B is the Brillouin frequency shift, λ_0 is the laser wavelength of 532 nm, and θ is the external scattering angle. On the other hand, the ISLS employs a pump-and-probe technique where the system is equipped with a pump laser with 1064-nm wavelength and a green probe laser with 532-nm wavelength (Talisker, Coherent Company) (Fu et al., 2017, 2018; Yang et al., 2015). Both pump and probe lasers have a pulse width of 15 ps. The pump laser is split into two excitation beams which are then recombined and focused at the sample position with a crossing angle of 20.3°. The probe laser with a beam size of \sim 30-40 μ m in diameter is incident upon the center of the sample at a Bragg angle of 10.15°. To minimize potential geometrical errors, these two excitation beams are precisely aligned to reflect back to one another from the diamond tables. Similar to the BLS system, the ISLS system is regularly calibrated using standard distilled water and glass. The green probe laser is delayed as long as 20 ns by an Aerotech linear stage. For each given delay time between the excitation and probe beams, the scattered signals are detected by a photodiode detector (ThorLabs DET 36A) and recorded by a computer using LabView software. The collected time-domain ISLS spectra were analyzed and Fourier-transformed to frequency-domain power spectra using the Origin Software to determine the V_P of the sample along the crystallographic direction at high pressures (Fu et al., 2018). For each sample, we collected both BLS and ISLS spectra for identical sample orientations at a 10° step with rotations about the compression axis of the DAC over a range of 180°-200° (Figs. 2, S5, and S6). It typically took \sim 1-2 hours and \sim 2-3 hours for the collection of each BLS and ISLS spectrum, respectively.

To confirm the orientations and single-crystal quality of the selected Fe6-Al4-Bgm and Fe12-Al11-Bgm for BLS and ISLS measurements at high pressures, XRD experiments were further performed on these crystals at 25 and 35 GPa using an incident X-ray wavelength of 0.3344 Å and a CCD detector at 13IDD beamline in GSE-CARS. To collect as many diffraction spots as possible and reliably determine the orientation information, diffraction patterns of the single-crystal Fe6-Al4-Bgm and Fe12-Al11-Bgm were collected by rotating $\pm 15^{\circ}$ about the vertical axis of the sample stage. Analyses of the diffraction peaks using the GSE-ADA/RSV software (Dera et al., 2013) showed consistent orientations between ambient conditions and high pressures with uncertainties of 0.2° (Fig. S2). The integrated XRD patterns show that the average FWHM of the crystals are $\sim 0.043^{\circ}$ and $\sim 0.052^{\circ}$ at ambient conditions and 35 GPa, respectively (Figs. S2c-d), indicating that the quality of the single crystals was preserved at high pressure. The XRD patterns also allow us to derive the lattice parameters and density of the crystals at high pressures needed for determination of their C_{ij} .

3. Results and data analysis

The use of both BLS and ISLS in this study allows us to measure high-quality V_S and V_P of Fe6-Al4-Bgm and Fe12-Al11-Bgm



Fig. 3. Compressional and shear wave velocities of single-crystal Fe6-Al4-Bgm and Fe12-Al11-Bgm as a function of azimuthal angles at 25 and 35 GPa. (a) and (b) show the velocities of Fe6-Al4-Bgm on two platelets with crystallographic orientations of (4.5, 0.9, 1.9) (black circles) and (2.0, 4.2, -2.1) (red circles) at 25 GPa and (4.5, 0.9, 1.9) (black circles) and (3.4, -3.5, 0.2) (red circles) at 35 GPa, respectively. (c) and (d) represent velocities of Fe12-Al11-Bgm on two platelets with crystallographic orientations of (6.1, -0.4, 1.4) (black circles) and (0.1, -3.2, 3.6) (red circles). Lines are best fits using Christoffel's equation to derive the full elastic constants of the orthorhomic-structured Bgm. V_{S1} and V_{S2} for each crystal platelet are plotted with solid and dashed lines, respectively, to distinguish the two perpendicularly polarized shear wave velocities. We note that only one V_S peak was detected for most crystal platelets in the selected crystallographic orientations. (For interpretation of the colors in the figure(s), the reader is referred to the web version of this article.)

Table 1

Elastic properties of single-crystal Fe6-Al4-Bgm and Fe12-Al11-Bgm at 25 and 35 GPa. Errors in parentheses are standard deviation $(\pm 1\sigma)$ of the elastic properties.

	Fe6-Al4-Bgm		Fe12-Al11-Bgm	
	25 GPa	35 GPa	25 GPa	35 GPa
C ₁₁ (GPa)	608.6 ± 21.6	653.6 ± 25.1	577.3 ± 2.5	626.8 ± 3.1
C ₂₂ (GPa)	636.5 ± 2.5	684.9 ± 3.3	653.4 ± 2.6	699.3 ± 3.6
C ₃₃ (GPa)	672.5 ± 4.3	715.5 ± 5.6	617.7 ± 3.5	649.3 ± 3.5
C44 (GPa)	241.8 ± 0.3	260.1 ± 0.2	207.8 ± 0.5	250.6 ± 1.8
C ₅₅ (GPa)	203.6 ± 0.5	220.6 ± 0.4	191.8 ± 0.3	209.5 ± 0.4
C ₆₆ (GPa)	202.0 ± 0.8	233.9 ± 0.6	220.1 ± 1.5	234.7 ± 0.8
C ₁₂ (GPa)	201.3 ± 10.9	209.2 ± 14.3	235.1 ± 5.4	234.9 ± 4.5
C ₁₃ (GPa)	219.7 ± 10.3	245.4 ± 13.1	228.0 ± 2.3	248.0 ± 2.5
C ₂₃ (GPa)	222.5 ± 2.5	258.2 ± 3.2	224.8 ± 2.1	251.7 ± 2.1
K_S (GPa)	355.6 ± 18.8	385.8 ± 22.5	357.8 ± 9.8	382.4 ± 10.1
G (GPa)	213.9 ± 9.5	231.8 ± 12.3	200.8 ± 4.2	220.8 ± 5.3
ρ (g/cm ³)	4.54 ± 0.01	4.69 ± 0.01	4.58 ± 0.01	4.71 ± 0.01
V_P (km/s)	11.88 ± 0.26	12.17 ± 0.27	11.69 ± 0.12	12.00 ± 0.13
V_{ϕ} (km/s)	8.85 ± 0.23	9.07 ± 0.24	8.84 ± 0.10	9.02 ± 0.11
V_S (km/s)	6.86 ± 0.14	7.03 ± 0.17	6.62 ± 0.07	6.85 ± 0.06

as a function of azimuthal angles at 25 and 35 GPa in selected crystals with optimal orientations to retrieve their full elastic constants with high precision (Figs. 2, S5, and S6). For each pressure, a set of nine single-crystal elastic constants of Fe6-Al4-Bgm and Fe12-Al11-Bgm can be derived using Christoffel's equations to fit the measured velocities (Fig. 3) (Every, 1980):

$$\left|C_{ijkl}n_{i}n_{j}-\rho v^{2}\delta_{ik}\right|=0$$
(3)

where C_{ijkl} is the elastic constants with full suffix notation, v are the measured velocities, ρ is the density derived from singlecrystal XRD measurements, n_i are the wave vector direction cosines and δ_{ik} is the Kronecker delta. As shown in Table 1, most C_{ij} of Fe12-Al11-Bgm and Fe6-Al4-Bgm can be well-constrained within less than 1% error except C_{12} of Fe12-Al11-Bgm with ~2% error and C_{11} , C_{12} , and C_{13} of Fe6-Al4-Bgm with 3-5% error. Calculation of the covariance matrix of the derived C_{ij} is consistent with the modeled results in the sensitivity test, further confirming reliability of the derived elasticity of our (Al,Fe)-bearing Bgm samples within uncertainties (Figs. 1 and S8). All C_{ij} of Fe6-Al4-Bgm and Fe12-Al11-Bgm increase with pressure from 25 to 35 GPa. Comparison of the single-crystal C_{ij} of Fe6-Al4-Bgm and

Fe12-Al11-Bgm with previous experimental (Fukui et al., 2016; Kurnosov et al., 2017; Lin et al., 2018; Sinogeikin et al., 2004; Yeganeh-Haeri, 1994) and theoretical results (Karki et al., 1997; Li et al., 2005; Oganov et al., 2001a; Wentzcovitch et al., 2004) at high pressures shows that our elasticity data fall between the upper and lower bounds of literature results on pure MgSiO₃ Bgm (Fig. S9). We note that Kurnosov et al. (2017) investigated the single-crystal elasticity of Fe10-Al10-Bgm with $Fe^{3+}/\Sigma Fe = 0.66$, which is similar in bulk composition to our Fe12-Al11-Bgm sample with Fe³⁺/ Σ Fe ratio of 0.8. Comparison of the sensitivity test of crystal platelets used in this study and Kurnosov et al. (2017) shows that the crystal orientations in Kurnosov et al. (2017) are sensitive for constraining some shear moduli, for example C₄₄ and C_{55} with high sensitivity, but not sensitive to constraining longitudinal (C_{11} , C_{22} , and C_{33}) and off-diagonal moduli (C_{12} , C_{13} , and C₂₃) (Fig. S7) (Lin et al., 2018). Furthermore, Kurnosov et al. (2017) used the BLS method to measure V_P and V_S of Fe10-Al10-Bgm up to 40 GPa where V_P in most directions would be blocked by diamond V_S peaks at pressures above ~20 GPa. The sensitivity test here indicates that the errors of the fitted C_{ii} increase significantly when the number of measured phonon directions decrease (Figs. 1 and S4). Therefore, the C_{ii} of single-crystal Fe10-Al10-Bgm reported in Kurnosov et al. (2017) should have large uncertainties up to 10% for C_{23} , C_{22} , C_{13} and C_{11} at 40 GPa (Lin et al., 2018) rather than less than 1% error in the reports by Kurnosov et al. (2017). That is, Kurnosov et al. (2017) significantly underestimated the uncertainties of their reported elastic constants. The use of ISLS method in this study allows us to measure high-pressure V_P as a function of all azimuthal angles for derivation of reliable C_{ij} of Fe12-Al11-Bgm and Fe6-Al4-Bgm.

Using the derived single-crystal C_{ij} of Fe6-Al4-Bgm and Fe12-Al11-Bgm at 25 and 35 GPa, we can calculate the aggregate adiabatic bulk (K_S) and shear moduli (G) using the Voigt-Reuss-Hill average with the following equations (Hill, 1952):

$$K_V = (C_{11} + C_{22} + C_{33} + 2(C_{12} + C_{13} + C_{23}))/9$$
(4)

$$K_R = D/E \tag{5}$$

$$G_V = (C_{11} + C_{22} + C_{33} + 3(C_{44} + C_{55} + C_{66}) - (C_{12} + C_{13} + C_{23}))/15$$
(6)

(9)

$$G_R = 15 / \left(\frac{4F}{D} + 3\left(\frac{1}{C_{44}} + \frac{1}{C_{55}} + \frac{1}{C_{66}}\right)\right)$$
(7)

where $K_V(G_V)$ and $K_R(G_R)$ are the upper Voigt and lower Reuss bounds of $K_S(G)$, respectively, and D, E, and F are three constants related to all nine C_{ij} , expressed as:

$$D = C_{13}(C_{12}C_{23} - C_{13}C_{22}) + C_{23}(C_{12}C_{13} - C_{11}C_{23}) + C_{33}(C_{11}C_{22} - C_{12}C_{12})$$
(8)
$$E = C_{11}(C_{22} + C_{33} - 2C_{23}) + C_{22}(C_{33} - 2C_{13}) - 2C_{12}C_{33} + C_{12}(2C_{23} - C_{12}) + C_{13}(2C_{12} - C_{13}) + C_{23}(2C_{13} - C_{23})$$

$$F = C_{11}(C_{22} + C_{33} + C_{23}) + C_{22}(C_{33} + C_{13}) + C_{12}C_{33} - C_{12}(C_{23} + C_{12}) - C_{13}(C_{12} + C_{13}) - C_{23}(C_{13} + C_{23})$$
(10)

 K_S and G are calculated as the average of their upper and lower bounds. The aggregate V_P and V_S can then be calculated using the equations:

$$V_P = \sqrt{(K_S + 4G/3)/\rho} \tag{11}$$

$$V_{\rm S} = \sqrt{G/\rho} \tag{12}$$

where ρ is the density of the sample from single-crystal XRD results at corresponding high pressures. *G* of Fe12-Al11-Bgm is about ~6(±1)% smaller than that of Fe6-Al4-Bgm, while K_S of the two samples are almost identical at 25 and 35 GPa. For aggregate velocities of (Al,Fe)-bearing Bgm, aggregate V_P and V_S of Fe12-Al11-Bgm are ~1.5(±0.3)% and ~2.6(±0.5)% lower than those of Fe6-Al4-Bgm, respectively, at the two experimental pressures.

The derived single-crystal C_{ij} of Fe6-Al4-Bgm and Fe12-Al11-Bgm also allow us to evaluate the azimuthal V_P anisotropy and V_S polarization anisotropy (AV_P and AV_S , respectively), defined as:

$$AV_{P} = 2(V_{P,max} - V_{P,min}) / (V_{P,max} + V_{P,min}) \times 100\%$$
(13)

$$AV_{S} = 2(V_{S1} - V_{S2})/(V_{S1} + V_{S2}) \times 100\%$$
(14)

where $V_{P,max}$ and $V_{P,min}$ represent maximum and minimum V_P of Bgm crystal, respectively, V_{S1} and V_{S2} are two orthogonally polarized V_S velocities for a given propagation direction (Mainprice, 2010). Our results show that single-crystal Fe6-Al4-Bgm exhibits azimuthal AV_P and maximum V_S splitting anisotropy of ~5.8% and ~9.0%, respectively, at 25 GPa and Fe12-Al11-Bgm shows AV_P of ~6.5% and maximum AV_S of ~7.7% (Figs. 6, S12, and S13). AV_P of Fe6-Al4-Bgm and Fe12-Al11-Bgm show increasing trends with increasing pressure, while the pressure effect on maximum AV_S varies between Fe6-Al4-Bgm and Fe12-Al4-Bgm: negative and positive pressure effects on maximum AV_S of Fe6-Al4-Bgm and Fe12-Al4-Bgm and Fe12-Al11-Bgm, respectively.

4. Discussion

4.1. Effects of combined Fe and Al substitution on the single-crystal elasticity of (Al,Fe)-bearing Bgm at high pressure

Early studies have indicated that significant amounts of Al and Fe could dissolve into Bgm in the Earth's lower mantle which could affect our understanding of the lateral and/or radial seismic heterogeneity (Frost et al., 2004; Irifune et al., 2010). It has been suggested that Fe and Al cations under lower-mantle conditions would replace A-site Mg and B-site Si, respectively, with a ratio



Fig. 4. Elastic constants of single-crystal (Al,Fe)-bearing Bgm as a function of combined Fe and Al substitutions at 25 and 35 GPa and room temperature. Open symbols show results from literature *ab initio* calculations, and solid symbols are experimental results. Open circles: MgSiO₃ Bgm (Karki et al., 1997); open squares: MgSiO₃ Bgm (Wentzcovitch et al., 2004); solid circles: Fe6-Al4-Bgm and Fe12-Al11-Bgm in this study; solid squares: Fe10-Al10-Bgm by Kurnosov et al. (2017) using a global fit model; solid triangles: recalculated results by Lin et al. (2018) using velocity data of Kurnosov et al. (2017) at 25.06 and 35.44 GPa. Black, red and blue symbols represent *C*₁₁, *C*₂₂, and *C*₃₃, respectively, in (a) and (d), while these symbols represent *C*₄₄, *C*₂₂, and *C*₃₃, respectively, in (b) and (e), and represent *C*₁₂, *C*₁₃, and *C*₂₃, respectively, in (c) and (f). Dashed lines are plotted to guide the eyes to demonstrate the first-order combined Fe and Al substitution effects on the *C*_{ij} of single-crystal (Al,Fe)-bearing Bgm. Uncertainties $(\pm 1\sigma)$ are smaller than symbols when not shown.

of almost 1:1, via charge-coupled substitution (Irifune et al., 2010; Lin et al., 2013; McCammon, 1997). It is thus important to understand the effects of Fe and Al substitution on the elasticity as well as seismic anisotropy of single-crystal (Al,Fe)-bearing Bgm at relevant lower-mantle *P*-*T* and compositional conditions. We should note that in pure Fe-bearing (Al-bearing) Bgm, Fe²⁺ would substitute A-site Mg^{2+} , and $Fe^{3+}(Al^{3+})$ would substitute both A-site Mg^{2+} and B-site Si⁴⁺. Considering the different substitution mechanisms between pure Al- or Fe-bearing Bgm and (Al,Fe)-bearing Bgm, the chemical effects on the elasticity of lowermantle Bgm could be different. In this study, we used Fe6-Al4-Bgm and Fe12-Al11-Bgm with Fe/Al ratios of \sim 1 and high Fe³⁺ content, where most Fe is Fe^{3+} and occupies A site, while Al^{3+} occupies B site. Here we refer such chemical compositions in (Al,Fe)-bearing Bgm as combined Fe and Al substitution and we will mainly discuss the combined Fe and Al substitution effects on the elastic properties of (Al,Fe)-bearing Bgm due to its geochemical and geophysical relevance (e.g., Irifune et al., 2010). We define Fe and Al contents in (Al,Fe)-bearing Bgm as (Fe+Al)/(Fe+Mg+Si+Al), referring to the average molar percentage of Fe and Al abundance.

The C_{ij} of Fe6-Al4-Bgm and Fe12-Al11-Bgm at 25 and 35 GPa are plotted as a function of average number ratio for combined Fe and Al substitution (Fig. 4). Due to the lack of reliable experimentally constrained C_{ij} for pure endmember MgSiO₃ Bgm at high pressure as well as the inconsistent high-pressure C_{ij} values from *ab initio* calculations due to different approximations (Karki et al., 1997; Li et al., 2005; Oganov et al., 2001a; Wentzcovitch et al., 2004), we first compared the C_{ij} of MgSiO₃ Bgm be-

tween experiments and *ab initio* calculations at ambient conditions (Fig. S10). The comparison shows that although slight differences exist between the C_{ij} from Karki et al. (1997) and Wentzcovitch et al. (2004), these two studies may provide consistent values for most C_{ii} of MgSiO₃ Bgm at ambient conditions (Fukui et al., 2016; Sinogeikin et al., 2004; Yeganeh-Haeri, 1994). Thus the C_{ii} of endmember MgSiO₃ Bgm from Karki et al. (1997) and Wentzcovitch et al. (2004) are taken as the reference at high pressure. In a first-order linear approximation, with the combined substitution of Fe and Al in (Al,Fe)-bearing Bgm, C11, C33, C44 and C55 decrease and C₆₆, C₁₂, C₁₃ and C₂₃ increase with increasing Fe and Al concentrations, while C_{22} seems to be insensitive with Fe and Al variances. Early ab initio calculations indicate that with the substitution of one Al^{3+} and one Fe^{3+} for one Si^{4+} and one Mg^{2+} in Bgm, both longitudinal and shear moduli would decrease, and the off-diagonal moduli would increase (Li et al., 2005). Our results on the combined Fe and Al substitution effects are consistent with *ab initio* calculations (Li et al., 2005) for most C_{ij} except C_{22} and C_{66} . Potential causes of the inconsistent trend for C_{22} and C_{66} might come from experimental uncertainties, limitations of prediction when employing GGA in *ab initio* calculations (Li et al., 2005), or that the (Al,Fe)-bearing Bgm samples in this study do not contain a precise 1:1 ratio of Fe^{3+} and Al substitution. Furthermore, we observe that the effects of combined Fe and Al substitution appears to be weakened on all C_{ij} with pressure increasing from 25 to 35 GPa. This observation is consistent with findings from earlier ab initio calculations (Li et al., 2005), that shows the difference in the elastic properties of pure MgSiO₃ and (Fe,Al)-bearing Bgm diminishes with pressure. We note that the comparison is based on C_{ii} data of (Al,Fe)-bearing Bgm in this study and MgSiO₃ Bgm from ab initio calculation (Karki et al., 1997; Wentzcovitch et al., 2004). Elasticity data of Fe10-Al10-Bgm from Kurnosov et al. (2017) are excluded due to high uncertainties, especially for offdiagonal moduli.

4.2. Effects of combined Fe and Al substitution on the elastic properties for an isotropic polycrystalline (Al,Fe)-bearing Bgm aggregate at high pressure

The effects of combined Fe and Al substitution on the elastic properties, K_S, G, V_P, and V_S, of polycrystalline (Al,Fe)-bearing Bgm aggregate are further examined at high pressures by comparing our results with previous studies (Chantel et al., 2012; Fu et al., 2018; Jackson et al., 2005; Karki et al., 1997; Kurnosov et al., 2017; Wentzcovitch et al., 2004). Similar to the comparison of single-crystal C_{ij}, theoretical results on MgSiO₃ Bgm are used as the endmember reference (Karki et al., 1997; Wentzcovitch et al., 2004). We note that the V_P and V_S for an isotropic polycrystalline Bgm aggregate calculated from single-crystal C_{ii} in ab initio calculations (Karki et al., 1997; Wentzcovitch et al., 2004) are fairly consistent with those of experimentally measured polycrystalline MgSiO₃ Bgm below ~21 GPa (Chantel et al., 2012) (Fig. S11). This affirms the reliability of aggregate properties of endmember MgSiO₃ Bgm from *ab initio* calculations at high pressure. Aggregate elastic properties of earlier experimentally measured polycrystalline Fe-bearing (Chantel et al., 2012; Fu et al., 2018) and Al-bearing Bgm (Jackson et al., 2005) were also plotted for comparison. As shown in Fig. 5, a linear relationship can be assumed for the combined Fe and Al substitution effects on aggregate V_P and V_S of (Al,Fe)-bearing Bgm. The best linear fits show that with the combined Fe and Al substitution in (Al,Fe)-bearing Bgm, both V_P and V_S of (Al,Fe)-bearing Bgm decrease significantly with $dV_P/dX \sim -0.0268$ km/s/mol% and $dV_S/dX \sim -0.0166$ km/s/mol% at 25 GPa (X is the average Fe and Al molar fraction as a percentage). The values of dV_P/dX and dV_S/dX slightly decrease to be \sim -0.0261 km/s/mol% and \sim -0.0131 km/s/mol%, respectively,



Fig. 5. Aggregate elastic moduli and sound velocities of (Al,Fe)-bearing Bgm as a function of combined Fe and Al substitution at high pressures and room temperature. (a) and (c): K_S and G at 25 and 35 GPa; (b) and (d): aggregate V_P and V_S at 25 and 35 GPa. Open circles are results from ab initio calculations and solid circles are from experimental measurements using BLS method except Chantel et al. (2012), who performed ultrasonic interferometry measurements. Solid red circles: Fe6-Al4-Bgm and Fe12-Al11-Bgm in this study; open black circles: MgSiO₃ Bgm (Karki et al., 1997); open red circles: MgSiO₃ Bgm (Wentzcovitch et al., 2004); solid blue circles: Fe-bearing Bgm with composition $Mg_{0.96(1)}Fe_{0.036(5)}^{2+}Fe_{0.014(5)}^{3+}Si_{0.99(1)}O_3$ (Fu et al., 2018); solid gray circles: Al-bearing Bgm containing 5.1 wt% Al₂O₃ (Jackson et al., 2005); solid olive circles: Fe10-Al10-Bgm (Kurnosov et al., 2017); solid pink circles: recalculated results by Lin et al. (2018) using velocity data of Kurnosov et al. (2017); solid orange circles: Fe-bearing Bgm with composition $Mg_{0.95}Fe_{0.04}^{2+}Fe_{0.01}^{3+}SiO_3$ (Chantel et al., 2012). Dashed gray lines are best linear fits to show the combined Fe and Al substitution effects on the aggregate elastic moduli and sound velocities. Uncertainties $(\pm 1\sigma)$ are smaller than symbols when not shown.

at 35 GPa, consistent with the weakening effects of chemical substitution on C_{ij} when pressure increases. We should note that the linear fit doesn't take into account results of pure Fe-bearing and Al-bearing Bgm due to the lack of combined Fe and Al substitution.

4.3. Effects of combined Fe and Al substitution on the single-crystal velocity anisotropy of (Al,Fe)-bearing Bgm at high pressure

The single-crystal elasticity of (Al,Fe)-bearing Bgm can be greatly affected by varying Fe and Al contents which in turn could provide clues for understanding seismic anisotropy of polycrystalline Bgm aggregate in the Earth's lower mantle. Based on the derived full set of C_{ii} of our (Al,Fe)-bearing Bgm, we calculated variations of V_P and V_S for Fe6-Al4-Bgm and Fe12-All1-Bgm as a function of wave propagation direction at 25 and 35 GPa (Figs. 6 and 7). Our results show that combined Fe and Al substitution in (Al,Fe)-bearing Bgm would affect not only the topology of V_P and $V_{\rm S}$ anisotropy, but also crystallographic direction of the highest V_P and AV_S . In particular, Fe6-Al4-Bgm shows the fastest V_P approximately along the [001] direction, and the direction of fastest V_P shifts towards the [010] direction for Fe12-Al11-Bgm at 25 GPa. This trend can be explained by the decrease of C_{11} and C_{33} with Fe and Al contents in Bgm, resulting in C_{22} being larger than C_{33} (Fig. 4). The maximum AV_S of Fe6-Al4-Bgm slightly decreases from ${\sim}9.0\%$ to ${\sim}8.23\%$ with pressure increasing from 25 to 35 GPa, while the maximum AV_S of Fe12-Al11-Bgm increases from \sim 7.68% at 25 GPa to \sim 11.06% at 35 GPa. This indicates significant Fe and Al substitution effects on the maximum AV_S of (Al,Fe)-bearing Bgm at high pressure. Furthermore, the highest V_S splitting anisotropy for Fe6-Al4-Bgm at 35 GPa is along the [001] direction with V_{S1} and V_{S2} of 7.45 km/s and 6.86 km/s, respec-



Fig. 6. V_P , V_{S1} and V_{S2} of single-crystal Fe6-Al4-Bgm and Fe12-Al11-Bgm as a function of propagation directions at 25 and 35 GPa. Red lines: Fe6-Al4-Bgm; blue lines: Fe12-Al11-Bgm. V_{S1} and V_{S2} are orthogonally polarized shear wave velocities: dashed lines are used for V_{S2} to distinguish them from V_{S1} (solid lines). The directions of fastest V_P and highest V_S splitting anisotropy for Fe6-Al4-Bgm are labeled with pink areas, while blue areas are for those of Fe12-Al11-Bgm.

tively. In contrast, Fe12-Al11-Bgm exhibits the highest V_S splitting anisotropy along the direction midway between [100] and [001] directions with V_{S1} and V_{S2} of 7.18 km/s and 6.43 km/s, respectively, at 35 GPa.

5. Geophysical implication

Global V_S tomography models indicate that V_S radial anisotropy is weak on a global scale at the topmost lower mantle (e.g., Montagner and Guillot, 2002; Panning and Romanowicz, 2006). However, regional seismology studies showed strong regional V_S radial anisotropy, 1-2% on average, at the topmost lower mantle of ~670-1000 km near subducted slabs with delay time ranging from less than 1 s to more than 6 s (e.g., Foley and Long, 2011; Wookey et al., 2002; Wookey and Kendall, 2004). In particular, significant trench-parallel anisotropy has been observed at the topmost lower mantle near the Tonga subduction zone, one of the best investigated subduction zones in the mid-lower mantle (e.g., Foley and Long, 2011; Wookey et al., 2002; Wookey and Kendall, 2004). Seismic studies indicated that V_{SH} is about 1-2% faster than

 V_{SV} for the horizontally propagating V_S at the Tonga-Kermadec subduction zone (Wookey et al., 2002; Wookey and Kendall, 2004).

The measured single-crystal elasticity of Fe6-Al4-Bgm and Fe12-Al11-Bgm at high pressures in this study could help us better understand the seismically-observed V_S radial anisotropy at the topmost lower mantle with depths of \sim 670-1000 km. Taking into account the high temperature conditions in the Earth's lower mantle, the C_{ii} of Fe6-Al4-Bgm and Fe12-Al11-Bgm at 25 and 35 GPa determined here at room temperature, are extrapolated to high P-T conditions along an expected lower-mantle geotherm (Katsura et al., 2010). The temperature derivatives of all C_{ii} (dC_{ii}/dT) are taken from analyses of *ab initio* calculations (Oganov et al., 2001b; Wentzcovitch et al., 2004; Zhang et al., 2013). As shown in Fig. S14, a linear pressure effect on dC_{ii}/dT can be assumed by fitting literature results (Oganov et al., 2001b; Wentzcovitch et al., 2004; Zhang et al., 2013). We should note that the deviations of dC_{ii}/dT at high pressure between best linear fit and theoretical data are small, the uncertainties of extrapolated high-temperature C_{ii} should be, on average, about 2-3%.

It's important to consider the microstructure information (crystal orientation, volume fraction, etc.) of the aggregates when applying single-crystal results to polycrystalline rocks in the Earth's lower mantle (Mainprice, 2010). In general, the elastic properties of a grain or crystal with a certain orientation in the polycrystalline rocks can be described by rotating the single-crystal properties into the specimen coordinate frame using the orientation matrix (Mainprice, 2010). The elastic properties of polycrystalline aggregates can be calculated by integrating over all possible orientations of the orientation distribution function (ODF) of the grains in the aggregates (Mainprice, 2010). To investigate the ODF of polycrystalline Bgm aggregate under mantle flow at lower-mantle P-T conditions, a survey of recent experimental and theoretical studies indicates that the CPO or texture of Bgm at high P-T remains an open research question owing to different techniques used in different studies (Cordier et al., 2004; Ferré et al., 2007; Mainprice et al., 2008; Merkel et al., 2003; Miyagi and Wenk, 2016; Tsujino et al., 2016). At room temperature, earlier in situ uniaxial DAC deformation studies found no evidence for texture development up to 32 GPa, probably due to insufficient strain (Meade et al., 1995; Merkel et al., 2003), while recent in situ uniaxial DAC deformation experiments observed significant texture development in Bgm and Bgm + Fp aggregates (Miyagi and Wenk, 2016; Wenk et al., 2006). In the results by Miyagi and Wenk (2016), a 001 texture development was observed in Bgm at pressures be-



Fig. 7. Seismic wave velocities of single-crystal (a) Fe6-Al4-Bgm and (b) Fe12-Al11-Bgm at 35 GPa. For simplicity, the crystal form and surface planes are adopted from orthorhombic olivine that has the same crystal system as Bgm and is well-known as an abundant upper mantle mineral. Crystallographic orientations are labeled on the surface plane. V_P , V_{S1} , and V_{S2} in km/s along the specific orientations are labeled with black, red, and blue colors, respectively. Arrows show the polarization of the shear waves.



Fig. 8. Shear wave splitting anisotropy of deformed (Al,Fe)-bearing Bgm polycrystalline aggregate at the topmost lower-mantle conditions. The modeled results are for *P*-*T* conditions at 24 GPa and ~1886 K corresponding to 670 km in depth (*a* and *c*) and at 35 GPa and ~2000 K for 920 km in depth (*b* and *d*) along an expected geotherm (Katsura et al., 2010). The modeling is conducted using a FOR-TRAN program to calculate the seismic anisotropy of deformed (Al,Fe)-bearing Bgm (Mainprice, 1990). Single-crystal elastic constants derived in this study are used for the calculations. The orientation distribution of crystals in deformed Fe6-Al4-Bgm and Fe12-Al11-Bgm are taken from recent shear deformation experiments at 25 GPa and 1873 K (Tsujino et al., 2016). The x axis indicates the shear direction, the y axis is perpendicular to the shear plane, and the z axis is perpendicular to the shear direction of the fastest shear wave.

low 55 GPa, which was likely due to the slip on (001) planes in the [100], [010], [110] directions; at pressures greater than 55 GPa, the texture changed to 100 maximum with a slip system on the (100) plane. In contrast to the deformation mechanism at room temperature, different texture developments in Bgm were observed for high P-T experiments using multi-anvil techniques (Cordier et al., 2004; Tsujino et al., 2016). With uniaxial stress relaxation experiments on MgSiO₃ Bgm at 25 GPa and 1673 K, Cordier et al. (2004) suggested a [100]-dominant slip direction, while recent shear deformation multi-anvil experiments on Mg_{0.97}Fe_{0.03}SiO₃ Bgm at 25 GPa and 1873 K showed that the dominant slip system of Bgm is [001](100), where the [001] axis is aligned mostly parallel to the shear direction and the [100] axis is aligned normal to the shear plane (Tsujino et al., 2016). We should note that the multi-anvil technique (Cordier et al., 2004; Tsujino et al., 2016) could provide more relevant lower-mantle P-T and stress conditions for deformation compared with earlier DAC experiments at room temperature (Miyagi and Wenk, 2016). Uniaxial stress relaxation experiments employed by Cordier et al. (2004) involved relatively high deviatoric stress that is not compatible with the condition of deformation at the topmost lower mantle. Thus, the slip system [001](100) reported by Tsujino et al. (2016) should be a more representative deformation mechanism for Bgm at topmost lower-mantle P-T conditions. Therefore, we used the derived ODF of deformed Bgm at high P-T from Tsujino et al. (2016), together with the single-crystal C_{ij} of Fe12-Al11-Bgm and Fe6-Al4-Bgm, to model the seismic anisotropy of deformed (Al,Fe)-bearing Bgm at the topmost lower mantle, using a FOR-TRAN program (Mainprice, 1990). The modeled results show that $V_{\rm S}$ splitting anisotropy of deformed Fe6-Al4-Bgm is ~0.9% at ~670 km depth, and decreases to be \sim 0.4% at \sim 920 km (Figs. 8a-b). In contrast, deformed Fe12-Al11-Bgm shows \sim 0.4% and \sim 0.8% V_S splitting anisotropy at 670 and 920 km depths, respectively, indicating an increase in V_S anisotropy of Fe12-Al11-Bgm with depth (Figs. 8c-d).

Seismic studies showed that stagnation depths of subducted slabs in different regions could vary, ranging from above to below the 660 km discontinuity, such as the Tonga-Kermadec, Java, Peru, and Kuril slabs (Foley and Long, 2011; Nowacki et al., 2015; Wookey et al., 2002; Wookey and Kendall, 2004). Most slabs that could extend into the lower mantle have been observed to stagnate at approximately 1000 km. The stagnation of subducted slabs at the topmost lower mantle has been generally attributed to the viscosity jump in the mid-lower mantle of 1000-1500 km depths (Forte and Mitrovica, 2001; Marquardt and Miyagi, 2015). The near-vertical subduction and near-horizontal stagnation of slabs at the topmost lower mantle would yield corresponding mantle flows and the deformation of (Al,Fe)-bearing Bgm in this region. As a result, the deformed (Al,Fe)-bearing Bgm with V_S anisotropy could be used to account for the seismically-observed 1-2% radial anisotropy at the topmost lower mantle. Considering the Fe partitioning between Fp and (Al,Fe)-bearing Bgm as well as Fe/Al solubility in Bgm in a pyrolitic composition with depth (Irifune et al., 2010), Bgm is expected to host about 6 mol% Al and 8 mol% Fe at ${\sim}24$ GPa (${\sim}670$ km in depth), and the Fe and Al contents in Bgm gradually increase up to 11 mol% and 10 mol%, respectively, at \sim 28 GPa (\sim 750 km in depth). The Fe and Al contents are expected to remain constant from 28 GPa up to 40 GPa (~1000 km in depth) (Fig. S15). Therefore, we used Fe6-Al4-Bgm and Fe12-Al11-Bgm to represent (Al,Fe)-depleted Bgm at a depth of \sim 670 km and relatively (Al,Fe)-rich Bgm at a depth of \sim 920 km at the topmost lower mantle. We note that literature results on the deformation mechanism and resultant effects on the elastic anisotropy of two-phase or multi-phase aggregates, that represent pyrolitic or peridotitic lower-mantle mineralogies, are mostly lacking and controversial (e.g., Miyagi and Wenk, 2016). Here we used simplified Bgm aggregate model without including Fp, Ca-Pv or other minor phases. Since (Al,Fe)-bearing Bgm is the most abundant mineral of the lower mantle, the modeled results of deformed Bgm aggregate should be representative for the interpretation of seismically-observed anisotropy at the topmost lower mantle. Shown as a schematic diagram of Tonga-Kermadec slab at the topmost lower mantle in Fig. 9, the flow direction changes from near-vertical at shallower depth (~670 km) to about horizontal flow at deeper depth (~900-1000 km) (e.g., Morra et al., 2010). As a result, the V_S splitting anisotropy induced by deformation of Fe6-Al4-Bgm at \sim 670 km would result in a V_{SV} about 0.9% higher than V_{SH} (insert in Fig. 9). With depth increasing to \sim 920 km, the deformation of Fe12-Al11-Bgm would generate \sim 0.8% V_S splitting anisotropy, showing that V_{SH} is about 0.8% higher than V_{SV} (insert in Fig. 9). We should note that as shown in Fig. 8 and early discussion on the pressure and chemical effects on the modeled V_{S} splitting anisotropy of Fe6-Al4-Bgm and Fe12-Al11-Bgm, the calculated near $\sim 1\%$ V_S splitting anisotropy at the topmost lower mantle comes from the increase of Fe and Al content in Bgm with depth, but not from pressure effects. These modeled results could provide plausible explanations to the distinct V_S splitting anisotropies at the topmost lower mantle near the Tonga-Kermadec subduction region: V_{SH} is about 1-2% higher than V_{SV} from the Tonga-Kermadec subduction zone to the Australian continental seismic stations (Wookey et al., 2002; Wookey and Kendall, 2004), while the V_{SV} is higher than V_{SH} , from the Tonga-Kermadec subduction zone at the western North America stations (Foley and Long, 2011).

6. Conclusion

In summary, we determined the single-crystal elasticity of (Al,Fe)-bearing Bgm with two compositions, Fe6-Al4-Bgm and Fe12-Al11-Bgm, at 25 and 35 GPa using a combination of BLS and ISLS. Our experimental results have shown that with Fe and Al contents increasing from Fe6-Al4-Bgm to Al12-Fe11-Bgm, C_{11} , C_{33} , C_{44} and C_{55} decrease, C_{66} , C_{12} , C_{13} and C_{23} increase, and



Fig. 9. Schematic cross-section of the Tonga-Kermadec slab, subducting into the mantle from east to west, with deformation of Bgm aggregate and resultant shear wave radial anisotropies. Taking Fe partitioning between Fp and (Al,Fe)-bearing Bgm and Al substitution in Bgm with depth into account (Irifune et al., 2010), we used Fe6-Al4-Bgm and Fe12-Al11-Bgm to represent Bgm composition at depths of ~670 km and ~920 km, respectively. At 670 km depth, the deformation of Bgm is caused by a near-vertical flow slab direction, whereas with depth increasing to ~920 km, the deformation is caused by a near horizontal flow. The dashed line with an arrow shows the flow direction of a subducting slab into the Earth's lower mantle. The inserts on the left show the V_S splitting anisotropy projected on the *xy* plane, resulting from deformation of Fe6-Al4-Bgm (top right) and Fe12-Al11-Bgm (bottom right). The *x* axis indicates the shear direction and the *y* axis is perpendicular to the shear plane. The black lines in the inserts show the polarization direction of the fastest shear wave.

 C_{22} varies little at the two experimental pressures. Our derived single-crystal C_{ii} provided crucial constraints on the combined Fe and Al effects on the aggregate V_P and V_S , as well as seismic anisotropy of (Al,Fe)-bearing Bgm at high pressure. Furthermore, with pressure increasing from 25 to 35 GPa, we have observed a weakening of the chemical effects of Fe and Al on the C_{ii} of (Al,Fe)-bearing Bgm. Together with literature shear deformation results on the Fe-bearing Bgm (Tsujino et al., 2016), the obtained single-crystal C_{ij} of (Al,Fe)-bearing Bgm allow us to model the seismic anisotropy of deformed (Al,Fe)-bearing Bgm at the topmost lower mantle. Taking into account the Fe and Al contents in (Al,Fe)-bearing Bgm increasing with depth as well as the geometry of a subducting slab at topmost lower mantle depth derived from mantle flow models, our seismic anisotropy model show that the deformed Fe6-Al4-Bgm at a depth of \sim 670 km would generate a \sim 0.9% V_S splitting anisotropy under near-vertical flow, while a 0.8% V_S splitting anisotropy could be induced by the deformation of Fe12-Al11-Bgm at a depth of ~920 km under horizontal flow due to stagnation of subducted slabs. Our results can be used to plausibly explain the seismically-observed 1-2% V_S radial anisotropy at the topmost lower mantle as the deformation of (Al,Fe)-bearing Bgm under mantle flow convection.

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Appendix A. Supplementary material

Supplementary material related to this article can be found online at https://doi.org/10.1016/j.epsl.2019.04.023.

References

- Chantel, J., Frost, D.J., McCammon, C.A., Jing, Z., Wang, Y., 2012. Acoustic velocities of pure and iron-bearing magnesium silicate perovskite measured to 25 GPa and 1200 K. Geophys. Res. Lett. 39.
- Cordier, P., Ungár, T., Zsoldos, L., Tichy, G., 2004. Dislocation creep in MgSiO₃ perovskite at conditions of the Earth's uppermost lower mantle. Nature 428, 837.
- Dera, P., Zhuravlev, K., Prakapenka, V., Rivers, M.L., Finkelstein, G.J., Grubor-Urosevic, O., Tschauner, O., Clark, S.M., Downs, R.T., 2013. High pressure single-crystal micro X-ray diffraction analysis with GSE_ADA/RSV software. High Press. Res. 33, 466–484.
- Every, A., 1980. General closed-form expressions for acoustic waves in elastically anisotropic solids. Phys. Rev. B 22, 1746.
- Ferré, D., Carrez, P., Cordier, P., 2007. First principles determination of dislocations properties of MgSiO₃ perovskite at 30 GPa based on the Peierls–Nabarro model. Phys. Earth Planet. Inter. 163, 283–291.
- Foley, B.J., Long, M.D., 2011. Upper and mid-mantle anisotropy beneath the Tonga slab. Geophys. Res. Lett. 38.
- Forte, A.M., Mitrovica, J.X., 2001. Deep-mantle high-viscosity flow and thermochemical structure inferred from seismic and geodynamic data. Nature 410, 1049.
- Frost, D.J., Liebske, C., Langenhorst, F., McCammon, C.A., Trønnes, R.G., Rubie, D.C., 2004. Experimental evidence for the existence of iron-rich metal in the Earth's lower mantle. Nature 428, 409.
- Fu, S., Yang, J., Lin, J.-F., 2017. Abnormal elasticity of single-crystal magnesiosiderite across the spin transition in Earth's lower mantle. Phys. Rev. Lett. 118, 036402.
- Fu, S., Yang, J., Zhang, Y., Okuchi, T., McCammon, C., Kim, H.I., Lee, S.K., Lin, J.F., 2018. Abnormal elasticity of Fe-bearing bridgmanite in the Earth's lower mantle. Geophys. Res. Lett. 45, 4725–4732.
- Fukui, H., Yoneda, A., Nakatsuka, A., Tsujino, N., Kamada, S., Ohtani, E., Shatskiy, A., Hirao, N., Tsutsui, S., Uchiyama, H., 2016. Effect of cation substitution on bridgmanite elasticity: a key to interpret seismic anomalies in the lower mantle. Sci. Rep. 6, 33337.
- Garnero, E.J., McNamara, A.K., 2008. Structure and dynamics of Earth's lower mantle. Science 320, 626–628.
- Hill, R., 1952. The elastic behaviour of a crystalline aggregate. Proc. Phys. Soc. A 65, 349.
- Irifune, T., Shinmei, T., McCammon, C.A., Miyajima, N., Rubie, D.C., Frost, D.J., 2010. Iron partitioning and density changes of pyrolite in Earth's lower mantle. Science 327, 193–195.
- Ismail, W.B., Mainprice, D., 1998. An olivine fabric database: an overview of upper mantle fabrics and seismic anisotropy. Tectonophysics 296, 145–157.
- Jackson, J.M., Zhang, J., Shu, J., Sinogeikin, S.V., Bass, J.D., 2005. High-pressure sound velocities and elasticity of aluminous MgSiO₃ perovskite to 45 GPa: implications for lateral heterogeneity in Earth's lower mantle. Geophys. Res. Lett. 32.
- Karki, B.B., Stixrude, L., Clark, S.J., Warren, M.C., Ackland, G.J., Crain, J., 1997. Elastic properties of orthorhombic MgSiO₃ perovskite at lower mantle pressures. Am. Mineral. 82, 635–638.
- Katsura, T., Yoneda, A., Yamazaki, D., Yoshino, T., Ito, E., 2010. Adiabatic temperature profile in the mantle. Phys. Earth Planet. Inter. 183, 212–218.
- Kurnosov, A., Marquardt, H., Frost, D., Ballaran, T.B., Ziberna, L., 2017. Evidence for a Fe³⁺-rich pyrolitic lower mantle from (Al,Fe)-bearing bridgmanite elasticity data. Nature 543, 543–546.
- Li, L., Brodholt, J.P., Stackhouse, S., Weidner, D.J., Alfredsson, M., Price, G.D., 2005. Elasticity of (Mg,Fe) (Si,Al)O₃-perovskite at high pressure. Earth Planet. Sci. Lett. 240, 529–536.
- Lin, J.-F., Mao, Z., Yang, J., Fu, S., 2018. Elasticity of lower-mantle bridgmanite. Nature 564, E18–E26.

- Lin, J.F., Mao, Z., Yang, J., Liu, J., Xiao, Y., Chow, P., Okuchi, T., 2016. High-spin Fe²⁺ and Fe³⁺ in single-crystal aluminous bridgmanite in the lower mantle. Geophys. Res. Lett. 43, 6952–6959.
- Lin, J.F., Speziale, S., Mao, Z., Marquardt, H., 2013. Effects of the electronic spin transitions of iron in lower mantle minerals: implications for deep mantle geophysics and geochemistry. Rev. Geophys. 51, 244–275.
- Mainprice, D., 1990. A Fortran program to calculate seismic anisotropy from the lattice preferred orientation of minerals. Comput. Geosci. 16, 385–393.
- Mainprice, D., 2010. 2.16 Seismic anisotropy of the deep Earth from a mineral and rock physics perspective. In: Mineral Physics: Treatise on Geophysics, vol. 437.
- Mainprice, D., Tommasi, A., Ferré, D., Carrez, P., Cordier, P., 2008. Predicted glide systems and crystal preferred orientations of polycrystalline silicate Mg-Perovskite at high pressure: implications for the seismic anisotropy in the lower mantle. Earth Planet. Sci. Lett. 271, 135–144.
- Mao, Z., Wang, F., Lin, J.-F., Fu, S., Yang, J., Wu, X., Okuchi, T., Tomioka, N., Prakapenka, V.B., Xiao, Y., 2017. Equation of state and hyperfine parameters of high-spin bridgmanite in the Earth's lower mantle by synchrotron X-ray diffraction and Mössbauer spectroscopy. Am. Mineral. 102, 357–368.
- Marquardt, H., Miyagi, L., 2015. Slab stagnation in the shallow lower mantle linked to an increase in mantle viscosity. Nat. Geosci. 8, 311.
- McCammon, C., 1997. Perovskite as a possible sink for ferric iron in the lower mantle. Nature 387, 694.
- Meade, C., Silver, P.G., Kaneshima, S., 1995. Laboratory and seismological observations of lower mantle isotropy. Geophys. Res. Lett. 22, 1293–1296.
- Merkel, S., Wenk, H.R., Badro, J., Montagnac, G., Gillet, P., Mao, H.K., Hemley, R.J., 2003. Deformation of (Mg_{0.9},Fe_{0.1})SiO₃ Perovskite aggregates up to 32 GPa. Earth Planet. Sci. Lett. 209, 351–360.
- Miyagi, L., Wenk, H.-R., 2016. Texture development and slip systems in bridgmanite and bridgmanite + ferropericlase aggregates. Phys. Chem. Miner. 43, 597–613.
- Montagner, J.-P., Guillot, L., 2002. Seismic anisotropy and global geodynamics. In: Reviews in Mineralogy and Geochemistry, vol. 51, pp. 353–385.
- Morra, G., Yuen, D., Boschi, L., Chatelain, P., Koumoutsakos, P., Tackley, P., 2010. The fate of the slabs interacting with a density/viscosity hill in the mid-mantle. Phys. Earth Planet. Inter. 180, 271–282.
- Nowacki, A., Kendall, J., Wookey, J., Pemberton, A., 2015. Mid-mantle anisotropy in subduction zones and deep water transport. Geochem. Geophys. Geosyst. 16, 764–784.
- Oganov, A.R., Brodholt, J.P., Price, G.D., 2001a. Ab initio elasticity and thermal equation of state of MgSiO₃ perovskite. Earth Planet. Sci. Lett. 184, 555–560.

- Oganov, A.R., Brodholt, J.P., Price, G.D., 2001b. The elastic constants of $MgSiO_3$ perovskite at pressures and temperatures of the Earth's mantle. Nature 411, 934–937.
- Okuchi, T., Purevjav, N., Tomioka, N., Lin, J.-F., Kuribayashi, T., Schoneveld, L., Hwang, H., Sakamoto, N., Kawasaki, N., Yurimoto, H., 2015. Synthesis of large and homogeneous single crystals of water-bearing minerals by slow cooling at deepmantle pressures. Am. Mineral. 100, 1483–1492.
- Panning, M., Romanowicz, B., 2006. A three-dimensional radially anisotropic model of shear velocity in the whole mantle. Geophys. J. Int. 167, 361–379.
- Sinogeikin, S.V., Zhang, J., Bass, J.D., 2004. Elasticity of single crystal and polycrystalline MgSiO₃ perovskite by Brillouin spectroscopy. Geophys. Res. Lett. 31.
- Tsujino, N., Nishihara, Y., Yamazaki, D., Seto, Y., Higo, Y., Takahashi, E., 2016. Mantle dynamics inferred from the crystallographic preferred orientation of bridgmanite. Nature 539, 81.
- Wenk, H.-R., Speziale, S., McNamara, A., Garnero, E., 2006. Modeling lower mantle anisotropy development in a subducting slab. Earth Planet. Sci. Lett. 245, 302–314.
- Wentzcovitch, R., Karki, B., Cococcioni, M., De Gironcoli, S., 2004. Thermoelastic Properties of MgSiO₃-perovskite: insights on the nature of the Earth's lower mantle. Phys. Rev. Lett. 92, 018501.
- Wookey, J., Kendall, J.-M., Barruol, G., 2002. Mid-mantle deformation inferred from seismic anisotropy. Nature 415, 777.
- Wookey, J., Kendall, J.M., 2004. Evidence of midmantle anisotropy from shear wave splitting and the influence of shear-coupled P waves. J. Geophys. Res., Solid Earth 109.
- Wu, X., Lin, J.-F., Kaercher, P., Mao, Z., Liu, J., Wenk, H.-R., Prakapenka, V.B., 2017. Seismic anisotropy of the D" layer induced by (001) deformation of postperovskite. Nat. Commun. 8, 14669.
- Xu, S., Lin, J.F., Morgan, D., 2017. Iron partitioning between ferropericlase and bridgmanite in the Earth's lower mantle. J. Geophys. Res., Solid Earth 122, 1074–1087.
- Yang, J., Tong, X., Lin, J.-F., Okuchi, T., Tomioka, N., 2015. Elasticity of ferropericlase across the spin crossover in the Earth's lower mantle. Sci. Rep. 5.
- Yeganeh-Haeri, A., 1994. Synthesis and re-investigation of the elastic properties of single-crystal magnesium silicate perovskite. Phys. Earth Planet. Inter. 87, 111–121.
- Zhang, Z., Stixrude, L., Brodholt, J., 2013. Elastic properties of MgSiO₃-perovskite under lower mantle conditions and the composition of the deep Earth. Earth Planet. Sci. Lett. 379, 1–12.