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Single crystal elasticity of majoritic garnets: Stagnant slabs and thermal anomalies at the base of the transition zone

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ABSTRACT

The elastic properties of two single crystals of majoritic garnet ($Mg_{3.24}Al_{1.53}Si_{3.23}O_{12}$ and $Mg_{3.01}Fe_{0.17}Al_{1.68}Si_{3.15}O_{12}$), have been measured using simultaneously single-crystal X-ray diffraction and Brillouin spectroscopy in an externally heated diamond anvil cell with Ne as pressure transmitting medium at conditions up to ~30 GPa and ~600 K. This combination of techniques makes it possible to use the bulk modulus and unit-cell volume at each condition to calculate the absolute pressure, independently of secondary pressure calibrants.

Substitution of the majorite component into pyrope garnet lowers both the bulk (K_S) and shear modulus (G). The substitution of Fe was found to cause a small but resolvable increase in K_S that was accompanied by a decrease in $\partial K_S/\partial P$, the first pressure derivative of the bulk modulus. Fe substitution had no influence on either the shear modulus or its pressure derivative. The obtained elasticity data were used to derive a thermo-elastic model to describe V_S and V_P of complex garnet solid solutions. Using further elasticity data from the literature and thermodynamic models for mantle phase relations, velocities for mafic, harzburgitic and lherzolitic bulk compositions at the base of Earth's transition zone were calculated. The results show that V_S predicted by seismic reference models are faster than those calculated for all three types of lithologies along a typical mantle adiabat within the bottom 150 km of the transition zone. The anomalously fast seismic shear velocities might be explained if laterally extensive sections of subducted harzburgite-rich slabs pile up at the base of the transition zone and lower average mantle temperatures within this depth range.

1. Introduction

Seismic velocity profiles of the Earth's interior provide essential information for constraining the thermal and chemical state of the mantle (Anderson and Bass, 1986; Irifune and Ringwood, 1987a; Ita and Stixrude, 1992). The correct interpretation of these profiles in terms of mantle mineralogy and chemistry, however, requires laboratory or computational data on the elasticity of candidate minerals at conditions of the Earth's mantle. In this context, knowledge of the thermo-elastic properties of garnet solid solutions are essential, since they make up a major proportion of both mafic and ultramafic rocks in the upper mantle and transition zone (Irifune and Ringwood, 1987a). Garnets recovered from the Earth's mantle crystallize in the cubic space group $Ia\bar{3}d$ forming a series of complex solid solutions that are described using the crystal-structural formula $^{VIII}X_3{}^{VI}Y_2{}^{IV}Z_3O_{12}$. Large cations, X = Mg, Ca, Fe^{2+}, occupy the 8-fold coordinated dodecahedral sites, medium sized cations, Y = Al, Fe^{3+}, Cr, occupy the octahedral sites, whereas the tetrahedral Z site is occupied by Si. At pressures above 5 GPa the coupled substitution of Si and Mg (and Fe) onto the Y site occurs in garnets within mantle assemblages as a result of the breakdown of both orthopyroxene and clinopyroxene. This, so called, majorite substitution increases the proportion of garnet in man-

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Table 1
Starting materials in wt.% of oxides.

	Pyrope glass	Mixture Py1	Mixture Py3	Enstatite glass	Fe-majorite	Mixtures A′, B′, C′, D′
Al_2O_3	25.29	19.95	22.3	–	12.91	A′: 50% enstatite glass – 50% mixture Py1 (10.56 wt.% H_2O)
MgO	44.71	23.66	26.45	40.15	26.96	B′: 50% enstatite glass – 50% mixture Py2 (7.92 wt.% H_2O)
SiO_2	29.99	35.27	39.43	59.85	42.8	C′: 50% enstatite glass – 50% mixture Py3 (5.91 wt.% H_2O)
Fe_2O_3	–	–	–	–	5.28	D′: 50% enstatite glass – 50% mixture Py4 (1.48 wt.% H_2O)
H_2O	–	21.12	11.81	–	12.04	
Sum	100	100	100	100	99.99	

Note: mixture Py2 = 25% pyrope glass + 75% mixture Py1; mixture Py4 = 75% pyrope glass + 25% mixture Py3.

tle rocks at the expense of pyroxenes in the Earth's deep upper mantle and transition zone (Ringwood, 1967). The Al-free garnet end-member is referred to as majorite, Mj ($Mg_4Si_4O_{12}$) and crystallizes with tetragonal symmetry due to ordering of Mg and Si on the octahedral sites. Pure Mj is stable at pressures between 16 and 23 GPa and temperatures above 1600 °C (Kato and Kumazawa, 1985; Angel et al., 1989). In upper mantle ultramafic rocks garnets are solid solutions that are dominated by the end member pyrope (Py, $Mg_3Al_2Si_3O_{12}$) but have sub-equal proportions of almandine (Alm, $Fe_3Al_2Si_3O_{12}$) and grossular (Gr, $Ca_3Al_2Si_3O_{12}$). With increasing pressure, however, the Mj end member becomes increasingly important and dominates in the transition zone (410–660 km depth). A key issue concerning the structure of the Earth's interior is the extent and scale at which the mantle can be considered homogeneous. A number of studies have proposed, for example, that the mantle may become richer in mafic material with depth (e.g. Anderson and Bass, 1986). One of the main expressions of such chemical heterogeneity in the mantle would be variation in the chemistry and proportion of garnet. Garnets constitute approximately 40% by volume of ultramafic compositions and 70% of mafic compositions (Anderson and Bass, 1986; Irifune and Ringwood, 1987a; Ita and Stixrude, 1992), but garnets formed from mafic assemblages will have greater Gr and Alm contents and in the transition zone less Mj compared to ultramafic assemblages. Knowledge of how the elastic properties of garnet change as the bulk chemistry changes is, therefore, important.

Several studies have investigated the elastic properties of Py–Mj garnets at room pressure and temperature (Bass and Kanzaki, 1990; O'Neill et al., 1991). Moreover elastic moduli measurements have also been performed at high pressure and room temperature, using ultrasonic techniques on polycrystalline aggregates (Rigden et al., 1994; Gwanmesia et al., 1998; Chen et al., 1999; Wang and Ji, 2001) and through the use of Brillouin spectroscopy on both single crystals (Conrad et al., 1999; Sinogeikin and Bass, 2000; Murakami et al., 2008) and powdered samples (Sinogeikin and Bass, 2002). Recent improvements in ultrasonic techniques coupled with synchrotron X-ray radiation have allowed sound velocity measurements on polycrystalline samples along the Py–Mj solid solution to be performed at simultaneous high P and T (Irifune et al., 2008; Gwanmesia et al., 2009; Liu et al., 2015). Furthermore the single-crystal elasticity of an iron-bearing pyrope was recently obtained simultaneously at high-pressures (up to 20 GPa) and high-temperature (750 K) using Brillouin spectroscopy and X-ray diffraction (Lu et al., 2013). While the value of the bulk and shear moduli, K_s and G, reported by these studies cover a relatively small range, the exact dependence particularly of K_s on Mj content is unclear, large discrepancies in elastic moduli pressure derivatives exist, the thermal properties are poorly constrained as is the effect of the Alm content. Consequently, the interpretations of seismic velocity gradients in the transition zone remain uncertain.

The aim of this study is, therefore, to constrain the elastic properties of majoritic garnets as a function of density, temperature and composition under hydrostatic conditions by employing a combination of single-crystal Brillouin scattering and X-ray diffraction measurements. The simultaneous measurement of elastic properties and density are used to also obtain absolute values of the experimental pressure, avoiding in this way any systematic errors that may be introduced through the use of secondary pressure calibrations. The elasticity data obtained are fitted to a self-consistent thermo-elastic model from which thermodynamic properties of the garnet end-members are estimated. Acoustic velocities of mafic, harzburgitic and lherzolitic assemblages are then calculated along a typical mantle adiabat at conditions of the Earth's transition zone by combining our garnet model with properties for coexisting minerals from the literature. The results are then compared with seismic reference models reported over the same depth interval to constrain the plausible mineralogy and temperature at the base of the Earth's transition zone.

2. Experimental methods

2.1. Sample synthesis and characterization

The growth of large crystals is usually facilitated by adding a flux to the starting material, such as H_2O, in order to lower the melting temperature and allow larger crystals to grow from the surrounding melt. The flux to starting material ratio is an important factor in determining the size of the final crystals. In order to assess the optimal H_2O content for the growth of large single crystals, four different majoritic garnet starting mixtures were prepared by mixing in a 50/50 proportion an enstatite glass and four pyrope mixtures (Py1, Py2, Py3 and Py4) with different H_2O contents (Table 1).

The four pyrope mixtures were then mixed with the enstatite glass to produce hydrous majoritic garnet starting mixtures with differing H_2O contents, A′, B′, C′, D′ (Table 1). These were loaded into a multi-chamber capsule fabricated from a 2 mm diameter rhenium rod.

High-pressure experiments aimed at producing majoritic garnets were carried out using a 5000 t multi-anvil apparatus at the Bayerisches Geoinstitut. A 18 mm edge length Cr_2O_3-doped (5 wt.%) MgO octahedron was used as a pressure medium with tungsten carbide cubes of 52 mm edge length and 11 mm truncation edge length (18/11 assembly). The pressure calibrations for the assembly used in this study are reported in Keppler and Frost (2005). The samples were first pressurized to 17 GPa followed by heating at 1900 °C for 5 min. After heating at high pressure, the experiments were quenched by shutting off the power and the run-products were recovered after decompressing for 18 h. The recovered capsules were embedded in epoxy resin, ground and polished for electron probe microanalysis. Single-crystals of majoritic garnet (up to ~200 μm in length) were obtained from the starting composition (mixture A′) that contained the largest amount of water (Fig. S1, supplementary information).

An iron bearing majoritic garnet with a similar composition to that recovered above was also prepared from a glass starting material that contained H_2O added as $Mg(OH)_2$ (Fe-majorite, see Table 1). An oxide mixture of Al_2O_3, SiO_2 and Fe_2O_3 was initially melted in air at 1600 °C for twenty minutes and then