Physics of the Earth and Planetary Interiors 271 (2017) 57–63

Contents lists available at ScienceDirect

Physics of the Earth and Planetary Interiors

journal homepage: www.elsevier.com/locate/pepi

High pressure elasticity of $FeCO_3$-$MgCO_3$ carbonates

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ARTICLE INFO

Article history:
Received 31 March 2017
Received in revised form 17 July 2017
Accepted 21 August 2017

Keywords:
Elastic tensor
Siderite
Magnesite
High pressure
IXS
DFT

ABSTRACT

We have determined the elastic stiffness moduli of $FeCO_3$ across the spin transition up to 60 GPa by inelastic X-ray scattering and density functional theory calculations. We have derived functions describing the dependence of the components of the elastic tensor of $Mg_{1-x}Fe_xCO_3$ solid solutions on pressure and concluded that there is a linear dependence of the C_{11}, C_{33}, C_{44} and C_{14} moduli on the composition parameter x. The elastic tensors were employed to calculate the sound velocities and velocity anisotropies of $Mg_{1-x}Fe_xCO_3$. These results allow an assessment of the potential seismic signature of deep mantle carbonates.

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1. Introduction

Carbonates play a significant role in the deep carbon cycle of the Earth. They can be transported to the interior of the Earth in subducting slabs, thus potentially contributing to the deep carbon storage in the lower mantle (Hazen and Schiffries, 2013). The most abundant carbonates at shallow depths are calcite/aragonite, $CaCO_3$, dolomite, $CaMg(CO_3)_2$ and magnesite, $MgCO_3$ (Turekian and Wedepohl, 1961; Luth, 1999). However, during subduction, calcium rich carbonates react with silicate minerals forming iron bearing magnesite $Mg_{1-x}Fe_xCO_3$ (Biellmann et al., 1993; Litasov, 2011; Seto et al., 2008) which is stable at lower mantle conditions (Wang et al., 1996; Fiquet et al., 2002; Isshiki et al., 2004). Knowledge of the elastic properties of $Mg_{1-x}Fe_xCO_3$ carbonates at Earth's mantle conditions is thus important for understanding the deep carbon cycle and is a prerequisite for the prediction of the seismic signature, that would be indicative for carbonates in the mantle.

At ambient temperature and up to 60 GPa both siderite, $FeCO_3$, and magnesite, $MgCO_3$, crystallize in space group $R\bar{3}c$, with octahedrally coordinated cations and planar CO_3 groups (Oh et al., 1973; Lavina et al., 2009). Such a symmetry results in 6 independent C_{ij} moduli: C_{11}, C_{33}, C_{44}, C_{12}, C_{13} and C_{14}. At 45 GPa $FeCO_3$ undergoes a spin transition associated with a 10% decrease of the unit cell volume (Mattila et al., 2007; Lavina et al., 2009). The bulk modulus increases by 18% across the spin transition from 317 GPa to 373 GPa (Lavina et al., 2009; Lavina et al., 2010). Different studies on $Mg_{1-x}Fe_xCO_3$ carbonates reporting the spin transition pressure (Lavina et al., 2010; Lobanov et al., 2015; Spivak et al., 2014; Cerantola et al., 2015; Müller et al., 2016; Fu et al., 2017) show that it lies within the region of 40–47 GPa. There is an ongoing discussion on whether this transition is "sharp", i.e. takes place over an interval of 2 GPa (Müller et al., 2016), or "gradual", i.e. takes place over an interval of 7 GPa (Cerantola et al., 2015).

Our knowledge of the pressure dependence of the elastic stiffness tensor of carbonates is currently very limited. Yang et al. (2014) measured the full elastic stiffness tensor of $MgCO_3$ up to 14 GPa at ambient temperature and additionally up to 750 K at ambient pressure by Brillouin scattering in a diamond anvil cell. They reported that the elastic stiffness moduli of $MgCO_3$ increase linearly with pressure and decrease linearly with temperature. Fu et al. (2017) measured the full elastic stiffness tensor of $Mg_{0.35}Fe_{0.65}CO_3$ up to 70 GPa at ambient temperature by Brillouin light scattering and impulsive stimulated light scattering in a

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http://dx.doi.org/10.1016/j.pepi.2017.08.004
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diamond-anvil cell. They observed a drastic softening of the C_{11}, C_{33}, C_{12}, C_{13} moduli and stiffening of C_{44} and C_{14} moduli across the spin transition in the mixed-spin state. Outside the region of the spin transition they observed a linear increase of all elastic moduli with pressure. Sanchez-Valle et al. (2011) measured the elastic tensor of $Mg_{1-x}Fe_xCO_3$ for four different compositions at ambient conditions and concluded that, within the resolution of their data, all elastic stiffness moduli follow linear trends upon substitution of Fe for Mg.

Previous high pressure DFT calculations on $FeCO_3$ (Shi et al., 2008; Hsu and Huang, 2016) report the pressure dependence of the bulk modulus without deriving the full elastic tensor. Shi et al. (2008) calculated the spin transition pressure of $FeCO_3$ to be at 28 GPa based on GGA + U calculations. They report an abrupt increase of bulk modulus at the spin transition from 218 GPa to 261 GPa. Hence, their values are in only moderate agreement with Lavina et al. (2009). Hsu and Huang (2016) investigated $Mg_{1-x}Fe_xCO_3$ carbonates with an iron concentration in a range of x = 0.125–1 employing LDA+U_{sc} calculations. They concluded that the spin transition occurs in the region of 45–50 GPa regardless of the iron concentration. They also calculated the pressure and temperature dependence of the bulk modulus of $Mg_{1-x}Fe_xCO_3$ carbonates taking into account the mixed-spin state. They predict a drastic softening of the bulk modulus along the spin transition which was confirmed experimentally in the case of $Mg_{0.35}Fe_{0.65}CO_3$ (Liu et al., 2014; Fu et al., 2017).

In order to quantify the change in the elasticity of pure $FeCO_3$ across the spin transition we performed an inelastic X-ray scattering (IXS) experiment and complementary DFT calculations to determine the full elastic stiffness tensor. We have investigated the reliability of our computational approach by computing the pressure dependence of the elastic stiffness tensor of $MgCO_3$, and by comparing our results with published data (Yang et al., 2014; Sanchez-Valle et al., 2011; Chen et al., 2006; Every and McCurdy, 1992). A combination of all experimental and theoretical data allows us to interpolate the elastic properties of $Mg_{1-x}Fe_xCO_3$ for any composition and pressure up to 60 GPa. From this data we can obtain sound velocities and velocity anisotropies of lower mantle $Mg_{1-x}Fe_xCO_3$ carbonates, which then can be employed in mineral physics models.

2. Experimental methods

Single crystals of $FeCO_3$ were synthesized by following the method developed by French (1971) and Cerantola et al. (2015). We have tested the quality of the crystals on an Xcalibur single crystal diffractometer or by synchrotron radiation. Crystals of highest quality were chosen for high pressure IXS experiments, their dimensions were $80 \times 50 \times 22\ \mu m^3$ (S18), $35 \times 30 \times 15\ \mu m^3$ (S15) and $25 \times 25 \times 10\ \mu m^3$ (A1). Crystals S18 and S15 were loaded into Boehler-Almax type diamond anvil cells with 350 μm and 300 μm diamond culet size, respectively, and rhenium gaskets with initial hole dimensions $160 \times 55\ \mu m^2$ (diameter × thickness) and $110 \times 40\ \mu m^2$, respectively, with Ne as pressure transmitting medium. Crystal A1 was loaded into a symmetric diamond anvil cell with bevelled diamonds with diameters of 250 μm, a rhenium gasket with initial dimensions $140 \times 60\ \mu m^2$ and He as pressure medium. Crystal S18 was measured at 2 GPa and 28 GPa, S15 at 15 GPa and A1 at 55 GPa. The pressure was measured before and after IXS measurements at each pressure point. Crystal quality degraded significantly with increasing pressure as indicated by the increase of intensity of the elastic line, see Fig. 1.

IXS measurements were performed at the ID28 beamline of the ESRF. The spectrometer was operating at 17.794 keV incident photon energy providing an instrumental energy resolution of 3 meV. The X-ray beam was focused using KB mirrors to a spot size of $20 \times 30\ \mu m^2$. At each pressure point energy scans were performed along the Γ-T direction, around convenient Bragg reflections (see Supplementary materials). At 55 GPa measurements along other directions were performed in addition. Before each IXS scan the UB matrix of the crystal was refined, to determine the exact orientation of the crystal and measure the lattice parameters used to determine the density of the sample.

Linear dispersion relations were fitted to the measured data in the vicinity of the Γ point, to obtain the sound velocities. Velocities of the longitudinal phonons were used to determine the C_{33} modulus, and velocities of the transverse phonons were employed to determine the C_{44} modulus by solving the Christoffel equation (Nye, 1985). Velocities obtained from additional measurements at 55 GPa were compared with calculated values.

3. Computational details

Spin-polarized density functional theory calculations were performed with commercial and academic versions of the CASTEP program (Clark et al., 2005) using the generalized gradient approximation formalized by Perdew et al. (1996) (PBE) with a plane wave basis set and ultrasoft pseudopotentials from the CASTEP 8.0 database. The maximum cutoff energy of the plane waves was 750 eV. A $12 \times 12 \times 12$ Monkhorst–Pack grid Monkhorst and Pack, 1976 was employed for sampling of the reciprocal space corresponding to a k-point separation of less than $\sim 0.022\ Å^{-1}$.

A Hubbard U of 4 eV was employed for the Fe d-electrons. Additional calculations showed that a variation of U by 10% had only a negligible influence on the elastic stiffness moduli. The calculations were considered to be converged once the maximal residual force acting on an atom was <0.01 eV/Å, the residual stress was <0.02 GPa, and the maximal energy change was $<5 \cdot 10^{-6}$ eV/atom. For the calculations of stress–strain relations two strain patterns were employed. The maximum strain amplitude was 0.003.

The calculations were done in 10 GPa pressure steps for both $MgCO_3$ and $FeCO_3$. In case of $FeCO_3$ we performed the calculation in pure spin state, i.e. in high-spin state from 0 to 40 GPa inclusive, and in low-spin from 40 to 60 GPa inclusive.

4. Results and discussion

4.1. IXS, high pressure elasticity of $FeCO_3$ and $MgCO_3$

Representative high-pressure IXS spectra of $FeCO_3$ are shown in Fig. 1. The velocities derived from low-q phonon dispersion relations of LA and TA branches measured along c* direction were used to determine the C_{33} and C_{44} moduli of the elastic tensor of $FeCO_3$, as shown in Fig. 2. We have performed complementary DFT calculations to determine the full elastic tensor and compared the results to our data (Fig. 2). Velocities obtained from additional measurements at 55 GPa are compared with calculated values in Fig. 3.

The experimental values of C_{33} and C_{44} moduli of high-spin $FeCO_3$ are in good agreement with the results of our calculations. The excellent correspondence between calculated and measured elastic moduli is almost certainly fortuitous as DFT-calculated elastic moduli are typically accurate to a few percent. At ambient pressure the calculated values of C_{12} and C_{13} are lower than the experimental values by 28% and 23%, respectively, other moduli are the same within the given error. We see a linear stiffening of all C_{ij} moduli with pressure, up to the transition pressure. After the spin transition all C_{ij} moduli stiffen abruptly with the exception of C_{12} which in the low spin phase has similar values to the ones

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