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The effect of cation-ordering on the elastic properties of majorite: An *ab initio* study

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Abstract

The effects of cation disorder and pressure on the structural and elastic properties of $MgSiO_3$ majorite (Mj100) and $MgSiO_3$–$Mg_3Al_2Si_3O_{12}$ solid solution (Py50Mj50) are modelled using the first principle simulations. Our results are consistent with the tetragonal phase as the stable structure for both compositions up to 25 GPa. Both pressure and disorder decrease the differences between c_{11} and c_{33}, and between c_{44} and c_{66}, indicating that the elastic properties move closer to cubic. The calculated bulk modulus and shear modulus are comparable with the reported experimental data. The bulk modulus of Mj100 varies little while the shear modulus decreases slightly with increasing cation disorder. The elastic properties of an ordered Py50Mj50 are nearly cubic in symmetry. Mg–Si disorder has much lower energy impact on Py50Mj50 than Mj100. In the Earth's mantle, variation of the Al content in the garnet will more significantly affect the seismic velocities than will the order/disorder of Si and Mg.

Keywords: majorite; cation disorder; elasticity; high pressure; seismic velocity

1. Introduction

Majorite rich garnet is expected to be the second most abundant mineral in the Earth's transition zone [1]. The formation of majorite will significantly affect the density of subducted basaltic crust within a pyrolite mantle [2]. Thus, the properties of majorite and their dependence on chemical composition will have a significant impact on radial and lateral variations in seismic velocities and buoyancy in this region. The end-member, Mg–Si, majorite is among the few minerals that have ferroelastic phase transitions that are often accompanied by softening of elastic moduli or high acoustic attenuation [3,4]. This transition is marked by the ordering of magnesium and silicon cations on the octahedral sites accompanied by a cubic to tetragonal phase transformation. Sinogeikin et al. [5] suggest that there is a discontinuous decrease in the elastic moduli across this transition. Their experimental data, which span a range in the pyrope–majorite solid solution, were interpreted as having a small discontinuous decrease in the region where the tetragonal phase is stable. Yeganeh-Haeri et al. [6], on the other hand, suggest a continuous decrease in elastic moduli as aluminium is replaced by an Mg–Si couple, with no discontinuity associated with the change in space group. This issue has an immediate implication for seismic velocities in the mantle which

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may have some dependence not only on the chemical composition of the garnet, but also on the degree of ordering of the Mg and Si on the octahedral site.

Experimental studies are quite limited in clarifying this issue. The experimental data of [5] could also be explained, within the resolved errors, by a gradual compositional effect on the elastic moduli with no effect of the phase transition. Furthermore, X-ray studies are weak in defining the state of order between Mg and Si owing to the similarity of their structure factors. Here we present the results of *ab initio* calculations. They indicate that while the presence of the tetragonal phase is definitive evidence of the ordered structure, the tetragonal phase may be metrically cubic (all axes of the same length). Thus, the elastic properties may be determined by the ordered structure, but still appear to be cubic in terms of cell dimension thus rendering the experimental data even more ambiguous. However, we find that while disorder appears to lower the shear modulus, the effect of composition is by far the dominant variable affecting the seismic velocity in the pyrope–majorite solid solution.

Majorite is unusual in that Mg and Si cations are significantly (i.e.>10%) disordered. Laboratory studies have shown that majorite garnet can transform from cubic (Ia–3d) to tetragonal ($I4_1/a$) at elevated temperature and pressure [3]. The tetragonal $MgSiO_3$ majorite garnet has Mg1(16f) and Mg2(8e) occupying the dodecahedral sites, Si1(4b), Si2(4a) and Si3(16f) occupying the tetrahedral sites, O1–O6(16f) occupies the corner of tetrahedral, and Mg(8c) and Si(8d) cations occupying the octahedral sites. Cation disordering occurs when Mg (8c) exchanges sites with Si(8d). We define here the compositional parameter x in $Mg_x^{8d}\ Mg_{1-x}^{8c}\ Si_{1-x}^{8d}\ Si_x^{8c}$ to represent the cations in the octahedral sites. Then complete ordering obtains for $x=0$ (tetragonal structure) and disorder (cubic structure) occurs at $x=0.5$. Angel et al. [7] report $x=0.2$ for $MgSiO_3$ majorite (0.2 Si on the Mg site). Even though the tetragonal structure has been reported for the synthesized majorite garnet [3,7–9], natural Mg–Fe rich majorite found in meteorite craters have been reported as being cubic (Ia–3d) [10,11] with Mg and Si randomly distributed.

For garnet, order–disorder is associated with the tetragonal–cubic phase transition. In the Earth's mantle, majorite exists in solid solution with pyrope. An experimental study [12] has reported the tetragonal structure for the majorite–pyrope join when the majorite content is over 75 mol% and the cubic structure for the ones with more aluminium. The data are excellent in defining the cell dimensions, but still unable to define the state of order, and therefore unable to confirm the cubic space group. The presence of Al in the solid solution also affects the elasticity [5,6,13–19]. Typically, elastic properties decrease very modestly as majorite replaces pyrope in the solid solution.

First principle simulation has successfully predicted structural and elastic properties of mantle minerals [20–23]. This approach can define atom positions in a periodic cell and simulate the cation substitution and ordering, especially at high pressure. We specify the atom positions in a large cell. We use density functional theory to compute the enthalpy, structural, and elastic properties of majorite garnet with defined atom configurations at mantle pressure. To simulate disorder, we use a sample box with 160 atoms and perturb only a few of these atoms. The arrangement of atoms on a larger scale is assumed to be periodic with the sample box. Thus, we are restricted to define the properties of systems that have specific violations of the ordered space group. Howver, the calculations provide some insights that are not accessible experimentally. For example, X-ray diffraction cannot define the Si–O bond distances for the Si atoms that are on the Mg sites and yield only the average of the M–O bond distance is defined. The calculations do provide this information.

2. Computation method

Computations were performed using the density functional theory (DFT) based VASP code with the projector augmented wave implementation [24,25] and a plane wave basis set with kinetic energy cut-off of 900 eV. The electron exchange and correlation is described within the generalized gradient approximation (GGA-PW91) [26,27]. The Γ-point is used for Brillouin zone sampling.

We used a unit cell with $I4_1/a$ symmetry containing 160 atoms (listed in Supplementary data Table S1 based on experimental data of [7]). These were used as the starting point for the calculations. The disordered atomic positions for different garnet models with $x=0$, 1/8, 2/8, 4/8 are given in Table S2 of the Supplementary data. The four configurations for the $x=1/8$ case represent all of the possible configurations for this degree of disorder with a cell containing 160 atoms. For higher values of disorder, the number of possible disordered arrangements grows rapidly. Not all possibilities were considered, rather the Mg and Si atoms were randomly chosen due to the high computation demand. A total of 10 configurations for majorite were considered. For each model, the lattice parameters, the cell shape, as well as ionic positions were allowed to relax. Calculations were performed between 0 and 30 GPa. Elastic moduli for the