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Elasticity of $(K,Na)AlSi_3O_8$ hollandite from lattice dynamics calculations

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ABSTRACT

We compute the elastic constants tensor and the seismic properties of $KAlSi_3O_8$ and $K_{0.8}Na_{0.2}AlSi_3O_8$ up to the ferroelastic transition using density-functional theory and density-functional perturbation theory in the ABINIT implementation. We observe a softening of the tetragonal shear with pressure that precedes the ferroelastic transition. The Reuss shear moduli become negative at respectively 23 GPa and 13 GPa for the two compositions considered in here. The ferroelastic transition is associated with a strong decrease of the horizontal shear wave velocities and a corresponding increase of the seismic anisotropy. The presence of Na enhances these features.

1. Introduction

The large alkaline and calc-alkaline cations like K, Na, Ba, Sr are usually incompatible with the silicatic mantle and thus they tend to fractionate in the Earth's crust. They can get entrained by the subduction and penetrate in the mantle. In this geological setting their major transport means are open-framework structures, like feldspars, certain micas and amphibole, and especially the mineral hollandite (Downs et al., 1995). At low and moderate thermodynamic conditions prevalent in the beginning and the early stages of the subduction process the main mineral hosts for K in the subducting slabs are the phengite micas, the feldspar, the wadeite and the amphiboles (Irifune et al., 1994; Dobrzhinetskaya and Green, 2007; Konzett and Fei, 2000). The stability field of hollandite within the thermochemical conditions of the upper mantle is reached at about 8–9 GPa, corresponding to depths of about 300 km (Irifune et al., 1994; Urakawa et al., 1994; Schmidt, 1996; Tutti et al., 2001; Akaogi et al., 2004; Yong et al., 2006; Dobrzhinetskaya and Green, 2007). Once formed the hollandite can stay within this form up to very high pressures and could potentially be transported even into the lower mantle (Hirao et al., 2008). The ferroelastic phase transition, characterized by a positive Clapeyron slope, appears at depths of about 400–500 km depending on the composition. Afterwards hollandite is stable throughout the Earth's mantle. The two structures, hollandite I, tetragonal, stable before the transition and hollandite II, monoclinic, stable after the transition are very similar. In the following we study the low-pressure polymorph, hollandite I that we will denote hereinafter simply as hollandite.

The crystal structure of hollandite (Fig. 1) consists of tunnels with a square cross-section, which run parallel to the fourfold axis. The tunnels are delimited by double chains of edge-sharing octahedra. The cations inside the tunnels are usually monovalent or divalent and the cations inside the octahedra are trivalent or tetravalent. The possible size mismatch between the cations inside the tunnels and the cations inside the octahedra may induce crystallographic distortions leading to ferroelastic transitions under pressure or apparition in incommensurate structures at low temperatures (Caracas, 2002; Wu et al., 1991). From the geoscientific point of view the wide tunnels are an ideal host for geochemically incompatible elements, like K, Na, Ba and Sr or other large non-alkaline elements, like Pb and U. However, within the Earth's geochemical setting the major cation is K, which can be partially replaced by Na. Experiments suggest maximum sodium limit of

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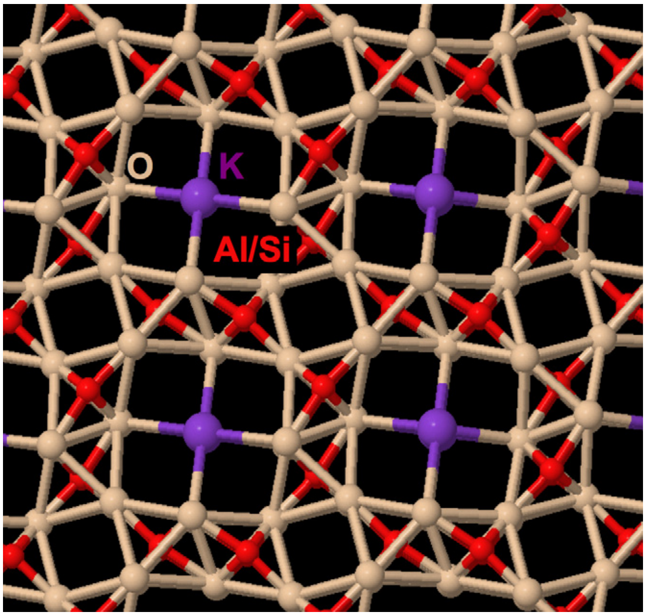

Fig. 1. Crystal structure of hollandite viewed along the fourfold axis.

about 40–50 at.% for characteristic upper mantle thermodynamics conditions (Yagi et al., 1994; Liu, 2006).

Recent in situ high-pressure studies of $KAlSi_3O_8$ hollandite (Sueda et al., 2004; Nishiyama et al., 2005; Ferroir et al., 2006; Hirao et al., 2008) reported a non-quenchable phase transformation from tetragonal to monoclinic symmetry at about 20 GPa. The high-pressure phase can be indexed with a monoclinic unit cell (space group I2/m) similar in structure with $BaMn_8O_{16}$ hollandite. The transition is described by the group–subgroup relation 4/m to 2/m for which the active representation is B_g of the point group 4/m.

Here we consider two cases: pure $KAlSi_3O_8$ and 80 at.% K–20 at.% Na, as $K_{0.8}Na_{0.2}AlSi_3O_8$, which are largely within the range of expected natural compositions from the Earth's upper mantle. We assume ideally disordered structures at all pressures with Si and Al randomly distributed inside the octahedra and K and Na randomly distributed on the K site, inside the tetragonal tunnels. All calculations are performed in the primitive unit cell of the conventional tetragonal I4/m one, which hosts one formula unit.

2. Computational details

We compute the full elastic constants tensor in the framework of the density functional perturbation theory (DFPT) (Baroni et al., 1987; Gonze et al., 1992; Gonze, 1997; Gonze and Lee, 1997; Baroni et al., 2001; Gonze et al., 2005a). Here the elastic constants are expressed as the derivative of the energy with respect to lattice strains (Hamann et al., 2005). The atomic relaxations due to strain are taken into account from the phonon and dielectric calculations by inverting a matrix containing the interatomic force constants, the couplings with the strains and the couplings with the electric fields. The elastic theory is implemented on top of the density functional theory (DFT) (Hohenberg and Kohn, 1964; Kohn and Sham, 1965) in the ABINIT package (Gonze et al., 2002, 2005) based on planewaves and pseudopotentials.

We use the local density approximation for the exchange-correlation energy, with Troullier–Martins type pseudopotentials. As usual with planewave basis sets, the numerical accuracy of the calculation can be systematically improved by increasing the cut-off kinetic energy of the planewaves and the density of the sampling of the Brillouin zone (Payne et al., 1992). We use a 35 Ha cut-off energy for the kinetic energy of the planewaves. We sample the reciprocal space using a $8 \times 8 \times 8$ regular grid of special k points according to the Monkhorst–Pack scheme (Monkhorst and Pack, 1976).

The classical method to study an intermediate term of a solid solution is the cluster expansion model. According to this approach the properties of the disordered solid may be inferred using the computed results for only several selected supercells with different representative atomic configurations and then making use of statistical physics. This model is straightforward and it can be applied to any type of disordered structure or solid solution, but the results are highly dependent on the quality of the sampling. Each individual calculation is more tedious because of larger system sizes and possible losses of symmetry due to the specific atomic configuration.

Here we adopt an alternative approach, the virtual crystal approximation (Bellaiche and Vanderbilt, 2000). For each of the disordered sites we construct a new pseudopotential called *alchemical*, which is obtained from mixing the atoms that participate in the solid solution in the appropriate amounts (Giantomassi et al., 2005,). In practice the *alchemical* pseudopotentials are obtained as follows: the local potentials of the original pseudopotentials are linearly mixed, the form factors of the non-local projectors are all preserved, and all considered to generate the alchemical potential, the scalar coefficients of the non-local projectors are multiplied proportionally and the core charge cutoff radius and functions are linear combinations of respectively the radii and the functions of the original pseudopotentials.

This approach uses small simulation cells and preserves the symmetry, but the mixing should be realized between chemically similar atoms. It is especially well suited for solid solutions that do not show ordering on any scale. The theoretical structures and their physical properties obtained using the alchemical pseudopotentials are in very good agreement to experimental data. This latter approach has already been successfully applied to compute physical properties for solid solutions, like dielectric tensors (Cohen, 2007) or Raman and elasticity (Caracas and Banigan, 2009). For example, in spinel, $MgAl_2O_4$, it has been shown that only a partial Mg–Al disordering can explain the experimental results, as the purely ordered structure would yield Raman signatures whose intensities and artificial peak splitting disagree with the experiments. For hollandite there is no indication about ordering on any scale of neither K/Na nor Si/Al. Consequently the alchemical approach should give more reliable results than the use of supercells, no matter how complex they can be (Mookherjee and Steinle-Neumann, 2009).

3. Results and discussion

Hollandite is tetragonal with space group I4/m and two formula units in the conventional unit cell. The large cations, i.e. K, Na, etc., lay on the 2a Wyckhoff positions; the octahedrally coordinated cations, i.e. Si and Al, are disordered on the 8h Wyckoff positions; the O atoms lay on 8h Wyckhoff positions. We perform the first-principles calculations using the primitive unit cell in order to avoid the phase-corrections of the wavefunctions (that would otherwise contribute from the neighboring Brillouin zone by folding back to the original zone). This same restriction is highly useful as it minimizes the computational effort by reducing the size of the unit cell. We chose the axis orientation such as the fourfold tunnel parallel to the c axis of the primitive unit cell.

The variation of the lattice parameters with pressure for the two compositions is summarized in Table 1. The Na-bearing hollandite has consistently smaller lattice parameters than the K-pure term. The change in density between the two compositions is