

Structure and properties of aluminosilicate garnets and katoite: an ab initio study

R.H. Nobes^a, E.V. Akhmatkaya^a, V. Milman^{b,*}, B. Winkler^c, C.J. Pickard^c

^a *FECIT, 2 Longwalk Road, Stockley Park, Uxbridge UB11 1AB, UK*

^b *MSI, The Quorum, Barnwell Road, Cambridge CB5 8RE, UK*

^c *KristallographieInstitut für Geowissenschaften, Olshausenstr 40, D 24098 Kiel, Germany*

Abstract

The structural properties of end-members of the aluminosilicate garnet family (pyrope, grossular, spessartine and almandine) and of one hydrogarnet (katoite) have been investigated as a function of applied pressure. The calculated static geometry, bulk modulus and its pressure derivative are in good agreement with available experimental data. The results of a systematic study of the effect of the size of the divalent cation on compressibility are presented. The bonding and dynamics of Mg in pyrope are investigated by using frozen phonon calculations. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Garnets are a chemically diverse group of minerals that are abundant in the Earth's crust and upper mantle [1]. Recent studies of synthetic end-members and their solid solutions have provided detailed insight into the crystal chemistry and structure of garnets (e.g., [2]). However, a number of open questions remain that can be best investigated by using atomistic modeling. The present paper addresses such issues as: the compression mechanism up to high pressures; the effect of hydrogarnet substitution, $\text{SiO}_4 \leftrightarrow \text{O}_4\text{H}_4$; and the dynamics and disorder of cations in garnets.

The garnets studied here include the four aluminosilicate end-members pyrope ($\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$), grossular ($\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$), almandine ($\text{Fe}_3\text{Al}_2\text{Si}_3\text{O}_{12}$) and spessartine ($\text{Mn}_3\text{Al}_2\text{Si}_3\text{O}_{12}$), as well as katoite ($\text{Ca}_3\text{Al}_2(\text{O}_4\text{H}_4)_3$), the Si-free hydrogrossular. These garnets crystallize in the space group $Ia\bar{3}d$ with 160 atoms per unit cell (232 atoms in the case of katoite). This system size makes ab initio modeling extremely demanding in terms of both memory requirements and floating-point performance.

The accuracy of methods that are computationally less demanding appears to be too low to investigate the structure and compressibility of garnets. For example, the ab initio perturbed ion (aiPI) technique has been used recently to study pyrope [4] and grossular [5]. This method represents the electronic structure of infinite systems by treating them as clusters embedded into a periodic lattice. The calculated bulk moduli of 155 GPa for

* Corresponding author.

¹ Tel.: +44-1223-413300; fax: +44-1223-413301.

E-mail address: vmilman@msicam.co.uk (V. Milman).

pyrope [4] and 121 GPa for grossular [5] are in error by 9% and 28%, respectively. The origin of the discrepancy between the experimental and calculated data is most probably due to large errors in the computed bond lengths, which deviate from experimental values by up to 9%. Thus the volume distribution between polyhedra is wrong and the compressibility is not described correctly.

It follows from these earlier results that one has to use a technique that goes beyond the cluster description, and is based on a more rigorous representation of electronic interactions. Hartree–Fock studies of large and complex structures such as garnets are computationally so demanding that only a minimal basis set can be used. The computed compressibility from such a calculation for pyrope [3] deviates significantly (23%) from the experimental result and hence cannot be used in a comparative crystal chemical study. It would also be rather difficult to use the HF method for garnets with heavy cations.

The aim of this paper is to demonstrate the accuracy of a density functional description of garnets. We start with a description of the computational approach. We then present a summary of a recent study of aluminosilicate garnets [6], followed by the results for katoite. Finally, we use the computed potential energy surface for Mg in pyrope to address the question of cation dynamics and disorder in garnets.

2. Computational details

The quantum-mechanical calculations performed here are based on density functional theory (DFT) [7]. Exchange–correlation effects were taken

into account by using the generalized gradient approximation (GGA) [8], as implemented by [9]. A spin-polarized version of the GGA was applied for Fe- and Mn-containing garnets. The total energy code CASTEP was used [10,11], which utilizes pseudopotentials to describe electron–ion interactions and represents electronic wavefunctions using a plane-wave basis set. Most calculations were performed for primitive cells, but the potential energy surface calculations in pyrope were performed with 160 atoms. Norm-conserving optimized potentials [12,13] were used to study pyrope, grossular, almandine and spessartine. An energy cutoff of 900 eV was employed.

Ultrasoft pseudopotentials [14] were subsequently incorporated into the CASTEP code [11] and were used to study the compression of katoite and to investigate Mg dynamics in pyrope, where the system size prohibits the use of norm-conserving potentials. An energy cutoff of 380 eV was found to be sufficient for these systems. A single Γ point was used for the Brillouin zone sampling for all the systems studied.

Geometry optimizations were performed with fixed lattice parameters and full relaxation of the internal coordinates. The calculated pressures were used to construct the equation of state (EOS), which was fitted to a third-order Birch–Murnaghan expression to obtain the bulk modulus, B , and its pressure derivative, B' . All calculations were performed on a Fujitsu VX vector processor.

3. Ground-state properties of garnets

The calculated equilibrium lattice constants and EOS parameters are presented in Table 1, and the

Table 1
Lattice constant, bulk modulus and its pressure derivative for garnets^a

	a (Å)			B (GPa)		B'	
	Experimental	Theoretical	Difference (%)	Experimental	Theoretical	Experimental	Theoretical
Pyrope	11.439	11.395	−0.4	171	170	4.4	4.3
Grossular	11.837	11.857	+0.1	168	166	4.3	4.3
Almandine	11.507	11.509	+0.02	175	176	3.0	4.2
Spessartine	11.606	11.616	+0.09	183	179	7.0	3.6
Katoite	12.570	12.645	+0.6	66; 52	56.3	4.1; 4.0	3.6

^a Experimental data are from [2].

accuracy of the calculated EOS is illustrated in Fig. 1. We obtained very good agreement with experiment for the equilibrium lattice constants as well as for the EOS. The effect of the metallic cation on compressibility is small, of the order of a few per cent of the bulk modulus, and it is thus

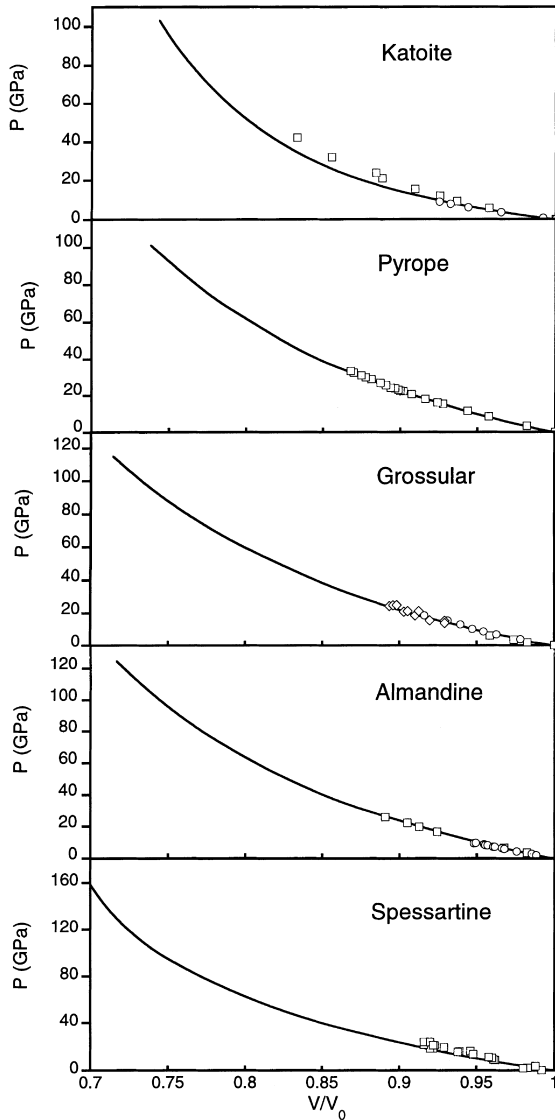


Fig. 1. Equation of state for garnets. Calculated results are shown with solid lines, and experimental data with symbols (katoite: \square [15], \circ [16]; pyrope: \square [17]; grossular: \square [18], \circ [19], \diamond [15]; almandine: \square [20], \circ [21]; spessartine: \square [22]).

crucial to be able to calculate B with an accuracy of a few GPa.

The internal structure is equally well described for all the garnets studied. The deviation of calculated bond lengths from the experimental values is always below 1–1.5%, which is within the limits of the accuracy of DFT.

Two experimental values for the compressibility of katoite have been presented. Energy-dispersive X-ray diamond anvil cell measurements up to 42 GPa gave $B = 66 \pm 4$ GPa and $B' = 4.1 \pm 0.5$ [15]. A Rietveld refinement of angle-dispersive neutron scattering data up to 9 GPa gave $B = 52 \pm 1$ GPa [16]. The calculated value of B of 56 GPa falls between these two experimental results.

4. Compression mechanism and the role of cation

Garnets consist of chains of corner-sharing SiO_4 tetrahedra and AlO_6 octahedra. The third type of coordination polyhedron in the structure is a triangular dodecahedron, XO_8 , occupied by metallic cations. The dodecahedra are the biggest polyhedra in the cell, contributing roughly one third to the cell volume. In the aluminosilicate garnets their bulk moduli are in the region of 120–130 GPa [6], significantly lower than the bulk moduli of garnets. Hence, the bulk modulus of the aluminosilicate garnets is not determined by the compressibility of the dodecahedra. Our results confirm that the main compression mechanism is the bending of the angle between the octahedra and tetrahedra [2]. This conclusion is supported by a linear correlation between the change of the Si–O–Al angle and the distortion parameters of all three types of polyhedra [6].

A small increase in the cation size in the sequence Mg–Fe–Mn causes an increase of the bulk modulus. The qualitative changes in the polyhedra under compression are similar in pyrope, almandine and spessartine. Grossular contains the biggest cation, Ca, and compression characteristics of this garnet are different. The bulk modulus of grossular is the lowest among the garnets considered here, primarily due to the different behavior of the AlO_6 octahedra under pressure.

The bulk modulus of katoite is much lower than that of grossular. We found that the bulk modulus of the tetrahedron drops from 341 GPa in grossular to 19 GPa in katoite. Additionally, the bulk modulus of the CaO_8 dodecahedron decreases from 131 to 55 GPa, so that the high compressibility of the dodecahedron also contributes to the low bulk modulus of katoite [16].

The nature of the hydrogen bonding in katoite under pressure is controversial. Neutron diffraction data up to 9 GPa suggest that the O...H bond length decreases under pressure, leading to stronger hydrogen bonding in the structure [16]. The O–H bond, however, was found to contract significantly at a rate of $\sim 0.012 \text{ \AA/GPa}$ [16]. This contradicts an earlier spectroscopic study [23] which interpreted the pressure shift of infrared and Raman bands as a lengthening of the O–H bond at high pressure. The calculated results are compared with experiment in Fig. 2. The theoretical curve shows a slight increase in the O–H bond length, from 0.96 to 0.99 \AA , over the pressure range of 100 GPa. It appears that diffraction data are not accurate enough to locate hydrogen positions unambiguously.

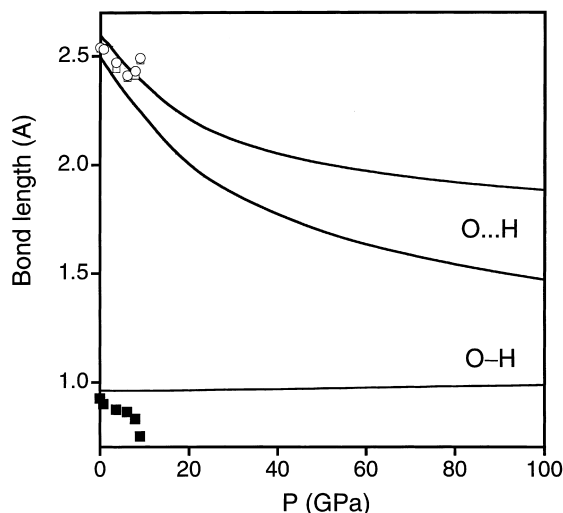


Fig. 2. Pressure dependence of the O–H and O...H bond lengths in katoite (two inequivalent hydrogen bond lengths are shown). Experimental data are from [16].

5. Bonding and dynamics of Mg in pyrope

The ionic radius of the Mg cation suggests that this cation is ‘too small’ for the dodecahedral site it occupies in pyrope. It has been suggested that Mg atoms are statically and/or dynamically disordered [2]. We studied the bonding and vibrational properties of Mg by calculating the potential energy surface (PES) for Mg displacements. The conventional unit cell with 160 atoms was used, and only one Mg atom was displaced. This setup allows us to investigate the modes that correspond to a pure hindered translational motion of Mg. We found that the lowest frequency for a pure Mg translation is 234 cm^{-1} , which should help to re-assign experimental vibrational frequencies [2,24].

The calculated PES is highly anisotropic and strongly anharmonic in one direction. There is no local minimum close to the global energy minimum, which means that there is no static subsite ordering. The Mg PES is illustrated in Fig. 3 for displacements perpendicular to the $\bar{4}$ axis. The data in Fig. 3 cannot be interpreted in a quasi-harmonic approximation unless small and large

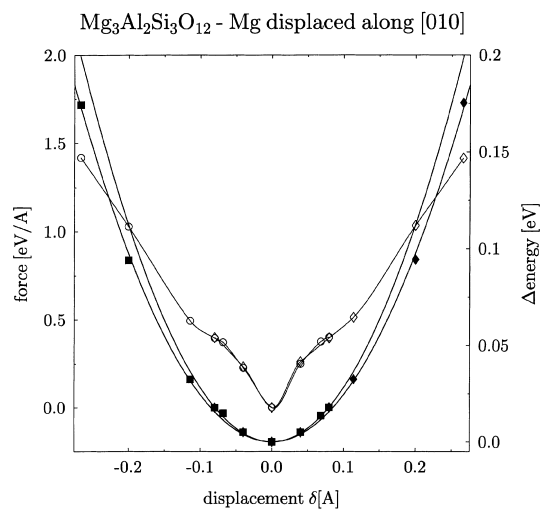


Fig. 3. Dependence of the total energy (solid symbols) and of the absolute value of restoring force (open symbols) on the displacement of the Mg cation perpendicular to the $\bar{4}$ axis. Different symbols refer to different, but symmetry-equivalent, displacements. The force on the Mg atom is not linearly dependent on displacement, and the total energy cannot be fitted with a single quadratic function.

displacements are fitted by different parabolas. This anharmonicity should result in a noticeable temperature-dependent shift of some of the Mg vibrational modes. It also follows that the phonon frequencies derived from the dynamical matrix in the harmonic approximation could be too large by 10%.

6. Conclusions

We have demonstrated that state-of-the-art quantum-mechanical methods as implemented on high-performance vector processors are sufficiently robust and accurate to be used as a quantitative tool for predictive studies of complex systems with more than 150 atoms in the unit cell. The results presented provide better insight into the properties and structure of garnets at ambient conditions and under pressure. It is conceivable that *ab initio* modeling will in the near future become an integral part of the experimental study of complex systems under extreme conditions.

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