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A theoretical investigation of the relative stabilities of Fe-free clinozoisite and orthozoisite

Abstract The relative stabilities of orthozoisite, $Ca_2Al_3[O|OH|Si_2O_7|SiO_4]$, space group *Pnma*, and the monoclinic polymorph, clinozoisite, space group $P2_1/m$, have been investigated using calculations based on density functional theory. It is found that orthozoisite is more stable than clinozoisite by about $1 \, kJ \, mol^{-1}$ at zero pressure in the athermal limit. The bulk moduli of the two polymorphs have been calculated to be $B_{ortho} = 117.5(1.7) \, GPa$ and $B_{clino} = 136(4) \, GPa$.

Key words Quantum mechanical calculations · Fe-free clinozoisite · Orthozoisite

Introduction

The relative stabilities of orthozoisite, $Ca_2Al_3[O|OH|Si_2O_7|SiO_4]$ (space group *Pnma*, Z = 4), and the monoclinic polymorph, clinozoisite (space group $P2_1/m$, Z = 2), at low temperatures have been the subject of controversy (see references in Jenkins et al. 1983 and Smelik et al. 2001). Conclusions based on phase relations observed in field studies are generally problematic, as natural samples contain variable amounts of iron, and this may influence the relative stabilities of the polymorphs. Unambiguous experimental reversal studies for Fe-free end members seem to be impossible due to the sluggishness of the reaction at low temperatures, and hence other methods need to be

used to determine the relative stabilities of the two polymorphs.

It is also surprising that the compressibility of the two polymorphs is only poorly determined. The molar volumes of the polymorphs are very similar, 136.19 and $136.83 \, g \, mol^{-1}$ for orthozoisite and clinozoisite, respectively (Dollase 1968). As the structures are closely related, to a first approximation the compressibilities should not differ much. However, no consensus with respect to the bulk moduli of the two polymorphs has yet been reached. For the bulk modulus of orthozoisite, values of 279 GPa (Holland et al. 1996), 102 GPa (Comodi and Zanazzi 1997) and 125 GPa (Pawley et al. 1998) have been derived from static, in situ high-pressure diffraction experiments. The bulk modulus of clinozoisite has been determined to be 154 GPa (Holland et al. 1996) or 127 GPa (Comodi and Zanazzi 1997). The poor agreement between the datasets does not currently allow any quantitative conclusion with respect to the contribution of the *PV* term to the Gibbs free energies of ortho- or clinozoisite.

In a recent calorimetric study (Smelik et al. 2001), standard enthalpies of formation for Fe-free clinozoisite had to be derived from data for orthozoisite by assuming an energy contribution of $4 \, kJ \, mol^{-1}$ due to the orthorhombic–monoclinic transition, but the validity of this assumption remains untested.

In the light of the lack of unambiguous experimental findings it seems worthwhile to establish the difference between the internal (or total) energies of the two phases and their bulk moduli. These have to be computed by quantum mechanical simulations, as models based on empirical potentials will not be sufficiently accurate. For solids with large unit cells, the quantum mechanical approach most often used is density functional theory (DFT) (Hohenberg and Kohn 1964; Kohn and Sham 1965; Parr and Yang 1989; Jones and Gunnarsson 1989; Kryachko and Ludena 1990). In contrast to the computation of free-energy differences (Alfe et al. 1999), the calculation of internal energies of the ground state in the

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athermal limit is straightforward, and this has been done here.

Computational details

The quantum mechanical calculations performed here are based on density functional theory, DFT. While DFT itself is exact (Hohenberg and Kohn 1964), practical calculations require an approximation for the treatment of the exchange and correlation energies. Here we use the generalised gradient approximation, GGA (Perdew et al. 1992). Results based on GGA calculations are generally in better agreement with experiment than those obtained with the local density approximation, LDA (Leung et al. 1991; Hammer et al. 1993; Goniakowski et al. 1996; Hamann 1996).

Total energy differences between polymorphs are usually small and their evaluation requires precise calculations of the total energies. The unit-cell volume of orthozoisite is about 900 Å^3, and so a computationally efficient approach is essential. Full geometry optimisations of complex, low-symmetry compounds like clinozoisite can only be performed if the stress tensor for a given configuration can be evaluated. A computational scheme in which the charge density and electronic wavefunctions are expanded in a basis set of plane waves can fulfil these requirements simultaneously. However, as it is impractical to consider tightly bound core electrons explicitly when using a plane-wave basis set, pseudopotentials have to be used to mimic the screening of the Coulomb potential of the nucleus by the core electrons. A number of approaches for the construction of pseudopotentials have been presented in the literature (Bachelet et al. 1982; Kleinman and Bylander 1982). The state-of-the-art is the efficient "ultrasoft" pseudopotentials, leading to calculations that require a comparatively small number of plane waves (Vanderbilt 1990; Kresse and Hafner 1994). Such ultrasoft pseudopotentials were used here, with a maximum cutoff energy of the plane waves of 380 eV. In addition to the cutoff energy, only one further parameter determines the quality of the calculations, namely the density of points with which the Brillouin zone is sampled. Here, we use a sampling of reciprocal space such that distances between grid points are less than 0.055 Å^{-1}. This is a rather strict criterion for obtaining ground-state properties of an insulator. Full geometry optimisation calculations were performed in which the space-group symmetry was constrained to either $Pnma$ or $P2_1/m$, for ortho- and clinozoisite, respectively. After the final self-consistency cycle, the remaining forces on the atoms were less than 0.02 eV Å^{-1}, and the remaining stress was less than 0.1 GPa. The present calculations are restricted to the athermal limit, in which temperature effects and zero-point motions are neglected. For all calculations we used academic and commercial versions of the CASTEP program, which has been described elsewhere (Payne et al. 1992; MSI 1998; Milman et al. 2000).

The bulk moduli of the two polymorphs were computed by fiting a third-order Birch–Murnaghan equation of state to equilibrium volumes computed at pressures ranging from 0–50 GPa. This approach has been shown to reproduce bulk moduli in silicates to within a few percent of the experimental values (Akhmatskaya et al. 1999).

Results

The results are given in Tables 1 and 2, where they are compared with experiment. The agreement between theory and experiment is well within the usual limits of DFT-based calculations. The experimental finding that the molar volume of clinozoisite is slightly larger, by about 0.6%, than that of orthozoisite is reproduced.

Structural details are also reproduced with the expected accuracy. For example, for orthozoisite it is found experimentally (Dollase 1968) that in the coordination polyhedron of the Si(2) there are two bonds of equal length of 1.621(6) Å, one bond with a length of 1.620 Å and one short bond of 1.582(6) Å. The quantum mechanical model has two bonds with 1.593 Å, one with 1.594 Å and one short one of 1.557 Å. The experimentally determined bond lengths in the coordi-

Table 1 Comparison of structural data for clinozoisite obtained from experiment (Dollase 1968) and theory

	Experimental			DFT–GGA		
a [Å]	8.879(5)			8.7767		
b [Å]	5.583(5)			5.5734		
c [Å]	10.1679(6)			10.1569		
β [°]	115.50(5)			115.72		
Volume ($\text{Å}^3 \text{ mol}^{-1}$)	227.469			223.810		
Density (g cm^{-3})	3.317			3.371		
Ca	0.76170	0.75000	0.15500	0.76266	0.75000	0.15527
Ca	0.60630	0.75000	0.42340	0.60642	0.75000	0.41638
Si	0.33820	0.75000	0.04780	0.33409	0.75000	0.04173
Si	0.67760	0.25000	0.27530	0.67607	0.25000	0.27444
Si	0.18220	0.75000	0.31580	0.18085	0.75000	0.31397
Al	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
Al	0.00000	0.00000	0.50000	0.00000	0.00000	0.50000
Al	0.28730	0.25000	0.22380	0.28749	0.25000	0.23081
O	0.23460	0.99720	0.45200	0.23081	0.99040	0.03921
O	0.30040	0.98670	0.35090	0.29771	0.98439	0.34914
O	0.78740	0.01280	0.34710	0.78537	0.01750	0.34908
O	0.05510	0.25000	0.13220	0.06075	0.25000	0.13189
O	0.03950	0.75000	0.14330	0.04212	0.75000	0.14365
O	0.05960	0.75000	0.40100	0.05973	0.75000	0.39768
O	0.51660	0.75000	0.17790	0.51237	0.75000	0.16953
O	0.50900	0.25000	0.29500	0.50495	0.25000	0.28629
O	0.64200	0.25000	0.10420	0.64779	0.25000	0.10869
O	0.07510	0.25000	0.42410	0.07318	0.25000	0.42425
H	0.04600	0.25000	0.34100	0.04842	0.25000	0.31845

Table 2 Comparision of structural data for orthozoisite obtained from experiment (Dollase 1968) and theory

	Experimental			DFT–GGA		
a [Å]		16.212(8)			16.0271	
b [Å]		5.559(6)			5.5323	
c [Å]		10.036(4)			10.0317	
Volume (Å^3 mol^{-1})		226.117			222.371	
Density (g cm^{-3})		3.337			3.393	
Ca	0.36670	0.25000	0.43760	0.36744	0.25000	0.43734
Ca	0.45180	0.25000	0.11500	0.45043	0.25000	0.11969
Si	0.08160	0.25000	0.10640	0.08335	0.25000	0.10375
Si	0.41040	0.75000	0.28210	0.41180	0.75000	0.28542
Si	0.16010	0.25000	0.43560	0.16071	0.25000	0.43331
Al	0.24960	0.99700	0.18990	0.25054	0.99675	0.18957
Al	0.10540	0.75000	0.30060	0.10653	0.75000	0.30264
O	0.13170	0.00000	0.14510	0.13236	0.00382	0.14364
O	0.10120	0.01500	0.43000	0.10267	0.01486	0.42676
O	0.35840	0.99000	0.24520	0.36005	0.98504	0.24553
O	0.21780	0.75000	0.30100	0.21864	0.75000	0.29818
O	0.22730	0.25000	0.31200	0.22832	0.25000	0.31253
O	0.27130	0.75000	0.06000	0.27444	0.75000	0.05915
O	0.99050	0.25000	0.16400	0.99379	0.25000	0.15994
O	0.99540	0.75000	0.29500	0.99843	0.75000	0.28478
O	0.42090	0.75000	0.44300	0.41854	0.75000	0.44394
O	0.26800	0.25000	0.07400	0.27149	0.25000	0.07775
H	0.26300	0.25000	0.97600	0.27027	0.25000	0.97769

nation tetrahedra of the Si(3) are $2 \times 1.620(6)$ Å, 1.648(6) Å and 1.670(6) Å (Dollase 1968), whereas the model gives 2×1.601 Å, 1.625 Å and 1.635 Å. So, while there is a small systematic shortening of the Si–O bonds, the distortions are reasonably well described. The O–H distance is calculated to be 1.004 Å, which is consistent with a weak-to-medium hydrogen bond (Winkler et al. 1989).

The calculations predict that orthozoisite is stable by about 1 kJ mol^{-1} with respect to clinozoisite. This energy difference is close to the uncertainty of the method. However, the polymorphs are rather similar and hence errors due to the methodology used should largely cancel out when differences between energies are taken. Also, in the present calculations the quality of the basis set and of the k-space sampling was rather high, and therefore this result is judged to be significant.

The equation of state calculations give bulk moduli of $B_{ortho} = 117.5(1.7)$ GPa and $B_{clino} = 136(4)$ GPa.

Discussion

At the level of theory employed here, and with the approximations made in the present calculations, orthozoisite is more stable by about 1 kJ mol^{-1} with respect to clinozoisite in the athermal limit. The finding of the present study is in contradiction to the suggestion that at low temperatures clinozoisite is the stable polymorph (for references see Smelik et al. 2001). All former studies, however, were based on extrapolations, with respect to either temperature or composition. We therefore believe that the present result provides new constraints for the derivation of the relative stabilities of the two polymorphs.

The current calculations emphasise that any kind of modelling of the two polymorphs needs to be very reliable in order to be able to address the origin of the difference of properties between them. In practise, this excludes the use of empirical rigid-ion (Burnham 1990) or core-shell type (Winkler et al. 1991) models as these will not be accurate enough. Modelling the temperature dependence of the relative stabilities of the two polymorphs based on observed vibrational frequencies, as has been done by Richet et al. (1992), can provide the slope of the univariant reaction boundary, but one point on this curve has to be fixed, and for this the current result can be used. However, the system studied here requires a very high accuracy, and it is not obvious that the error made in the derivation of the phonon density of state in a Kieffer-type model (Kieffer 1985) is negligible.

As has been mentioned in the introduction, the bulk moduli reported in the literature differ significantly, ranging from 279 GPa (Holland et al. 1996) to 102 GPa (Comodi and Zanazzi 1997) for orthozoisite and from 154 GPa (Holland et al. 1996) to 127 GPa (Comodi and Zanazzi 1997) for clinozoisite. Our calculations clearly support a value close to that of 125 GPa (Pawley et al. 1998) for orthozoisite and suggest that the true value for clinozoisite is about 136 GPa, i.e. between the two values reported so far.

In addition to the results presented here, the energetics of the incorporation of Fe into the symmetrically inequivalent sites can be studied. This, then, is a more geologically relevant model, but our own preliminary calculations have shown that this requires the use of spin-polarised calculations based on ultrasoft pseudopotentials with "non-linear core corrections" (Louie et al. 1982). These computationally expensive calculations are currently in progress.

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