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A new $Ca_3MgSi_2O_8$ compound and some of its thermodynamic properties

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ABSTRACT

A new calcium magnesium orthosilicate with the composition $Ca_3MgSi_2O_8$ was synthesized by a solid-state reaction process at 1.2 GPa and 1373 K for 7 days. We refined the crystallographic structure of this new compound using single-crystal X-ray data, and obtained some of its thermodynamic properties by performing some first-principles simulations. Our single-crystal X-ray analysis has shown that this new compound is monoclinic with the space group $C2/c$, and its unit-cell parameters are a = 9.344(4) Å, b = 5.3308(3) Å, c = 13.290(6) Å, α = 90°, β = 92.072(7)°, γ = 90°, and V = 658.7(6) Å^3. The compressibility of this new compound was studied with the CASTEP code using density functional theory and planewave pseudopotential technique, which led to an isothermal bulk modulus B_0 of 99(2) GPa with a pressure derivative B_0' of 3.5(5). The phonon dispersions and vibrational density of the states (VDoS) of this new compound were calculated by using density functional perturbation theory. Subsequently, the VDoS was combined with a quasi-harmonic approximation to compute the isobaric heat capacity (C_p) and standard vibrational entropy (S^0_{298}), yielding $C_p = 3.927(2) \times 10^2 - 1.159(6) \times 10^3 T^{-0.5} - 1.054(4) \times 10^7 T^{-2} + 1.362(8) \times 10^9 T^{-3}$ J mol^{-1} K^{-1} for the T range of 298–1000 K and S^0_{298} = 270.5(60) J mol^{-1} K^{-1}.

1. Introduction

The calcium magnesium orthosilicates have attracted much attention for their wide applications as cements, photoluminescent materials and bioactive materials due to their versatile structures as well as interesting physical and chemical properties [1–3]. These compounds are also found as mineral inclusions in diamonds originated from the Earth's mantle [4], and may be used to estimate the formation P-T conditions of the diamonds [5].

The composition $Ca_3MgSi_2O_8$ was previously demonstrated to crystallize into the phase merwinite (space group $P21/a$, Z = 4), one of the calcium magnesium orthosilicates. Since the structure of merwinite is much more closely-packed than that of olivine, merwinite has been proposed as a possible stable phase in the upper mantle of the Earth [6]. Indeed, Liu experimentally demonstrated that merwinite was stable at 1273 K and 20 GPa [7]. In the lower mantle of the Earth, the perovskite-structured compounds $MgSiO_3$ and $CaSiO_3$ were thought to be the predominant phase. It has been shown that the crystal structure of merwinite consists of a perovskite-like layer of [MgO_6] octahedra and a double-layer of [SiO_4] tetrahedra, stacking alternatively in the [111] direction of an ideal cubic perovskite structure [8]. The close relationship between the structure of merwinite and those of the $MgSiO_3$ and $CaSiO_3$ perovskites is very meaningful: Since the $MgSiO_3$ and $CaSiO_3$ perovskites are usually unquenchable, a good understanding about the structure and properties of merwinite may lead to better understanding of the structures and physical-chemical properties of the $MgSiO_3$ and $CaSiO_3$ perovskites.

In this work, we synthesized a new compound, with the composition $Ca_3MgSi_2O_8$ but a structure slightly different to that of merwinite, using a solid-state reaction method. The crystallographic details of this new phase were obtained by performing single-crystal X-ray diffraction analysis. First-principles calculation was engaged to study some of the thermodynamic properties of this new phase. With the CASTEP code, the compressibility was determined by using density functional theory and planewave pseudopotential technique, and the phonon dispersions and vibrational density of the states (VDoS) were calculated by using density functional perturbation theory. The VDoS was further combined with a quasi-harmonic approximation to compute the isobaric heat capacity (C_p) and standard vibrational entropy (S^0_{298}).

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2. Experimental and theoretical section

2.1. Synthesis

A new calcium magnesium orthosilicate with the composition $Ca_3MgSi_2O_8$ was synthesized by a solid-state reaction method. The starting material was made as following: (1) pure chemicals $CaCO_3$ (Alfa Aesar, powder, 99.9%), MgO (Alfa Aesar, powder, 99.9%) and SiO_2 (Alfa Aesar, powder, 99.9%) were pretreated at 1 atm and 723 K for 72 h, mixed in a mole ratio 3:1:2, and ground and homogenized in a agate mortar; (2) this mixture was pressed into a pellet and degassed in a Pt crucible at 1 atm and 1273 K for 48 h; (3) the degassed pellet was crushed into a fine powder, which was further stored in a drying oven at 383 K for later synthesizing experiment. The starting material was loaded into a Pt capsule (10 mm in length and 2.5 mm in diameter), which was sealed at both ends using an arc-welding technique. Our synthesizing experiment was carried out with a piston-cylinder apparatus installed in the High-Pressure Laboratory of Peking University (Depths of The Earth Company Quickpres [9,10]). The experimental assembly and high-*P* experimental technique were generally identical to those reported in [11]. Our sample was synthesized at 1.2 GPa and 1373 K with a heating time of 7 days.

2.2. Characterization

The synthetic product was polished with a series of diamond pastes, washed with an ultrasonic washing machine, carbon-coated and examined with an electron microprobe (EMP; JEOL JXA-8100). The analyses were carried out in twenty-two randomly-selected areas. The sample was then slowly ground down to a fine powder and checked with a powder X-ray diffractometer (Rigaku D/Max 2550V/PC with graphite-monochromated Cu Kα radiation) at ambient conditions.

2.3. Single-crystal X-ray diffraction

Suitable single crystal of the new $Ca_3MgSi_2O_8$ compound was selected for single-crystal X-ray diffraction analysis. Intensity data was collected on a Bruker Smart ApexII Quazar micro-focused diffractometer using Mo Kα radiation (λ = 0.71073 nm). The raw data was processed and corrected for the absorption effects using SAINT+ and SADAB. An initial structure solution was obtained via direct methods and refined by a full-matrix least-squares method using the SHELXT software included in the SHELXTL package. All heaviest atoms were first located unambiguously in the Fourier maps, and then the O atoms were found in the subsequent difference maps. All atoms were refined with anisotropic displacement parameters. The final cycles of the least-squares refinement including atomic coordinates and anisotropic thermal parameters for the atoms [I > 2sigma(I)] converged at R_1 = 0.0527, wR_2 = 0.1310, and S = 1.035 for this new $Ca_3MgSi_2O_8$ compound.

2.4. Computational method

The first-principles simulation carried out to investigate the compressibility of the new $Ca_3MgSi_2O_8$ compound was completed with the CASTEP code using density functional theory [12,13] and planewave pseudopotential technique [14]. The exchange-correlation interaction was treated by the generalized gradient approximation (GGA) with the Perdew-Burker-Ernzerhof (PBE) functional [15], and a convergence criterion of 10^{-6} eV/atom was used in the self-consistent field calculations. We employed a planewave basis set with a cutoff of 990 eV to expand the electronic wave functions, and a norm-conserving pseudopotential to model the ion-electron interaction [16,17]. We sampled the irreducible Brillouin zone with a 3 × 3 × 1 Monkhorst-Pack grid [18]. The effects of using larger cutoff and k point mesh on the calculated properties were found to be insignificant. The computation cell contained four $Ca_3MgSi_2O_8$ molecules (in total 56 atoms), with the initial structure model from our single-crystal X-ray analysis. The equilibrium lattice parameters and internal coordinates at different pressures were optimized by minimizing the Hellmann-Feynman force on the atoms and simultaneously matching the stress on the unit cell to the target stress. These theoretical techniques were used in our previous studies targeting the structures and thermodynamics of some silicate minerals [19,20].

Based on the optimized structure with the GGA + PBE method, the phonon dispersions and VDoS of the $Ca_3MgSi_2O_8$ compound were calculated by diagonalizing the dynamical matrix whose elements were obtained using density functional perturbation theory [21,22]. The q-vector grid spacing for interpolation was 0.07 $Å^{-1}$, which represented the average distance between the Monkhorst-Pack q-points used in the dynamical matrix calculations. The phonon dispersions were obtained at the high symmetry points (L, M, A, G, Z, V). The coordinates of these points on the surface of the Brillouin zone were L = ($-^1/_2$ 0 $^1/_2$), M = ($-^1/_2$ $-^1/_2$ $^1/_2$), A = ($-^1/_2$ 0 0), G = (0 0 0), Z = (0 $-^1/_2$ $^1/_2$), V = (0 0 $^1/_2$).

3. Results and discussion

3.1. Phases in synthetic material

The electron back-scatter images (Fig. S1) indicate that there is just one crystalline phase appearing in our synthetic product, but the powder X-ray diffraction data (Fig. 1) show that another crystalline phase with a small proportion occurs. This minor phase could be a pyroxene, as implied by the powder X-ray diffraction data. The 22 EMP analyses suggest a chemical formula of $Ca_{3.04(2)}Mg_{1.00(1)}Si_{1.98(1)}O_8$ for the major phase, close to an idealized formula of $Ca_3MgSi_2O_8$.

3.2. Single-crystal structure

The single-crystal analysis of the new $Ca_3MgSi_2O_8$ compound reveals that it crystallizes in the *C*2/*c* space group, rather than in the *P*21/*a* space group of the merwinite, with a = 9.344(4) Å, b = 5.308(3) Å, c = 13.290(6) Å, α = 90°, β = 92.072(7)°, γ = 90°, and V = 658.7(6) $Å^3$ (Table 1), in agreement with those obtained by our powder X-ray diffraction pattern (Fig. 1).

Each asymmetric unit contains one distinct Mg site, one distinct Si site, two distinct Ca sites and four distinct O sites (Fig. S2), and their coordinates and equivalent isotropic displacement parameters are listed in Table S1. As shown in Fig. 2 and Table S2, the Mg atom is

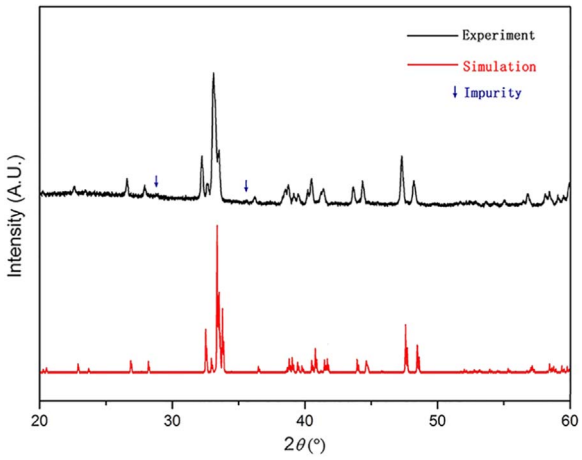

Fig. 1. Experimental and simulated powder X-ray diffraction patterns of the new $Ca_3MgSi_2O_8$ compound. The simulated pattern is based on the structure refined by our single-crystal X-ray diffraction analysis. The arrows indicate those extremely weak peaks in the experimental powder X-ray diffraction pattern, which do not belong to the new $Ca_3MgSi_2O_8$ compound.

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