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First-principles studies of pressure-induced phase transitions in SiO₂

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Abstract

Structural stability is investigated for the CaCl₂ structure of SiO₂ by using a first-principles linear response theory. Softening of modes is found in the direction of the Γ -X (100) axis in k -space at 810 GPa. The results of the present work strongly support the assertion that the $P2_1/n$ structure is very reasonable suggestion for the post-CaCl₂ structure.

1. Introduction

Recent theoretical studies of pressure-induced phase transformations in SiO₂ have revealed that the mechanism for the cristobalite-to-stishovite transformation is a two-step process involving, first, rotation of SiO₄ tetrahedra followed by a translation to yield the six-coordinated stishovite structure [1]. Compression of the stishovite phase to the CaCl₂ structure has been investigated in detail both experimentally and theoretically by several groups and has been indicated to be resulting from lattice instabilities associated with a vanishing shear modulus [2, 3]. The question of the stability and transition mechanisms of post-CaCl₂ structure has been addressed by many groups [4–8]. A recent study has employed first-principles molecular dynamics simulation based on the Parrinello–Rahman algorithm in the Car–Parrinello method to explore the possible structures that may occur at high pressures and their stability relative to structures that have been suggested previously [1]. This study predicted that the six-coordinated CaCl₂ structure transforms at 300 K and under hydrostatic conditions to a six-coordinated monoclinic structure with $P2_1/n$ symmetry, which remains stable to very high pressures and then transforms to another more highly coordinated monoclinic structure with $P2_1/m$ symmetry.

In this study, the mechanism for transformation to the structures obtained in [1] is investigated by using first-principles calculations. Phonon calculations are performed for the CaCl₂ phase and detailed discussions for the CaCl₂-to- $P2_1/n$ transition are given here.

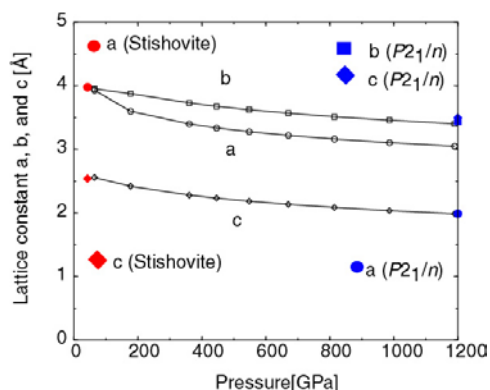


Figure 1. Pressure dependences of the lattice constants for the CaCl_2 structure: the filled circle and diamond specify the lattice constants a and c of stishovite at 42 GPa [11], respectively. The filled circle, square, and diamond specify the average lattice constants a , b , and c of the $P2_1/n$ structure at 1.2 TPa [1]. Note that the choices of a - and c -axes in the CaCl_2 structure are different from those for the $P2_1/n$ structure. However, the unique axis b is the same in each case.

(This figure is in colour only in the electronic version)

2. Computational method

A first-principles pseudopotential method based on the density functional theory is used to obtain the structure optimized for different constant volumes [9]. To perform the phonon calculation, a first-principles linear response technique [9] is used. The phonon band structures are then calculated by calculation of the dynamical matrices on a $(4, 4, 4)$ Monkhorst–Pack k -point mesh for integrations over the Brillouin zone. Troullier–Martins-type pseudopotentials are used [10] within a local density approximation. The maximum kinetic energy of the plane waves included in the basis is 35 Hartree. The criterion for forces to optimize the structures is 5.0×10^{-5} Hartree Bohr $^{-1}$.

3. Results and discussion

The CaCl_2 structure has an orthorhombic unit cell with $Pnmm$ symmetry. Si atoms are at $2a$: $(0, 0, 0)$, $(1/2, 1/2, 1/2)$; and O atoms are at $4g$: $(u_1, u_2, 0)$, $(-u_1, -u_2, 0)$, $(-u_1 + 1/2, u_2 + 1/2, 1/2)$, and $(u_1 + 1/2, -u_2 + 1/2, 1/2)$. Note that $Pnmm$ is a subgroup of $P4_2/mnm$ (stishovite; rutile structure) and a supergroup of $P2_1/n$.

Firstly, structures of the CaCl_2 structure are optimized for several different constant volumes. The pressure dependences of the lattice constants are shown in figure 1. Pressure is given at each volume for calculating the stress tensor. It is found that the lattice constants of the CaCl_2 structure are continuously connected to those of both low- and high-pressure structures except for the lattice constant a of the CaCl_2 structure. The reason for this is revealed in the discussion of phonon dispersion curves in this work. Figure 1 indicates no discontinuity in the lattice constant, which implies that the transitions from stishovite to CaCl_2 structure and from CaCl_2 to $P2_1/n$ structure are second- or higher-order transitions. Such continuous change is also observed in the internal parameters, u_1 and u_2 , as shown in figure 2. These results for the low-pressure range agree with previous work [12].

A previous work indicated the CaCl_2 structure to be stable over a long range, according to the total energy found from a first-principles study [1]. In this work, structural stability is investigated on the basis of lattice vibration energy. Phonon dispersions at 64 GPa at the $\Gamma(000)$ point are shown in figure 3. This is a typical phonon dispersion for a CaCl_2 structure under 810 GPa. On all symmetrical axes, the phonon frequencies are positive, which implies that all vibration modes in the CaCl_2 structure are stable and that the structure is stable under 810 GPa.

The phonon dispersions at 810 GPa are shown in figure 4. The modes have negative frequencies on the Γ –X (100) axis in k -space. This implies that the CaCl_2 structure cannot

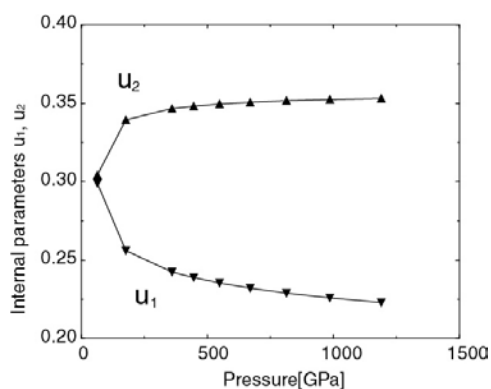


Figure 2. Pressure dependences of the internal parameters of the CaCl₂ structure. These sites are occupied by oxygen.

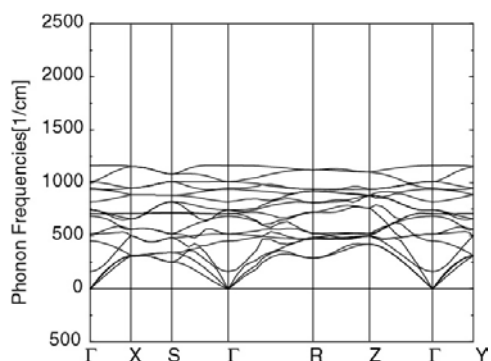


Figure 3. Phonon frequencies of the CaCl₂ structure at 64 GPa.

be formed above 810 GPa and it must transform to another structure at that pressure. This is consistent with previous work [1].

Figure 4 implies that the a -axis in real space becomes unstable first. This is enough evidence to convince us that there is a change in the lattice constant a . This explains the discrepancy between the lattice constant a of the CaCl₂ structure and the lattice constant c of the $P2_1/n$ structure.

The lattice constants a and c are unstable above 810 GPa from dispersion curves for higher pressure, which implies that the a - c plane is unstable. Therefore, the angle between the a - and c -axes (angle β) is no longer fixed at 90°. This is considered to promote the structural transformation from CaCl₂ to the $P2_1/n$ structure.

The phonon calculation indicates that the $P2_1/n$ structure is a very reasonable suggestion for the post-CaCl₂ structure.

4. Conclusions

The mechanism of the transformation from the CaCl₂ structure to the $P2_1/n$ structure is investigated by using the first-principles linear response technique. The phonon band structures obtained indicate phonon anomalous at 810 GPa. The behaviour of the Γ -X axis is consistent with the change of the lattice constant a . From the dispersion curves for higher pressure the a - c plane becomes unstable. These results strongly support the assertion that the post-CaCl₂ structure is a $P2_1/n$ structure.

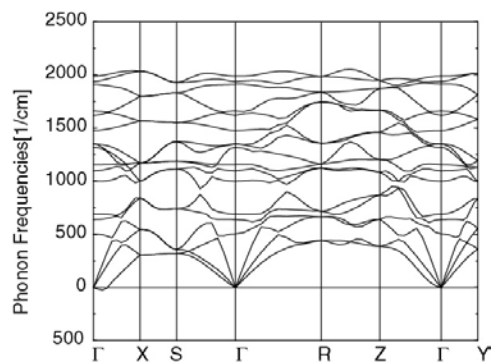


Figure 4. Phonon frequencies of the CaCl_2 structure at 810 GPa.

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