First principle calculations of materials deep inside the earth

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The structural properties of CaO and SrO are investigated up to 100 GPa for CaO and 60 GPa for SrO using the first-principle plane wave pseudopotential method within the Local Density Approximation (LDA) and Generalized Gradient Approximation (GGA), in which the ultra-soft and the norm-conserved pseudopotentials are employed. The calculated equilibrium lattice constants under external high pressure reproduce the experimental ones. The structural phase transitions from the low-pressure NaCl to the high-pressure CsCl structures are also estimated by the enthalpy calculations, which also reproduce the experimental results.

Introduction

The structural and elastic properties of materials under high-pressure conditions have been extensively studied both experimentally and theoretically. These kinds of studies have provided us fundamental changes in bonding natures of many materials under deep earth conditions. The theoretical studies have been performed using the classical Molecular Dynamics (MD) and first-principle (*ab initio*) electronic structure calculational methods. For these first-principle studies the Hartree-Fock based, the augmented plane wave and the pseudopotential plane wave calculational methods were employed.

The high-pressure behaviors of the alkaline-earth oxides have been widely studied [1–7] both experimentally and theoretically, because they have wide varieties of applications and importance as prototype oxides. Then the structural properties of CaO and SrO were studied here theoretically using the plane wave pseudopotential method within the Local Density Approximation (LDA) and the Generalized Gradient Approximation (GGA), up to 100 and 60 GPa for CaO and SrO, respectively, in which the ultra-soft and the norm-conserved pseudopotentials are employed. The best agreement between calculations and experiments are obtained when the ultra-soft potential within GGA are used. The observed pressure-induced volume compression for both CaO and SrO were well reproduced by the calculated ones. The structural phase transitions from the low-pressure NaCl (B1) to the high-pressure CsCl (B2) structures in CaO and SrO occur at 53–70 and 32–40 GPa, respectively. The transition pressures taken from the enthalpy calculations were 65.2 and 37.0 GPa for CaO and SrO, respectively, which reproduced the experimental results very well.

Calculating procedures

The structural properties of CaO and SrO were studied using the Density Functional Theory (DFT) and the plane wave pseudopotential method within the Local Density Approximation (LDA) and the Generalized Gradient Approximation (GGA). Here the ultra-soft and optimized, norm-conserving, nonlocal pseudopotentials were employed. All the calculations have been performed using the CASTEP (CAmbridge Serial Total Energy Package) code[8] on the Fujitsu VPP700E in RIKEN.

At first, total energies and lattice constants of the primitive cells with the NaCl structure ($Fm\bar{3}m$ symmetry) for CaO were calculated changing the cutoff energy, *i.e.* 260, 300, 340 and 380 eV cutoff for ultra-soft and 600, 750, 900 and 1000 eV cutoff for norm-conserving potentials, and the number of sampling k points, *i.e.* 10, 20 and 35 special k points, in order to check the dependence of the resulting lattice constant on the cutoff energy and the number of sampling k points. Resulting differences of the lattice constants between three kinds of k samplings were less than 0.01 Å. Then the results in the case of 10 k-point sampling were plotted on Figs. 1 and 2. From these results, the lattice constant of CaO was best

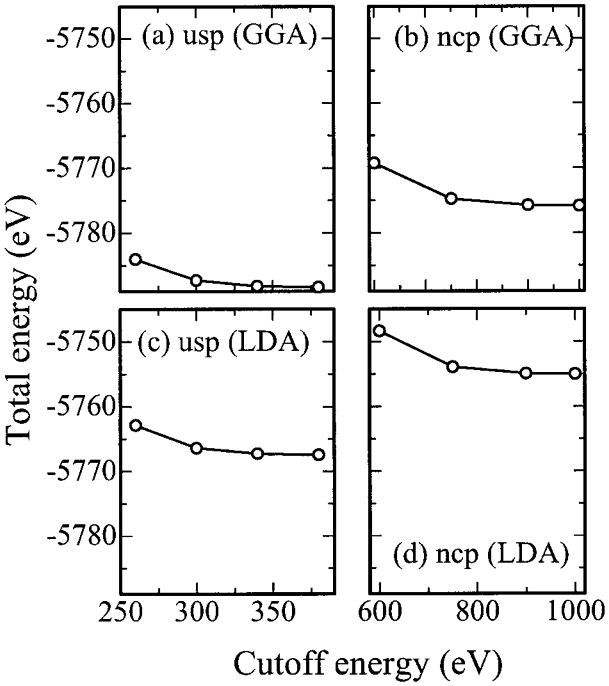

Fig. 1. Calculated total energies of CaO at zero-pressure using (a) ultra-soft potential within GGA, (b) norm-conserved potential within GGA, (c) ultra-soft potential within LDA and (d) norm-conserved potential within LDA.

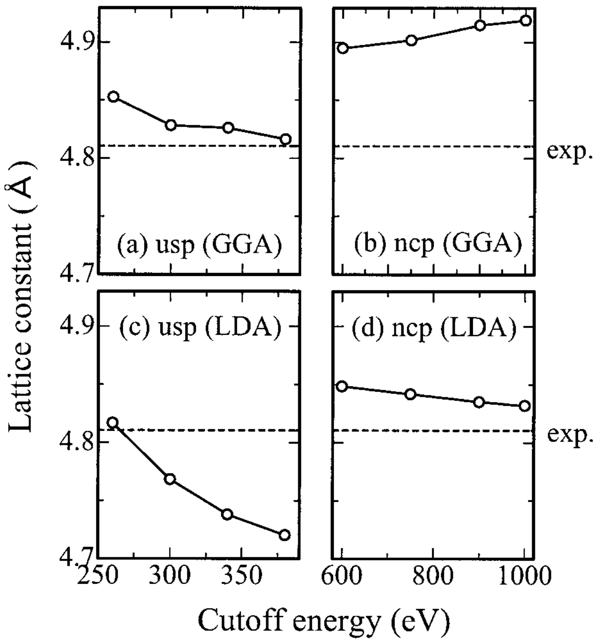

Fig. 2. Calculated equilibrium lattice constants of CaO at zero-pressure using (a) ultra-soft potential within the GGA, (b) norm-conserved potential within GGA, (c) ultra-soft potential within LDA and (d) norm-conserved potential within LDA. Experimental lattice constant is indicated by dashed line.

reproduced when the ultra-soft potential within the GGA was used. Then the ultra-soft pseudopotential within the GGA was adopted for all the calculations of structural properties of CaO and SrO under external high pressure, where the cutoff energy and the number of k-points were fixed at 380 eV and 10 special k-points. Next single primitive cells of CaO and SrO with B1 (NaCl type) and B2 (CsCl type) structures were optimized at several pressures by minimizing the total energies and stresses, in which the crystal symmetries were fixed at $Fm\bar{3}m$ and $Pm\bar{3}m$ for B1 and B2 phases, respectively.

Results and discussions

The calculated equilibrium lattice constants for CaO and SrO at zero-pressure and zero-temperature are summarized on Table 1, which are compared with the experimental and other calculated results. The calculated pressure-volume results were fitted to the fourth order Birch-Murnaghan equation of state[9] expressed by

$$P = 3K_0 f(1+2f)^{5/2}(1+af+bf^2)$$

where

$$f = \frac{1}{2}\left[\left(\frac{V_0}{V}\right)^{2/3} - 1\right]$$

$$a = \frac{3}{2}(K_0' - 4)$$

$$b = \frac{3}{2}\left[K_0 K_0'' + K_0'(K_0' - 7) + \frac{143}{9}\right].$$

These fittings yield the zero-pressure bulk moduli K_0 and their first and second pressure derivatives K_0' and K_0'', which are also summarized on Table 1. The calculated volume compression data for CaO and SrO with both B1 and B2 phases at several pressures are compared with the observed ones in Fig. 3. Agreements between calculations and experiments are fairly good.

Table 1. Comparison of lattice constants(a_0), bulk modulus(K_0) and its first and second pressure derivatives (K_0', K_0'') at zero-pressure for B1 phase of CaO and SrO between calculations and experiments.

	a_0, Å	K_0, GPa	K_0'	K_0''
CaO				
Theory				
this study	4.8163	109	4.41	−0.045
Karki and Crain[1]	4.8382	117	4.41	−0.049
Mehl et al.[2]	4.820	102	4.33	
Bukowinski[3]	4.782	109	4.62	
Kalpana et al.[4]	4.711			
Experiments				
Wyckoff[10]	4.8105			
Mammone et al.[5]		115	4.10	
Richet et al.[6]		111	4.2	
Chang and Grahm[7]		111	4.80	
SrO				
Theory				
this study	5.1697	90	3.71	0.019
Kalpana et al.[4]	5.06			
Experiments				
Wyckoff[10]	5.1602			

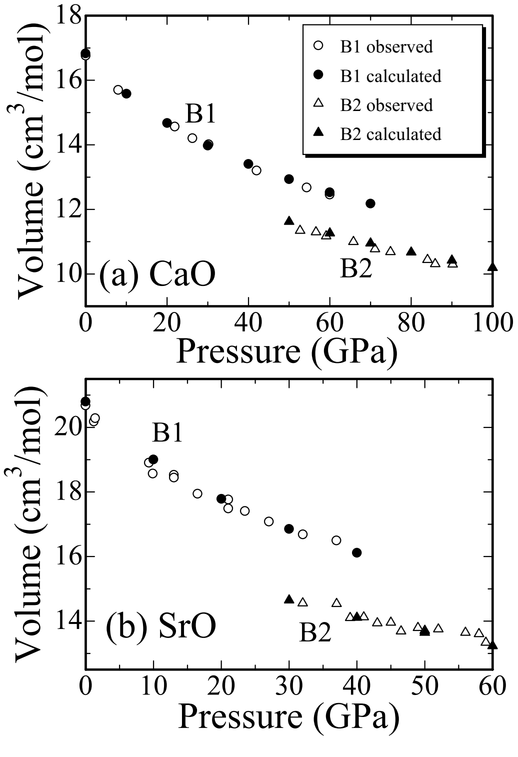

Fig. 3. Observed and calculated volume compression data for (a) CaO and (b) SrO. The experimental data are taken from Ref. 6 for CaO and Ref. 11 for SrO.

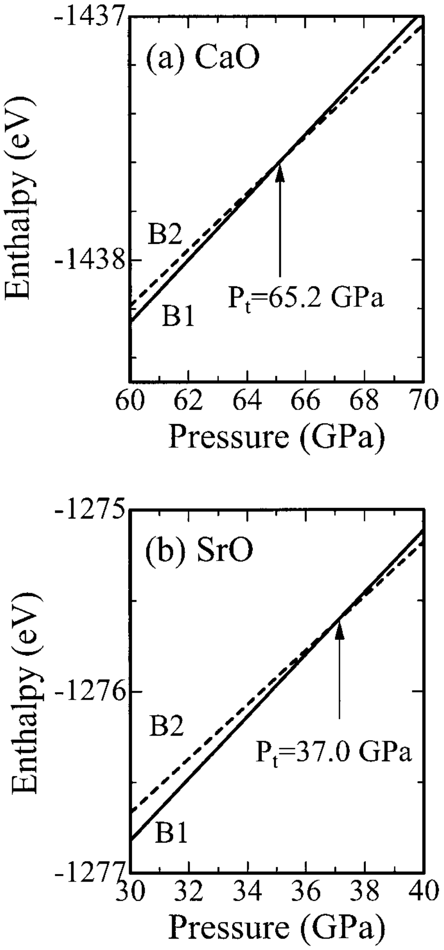

Fig. 4. Calculated enthalpies (zero-temperature free energies) for B1 (solid line) and B2 (dashed line) phases.

We have also calculated the enthalpy, *i.e.* free energy (E+PV) at zero-temperature, for both B1 and B2 phases, in order to investigate the critical pressure where the structural phase transitions from B1 to B2 phases occur. Resulting enthalpies depending on the external pressure are shown in Fig. 4, which indicate the structural phase transitions from B1 to B2 phases occur at 65.2 and 37.0 GPa for CaO and SrO, respectively. These calculated transition pressures fall within the experimental ranges 53–70 and 32–40 GPa for CaO and SrO, respectively.

Summary

The first-principle plane wave pseudopotential calculations were performed for the analysis of the structural properties of CaO and SrO under high-pressure conditions. The calculating results reproduced not only the observed pressure-induced volume compressions but also the experimental transition pressures from low-pressure B1 to high-pressure B2 phases.

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