The effects of the Earth D"-leyar high pressure on electrical, optical and structural properties of MgSiO3

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Abstract

High-pressure behavior of Perovskit and Post-Perovskit of MgSiO3 is studied based on density functional simulations within generalized gradient approximation (GGA) and first principal calculations. All calculations are performed by using the linear augmented plane waves plus perfect potential (FP+LAPW). We have chosen our pressure to be 86 GPa and 116 GPa to have both below and above the phase transition pressure. For Perovskit (Post-Perovskit) phase under 86 GPa, it can be seen that the electrical gaps are 11 eV (8 eV) and 9.1 eV for Post-Perovskit phase under 116 GPa. We have optimized energy in respect to volume and obtained the optimized equilibrium lattice constants of MgSiO3 in Perovskit (Post-Perovskit) structure. Our results for the volume module are in great consistency with experimental results and also with theoretical results obtained by others. The optical gaps were found to be 9.7 eV (8 eV) for Perovskit (Post-Perovskit) at 86 GPa and 9eV for Post-Perovskit under 116 GPa. These results show that the optical gap is an increasing function of pressure like that of the electrical gape.

1.Introduction

From seismic observations, it is well known that a boundary between the solid silicate mantle and the liquid iron core (CMB) exists at a depth of 2900 km. Recent seismic studies have shown that the region above the CMB, called the D" layer, contains strong seismic anomalies.CMB is the interface with the largest contrast in physical properties like density, elastic moduli, electrical conductivity within the Earth's interior. It is through the CMB that the liquid outer core has transferred massive quantities of thermal energy to the mantle over the course of geologic history. The D″ layer, just above the CMB, has therefore attracted a great deal of interest in seismology and mineral physics because this layer may play a key role in the dynamic and thermal evolution of the Earth's mantle. The recent experimental identification of the postperovskite phase transition in MgSiO3(Murakami et al.,2004) [e.g., [1-3]], which occurs under P–T conditions thought to exist at the bottom of the mantle (~125GPa,2700Km) may offer new insight into the properties of D″ region. Theoretical calculations (Iitaka et al., 2004; Tsuchiya et al., 2004a; Oganov and Ono, 2004; Stackhouse et al., 2005; Wentzcovitch et al., 2006) and interpretations of seismic data (Hernlund et al., 2005) suggest that the perovskite-to-post-perovskite phase transition and the properties of this new phase could reasonably explain most of the seismic characteristics of the D″ discontinuity. Recently,anomalies in the electrical conductivity at the base of the lower mantle have also been observed [e.g., [4-5]]

Pv Phase are compositions with general formula ABX3 Which A and B are metallic Cations and of course usually Oxygen is replaced with X. PPv phase have the Pv ideal structure too,

which is changed under pressure. In the case of MgSiO3, it is creat with rotation of SiO6 octahedral

it has been revealed that there are some interesting differences in perovskit and post perovskit phases for MgSiO3. These findings are used to explain the behavior of the Earth D-layer and simulation of surface conductivity in Earth. As a result of practical difficulties in exploring the inner layers of the Earth, it seems necessary to study the theory of these layers. In this paper, we obtain some important results about electrical properties of perovskit and post perovskit phases for MgSiO3. These properties could account for the conductivity of the inner layers of Earth on the basis of the phase transition in MgSiO3 crystal structure.

In this paper, firstly, the structural properties both Pnma phase and Cmcm phase for MgSiO3 are investigated. The phase transition pressure from Pnma to Cmcm phase is found and corresponding equilibrium structural parameters are given as well. Secondly, we discuss the electronic properties of Pnma structure and Cmcm structure of MgSiO3 under phase transition pressure. Finally, optical properties of both phases at phase transition pressure are discussed.

2. Computational Details

Calculations are performed using the all-electron linear augmented-plane wave plus local orbitals (LAPW+lo) 9 method as implemented in WIEN2k,10 with the PBE generalized gradient approximation (GGA) exchange correlation functional. A plane wave cut off is RKmax=7.0. In the LAPW+lo method, the wave functions are expanded in spherical harmonics inside nonoverlapping atomic spheres of radius RMT and in plane waves in the remaining space of the unit cell (the interstitial region) [e.g., [6-8]. The maximum value for partial waves inside the atomic sphere is taken to be lmax=10. Fully relativistic approximation is used for core electrons, and scalar relativistic approximations are used for valence electrons of 2s2p3s for Mg and 2p3s3pfor Si and 2s2p for O. Highly accurate Brillion zone integrations are performed using the modified special k-points technique of Monkhorst and Pack (MP). The self-consistency cycles have been performed with 1500 k points in the irreducible Brillouin zone (IBZ). We select force convergence to 1.0 mRy/a.u. during structure relaxation and charge convergence to 0.001 during self-consistency cycles.

In this section, we study the high pressure behavior of ppv (pv) with Cmcm (Pnma) with 10(20) atoms at 86 GPa and 116GPa. In this case, the muffin-tin radii (RMT) are 1.83 a.u, 1.5 a.u and 1.5 a.u for Mg, Si and O, respectively.

3.1. Structural properties

The pressure is an important factor in phase transition in crystal structures, so we have optimized energy in respect to volume and obtained The optimized equilibrium lattice constants of MgSiO3 in Perovskite (Post-Perovskite) structure.

The structures of Pnma and Cmcm phases of MgSiO3 are optimized under the pressure range from 0 to 140 GPa. The optimized equilibrium lattice constantsof MgSiO3 in Perovskite (Post-Perovskite) structure are a= 4.7123 (2.476)°A, b=6.5307 (8.1493)°A, c=4.3329 (6.1018)°A.

These energy points are then used to fit the parameters of the 3rd order Birch-Murnaghan equation of state (EOS), respectively. The values of the fitted parameters are reported in

Table 1 together with other theoretical results and experimental values at zero pressure. Our results are in good agreement with available literatures.

3.2. electronic properties

In figure 2, The total density of states (DOS) for Pnma phase and Cmcm phase of MgSiO3 is calculated. According to this figure, the energy gape in Pnma (Cmcm) is about 11 eV (8 eV) at 86 GPa. This shows that the conductivity at 86 GPa and 9.1 eV for Post-Perovskit phase under 116 GPa, increases when we have a phase transition from pv to ppv.

*When the Cmcm phase of MgSiO3 is compressed, on t*he one hand, the peaks of DOS in the valence bands tend to shift to the lower energy and the peaks of DOS in the conduction bands tend to shift to the higher energy. On the other hand, the peak values of DOS in the valence bands and conduction bands decrease. This can be understood from the fact that the overlap of the bonds increases. The biggest peak value of DOS for the Pnma structure of MgSiO3 is much higher than

that of the Cmcm structure of MgSiO3. By means of the partial DOS of MgSiO3, we know that the valence bands near the Fermi level, for both Pnma and Cmcm structure, mainly originate from the O-p states. There are strong O1-p states and O2-p states hybridization in both Pnma structure and Cmcm structure of MgSiO3. also we can see that compared with the Cmcm structure of MgSiO3 under the transition pressure 86GPa, the conduction bands of Pnma structure of MgSiO3 under the ambient pressure are extended to higher energy location. It means that the band gap of Pnma phase of MgSiO3 is higher than that of the Cmcm structure of MgSiO3. Moreover, it can be found that the energy gap becomes wider for both Pnma and Cmcm structures with the pressure increasing. This is because the external pressure makes conduction band shifting to higher energy region while valence band shifting to lower energy region.

3.3 optical properties

The optical properties are studied through the dielectric function. The dielectric tensor is defined as:

$$\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega) \tag{1}$$

Where $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$ are the real part and the imaginary part of the dielectric tensor, respectively. The $\varepsilon(\omega)$ is calculated within the random phase approximation based on the calculated band structure. From the imaginary part of the dielectric tensor component the corresponding real part is obtained by Kramer-Kronig relationship[e.g., [9].

$$\varepsilon_1(\omega) = 1 + \frac{2}{\pi} P \int_{\circ}^{\infty} \frac{\omega' \varepsilon_2(\omega)}{\omega'^2 - \omega^2} d\omega' \tag{2}$$

Where *P* stands for the principal value of the integral and ω is the angular frequency of light. $\varepsilon_2(\omega)$ can be given by calculating the momentum matrix elements between the occupied and unoccupied wave functions with selection rules. Given the imaginary part of dielectric function, all the other optical constants such as reflectivity and optical conductivity can be derived. Thus we only present the imaginary of dielectric tensor component (figure3). The dielectric tensor is symmetric with up to six independent components according to the

symmetry of the crystal. For orthorhombic crystal, there are three independent components, i.e, ε_2^{xx} , ε_2^{yy} and ε_2^{zz} .

For the Pnma structure at ambient pressure, it is observed that there are three distinct peaks in ε_2^{xx} at 8.83, 10.41, and 12.49, accompanied with a noticed peak at 17.29eV. Former three peaks primarily originate from the transition of O *p* to Si *s* bands, O *p* to Mg *s* bands, and O *p* to Si *p* bands, respectively. The forth peak at 17.29 eV comes from the transition of O *p* to Mg *p* bands. Comparing Fig.5 (b)with (a), we find not only the line shapes of $\varepsilon_2(\omega)$ is a little changed but also there is a small shift forward high-energy region (blue shift) when the Pnma structure is compressed to 86 GPa. For the Cmcm structure under 86 GPa, the spectrum is quit different from that of Pnma structure under ambient pressure. It can be seen that there is one clear peak at about 12.72 eV, which comes from the transition of O *p* to Si *s* bands as well as three little peaks around 10.48, 14.95 and 16.31 eV, which originate from the transition of O *p* to Mg *s* bands, O *p* to Si *p* bands, and O *p* to Mg *p* bands, respectively.

Conclusion

In this paper, we have examined the optical and electronical properties of MgSiO3. The dielectric function in this compound, even in an orthorhombic phase, has not changed considerably in the directions of x and y, so we conclude that the pressure and crystal symmetry changes do not strikingly affect the isotropy of this function. By considering the total state density and optical conductivity, we understand that the most probable transitions are those from O *2p* to Mg *2s* bands. This component has a large optical gap and its refraction indexes have approximately same values in the directions of x and y and by a good approximation, we can assume that the refraction index in the z direction is between 11-16 eV. Further more, the Plasmon oscillations occur in high energies in this component.

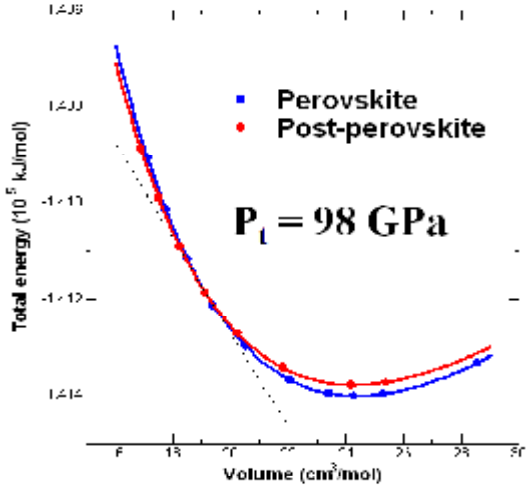

Fig 1. The total energy as a function of volume for Cmcm phase and Pnma phase of MgSiO3.

Table1. Third-order Birch-Murnaghan EOS of perovskite and post-perovskite structures, (* ref [4]).

	Pv	PPv
Bulk modulus [GPa], B_0	248, 230.05*	222, 223.7*
dB/dP	3.9, 4.14*	4.2, 4.15*
Ambient volume, V_0	24.704[cm^3/mol]	24.662[cm^3/mol]

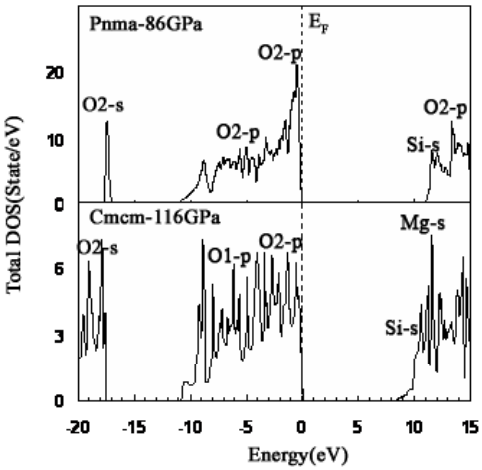

Fig 2. Total density of states per molecular volume of MgSiO3 for Pv and PPv phases.

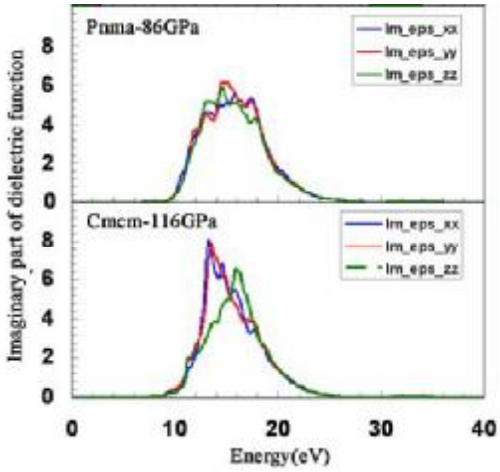

Fig 3. Imaginary part of dielectric function for Pv and PPv phases.

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