Journal of Materials, Processing and Design (2021) 5: 76-79
Clausius Scientific Press, Canada
DOI: 10.23977/jmpd.2021.050116
ISSN 2516-0923

Thermodynamic, Mechanical and Electronic Structure Properties of Wollastonite with Different Crystal Forms

Haiqi Li

Nanjing University of Technology, Nanjing, Jiangsu 211816, China

Keywords: First principle, Calcium silicate, Mechanical properties

Abstract: This paper uses the first principle calculation method based on density functional theory to analyze the mechanical and thermodynamic properties of β-CaSiO3 and α-CaSiO3 under different isostatic pressures. Based on the plane-wave pseudopotential method and the proton balance equation (PBE) in the generalized gradient approximation (GGA), the elastic constants, flexibility constants, bulk modulus, shear modulus, Young's modulus and Poisson's ratio of two calcium silicate crystals under different pressures are calculated by using the exchange correlation function to judge the mechanical properties of calcium silicate, such as ductility, brittleness, hardness and plasticity. The results show that the Young's modulus and rigidity are the largest under the pressure of 6Gpa and when the pressure is 10Gpa, the Poisson's ratio is the largest, indicating that its plasticity is the best.

1. Introduction

The purpose of this experiment is to study the mechanical, thermodynamic and acoustic properties of β-$CaSiO_3$ and α-$CaSiO_3$ under different isostatic pressures. Firstly, we should optimize the structure of the two wollastonite crystal forms to obtain the lowest energy and the most stable cell. Secondly, we can set the pressure: 0, 2, 4, 6, 8 and 10Gpa. Then, based on the pressure structure, the elastic constant is calculated. Through this calculation, we can get the elastic constant matrix, flexibility constant matrix, bulk modulus, shear modulus, etc. Using these physical quantities, we can calculate the relevant Young's modulus and Poisson's ratio.

2. Study on Mechanical Properties of Two Wollastonite Crystals

Stiffness refers to the ability of a material to resist elastic deformation when subjected to external forces. The stiffness of the material is the elastic modulus of the material. The larger the elastic modulus of the material, the smaller the elastic deformation under the corresponding pressure.

The elastic stiffness matrix is a 6×6 matrix. Due to the different symmetry of crystal systems, different crystal systems have different independent components. When there is a plane of symmetry, the independent elastic constant of monoclinic system becomes 13.

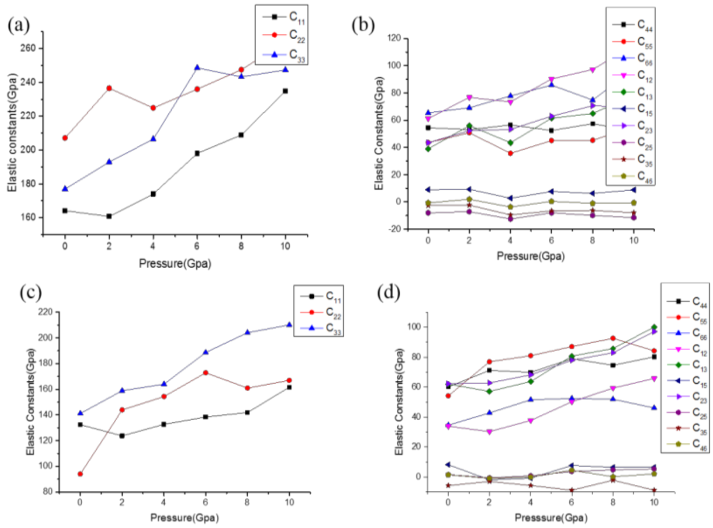

Fig. 1 Variation of elastic constant of calcium silicate with pressure. (a) Variation of elastic constant of α-$CaSiO_3$ calcium silicate with pressure (b) Variation of elastic constant of α-$CaSiO_3$ calcium silicate with pressure (c) Variation of elastic constant of β-$CaSiO_3$ calcium silicate with pressure (d) Variation of elastic constant of β-$CaSiO_3$ calcium silicate with pressure

Based on the importance of elastic properties to solids, the elastic properties of α-$CaSiO_3$ and β-$CaSiO_3$ are exploded. $CaSiO_3$ has thirteen independent elastic constants C_{ij}. Figure 1 (a) and (b) show the variation of elastic constant of α-$CaSiO_3$ with pressure. Figure 1 (c) and (d) show the variation of elastic constant of β-$CaSiO_3$ with pressure. C_{11} of β-$CaSiO_3$ is smaller than C_{22} and C_{33}, indicating that the incompressibility of β-$CaSiO_3$ along [100] direction is less than that along [010] and [001]. This means that the nature of the chemical bond is weaker in the [001] direction than in the [010] and [001] directions. The maximum value of C_{33} indicates the maximum incompressibility in the [001] direction. On the contrary, except for the maximum value of C_{33} when the pressure is 6Gpa, under other pressure conditions, the value of C_{22} of β-$CaSiO_3$ is the largest, that is, the incompressibility is the largest in the [010] direction. C_{11} of α-$CaSiO_3$ is smaller than C_{22} and C_{33}, indicating that the elastic constant of α-$CaSiO_3$ decreases with the increase of lattice parameters. According to the mutual inverse matrix of crystal elastic stiffness matrix and elastic flexibility coefficient matrix, the elastic flexibility matrix of crystal can be obtained through the following formula, and the elastic flexibility coefficient under GGA theory can be calculated [1]:

$$[C] = \frac{[S]^*}{|S|} \quad (3\text{-}1)$$

The calculated elastic constant C_{ij} can estimate the values of volume and shear modulus according to the Voigt-Reuss-Hill (VRH) approximation. Bulk modulus is the applied pressure of resistivity on volume change to a certain extent. On the contrary, the shear modulus represents the deformation of resistivity against shear stress. In Voigt estimation, formula 3-2 gives the bulk modulus (B_V) and shear modulus (G_V) of monoclinic CaSiO3. In the Reuss prediction, B_R and G_R are given by the elastic constant C_{ij}.

$$\begin{aligned} 9B_V &= (C_{11}+C_{22}+C_{33})+(C_{12}+C_{13}+C_{23}), \\ 15G_V &= (C_{11}+C_{22}+C_{33})-(C_{12}+C_{13}+C_{23})+3(C_{44}+C_{55}+C_{66}) \\ B_R &= [(S_{11}+S_{22}+S_{33})+2(S_{12}+S_{13}+S_{23})]^{-1} \\ G_R &= 15[4(S_{11}+S_{22}+S_{23})-4(S_{12}+S_{13}+S_{23})+3(S_{44}+S_{55}+S_{66})] \end{aligned} \quad (3\text{-}2)$$

Voigt approximation and Ruess approximation are only valid for equithermal materials, but not for anisotropic materials. For anisotropic crystals, Hill obtained the average results of the maximum and minimum isotropic elastic modulus in Voigt and Reuss approximation. The Voigt-Reuss-Hill approximate model with certain practicability is:

$$B_H = \frac{1}{2}(B_V + B_R), \quad G_H = \frac{1}{2}(G_V + G_R) \qquad (3\text{-}3)$$

For isotropic materials, Young's modulus E and Poisson's ratio V can be obtained by the following formula:

$$E = \frac{9BG}{3B+G}, \quad v = \frac{3B-2G}{2(3B+G)} \qquad (3\text{-}4)$$

Table 3 -5 Bulk Modulus, Shear Modulus, Young's Modulus and Poisson's Ratio of B-Casio$_3$ under Different Isostatic Pressures

press	B_V	B_R	B_H	G_V	G_R	G_H	E	V
0	76.04	70.145	73.1	43.75	38.95	41.35	104.37	0.262
2	80.813	77.61	79.21	56.62	52.32	54.47	132.94	0.22
4	87.83	85.23	86.53	59.24	55.35	57.3	140.82	0.229
6	101.99	97.72	99.854	63.095	57.24	60.17	150.32	0.249
8	107	101.68	104.34	62.39	56.73	59.56	150.12	0.26
10	118.3	112.72	115.51	60.48	54.45	57.47	147.88	0.29

Table 3 -6 Bulk Modulus, Shear Modulus, Young's Modulus and Poisson's Ratio of A-Casio$_3$ under Different Isostatic Pressures

press	B_V	B_R	B_H	G_V	G_R	G_H	E	V
0	92.82	91.47	92.14	59.62	56.79	58.2	144.23	0.24
2	106.66	104.13	105.4	61.6	58.6	60.1	151.5	0.26
4	105.04	102.51	103.77	62.99	56.41	59.7	150.28	0.259
6	123.5	122.75	123.13	67.84	61.94	64.89	165.58	0.28
8	129.45	128.43	128.94	66.57	62.16	64.36	165.34	0.286
10	141.24	140.15	140.69	73.15	67.02	70.1	180.35	0.2864

As you can see, for α-$CaSiO_3$ and β-$CaSiO_3$, B is always greater than G, which indicates that the shear modulus is the main factor affecting the mechanical stability of crystalline materials. Besides, under the same pressure, the bulk modulus of α-$CaSiO_3$ is greater than β-$CaSiO_3$. Because the bulk modulus represents the force that hinders volume deformation under pressure, so α-$CaSiO_3$ has greater resistance. Similarly, because the shear modulus represents the resistance of shear deformation under applied pressure, it can be obtained from the results calculated by MS, the shear modulus of α-$CaSiO_3$ is higher, so the resistance to shear deformation is greater. Young's modulus E and Poisson's ratio are very important in various applications. The greater the value of Young's modulus, the harder the material. The value of Young's modulus of the two crystal forms is the largest when the pressure is 6Gpa. Poisson's ratio provides information about the shear stability and chemical bonding properties of materials. As shown in the table, α-$CaSiO_3$ and β-$CaSiO_3$ reached the maximum when the pressure was 10GPa. This value indicates that the plasticity of the two crystalline wollastonites is the best when the pressure is 10GPa.

The v value of Poisson's ratio of covalent bond force is small (v= 0.1). Poisson's ratio of ionic materials v value(v= 0.25) is higher [2]. The range of Poisson's ratio fluctuates between - 1 ~ 0.5.

The greater the Poisson's ratio, the better the plasticity of the material. It is worth noting that, as shown in Figure 1, the Poisson's ratio of β-$CaSiO_3$ at pressure conditions of 0, 2, 8 and 10Gpa exceeds 0.25, which indicates that $CaSiO_3$ has obvious ionic properties. Except 0Gpa, the Poisson's ratio of α-$CaSiO_3$ is greater than 0.25. It can be seen the pressure conditions corresponding to the large plasticity of wollastonite. But whether it's α-$CaSiO_3$ or β-$CaSiO_3$, their Poisson's ratio is very small, indicating that they are relatively stable to shear deformation.

3. Conclusion

Based on the first principle calculation, the elastic constants of two kinds of wollastonite crystals are calculated and analyzed by using the exchange correlation functional: PBE under GGA. The experimental data show that, β-$CaSiO_3$ has the largest elastic constant C_{33}, that is, the incompressibility along the [001] direction is stronger. The elastic constant C_{22} of α-$CaSiO_3$ is the largest, that is, the incompressibility along the [010] direction is stronger. The Young's modulus and rigidity of the two crystalline wollastonites are the largest when the pressure is 6Gpa. When the pressure is 10Gpa, the Poisson's ratio is the largest, indicating that its plasticity is the best. Shear modulus of α-$CaSiO_3$ is higher than β-$CaSiO_3$, so the ability to resist shear strain is stronger. This shows that β-$CaSiO_3$ under 4Gpa, α-$CaSiO_3$ under 8Gpa have the strongest resistance to mechanical pressure.

References

[1] Chen Hongsun. Metal Elastic Anisotropy [M]. Beijing:Metallurgical Industry Press, 1996, 20- 80.

[2] Rahman M A , Rahaman M Z , Rahman M A . The structural, elastic, electronic and optical properties of MgCu under pressure: A first-principles study[J]. International Journal of Modern Physics B, 2016, 30(27):084101-.