Crystal structure and band gap studies of hydrogarnet calculated results by density functional theory

Lijun Pan[1, a], Wanchao Chao[2], Yan Kun[2]

[1] College of Physics and Electronic Engineering, Zhengzhou Normal University, Zhengzhou, 450044, China

[2] Zhengzhou Research Institute of CHALCO, Zhengzhou, 450041, China

[a]email:lijunpan515@163.com

Keywords: Garnet; Crystal structure; Electronic properties; Density functional theory

Abstract. Herein, we investigate the hydrogarnet sample by X-ray diffraction and calculated the related garnets included grossular, katoite and hydrogrossular by density functional theory to investigate the effect of silicon composition. The results of X-ray diffraction suggests that the chemical formula should be $C_{a2.93}Al_{1.97}Si_{0.64}O_{2.56}(OH)_{9.44}$. The optimized lattice parameters are in good agreement with the available data. We demonstrated the structural details of oxygen tetrahedron with or without silicon and found the stability and the band gap of garnet to be selectively modified by controlling the distribution and concentration of silicon atoms at different structural deformation levels. Moreover, the hydrogrossular configuration with the silicon atoms in separate manner is favored of the high stability and large band gap. It is firstly proposed that the band gap of hydrogarnet should be 3.17-3.65 eV by first-principles calculations. This was explained by the majority of the DOS contributions from the electrons in O and Ca atoms. It is believed that our research contributes to the mechanism of silicon distribution in garnet and helps the further disposal and treatment of silicate mud.

Introduction

Garnet as a common component in silicate mud belong to a cubic structure in space group Ia3d with the general formula $3XO \cdot Y_2O_3 \cdot mSiO_2 \cdot (6-2m)H_2O$, where the X, Y site is occupied by divalent cation and trivalent cation, respectively. The structure of garnet may be constructed by three types of cation-oxygen polyhedron: X for the eight-coordinated dodecahedron, Y for the six-coordinated octahedron and the Si for the tetrahedron. The m varies from 0 to 3 due to the substitution of silicon-oxygen tetrahedron at different levels [1] [2]. In the past several decades, large efforts have been devoted to investigate garnets. Generally, there are katoite $Ca_3Al_2(O_4H_4)_3$ [1] [3] [4], grossular $Ca_3Al_2Si_3O_{12}$ [5-7] [9], hydrogrossular [1] [2] [8]. In fact, the family of hydrogrossular may extend to $Ca_3Fe_2Si_3O_{12}$ [9] [12], $Mg_3Al_2Si_3O_{12}$ [9] [12] $Fe_3Al_2Si_3O_{12}$ [9], $Mn_3Al_2Si_3O_{12}$ [9] [13] and so on if the substitution of divalent and trivalent cation is considered.

The garnet has structural deformation to some extent either by the replacement of $(SiO_4)^{4-}$ by $(O_4H_4)^{4-}$ or by the substitution of divalent and trivalent cations. Start from the katoite, Lager *et al.* confirmed that the value of lattice parameter is about 12.5695 Å, which decreases as the Si atoms are introduced [2] [4], which conforms to the result [14]. On the whole, the OH tetrahedron may be regarded as a H-associated point defect [2], in which the short O-H bond from 0.65-0.74 Å [2] [4] [8] or 0.93-0.96 Å [1] [7] [15] implies the disorder degree of tetrahedron. In addition, this is the similar lattice disorder case for the substitution of divalent and trivalent cations in henritermierite [16] and pyrope and grossular [17]. The electronic properties of garnet series which are influenced by the structural distortion are worth of investigating carefully [14] [18-21]. Cano *et al.* showed that grossular has a direct band gap of 5.22 eV [14]. The first-principles studies may provide the reliable results in garnets, for examples, that of yttrium gallium garnet and yttrium iron garnet was determined to be 3.51 eV [20], 2.18 eV [21], respectively. In summary, the mentioned above

researches based on the density functional theory have reproduced the experimental results well. Little is known about the complex structure of hydrogrossular.

In the present work, the structure and electronic properties of garnet minerals including grossular, katoite and hydrogrossular are demonstrated by a combination of first-principles calculations and experiments for the purpose of investigating the effect of Si^{4+}. To our knowledge, no analogous calculation has been carried out. Specifically, the calculated band gap was compared with respect to the optical band gap.

Method

The samples were prepared and provided by Zhengzhou Research Institute of CHALCO. XRD measurements were carried out with Cu Kα radiation, employing Bruker D8 diffractometer at 40 mA and 40 KV, a scan step size of 0.05^o and 2θ range from 3° to 90°. We adopted herein a first-principles approach with the Vienna *ab initio* simulation Package (VASP) [22]. Briefly, the total energies have been calculated within generalized gradient approximation (GGA) [23] and periodic boundary conditions with the energy cutoff 400 eV, with the energy and the force convergence criterion on each atom fixed to be 0.0001 eV and 0.01 eV/Å, respectively. The number of atoms in grossular, katoite in per unit cell is 160, 232, respectively. While that of hydrogrossular is 217 or 214 which is related to the amount of Si. The calculations are checked using a 3×3×3 Monkhorst-pack k-point mesh [24] to ensure a sufficient number of k points in the irreducible Brillouin Zone (BZ).

Results and Discussion

The X-ray power patterns of the garnet sample are shown in Fig.1. The peaks indexing confirms the sample with the stoichiometry of $Ca_{2.93}Al_{1.97}Si_{0.64}O_{2.56}(OH)_{9.44}$ first proposed by Sacerdoti and Passaglia [8] (ICSD-No.49772), who measured the experimental cubic cell parameter α, the value of which is 12.38 Å and established all of the Ca, Al and O atomic positions with the full occupancy. However, there are about 5.1 Si atoms per unit cell. The Si atoms have uncertain positions with the occupancy of 0.214 and twenty four possible sites; we adopted two calculated hydrogrossular models with five Si atoms or six ones. Two extremes for the largest and smallest Si-Si distance between each other are computed. It may be divided into four types: five Si with the largest distance (5Si-L), five Si with the smallest distance (5Si-S), six Si with the largest distance (6Si-L) and six Si with the smallest distance (6Si-S).
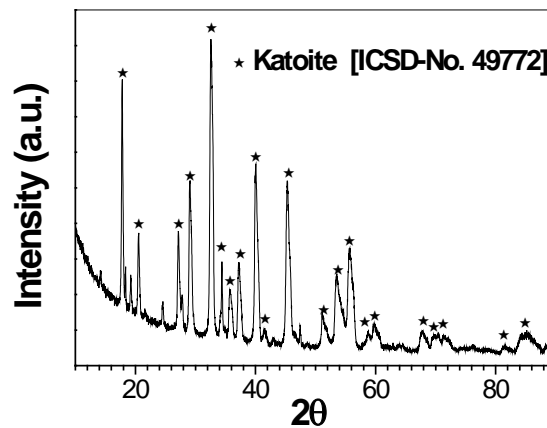

Fig. 1. X-ray power diffraction pattern of the sample, the Bragg reflex positions of $Ca_{2.93}Al_{1.97}Si_{0.64}O_{2.56}(OH)_{9.44}$ are marked.

The structure of grossular which contains 24 calcium, 16 aluminum, 24 silicon and 96 oxygen atoms in per unit cell is shown on the left side of Fig.2 and that of katoite is depicted on the right

side. The transformation from katoite to grossular or hydrogrossular may be regarded as the total or partial $(SiO_4)^{4-}$ substitution of $(O_4H_4)^{4-}$, the scheme of which is demonstrated in the middle of Fig.2.
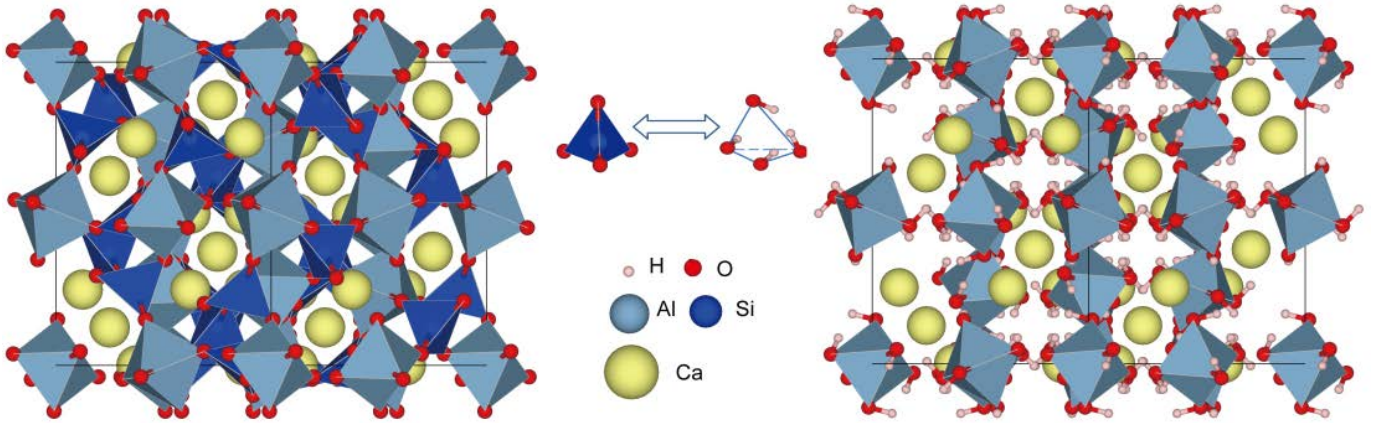

Fig.2. The side view of grossular (on the left), the scheme of $(SiO_4)^{4-}$ substitution of $(O_4H_4)^{4-}$ (on the upper middle) and the side view of katoite (on the right).

The lattice parameter of grossular is consistent with the previous studies [2] [4] [7] [14], and the value of katoite is 12.38 Å, slightly lower but close to the results [2] [4] [7]. Both of them have lower formation energies than partial Si substituted configurations due to the higher symmetry. The stable structure is obtained as the Si atoms separate as far as possible for five and six Si cases. The O-H bond length in our calculations has the range of 0.97-1.00 Å, which approve of the studies [1] [7] [15]. It is deduced that the O-H bond length is independent of the chemical compositions.

The optimized structure of $(O_4H_4)^{4-}$ tetrahedron in katoite is shown in Fig.3. There are two types of O-O distances: the values are 3.10 Å and 2.89 Å, both of which are in good agreement with the references [2]. The atomic hydrogen distribution in previous studies [1] [2] [4] [8] [15] may be summarized as "hand in hand" manner that the hydrogen atoms extend toward each other, while, the manner of ours is regarded as the "end to end" that the hydrogen atoms are almost direct along the tetrahedral edges with the $\angle$O-O-H angle of 5.95°. It is first revealed by first-principles approach.
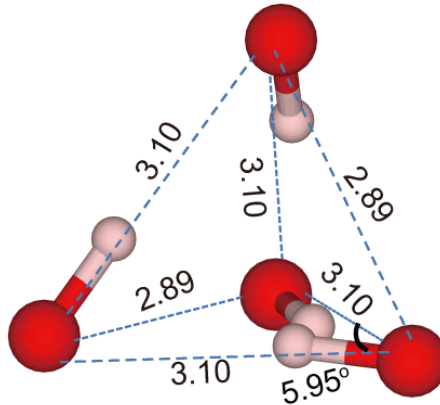

Fig.3. The side view of the optimized structure of $(O_4H_4)^{4-}$ tetrahedron in katoite.

In the following, the electronic properties of hydrogrossular were shown in Fig.4. All of them are direct gap type. The band gap of grossular is calculated to be 5.25 eV, which is identical to the calculation [14]. We found that the total density of states near the Fermi level is mainly attributed to the energy states of O and Ca atoms and the Si contribution which has little effect. It is inferred that the electrons bonded to Ca-O are relatively "active" while the electrons are restricted strongly by the Si-O bond. The gap of katoite is calculated to be 4.78 eV. It is realized that the band gap which is mainly affected by the electrons in O and Ca atoms in the valence band maximum (VBM) and conduction band minimum (CBM). It is seen that the O atoms and Ca atoms as the first and second

contributor provide the main responsibility near the Fermi level. The band gaps of 5Si-L, 5Si-S configurations may be calculated to be 3.65 eV and 2.94 eV, respectively. Similar, 6Si-L has a gap of 3.17 eV, larger than that of 6Si-S, the value of which is 2.92 eV. The difference which is ascribed to the decrease of conduction band minimum is aroused by Si distribution.
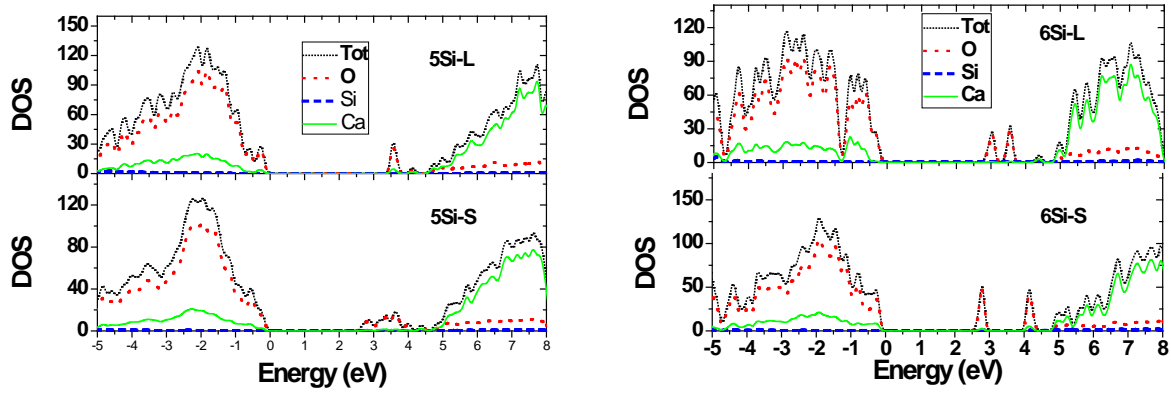

Fig. 4. The total density and partial of states of hydrogrossular for five Si atoms (Fig.6a), and six Si ones (Fig.6b).

The band gaps and CBM, VBM as functions of lattice parameters for different compounds are presented in Fig.5. The band gap and CBM of katoite are labeled by red circle. The gaps of Si substituted configuration decreases with the increasing of lattice parameter; this tendency is consistent with the curve of CBM. As shown, the variation of VBM is limited in a small scope. It may be deduced that the CBM plays a main role in the variation of band gap rather than VBM. On the whole, our calculations revealed that the Si substitution may be used to selectively modify the band gap by altering the CBM.
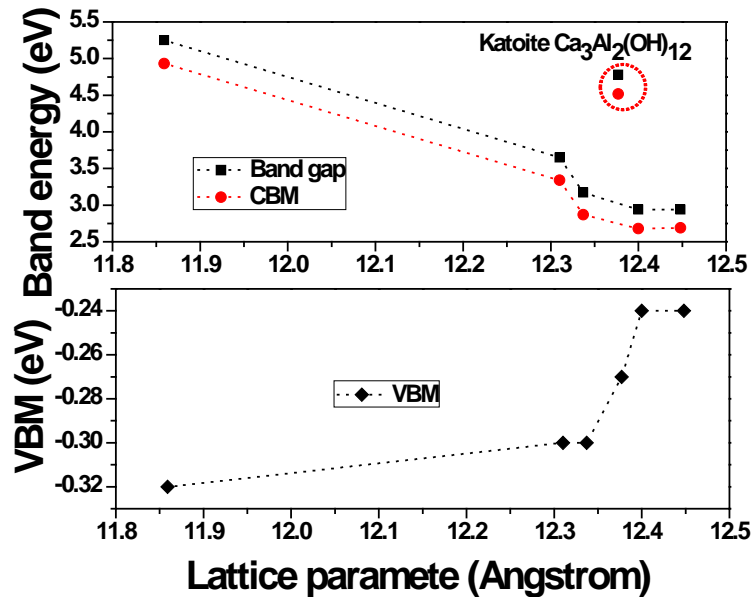

Figure 5. The band gaps and values of CBM, VBM as functions of lattice parameters for different compounds, the grossular and katoite are labeled in red circle.

Conclusions

In this paper, we have investigated the chemical compositions of hydrogrossular sample by X-ray diffraction with the stoichiometry of $Ca_{2.93}Al_{1.97}Si_{0.64}O_{2.56}(OH)_{9.44}$. By density functional theory, we found that $(SiO_4)^{4-}$ tetrahedron involved of Si-O and O-O$^{(1)}$ distances provide the mainly

contribution to the distortion. The stable structure is obtained with the Si atoms separate as far as possible. The stability of configuration linearly decreases as the lattice parameter increases except the katoite. We also proposed that the hydrogen atoms in $(O_4H_4)^{4-}$ tetrahedron trend to "end to end" manner along the tetrahedral edges with the $\angle$C-C-H angle of 5.95°. The gaps of Si substituted configuration decreases with the increasing of lattice parameter; this tendency is consistent with the curve of CBM, which indicates that the CBM plays a main role in the variation of band gap rather than VBM. The majority of the DOS contributions come from the electrons in O 2p states and Ca 3p states. The photon band gap should be in range of 4.27 eV to 4.75 eV combining the results of the absorption spectra and reflectance spectra. The 5Si-L and 6Si-L configurations having the largest gap of 3.65 eV are possible candidates considering the structural stability and energy band gap. Our calculations reveal that the Si substitution may be used to selectively modify the stability and the band gap by altering the CBM with the large gap and high stability for small lattice parameter. It is expected that our studies should be favorable to the further understanding of the hydrogrossular.

Acknowledgement

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