journal

Theoretical Calculation and Measurement of the Hardness of Diopside

Morten M. Smedskjaer,[‡] Martin Jensen,[‡] and Yuan-Zheng Yue[†]

Section of Chemistry, Aalborg University, DK-9000 Aalborg, Denmark

In the present paper, we test the suitability of a previously proposed model by Gao *et al.*[9] for describing the hardness of more complicated, multicomponent crystals by both calculating and measuring the hardness of a diopside crystal. We analyze the limitations of the model and suggest that factors like load and temperature should be considered in the model. The calculated value of hardness of the diopside crystal is compared with the Vickers hardness values measured at different loads. A good agreement is found between the calculated hardness and the value measured at 25°C at a load of 0.5 N. Crystal orientation and measurement temperature have an impact on the experimental value of hardness of the crystals.

I. Introduction

Hardness is an important mechanical property for the application of various materials. A general definition of hardness is the mechanical resistance of a solid object to permanent change.[1] Various experimental methods for determining hardness are available, e.g., Vickers, Brinell, Rockwell, and Knoop.[1,2] The principle of these methods is to measure indentation hardness, i.e., a harder material is indented to a sample at a selected load with the size of the indented hole being related to the hardness of the material.[1,3]

From an industrial point of view, it is desirable to predict the hardness of a new material before manufacturing. If prediction is feasible, it could furthermore contribute to the development of new superhard materials. A superhard material can be defined as a material with microhardness exceeding 40 GPa.[4] The search for new superhard materials has attracted interest[5,6] as superhard materials could be used as wear-resistant coating or as cutting and polishing tools. To find or synthesize superhard materials, it is important to investigate the relationship between hardness and other mechanical properties, like shear and bulk moduli.[5,7] From the existing results, it is concluded that hardness cannot be quantitatively described by shear or bulk moduli. An example illustrating this is HfN possessing a bulk modulus of 422 GPa, which is approaching that of diamond (443 GPa), but its hardness is only 17 GPa in comparison with diamond's hardness of 96 GPa.[5]

As no relationship between hardness and other macroscopic properties has been established, it is necessary to develop a method to directly calculate the hardness of a material. Some promising efforts have been made in the search for such a method. It has been established that bulk modulus can be related to the amount of bonds per volume.[8] More importantly, a method for calculating hardness is developed by considering the strength of each individual bond and the amount of bonds per volume, i.e., on the first principle calculations of chemistry. Gao *et al.*[9] have

succeeded in calculating the hardness of covalent crystals, and concluded that hardness is an intrinsic property. The method is applicable for polar covalent crystals,[9] oxide crystals with some ionic character,[10] and nitride spinel.[11] A crucial step of the method is to split the complex crystal into pseudobinary crystals, each containing only one chemical bond, using the approach proposed by Zhang.[12]

Diopside ($CaMgSi_2O_6$) is in this work chosen as the example to study the validity of the approach of Gao *et al.*[9] on complex minerals (containing more than three elements). If the method proposed by Gao *et al.*[9] is proven to apply to diopside, by comparing the calculated data with the measured data, it would become possible for the method to be used for the hardness calculation of other complex minerals, i.e., the universality of the method would be strengthened. Moreover, diopside is chosen for the following two reasons. First, diopside is the dominant crystalline phase occurring in the heat-treated basaltic glasses and in many other heat-treated aluminosilicate systems.[13–17] The diopside phase has a strong impact on the thermal and mechanical properties of those systems. Second, the crystallographic and bonding data are available in the literature. Another aim of this work is to discuss the limitations of the method and give suggestions for improvement.

II. Theory

In a multicomponent crystal (a crystal constituted by more than two different atoms), bonds are found between different atoms and the crystal thus consists of various chemical bonds. In Gao *et al.*,[9] the hardness of each individual chemical bond is calculated. Hence, before the calculation, the multicomponent crystal must be split into pseudobinary crystals containing only one chemical bond. The work described in Gao[10] is based on the theoretical approach devolved by Zhang,[12] which is expounded in the following section. Afterwards, the approach of Gao *et al.*[9] and Gao[10] is presented before the calculation of the hardness of diopside is carried out.

(1) Decomposition into Pseudobinary Crystals

To perform the decomposition of a complex crystal, it is necessary to have information on the crystal structure plus crystallographic data revealing the different chemical bonds. As solely one chemical bond confines the pseudobinary crystal, the latter can be denoted as A_aB_b. Starting by considering atom A, it must be known which atom(s) A is bonded to in the multicomponent crystal. In addition, the following information must be available: (i) the number of B atoms that atom A is bonded to ($N(B-A)$); (ii) the nearest coordination number of A, i.e., the number of B atoms *and* other atoms that atom A is bonded to (N_{CA}); and (iii) the number of A atoms in the pseudobinary crystal A_aB_b (a). The equivalent procedure must be applied when considering atom B.[12]

When decomposing the multicomponent crystal, a number of pseudobinary crystals arise. The pseudobinary crystals can be added to give the composition of the entire multicomponent crystal. The pseudobinary crystals in this sum must be weighted according to how many times they are present in the multicomponent crystal. The weight of atom A in A_aB_b can be calculated

by the following formula[12]:

$$\text{Weight of atom } A = \frac{N(B-A) \cdot a}{N_{CA}} \qquad (1)$$

The weight of atom B in A_aB_b is calculated equivalently.

(2) Hardness of Each Pseudobinary Crystal

When indenting a material, rearrangement of atoms will occur in the indented area, i.e., electron–pair bonds must be broken and then reformed. When the bonds are broken, two unpaired electrons arising from the former bond exist. From an energetical point of view, this is equal to two electrons being excited from the valence band to the conduction band. Therefore, the activation energy required for plastic deformation is twice the band gap, E_g.[18] This mechanism of hardness is valid for covalent and polar covalent substances where bonding is localized.[9] In this case, hardness is considered to be intrinsic by Gao *et al.*[9] and can be evaluated as the sum of the resistance of each bond per unit area.[19] The resistance force of each bond can be described by the band gap and the number of bonds per unit area determined by the density of valence electrons.

The hardness of a binary crystal composed of a μ bond is calculated as follows[9]:

$$H_v^\mu(\text{GPa}) = A(N_e^\mu/2)^{2/3} E_g^\mu \qquad (2)$$

where A is a constant and N_e^μ is the number of valence electrons per cubic Ångstrøm. Thus, hardness is determined by the bond density and the strength of the bond. E_g^μ can be substituted by E_h^μ (the pure covalent contribution to E_g^μ) and f_i^μ (ionicity)[9]:

$$H_v^\mu(\text{GPa}) = 0.630A(N_e^\mu)^{2/3} e^{-\alpha f_i^\mu} E_h^\mu \qquad (3)$$

where α is a constant. A and α are determined by an experimental correlation between hardness and ionicity. Gao *et al.*[9] have found that $A = 14$ and $\alpha = 1.191$ when 10 crystals are used in the analysis. Therefore, Eq. (3) reduces to

$$H_v^\mu(\text{GPa}) = 8.82(N_e^\mu)^{2/3} e^{-1.191 f_i^\mu} E_h^\mu \qquad (4)$$

It should be noted that the hardness will only have the unit of GPa if N_e^μ, E_h^μ, and f_i^μ are inserted as Å^{-3}, eV, and dimensionless, respectively. The various terms required for calculating the hardness of a pseudobinary crystal are described in Sections II(2)(A)–(C).

(A) Calculation of N_e^μ: The calculation of N_e^μ requires knowledge of several parameters that will be calculated preliminarily. First, the number of effective valence electrons $((Z^\mu)^*)$ must be calculated. When considering atoms without d-electrons, $(Z^\mu)^*$ can be replaced by the number of valence electrons (Z^μ).[20] With the knowledge of $(Z^\mu)^*$ and N_C (nearest coordination number) for both atom A and atom B, the number of effective valence electrons per μ bond $((n_e^\mu)^*)$ can be determined by Eq. (5).[10]

$$(n_e^\mu)^* = (Z_A^\mu)^*/N_{CA} + (Z_B^\mu)^*/N_{CB} \qquad (5)$$

Furthermore, the number of bonds per unit volume (N_b) for each bond type must be known. This value can, e.g., be obtained by knowing the unit cell volume of the given crystal and the number of each bond type in the unit cell. N_b is needed in the calculation of the bond volume (v_b^μ):

$$v_b^\mu = \frac{(d^\mu)^3}{\sum (d^v)^3 N_b^v} \qquad (6)$$

where d is the bond length and v denotes an arbitrary bond in the multicomponent crystal. Now it is possible to calculate N_e^μ[10]:

$$N_e^\mu = (n_e^\mu)^*/v_b^\mu \qquad (7)$$

(B) Calculation of E_h^μ: The calculation of E_h^μ requires only the value of d^μ[21]:

$$E_h^\mu = \frac{39.74}{(d^\mu)^{2.48}} \qquad (8)$$

where the unit of E_h^μ is eV if the unit of d^μ is Å.

(C) Calculation of f_i^μ: Now, the decomposition of the multicomponent crystal is to be utilized. n is the ratio of atom B to atom A in the pseudobinary crystal. It is necessary to know n in order to calculate the average coordination number (N_c^μ)[10]:

$$N_c^\mu = N_{CA}/(1+n) + nN_{CB}/(1+n) \qquad (9)$$

When N_c^μ is calculated, the structural correction factor b^μ can be estimated[22]:

$$b^\mu = \beta(N_c^\mu)^2 \qquad (10)$$

where β is a constant that can be estimated to $0.089 \pm 10\%$.[22] Furthermore, the Thomas–Fermi screening wave number (k_s^μ) of the valence electron in the μ bond must be calculated[21]:

$$k_s^\mu = \left(\frac{4 \sqrt[3]{3\pi^2 N_e^\mu}}{a_B \pi} \right)^{1/2} \qquad (11)$$

where a_B is the constant Bohr radius (0.529 Å). b^μ and k_s^μ are utilized when calculating C^μ (the ionic contribution to E_g^μ)[10]:

$$C^\mu = 14.4 b^\mu \left| (Z_A^\mu)^* + \Delta Z_A^\mu - n(Z_B^\mu)^* \right| e^{-k_s^\mu r_0^\mu}/r_0^\mu \qquad (12)$$

where ΔZ_A^μ is a correction factor that accounts for d-electron effects and r_0^μ is half of the bond length. In Gao,[10] the absolute value is not utilized, but this could lead to C^μ having a nonsense negative value. Z_B^μ denotes the number of valence electrons in the B anion and will be larger than Z_A^μ as this denotes the number of valence electrons in the A cation. In the opinion of the authors, the value $Z_A^\mu - nZ_B^\mu$ will never be positive. However, the sign of C^μ is unimportant. The reason for this is that C^μ is only used in the calculation of the ionicity, which can be expressed as follows[21]:

$$f_i^\mu = \frac{(C^\mu)^2}{(E_h^\mu)^2 + (C^\mu)^2} \qquad (13)$$

(3) Hardness of a Multicomponent Crystal

The hardness (H_v) of a multicomponent crystal is a geometric average of all bonds in the pseudobinary crystals that accounts for the fact that soft bonds break before hard bonds. Therefore, it should be calculated as follows[9]:

$$H_v = \left(\prod^\mu (H_v^\mu)^{n^\mu} \right)^{1/\sum n^\mu} \qquad (14)$$

where n^μ is the number of μ bonds comprising the multicomponent crystal.

(4) Calculating the Hardness of Diopside

Diopside is a monoclinic $C2/c$ pyroxene with the cell dimensions 9.743, 8.923, and 5.251 Å for a, b, and c, respectively. β is 105.93°.[23] The schematic microstructure is shown in Fig. 1.
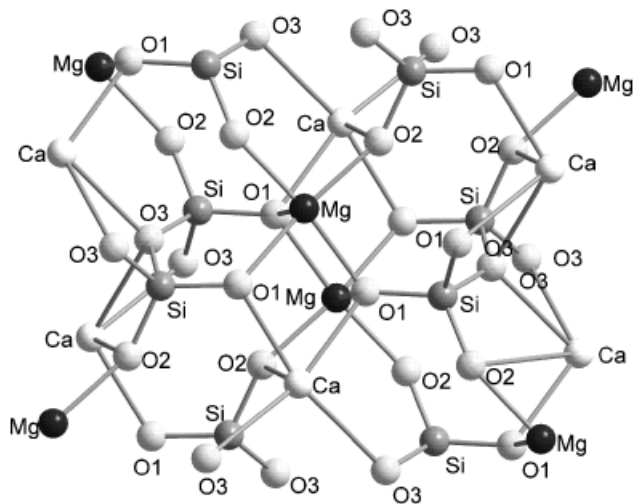
Fig. 1. Schematic representation of the microstructure of the diopside crystal.

From Cameron *et al.*,[24] Raudsepp *et al.*,[25] Gordon *et al.*,[26] and Levien and Prewitt,[27] it is established that diopside has 11 different types of bonds that all occur twice. Furthermore, the 6 oxygens are different because they have different coordination numbers and/or bind to different cations. Therefore, the oxygens are all labeled, e.g., O(1). In contrast to this, Ca, Mg, and Si have constant coordination numbers and only bind to oxygen. Table I assembles the information about the different bonds in diopside and the length of the bonds.

(A) Decomposition of Diopside into Pseudobinary Crystal Subformulas: By applying Eq. (1) to all the bond types presented in Table I, the following decomposition of diopside is obtained:

$$CaMgSi_2O_6 = CaMgSi_2O(1)O(1')O(2)O(2')O(3)O(3')$$

$$= \frac{2 \cdot 1}{8} Ca \frac{1 \cdot 1}{3} O(1) + \frac{2 \cdot 1}{8} Ca \frac{2 \cdot 1}{4} O(2)$$

$$+ \frac{2 \cdot 1}{8} Ca \frac{2 \cdot 1}{4} O(3) + \frac{2 \cdot 1}{8} Ca \frac{2 \cdot 1}{4} O(3')$$

$$+ \frac{2 \cdot 1}{6} Mg \frac{1 \cdot 1}{3} O(1) + \frac{2 \cdot 1}{6} Mg \frac{1 \cdot 1}{1} O(1')$$

$$+ \frac{2 \cdot 1}{6} Mg \frac{1 \cdot 1}{1} O(2') + \frac{1 \cdot 2}{4} Si \frac{1 \cdot 1}{3} O(1)$$

$$+ \frac{1 \cdot 2}{4} Si \frac{2 \cdot 1}{4} O(2) + \frac{1 \cdot 2}{4} Si \frac{2 \cdot 1}{4} O(3)$$

$$+ \frac{1 \cdot 2}{4} Si \frac{2 \cdot 1}{4} O(3')$$

$$= \frac{1}{4} CaO(1)_{4/3} + \frac{1}{4} CaO(2)_2 + \frac{1}{4} CaO(3)_2$$

$$+ \frac{1}{4} CaO(3')_2 + \frac{1}{3} MgO(1) + \frac{1}{3} MgO(1')_3$$

$$+ \frac{1}{3} MgO(2')_3 + \frac{1}{2} SiO(1)_{2/3} + \frac{1}{2} SiO(2)$$

$$+ \frac{1}{2} SiO(3) + \frac{1}{2} SiO(3') \quad (15)$$

As diopside has been split into pseudobinary crystals, the hardness of each bond can be calculated. The calculation of the hardness of the CaO(1) bond will exemplify the methodology. Afterwards, the bond parameters of the other bonds, which are used for calculating the overall hardness, will be presented in Table II.

(B) Bond Parameters for Diopside: Ca and O have no d-electrons and therefore $(Z_{Ca}^{CaO(1)})^* = 2$ and $(Z_{O(1)}^{CaO(1)})^* = 6$. As Ca is bonded to 8 oxygens, $N_{CCa} = 8$, and as O(1) is bonded to one Ca, Mg, and Si, $N_{CO(1)} = 3$. According to Eq. (5), $(n_e^{\mu})^*$ is then 2.25. As all the bonds in diopside occur with the same

Table I. Bond Types and Lengths in Diopside

Center atom	Bond type	N	Bond length (Å)
Ca	CaO(1)	2	2.363
	CaO(2)	2	2.347
	CaO(3)	2	2.561
	CaO(3')	2	2.721
Mg	MgO(1)	2	2.119
	MgO(1')	2	2.061
	MgO(2')	2	2.051
Si	SiO(1)	1	1.602
	SiO(2)	1	1.589
	SiO(3)	1	1.669
	SiO(3')	1	1.687
O(1)	O(1)Ca	1	2.363
	O(1)Mg	1	2.119
	O(1)Si	1	1.602
O(1')	O(1')Mg	1	2.061
O(2)	O(2)Ca	2	2.347
	O(2)Si	2	1.589
O(2')	O(2')Mg	1	2.051
O(3)	O(3)Ca	2	2.561
	O(3)Si	2	1.669
O(3')	O(3')Ca	2	2.721
	O(3')Si	2	1.687

The bond lengths are given at room temperature.[25] N is the number of a specific ligand that is bonded to the central atom.

frequency per unit volume, N_b is constant for all the bonds in diopside. By counting the number of bonds in the unit cell of diopside (cf. Table I), N_b can be calculated by dividing this number (2) with the unit cell volume (438.97 Å³).[23] That is, $N_b = 4.556 \cdot 10^{-3}$ Å^{-3}. For CaO(1), $v_b^{CaO(1)}$ can then be calculated using the bond length given in Table I and by insertion into Eq. (6). This gives $v_b^{CaO(1)} = 26.93$ Å³. Therefore, $N_e^{CaO(1)}$ is:

$$N_e^{CaO(1)} = 2.25/26.93 \text{ Å}^3 = 0.0836 \text{ Å}^{-3} \quad (16)$$

With a bond length of 2.363 Å for CaO(1), $E_h^{CaO(1)}$ is calculated according to Eq. (8):

$$E_h^{CaO(1)} = \frac{39.74 \text{ eV} \cdot \text{Å}^{2.48}}{(2.363 \text{ Å})^{2.48}} = 4.71 \text{ eV} \quad (17)$$

The next step is the calculation of $f_i^{CaO(1)}$. According to Eq. (15), the ratio between O(1) and Ca is 4/3 (i.e., $n = 4/3$). All the information needed to calculate N_e^{μ} by Eq. (9) is now available: $N_c^{CaO(1)} = 5.14$. This value can directly be used to calculate $b^{CaO(1)}$ to be 2.35 using Eq. (10). $k_s^{CaO(1)}$ is then calculated to be 1.80 Å^{-1} using Eq. (11). This and other now-known values are inserted into Eq. (12) and $C^{CaO(1)}$ is determined to 20.4 eV. By

Table II. Bond Parameters for the Bonds Confining Diopside

Bond type (μ)	N_e^{μ} (Å^{-3})	E_h^{μ} (eV)	f_i^{μ} (—)	H_v^{μ} (GPa)
CaO(1)	0.0836	4.71	0.949	2.56
CaO(2)	0.0663	4.79	0.977	2.16
CaO(3)	0.0510	3.86	0.978	1.46
CaO(3')	0.0426	3.32	0.979	1.11
MgO(1)	0.120	6.17	0.813	5.04
MgO(1')	0.354	6.61	0.672	13.1
MgO(2')	0.360	6.69	0.671	13.4
SiO(1)	0.358	12.3	0	54.9
SiO(2)	0.305	12.6	0.323	34.3
SiO(3)	0.263	11.2	0.326	27.1
SiO(3')	0.255	10.9	0.339	25.7

squaring $C^{\text{CaO(1)}}$ and $E_h^{\text{CaO(1)}}$, $f_i^{\text{CaO(1)}}$ can be determined to be:

$$f_i^{\text{CaO(1)}} = \frac{(20.4 \text{ eV})^2}{(20.4 \text{ eV})^2 + (4.71 \text{ eV})^2} = 0.949 \qquad (18)$$

The hardness of the CaO(1) bond is calculated:

$$H_v^{\text{CaO(1)}} = 8.82 \frac{\text{GPa} \cdot \text{Å}^2}{\text{eV}} (0.0863 \text{ Å}^{-3})^{2/3} 4.71 \text{ eV} \cdot e^{-1.1910 \times 949}$$
$$= 2.56 \text{ GPa}$$

$$(19)$$

The bond parameters for all 11 bonds in diopside are listed in Table II. It can be observed that the SiO bonds are the hardest because of their covalent nature.

The hardness of the multicomponent crystal diopside can be calculated. This is done by inserting the hardness of the pseudo-binary crystals given in Table II into Eq. (14). All hardness values are given in GPa and $n^\mu = 2$ as all bonds occur twice in CaMgSi$_2$O$_6$.

$$H_v = (2.56^2 2.16^2 1.46^2 1.11^2 5.04^2 13.1^2 13.4^2 54.9^2 34.3^2 27.1^2 25.7^2)^{1/22}$$
$$= 8.15 \text{ GPa}$$

$$(20)$$

The calculated value is the geometric average. The weighted average hardness of the bonds in Table II is 16.4 GPa. This shows that the soft bonds are of greater importance to the overall hardness than the strong bonds.

III. Experimental Procedure

Two samples from a diopside mineral (from the state of Minas Gerais in Brazil) were cut into samples with dimensions of $3.0 \times 1.5 \times 1.0$ cm^3 using a Secotom-10 diamond-coated blade (Struers A/S, Ballerup, Denmark). One of the samples was heat treated in a furnace (K10, Scandiaovnen A/S, Allerød, Denmark) at 1100°C for 30 min under atmospheric conditions and subsequently exposed to room temperature. Both samples were ground and polished with LaboPol-5 (Struers). The final step of the polishing was carried out using silicon carbide paper with a grit size of P4000 (Struers).

Vickers microhardness was measured using a Duramin indenter (Struers). All indentations had a duration of 5 seconds. The hardness of the heat-treated sample was measured 40 times at 0.49 N. The other sample was measured at 0.25, 0.49, 0.98, and 1.96 N, with 40 measurements at each load. The choice of the loads and the number of repetitions have been considered in accordance with the issues described by Quinn and Quinn.[28]

IV. Results and Discussion

Figure 2 shows the dependence of the hardness of the untreated diopside on load applied during indentation. The hardness of the heat-treated diopside was measured at 0.49N. The development of hardness against load has been fitted using Kick's law.[29] Kick's law is not theoretically applicable to Vickers hardness as it was developed for the Brinell test, but can anyway provide a good empirical fit to Vickers hardness measurements.[28] Kick's law is stated as follows:

$$P = C \cdot d^n \qquad (21)$$

where P is the load, C is a constant, d is the measured impression size, and n is the logarithmic exponent. By definition, hardness is[28]:

$$H = \alpha \frac{P}{d^2} = \alpha \frac{Cd^n}{d^2} \qquad (22)$$

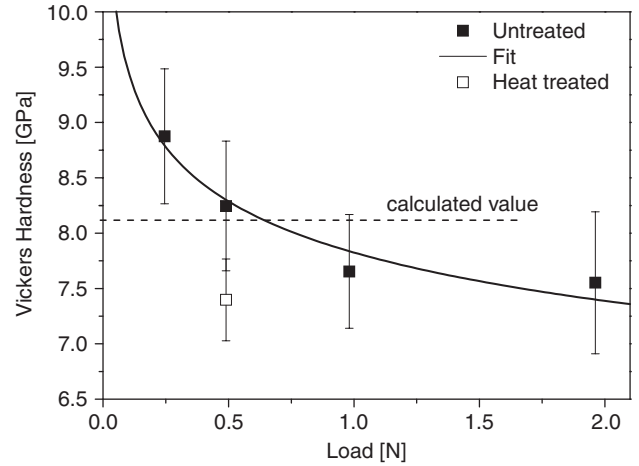where α is dependent on the indenter geometry.

Fig. 2. Vickers hardness of diopside measured at various loads. The diopside sample that has been heat treated at 1100°C for 30 min is measured at 0.49 N. Each point corresponds to a mean of 40 indentations. The results obtained from the untreated sample are fitted to Kick's law.

It is obvious from Fig. 2 that Kick's law (with $n = 1.85$) describes the load dependency well. This load dependency is well demonstrated in the literature for other materials.[30–33] Therefore, the hardness of diopside and other materials cannot be described by a single value. This load dependency is not accounted for in the hardness calculation. In addition to this, the hardness test method and the duration of indentation also affect the hardness, but these issues will not be discussed here. The results show that hardness is constituted by both intrinsic and extrinsic effects. Extrinsic effects are partially accounted for in the experimental correlation leading to the semi-empirical Eq. (4) as the experiments are always affected by the limitation of extrinsic factors.

In Section II(4), the hardness of diopside was calculated to be 8.15 GPa. Considering the standard deviations presented in Fig. 2, this calculated value is in agreement with the hardness measured at three of the four loads. However, the load dependency of hardness is neglected in e.g., Gao *et al.*[9] when measured and calculated values are compared. Thus, it is problematic to confirm the calculated values with the measured ones and some loads may even be erroneous. The theoretical calculations are based on bond breaking in the indented area. Therefore, load resulting in crack formation cannot be used if the theoretical and measured values are to be compared. Lawn and Marshall[34] and Lawn and Evans[35] claim that cracking occurs above a certain load (called the threshold load). Below this load, the indentation leads to deformation behavior, whereas above the threshold it shows fracture behavior. Similar behavior has been observed by Dériano *et al.*[36] However, no definite threshold load can be stated as different materials possess different brittleness.

The visual result of the heat treatment of diopside is a change in color from green to brownish, which is due to the oxidation of iron. The heat-treated sample is at the limit of having a significantly lower hardness than the untreated sample, i.e., intrinsic and/or extrinsic effects seem to have been altered. At 1100°C, the bond lengths in diopside have increased which results in lower hardness. However, because of the cooling rate used, the increased bond lengths cannot be frozen in upon cooling. The intrinsic contribution to the altered hardness must then be due to the formation of new bond types and/or changed bond density. Extrinsic effects such as vacancies, dislocations, and strains can also alter the hardness. The formation of new bond types is possible due to the oxidation of iron. Ferrous iron is regarded as a network modifier, whereas ferric iron is a network former. In the case where no new bond types are formed upon heating, the hardness of the heated material can be calculated. This is done by taking the increased bond lengths and unit cell volume into

account in the method described in Section II(*2*). Using the work of Cameron *et al.*,[24] the bond lengths and unit cell volume against temperature have been linearly extrapolated to 1100°C. The hardness of diopside in an inert atmosphere at 1100°C can be calculated to be 7.71 GPa. Dorner and Stöckhert[37] have measured the Vickers hardness of diopside to be 4.9–6.1 GPa at temperatures between 300° and 750°C with a load of 0.5 N. Their values are 2–3 GPa lower than the hardness reported here. The discrepancy can, in addition to the elevated temperature, be ascribed to a loading period of 10 s, which is longer than that used in the present work.

In crystals, the different planes can contain different bonds and therefore the hardness of a crystal may be dependent on the orientation of the crystal concerning the Miller indices. This has, for instance, been experimentally confirmed for SiC and MgO.[38,39] The crystal orientation effect is not accounted for in the calculation method. Starting from the measured hardness of diopside, this value does not seem to be influenced by the orientation as the standard deviation is rather low.[28] This can arise from two factors. Firstly, the indentation can be an average hardness of many microcrystals. Secondly, the hardness of diopside is only weakly dependent on crystal orientation, which has been confirmed at elevated temperatures.[37] In cases where the conditions are not fulfilled, the crystallographic data used in the hardness calculation must arise from the same orientation in which the indentation is performed.

It is important to recall that the calculated hardness is associated with uncertainty as the parameter β has an uncertainty of 10%. This results in a change in the calculated hardness of 3% for the case of diopside. Furthermore, the empirical fit leading to the parameters α and A of Eq. (4) is associated with uncertainty. In particular, the utilization of SiC as one of 10 crystals in the fit is debatable as the hardness of SiC varies between 20.9 and 29.0 GPa depending on the crystal orientation.[38] Reestablishing the empirical fit from Gao *et al.*[9] by removing SiC and using the data given in Table I in Gao *et al.*[9], $A = 13$ and $\alpha = 1.076$. Using these values, the hardness of diopside can be recalculated to be 8.14 GPa, i.e., a change of only 0.05%. Even though the use of SiC is debatable, it has a negligible effect on the calculated hardness.

V.　Conclusion

The hardness of diopside has been calculated to be 8.15 GPa, which is in accordance with the measured values. This indicates that the calculation method is applicable to complicated crystals such as pyroxenes even though they possess some ionic character. Therefore, the model proposed by Gao *et al.*[9] can be a good approximation to calculate the hardness of multicomponent crystals. In order for the model to be more precise, we suggest that the load, geometry, and temperature dependency of hardness should be specified in the model. The temperature dependence of the unit cell volume is discussed. The calculated and measured indentation hardness must be compared for the same load and crystal orientation.

References

[1]J. I. Gersten and F. W. Smith, *The Physics and Chemistry of Materials*. John Wiley & Sons, Inc., New York, 2001.

[2]S. Frank, "Portable Hardness Testing—Principles and Applications," *e-J. Nondestruct. Testing.*, **7** [10] (2002).

[3]D. R. Askeland, *The Science and Engineering of Materials*. Chapman & Hall, London, 1996.

[4]C.-M. Sung and M. Sung, "Carbon Nitride and Other Speculative Superhard Materials," *Mater. Chem. Phys.*, **43**, 1–18 (1996).

[5]D. M. Teter, "Computational Alchemy: The Search for New Superhard Materials," *Mater. Res. Soc. Bull.*, **23**, 22–27 (1998).

[6]R. B. Kaner, J. J. Gilman, and S. H. Tolbert, "Designing Superhard Materials," *Science*, **308**, 1268–9 (2005).

[7]A. Y. Liu and M. L. Cohen, "Prediction of New Low Compressibility Solids," *Science*, **245**, 841–2 (1989).

[8]C. Li and P. Wu, "Correlation of Bulk Modulus and the Constituent Element Properties of Binary Intermetallic Compounds," *Chem. Mater.*, **13**, 4642–8 (2001).

[9]F. M. Gao, J. L. He, E. D. Wu, S. M. Liu, D. L. Yu, D. C. Li, S. Y. Zhang, and Y. J. Tian, "Hardness of Covalent Crystals," *Phys. Rev. Lett.*, **91**, 015502 (2003).

[10]F. M. Gao, "Hardness Estimation of Complex Oxide Materials," *Phys. Rev. B*, **69**, 094113 (2004).

[11]F. M. Gao, R. Xu, and K. Liu, "Origin of Hardness in Nitride Spinel Materials," *Phys. Rev. B*, **71**, 052103 (2005).

[12]S. Y. Zhang, "Investigation of Chemical Bonds on Complex Crystals," *Chin. J. Chem. Phys.*, **4**, 109–15 (1991) (in Chinese).

[13]M. Moesgaard, H. D. Pedersen, Y. Z. Yue, and E. R. Nielsen, "Crystallization in Stone Wool Fibres," *J. Non-Cryst. Solids*, **353**, 1101–8 (2007).

[14]S. Yilmaz, O. T. Özkan, and V. Günay, "Crystallization Kinetics of Basalt Glass," *Ceram. Int.*, **22**, 477–81 (1996).

[15]B. K. Khan, I. A. Kravchenko, Z. D. Bogatyreva, and V. Y. Khorunzhii, "Crystallization Properties of Glasses Based on Ferronickel Slag," *Glass Ceram.*, **42**, 65–9 (1985).

[16]P. M. Sørensen, M. Pind, Y. Z. Yue, R. D. Rawlings, A. R. Boccaccini, and E. R. Nielsen, "Effect of the Redox State and Concentration of Iron on the Crystallization Behavior of Iron-Rich Aluminosilicate Glasses," *J. Non-Cryst. Solids*, **351**, 1246–53 (2005).

[17]V. Žnidarši-Pongrac and D. Kolar, "The Crystallization of Diabase Glass," *J. Mater. Sci.*, **26**, 2490–4 (1991).

[18]J. J. Gilman, "Flow of Covalent Solids at Low Temperatures," *J. Appl. Phys.*, **46**, 5110–3 (1975).

[19]F. M. Gao, "Theoretical Model of Intrinsic Hardness," *Phys. Rev. B*, **73**, 132104.1 (2006).

[20]X. L. Chen, Q. Y. Tu, M. He, L. Dai, and L. Wu, "The Bond Ionicity of MB₂ (M = Mg, Ti, V, Cr, Mn, Zr, Hf, Ta, Al and Y)," *J. Phys.: Condens. Mater.*, **13**, 723–7 (2001).

[21]J. C. Phillips, "Ionicity of the Chemical Bond in Crystals," *Rev. Mod. Phys.*, **42**, 317–56 (1970).

[22]B. F. Levine, "Bond Susceptibilities and Ionicities in Complex Crystal Structures," *J. Chem. Phys.*, **59**, 1463–86 (1973).

[23]D. R. Lide, *CRC Handbook of Chemistry and Physics*. CRC Press, London, U.K., 2006.

[24]M. Cameron, S. Sueno, C. T. Prewitt, and J. J. Papike, "High-Temperature Crystal Chemistry of Acmite, Diopside, Hedenbergite, Jadeite, Spodumene, and Ureyite," *Am. Mineral.*, **58**, 594–618 (1973).

[25]M. Raudsepp, F. C. Hawthorne, and A. C. Turnock, "Crystal Chemistry of Synthetic Pyroxenes on the Join CaNiSi₂O₆-CaMgSi₂O₆ (Diopside): A Rietveld Structure Refinement Study," *Am. Mineral.*, **75**, 1274–81 (1990).

[26]W. A. Gordon, D. R. Peacor, P. E. Brown, E. J. Essene, and L. F. Allard, "Exsolution Relationships in a Clinopyroxene of Average Composition Ca0:43Mn0:69Mg0:82Si₂O₆: X-ray Diffraction and Analytical Electron Microscopy," *Am. Mineral.*, **66**, 127–41 (1981).

[27]L. Levien and C. T. Prewitt, "High-Pressure Structural Study of Diopside," *Am. Mineral.*, **66**, 315–23 (1981).

[28]J. B. Quinn and G. D. Quinn, "Indentation Brittleness of Ceramics: A Fresh Approach," *J. Mater. Sci.*, **32**, 4331–46 (1997).

[29]F. Kick "Das Gesetz der Proportionalen Widerstände und Seine Anwendung," Leipzig Felix Edition, 1885.

[30]H. Li and R. C. Bradt, "The Indentation Load/Size Effect and the Measurement of the Hardness of Vitreous Silica," *J. Non-Cryst. Solids*, **146**, 197–212 (1992).

[31]D. J. Clinton and R. Morrell, "Hardness Testing of Ceramic Materials," *Mater. Chem. Phys.*, **17**, 461–73 (1987).

[32]R. Roesky and J. R. Varner, "Influence of Thermal History on the Crystallization Behavior and Hardness of Glass–Ceramic," *J. Am. Ceram. Soc.*, **74**, 1129–30 (1991).

[33]P. M. Sargent and T. F. Page, "Influence of Microstructure on the Microhardness of Ceramic Materials," *Proc. Br. Ceram. Soc.*, **26**, 209–24 (1978).

[34]B. R. Lawn and D. B. Marshall, "Hardness, Toughness, and Brittleness: An Indentation Analysis," *J. Am. Ceram. Soc.*, **62**, 347–50 (1979).

[35]B. R. Lawn and A. G. Evans, "A Model for Crack Initiation in Elastic/Plastic Indentation Fields," *J. Mater. Sci.*, **12**, 2195–9 (1977).

[36]S. Dériano, A. Jarry, T. Rouxel, J.-C. Sangleboeuf, and S. Hampshire, "The Indentation Fracture Toughness (K_C) and Its Parameters: The Case of Silica-Rich Glasses," *J. Non-Cryst. Solids*, **344**, 44–50 (2004).

[37]D. Dorner and B. Stöckhert, "Plastic Flow Strength of Jadeite and Diopside Investigated by Microindentation Hardness Tests," *Tectonophysics*, **379**, 227–38 (2004).

[38]P. T. B. Shaffer, "Effect of Crystal Orientation on Hardness of Silicon Carbide," *J. Am. Ceram. Soc.*, **47**, 466 (1964).

[39]M. Y. Khan, L. M. Brown, and M. M. Chaudhri, "The Effect of Crystal Orientation on the Indentation Cracking and Hardness of MgO Single Crystals," *J. Phys. D: Appl. Phys.*, **25**, 257–65 (1992).　□