Impacts of first principles calculations in engineering ceramics

Isao TANAKA*³,⁴,⁵

*Department of Materials Science and Engineering, Kyoto University, Sakyo, Kyoto 606–8501, Japan
³Japan Fine Ceramics Center, Atsuta, Nagoya 456–8587, Japan

With rapid progress of high performance computers and algorithm, we are now capable to obtain physical properties and thermodynamical quantities of substances through first principles calculations with the accuracy comparable to experiments. Here, the author makes a short review of our works related to the use of first principles calculations for the study of engineering ceramics. It includes 1) chemical bonding of SiAlONs and solute arrangements, 2) phonon calculations and related properties, 3) theoretical lattice thermal conductivity, 4) cluster-expansion method to study solid solution and order/disorder phenomena, and 5) materials informatics approach for discovery of low thermal conductivity materials.©2016 The Ceramic Society of Japan. All rights reserved.

Key-words : DFT calculations, Chemical bonding, Phonon, Thermal properties, Thermal conductivity, Order–disorder transition, Materials informatics

1. Introduction

Electronic structure calculations within density functional theory (DFT) are commonly called first principles calculations, since they are based entirely upon physical principles of quantum mechanics. Their usefulness can be recognized when compared with calculations using empirical parameters such as classical molecular dynamics calculations. Such classical calculations can adequately describe materials only when the systems are close to references used to obtain empirical parameters. In other words, they cannot be used for chemical elements with ionic states that are not included in references. The accuracy of the calculations is not guaranteed when they are used for lattice imperfections unless they are explicitly included as references. First principles calculations do not have such problems. With developments of high performance computing systems as well as highly efficient computational codes, first principles calculations are making strong impacts on materials science. Some examples based on the author’s own work on engineering ceramics will be given.

2. Chemical bonding in SiAlON

Formation of solid solution for Si₃N₄ by concurrent substitution of Si by Al and N by O was first reported in early 1970s.¹²,³ The solid solution has been called SiAlON. Since the primitive unit cell of β-Si₃N₄ contains 2 formula units, β-SiAlON is commonly expressed as β-Si₃₋ₙ₋ₓAlₓOₓN₄₋₂ in which the z-value corresponds to the solute concentration. The maximum solubility obtained by experiments was z ≈ 4 at 1700–1800 K.⁵ Note that the solubility was typically determined in samples after sintering and furnace cooling down to the room temperature.

The present authors made a series of experiments to sinter high cation-purity silicon nitride and SiAlON powders that were synthesized by imide decomposition method. Glass-encapsulated hot isostatic pressing method was adopted to sinter β-SiAlONs ranging from z = 0 to 3.8 without additives to full density.⁵⁻⁷ Young’s modulus was found to decrease linearly with the increase of z as shown in Fig. 1(a).⁹ Similar dependence on z was found for the Vickers hardness.⁶⁻⁷ In 1992, the electronic origin of the remarkable softening was discussed with first principles calculations using cluster models composed of 13 atoms.⁵ The presence of Al and O was found to weaken the covalent chemical bonding significantly. This can be visualized by plotting the charge density contour as in Fig. 1(b), which can be quantified by the bond overlap population as shown in Fig. 1(c). A decade later, more accurate first principles calculations were systematically made.⁶⁻⁷ Formation energy of the solid solution with reference to β-Si₃N₄, α-Al₂O₃ and AlN is plotted as a function of the number of the nearest neighbour Al–O bonds per unit cell in Fig. 1(d).⁸ An obvious preference to form Al–O bonds in SiAlONs was found for the whole range of z, which was later experimentally confirmed by Al–K edge X-ray absorption near edge structures.⁹

3. Impacts of phonon calculations

According to the Hellmann–Feynman theorem, forces acting on atoms can be computed through first principles calculations. They are used to optimize the atomic arrangement of a given system, in other words to obtain the equilibrium structure. When an atom in the equilibrium structure is deliberately displaced, forces occur to restore the structure as shown in Fig. 2. Note that a supercell should be used to compute reasonable restoring forces. The forces by such a finite displacement method can be used to compute phonon frequencies within harmonic approximation. Once phonon density of states is obtained, thermal properties of crystals, such as specific heat at constant volume, Cᵥ, Helmholtz free energy, F, and entropy, S can be calculated according to the Bose-Einstein statistics. One can compute the phonon states as a function of volume to quantify specific heat at constant pressure, Cᵥ, thermal expansion coefficient, α, and Gibbs free energy, G, within the quasi-harmonic approximation. Togo has developed a code phonopy that can make such first principles phonon calculations routinely.¹⁰ Typical outputs for the thermal properties for AlN are shown in Fig. 3. Gibbs free energy is essential for discussion of phase transition. Figure 4 shows two examples of Gibbs free energy as a function of temperature. As for ZrO₂, the Gibbs free energy of the tetragonal structure is smaller than the
monoclinic structure at above 1350 K, which well agrees to the phase transition temperature observed by experiment. The Gibbs free energy of $\gamma$-Si$_3$N$_4$ is smaller than that of $\alpha$-Si$_3$N$_4$ in the whole temperature range, which means that $\alpha$-Si$_3$N$_4$ is a high pressure form having much higher Gibbs free energy under the ambient pressure. By experiments, both of $\alpha$- and $\beta$-Si$_3$N$_4$ are known to be synthesized under ambient conditions. But their hierarchy can be anticipated by the experimental fact that $\beta \rightarrow \alpha$ phase transition is much more frequently observed than the back transition. Since information of such thermal properties and thermodynamical quantities are essential in materials research, capability of such theoretical calculations provides strong impacts. A database for such phonon calculations, phonondb, is under construction and has been made open for public users.

Phonon calculations as described above are useful only when the harmonic approximation is valid. Quasiharmonic approximation can take account only a part of phonon anharmonicity. If one needs to compute lattice thermal conductivity (LTC), such approximations are not useful since harmonic phonons do not interact to make lattice thermal resistivity, a reciprocal of LTC. Third order force constants, which play essential role on LTC, can be computed by making finite displacements of two atoms instead of one as in Fig. 2. Phonon lifetime can then be computed, which is used to solve Boltzmann transport equation to obtain LTC within relaxation time approximation. Such computations are, however, a few orders of magnitudes more demanding than the harmonic phonon calculations. Very recently, Togo has launched a code phono3py that can handle such LTC calculations from first principles. Typical results of LTC at 300 K are compared with experimental data in Fig. 5. They are generally in good agreement. Since measurement of intrinsic LTC requires a high quality single crystal, the number of experimental data of LTC for ceramic materials are limited. Construction of reliable theoretical database is therefore invaluable. Application of such database will be described in chapter 5.

4. Impacts of cluster expansion calculations

Incorporation of alloying elements is a common strategy for emergence or modification of functionalities in ceramics. It is therefore useful to perform first principles calculations for solid solutions. However, an ordinal first principles band-structure calculation cannot be applied to a solid solution in a straightforward manner since the band-structure calculation is based upon a
periodic boundary condition. Strictly speaking, a randomly disordered solid solution should not have such artificial periodicity. Expansion of the unit cell, or use of a supercell, is a common strategy to reduce the artificial effects. However, except for the system that can be handled within the dilute limit, there is a wide variety of solute arrangements within a given solute concentration and the supercell size. It is not realistic to perform first principles calculations for all of such configurations exhaustively. Cluster expansion (CE) method is a statistical mechanical approach useful to handle solid solutions. CE gives an effective
representation of the configuration-dependent properties, such as the internal energy. In a binary system, the configuration-dependent property, Ξ, is expressed using pseudo-spin configuration variable σᵢ for lattice site i as

\[ Ξ = V₀ + \sum_i V_i σ_i + \sum_{i,j} V_{ij} σ_i σ_j + \sum_{i,j,k} V_{ijk} σ_i σ_j σ_k + \cdots \]

where \( V_0 \) and \( ϕ_α \) are called effective cluster interaction (ECI) and correlation function of cluster α, respectively. The use of the special quasi-random structure (SQS)\(^{17}\) is one of simple ways to estimate Ξ of a randomly disordered solid solution using first principles calculations. SQS is generated for a large supercell unless strong tendency to deviate from the random solute arrangements is anticipated. The cluster expansion and Monte Carlo simulations.\(^{19}\) Experimental data from different reports are shown by different symbols. They were given in ref. 19.

\[ \text{Etr} = \frac{v_f f}{C_3} \frac{\sigma}{\sqrt{v_f f}} \]

where \( v_f f \) denote the predicted value of \( \zeta_\text{tr} \) at \( 300 \text{K} \) by the regression using a set of predictors, \( x^* \). \( \sigma(x^*) \) is the prediction variance at \( x^* \). In ref. 16, crystalline volume, density and elemental predictors were used as predictors. The highly ranked compounds are summarized in Fig. 19. First principles anharmonic lattice dynamics calculations were performed for these highly ranked compounds, which actually showed very low LTC. In this study, the first prediction trial succeeded in discovery of low LTC compounds satisfactorily. If it had not been successful, the model should have been updated using kriging method.

5. Informatics approach for discovery of low thermal conductivity materials

Thermoelectrics are essential for utilizing waste heat. In order to increase the conversion efficiency, the thermoelectric figure of merit should be increased. Since the figure of merit is inversely proportional to thermal conductivity, many efforts have been placed to decrease the thermal conductivity. Lattice thermal conductivity, LTC, is the major part of the conductivity in most of ceramic materials. As described in chapter 3, it is now possible to compute LTC from first principles with the accuracy comparable to experiments. However, the computation is still demanding and practically possible only for a small number of simple compounds.

Recently, we reported LTC of 101 compounds through first principles anharmonic lattice dynamics calculations.\(^{16}\) The data was supplied to Gaussian process regression in order to make a model to predict LTC with a purpose to discover low LTC compounds among a library containing 54,779 compounds. The compounds in the library were ranked according to the Z-score given by

\[ Z(x^*) = \frac{f(x^*) - f_{\text{mean}}}{\sqrt{\sigma(x^*)}} \]

where \( f(x^*) \) denote the predicted value of \( -\log \zeta_\text{LTC} \) (LTC at 300 K) by the regression using a set of predictors, \( x^* \). \( \sigma(x^*) \) is the prediction variance at \( x^* \). In ref. 16, crystalline volume, density and elemental predictors were used as predictors. The highly ranked compounds are summarized in Fig. 7. First principles anharmonic lattice dynamics calculations were performed for these highly ranked compounds, which actually showed very low LTC. In this study, the first prediction trial succeeded in discovery of low LTC compounds satisfactorily. If it had not been successful, the model should have been updated using kriging method.

| Ranking | Z-score | Compound | Computed LTC at 300K (W/mK) |
|---------|---------|----------|-----------------------------|
| 1       | 1.90    | PbBrI₂   | 0.10                        |
| 2       | 1.76    | PbI₂Br  | 0.13                        |
| 3       | 1.58    | PbRh₂Br₃| 0.08                        |
| 4       | 1.56    | PbCl₂   | 0.18                        |
| 5       | 1.56    | PbClI₂  | 0.09                        |
| 6       | 1.44    | PbBrI(3mn)| 0.29                     |
| 7       | 1.43    | PbBrI(P6₃mc)| 0.29                   |

Fig. 6. Degree of inversion \( x \) in spinel MgAl₂O₄, i.e., \((\text{Mg}_{1-x}\text{Al}_x)\text{[Mg}_2\text{Al}_{2-x}]\text{O}_4\), estimated by the combination of first principles calculations, the cluster expansion and Monte Carlo simulations.\(^{19}\) Experimental data from different reports are shown by different symbols. They were given in ref. 19.

Fig. 7. Result of virtual screening for 54,779 compounds with actual lattice thermal conductivity (LTC) calculated by the first principles anharmonic lattice dynamics calculations.\(^{16}\) Only highly ranked compounds are shown.
$f_{\text{best}}$ corresponds to the lowest LTC value among “observed” compounds, which can be updated at each kriging step.

This type of method, called virtual screening with Baysian optimization in general, should be useful for searching materials for many different applications in which chemistry of materials need to be optimized.

Acknowledgement This work was supported by a Grant-in-Aid for Scientific Research (A) (Grant No. 15H02286) and a Grant-in-Aid for Scientific Research on Innovative Areas “Nano Informatics” (Grant No. 25106005) from the Japan Society for the Promotion of Science (JSPS).

References
1) K. Oyama and O. Kamigaito, Jpn. J. Appl. Phys., 10, 1637 (1971).
2) K. H. Jack and W. I. Wilson, Nat. Phys. Sci., 238, 28–29 (1972).
3) T. Ekström and M. Nygren, J. Am. Ceram. Soc., 75, 259–276 (1992).
4) I. Tanaka, G. Pezzotti, T. Okamoto, Y. Miyamoto and M. Koizumi, J. Am. Ceram. Soc., 72, 1656–1660 (1989).
5) Y. Fujiwara, I. Tanaka, T. Okamoto, S. Kume and Y. Miyamoto, J. Ceram. Soc. Japan, 98, 360–364 (1990).
6) I. Tanaka, S. Nasu, H. Adachi, Y. Miyamoto and K. Niihara, Acta Metall. Mater., 40, 1995–2001 (1992).
7) T. Ekström, P. O. Käll, M. Nygren and P. O. Olsson, J. Mater. Sci., 24, 1853–1861 (1989).
8) K. Tatsumi, I. Tanaka, H. Adachi and M. Yoshiya, Phys. Rev. B, 66, 165210 (2002).
9) W. Y. Ching, M. Z. Huang and S. D. Mo, J. Am. Ceram. Soc., 83, 780–786 (2000).
10) K. Tatsumi, T. Mizoguchi, S. Yoshioka, T. Yamamoto, T. Suga, T. Sekine and I. Tanaka, Phys. Rev. B, 71, 033202. (2005).
11) A. Togo and I. Tanaka, Scr. Mater., 108, 1–5 (2015).
12) A. Kuwabara, T. Tohei, T. Yamamoto and I. Tanaka, Phys. Rev. B, 71, 064301 (2005).
13) A. Kuwabara, K. Matsunaga and I. Tanaka, Phys. Rev. B, 78, 064104 (2008).
14) http://phonondb.mtl.kyoto-u.ac.jp/.
15) A. Seko, A. Togo, H. Hayashi, K. Tsuda, L. Chaput and I. Tanaka, Phys. Rev. B, 91, 094306 (2015).
16) A. Seko, A. Togo, H. Hayashi, K. Tsuda, L. Chaput and I. Tanaka, Phys. Rev. Lett., 115, 205901 (2015).
17) A. Zunger, S.-H. Wei, L. G. Ferreira and J. E. Bernard, Phys. Rev. Lett., 65, 353–356 (1990).
18) A. Seko, Y. Koyama and I. Tanaka, Phys. Rev. B, 80, 165122 (2009).
19) A. Seko and I. Tanaka, J. Phys.: Condens. Matter, 26, 115403 (2014).

Isao Tanaka is Professor in the Department of Materials Science and Engineering, Kyoto University and also a senior scientist in Nanostructures Research Laboratory, Japan Fine Ceramics Center. Trained as a metal physicist, he received his B.E. and M.E. from Kyoto University and his Ph.D. from Osaka University. In 1987, he joined ISIR, Osaka University where he started to work on engineering ceramics. He then returned to Kyoto University in 1993. Since then he has been in Kyoto University.