

The evaluation of ultrasoft pseudopotential in predicting material properties of ionic systems by an ab-initio pseudopotential method

In Yong Kang, Yoon-Suk Kim, Yong-Chae Chung*, Hanchul Kim^a, Deok-Soo Kim and Jay J. Kim

CPRC, Hanyang University, Seoul 133-791, Korea

^aMaterial Evaluation Center, Korea Research Institute of Standards and Science, Taejeon 305-600, Korea

The equilibrium lattice constants for various rock salt structure type compounds were predicted by an ab-initio pseudopotential method adapted in the Vienna Ab-initio Simulation Program (VASP), and the values were compared with the experimental lattice constants found in the literature to check the transferability of the pseudopotential of each atom. The results clearly indicate that a well-transferable pseudopotential is essential to predict the material properties of complex ionic systems consisting of many different kinds of atoms.

Key words: ab-initio method, DFT, ultrasoft pseudopotential, transferability.

Introduction

Ab-initio approaches to predict material properties have been widely applied in various science subjects, i.e. physics, chemistry, materials science etc. [1, 2]. Among the various approaches, the one based on Density Functional Theory (DFT) is preferable for application in the materials science field, since DFT can efficiently handle periodic bulk materials as well as surfaces and interfaces [3]. In the DFT scheme, the problem is eventually narrowed by solving the Kohn-Sham equation [4] and, in the calculation procedure, the pseudopotential plane wave scheme has been chosen to increase the efficiency in terms of computing resources [5-7].

In applying the pseudopotential scheme to complex oxide systems, however, special care should be taken since the contribution of the pseudopotential of each atom to the whole system cannot be clearly understood at first glance. In fact, when the pseudopotential is devised for each atom, the environment of the atom is not considered at all. Each pseudopotential contains only the information of the corresponding atom and not the information of the atom's environment. Nevertheless, the devised pseudopotential corresponding to the specific atom should ideally have the same characteristics irrespective of the environment of the specific atom.

In this study, we calculated the primary bulk material property, the equilibrium lattice constant, of various rock salt type oxide systems by an *ab-initio* pseudo-

potential method to evaluate the transferability of each atom's pseudopotential.

Calculation Procedures

The Vienna *Ab-initio* Simulation Program (VASP) code was employed in this study [8-10]. In the calculation, we selected Mg, Ca, Sr and Ba ions for cation site elements and O, S, Se and Te ions for anion site elements of the rock salt structure. To evaluate the exchange-correlation potential of the Kohn-Sham equation, Local Density Approximation (LDA) was chosen. For all of the atoms, ultrasoft pseudopotential was employed to calculate the total energy of the system.

In each calculation the values of the k-point and the cutoff energy were selected in the range that guarantees the convergence of the total energy. With the selected values of k-point and cutoff energy, the total energy calculation was performed changing the unit cell volume. From the data set of total energy versus unit cell volume, the equilibrium lattice constant was easily derived from the Birch-Murnaghan Equation of State (EOS) method [11].

Results

In Table 1, the calculated equilibrium lattice constants for all of the combinations of the selected atoms are compared with the experimental equilibrium lattice constants found in the literature [12]. In the table, the relative error of the calculated equilibrium lattice constant is listed as a percent of the experimental value. Since the value of relative percent error indicates the magnitude of the deviation of the calculated value from the experimental value, it is the value that indicates the

*Corresponding author:
Tel : +82-2-2290-0507
Fax: +82-2-2281-5308
E-mail: yongchae@hanyang.ac.kr

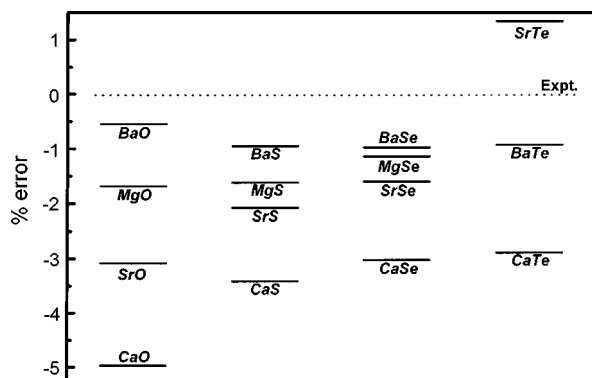
Table 1. Comparison of the predicted equilibrium lattice constants with the experimental values

Compounds		A_0 (Å)	Expt. (Å)	% error
Oxide	MgO	4.1405	4.2112	-1.679
	CaO	4.5714	4.8105	-4.970
	SrO	5.0014	5.1602	-3.077
	BaO	5.4927	5.5230	-0.549
Sulfide	MgS	5.1194	5.2033	-1.612
	CaS	5.4961	5.6903	-3.413
	SrS	5.8951	6.0198	-2.072
	BaS	6.3269	6.3875	-0.949
Selenide	MgSe	5.3892	5.4510	-1.134
	CaSe	5.7317	5.9100	-3.017
	SrSe	6.1305	6.2300	-1.597
	BaSe	6.5358	6.6000	-0.973
Telluride	CaTe	6.1617	6.3450	-2.889
	SrTe	6.5570	6.4700	1.345
	BaTe	6.9213	6.9860	-0.926

accuracy of the calculation.

As shown in Table 1, the magnitude of percent error for every anion increases when the cation element changes as $Ba \rightarrow Mg \rightarrow Sr \rightarrow Ca$. In other words, for the case of the oxides the percent error increases in the order $BaO \rightarrow MgO \rightarrow SrO \rightarrow CaO$. The same trend for the calculated equilibrium constants can be seen for sulfides, selenides, and tellurides. (In the telluride case, the data for MgTe were not listed due to unavailability of the experimental value in the literature.)

To find the anion dependency on the specific cation as well as the cation dependency on the specific anion, the relative percent error is graphically represented in Fig. 1 for each calculated rock salt type compound. In the figure, we can clearly see that the calculated equilibrium lattice constants for compounds formed with Ba cation, such as BaO, BaS, BaSe and BaTe, have rather small and uniform errors around 1%. However, the calculated equilibrium lattice constants for compounds formed with Ca cation, such as CaO, CaS, CaSe and

**Fig. 1.** Graphical representation of the % error of the predicted equilibrium lattice constants of various rock salt structure type compounds.

CaTe, have rather large errors compared to the Ba case. In addition, the range of percent error for compounds formed with S and Se anions turned out to be rather small compared to the cases of O and Te. From this simple calculation we showed that the pseudopotential of a specific atom behaved very differently depending on its environment. This tells us that one should be very careful in employing pseudopotential schemes to calculate material properties of complex material systems consisting of many different kinds of atoms. Otherwise, one cannot predict the desired material properties by *ab-initio* calculation as accurately as we would like.

Conclusions

In this study, equilibrium lattice constants for various rock salt structure type compounds were calculated by *ab-initio* pseudopotential method. From comparison with experimental values found in the literature, the transferability of a particular atom's pseudopotential was tested. The calculation results show that the percent error, which represents the amount of deviation of the calculated value from the experimental value, varies widely depending on the constituent atoms. The result of this study certainly emphasizes the importance of the well-transferable pseudopotential in calculating material properties by the *ab-initio* pseudopotential method, especially for complex systems which consist of many different kinds of atoms.

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