First-Principles Study of Thermal Expansion Coefficient of Complex Oxides for Thermal Barrier Coating

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Operating temperatures of gas turbine engines can be increased by ceramic thermal barrier coating (TBC) on turbine blades, to improve energy conversion efficiency [1]. This can be done if oxides are used for top coating of TBC, because it lowers the temperature at alloy-based blade surface due to its low thermal conductivity [2]. While conventional materials including yttria stabilized zirconia (YSZ) having fluorite crystal structure performs well [3], it is desired to find and develop materials with improved properties for TBC to achieve higher energy conversion efficiency, which requires the materials to simultaneously acquire multiple properties [4]. One of the important properties is coefficient of thermal expansion (CTE). The difference in CTEs between top coating and underlying layer may lead to fractures along the interface or spallation of the TBC after thermal cycling [5]. However, even though thermal expansion can be easily measured, critical factors that govern CTE of oxides remain still unclear, since factors determining thermal expansion are often attributed only to Grüneisen parameter [6]. Moreover, it is difficult to obtain intrinsic values of CTE of oxides, since microstructure and any inhomogeneity in practical materials significantly affect experimental CTE values [7]. Lack of these understanding is one of impediments for data-driven materials design for top coating or in other ways.

In this study, theoretical calculations and evaluations of CTE of oxides, which have FCC-like cationic sublattice, have been systematically done by using lattice dynamics technique in conjunction with ab initio calculations. Equilibrium structures at 0 K are calculated by ab initio calculations and free energy is calculated as a function of temperature. The same is done for other volumes to find equilibrium volumes as a function of temperature from which CTE can be calculated. The computational method allows us to obtain unique value of CTE of materials under the same conditions and to evaluate the impact of each factor on CTE, namely atomic mass, bulk modulus, and atomic bond length, in a separate manner. As a first step of the understanding, evaluation of the impact of atomic mass alone, which presumably governs atomic vibration, has been conducted.

Firstly, calculations of CTE values of rare earth oxides ($Ln_2O_3$, $Ln$: lanthanide) in C-type crystal structure, which is similar to that of fluorite YSZ as shown in Fig. 1, have been conducted. In addition, focusing on La$_2$O$_3$, CTEs of fictitious states where only atomic mass of La was intentionally changed to that of other lanthanide elements, while its structure including lattice constants and interatomic bonding were kept unchanged. In order to identify the influence only of atomic masses on CTE, comparison of these two cases has been made.

Different tendencies were observed in the two cases from Fig. 2. In the fictitious $Ln_2O_3$ cases where only atomic mass was changed, the magnitude of change in CTE is significantly smaller than their original $Ln_2O_3$. These results indicate that the impact of atomic mass on CTEs of the oxide is negligibly small, suggesting that other
factors have more impact for it. Although it is not shown in the figure, the same trend is found in other classes of oxides. For divalent oxides, MO (M: Mg, Ca, Sr), not only stable rock salt structure but also zinc blende structure are assumed for better understanding. Comparison between the original oxides and the fictitious oxides revealed the impact of atomic mass is negligibly small irrespective of crystal structures. These understanding help us to explore materials having optimal CTE without deteriorating other properties for practical use as TBC materials.

Acknowledgment: This study is supported by Grant-in-Aid for Scientific Reserch on Innovative Areas “Exploration of nanostructure-property relationship for materials innovation” (Grant No. 25106005) from the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan