

Statistical Thermodynamics of Oxides by Combination of Cluster Expansion Method and First Principles Calculations

Isao Tanaka^{1,2}, Atsuto Seko³, Atsushi Togo¹ and Fumiyasu Oba¹

1 Department of Materials Science and Engineering, Kyoto University, Kyoto, 606-8501, Japan

2 Nanostructures Research Laboratory, Japan Fine Ceramics Center, Nagoya, 456-8587, Japan

3 Pioneering Research Unit for Next Generation, Kyoto University, Kyoto 606-8501, Japan

Recent advances in computational power and numerical techniques enable us to perform a large set of first principles calculations systematically with high numerical accuracy. Such computational results can be used to evaluate the thermodynamical quantities. The cluster expansion (CE) method has been widely used as a tool to take account the statistical thermodynamics of crystalline solutions. In the research group of the present authors, efforts to develop a robust procedure for the CE of non-close packed structures have been pursued[1-8]. Here the results of a series of non-stoichiometric SnO_{2-x} compounds are presented.

SnO_2 with a rutile structure is the most popular compound in the Sn-O binary system. A mono-oxide SnO with a litharge structure has also been well studied. Other than these two compounds, presence of a few other phases, such as Sn_2O_3 , Sn_3O_4 and Sn_5O_6 , has been reported in literature. However, their stability and structure have not been clearly known. SnO_2 and SnO have common structural features: the sublattice of Sn atoms can be approximated by a body-centered-tetragonal structure. Six oxygen atoms are coordinated to each Sn atom in SnO_2 . In SnO, half the oxygen atoms are removed from SnO_2 . From the inspection of these structures, we have adopted the oxygen sublattice model for the intermediate structures in which SnO_{2-x} ($0 < x < 1$) is described by the arrangements of oxygen atoms and vacancies on the oxygen sublattice of the rutile SnO_2 . First principles calculations were performed for 750 ordered structures. A set of 28 clusters up to quadruplets were chosen from a pool of 262 clusters. Stable structures were explored using supercells with size up to $12 \times 12 \times 12$ (10,368 atoms).

Figure 1 shows the calculated formation energies relative to the energies of litharge SnO and rutile SnO_2 . Only Sn_3O_4 and Sn_2O_3 are found to be located on the convex hull of the formation energy. The predicted structures of Sn_3O_4 , Sn_2O_3 and Sn_5O_8 are

schematically drawn in Fig. 1. As can be seen, oxygen vacancies are commonly aligned along the plane corresponding to the (101) plane of SnO₂. The (101)-layered structures can also be seen in all of sub-dioxides including Sn₃O₅ and Sn₇O₁₂. They can be expressed as a series of homologous structures of the form Sn_{*n*+1}O_{2*n*} with alternating *n* layers of SnO₂-like bands and a (101) vacancy layer.

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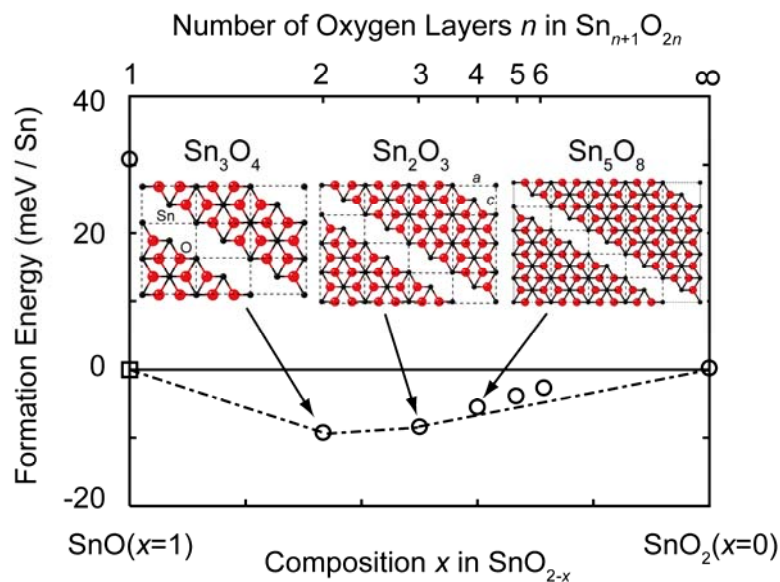


Fig 1 Computed formation energies of homologous Sn_{*n*+1}O_{2*n*} and their schematic structures.