Structure and Phase Stability of Nonstoichiometric Compounds of Tin Oxides

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The oxides with quadrivalent cations often form a rutile-type structure. Two minerals with this structure known as rutile (TiO2) and cassiterite (SnO2) have been popular subjects of fundamental studies for over a century. These oxides are also important in modern technology as catalysts and in spintronic and optoelectronic applications. Both of them often show oxygen deficiency, which plays a central role in determining their properties and chemical activities. In the Ti-O system, a series of nonstoichiometric compounds or homologous compounds are known to exist and are called “Magnéli phase”. Many studies have also been carried out on the nonstoichiometric compounds of SnO2-x. However, the structures and stabilities are much less understood. Although several phase diagrams have been reported for the Sn-O binary system, they do not agree with each other. To determine the unknown structures and their stability, a theoretical approach combining first-principles calculations with a cluster expansion technique can be a powerful tool. In the present study, a systematic study of the nonstoichiometric compounds in the Sn-O binary system is carried out by the combined approach[1].

Stable structures for Sn3O4 and Sn2O3 are found by simulated annealing (SA) as shown in Fig. 1. In the predicted structures, oxygen vacancies are aligned along the plane corresponding to (101) of SnO2. They are composed of SnO2-like and SnO-like local structures. Similar structures for the other oxygen-deficient compounds using various sizes of supercells were also predicted by SA. The (101)-layered structures can be expressed as a series of homologous structures of Snn+1O2n with alternating n layers of SnO2-like bands and a (101) vacancy layer. Figure 2 shows the theoretical XRD patterns of the stable structures for Sn3O4 and Sn2O3 compared with the experimental powder XRD patterns. The theoretical XRD patterns for the predicted (101)-layered structure of Sn3O4 and Sn2O3 are very close to each other, reflecting the similarities of the structures based on the common SnO and SnO2-like units. The peak positions and relative intensities of the theoretical XRD patterns are close to those of the experimental XRD patterns. The agreements of the theoretical and experimental XRD patterns indicate that the Sn3O4 and Sn2O3 phases observed experimentally in tin oxide systems correspond to the (101)-layered structures based on the rutile structure.

The electronic structures of the homologous phases can be most clearly compared with the projected density of states (PDOS) of Sn atoms. Figure 3 shows the PDOS of two kinds of Sn atoms in Sn3O4 along with the PDOS of Sn atoms in SnO2 and SnO. The Sn(a) atoms, as highlighted in Fig. 3, are coordinated by six oxygen atoms. The relative positions of the Sn-5s and 5p PDOS and their energies with respect to the Fermi energy are analogous to those of the quadrivalent Sn atom in rutile SnO2. The Sn(b) in Fig. 3, on the other hand, is analogous to the divalent Sn atom in SnO. These results imply that Sn(a) and Sn(b) in Sn3O4 are quadrivalent and divalent, respectively. No other kinds of Sn atoms are present, which indicates the absence of trivalent Sn in Sn2O3.

In summary, we investigated the structures and phase stabilities of rutile-type tin oxides, combining first principles calculations with the cluster expansion technique, in particular, those of the controversial Sn2O3 and Sn3O4 intermediate compounds. We predicted a homologous series of Snn+1O2n in which oxygen vacancies are layered on (101) planes. The theoretical structures are consistent with experimental x-ray diffraction profiles. The homologous structures consist of quadrivalent and divalent tin atoms. No trivalent Sn atoms are formed.

References
FIG. 1. Predicted stable structures for Sn$_3$O$_4$ and Sn$_2$O$_3$. The blue solid lines show unit cells.

FIG. 2. Theoretical XRD patterns (Cu-$K\alpha$) of the predicted structures for Sn$_3$O$_4$ and Sn$_2$O$_3$ compared with the experimental XRD patterns.

FIG. 3. PDOS of (a) sixfold-coordinated Sn and (b) asymmetrically oxygen-coordinated Sn in the (101)-layered Sn$_2$O$_3$. The PDOS of Sn atoms in rutile SnO$_2$ and that of Sn atoms in litharge SnO are shown for comparison.