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Stability, thermodynamic and mechanical properties of the compounds in the Ag–Sn–O system

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ABSTRACT

The stability and mechanical properties of the compounds in the Ag/SnO_2 composite by reaction synthesis are investigated with the advantage of density functional theory. Cohesive energy and formation enthalpy show that the calculated compounds are stable and the stability is aligned as $Ag_2O < SnO \sim Ag_2SnO_3 < Ag_6O_2 \sim SnO_2$. Similar results are also obtained by the Milliken population analysis. The crystal structures of $Ag_8Sn_4O_{12}$ (supercell of Ag_2SnO_3) could be produced by the reaction between $2 \times Ag_6O_2$ and $4 \times SnO_2$; the formation energy is about −164.95 kJ/mol. The thermodynamical data of these compounds are calculated using Debye's quasi-harmonic approximation, such as heat capacity and Gibbs free energy. Bulk modulus, Young's modulus and shearing modulus values are obtained by the Voigt–Reuss–Hill method.

1. Introduction

Silver and tin alloys have been frequently used in a variety of industrial applications, such as lead-free solders, electric contact materials, gas-sensitive sensor, etc. The metal oxides and other multi-component compounds are usually observed in electric contact materials [1–4]. Ag/CdO composite has excellent performance and can be fabricated easily into many electric devices. However, as Cd is a hazardous element and also due to other environmental concerns, Cd-free electric contact materials are now emphasized and studied extensively by many researchers [4,5]. Ag/SnO_2 composite should be one of the most important candidates for electric contact materials. The Ag/SnO_2 composite is preferred because of its excellent performances and can be easily fabricated with the conventional method. However, silver tin oxide is much more difficult to prepare because of the poor metallurgical properties [5–7]. Chen et al. [2] and Feng et al. [4] have reported that good mechanical and electrical performances of Ag/SnO_2 composite are achieved by the reactive synthesis method. In addition, the advanced Ag/SnO_2 composites were fabricated by Ag–Sn alloy and Ag_2O. In this progress, the metal of tin was oxide and some compounds such as SnO, modulated crystal structures of Ag_2SnO_3 and Ag_6O_2 were presented in Ag/SnO_2 composite from the experiment [8]. These precipitated compounds were not well reported in the Ag/SnO_2 composites all the time. With the fast development of Ag/SnO_2-based electric contact materials, it is important to investigate the ground-state properties of the precipitated phases in Ag/SnO_2 composite. On the one hand, the evaluations of bulk ground-state properties, such as lattice constants, bond lengths and bulk modulus, playing a remarkable role in materials science and it is helpful for us to understand the mechanical properties of the materials [9–11]. On the other hand, the thermodynamic parameters of the compound under high temperatures have attracted extensive attentions in the field of material science and engineering [12,13].

Based on the first principles study and Debye's quasi-harmonic approximation, the thermal properties, bulk modulus, elastic constant and the Debye temperature of these compounds in the Ag/SnO_2 composite are obtained [14–18], and which can provide some valuable insights on understanding Ag/SnO_2 electric contact materials.

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2. Computational methods and details

The whole researches were carried out using first principles calculations based on density functional theory (DFT) as implemented in CASTEP code [19]. Ultrasoft pseudo-potentials were employed to represent the interactions between ionic core and valence electrons. The exchange correction energies for LDA and GGA should be CA-PZ and PBE scheme, respectively [20–22]. The average forces acting on ions were finally reduced to 1.0×10^{-6} eV/atom, the Monkhorst–Pack scheme was used for **k** point sampling in the first irreducible Brillouin zone (BZ), and we used $12 \times 12 \times 12$ for all structures. Valence electrons included in this study for distinct atoms are O $2s^2$ $2p^4$, Ag $4d^{10}$ $5s^1$ and Sn $5s^2$ $5p^2$. The maximum energy cutoff value was 580.0 eV for plane wave expansions.

Density functional perturbation theory (DFPT) [23], which is a combination of density functional theory with electron-density linear-response, has been applied to calculate thermodynamical properties of the compound. Its main advantage is to reduce the computational cost for obtaining phonon frequencies throughout the Brillouin zone by using supercells. It is somewhat different from the direct methods such as molecular dynamics simulations and frozen-phonon calculations (the size of unit cell must be large enough to match wavelength of the phonon mode). In fact, the thermodynamic properties of Al [14], Ag [15], Cu [16], AlLi [17], NiAl and PdTi [18] are successfully predicted using *ab initio* DFPT calculations.

3. Results and discussion

3.1. Stability and reaction synthesis of the compounds in Ag/SnO_2 composite

In this paper, the crystal structures of the studied phases in Ag/SnO_2 composite are shown in Fig. 1. All of the crystal structures are constructed according to experimental data based on X-ray diffraction method [24–32]. The calculated crystal parameters and

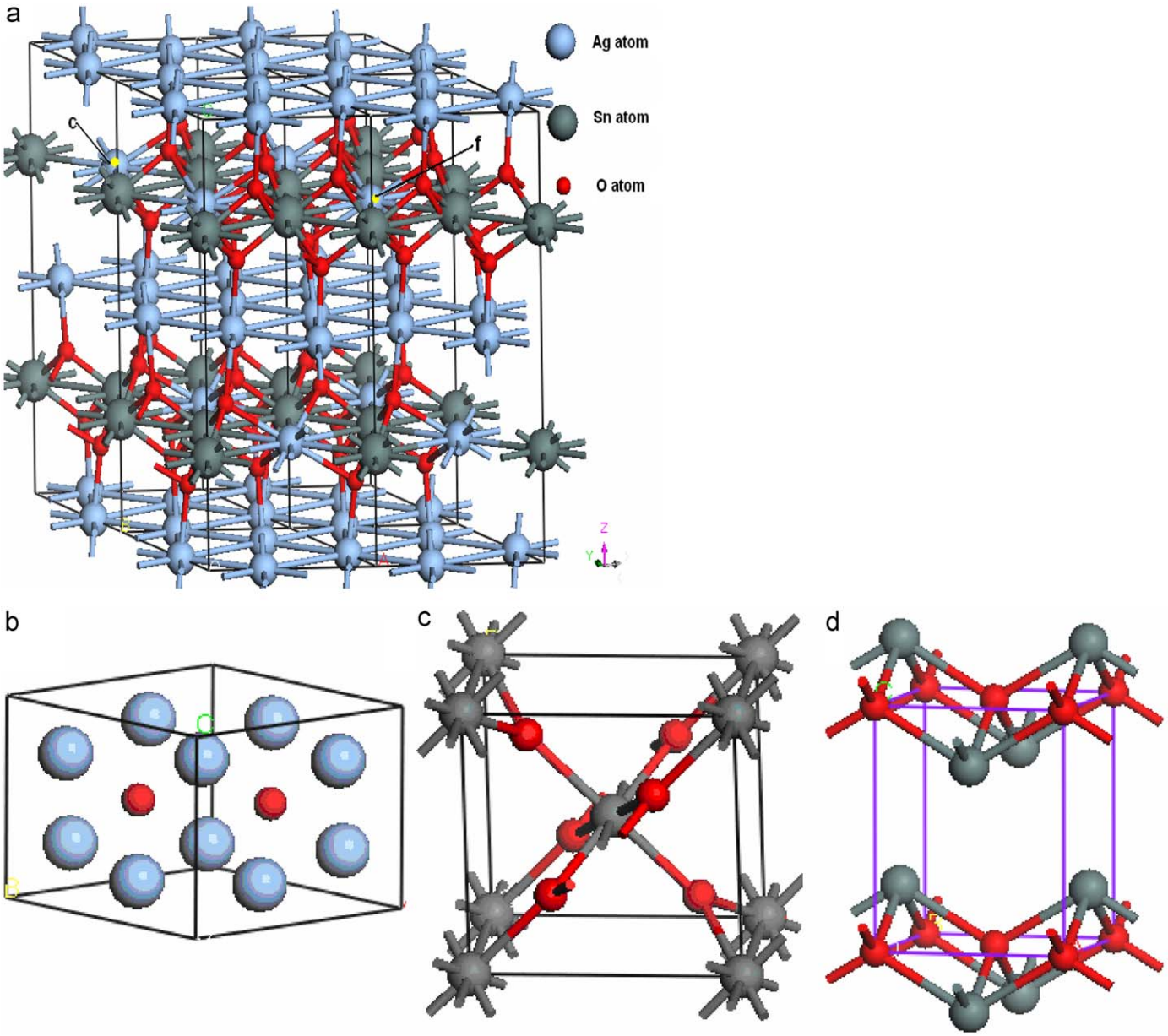

Fig. 1. Crystals of phases in the Ag–Sn–O system fabricated by reactive synthesis: (a) Ag_2SnO_3, (b) Ag_6O_2, (c) SnO_2, and (d) SnO.