Energetic stability, structural transition, and thermodynamic properties of ZnSnO₃

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First principles calculations were performed on ZnSnO₃ polymorphs to understand their energetic stability and structural transition under high pressure environments. The experimentally-identified ilmenite (IL)-type and LiNbO₃ (LN)-type ZnSnO₃ may coexist at zero pressure considering the effect of zero point energy. IL-type ZnSnO₃ becomes unstable under high pressure due to the appearance of imaginary frequency in phonon spectra. Enthalpy differences suggest that the phase transition occurs at 34.5 GPa from LN-type structure to a monoclinic CdSnO₄-type. Thermodynamic properties including Helmholtz free energy, specific heat at constant volume and Debye temperature were also calculated. © 2011 American Institute of Physics. [doi:10.1063/1.3562013]

Perovskite-type oxides (ABO₃) have attracted considerable attentions due to their potential applications as the ferroelectric, piezoelectric, pyroelectric, and nonlinear optical materials. Zinc stannate, ZnSnO₃, with polar IlNbO₃(LN)-type structure (space group of R3c) has recently been synthesized upon high pressurization above 7 GPa with an estimated polarization of 79 μC/cm². Meanwhile, the heteroepitaxial Zn-based oxide thin film was also fabricated with a high ferroelectric polarization of 47 μC/cm². It is, thus, expected that ZnSnO₃ would be an excellent candidate for lead-free ferroelectric materials.

For ZnSnO₃, various structures have been found in the experiments. In addition to LN-type structure, ilmenite (IL)-type ZnSnO₃ was synthesized by an ion exchange method, and nanostructured hexagonal and cubic perovskite-type structures were also observed. Theoretical calculations based on density functional theory (DFT) were performed to understand their structural, electronic and optical properties. Spontaneous polarization, dynamical and nonlinear optical properties were theoretically investigated to understand origins of physical properties of ZnSnO₃. A recent DFT study on the structural and electronic properties of ZnSnO₃ compositions reported a phase transformation from Zn₂SnO₄–1/2SnO₂ mixed phases to LN-type ZnSnO₃ under a low pressure of 2 GPa, below the critical transition pressure observed experimentally (~7 GPa). Despite that both IL and LN structure types were synthesized previously under ambient conditions, recent high pressure experiments only reported the synthesis of LN-type with no evidence of the formation of IL-type phase. The fundamental understanding of structural properties of ZnSnO₃ will be critical for designing and developing ferroelectric oxides. The phase transformation process among different polymorphs under high pressure conditions is not fully understood yet. In addition, limited thermodynamic properties are available due to the difficulty of synthesizing high quality samples for measurements.

In this letter, first principles techniques were employed to investigate the relative phase stability of ZnSnO₃ polymorphs under high pressure environments to understand the stability of crystal structure and their physical and thermodynamic properties. Our calculations indicate that IL-type and LN-type ZnSnO₃ may coexist at zero pressure considering the effect of zero point energy (ZPE). IL-type ZnSnO₃ becomes unstable under high pressure based on the calculations of phonon spectra. In contrast, LN-type phase is favorable above 7.1 GPa, in excellent agreement with experimentally determined critical pressure for synthesizing stable LN-type phase by solid synthesis route. Furthermore, a phase transition occurs at 34.5 GPa from LN-type structure to an orthorhombic CdSnO₄-type structure. These results provide theoretical insights in understanding the phase stability, which forms a scientific basis for designing materials by high pressure.

Calculations of ZnSnO₃ phases were performed with CASTEP code based on DFT. The exchange and correlation functional was treated by generalized gradient approximation-Perdew-Burke-Ernzerhof. The cutoff energy of 380 eV and k-points of 6 × 6 × 6 for all hypothetical structures were applied to calculate the total energy and enthalpy. The phonon dispersion and phonon density of states (PDOS) of IL-type and LN-type ZnSnO₃ was obtained with a cutoff energy of 660 eV using the linear response method. The cubic (c-) and hexagonal (h-) ZnO, tetragonal rutile SnO₂, and hexagonal SnO₂ mixed phases to LN-type ZnSnO₃ under a low pressure of 2 GPa, below the critical transition pressure observed experimentally (~7 GPa). Despite that both IL and LN structure types were synthesized previously under ambient conditions, recent high pressure experiments only reported the synthesis of LN-type with no evidence of the formation of IL-type phase. The fundamental understanding of structural properties of ZnSnO₃ will be critical for designing and developing ferroelectric oxides. The phase transformation process among different polymorphs under high pressure conditions is not fully understood yet. In addition, limited thermodynamic properties are available due to the difficulty of synthesizing high quality samples for measurements.

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and cubic spinel Zn$_2$Sn$_3$O$_7$ were adopted for enthalpy calculations.

Six possible structures for ZnSnO$_3$ were considered including cubic perovskite (space group: Pm-3m),$^{14}$ IL-type (space group: R-3),$^{10}$ LN-type (space group: R3c) structures,$^{8}$ CdSnO$_3$-type (space group: Pnma),$^{25}$ HgSnO$_3$-type (space group: R-3c),$^{2}$ and post perovskite (ppu)-type (space group: Cmcm) structure.$^{23}$ For each structure, the lattice parameters and atomic positions were fully optimized. The calculated lattice parameters shown in Table I are in good agreements with experimental results.$^{8,10}$ The calculated total energies versus volume (E-V curve) of the possible structures are shown in Fig. 1(a). Among all possible structures, LN-type structure has the lowest total energy at $T=0$ K; whereas total energy of the cubic perovskite structure is much larger than that of LN-type structure, and the difference can be as large as 3.76 eV/f.u. The larger energy difference suggests that the cubic perovskite phase of ZnSnO$_3$ is difficult to form under ambient conditions. Also, the total energy of the CdSnO$_3$-type phase intersects with that of both IL-type and LN-type phases, suggesting that structural modifications may occur under extreme environments. For experimentally synthesized IL-type and LN-type phases, no phase transition can be observed under studied conditions. These polymorphs can be stabilized under extreme conditions, such as high pressure or high temperature, as demonstrated by experimental observations.$^{8}$ In view of the structural transition of ZnSnO$_3$, we also calculated the enthalpy difference of mixed constituent oxides (ZnO + SnO$_2$) at ambient conditions. These polymorphs can be stabilized under extreme conditions, such as high pressure or high temperature, as demonstrated by experimental observations.$^{8}$

We, thus calculated the difference in total energy of ZnBO$_3$ ($B=$Si, Ge, Sn, and Pb) in both IL-type and LN-type structures as shown in Fig. 1(b). The difference in total energy decreases monotonically from Si phase (0.60 eV), Ge phase (0.37 eV) to Sn (0.09 eV) phase, suggesting that IL-type phase is energetically favorable as compared with LN-type phase; while for Pb-containing phase, LN-type phase is more favorable than IL-type phase. The total energy difference between IL-type and LN-type ZnSnO$_3$ is small within the range in which ZPE correction may become important for their relative structural stability.$^{29}$ The ZPE derived from the PDOS (Refs. 30 and 31) are 0.23 eV/unit and 0.31 eV/unit for IL-type and LN-type structures, respectively. Considered the effect of ZPE, the total energy difference between IL-type and LN-type is only $\sim 0.005$ eV/unit, which suggests that these two phases may coexist under ambient conditions. Moreover, the phonon spectra of IL-type and LN-type phases in both zero and high pressures (up to 10 GPa) were calculated to understand the structural stability of ZnSnO$_3$ polymorphs as displayed in Figs. 2(a) and 2(b). It can be seen that at zero pressure, all phonon branches of both phases have real frequency, indicating that these two phases are thermodynamically stable. However, at enhanced pressures (e.g., 1.5 GPa, 3 GPa, 5 GPa up to 10 GPa), IL-type phase becomes unstable, as evidenced by the appearance of imaginary frequency in the $\Gamma$-F direction, explaining why IL-type phase cannot be easily obtained in the high pressure experiment.$^{21}$

To further understand the effect of the possible synthesis routes in experiments, we also calculated the formation enthalpy $\{\Delta H=E_{\text{total}}(\text{ZnSnO}_3)-[E_{\text{total}}(\text{ZnO})+E_{\text{total}}(\text{SnO}_2)]\}$. All of the proposed phases of ZnSnO$_3$ have positive formation enthalpies (see Table I), suggesting that these polymorphs are not energetically favorable and cannot be synthesized by solid synthesis routes (ZnO+SnO$_2$=ZnSnO$_3$) at ambient conditions. These polymorphs can be stabilized under extreme conditions, such as high pressure or high temperature, as demonstrated by experimental observations.$^{8}$

![FIG. 1.](image1.png)

![FIG. 2.](image2.png)
the phase transition from LN-type structure to the orthorhombic CdSnO$_3$-type structure occurs at 34.5 GPa. $P_C$ of ZnSnO$_3$ is significantly larger than that of ZnGeO$_3$ (15.6 GPa) (Ref. 32) and MgGeO$_3$ (17.9 GPa) (Ref. 33) as observed in the experiments.

The temperature dependence of thermodynamic properties, such as Helmholtz-free energy, $\Delta F$, specific heat at constant volume, $C_V$, and even Debye temperature, $\Theta_D$, for both IL-type and LN-type phases can be derived from PDOS, as shown in Fig. 4. The calculated $\Delta F$ indicates that IL-type phase is more energetically favorable as compared to LN-type phase. The occurrence of IL-type phase in the experiment is thus highly dependent on the synthesis route. From Fig. 4, we found that at low temperature, $C_V$ exhibits a sharp increase up to about 400 K, and at high temperature, $C_V$ is close to a constant, so-called Dulong–Petit limit. $C_V$ of LN-type phase is smaller than that of IL-type phase in the studied range of temperature. At 300 K, $C_V$ of IL-type ZnSnO$_3$ (108.9 J/mol K) is similar to that of BaSnO$_3$ (103 J/mol K), but much larger than those of ZnSiO$_3$ (85.1 J/mol K), MgSiO$_3$ (78.4 J/mol K) or MgGeO$_3$ (87.3 J/mol K) (Ref. 38) with the same structure. Debye temperature of IL-type phase [Fig. 4] is significantly smaller than that of the LN-type phase with increasing temperature. For LN-type ZnSnO$_3$, $\Theta_D$ is 662 K at 300 K; whereas $\Theta_D$ of ZnSnO$_3$ (500 K) is relatively smaller than that of MgGeO$_3$ (777 K) at 300 K (Ref. 39) with the same IL-type structure. There are currently no reports on thermodynamic parameters in both experiments and calculations for ZnSnO$_3$. Therefore, our calculations may provide a prediction and stimulate the continued studies in the either experiments or simulations.

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![FIG. 3. (Color online) Calculated enthalpy differences, $H_{\text{IL}} - H_{\text{LN}}$, among mixed constituent oxides [ZnO+SnO$_2$, (Zn$_2$Sn$_{1-x}$O$_3$)$_{1/2}$], IL-type, and LN-type ZnSnO$_3$ (a) and $H_{\text{IL}} - H_{\text{LN}}$, between LN-type and CdSnO$_3$-type phases (b) as a function of pressure ($P$) at $T=0$ K.](image)

![FIG. 4. (Color online) Calculated Helmholtz free energy, $\Delta F$, specific heat at constant volume, $C_V$, and Debye temperature, $\Theta_D$, as a function of temperature of both IL-type and LN-type ZnSnO$_3$.](image)