

Crystallographic Phase Stabilities and Electronic Structures in AgNbO₃ by First-Principles Calculation.

Akio SHIGEMI, Takahiro WADA

Department of Materials Chemistry, Ryukoku University, Seta, Otsu 520-2194, Japan

We have primarily used Pb(Zr,Ti)O₃ (PZT) as piezoelectric materials. Recently, lead-free piezoelectric ceramic materials have come under the spotlight from the viewpoint of environmental protection. ANbO₃ (*A* = Li, Na and K) has been studied as a candidate for a lead-free piezoelectric material that can replace PZT. We have theoretically studied the ANbO₃ (*A* = Li, Na and K) system [1-3] using a plane-wave pseudopotential method (CASTEP code) [4]. In a previous study, we evaluated the formation enthalpies of the various sodium niobate (NaNbO₃) phases [1,3]. The formation enthalpies obtained for the various phases, e.g., cubic (*Pm3m*), tetragonal (*P4/mbm*), orthorhombic (*Ccmm*, *Pnmm*, *Pbma*) and rhombohedral (*R3cR*) phases, decrease with decreasing crystal symmetry, and the lowest symmetry rhombohedral (*R3cR*) phase was found to have the lowest formation enthalpy. This result corresponded to the experimental result that the rhombohedral phase was stable at ultra low temperatures. On the other hand, silver niobate (AgNbO₃) in the perovskite structure shows weak ferroelectricity at room temperature and undergoes several phase transitions with temperature. AgNbO₃ assumes several phases that crystallize in the perovskite structure similar to NaNbO₃.

In this study, in order to investigate the phase stability of AgNbO₃, the formation enthalpies of both physically the realized cubic (*Pm3m*), tetragonal (*P4/mbm*) and orthorhombic (*Cmcm*, *Pbcm*) phases as well as the virtual phases, the orthorhombic (*Pc2₁b*) and rhombohedral (*R3cR*) phases, which are observed in NaNbO₃, have been obtained using a plane-wave pseudopotential method. By the use of the Neumann-Knopp law [5], the formation enthalpy at temperature *T* for various AgNbO₃ phases can be approximately expressed as the following equation (Refer to [2]):

$$\Delta H_f^T(\text{AgNbO}_3) \approx E_t(\text{AgNbO}_3) - [E_t(\text{Ag}) + E_t(\text{Nb}) + 3E_t(\text{O})], \quad (1)$$

where ΔH_f is the formation enthalpy and E_t is the total energy per formula unit at 0 K. The determined formation enthalpies for various AgNbO₃ phases are plotted in FIG. 1. The theoretical value for cubic AgNbO₃ phase is estimated to be -941.6 kJ/mol. We previously reported that the theoretical value for the cubic NaNbO₃ phase, i.e., $\Delta H(\text{NaNbO}_3)$ was -1291.5 kJ/mol, which agreed with the experimental formation enthalpies [6] within an error of $\pm 3\%$. From this fact, we consider the theoretical formation enthalpies of AgNbO₃ are reliable to the same level of accuracy. The theoretical formation enthalpy for the AgNbO₃ decreases with decreasing crystal symmetry. Although the orthorhombic (*Pbcm*) phase with lower symmetry has the lowest formation enthalpy among the physically realized phases, the virtual rhombohedral (*R3cR*) phase with the lowest symmetry has the lowest formation enthalpy among all phases. In light of formation enthalpies, the rhombohedral phase of AgNbO₃ is most stable at low temperatures. There, we believe that the rhombohedral (*R3cR*) phase exists at extremely low temperatures.

Additionally, we have investigated the electronic structure of the various AgNbO₃ phases, and discuss these results in comparison with the electronic structures of NaNbO₃. The electronic structures of the various phases of AgNbO₃ and NaNbO₃ are calculated within the generalized gradient approximation (GGA-PBE). The TDOS and PDOS for the various AgNbO₃ phases are shown in FIG. 2. In normal perovskite compounds such as NaNbO₃, i.e., in the perovskite compounds having an *A*-site atom without *d* orbital electrons, the top of the valence band consists of only O 2p components, and the orbital component of Na at *A*-site does not appear in the valence band. In this case, the chemical bonding between the Na 3s and O 2p orbitals is ionic while the chemical bonding between Nb 4d and O 2p orbitals is partially covalent. On the other hand, even though the Ag 4d and O 2p components in AgNbO₃ lie in the valence band, the filled Ag 4d electrons may affect on the bonding of the O atoms. Therefore, the chemical bonding between Ag and O atoms becomes ionic with some covalent component and the chemical bonding between the Nb 4d and O 2p orbitals is partially covalent. In the various phases both AgNbO₃ and

NaNbO₃, the theoretical bandgaps of the anti-ferroelectric and ferroelectric phases with lower symmetry are wider than those of paraelectric phases due to the contribution of the Nb-O short bonds.

References

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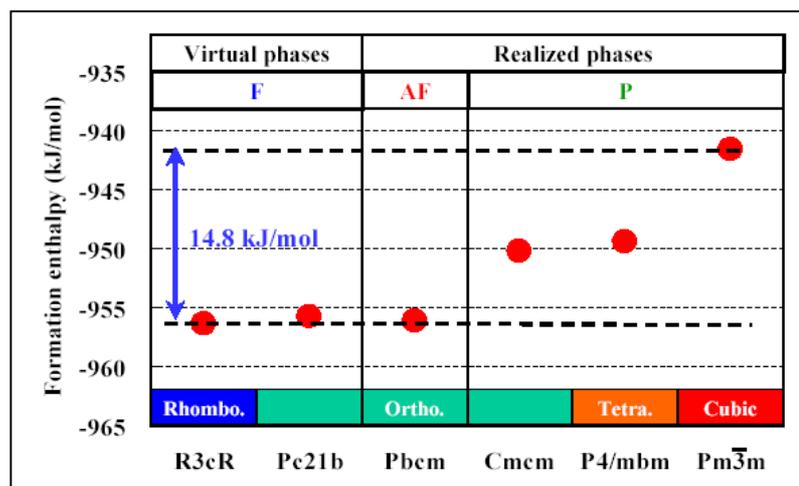


FIG. 1. Theoretical formation enthalpies for various AgNbO₃ phases. P, AF, F denote paraelectric, anti-ferroelectric and ferroelectric phases, respectively.

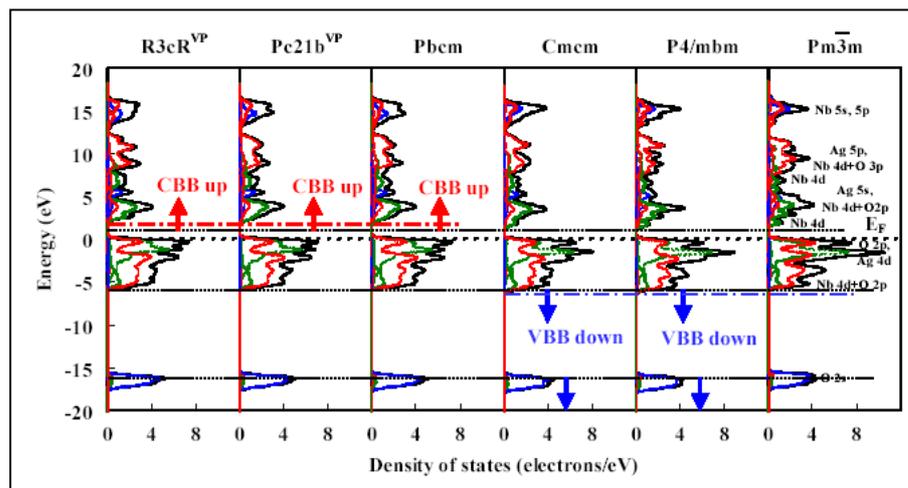


FIG. 2. Total and partial densities of states (TDOS and PDOS) for various AgNbO₃ phases. Black, blue, red and green lines are shown total, s, p and d components, respectively. Conduction band bottom: CBB, valence band bottom: VBB. The energy level of valence band top is set to 0 eV (= Fermi energy: E_F).