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First principles calculations on elasticity, electronic structure and bonding properties of antiperovskites $ANTi_3$ (A = Al, In and Tl)

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ABSTRACT

We use an ab initio pseudopotential plane wave (PP-PW) method within the generalized gradient approximation (GGA) and the local density approximation (LDA) to study the structural, elastic and electronic properties of the unexplored antiperovskite $ANTi_3$ compounds. The elastic constants C_{11}, C_{12}, C_{44} and their pressure dependence are calculated. We derived the bulk, shear and Young's moduli for ideal monocrystalline and for polycrystalline $ANTi_3$ aggregates which we have classified as ductile in nature. Band structures reveal that these compounds are conductors. The covalent ionic bands nature is due to the strong hybridization between Ti 3*d* and N 2*p* states. The Ti 3*d* states play dominant roles near the Fermi levels for all these compounds. The energy difference between spin polarized calculations and the nonspin polarized calculations indicate that $ANTi_3$ compounds exhibit magnetism at their equilibrium lattice constants.

1. Introduction

Intermetallic perovskite nitrides or carbides (formula AXM_3) where X is a main group (III–V) element, A is either carbon or nitrogen, and M is a transition metal [1] display also, a wide range of interesting physical properties and have numerous technological applications, such as giant magnetoresistance [2]. It is called as antiperovskite structure because the transition metals are located at the corners of the octahedron cage in contrast to the ordinary perovskite structure [3]. The intermetallic antiperovskite AXM_3 are related to both classical intermetallics of $AuCu_3$ type and classical oxide perovskites such as $CaTiO_3$ [4]. Among them, $MgCNi_3$ is the first oxygen-free superconductor at 8 K [5], which oriented many experimental and theoretical works towards the investigation of the physical properties of this compound; especially its superconductivity, however, the nature of its superconductivity is still controversial [6]. In order to found uniform behavior in this type of materials, some attention has been paid to the related compounds such as $AlCNi_3$, $CdCNi_3$, $GaCNi_3$, $InCNi_3$ and $ZnCNi_3$. Only $CdCNi_3$ was a superconductor at ~3.4 K [7,8]. The T_c temperature is relatively close to those found recently for the new superconductor $ZnNyNi_3$ at ~3 K [8]. On another hand, the lower T_c of $CdCNi_3$ than that of $MgCNi_3$ was explained by the smaller density of states at the Fermi energy and the enhanced ferromagnetic correlation in $CdCNi_3$ [6].

In order to search a new superconductors antiperovskites, Schaak et al. [4] have synthesized intermetallic perovskite borides and carbides AXM_3 compounds (A = Mg, Ca, Sc, Y, Lu, Zr, Nb; X = B, C; M = Ni, Ru, Rh, Pd, Pt) either by arc melting. The authors have showed that many of these compounds exist over a wide range of stoichiometries, which could critically influence their superconducting properties. Very recently, Cao et al. [8] have synthesized new intermetallic antiperovskite type ternary nitrides $InNCo_3$ from In_2O_3 and Co powders under NH_3 atmosphere at 600 °C with spin glass like behavior. Besides the experimental efforts, many theoretical investigations were also carrying out, especially on the electronic structure and magnetic properties [3,4,6,8,9]. Shim et al. [9] as an example, have performed first principles electronic structure and magnetic calculations using local density approximation LSDA on $GaCMn_3$ and related antiperovskite Mn compounds $ZnNMn_3$, $ZnCMn_3$, and $SnCMn_3$. The authors have confirmed that $SnCMn_3$ compound has a complicated magnetic structure with unstable ferromagnetic FM phase. Mn-based antiperovskite nitrides $ANMn_3$ (A = Cu, Zn, Ga, Ge, etc.) show large negative thermal expansion triggered by AFM or FM transition [8]. It is our ambition to carrying out a ab initio calculation since it was expected

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that the use of new 3d transition metal in antiperovskite nitrides or carbide fascinating the physical properties.

The ternary titanium nitrides $ANTi_3$, where A is from the group III, are isostructural to $MgCNi_3$ and belong to the antiperovskite type compounds. The ideal cubic antiperovskite structure for $ANTi_3$ compounds (#221) contains one formula with the *Wyckoff* positions of the atoms are A 1a (0, 0, 0), N 1b (0.5, 0.5, 0.5) and Ti 3c (0, 0.5, 0.5).

In the present study, lattice parameter, elastic constants, bulk, shear, and Young's moduli and Debye temperature, as well as the electronic structures and magnetic properties of $AlNTi_3$, $InNTi_3$ and $TlNTi_3$ were determined, probably for the first time, in order to fully take advantage of these compounds for eventual technological applications such as superconductivity. Some relationships between the various properties were studied. In addition, we have also compared the properties of $ANTi_3$ with those obtained for $ACTi_3$ compounds.

2. Calculation method

First-principles methods have already used to explore a variety of material properties and shown a good accuracy in the study of many physical and chemical properties for a wide scale of materials [10]. All our investigations were based on density functional theory (DFT). The exchange–correlation potential is treated within the local density approximation (LDA), developed by Ceperley and Alder and parameterized by Perdew and Zinger (CAPZ) [11,12], as well as the generalized gradient approximation (GGA) of Perdew et al. [13] as invoked by the framework package CASTEP Cambridge Serial Total Energy Package [14]. Interactions of electrons with ion cores were represented by the Vanderbilt-type ultrasoft pseudopotential for (N and C), Sn and Mn atoms [15].

The kinetic cut-off energy for the plane wave expansion is taken to be 400 eV, which was large enough to obtain good convergence. In the Brillouin zone integrations, $8 \times 8 \times 8k$ points were determined according to Monkhorst–Pack scheme [16].

Based on the Broyden–Fletcher–Goldfarb–Shenno (BFGS) [17] minimization technique, the system reached the ground state via self-consistent calculation when the total energy is stable to within 5×10^{-6} eV/atom, less than 10^{-2} eV/Å for the maximum ionic Hellmann–Feynman force and maximum stress within 2×10^{-2} eV Å^{-3}.

The elastic coefficients were determined by applying a set of given homogeneous deformations with a finite value and calculating the resulting stress with respect to optimizing the internal atomic degrees of freedoms [18]. The criteria for convergences of optimization on atomic internal freedoms were selected as the difference of total energy within 10^{-6} eV/atom, ionic Hellmann–Feynman force within 2×10^{-3} eV Å^{-1} and maximum ionic displacement within 10^{-4} Å. One strain pattern, with nonzero first and fourth components, in which, two positive and two negative amplitudes were used, gives stresses related to all three independent elastic coefficients for the cubic system.

3. Results and discussion

3.1. Structural properties

First, the equilibrium lattice constants a (Å) for the ideal stoichiometric unexplored antiperovskite $ANTi_3$ with (A = Al, In and Tl) were calculated. The results are listed in Table 1, which are very close to the measured ones [19,20] with small differences due to the reliability of the present first-principles computations. Better theoretical results are obtained with the GGA, since its known that the use of LDA gives slight underestimation (overestimation) of the lattice constants (bulk modulus) [6]. The calculated lattices parameter of $ANTi_3$ compounds increases in the following sequence: a_0 ($ALNTi_3$) < a_0 ($InNTi_3$) < a_0 ($TlNTi_3$). This can be understood from the fact that the atomic radius of Tl (1.7 Å) is larger than that of In (0.8 Å) and Al (0.535 Å) [21].

The bulk modulus B at zero pressure and its pressure derivative B' are calculated by fitting pressure volume data to a third order Birch–Murnaghan equation of state (EOS) [22], employing a dense sampling technology in the low pressure region. Hence our results for B are good and accurate (Fig. 1). Since we are note aware with any previous theoretical result on $ANTi_3$ compounds, our values of B are compared to those calculated for $ACTi_3$ by Medkour et al. [23] which were somewhat close to our one. In addition, our results were compared to those obtained for the first antiperovskite superconductor $MgCNi_3$: the measured value of the bulk modulus of $MgCNi_3$ is ~157 GPa [24], while the calculated ones are ~172 and ~207 GPa using GGA and LDA, respectively [6].

Table 1
Calculated a_0 (in Å), B_0 (in GPa) and B' (calculated from Birch–Murnaghan EOS fitting) compared to experiment data.

	Present work		Experiments
	GGA	LDA	
$AlNTi_3$			
a_0	4.1123	4.051	4.112 [19]
B_0	162.88 ± 0.13	183.41 ± 0.21	
B'	4.054 ± 0.01	4.027 ± 0.02	
$InNTi_3$			
a_0	4.195	4.116	4.190 [20]
B_0	152.961 ± 0.14	183.41 ± 0.21	
B'	4.220 ± 0.01	4.027 ± 0.02	
$TlNTi_3$			
a_0	4.204	4.124	4.191 [20]
B_0	152.557 ± 0.5	183.40 ± 0.19	
B'	4.335 ± 0.05	4.029 ± 0.02	

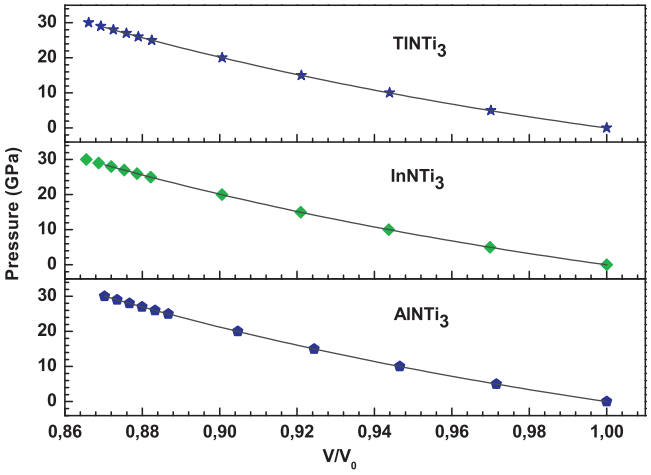

Fig. 1. Calculated pressure–volume relation for $ANTi_3$ compounds. V_0 is the equilibrium volume. The solid lines are given by the Birch–Murnaghan equation of state; parameters are listed in Table 1.

3.2. Elastic properties

The elastic constants of $ANTi_3$ compounds are listed in Table 2. The errors quoted for C_{ij} values are associated with the deviation of the stress strain relationship from linearity [25]. The three independent elastic constants in a cubic symmetry (C_{11}, C_{12}, and C_{44}) were estimated by calculating the stress tensors on applying strains to an equilibrium structure with applied pressure up to 30 GPa. Kumar et al. [24] has reported in experimental work that no phase transition for $MgCNi_3$ was observed for applied pressure up to 32 GPa. All C_{ij} constants for $ANTi_3$ compounds are positive and satisfy the criteria [26] for mechanically stable crystals else the ones obtained from GGA calculations for $InNTi_3$. This result can be explained by the underestimation associated with the use of GGA but experimental confirmation is necessary:

$$C_{44} - P > 0 \quad (1)$$

$$\frac{(C_{11} - C_{12})}{2} - P > 0 \quad (2)$$

$$\frac{(C_{11} + 2C_{12} + P)}{3} > 0 \quad (3)$$