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A Theoretical Study of Structural, Electronic and Elastic Properties of the Antiperovskite $SnNCa_3$

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Abstract: The structural, mechanical, electronic and phonon properties of antiperovskite $SnNCa_3$ compound in the cubic phase were systematically investigated by means of the density functional theory. The computed lattice constants and bulk modulus are well in accordance with the literature. The mechanical stability of the compound was examined via obtained elastic constants. The results indicated that $SnNCa_3$ antiperovskite compound is mechanically stable and brittle based on the Pugh`s criteria. The electronic band structure of the compound suggest that the material is metallic; the largest contribution to the conductivity are due to electrons of Sn-5p, N-2p and Ca-3d orbitals. In addition, phonon distribution curves and their corresponding density of states were obtained for the first time using the linear response approach by means of the density functional perturbation theory. The phonon properties investigation exhibited that $SnNCa_3$ antiperovskite compound is dynamically stable.

Antiperovskit $SnNCa_3$ Bileşiğinin Yapısal, Elektronik ve Elastik Özelliklerinin Teorik Olarak İncelenmesi

Anahtar Kelimeler
İlk tepki hesaplaması,
DFT,
Elektronik özellikler,
Elastik sabiti,
Fonon

Özet: Kübik fazdaki antiperovskit $SnNCa_3$ bileşiğinin yapısal, mekanik, elektronik ve fonon özellikleri yoğunluk fonksiyonel teorisi kullanılarak sistematik olarak incelenmiştir. Hesaplanan örgü sabitleri ve bulk modülleri literatürdeki verilerle mükemmel bir uyum içerisindedir. Bileşiğin mekanik kararlılığı elde edilen elastik sabitlerinden yola çıkılarak değerlendirilmiştir. Sonuçlar bileşiğin mekanik kararlı olduğunu göstermiştir. Pugh kriterine göre ise de bileşik kırılgandır. Bileşiğin elektronik bant yapısı metalik karakterde olduğunu göstermiş olup, iletkenliğe en büyük katkı Sn-5p, N-2p ve Ca-3d orbitallerindeki elektronlardan gelmektedir. Fonon dağılım eğrileri ve onlara karşılık gelen durum yoğunlukları yoğunluk fonksiyonel pertürbasyon teorisi çerçevesinde lineer tepki yaklaşımı kullanılarak ilk defa elde edilmiştir. Elde edilen fonon eğrilerine göre $SnNCa_3$ anti perovskit bileşiği dinamik kararlıdır.

1. Introduction

Perovskite materials, ABX_3 where A and B are cations, X is an anion, have been great of interest owing to their unique chemical and structural properties. These materials can be synthesised with a wide range of elements where large (ionic radius) cations sit in the A site and small cations sit on the B site. As a results of these features, they can be used in semiconductors, fuel cells, batteries, sensors, membrane reactors, hydrogen production and so on [1].

Antiperovskite materials on the other hand possess similar crystal structure only by interchanging the positions of cations and anions. Having good thermoelectric properties and broad band gaps made these materials attractive for researchers for the last two decades. These materials have the ability to extract waste heat and turn it into electricity which made them interesting for any industrial application [2]. Due to these thermoelectric and superconducting features, antiperovskite materials have been studied by many researchers [3-14]. A group of calcium nitrides ($MNCa_3$ with M = P, As, Sb, Bi, Ge, Sn, Pb) were synthesised by Chern *et al.* [5] and reported a change from cubic to orthorhombic structure for $PNCa_3$ and $AsNCa_3$ owing to small radius of P and As. The density functional theory calculation was carried out by Moakafi *et al.* [7] for $SbNCa_3$ and $BiNCa_3$ cubic

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antiperovskite compounds and reported that both compounds are semiconductors. Haddadi *et al.* [14] conducted an ab initio calculation for $XNCa_3$ (X=Ge, Sn and Pb) and found that all compounds are electrical conductors and metallic in nature. The physical properties of $TlNCa_3$ [15] and $AuNCa_3$ [16] have been studied and reported having metallic character for both compounds. Also, magnezyum based antiperovkites namely; $AsNMg_3$ and $SbNMg_3$ were synthesised and reported as ionic semiconductors [8, 17, 18]. The electronic properties of $MNSr_3$ and $MNBa_3$ (M=Sb, Bi) antiperovskite compounds were investigated [19] and described as semiconductor materials.

As mentioned above that calcium nitrides have been taking great interest from the researchers owing to their outstanding features. In addition to this, the properties of antiperovskites such as magnetic, optic, thermoelectric and mechanical dependent upon their electronic properties. Even, a slight change in electronic properties can result in variations previously listed properties. Hence, it is important to reveal a material's electronic structure, density of states and phonon properties fully before undertaking further investigation or application. The theoretical investigation using first principles calculations offer revealing those properties with high accuracy. Motivated by listed reasons above, this study presents a detailed investigation of cubic antiperovskite $SnNCa_3$ compound's electronic, magnetic, structural and dynamic properties in the frame of density functional theory.

2. Material and Method

The first-principles calculations were carried out using the Quantum-ESPRESSO program package [20]. All calculations were done with the Density functional theory (DFT) within the generalized gradient approximation (GGA) using the Perdew-Burke-Ernzerhof (PBE) [21] parameterization for the exchange-correlation potential. The integral over the irreducible Brillouin zone was performed with a 8×8×8 k-point mesh. A kinetic energy cut off 70 Ry was employed for the plane-wave expansion of the electronic states. The electron charge density was expanded to a plane wave set up to an approximate kinetic energy cut-off of 700 Ry. Methfessel-Paxton type smearing was applied for integration up to the Fermi surface with σ = 0.01 Ry smearing parameter [22] so as to get a smooth density of states. Whilst investigation of the electronic structure, a finer grid 24x24x24 k-point was preferred in order to obtain high-quality charge density. The lattice-dynamical properties were computed within the framework of density functional perturbation theory (DFPT) in the linear response approach. Eight dynamical matrices were evaluated for phonon wave vectors on a 4x4x4 q-point mesh. The dynamical matrices at arbitrary wave vectors were evaluated by Fourier interpolation on this mesh. By minimising the total energy as a function of the lattice parameters, the ground state of compound was obtained.

Elastic constants can provide information about stiffness of a material against an externally applied strain, thus mechanical stability. Various properties such as melting temperature and strength can also be estimates indirectly from elastic constants [23]. It is possible to calculate the elastic constants from the slopes of the acoustic modes in the full phonon spectra [24, 25]. Sound velocities correspond to the small wave behaviour of acoustic phonons. These velocities are related to C_{11}, C_{12} and C_{44} as described in references [3, 26]. Once the single crystal elastic constants are calculated, the relevant polycrystalline properties such as Bulk modulus (B), Young's modulus (E), Shear modulus (G) are derived using the following standard relationships:

$$B = \frac{C_{11} + 2C_{12}}{3} \quad (1)$$

$$G = \frac{C_{11} - C_{12} + 3C_{44}}{5} \quad (2)$$

The Young's modulus (E) for mechanical engineering design is an important parameter and is defined in the following:

$$E = \frac{9BG}{3B + G} \quad (3)$$

The Poisson's ratio is also relevant and is defined as the rate of extension of the lateral contraction as follows:

$$\sigma = \frac{1}{2}\left(1 - \frac{E}{3B}\right) \quad (4)$$

3. Results

$SnNCa_3$ antiperovskite compound with the space group Pm-3m (#No: 221) has the chemical formula of AXB_3 with the 1:1:3 stoichiometric ratio where A and B presents cations and X presents an anion. The cubic phase of $SnNCa_3$ is illustrated in Figure 1 where Sn atoms are positioned at corners (0, 0, 0), N atoms are placed at (0.5, 0.5, 0.5) and Ca atoms are sit at (0.5, 0, 0).

The point where the pressure is minimum where the system is in equilibrium is chosen as the lattice constant of $SnNCa_3$ antiperovskite cubic compound. The minimum pressure point is determined by carrying out optimisation. The computed lattice constant and bulk modulus are given in Table 1 together with experimental and theoretical results in the literature.

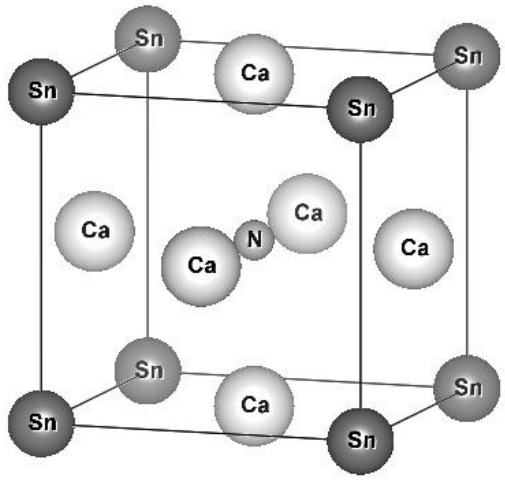

Figure 1. The crystal structure of $SnNCa_3$ in the cubic phase.

Table 1. The computed value of lattice constant (Å) and bulk modulus (GPa).

Comp.	Ref.	*a*	*B*
$SnNCa_3$	This work	4.898	54.17
	Exp. [5]	4.946	-
	Wien2k PBE-GGA [4]	4.915	54.23
	Wien2k Wu-Cohen [4]	4.850	60.51
	CASTEP GGA [14]	4.863	56
	CASTEP LDA [14]	4.771	65

The computed lattice constant in this study is about 1% smaller than the reported experimental value in the literature [5]. On the other hand, the computed bulk modulus of $SnNCa_3$ is well accordance with the reported values in the literature [4, 14] as can be seen from Table 1.

Electronic band structure and density of states were computed along high symmetry directions to investigate the electronic properties of the $SnNCa_3$ antiperovskite compound. Figure 2 presents the electronic structure of $SnNCa_3$ in the cubic phase while the total and partial density of states is given in Figure 3.

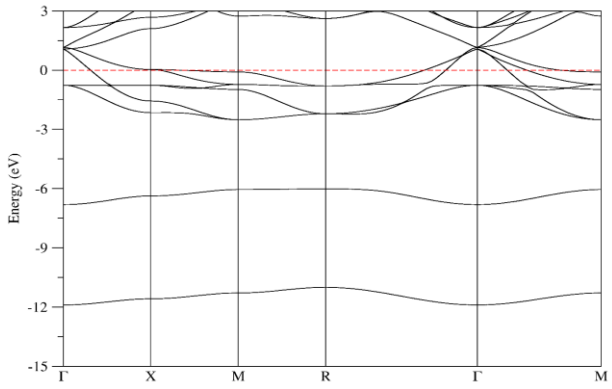

Figure 2. The computed electronic structure of $SnNca_3$ in the cubic phase.

The Fermi energy is subtracted from all band energies and taken as zero and shown with a dashed line in figures. As can be seen from Figure 2 that the Fermi energy level is cut by the conduction and valence band as the density of states in Figure 3 exhibits no gap at the Fermi level. Therefore, it can be said that $SnNCa_3$ antiperovskite compound has metallic character. The total density of states is found as $n(E_F)$= 3.148 states/eV cell at the Fermi level. This value is an indication of degree of metallicity. Also, the stability of a material is linked with the low density of states at the Fermi energy level. Therefore, the total density of states can be used to determine the most stable material among studied materials. As the value of $n(E_F)$ gets less, the material becomes much stable. However, only one material is considered in this study, thus no comparison is made.

The total and partial density of states of $SnNCa_3$ is demonstrated in Figure 3 in order to reveal the interactions between orbitals. As can be seen from partial density of states in Figure 3 that the contribution to the band above the Fermi level is owing to Sn-5p, N-2p and Ca-3d states whereas Sn-5s and N-2s states (between -6eV and -12 eV) contribute below the Fermi level. The electronic properties presented in this study is in a good agreement with [4, 14].

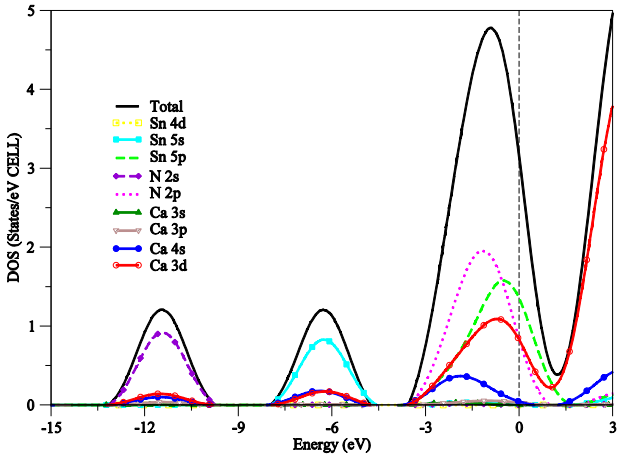

Figure 3. The computed total and partial density of states of $SnNCa_3$ in the cubic phase.

The elastic properties of a compound provides information about the crystal's mechanical, structural properties and their relationship [27]. Cubic structures have three different elastic constants; C_{11}, C_{12} and C_{44}. The elastic constants (C_{ij}) are computed by obtaining the total energy change via application of small strains to the lattice. From the differences in energy the elastic constants and bulk modulus (B), shear (G) and Young modulus (E) and Poisson ratio (σ) are calculated. The elastic constants of $SnNCa_3$ are given in Table 2 while mechanical parameters are presented in Table 3.

Table 2. The computed elastic constants (GPa) of $SnNCa_3$.

Comp.	Ref.	C_{11}	C_{12}	C_{44}
$SnNCa_3$	This work	97.309	32.600	42.4
	CASTEP GGA [14]	90	39	45
	CASTEP LDA [14]	104	44	47

Born criteria [28] for stability of elastic constants for a cubic phase is;

$$C_{11} > 0, \left(\frac{C_{11}}{C_{12}} > 1\right), (C_{11}^2 - C_{12}^2) and\ (C_{11} + 2C_{12}) > 0 \qquad (5)$$

As Table 2 indicates that the stability conditions are satisfied for $SnNCa_3$ compound. Thus, it can be said that $SnNCa_3$ is mechanically stable in the cubic phase with Pm-3m (#No: 221) group. These criteria also imply that C_{12} should be smaller than C_{11} and B must take an intermediate value between C_{11} and C_{12}. Thus, B;

$$C_{11} > B > C_{12} \qquad (6)$$

As can be seen from Table 1 and Table 2 that the bulk modulus and elastic constants that are obtained in this study confirm the Equations 5 and 6.

Table 3. The computed bulk modulus (GPa), shear modulus G (GPa), B/G ratio, Young's modulus E (GPa), Poisson's ratio σ of $SnNCa_3$.

Comp.	*B*	*G*	*B/G*	*E*	σ
$SnNCa_3$	54.17	38.10	1.42	92.59	0.22

The bulk and shear modulus in Table 3 suggest that $SnNCa_3$ can resist volume change under pressure since bulk modulus (B) is higher than that of shear modulus (G). In addition, B/G ratio is calculated to obtain information about brittleness and ductility of the material. The B/G ratio obtained in this study is 1.42 which suggest that $SnNCa_3$ antiperovskite compound is brittle due to the fact that this value is lower than 1.75. According to the Pugh criteria [29] if a material's B/G ratio is higher than 1.75, the material is ductile if it is lower, the material is brittle. The Poisson`s ratio for this material is computed as 0.22. It is said that if the Poisson`s ratio is around 0.1, the material has covalent bonding if that ratio is around 0.25, the material has ionic bonding [29, 30]. According to this assumption, $SnNCa_3$ antiperovskite compound should have ionic bonding, however this is not definitive. Therefore, in this study, the G/B ratio and Cauchy pressure (C_P=C_{12}−C_{44}) is also computed. The G/B ratio of $SnNCa_3$ is obtained as 0.7 which is similar to covalent materials ratios [29, 31]. Moreover, the Cauchy pressure of this material is negative which is a characteristic of covalent material [29, 31]. Thus, it can be concluded that $SnNCa_3$ antiperovskite compound has covalent bonding.

The phonon dispersion curve of $SnNCa_3$ is given in Figure 4 in the cubic phase.

$SnNCa_3$ has fifteen phonon modes (owing to 3N freedom degrees); twelve of being optical and three of them being acoustical. Because of the symmetry, the distinct number of phonon branches reduced along the principal Γ-X and M-R-Γ high symmetry directions. Phonon modes is reduced to 10 in the Γ-X high symmetry directions and 11 in the M-R-Γ high

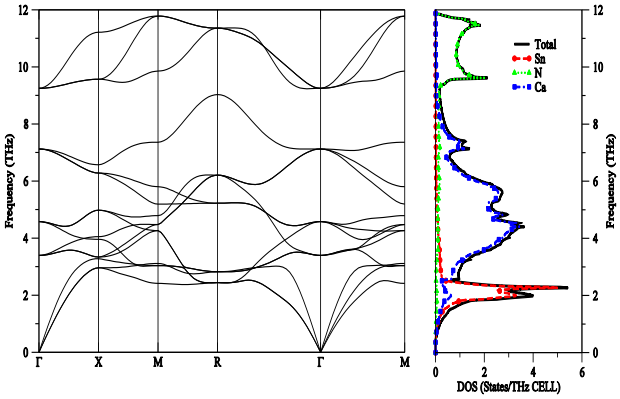

Figure 4. The phonon dispersion curves, total and projected density of states of $SnNCa_3$ in the cubic phase.

symmetry directions. The phonon modes are in the positive phonon frequency regions, hence $SnNCa_3$ is dynamically stable. The phonon dispersion curves indicate that the acoustic phonon frequencies are mostly due to Sn and Ca atoms with being higher effect of Sn atoms. Since Sn atoms are heavier than Ca and N atoms which result in lower vibration. Ca atoms vibrate mostly within nine optic modes in the mid frequency region as Sn atoms vibrate in the lower frequency region and N atoms vibrate in the high frequency region. The optic phonon frequencies are; 3.394, 4.578, 7.124 and 9.249 THz in the centre of Brilliouin zone. Unfortunately, there is no experimental or theoretical data in the literature for comparison with $SnNCa_3$ antiperevskite compound. Phonon dispersion curves and phonon density of states are obtained for the first time in this study and added to the literature.

4. Discussion and Conclusion

Structural, electronic, elastic and phonon properties of $SnNCa_3$ antiperovskite compound's properties with the space group Pm-3m (#221) were investigated using the GGA-PBE approach within the density functional theory. The lattice constant and bulk modulus of $SnNCa_3$ were obtained. By comparison with the literature, it is seen that the obtained results are well agree with the available data. The electronic band structures and the density of states indicated that $SnNCa_3$ antiperovskite compound is metallic in nature. The largest contribution to the conductivity are due to electrons of Sn-5p, N-2p and Ca-3d orbitals. The elastic constants evolution revealed that $SnNCa_3$ antiperovskite compound is mechanically stable. Bulk and shear modulus of the compound suggest that $SnNCa_3$ can resist volume change under pressure. In addition, $SnNCa_3$ is found to be brittle and covalent based on the B/G ratio, the G/B ratio and Cauchy pressure. The phonon properties investigation exhibits that $SnNCa_3$ antiperovskite compound is dynamically stable. This study carried out a systematic investigation to reveal all properties of $SnNCa_3$ antiperovskite compound including phonon and presented new data for future investigations and applications.

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