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MAX phases Nb_2AC (A = S, Sn): An *ab initio* study

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ABSTRACT

An *ab initio* investigation of structural parameters, elastic, electronic, thermodynamic and optical properties of MAX phases Nb_2AC (A = S, Sn) has been carried out by the plane wave pseudopotential method based on density functional theory (DFT). The effect on results of substitution of heavier Sn atoms for the lighter S atoms in the nanolaminate network has been made. The analysis of the electronic band structure shows that these compounds are electrical conductors, with contribution predominantly from the Nb 4*d* states. The temperature and pressure dependence of bulk modulus, Debye temperature, specific heats, thermal expansion coefficient of the nanolaminates are calculated for the first time using the quasi-harmonic Debye model with phononic effects. The estimated values of electron–phonon coupling constants ($\lambda \sim 0.49$, ~ 0.59) imply that Nb_2SC and Nb_2SnC are moderately coupled superconductors. Further first time detailed analysis of all optical functions reveals that Nb_2SC is a better dielectric material, and also both the phases, having similar reflectivity spectra, show promise as good coating materials in the energy regions 10–16.5 eV.

1. Introduction

The group of materials known as $M_{n+1}AX_n$ (MAX) phases since after the discovery by Nowotny et al. [1] have attracted great interest in the scientific communities worldwide [2–25] owing to a remarkable combination of properties, which are characteristic both of metals and ceramics. Furthermore out of a total of about 60 synthesized MAX phases [3], seven low-T_c superconductors have so far been identified. These are: Mo_2GaC [4], Nb_2SC [5], Nb_2SnC [6], Nb_2AsC [7], Ti_2InC [8], Nb_2InC [9], and Ti_2InN [10].

Sakamaki et al. [5] in 1999 reported the discovery of a new class of layered superconductor known as carbosulfide, Nb_2SC, which was in fact synthesized in 1968 by Beckmann et al. [11]. The electronegativity of C is same as S and as a result C-containing sulfide will be of particular interest in that it may cause a change in the structural dimensionality and physical properties of sulfide. Bortolozo et al. [6] report a study of the conductivity properties of Nb_2SnC sintered at both ambient and high pressure. The investigation revealed that this compound shows superconducting transition at ~7.8 K. The sample, when heat treated under high pressure, exhibited sharp T_c in both transport and magnetization properties. Prior to this El-Raghy et al. [25] synthesized Nb_2SnC along with other MAX phases and made several measurements.

The two MAX phases under consideration in this study possess a layered hexagonal structure (where blocks of transition metal carbides [MC] formed by edge-shared M_6C octahedra are sandwiched with *A* atomic sheets) and thus are similar to other groups of layered SCs such as high-T_c oxides and MgB_2. Halilov et al. [12] suggested that superconductivity in Nb_2SC arises due to pairing of electrons of S atoms arranged in planar networks. Since, according to the BCS theory $T_c \sim (\text{atomic mass})^{-1/2}$, the higher T_c of Nb_2SnC as compared to that of Nb_2SC (substitution of heavier Sn for the lighter S) clearly indicates that the pairing mechanism in these phases should have a different nature. Shein et al. [13] believe that the major role in the superconductivity of nanolaminates is played by the states of carbide (Nb–C) molecular layers. These layers, like the structure of the known superconductor NbC ($T_c \sim 11$ K) are composed of [Nb_6C] octahedra.

The electronic structures of Nb_2SC and Nb_2SnC have been carried out by Shein et al. [13] using FLAPW within GGA. Also Bouhemadou [14] has performed first-principles calculations for the structural, elastic properties of only Nb_2SnC under pressure by employing PP-PW approach based on DFT within the local density approximation (LDA). Kanoun et al. [17] investigated structural, elastic, electronic and dielectric function of four 211 MAX phases including Nb_2SnC. Shein and Ivanovskii [15] presented a theoretical study of the elastic properties for six superconducting MAX phases: Nb_2SC, Nb_2SnC, Nb_2AsC, Nb_2InC, Mo_2GaC, and Ti_2InC using VASP code in projector augmented wave formalism. Recently Romero and Escamilla [16] studied the pressure dependence of elastic and electronic properties of Nb_2SnC.

In view of the above discussions, it is clear that Nb_2SC has been subjected to limited theoretical study. Furthermore full optical as well as finite-temperature and finite-pressure thermodynamical

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Table 1
Calculated lattice parameters (a and c, in Å), ratio c/a, and internal parameters z_{Nb} for MAX phases Nb_2SC and Nb_2SnC.

Phases	a	c	c/a	z_{Nb}	Ref.
Nb_2SC	3.290	11.670	3.550	0.0956	This
	3.294	11.553	3.510	0.0964	[5] Exp.
	3.294	11.783	3.577	0.0960	[13]
	3.320	11.709	3.530	0.0952	[15]
Nb_2SnC	3.260	13.910	4.270	0.0820	This
	3.220	13.707	4.256		[6] Exp.
	3.241	13.802	4.258		[19] Exp.
	3.252	13.844	4.257	0.0830	[13]
	3.200	13.534	4.228	0.0846	[14]
	3.277	13.903	4.242	0.0828	[15]
	3.263	13.906	4.262	0.0821	[16]
	3.244	13.754	4.240	0.0830	[17]

investigations are absent for both the nanolaminates. The situation demands focus on areas where little or no work has been carried out. All these motivate us to perform such calculations on Nb_2SC and Nb_2SnC in addition to revisiting the existing theoretical works using methodology different from those used in previous published works [13–15]. The parameters of optical properties (dielectric function, absorption spectrum, conductivity, energy-loss spectrum, refractive index and reflectivity) for both the phases will be calculated and discussed. The paper is divided in four sections. In Section 2, we briefly describe the computational techniques used in this study. The results obtained for the structural, elastic, electronic, thermodynamic and optical properties for Nb_2SC and Nb_2SnC phases are presented and discussed in Section 3. Finally, Section 4 summarizes the main conclusion of the present work.

2. Computational methods

The zero temperature energy calculations presented in this work were performed by employing CASTEP code [26] which utilizes the plane-wave pseudopotential based on the framework of density functional theory (DFT). The electronic exchange–correlation energy is treated under the generalized gradient approximation (GGA) in the scheme of Perdew–Burke–Ernzerhof (PBE) [27]. The interactions between ion and electron are represented by ultrasoft Vanderbilt-type pseudopotentials for Nb, S, Sn and C atoms [28]. The basis set of valence electronic states was set to be $4d^4 5s^1$ for Nb, $3s^2 3p^4$ for S, $4d^{10} 5s^2 5p^2$ for Sn, $2s^2 2p^2$ for C. The correlation functional GGA-PBE was used in the calculations plane-wave basis set with 500 eV energy cut-off. For the sampling of the Brillouin zone a Monkhorst–Pack grid [29] of $10 \times 10 \times 3$ k-points for Nb_2SC, $13 \times 13 \times 3$ k-points for Nb_2SnC were employed. All the structures were relaxed by BFGS methods [30]. For the geometry optimization, the convergence tolerances were set as follows: 1×10^{-5} eV/atom for the total energy, 0.002 eV/Å for the maximum force on atoms, 0.05 GPa for the maximum stress, 1×10^{-3} Å for the maximum atomic displacement.

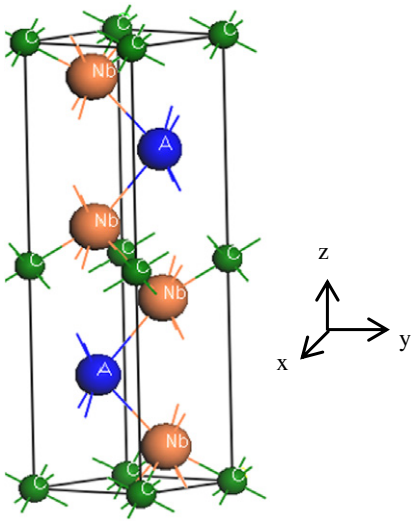

Fig. 1. Crystal structure of layered MAX phases: Nb_2AC (A = S, Sn).

The thermodynamic properties of Nb_2SC and Nb_2SnC were investigated using the quasi-harmonic Debye model, the detailed description of which can be found elsewhere [31,32]. Here we have calculated the bulk modulus, volume thermal expansion coefficient (VTEC), specific heats and Debye temperature at different temperatures and pressures. For this purpose we used $T = 0$ K, $P = 0$ GPa energy–volume calculation based on DFT method to obtain necessary E–V data employing the third order Birch-Murnaghan EOS [33].

3. Results and discussion

3.1. Structural and elastic properties

The Nb_2AC (A = S, Sn) phases possess the hexagonal structure which crystallizes in the space group $P6_3/mmc$ (No. 194) and has 8 atoms in one unit cell, where blocks of transition metal carbides [NbC] (formed by edge-shared Nb_6C octahedra) are sandwiched with A atomic sheets (see Fig. 1). The Wyckoff positions of atoms in Nb_2AC are – C: $2a$ [(0, 0, 0), (0, 0, 1/2)], A: $2d$ [(1/3, 2/3, 3/4), (2/3, 1/3, 1/4)], and Nb atoms: $4f$ [(1/3, 2/3, z_{Nb}), (2/3, 1/3, z_{Nb} + 1/2), (2/3, 1/3,$-z_{Nb}$), (1/3, 2/3, $-z_{Nb}$ + 1/2)] (see [2,3]).

The calculated fully relaxed equilibrium values of the structural parameters of the two phases are presented in Table 1 together with other theoretical [13–17] and experimental results [5,6,19]. The comparison shows that the calculated values are in good agreement with the available experimental results.

Table 2
Calculated C_{ij}, (in GPa), B (in GPa), G (in GPa), Y (in GPa), v, A, A_1, k_c/k_a for Nb_2SC and Nb_2SnC.

Phases	C_{11}	C_{12}	C_{13}	C_{33}	C_{44}	B	G	Y	v	A	A_1	k_c/k_a	Ref.
Nb_2SC	320.1	100.8	152.5	327.2	125.2	196.8	107.7	273.2	0.270	1.14	1.46	0.66	This
	303.6	116.9	155.1	315.7	88.1	220.9	88.6	234.5	0.323	0.94	1.14	0.69	[15]
Nb_2SnC	265.3	94.6	122.6	261.7	108.2	163.4	88.9	225.8	0.270	1.26	1.53	0.82	This
	315.0	99.0	141.0	309.0	124.0	210.2[a]	106.8	274.0[a]	0.282[a]	1.15[b]	1.45[b]	0.78[b]	[14]
	254.8	100.8	120.0	243.0	58.9	171.1	66.8	177.3	0.327	0.77	0.91	0.94	[15]
	286.5	91.5	126.8	288.5	99.8	171.1	93.3	236.9	0.271	1.02[b]	1.24[b]	0.77[b]	[16]
	340.9	105.6	169.0	320.6	183.3	209.0	125.8	314.5	0.250	1.56[b]	2.27[b]	0.72[b]	[17]
	268.0	86.0	119.0	267.0	98.0	161.0	89.0	225.4[b]	0.266[b]	1.08[b]	1.32[b]	0.78[b]	[18]

[a] Errors corrected using the published data [14].
[b] Estimated using published data of respective authors.