Intercalation of alkali metals (Li, Na, and K) in molybdenum dinitride (MoN_2) and titanium dinitride (TiN_2) from first-principles calculations

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ABSTRACT

We studied ternaries of nitrogen-rich titanium and molybdenum compounds combined with alkali metals (Li, Na, and K) as potential layered materials. LiMoN_2 has already been synthesized with layered structure corresponding to intercalated 3R-MoS_2 , however efforts to completely deintercalate Li from LiMoN_2 were unsuccessful. We studied ternaries MAN_2 (A: Ti, Mo and M: Li, Na, K) having layered crystal structures, their deintercalation, and the layered binaries TiN_2 and MoN_2 within density-functional theory. We find that LiMoN_2 and NaMoN_2 have a layered structure isotypic to 2H-MoS_2 with Li and Na ions filling interlayer spaces whereas LiTiN_2 and NaTiN_2 are isotypic to $\alpha\text{-NaFeO}_2$. Both KMoN_2 and KTiN_2 have a different kind of structure isotypic to SrTiN_2 which differentiates K from Li and Na. Ternaries Li(Na)MoN_2 and Li(Na)TiN_2 are all metals and the alkali metal atoms are present as ions in these structures. Partially deintercalated ternaries suggest that layers can interact strongly and the material can lose its layered form. Furthermore, we find that binary MoN_2 having a layered structure is not stable since monolayer MoN_2 has a positive formation energy and N atoms belonging to neighboring layers interact and form N_2 dimer in between Mo layers in which case formation energy becomes negative indicating that structure becomes more stable. These results can explain the decomposition of LiMoN_2 during the experimental trials of complete deintercalation. In contrast, TiN_2 has a negative formation energy already without interaction of N atoms belonging to neighboring layers.

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1. Introduction

Binaries of transition metal (TM) nitrides, TMN_x , have been studied for values of $x \leq 1$. However, nitrogen-rich ($x > 1$) binary transition metals have rarely been reported. This is thought to be due to the strong binding of two N atoms forming a N_2 molecule which can be released as gas. A different path to obtain nitrogen-rich binaries can be considered. For example, ternaries with alkali metal or alkaline earth metal atoms results in layered structures. Transition metal sulfides, selenides and oxides present many examples of layered structures. Transition metal layers are sandwiched between sulfur layers and these layers are separated with the ionic alkali metal layers which can be deintercalated. MAS_2 with A being one of Sc, Y, Ti, Zr, Hf, V, Nb, Ta, Cr and M being one of the alkali metal atoms (Li, Na, K) are among the examples of layered ternaries with an alkali metal atom [1–13]. There have been attempts to obtain ternaries of nitrides and LiMoN_2 , LiWN_2 , NaTaN_2 ,

CaTaN_2 , NaNbN_2 , SrZrN_2 , SrHfN_2 have been synthesized and formed layered structures similar to sulfides [14–17]. However, a complete picture of transition metal dinitrides is lacking.

MoN_2 has been recently synthesized at a relatively low pressure and from the comparison of the XRD data with calculation results, a layered structure having ABC stacking isotypic to 3R-MoS_2 was proposed as the crystal structure in which MoN_2 units in every layer has a local structure of a triangular prism formed by N atoms around Mo atoms (known as the H phase as in 2H-MoS_2) [18]. However, from first-principles structure search calculations the layered R3m structure is found to be unstable and a non-layered structure of $\text{P6}_3\text{mmc}$ symmetry is found to be the ground state structure [19]. Previously, LiMoN_2 has been synthesized also having a rhombohedral crystal structure of 3R-MoS_2 with Li filling the interlayer spaces (galleries) [14]. However, in this experimental study, attempts of deintercalating all the Li atoms in layered MoN_2 through chemical or electrochemical methods were unsuccessful. The inability of complete deintercalation was thought to be due to either difficulty of Li diffusion or high binding energy at low Li concentrations.

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In order to understand layered MoN_2 isotypic to MoS_2 and its intercalation/deintercalation (inserting/removing alkali metal atoms to/from the structures), MoS_2 can guide us. With Li intercalation of MoS_2 , a structural phase change has been observed such that 2H-MoS_2 transforms into 1T-MoS_2 . 2H-MoS_2 has a local structure of a triangular prism around Mo atoms and 1T-MoS_2 has a local structure of a octahedron. Experimentally it has been shown that upon annealing above 200°C , 1T-MoS_2 can transform into 2H-MoS_2 having similar optical properties such as photoluminescence exhibited by the mechanically exfoliated monolayer [20]. In particular, exfoliation of MoS_2 after Li intercalation inside an ionic liquid such as water (chemical exfoliation) assisted by ultrasonication and transferring the monolayers or few-layers to a substrate has been shown to be successful [21]. In this method, Li reacts with hydroxide and hydrogen gas is observed to be released. However, with Li intercalation structure changes to 1T-MoS_2 . 2H-MoS_2 structure is recovered with annealing. A similar kind of structural change can happen in MoN_2 . Investigation of this structural change should add to the understanding of the recently synthesized MoN_2 which is proposed to be a layered material.

In this work, we explored layered structures of ternary transition metal dinitrides with the chemical formula MAN_2 (A: Ti, Mo and M: Li, Na, K) and investigated the issues related to the deintercalation of LiMoN_2 encountered in the experiments. We also investigated the crystal structures of binaries TiN_2 and MoN_2 both in bulk and in two-dimension, and the associated electronic structures.

2. Method

We used Quantum-Espresso software for density-functional theory calculations using plane-wave basis set [22]. Semi-local Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional is used [23]. Ultrasoft pseudopotentials are used to replace core electrons and the states taken as valance are $3s^2 4s^2 3p^6 3d^2$, $4s^2 5s^1 4p^6 4d^5$, $2s^2 2p^3$, $2s^1$, $3s^1$, and $3s^2 4s^1 3p^6$ for Ti, Mo, N, Li, Na, and K, respectively. Monkhorst-Pack scheme is used to generate grid of k-points [24]. The energy cut-off of the wavefunctions and the charge density are 60 Ry and 740 Ry. Marzari-Vanderbilt smearing method with a smearing width of 0.01 Ry is used for the metallic systems [25]. Structure optimization is carried out by minimizing the stress and interatomic forces with convergence thresholds of 0.5 Kbar and 10^{-3} Ry/Bohr, respectively. Brillouin zone of MAN_2 compounds are sampled with k-point grids of $8 \times 8 \times 3$ for the 3R structure, $8 \times 8 \times 4$ for the 2H-a, 2H-b, and SrTiN_2 structures, $8 \times 8 \times 4$ for the 1T-a structure, $8 \times 8 \times 8$ for the 1T-b structure. Lattice constant and formation energy of rock-salt TiN are calculated as $a = 4.248 \text{ \AA}$ and -3.45 eV/TiN and are comparable to the experimental measurements of $a = 4.244 \text{ \AA}$ and -3.49 eV/TiN [26]. Hexagonal structure of $\delta\text{-MoN}$ is also considered and the lattice constants and formation energy of this system are calculated as $a = 5.776 \text{ \AA}$, $c = 5.702 \text{ \AA}$, and -0.659 eV/MoN where experimental measurements of $a = 5.733$ and $c = 5.611$ are comparable as well [27].

3. Results

A ternary phase of transition metal dinitride with an alkali metal, LiMoN_2 , has been experimentally obtained and the structure is reported to have rhombohedral symmetry as depicted in Fig. 1c [14]. We begin the discussion with LiMoN_2 and extend it to ternaries with Na and K. We also studied structures in which Mo is replaced with Ti, therefore we have 6 different ternaries with the chemical formula MAN_2 (M: Li, Na, K, and A: Ti, Mo). Except LiMoN_2 , these ternary transition metal dinitrides have not been

synthesized and the crystal structures of these materials are unknown. Ternaries of group IV transition metal (Ti, Zr, Hf) dinitrides with alkaline earth metals Sr and Ba have been synthesized [16]. Two different structures have been observed, KCoO_2 and $\alpha\text{-NaFeO}_2$. $\alpha\text{-NaFeO}_2$ structure with space group $R\bar{3}m$:R is depicted in Fig. 1e and labeled as 1T-b in this work since individual AN_2 layers have the structure of 1T-MoS_2 where coordination of S atoms around Mo atoms is octahedral. This is similar to the case of Li intercalation of MoS_2 where a structural change occurs from H-MoS_2 (trigonal prismatic coordination) to T-MoS_2 (octahedral coordination) after intercalation [20]. Additionally, we included LiTiS_2 structure [5], here labeled as 1T-a (see Fig. 1d), which is also an example for 1T phase with a different stacking of 1T-b. Two different stacking of intercalated 2H-MoS_2 structures with space group $\text{P6}_3\text{mmc}$ are included and labeled as 2H-a and 2H-b (Fig. 1a and b). The other structure, KCoO_2 is depicted in Fig. 1f and labeled as SrTiN_2 with P4/nmm space group since this material has been synthesized and adopts this structure and has interesting properties such as thermoelectricity [28]. In total, we tried five different layered structures and a non-layered structure (SrTiN_2); 2H-a, 2H-b, 3R- MoS_2 , 1T-a, 1T-b, and SrTiN_2 (Fig. 1). Although, a comprehensive structure search is not carried out here, these structures have been observed and we already know that LiMoN_2 adopts a layered structure and replacing Li with Na or K can result in similar structures. Therefore, we restricted our structure search for these six structures.

Calculated formation energies of these ternaries are reported in Table 1. LiMoN_2 and NaMoN_2 exhibit the same energy order and 2H-a structure (Fig. 1a) is the energetically most favored. Although the experimentally reported structure of LiMoN_2 has ABC type stacking with rhombohedral symmetry (3R), we found that AB stacking (2H-MoS_2) to be slightly more favorable. The energy difference between the AB stacking (2H) and ABC stacking (3R) for LiMoN_2 is about 60 meV/ LiMoN_2 which is 15 meV/atom. However these results are within PBE approximation for the ground state electronic structure and the energy contribution from lattice vibrations are not taken into account which can effect the energy order in this small energy window. In-plane lattice constant (a) and the interlayer distance between Mo layers ($d_{\text{Mo-Mo}}$) for the both structures 2H and 3R are comparable to the experimental measurements of the reported 3R structure (Table 1). In contrast to Li and Na, KMoN_2 has a different energy order and the energetically most favored structure is the SrTiN_2 structure. The energy difference with the second most energetically favored structure is large, more than twice, by 0.8 eV/ KMoN_2 , therefore SrTiN_2 structure is very stable compared to the rest of the structures for KMoN_2 . In the case of ternaries with Ti, we find different energetics for these structures compared to Mo. Instead of the H phase preferred by ternaries LiMoN_2 and NaMoN_2 , T phase is energetically favored for LiTiN_2 and NaTiN_2 . Energetically the most favored structure is the 1T-b structure and the energy difference with respect to the rest of the structures is large. Similar to KMoN_2 , KTiN_2 also prefers the SrTiN_2 structure among the structures that we have tried here. Therefore, in both cases of transition metal dinitrides of Mo and Ti, K exhibits a different kind of structure (non-layered) than Li and Na which results in intercalated layered structures either in H or T phase. In the favored structure of KMoN_2 and KTiN_2 , there are layers of MoN (or TiN) with a square lattice separated by two layers of KN (see Fig. 1f and g). However, the ternaries with Li or Na results in an hexagonal lattice isotypic to MoS_2 (H or T phase) in which layers of MoN_2 or TiN_2 are separated with the alkali metal layers.

Electronic structures and the density-of-states (DOS; total and projected to atomic orbitals) of these materials, LiMoN_2 (2H-a), NaMoN_2 (2H-a), KMoN_2 (SrTiN_2), LiTiN_2 (1T-b), NaTiN_2 (1T-b), and KTiN_2 (SrTiN_2) are presented in Fig. 2. Both LiMoN_2 and NaMoN_2 are metallic and have very similar electronic structures. There is no

Fig. 1. Layered structures considered for the ternaries MAN_2 .

Table 1

Formation energy, E_f (eV/f.u.) is defined with respect to bulk transition metal, N_2 molecule and the energy of bulk alkali metal. Experimental lattice constants of $LiMoN_2$; $a = 2.867$ Å, $d_{Mo-Mo} = 5.250$ Å [14].

	a	d_{Mo-Mo}	E_f		a	d_{Ti-Ti}	E_f
$LiMoN_2$ (3R)	2.91	5.29	-1.96	$LiTiN_2$ (3R)	3.01	5.00	-2.78
(2H-a)	2.92	5.21	-2.02	(2H-a)	3.03	4.81	-2.95
(2H-b)	2.90	5.36	-1.91	(2H-b)	2.99	5.16	-2.53
(1T-a)	2.93	5.35	-1.54	(1T-a)	2.98	5.19	-2.92
(1T-b)	2.96	5.13	-1.74	(1T-b)	3.02	4.86	-3.40
($SrTiN_2$)	3.87	5.74	-1.22	($SrTiN_2$)	3.62	6.07	-2.37
$NaMoN_2$ (3R)	2.96	5.91	-1.26	$NaTiN_2$ (3R)	3.08	5.64	-2.11
(2H-a)	2.96	5.81	-1.35	(2H-a)	3.08	5.52	-2.25
(2H-b)	2.95	5.99	-1.16	(2H-b)	3.07	5.76	-1.96
(1T-a)	2.99	5.92	-0.91	(1T-a)	3.06	5.73	-2.41
(1T-b)	3.01	5.96	-1.14	(1T-b)	3.08	5.49	-2.73
($SrTiN_2$)	3.92	6.20	-1.20	($SrTiN_2$)	3.72	6.55	-2.20
$KMoN_2$ (3R)	3.01	6.63	-0.53	$KTiN_2$ (3R)	3.13	6.34	-1.53
(2H-a)	3.01	6.51	-0.63	(2H-a)	3.13	6.29	-1.66
(2H-b)	3.00	6.70	-0.45	(2H-b)	3.12	6.42	-1.41
(1T-a)	3.05	6.59	-0.28	(1T-a)	3.12	6.42	-1.86
(1T-b)	3.07	6.41	-0.53	(1T-b)	3.13	6.26	-2.13
($SrTiN_2$)	4.01	6.93	-1.33	($SrTiN_2$)	4.01	6.92	-2.30

contribution to the valance band from Li 2s or Na 3s orbitals indicating the ionic character (charge transfer) of these alkali metal atoms in these layered materials. A difference regarding the electronic behavior between $LiMoN_2$ and $NaMoN_2$ is that, along the path $\Gamma-A$ in the Brillouin zone, there is a band that crosses the Fermi level in the electronic structure of $LiMoN_2$ which does not cross the Fermi level in the case of $NaMoN_2$. This path in the Brillouin zone corresponds to the out-of-plane direction in the crystal structure which indicates that the electronic transport properties in out-of-plane direction for these two layered structures can be different. We did not check spin polarization for these two

materials since experimentally $LiMoN_2$ is paramagnetic. $KMoN_2$ is found to be semi-metal. Upon projecting the states to atomic Mo 4d orbitals we find that conduction band minimum and valance band maximum is dominated by Mo 4d electrons. Partial occupation of these Mo 4d orbitals and vanishing energy gap between localized and delocalized d electrons as found within PBE approximation may not be a good enough approximation and there might be a finite gap between conduction band and valance band. However, we did not study strong electronic correlation here. We also find that anti-ferromagnetic solution to be more favorable by about 24 meV/ $KMoN_2$ with respect to non-magnetic solution, also favored over ferromagnetic solution, and the spin polarized states occupy the Mo 4d orbitals. Amount of the magnetization is $1.49 \mu_B/\text{cell}$ and there are two Mo sites per cell. Therefore, Mo atoms in the square lattice of MoN layer (Fig. 1g) in $KMoN_2$, have alternating spin directions. Similar to Mo, the ternaries of Ti are metallic as well without the presence of Li 2s, Na 3s, and K 4s electrons in the valance band indicating their ionic character in these systems. One of the differences between Mo and Ti is that the states at and around the Fermi level are dominantly of N 2p without a contribution from Ti 3d states for the ternaries of Ti whereas for Mo, there is about equal contribution from N 2p and Mo 4d states. Moreover, in the case of $KMoN_2$, the Mo 4d states contribute more than N 2p to the states at and around Fermi level.

Intercalation and deintercalation of $LiMoN_2$ has been experimentally investigated. Both with chemical and electrochemical methods, a complete deintercalation of Li from $LiMoN_2$ could not be achieved. Either oxidative strength of the chemicals used was insufficient or decomposition of MoN_2 has been observed below a certain Li concentration. Here, we optimized the structures with low Li or Na concentration in layered MoN_2 corresponding to the stoichiometries $Li_{0.125}MoN_2$ and $Na_{0.125}MoN_2$ in stage 2 structure which corresponds to one empty gallery (interlayer space) and one filled gallery (Fig. 3). Although, existence of this particular structure

Fig. 2. Band structures of MMoN_2 and MTiN_2 for the energetically favored structures indicated in parenthesis.

in this particular stage is unknown, we think that optimized structure of this structure can give us a hint regarding the unsuccessful attempts of complete deintercalation of LiMoN_2 in the experiments. As can be seen in Fig. 3, the interlayer distance ($d_{\text{Mo-Mo}} = 3.22 \text{ \AA}$ for both structures intercalated with Li or Na) of the empty gallery is much smaller than the typical van der Waals distance known for layered materials such as transition metal dichalcogenides and the N atoms of one layer are close enough to the Mo atoms of the neighboring layer to form stronger bonds such as covalent bonds or other types of bonds stronger than van der Waals interaction. Therefore the material is losing its layered form during deintercalation which could be one of the reasons of the inability of the complete deintercalation of Li from LiMoN_2 .

However, decomposition of the material has also been observed in the experiment and these results alone do not explain this observation. We have investigated the deintercalation of ternaries with Ti in another recent work and found similar results to the case of ternaries with Mo, therefore we do not discuss here [29].

Since there are problems with complete deintercalation of the ternary LiMoN_2 and NaMoN_2 and also decomposition of the material has been observed at low Li concentration, formation energy of binary MoN_2 , specifically the layered structure, can be helpful for understanding these issues. The interlayer binding energy in a layered material is very small compared to the energy of formation of individual layer. Therefore, in order to obtain a layered material, a single layer should be stable. We calculated the formation energy of

Fig. 3. Optimized structures of $M_{0.125}\text{MoN}_2$. (a) and (b) top view, (c) and (d) side views.

a single sheet of MoN_2 for both types of structures which are trigonal prismatic (H) and octahedral (T) depicted in Fig. 4. Monolayer T- MoN_2 is energetically much more favorable than H- MoN_2 by an energy difference of 0.28 eV/ MoN_2 , however both of the structure have large positive formation energies (Table 2). This result, that is separate bulk molybdenum metal and nitrogen molecule being energetically more favorable than these structures indicates the instability of MoN_2 as a layered material isotypic to MoS_2 . Furthermore, we optimized various structures for different stackings of both T- MoN_2 and H- MoN_2 (Fig. 5) in order to gain insight about the problems encountered with deintercalation of LiMoN_2 . The optimized structures presented in Fig. 5 show that N atoms initially belonging to a layer are interacting with the N atoms of a neighboring layer and forming N_2 dimers in between Mo layers for certain stacking modes in line with previous findings [19,30]. From the calculated formation energies (Table 2) it is understood that these structures with N_2 dimers in between Mo layers are the most energetically favored and moreover the only structures that have negative formation energies are these structures which are the structures labeled as P_0 and P_3 and obtained from an initially layered structure corresponding to a stacking of H- MoN_2 . These

Fig. 4. Two different structural phases (H and T) of monolayer AN_2 . (e) and (f) Hydrogen terminated structures.

results can explain the decomposition of the ternary LiMoN_2 at low Li concentration. N_2 dimers can form at low Li concentration and released from the material. Binary TiN_2 presents both similarities and differences to the binary MoN_2 . The difference between two is that monolayer TiN_2 has a negative formation energy for the H phase indicating the relatively better binding of Ti to N compared to Mo. Moreover, the phase change from T phase for the intercalated ternary TiN_2 to the H phase for the binary TiN_2 presents a similarity to the case of intercalation of MoS_2 . However, looking at the formation energies of the various different stacking modes of the bulk, we understand that N atoms belonging to neighboring TiN_2 layers interact strongly, therefore the structure loses the layered nature similar to the case of Mo. As a result, obtaining a layered binary TiN_2 can be as difficult as it is for the layered binary MoN_2 .

Additionally we obtained the electronic structure of monolayer T- MoN_2 which is energetically more favored than H- MoN_2 . The monolayer H- MoN_2 is found to be a ferromagnetic metal and T- MoN_2 is found to be a semi-metal (Fig. 6) and does not exhibit spin-polarization. For the case of TiN_2 , H phase is found to be much more favored than the T phase and have a large negative formation energy indicating the strong interaction of Ti with N. We do not discuss the electronic structure of monolayer H- TiN_2 here which we have presented in a recent study [29]. Moreover, hydrogen (H) termination of the monolayers can be considered in order to stabilize the structures. Here, we considered H termination on the N sites of both T and H phases. Formation energies become negative for the both H and T phases of MoN_2 and TiN_2 . Structural phase change is present in both cases. H- H_2MoN_2 becomes more favorable than the T phase and T- H_2TiN_2 becomes more favorable than the H phase. Electronic structures of the H terminated systems are presented in Fig. 6. H- H_2MoN_2 acquires a band gap of about 2 eV

Table 2
Formation energies E_f (eV/f.u.) with respect to bulk transition metal and N_2 molecule, in-plane lattice constant a and interlayer distance between transition metal planes d_{Mo-Mo} (d_{Ti-Ti}).

		A: Mo			A: Ti		
		E_f	a	d_{Mo-Mo}	E_f	a	d_{Ti-Ti}
Bulk	1T-AN ₂ (S ₀)	+1.20	3.00	5.34	+0.46	3.11	4.52
	1T-AN ₂ (S ₁)	+1.03	3.43	3.18	+0.18	3.36	3.26
	1T-AN ₂ (S ₂)	+0.44	3.05	4.06	-1.99	3.32	4.39
	1T-AN ₂ (S ₃)	+0.01	2.91	3.99	-1.82	3.07	3.64
	2H-AN ₂ (P ₀)	-0.79	2.93	3.90	-1.92	3.06	3.66
	2H-AN ₂ (P ₁)	+1.34	3.08	3.82	-1.55	3.23	4.76
	2H-AN ₂ (P ₂)	+1.46	3.00	5.12	-1.53	3.22	4.77
	2H-AN ₂ (P ₃)	-0.82	2.94	3.88	-2.06	3.04	3.69
	3R-AN ₂	+1.47	3.00	5.09	-1.53	3.22	4.78
Monolayer	T-AN ₂	+1.21	3.01	—	+0.55	3.14	—
	H-AN ₂	+1.51	2.99	—	-1.53	3.22	—
	T-H ₂ AN ₂	-0.98	2.96	—	-3.50	3.10	—
	H-H ₂ AN ₂	-2.11	2.95	—	-3.22	3.04	—

Fig. 5. (a)–(d) Different stackings of bulk 1T-MoN₂, (e)–(h) different stackings of 2H-MoN₂, and (i) ABC stacking with rhombohedral symmetry 3R-MoN₂ after optimization.

and T-H₂TiN₂ acquires a band gap of about 0.7 eV obtained with PBE functional.

As a result, a different approach to obtain layered forms of MoN₂ and TiN₂, as a monolayer or layered bulk, could be through chemical exfoliation of MAN₂ with M being one of the alkali metal atoms Li or Na inside an ionic liquid such as water, and later, by annealing, energetically favored structure T-MoN₂ and H-TiN₂ might be obtained as it has been performed to obtain 2H-MoS₂ [20]. Additionally, after the chemical exfoliation, monolayers could be transferred to a suitable substrate and the structure, although not favored, could be preserved on a substrate or sandwiched between layers of another 2D material such as graphene, *h*-BN or 2H-MoS₂ without performing annealing. Chemical elements such as hydrogen can further stabilize monolayers suspended inside water.

Furthermore, H terminated and stabilized monolayers can be restacked to form layered bulk forms of these nitrides. One can consider a battery application of these layered transition metal dinitrides. Li(Na)TiN₂ and Li(Na)MoN₂ have theoretical capacities of 351 mA h/g and 215 mA h/g, respectively. Considering the natural abundance of Ti, having the second lowest atomic mass among transition metals, higher theoretical capacity, and stronger interaction with N atoms, Ti is more attractive as a possible electrode for electrochemical battery application.

4. Conclusion

We studied layered structures of alkali metal transition metal dinitrides, MAN₂ (A: Ti, Mo and M: Li, Na, K). Among these

Fig. 6. Band structures of monolayers of TiN₂ and MoN₂ for the energetically favored structures (in T or H phase) and the effect of hydrogen (H) termination of the N sites on the electronic structures.

materials only LiMoN₂ has been experimentally synthesized. Although having a layered structure isotypic to MoS₂, complete deintercalation of Li from LiMoN₂ was unsuccessful in the experiments which is thought to be due to either difficulty of Li diffusion or high binding energy at low Li concentration. Decomposition of the material has also been observed during the trials of complete deintercalation. Through density-functional theory calculations, we understand that these issues are related to the fact that at low Li (or Na) concentration, neighboring layers interact with each other and the interlayer distance becomes much smaller than the typical van der Waals distance found in known layered materials such as transition metal dichalcogenides. Moreover, single layer of binary MoN₂ either in trigonal prismatic phase (H) or in octahedral phase (T) has a large positive formation energy with respect to bulk molybdenum metal and N₂ molecule indicating the instability of the structures. In the bulk, after optimizing different stackings of layered structures we found that N₂ dimers can form in between Mo layers and these structures are the only ones having negative formation energies. These results can explain the decomposition of the material observed in the experiments. However, in case of Ti, formation energy of the binary phase TiN₂ is negative with or without strong interaction of N atoms belonging to neighboring layers. Therefore, TiN₂ is more stable than MoN₂. Although, TiN₂ can exhibit similar difficulties with complete deintercalation as well due to same reasons that we found for the case of Mo. Monolayers of binary MoN₂ might be possible to obtain by binding

hydrogen on both side of the monolayers which can be achieved through chemical exfoliation of LiMoN₂ or NaMoN₂ inside water as it has been performed for intercalated MoS₂. Monolayer of TiN₂ has negative formation energy with and without H termination on the N sites. Structural change between H and T phases upon termination of N sites with H atoms is found for both TiN₂ and MoN₂ monolayers, in addition to an increase in the band gap of the materials. The theoretical capacity of Li(Na)TiN₂ is 351 mA h/g if used as an electrochemical battery electrode and considering the natural abundance and lower atomic mass of Ti compared to the rest of the transition metals, these materials can be attractive in battery application. After comparing the energies of different structures we found that KTiN₂ and KMoN₂ crystallize in a different structure (non-layered) than Li(Na)MoN₂ and Li(Na)TiN₂ (layered). We found that the crystal structure of KTiN₂ and KMoN₂ is isotypic to SrTiN₂ which has been studied for its thermoelectric property. Within PBE approximation, KMoN₂ is found to be semi-metallic and an anti-ferromagnetic spin alignment on Mo *d* orbitals is energetically more favored over non-magnetic and ferromagnetic ground states. All the other ternaries studied here are found to be metallic.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.cocom.2018.e00335>.

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