Usage Report for Fiscal Year 2018

Project Title: Design of Novel Ordered Double Transition Metal Carbides

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1. Background and purpose of the project, relationship of the project with other projects

The possibility of chemical exfoliation of layered bulk structures has brought great hope to synthesis novel 2D materials with unique electronic and mechanical properties in the future. In this regard, many members of the family of layered transition metal carbides and nitrides, known as MAX phases have been exfoliated into 2D transition metal carbides and nitrides. For examples, Ti_2AlC, Ti_2AlN, V_2AlC, Nb_2AlC, Ti_3AlC_2, Ti_3SiC_2, Ti_4AlN_3, V_4AlC_3, Nb_4AlC_3, Ta_4AlC_3, Mo_2ScAlC_2, Mo_2TiAlC_2, and many others have already been exfoliated into their corresponding 2D Ti_2C, Ti_2N, V_2C, Nb_2C, Ti_3C_2, Ti_3C_2, Ti_4N_3, V_4C_3, Nb_4C_3, Ta_4C_3, Mo_2ScC_2, Mo_2TiC_2, respectively.

As seen above, many of the Al-containing MAX phases have already been exfoliated into 2D MXenes. This motivated experimentalists to focus on the Al-containing layered materials such as MAB phases as promising candidates for obtaining new 2D materials. In detail, MAB phases are orthorhombic crystals with the chemical formula of MAlB, M_2AlB_2, $M_3Al_2B_2$, M_3AlB_4, and M_4AlB_6, see Figure 1. Experimentally, MAlB (M = Mo, W), M_2AlB_2 (M = Cr, Mn, Fe), $Ru_3Al_2B_2$, Cr_3AlB_4, and Cr_4AlB_6 have been synthesized. In recent experiments, it has been shown that MoAlB can be partially exfoliated into 2D MoB by removing Al atoms [J. Am. Chem. Soc. 140, 8833 (2018)].

2. Specific usage status of the system and calculation method

I have extended the family of MAB phases and studied the dynamic stability and formation energies of MAlB, M_2AlB_2, $M_3Al_2B_2$, M_3AlB_4, and M_4AlB_6 (M = Sc, Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W, Mn, Tc, Fe, Ru, Co, Rh, and Ni) by using density functional theory calculations and set of phonon calculations. Then, I have investigated the exfoliation possibility of the stable MAB phases into 2D MB phases.

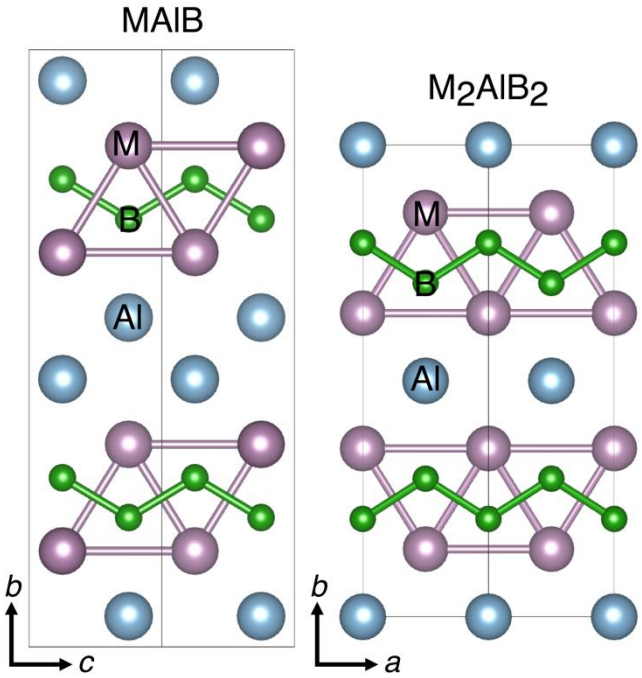

Figure 1. Some crystal structures of MAB phases.

3. Result

In order to find out which of the dynamically stable MAB phases can be realized experimentally, I have calculated the formation enthalpy of the MAB phases with respect to the combinations of most competitive phases. In excellent agreement with experimental observation, the Cr, Mo, W, Mn, and Fe-based MAB phases find negative ΔH indicating their synthesis possibility in the experiment. Moreover, my calculations indicate that there is a high possibility to realize Sc, Ti, V, and Tc-based MAB phases experimentally in the future.

As mentioned before, Al-containing layered MAB phases are of interest for obtaining novel 2D materials. Currently, our theoretical and experimental knowledge on exfoliation possibility of MAB phases are very little. Exfoliation is a dynamic chemical process which depends on the type of

etchant, its concentration, the time duration of the treatment, and temperature. It is very difficult and time-consuming to simulate the exfoliation process by performing molecular dynamics simulations. Hence, in order to shed light on exfoliation possibility of MAB phases, performing a set of static calculations to measure the bond strength properties is the only effective way to study this family systematically. This is because, in a successful chemical process, the bonds between an Al atom and its neighboring Al, M, and B atoms should be broken without destroying the other bonds. The weaker the M−Al bonds, the higher the exfoliation possibility. The strength of bonds in materials could be approximately measured *e.g.*, using force constant calculations [Phys. Chem. Chem. Phys. 20, 8579 (2018)].

Figure 2 summarizes the results of force constant calculations for various M-B, M-Al, M-M, Al-Al, Al-B, and B-B bonds in MAB phases. It is seen that generally as the atom−atom distance increases, the bond strength decreases. Figure 2 shows that B−B and M−B are stiffer than the M−Al, M−M, Al−Al, and Al−B. B−B, M−B, and M−M are the bonds which construct the MB, M_2B_3, and M_3B_4 block units in MAB phases and since they are stronger than M−Al, Al−Al, and Al−B bonds, it implies the possibility of exfoliation of MAB phases by breaking the bonds between Al and neighboring M, Al, and B atoms without hurting the 2D MB, M_2B_3, and M_3B_4 backbones. In MAX phases the strong M−X (X = C or N) bonds construct the backbones, $M_{n+1}X_n$ MXenes. Our calculations indicate the strength of B−B bonds in MAB phases are as strong as M−X (X = C or N) bonds in MAX phases. This can be a sign that 2D MB, M_2B_3, and M_3B_4 may remain stable after exfoliation process as seen in the case of $M_{n+1}X_n$ MXenes.

4. Conclusion

Recently, a layered family of Al-containing transition metal borides, known as MAB phases have received attention for obtaining 2D transition metal borides: 2D MB, M_2B_3, and M_3B_4. Currently, MAB phases have a few members, mainly made of Cr, Mo, W, Mn, and Fe. By performing this study, I have shown that in addition to the above MAB phases, it might be possible to realize Sc, Ti, V, and Tc-based MAB phases. The bond strength analyses indicate the B−B and M−B bonds are stronger than M−Al, Al−B, and Al−Al bonds, implying the exfoliation possibility of MAB phases into 2D transition metal borides.

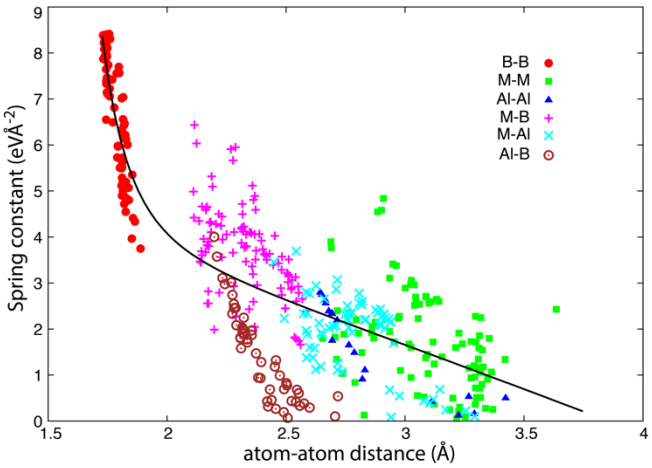

Figure 2. Evaluating the strength of the bonds by force constant calculations.

5. Schedule and prospect for the future

Currently, I am extending the above study by investigating the possibility of formation of ordered double transition metals in MAX and MAB phases.

Fiscal Year 2018 List of Publications Resulting from the Use of the supercomputer

[Paper accepted by a journal]

1) Mohammad Khazaei, Anavish Mishra, Natarajan S. Venkataramanan, Abhishek K. Singh, Seiji Yunoki, "Recent advances in MXenes: from fundamentals to applications", Current Opinion in Solid State & Materials Science (2019), in press. DOI: https://doi.org/10.1016/j.cossms.2019.01.002.

2) Mohammad Khazaei, Vei Wang, Cem Sevik, Masao Arai, Seiji Yunoki, "Electronic structures of iMAX phases and their two-dimensional derivatives: A family of piezoelectric materials", Physical Review Materials 2, 074002 (2018).

[Others (Book, Press release, etc.)]

Book chapter:

1) Mohammad Khazaei, Ahmad Ranjbar, Yunye Liang, and Seiji Yunok "Electronic properties and applications of MXenes from ab initio calculations perspective", included in the book "2D Transition Metal Carbides and Nitrides (MXenes): Structure, Properties, and Applications" edited by B. Anasori and Y. Gogotsi. Publisher: Springer-Nature, in press (2019).