Usage Report for Fiscal Year 2017

Project Title:

Computational discovery of novel ternary boride phases

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

Ternary borides are a family of M-A-B compounds (known as MAB phases), where M= Sc, Ti, Zr, Hf, V, Nb, Hf, Cr, Mo, W, A = Al, Ga, In, Si, Ge, and B= boron. MAB phases can be considered as part of a larger family of M-A-X compounds (known as MAX phases) with chemical formula of M_nAX_{n+1}, where X= carbon or nitrogen, and n= 1-3. Recently, MAX phases have been exfoliated into two-dimensional transition metal carbides and nitride (M_nX_{n+1}) so-called MXenes, by removing the "A" element using acid solutions. The crystal structure of MAX phases and MXenes are shown in Figure 1. The main difference between MAX and MAB phases is in their crystal structures. MAX phases are layered hexagonal structures while MAB phases possess mainly orthorhombic.

We have already discovered many new MAB phases and investigated their exfoliation process. Actually, we have suggested a method to investigate the exfoliation possibility of MAX and MAB phases. We report the results for the MAX phases that its related paper has been accepted for publication in Physical Chemistry Chemical Physics, in press (2018). The results for the discovered MAB systems and their exfoliation possibility is in preparation.

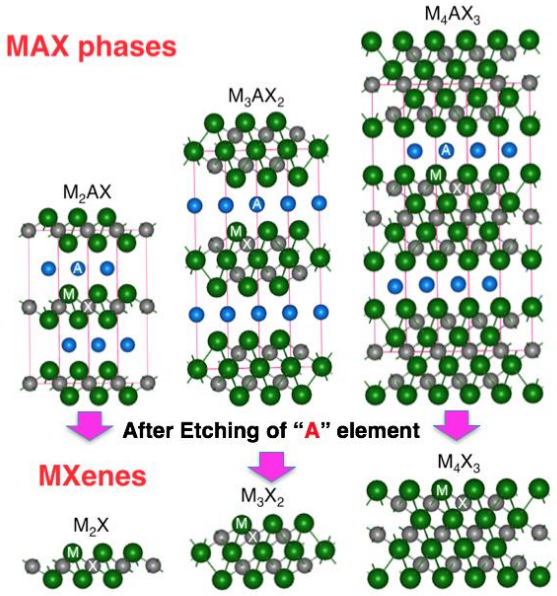

Figure 1: Typical structures of M_2AX, M_3AX_2, and M_4AX_3 MAX phases, and their derived two-dimensional M_2X, -M_3X_2, and -M_4X_3 MXenes.

The chemical exfoliation process is a very complicated dynamical process, which is very difficult to model and simulate with all the details. Nevertheless, we can still gain great insights through studying the bond strength and the exfoliation energy because it is expected that MAX phases with weaker M-A bonds are promising for the successful exfoliation process.

2. Specific usage status of the system and calculation method

By using a set of first-principles calculations based on density functional theory (DFT), we have studied the electronic structures, static exfoliation energies, force constants, and bond strengths of the 82 crystalline MAX phases.

In order to evaluate the force constants of the bonds in MAX phases, we have performed a set of phonon calculations on the 82 experimentally crystalline MAX phases. As expected and consistent with the experimental results, no negative phonon frequencies are found in the phonon spectra of these MAX phases. This indicates that these MAX phases are dynamically stable.

The static exfoliation energy $E_{Exfoliation}$ of a bulk MAX phase into 2D MXenes is calculated through $E_{Exfoliation}$= -[E_{tot}(MAX phase)- 2 E_{tot}(MXene)- 2 E_{tot}(A)]/(4S), where E_{tot}(MAX phase), E_{tot}(MXene) and E_{tot}(A) stand for the total energies of bulk MAX phase, 2D MXene, and A element, respectively. Here, $S = \sqrt{3}a^2/2$ is the surface area and a is the lattice parameter of the MAX phase. Exfoliating a MAX phase, each unit cell of the MAX phase generates two MXene layers with totally 4 surfaces. Hence, the exfoliation energy is divided by 4 in the above formula. The total energy of A element, E_{tot}(A), is estimated from its most stable bulk structure.

3. Result

Here, M_1 and M_2 represent transition metals belonging to the first and second layers of transition metals close to the A element, and the X layer is sandwiched between M_1 and M_2 layers. The results of the force constants for these bonds are summarized in Fig. 2. A general trend can be revealed that shorter bonds are stiffer. It is also observed that the force constants of the M_1-X bonds are significantly larger than those of other bonds. This indicates that the M_1-X bonds are the strongest in the MAX phases, which is the main reason for the stability of these MAX phases and the resulting MXenes. Since the force constants of the M_1-A bonds are smaller than those of the M_1-X bonds, implying that the M_1-A bonds are weaker than the M_1-X bonds, it is expected that the bulk modulus of MAX phases is not larger than that of their corresponding

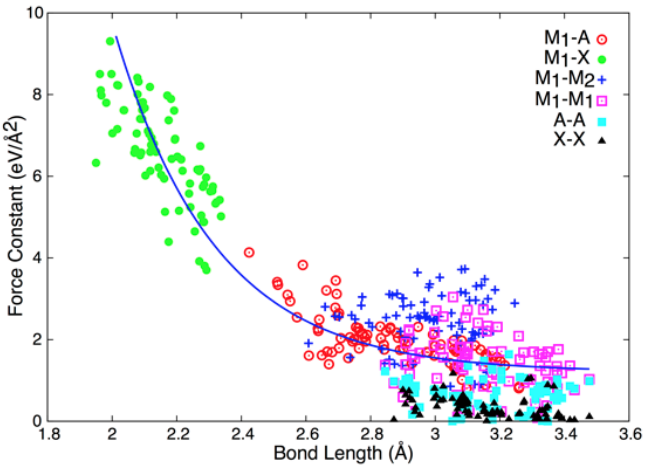

Figure 2: Calculated force constants of different bonds versus the corresponding bond lengths for the 82 experimentally synthesized MAX phases. The line is a guide to the eye.

binary MX compounds.

In order to examine which of the MAX phases are well-suited for the successful exfoliation into 2D MXenes, the total force constant FC_A --- the summation of force constants of all springs that connect an A atom to its neighboring atoms --- is a very useful quantity. As a simple criterion, we can expect that MAX phases with smaller FC_A can be considered as promising candidates for the exfoliation process. In this respect, Ti_2AlC, V_2AlC, Ti_3AlC_2, Zr_3AlC_2, Ti_4AlN_3, Nb_4AlC_3, Mo_2TiAlC_2, Cr_2TiAlC_2, Mo_2ScAlC_2, and $Mo_2Ti_2AlC_3$ are the list of MAX phases that have already been exfoliated to Ti_2C, V_2C, Ti_3C_2, Zr_3C_2, Ti_4N_3, Nb_4C_3, Mo_2TiC_2, Cr_2TiC_2, Mo_2ScC_2, and $Mo_2Ti_2C_3$, respectively. All these compounds contain Al in the MAX phases. The minimum (maximum) FC_A is for Zr_3AlC_2 (V_2AlC). Therefore, we expect that by using appropriate acids in the experiments it might be possible to break the bonds as strong as the V-Al bond. Based on this criterion, we screen our data for 82 compounds with FC_A less than 21.855 eV/Å^2.

The exfoliation process would be successful experimentally only if the obtained 2D MXenes are structurally perfect. This requires that the M_1-M_1, M_1-M_2, and M_1-X bonds should be stronger than the M_1-A and A-A bonds. Otherwise, during the exfoliation process, other bonds may also be broken besides the M1-A bonds. In such a case, either the MXenes would not be formed at all or they would be

formed with many M and X defects. Since the M_1-X bonds are the strongest in MAX phases, we calculate the total force constant FC_X --- the summation of force constants of all springs that connect an X atom to its neighboring atoms --- and compare it with the FC_X of MAX phases experimentally exfoliated into MXenes. We find that the maximum (minimum) of FC_X is for V_2AlC (Zr_3AlC_2). Therefore, in order to successfully synthesize MXenes, FC_X should at least be as large as that for Zr_3AlC_2 (40.511 eV/ eV/Å^2). Based on this criterion, we re-screen the results of FC_X in all 82 MAX phases.

As we described above, the chemical exfoliation is a complicated dynamical process with subtle details. Hence, it is extremely difficult to simulate such processes computationally. However, the calculation of the static exfoliation energy would help us to screen MAX phases for the successful exfoliation process into 2D MXenes. Here, we evaluate the exfoliation energy $E_{Exfoliation}$ for the 82 different MAX phases. The definition of $E_{Exfoliation}$ is given in the section of methods of calculations. Among the MAX phases experimentally exfoliated into MXenes, Zr_3AlC_2 (V_2AlC_2) shows the lowest (largest) $E_{Exfoliation}$ (eV/area), 0.131 (0.205) eV/Å^2. Therefore, we expect that the MAX phases with an exfoliation energy lower than 0.205 eV/Å^2 have a better chance to be exfoliated into MXenes.

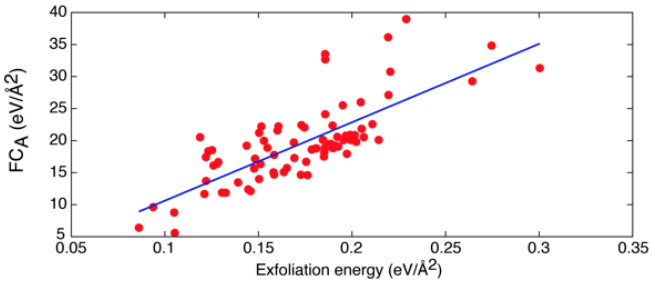

Figure 3: Force constant FCA versus exfoliation energy.

Figure 3 shows the total force constant FC_A for the A atoms versus the exfoliation energy. It is clearly observed that the total force constant FC_A is strongly correlated with the exfoliation energy: the MAX phases with smaller FC_A have a lower exfoliation energy.

Combining all the above analyses, we can finally conclude that the best candidates of MAX phases for the successful exfoliation into 2D MXenes are those MAX phases with small total force constants of the A atoms, large total force constants of the M and X atoms, and low exfoliation energy.

We predict that in addition to the 10 MAX phases that have already been exfoliated experimentally, the following 37 MAX phases are promising candidates for the successful exfoliation. Since the exfoliation energy is more directly related to the chemical exfoliation process than the other two criteria, we prioritize this criterion to sort these 37 promising candidates from the smallest to the largest exfoliation energies. Therefore, in the following list, we predict that the first (last) MAX phase is the most (least) promising candidate for successful exfoliation: 1) Ti_2CdC, 2) Zr_2AlC, 3) Ti_3AuC_2, 4) Ti_5AlC_4, 5) Zr_2InC, 6) Hf_2AlC, 7) Ti_2GaC, 8) Ti_4GaC_3, 9) Hf_2InC, 10) Nb_5AlC_4, 11) Hf_2TlC, 12) Ti_2InC, 13) Ti_2TlC, 14) Nb_2GaC, 15) Hf_2PbC, 16) Ta_5AlC_4, 17) Ti_3SiC_2, 18) Ti_4SiC_3, 19) Ti_3GeC_2, 20) Nb_2InC, 21) Ti_2GeC, 22) Ti_4GeC_3, 23) Hf_2SnC, 24) Mo_2GaC, 25) Ti_2SiC, 26) Ta_2GaC, 27) Cr_2GaN, 28) Ti_3IrC_2, 29) V_2GaC, 30) Ti_2InN, 31) Ta_2AlC_2, 32) Ti_2PbC, 33) Ta_2AlC, 34) Cr_2GaC, 35) V_4AlC_3, 36) V_3AlC_2, and 37) Ti_2SnC. Therefore, we expect the following 2D MXenes can be synthesized: Ti_2C, Ti_3C_2, Ti_4C_3, Ti_5C_4, Ti_2N, Zr_2C, Hf_2C, V_2C, V_3C_2, V_4C_3, Nb_2C, Nb_5C_4, Ta_2C, Ta_5C_4, Cr_2C, Cr_2N, and Mo_2C.

4. Conclusion

MAX phases can be a great source for the synthesis of novel 2D materials with exceptional properties. So far, around 82 different crystalline and numerous alloy MAX phases have been synthesized. Here, we have provided an insight into the exfoliation possibility of various crystalline MAX phases. Our systematic analyses show that in all MAX phases, the M_1-X bonds are stiffer and stronger than the M_1-A bonds. The large stiffness of the M_1-X bonds is

attributed to the greater orbital mixing and higher ionicity of the M_1-X bonds than those of the M_1-A bonds. The total force constant for the A atoms in MAX phases is found to be linearly correlated with the chemical exfoliation energy, and therefore the force constant can be used to investigate the bond strength and the exfoliation likelihood in MAX phases.

5. Schedule and prospect for the future

We are applying the above analysis on other layered materials to investigate their exfoliation possibilities.

Fiscal Year 2017 List of Publications Resulting from the Use of the supercomputer

[Publication]

1) **Mohammad Khazaei**, Ahmad Ranjbar, Keivan Esfarjani, Dimitri Bogdanovski, Richard Dronskowski, Seiji Yunoki, Insights into exfoliation possibility of MAX phases to MXenes, accepted for publication in Phys. Chem. Chem. Phys. (2018).

2) Yunye Liang, **Mohammad Khazaei**, Ahmad Ranjbar, Masao Arai, Seiji Yunoki, Yoshiyuki Kawazoe, Hongming Weng, Zhong Fang, "Theoretical prediction of two-dimensional functionalized MXene nitrides as topological insulators", in submission, Phys. Rev. B 96, 195414 (2017).

3) **Mohammad Khazaei**, Ahmad Ranjbar, Masao Arai, Taizo Sasaki, Seiji Yunoki, "Electronic structures and applications of MXenes: a theoretical review", J. Mater. Chem. C 5, 2488 (2017).

Note: This paper was the first paper that I published with my supercomputer account. I was not aware that I should include the acknowledgment. In the other publications, I have included it.

[Oral presentation at an international symposium]

1) **Mohammad Khazaei**, "Electronic structures of MAX phases and MXenes", The 9th conference of the Asian Consortium on Computational Materials Science (ACCMS-9), Kuala Lumpur, Malaysia, August 8-11, 2017. (Invited talk)

2) **Mohammad Khazaei**, "Insight into exfoliation possibility of MAX Phases to MXenes", Asian Consortium on Computational Materials Science-Virtual Organization, ACCMS-VO12, Sendai, Tohoku University, Dec. 17-19.

3) **Mohammad Khazaei**, "Application of DFT calculations for predicting the structural and electronic properties of materials", The 8th AICS International Symposium on "Roadmap on computer science and computational science in the future AICS and HPC communities", February 7-8, 2017, RIKEN AICS, Kobe, Japan.