NDnano
Notre Dame Nanoscience and Technology

NDnano Summer Undergraduate Research
2023 Project Summary

1. Student name & home university:
   Robin Kucsera, Budapest University of Technology and Economics

2. ND faculty name & department:
   Prof. Laszlo Forro, Department of Physics & Astronomy

3. Summer project title:
   Tailoring the electronic properties of Ti-based MXenes

4. Briefly describe new skills you acquired during your summer research:
   During the research, I learned how to handle nanomaterials and how to insert atoms into their structure. In addition, I learned the basic usage of new spectrometric devices such as VSM, Microwave resistance, and Raman spectroscopy.

5. Briefly share a practical application/end use of your research:
   The intercalation of Ti_3C_2 MXene can be further utilized in the semiconductor industry because it enables the fine-tuning of the electronic properties of the material. Furthermore, like other MXenes, it can be used for energy storage, in forms such as capacitors or batteries.

6. 50- to 75-word abstract of your project:
   MXenes are a family of two-dimensional compounds that have been discovered recently. The properties of Ti_3C_2, as a novel material, are still not yet well-known. One of the key questions is how well we can introduce and accommodate metals into their composition to improve their electronic capabilities. The layered structure of the MXenes could serve as a good host for intercalation compounds. During the project, I tried vapor and liquid ammonia-based intercalation methods with potassium and calcium.

7. References for papers, posters, or presentations of your research:

[1] Armin Vahid Mohammadi *et al*., The world of two-dimensional carbides and nitrides (MXenes).Science372,eabf1581(2021)

[2] Hong, W., Wyatt, B.C., Nemani, S.K. *et al*. Double transition-metal MXenes: Atomistic design of two-dimensional carbides and nitrides. MRS Bulletin 45, 850–861 (2020)

[3] M. S. Dresselhaus & G. Dresselhaus (2002) Intercalation compounds of graphite, Advances in Physics, 51:1, 1-186

[4] Márkus, B.G., Szirmai, P., Kollarics, S., Náfrádi, B., Forró, L., Chacón-Torres, J.C., Pichler, T. and Simon, F. (2019), Improved Alkali Intercalation of Carbonaceous Materials in Ammonia Solution. Phys. Status Solidi B, 256: 1900324

[5] Freeman J. Dyson, Electron Spin Resonance Absorption in Metals. II. Theory of Electron Diffusion and the Skin Effect, Phys. Rev. 98, 349 – Published 15 April 1955

[6] Donovan, S., Klein, O., Dressel, M. *et al*., Microwave cavity perturbation technique: Part II: Experimental scheme. Int J Infrared Milli Waves 14, 2459–2487 (1993).

One-page project summary that describes problem, project goal and your activities / results:

MXenes are a material family whose first variants were discovered in 2011. Since then, numerous other members of the family have been discovered, and many more are predicted by theoretical calculations. They are all two-dimensional layered metal carbides, nitrides, or carbonitrides [1]. One member is the titanium-based 3-2 carbide: Ti_3C_2, in which each carbon layer is sandwiched between two titanium layers. The goal of the project was to try to improve the nanolayers' electronic capabilities by intercalation, as it has not been well-studied in the case of titanium carbide.

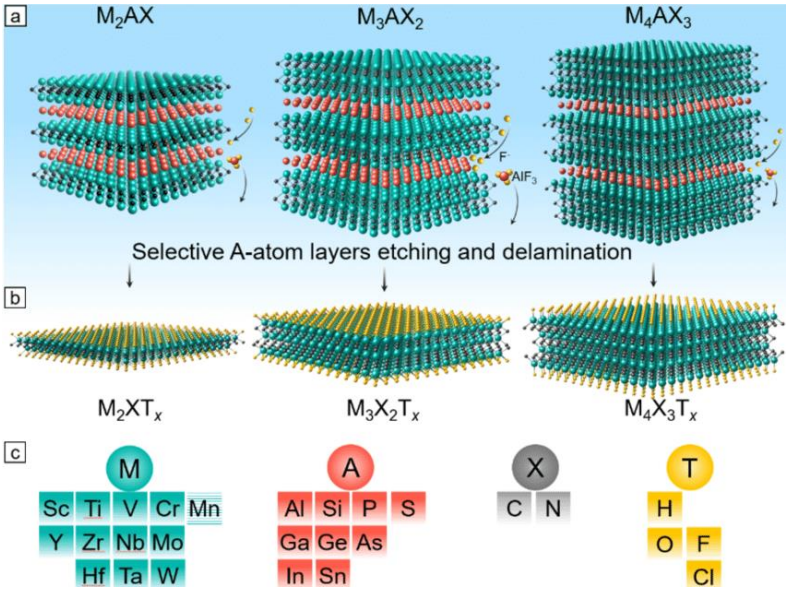

Figure 1. MXene precursors, the possible elements they are made of and their synthesis through etching. After etching, termination groups appear at the side of the MX sheets.[2]

The precursor of the MXenes is the so-called MAX phase, which consists of layers of the following materials: a transition metal (M=Ti, Nb, V, etc.), a light metal (A=Al, Si, etc.), and carbon or nitrogen (X=C, N). The layered crystal formed by these elements will go through an etching process where the light metal atoms are removed from the structure. After the etching process, the MX sheets are revealed, but the process leaves behind termination groups (*T*) on the surface of these sheets. Thus, the resulting material is often noted as $M_{n+1}X_nT_x$. The process is depicted in Figure 1. The termination groups also play an important role in the stability of the separated layers. Despite these termination groups, the sheets are still connected by van der Waals forces. In the intercalation process, we insert dopant atoms between the carbide layers. We expect that this way, the dopant can donate charge carriers to the MX and increases its conductivity, similar to the case of graphite [3].

In my summer research, I tried to achieve the intercalated state with two different inclusion methods. One of which is the two-zone vapor chamber method. I prepared a quartz tube with indents using a gas-welder torch so that the dopant and MX would not touch. A prepared ampoule is shown in Figure 2.

Figure 2. A sample prepared with potassium for the vapor chamber method.

After measuring the required amount of MX, I put it in the tube and heated it at 200 °C for 1 hour in a vacuum system to dehydrate it. Then, I transferred the tube, still under vacuum, into a glovebox, where I placed the air-reactive potassium/calcium into the tube. The metal cannot fall entirely through, as it gets stuck on the indents. After connecting it to the vacuum system, I sealed the tube with the torch. Then the MX with the dopant was placed into a furnace at an elevated temperature of 300-350 °C for potassium and 500-530 °C for calcium for several (5-40) hours. Later in the characterizations, I did not find a good correlation between these parameters. The process needs further investigation.

Other samples were prepared in liquid ammonia. Alkali and alkaline earth metals are known to dissolve in liquid NH_3. I prepared the sample in a similar fashion to the vapor-based ones, but I put the cleaned MX in a flask-ended tube to aid mixing of the ingredients. After the dopant was in the flask, I introduced 900 mbar of gaseous ammonia into the vacuum system separated from the vacuum pumps. Then, I cooled the tube with liquid nitrogen until the ammonia condensed. For the reactions to properly proceed, they needed to be kept at a low temperature of -40 – -50 °C. For this process, I placed the bottom of the flask into an alcohol-mix bath (90% ethyl alcohol, 5% methyl alcohol, 5% isopropyl alcohol) that I kept cold with liquid nitrogen. To further accelerate the process, the alcohol beaker was immersed in a hydroponic bath for 30 minutes. After 30 minutes, the tube was gradually heated up to room temperature [4]. Because the prepared samples are sensitive to oxygen and moisture, they must be sealed in an inert gas atmosphere (or vacuum). In my case, they were sealed in a low-pressure (~30 mbar) helium atmosphere.

The prepared samples were then characterized using four techniques: Electron Spin Resonance (ESR), Microwave Resistance, Vibrating Sample Magnetometry (VSM), and Raman spectroscopy. The most prominent results were obtained by ESR. This can be seen in Figure 3. The change of the spectrum along the magnetic field compared to the reference material's signal indicates a change in composition but does not identify the position of the dopant adatoms, as it is a more complex question. We suspect that intercalation is happening, as the appearing double peaks are also asymmetrical. It is possible that a Dysonian component [5] is mixed in as well (among the usual derivative Lorentzian peaks). This kind of line shape is observed when the microwaves cannot penetrate uniformly through the sample due to the skin effect. The appearance of such a feature would indicate the presence of conducting electrons, which is a feature of metallic character. I tried to confirm this with microwave resistance measurements [6], but I did not find any correlations in the conductivity of the samples and other parameters that were different between the samples. In the VSM measurement, I did not experience any phase transition between 1.8-300 K, but in the hysteresis curves at low temperatures, I noticed a change. The reference signal had a paramagnetic component that saturated quickly, but in both types of new samples, this saturation occurred at much higher fields and at orders of magnitude bigger amplitude. This could be caused by potassium and calcium flakes being mixed with the MX, but the microscopic pictures from Raman spectroscopy confirmed that this was not the case. Unfortunately, the intercalation has not been supported by Raman measurements yet as the intercalated MX is air-sensitive and held in a quartz tube, which did not let us collect a reasonable Raman spectrum.

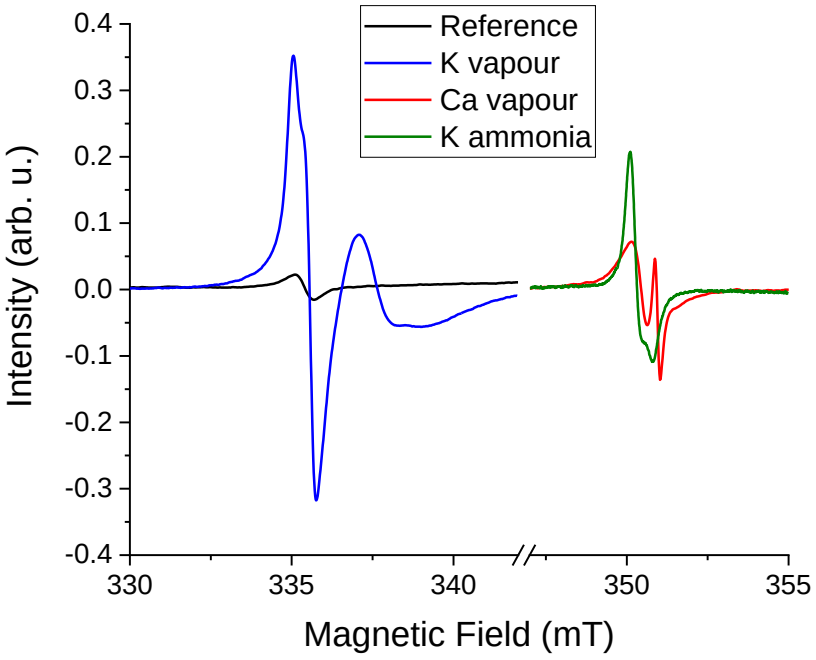

Figure 3: ESR spectra of the prepared intercalated species (K and Ca) compared to the starting material (Reference). Please note the stark difference between the obtained materials and the reference.