Remarkable 3D MAX Phases & 2D Wonder Materials MXenes

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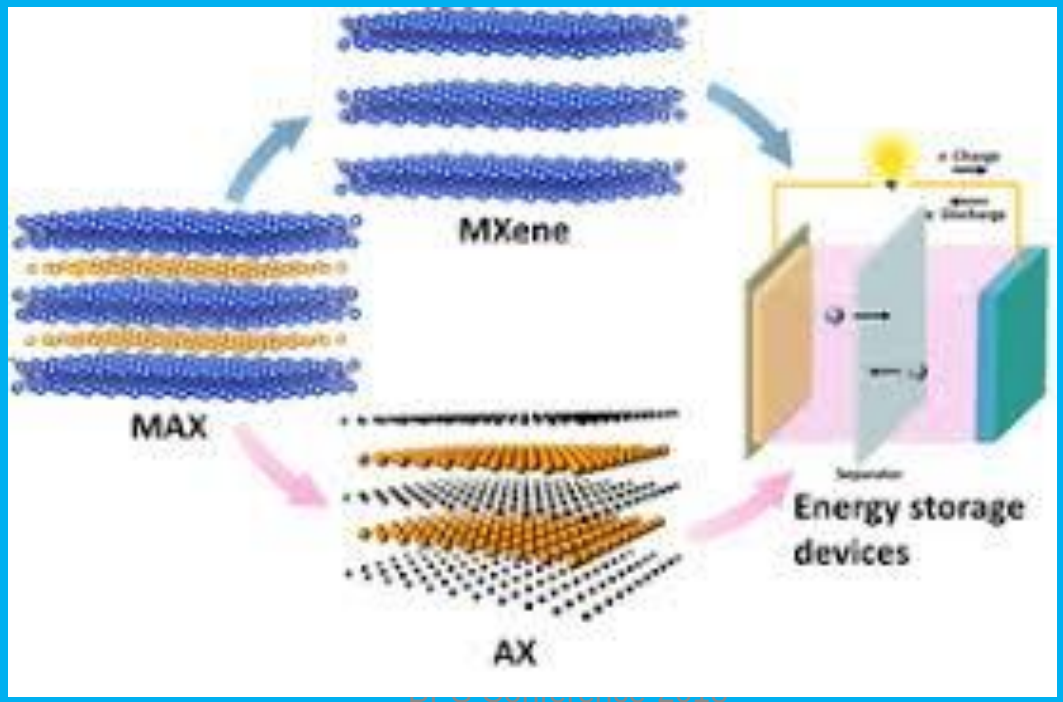
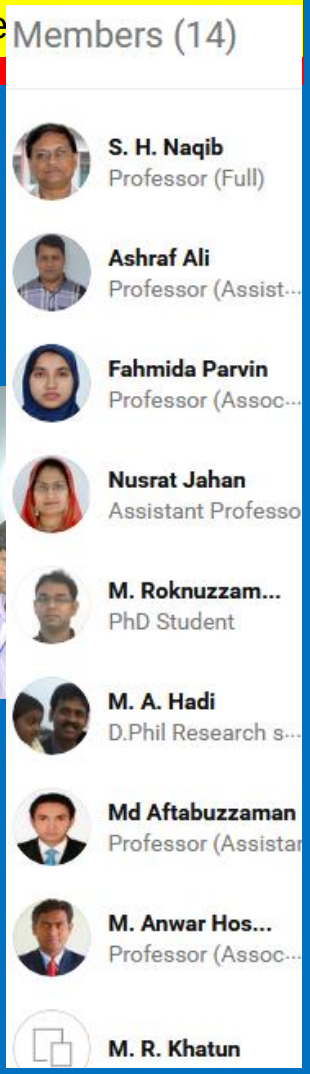


Outline

Any shape that only has a surface area is a 2-D shape while shapes with volume are

- **3D MAX Phase Materials (Nanolaminate):**
  - Exciting new class of materials – Why ?
  - MAX phases: Bridging the gap between metals & ceramics
  - Applications
- **Our Research on MAX Phases** ➔
  - Prediction of yet unobserved phases
  - Substitution – strengthening study: $(Ti, V)_2AlC_2$ etc.
  - Superconducting MAX phases
- **2D MXenes derived from 3D MAX Phases**
  - Stories of new wonder materials

Lab: A K M A Islam



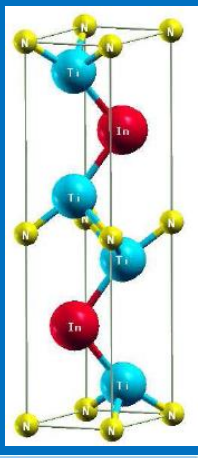
3D MAX Phase

Now > 70 phases-- most discovered & produced in powder form in the 60's by H. Nowotny & coworkers.

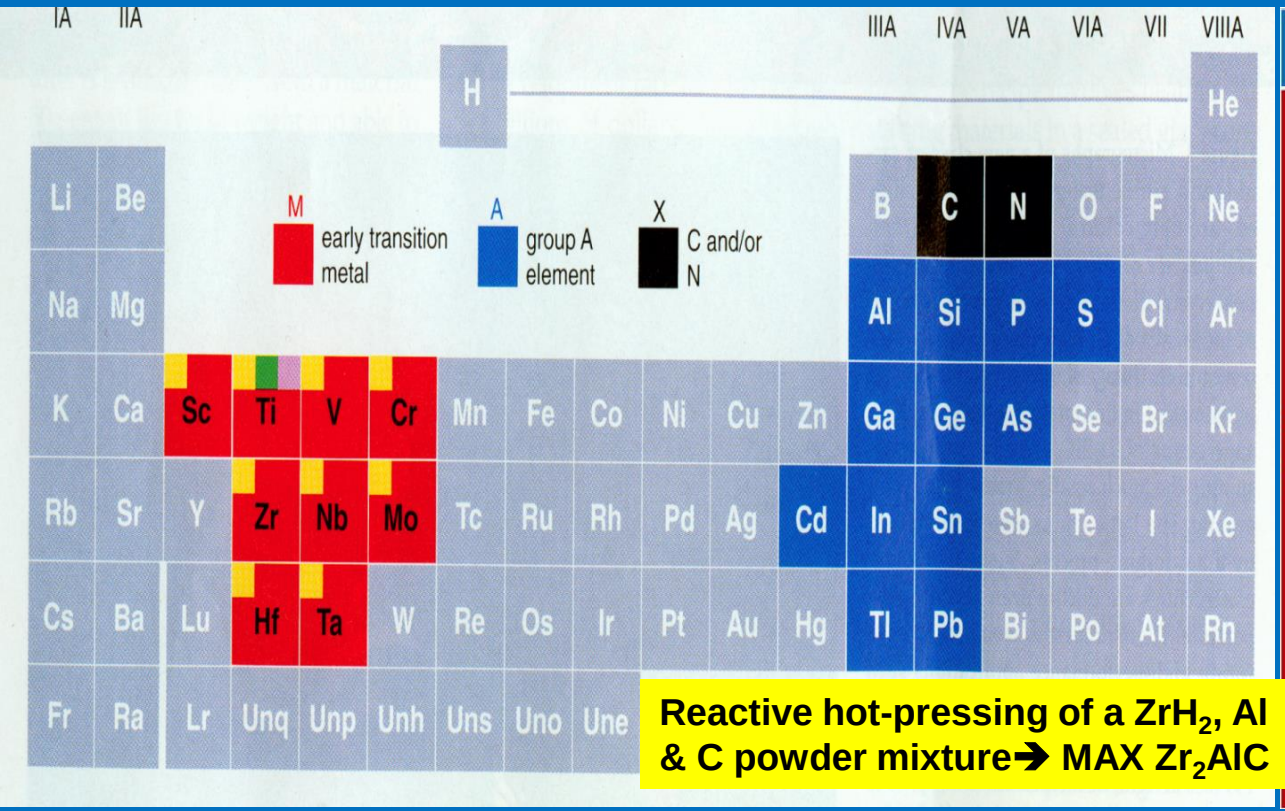
Formula: $M_{n+1}AX_n$

- **M** is an <u>early transition</u> metal
- **A** is an <u>A-group</u> element
- **X** is either C or N

First fabricated in bulk & characterized
(Dr. Barsoum Group at Drexel University, USA)



Ti_2InN



MAX Materials

M element	A-group element: s^2 (group 12)	s^2p^1 (group 13)	s^2p^2 (group 14)	s^2p^3 (group 15)	s^2p^4 (group 16)
211 Phases					
3d	Ti_2CdC	Sc_2InC Ti_2AlC Ti_2GaC Ti_2InC Ti_2TlC V_2AlC V_2GaC Cr_2GaC Ti_2AlN Ti_2GaN Ti_2InN V_2GaN Cr_2GaN	Ti_2GeC Ti_2SnC Ti_2PbC V_2GeC Cr_2AlC Cr_2GeC	V_2PC V_2AsC	Ti_2SC
4d		Zr_2InC Zr_2TlC Nb_2AlC Nb_2GaC Nb_2InC Mo_2GaC Zr_2InN Zr_2TlN	Zr_2SnC Zr_2PbC Nb_2SnC	Nb_2PC Nb_2AsC	Zr_2SC Nb_2SC
5d		Hf_2InC Hf_2TlC Ta_2AlC Ta_2GaC	Hf_2SnC Hf_2PbC Hf_2SnN		Hf_2SC
312 Phases					
3d		Ti_3AlC_2 V_3AlC_2	Ti_3SiC_2 Ti_3GeC_2 Ti_3SnC_2		
5d		Ta_3AlC_2			
413 Phases					
3d		Ti_4AlN_3 V_4AlC_3 Ti_4GaC_3	Ti_4SiC_3 Ti_4GeC_3		
4d		Nb_4AlC_3			
5d		Ta_4AlC_3			

Reactive hot-pressing of a ZrH_2, Al & C powder mixture➔ MAX Zr_2AlC

Exciting MAX Phases

The term "MAX phases" was coined in the late 1990s.

Renewed interest in MAX Phases after Barsoum & El-Raghy's report in 1996 on the synthesis of phase-pure bulk T_3SiC_2 samples & their unusual combination of properties.

Since then, Research on the MAX phases has exploded.

According to ISI, to date > 1,200 papers have been published on one MAX phase alone, T_3SiC_2, with roughly half of those published in the past 6 years.

Exciting MAX: Bridging the Gap between Metals & Ceramics

Metals possess:

- Good electrical & thermal conductivity, low hardness, machinability, damage tolerance & thermal shock resistance

Ceramics possess:

- High-T strength, high elastic moduli, oxidation & corrosion resistance.

➔ MAX materials possess both attributes - Exciting !!!!

So MAX materials are exciting new class of materials which bridge the Gap between Metals & Ceramics

MAX - New Class of Materials : Bridging the Gap between Metals & Ceramics

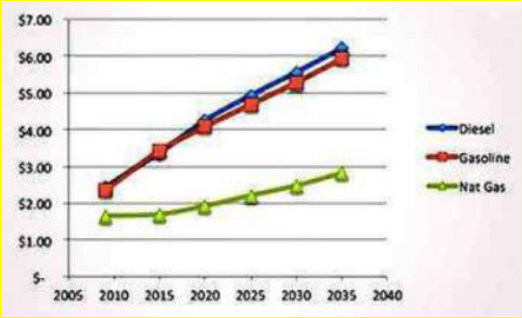
Properties	Ceramic	Metal	MAX Phase Materials
Hardness	H^+	L	G
Elastic Moduli	H^+	G	G
High-T strength	G	L	G
Thermal Expansion	L	G	G
Ductility	L	G	G
Oxidation resistance	H	L	G-H
Corrosion resistance	G-H	L	G
Resistance to wear	G	L	G
Electrical Conductivity	L^-	G	G
Thermal Conductivity	L^-	G	G

Possess both attributes (combine both Ceramic & Metal properties)

Soft & machinable, yet also heat-tolerant, strong & lightweight

Major Challenges in Engineering & MAX Materials

We need versatile materials for developing technologies.: Durable & high performance in extreme environments



Now

1. Simple Facts from Thermodynamics!

- **Efficiency of any fuel-burning engine: $e \propto T_{operating}$**
- **Raise engine *temp.* by 1 ^{o}C ➔ Fuel savings of the world's jet alone worth ~ $1 b/year.**
- **Similar strategy to increase vehicle efficiency by 1 km/litre would save ~ 1 m barrels of oil a day.**
- **A jet engine made from a material 50% lighter in weight & able to run 200 to 300 degrees hotter would have a staggering economic impact.**

2. Today's jet engines are not running hotter for a simple reason :

- **No material exists that can take that kind of heat while spinning furiously.**

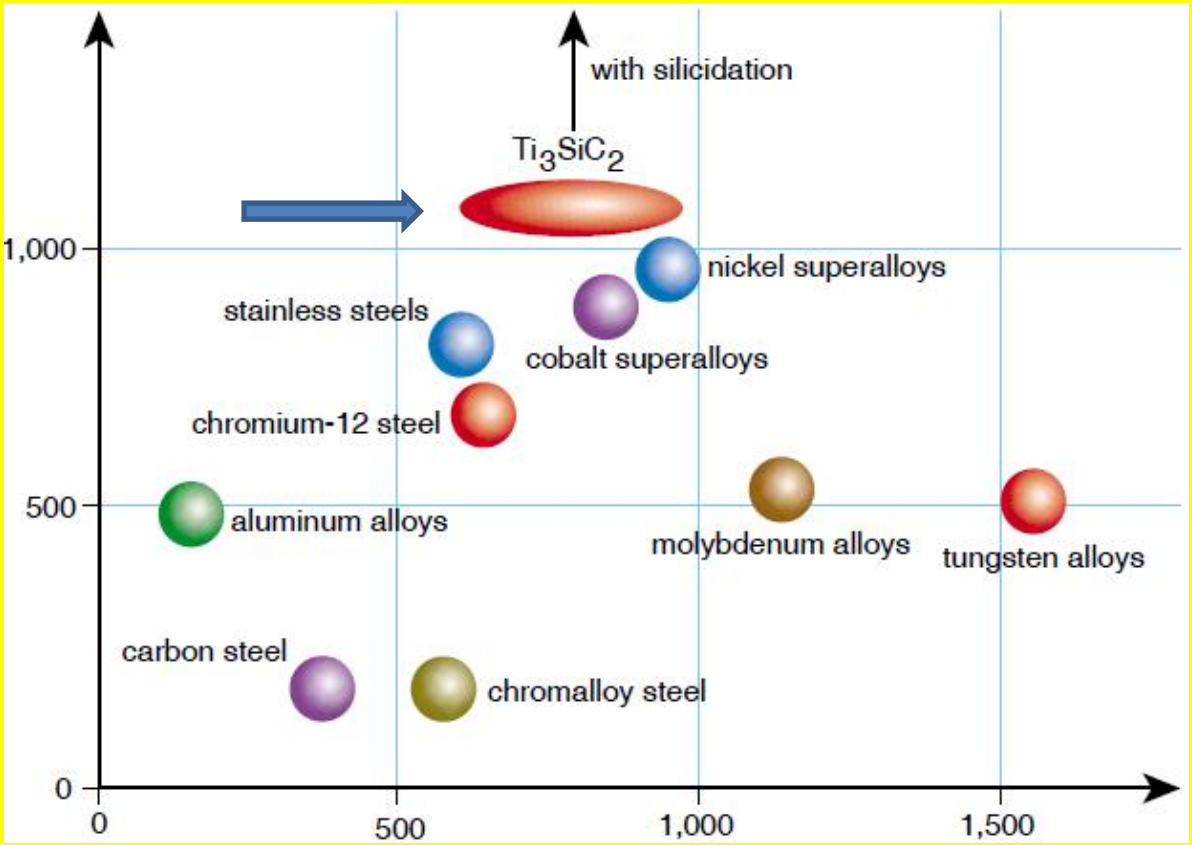
  The same goes for the internal-combustion engine; if a car engine could be built with a temp-tolerant material, its radiator, water pump & cooling water could be thrown away.

- **Such an efficient, lighter & higher-*T* engine would squeeze more *km* from *every litre* of fuel.**

- **Stiff, lightweight, machinable, made from relatively inexpensive raw materials, resistant to oxidation & thermal shock, & capable of remaining strong up to $T > 1300\ ^{o}C$ in air.**
- **An ideal high-performance structural material for, say, jet engines would have all these qualities.**
- **<u>MAX materials form such a new class of solids</u> – since these turn out to be surprisingly soft & machinable, yet also heat-tolerant, strong & lightweight.**

Materials in demanding applications <u>not only must retain their strength, but also need to resist oxidation</u>:

Ti_3SiC_2 possesses both



OUR Research on MAX Phases at RU + IIUC

- **Prediction of yet unobserved phases**
  - First-principles investigation + Gibbs energy
  - Thermodynamic, Electronic & Optical properties
- **Substitution – strengthening study:**
  - $Ti_{2-x}V_xAlC$, $Ti_2Si_xAl_{1-x}C$ etc.
- **Superconducting MAX Phases** (Thermal + optical prop)
  - Nb_2SC, Nb_2SnC, Nb_2AsC, Nb_2InC
  - Ti_2InC, Ti_2InN
  - Mo_2GaC

Publication on MAX Phases = 24

A K M A Islam *et al.*

During Last 6 years (2011 - 2018 Feb)
Total Publication = 53, Publ. on MAX Phases only = 24

Year	No.	Journals
2018	2	J. Alloys & Comp, Mater. Res Express
2017	6	J. Alloys & Comp, Phys. Stat. Solidi, Comp. Mater. Sci, Chin. Phys B
2016	5	J.Phys: CMP, Comp.Mat. Sci, Chin.Phys B, Phys.Stat.Solidi
2015	2	Int.J.Mod.Phys., J.Sci.Res
2014	1	Int. J.Mod.Phys.
2013	4	Comp.Mater.Sci, Cond.Matter Phys., Int. Comp.Mater. Phys.
2012	3	Physica B:CondMatter, ISRN Cond. Matter Phys,
2011	1	Physica B:Cond.Matter

Prediction of Yet Unobserved New MAX Phases

Stability of a MAX phase can be studied by comparing total energy

Energy difference $\Delta G(T, p)$ between the energy of MAX & that of the competing phases (thermodynamically favorable) is calculated using:

$$G(T, p) = E_{tot} + (E_{ZPE} - T S_{vib}) + p V$$

Here *G* = *Gibb's free energy*, E_{tot} = Total *E* (from electronic structure calc.) , 2nd term = ZPE, & 3rd term = vibrational entropic

$T = 0$, $P = 0$: $\Delta E > 0$, unstable; $\Delta E < 0$, stable

Finite *T*, Finite *P* : $\Delta G > 0$, unstable; $\Delta G < 0$, stable

$T = 0,\ P = 0$: $\Delta E > 0$, unstable; $\Delta E < 0$, stable

Finite T, Finite P : $\Delta G > 0$, unstable; $\Delta G < 0$, stable

Phase	Competing phases	$\Delta E = E_{MAX} - E_{CP}$ (eV/f.u.)	Reported occurrence
Ti_2SiC	4/9 Ti_3SiC_2 + 1/9 $TiSi_2$ + 1/9 Ti_5Si_3C Ti_3SiC_2, $TiSi_2$, Ti_5Si_3	0.014 - 0.032	No
Ti_3SiC_2	9/5 TiC + 1/5 $TiSi_2$ + 1/5 Ti_5Si_3C	- 0.202	Yes
Ti_4SiC_3	Ti_3SiC_2 + TiC Ti_3SiC_2 + TiC	0.012 - 0.232	Yes≠
Ti_5SiC_4	Ti_3SiC_2 + 2 TiC Ti_3SiC_2 + 2 TiC	0.043 0.37 ?	No
$Ti_5Si_2C_3$	Ti_3SiC_2, $TiSi_2$, Ti_5Si_3 3/2 Ti_3SiC_2 + 1/7 $TiSi_2$ + 1/14 Ti_5Si_3	0.36	Intergrown phase (IP) hybrid “523” and “725” MAX phases
$Ti_7Si_2C_5$	Ti_3SiC_2, TiC 2 Ti_3SiC_2 + TiC	0.392	IP (2004), Yes (2011)

a. Substitution (solid solution) of MAX phases

b. Superconducting MAX phases

The following properties are studied

Thermodynamic properties

- ***T*** **&** ***P*** **dependence of Debye temp.**
- ***T*** **dependence of** C_p**,** C_p
- ***T*** **and** ***P*** **dependence of thermal expansion**

Elastic properties

- C_{ij}**,** ***B*****, shear modulus** ***G*****,** ***Y*****,** **ν**
- **Vickers hardness, brittleness**

Electronic properties

- **Electronic band structure, Total & partial DOS, Phonon etc**

Optical properties + Thermoelectric Properties

- **Dielectric constants, Photoconductivity**
- **Reflectivity spectrum**

Solid solution -- strengthening study

- Ti_2AlC can be strengthened by substituting Ti with V to form $(Ti,V)_2AlC$ solid solutions.
- V is smaller, & has 1 more valence electron than Ti The weak interaction *transition metal-Al* bonds are reinforced & strengthened.
- *B*, Vicker's hardness & other aspects are also studied.

New Solid Solution of MAX Phases

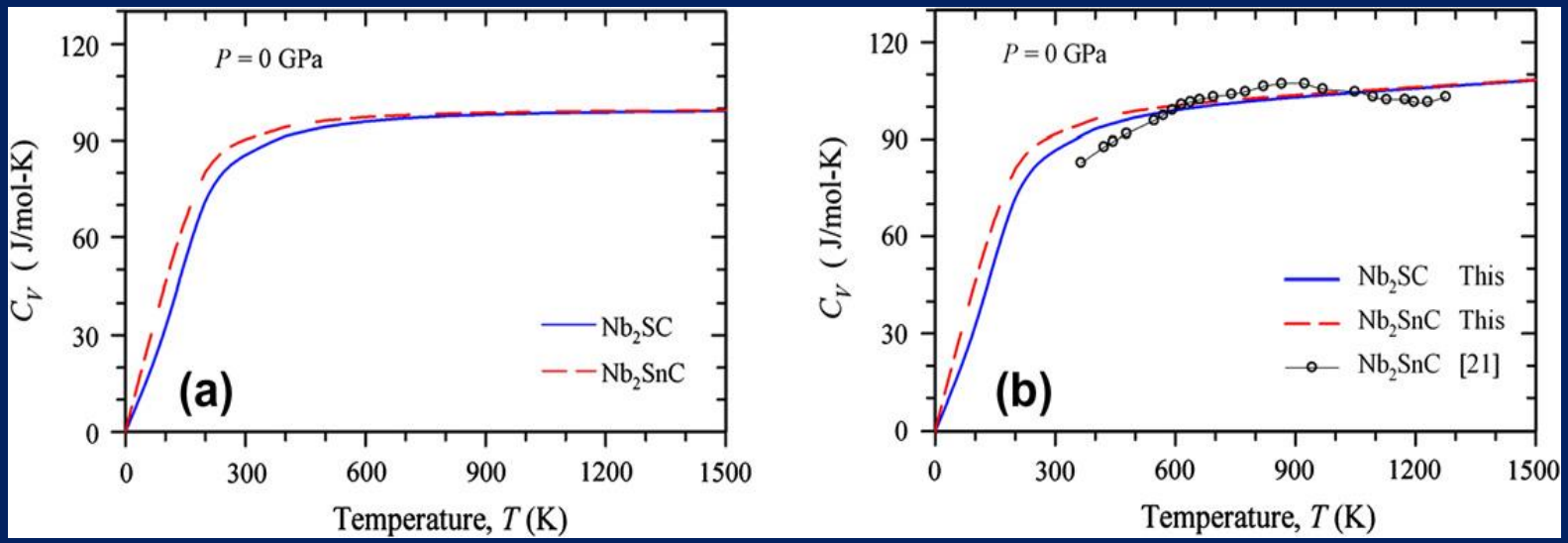
M. Naguiba, et al. Mater.Res.Lett. 2014 Vol. 2, No. 4, 233–240

- **Previously unreported Al containing solid solution $M_{n+1}AX_n$ phases have recently been synthesized.**

  $(Ti_{0.5},V_{0.5})_3AlC_2$, $(Nb_{0.5},V_{0.5})_2AlC$, $(Nb_{0.5},V_{0.5})_4AlC_3$, $(Nb_{0.8}, Zr_{0.2})_2AlC$

- **Rietveld analysis of powder X-ray diffraction patterns was used to calculate the lattice parameters & phase fractions.**
- **Heating Ti, V, Al & C elemental powders—in the molar ratio of 1.5:1.5:1.3:2—to 1, 450 ◦C for 2 h in flowing argon, resulted in a predominantly phase pure sample of $(Ti_{0.5},V_{0.5})_3AlC_2$**
- ***The other compositions* were not as phase pure & further work on optimizing the processing parameters needs to be carried out if phase purity is desired.**

Thermodynamic properties



$$C_p - C_V = \alpha_V^2(T)BVT$$

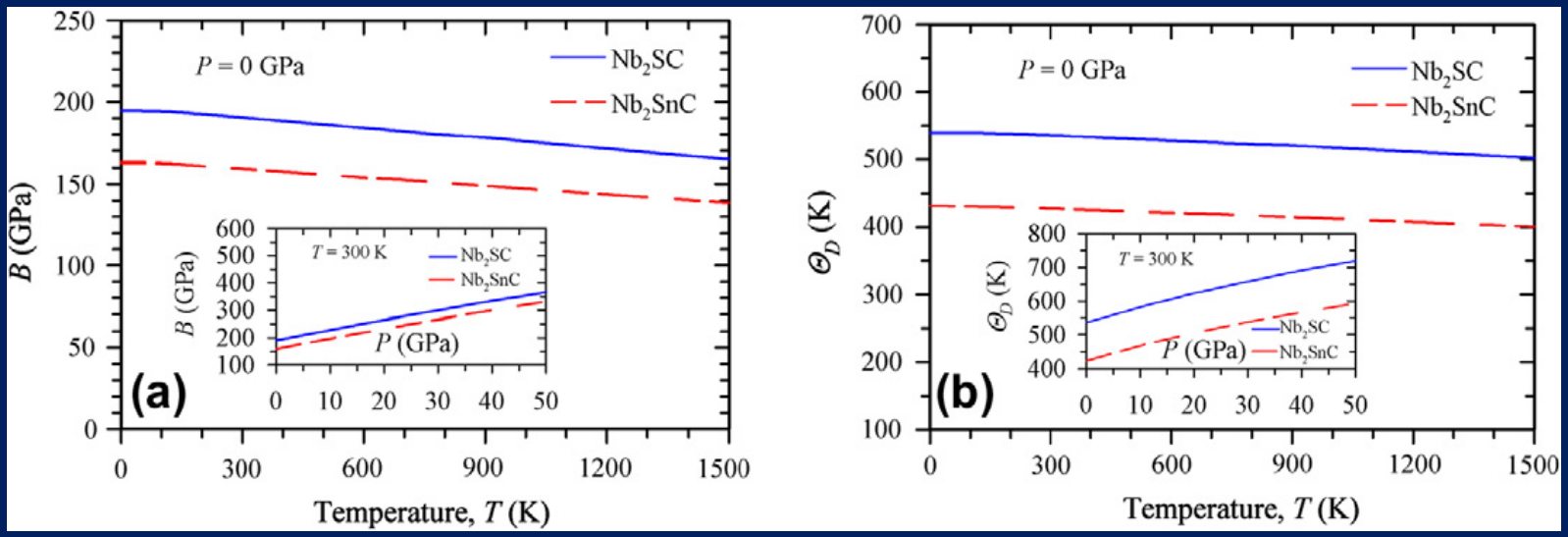
At low T up to ~10 ^oC, $C_P = \gamma T + \beta T^3$

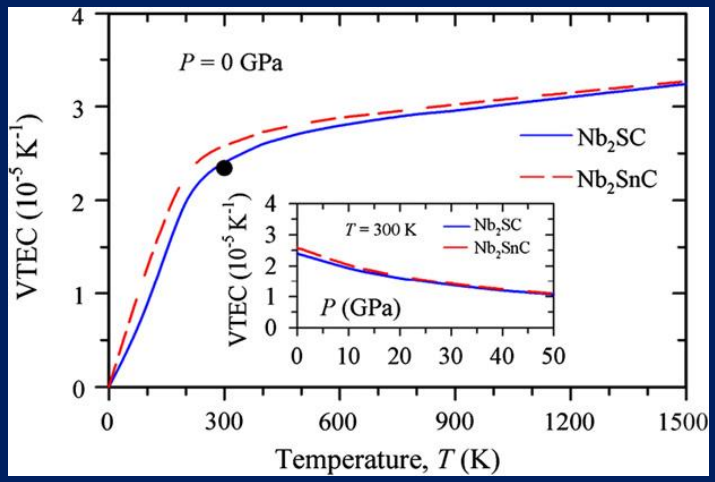
γ and β are the coefficients of electronic & lattice heat capacities.

A plot of C_P/T *vs* T^2 should yield a straight line with slope β & intercept γ.

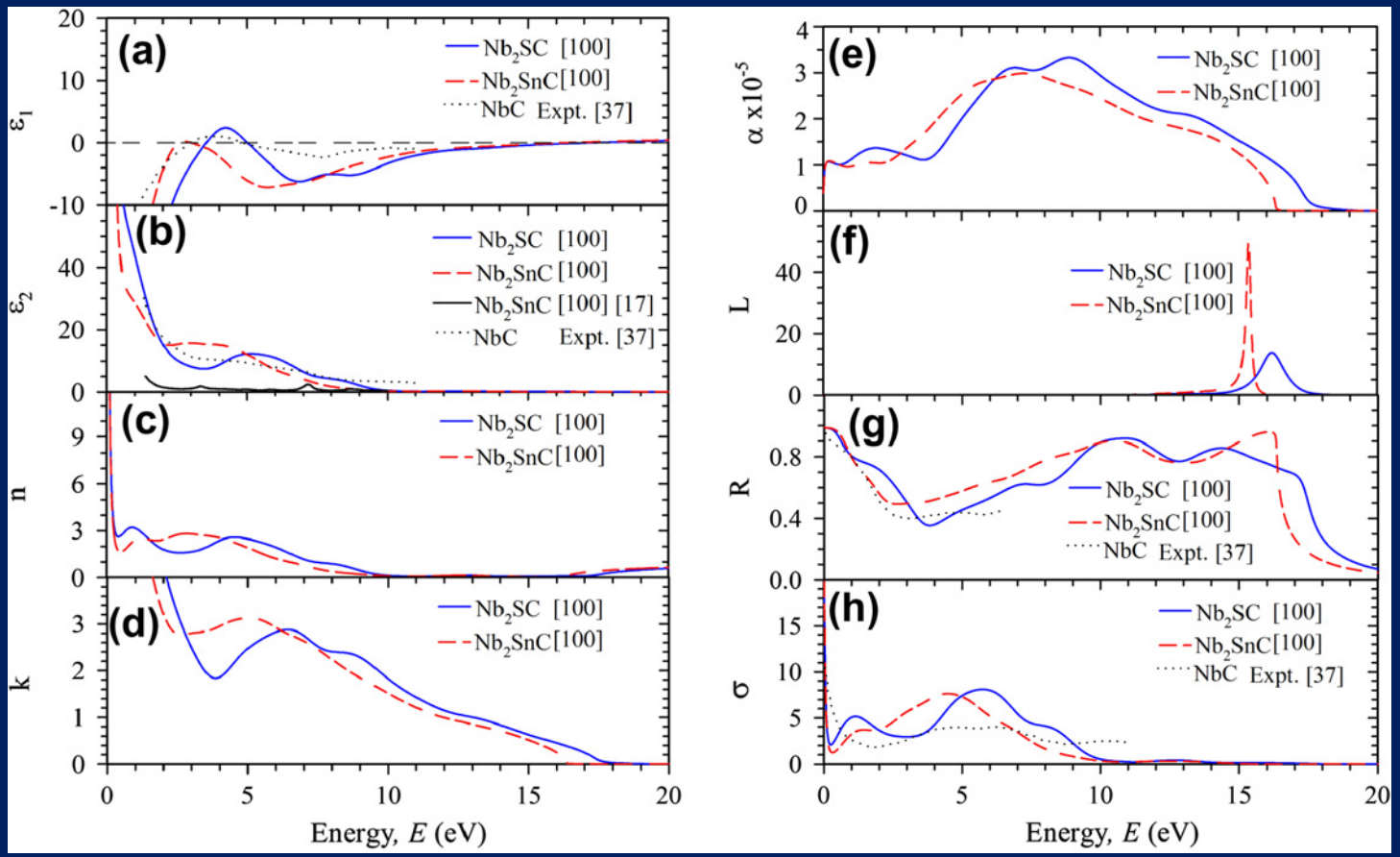
λ (e-ph coupling constant) is obtained via $\gamma = (1+\lambda)\, k_B^2\, N(E_F)/3$.

Thermodynamic Properties – *contd.*



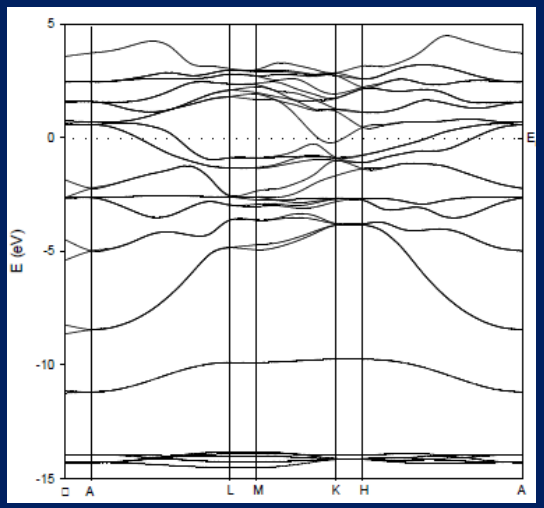


Optical Properties



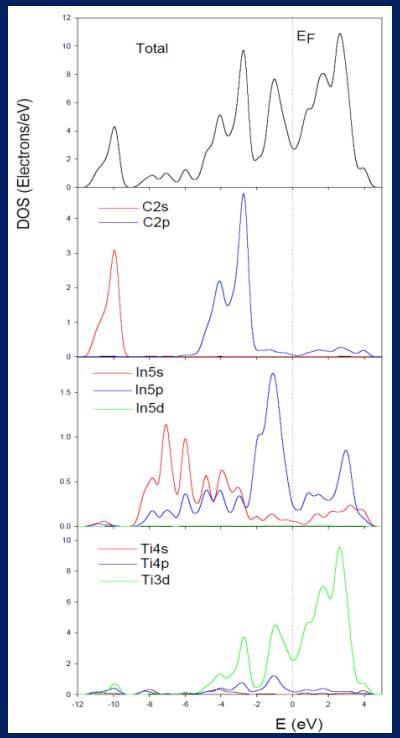
(a) Real and (b) imaginary part of dielectric function, (c) real and (d) imaginary part of refractive index, (e) absorption coefficients, (f) loss function, (g) reflectivity and (h) real part of photoconductivity

Superconductors Ti_2InC and Nb_2SC

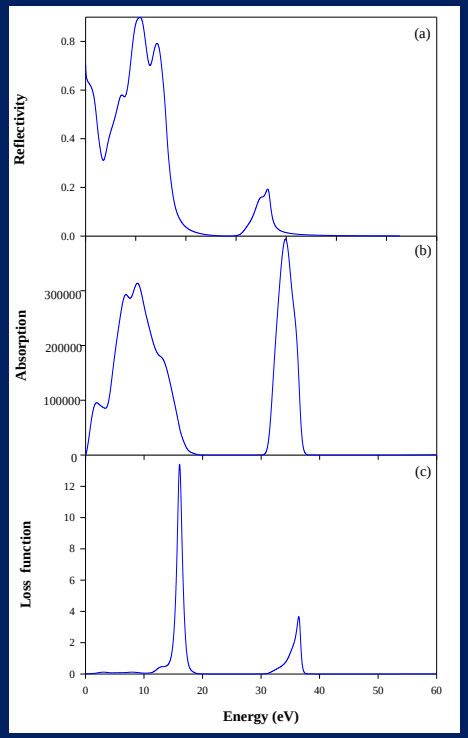


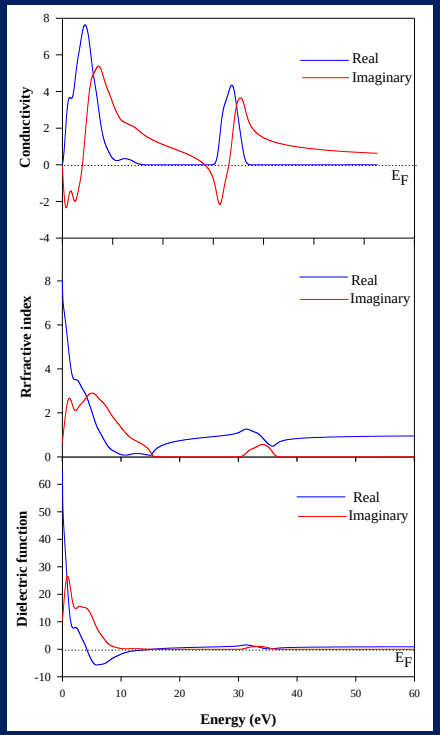
Band structure of Ti_2InC

(T_c = 3.1 K)



Total & partial DOS of Ti_2InC





Optical constants of Nb_2SC (T_c = 5 K)

Can calc, *el-phonon* coupling constant

Outlook

Finally, the question: to what extent can the properties of the MAX phases be tuned?

- Future research direction would be systematic exptl. studies of MAX phase solid solutions to elucidate the role of chemistry on phase stability and properties.
  - To engineer the band structure by appropriate dopants, so as to achieve desired properties (shifting Fermi level to tune material from metal to semiconductor in a controlled manner).
  - Combinatorial thin-film materials synthesis will be useful to identify MAX phase solid solutions with attractive, and quite possibly novel, properties.

WONDER MATERIALS - Major Breakthrough in Materials Science

- ***Graphene*** **was the first 2D wonder material**

  Discovery: 2004

- ❑ **Isolated at Manchester Univ - Nobel Prize in Physics 2010**

  ➔ **A Geim & K Novoselov for ground-breaking expts regarding 2D graphene**

- **Now *MXene* – New 2D wonder material**

  Discovery 2011

- ❑ **Derived from parent 3D MAX phases**
- ❑ ***"MXenes"*** **are produced by <u>etching</u> *A-atom* layer from MAX phases**
- ❑ ***MXenes*** **adopt 3 structures, as inherited from the parent MAX phases: M_2X, M_3X_2, & M_4X_3**

Surface of a sheet of paper is two-dimensional - can exist as 3, 5, or 7 atomic layers

Any shape that only has a surface area is a 2D shape while shapes with volume are 3D shape

MXenes – New 2D Wonder Materials

Discovery

MXenes, 2D materials, are *derived from parent* 3D MAX *phases.*

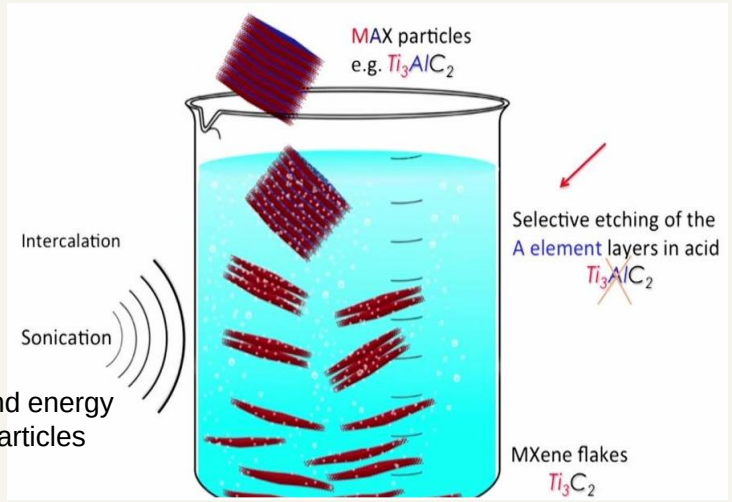
- **"*MXenes*" are produced by etching *A-atom* layer from MAX phases -- "ene" is affixed to emphasize their similarity to *Graphene***
- ***MXenes*** adopt 3 **structures**, as inherited from the **parent MAX phases: M_2X, M_3X_2, & M_4X_3**

These 2D sheets/structures *MXenes* possess greatly different properties – behavior typical of 2D *Graphene* materials.

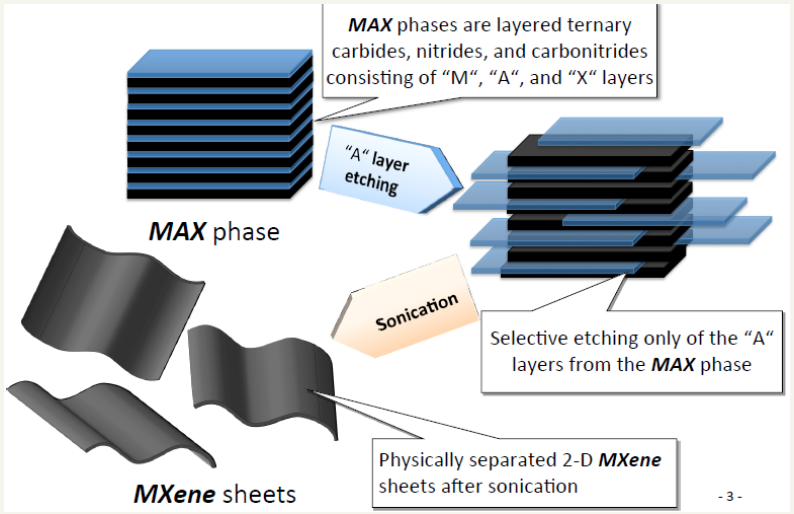
Synthesis of *Mxene* from MAX Phase

Etching process: **simply immerse MAX phase in hydrofluoric acid at room-T.**

Sonication



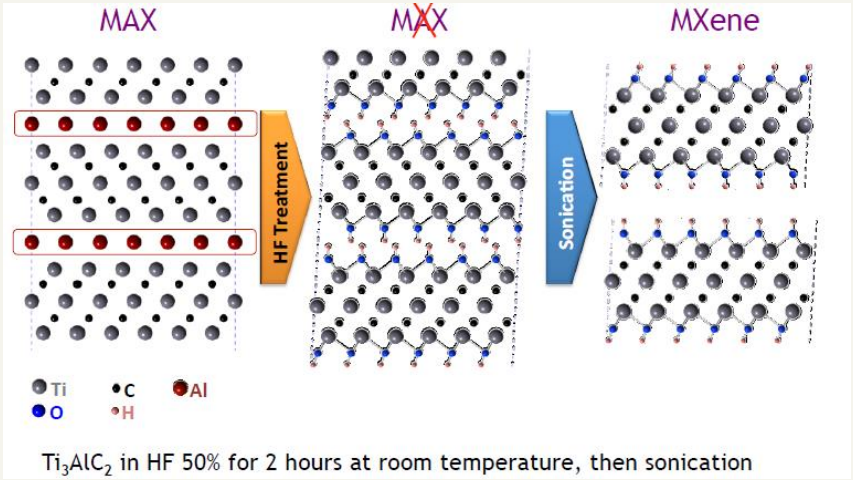
Apply sound energy to agitate particles



Solution approach to Ti_3AlC_2 Exfoliation & Dispersion

Exfoliate: Wash & Shed flakes from surface

Intercalation : Insertion of a molecule (or ion) into compounds with layered structures

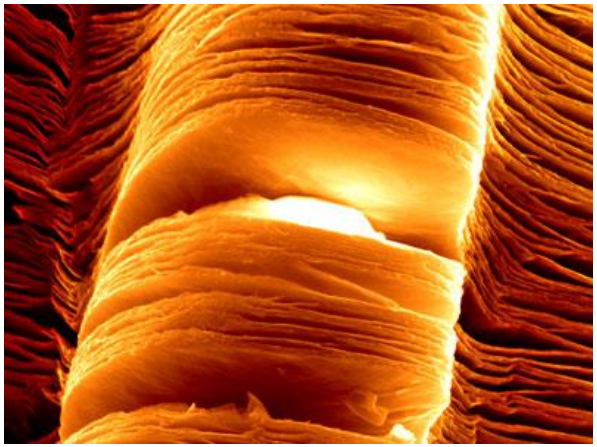


structures

MXene singled out

Intercalation is the insertion of a molecule (or ion) into compounds with layered structures

HF-etching of Ti_3AlC_2



Exfoliated MXene nanosheets.

(mage: B Anasori, Drexel Univ)

Magnification = 20,000

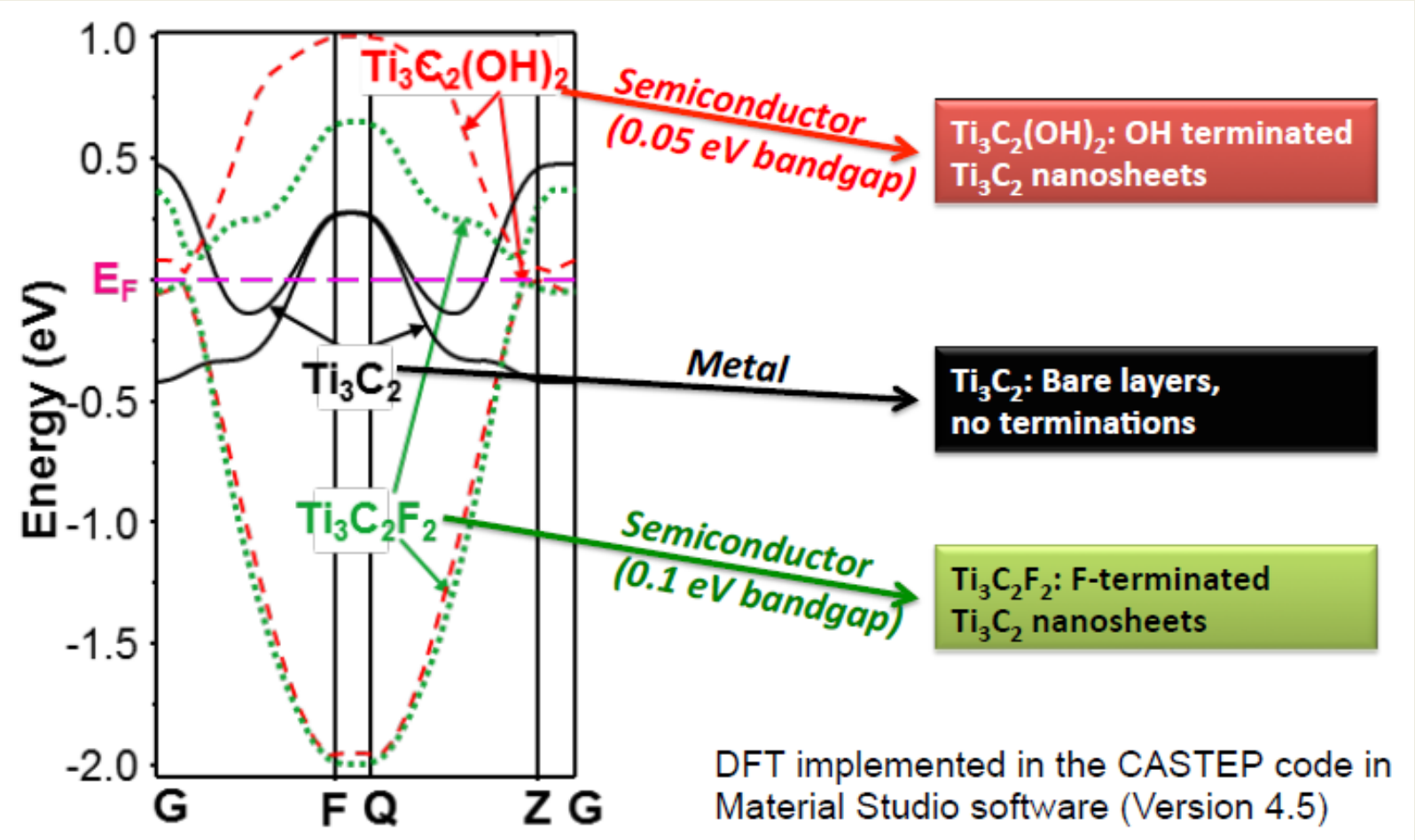
split into thin flakes
Exfoliate: wash to get rid of flakes

Singled out:

Researchers have also figured out how to break layers of MXenes, which are typically stacked like Pringles potato chips, apart. So far, they've made MXene paper, & are studying what is a single MXene layer can do.

Electronic Structure of MXenes

DFT calculations showed that MXenes' band gap can be tuned by changing the surface termination, *e.g.* bare MXene is metallic conductors, while OH or F terminated are semiconductors with small band gap.



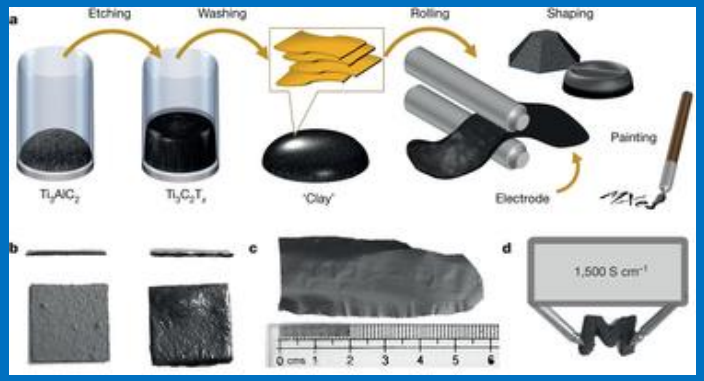
M. Naguib, et al. *Advanced Materials* 23 (2011) 4248-4253

Why's *MXene* good, then?

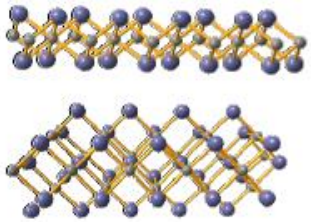
3 main properties of *MXene* that should catch our eyes are:

1. **It's hydrophilic. That means, unlike graphene, it loves water. And that's good news.**
2. **It's very malleable. Can mold it into complicated forms, or roll or press it very flat – both of which are potentially very handy for a material with conductivity.**
3. **The material has a very healthy capacitance of 900 F/cm^3 – performance will improve further. *MXene* lost no capacitance after >10,000 charge cycles.**

This clay-like material, made from etched MXene and water, is not only easier and safer to produce than current electrode material, it's also has twice the capacitance!



Applications



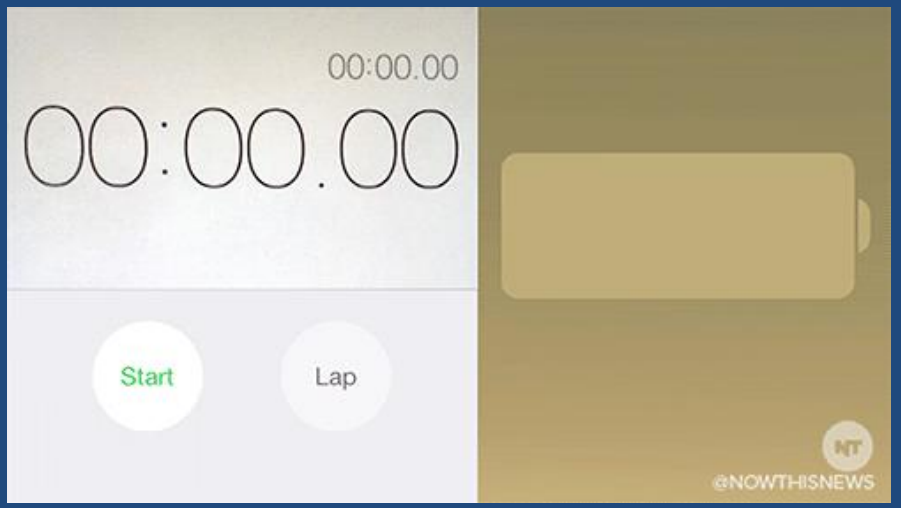
- **Electrical energy storage**
  - **Pseudocapacitors, Li-ion batteries, Hybrid devices**
- **Composite Materials**
  - **Conductive, high-strength, low-permeability polymers, high strength & high toughness ceramic-metal composites**
- **Sensors – *e.g. electrochemiluminescent sensor*** **(2018)**
- **2D and flexible electronics**
- **Spintronic Devices - 2D information superhighway**
- **2D MXenes make photonic diodes** **(18 Jan 2018)**
- **MXenes can contain 'Electromagnetic Pollution'**
  - Buzzing sound/em noise, caused by radio waves, can originate from anything that creates, carries or uses an electric current, including TV & internet cables, cell phones, tablets & laptops.
- **Use in Cell Phones that Charge in Seconds** **(15 Aug 2017)**
  https://phys.org/news/2016-09-electromagnetic-pollution-mxene-mobile-devices.html#jCp

MXene: A Breakthrough for Battery Charging?

July 30, 2017 by Sarah Chan

- **No one enjoys waiting for their phone to charge — but using a phone with low battery can be even more stressful. Fortunately, researchers from Drexel University have developed a new battery electrode design that has the potential to eliminate both of those problems. They recently published their work in the journal *Nature Energy*.**
- **The team, led by Dr. Yury Gogotsi, created the new electrode design from a highly conductive, 2-D MXene.**

  What sets MXene apart from traditional battery designs is its ability to open up more paths for ions to move quickly throughout the material.



giphy.gif https://i1.wp.com/media.giphy.com/media/xTiTnGs6ugGmS0tKCY/giphy.gif?w=1023&ssl=1

Ternary ceramics turn out to be surprisingly soft & machinable, yet also heat-tolerant, strong & lightweight

Further Could the electric clay *MXene* derived from 3-D MAX phases be the world's next wonder-material?

➔ **It's hard to guess what the next couple of years will bring to this new area of materials science.**

But it's clear that this is only the beginning.

Thank you