

Genomic Approach to Screen the Stability, Mechanical and Electronic Properties of MAX-Phase Compounds

Wai-Yim Ching, Sitaram Aryal, Ridwan Sakidja

Department of Physics and Astronomy
University of Missouri-Kansas City, USA

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Outline

- I. Project outline
- II. Introduction to MAX phases
- III. Genomic approach to study MAX phases
- IV. Computational methods
- V. Analysis of results**
- VI. Conclusions and future work

I. Project outline

LARGE SCALE SIMULATIONS OF THE MECHANICAL PROPERTIES OF LAYERED TRANSITION METAL TERNARY COMPOUNDS FOR FOSSIL ENERGY POWER SYSTEM APPLICATIONS

NETL Project DE-FE0005865 (Technical Manager: Richard Dunst)

PI: Wai-Yim Ching, University of Missouri-Kansas City

Co-PIs: Paul Rulis and Lizhi Ouyang

I. Project outline and significance

Simulations on the transition metal layered alloys, MAX phases. The objectives are:

- (1) to understand the fundamental mechanical and electronic structures of the MAX phase alloys and to predict the useful new phases;
- (2) to perform multi-axial compression and tensile experiments;
- (3) to develop new methods for calculating thermomechanical properties at high T & P.
- (4) to explore the effect of grain boundaries and interfaces of the MAX phases;
- (5) to establish collaborations with experimental scientists.

II. Statement of project objectives (OSPO) (SCOPE OF WORK) two phases:

Phase I (first 2 years): fundamental mechanical properties, electronic structure and bonding of MAX phases & execution of multi-axial tensile/compression simulations.

Phase II (third year): mechanical properties at high T, P, & corrosive environments, modeling of microstructures and interfaces in MAX phases.



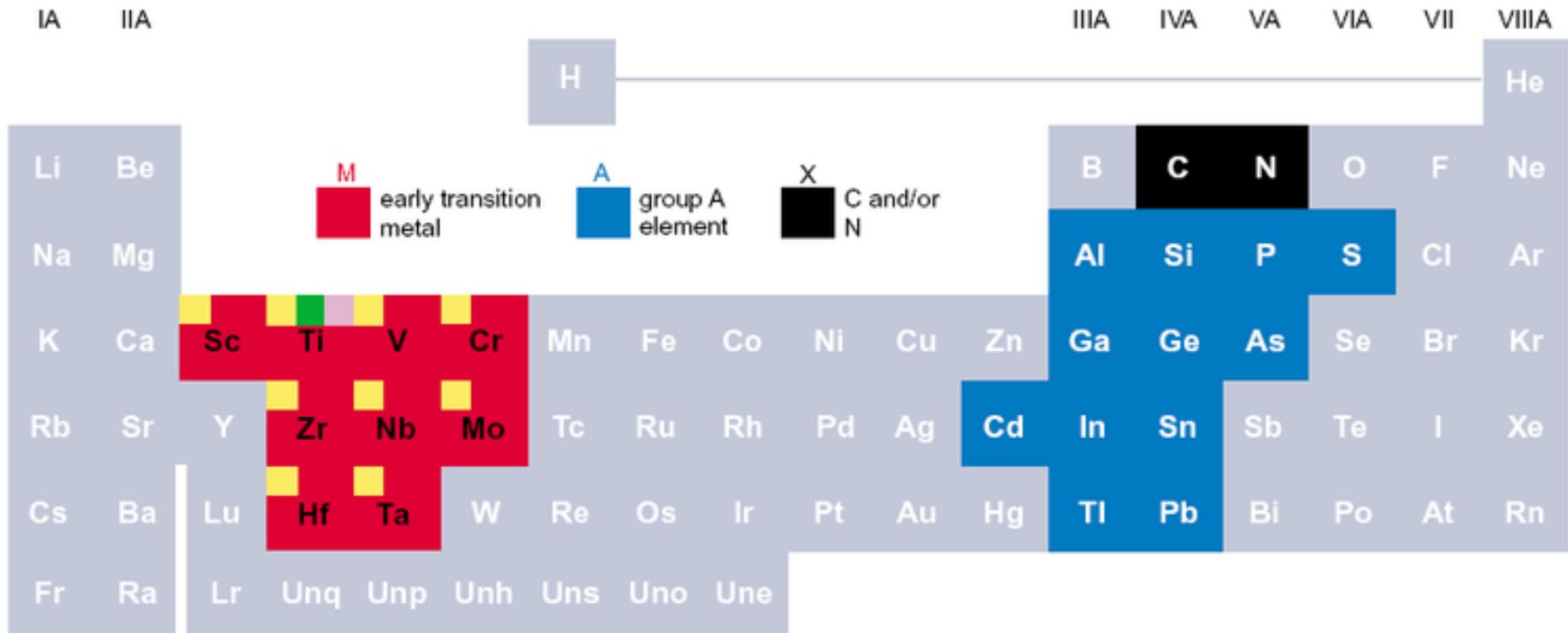
II. Introduction to MAX Phases

Why MAX phases? A novel intermetallic compound with unique properties serving as a **model system**.

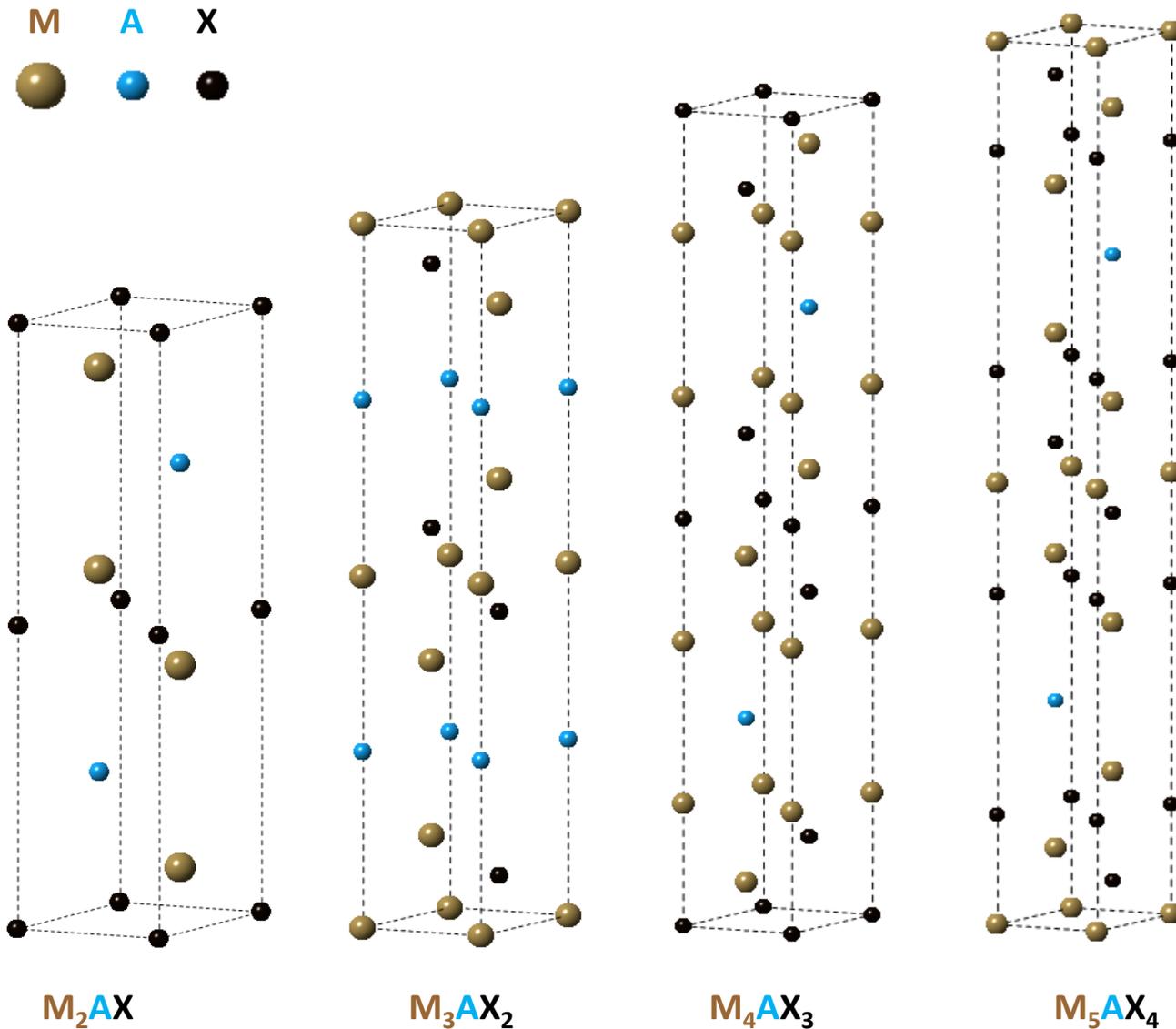
What is MAX? Layered Ternary Transition Metal Carbides and Nitrides

Formula: $M_{n+1}AX_n$ where **M** — Early Transition Metal; **A** — A-group element; **X** — Carbide or Nitride, $n = 2, 3, 4, 5$. ($n = 1$ also possible)

Most phases are 211 or 312 compounds; 413 and 514 are very rare.



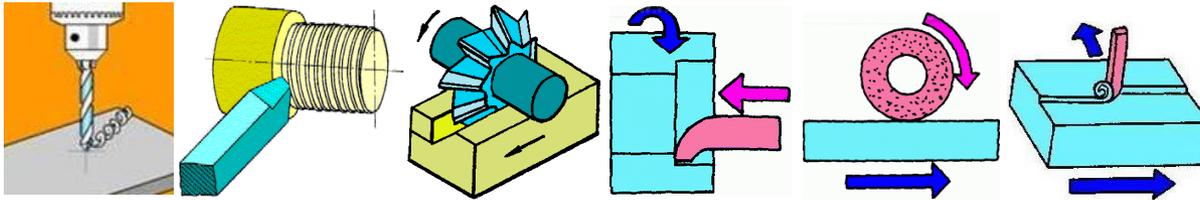
Layered hexagonal structure of 211, 312, 413, 514 MAX phases



Special properties of MAX phases compounds

Advanced Properties:

Like a Metal: thermally and electrically conductive, thermal-shock resistant, machinable, and damage tolerant;



Images from the Internet

Like Ceramics: light weighted, stiff, refractory and oxidation resistant, not too expensive.

Mechanical properties of MAX phases are very complicated! Some are very promising, others are detrimental, depending on structure, composition and interatomic bonding.

Applications of MAX phases (realized and projected):

- High-temperature structural applications;
- Porous exhaust gas filters for automobiles;
- Heat exchangers; Heating elements;
- Wear and corrosion protective surface coatings;
- Electrodes, resistors, capacitors, rotating electrical contacts;
- Nuclear applications;
- Bio-compatible materials;
- As sensor materials; cutting tools, nozzles, tools for die pressing;
- Impact-resistant materials; projectile proof armor, bullet proof vest, etc.

MAX as Advanced Materials in Fossil energy power plants? YES!

This is the one of the main goals for this project with NETL!

Using ab initio computation to explore new cost effective materials for advance applications based on fundamental understanding!

III. Genomic approach to mechanical properties

This is a significant expansion of the scope of investigation in Phases II.
MAX is an ideal system to test genomic approach in metallic materials

- ♠ There are many attempts and published papers on the calculation of mechanical properties of the MAX phases.
- ♠ A far more ambitious approach => **All MAX phases** to be screened and studied using a genomic approach.
- ♠ **Construction of a complete data base for All possible MAX phases for data mining and machine learning.**
- ♠ Consider trends in the rows and columns of elements **M**, and **A**.
- ♠ Consider difference between **X=C** and **X=N** and trends in n.
- ♠ Consider correlations between **M**, **A**, **X**.
- ♠ Consider connections to electronic structures and bonding.
- ♠ Predict the stable and better MAX phases that has not been synthesized and may have outstanding properties.

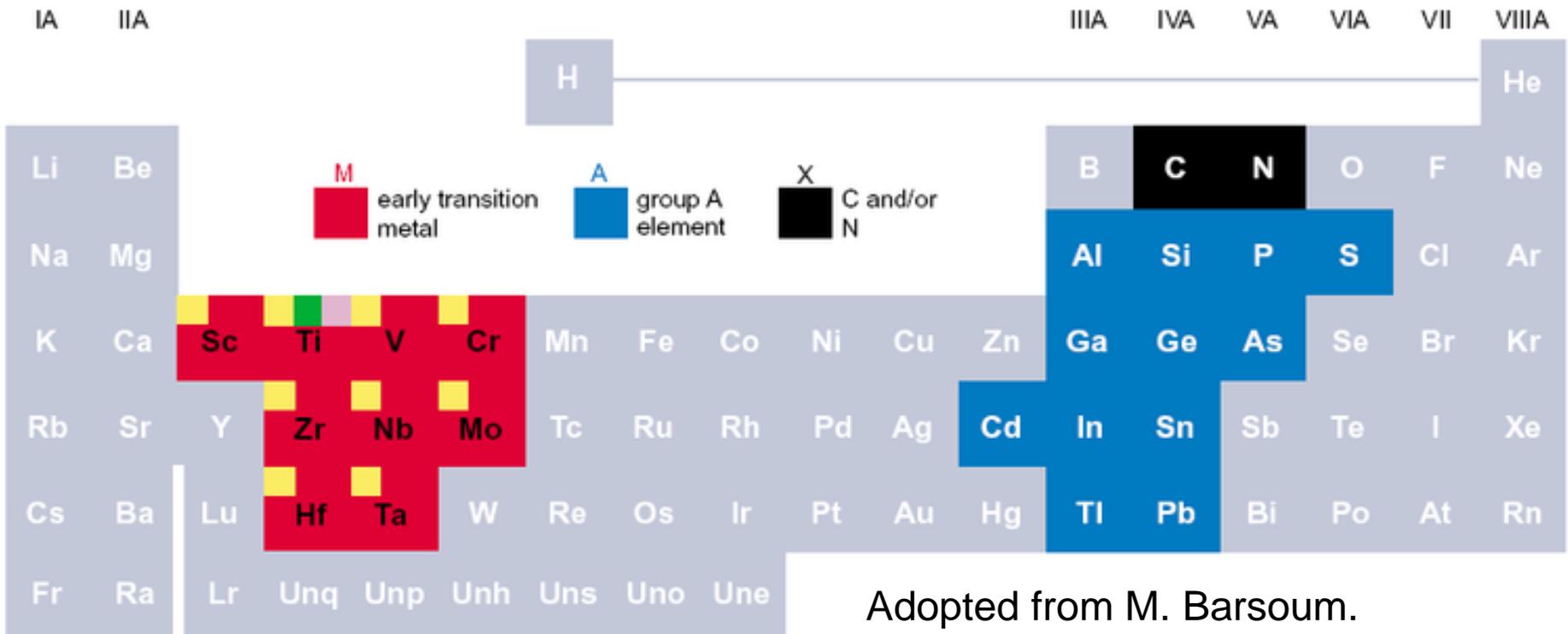
Possible MAX phase considered: $9 \times 11 \times 2 \times 4 = 792!$

M (9) in different columns: Sc (III_A); Ti, Zr, Hf (IV_A); V, Nb, Ta (V_A); Cr, Mo (VI_A).

A (11) in different columns: Al, Ga, In, Tl (III_B); Si, Ge, Sn, Pb (IV_B); P, As (V_B); S (VI_B).

X (2) = C (IV_B) or N (V_B).

$n = 1 \Rightarrow$ 211 phase, $n = 2 \Rightarrow$ 312 phase, $n = 3 \Rightarrow$ 413 phases, $n = 4 \Rightarrow$ 514 phase.



IV. Computational methods (DFT-based calculations)

Mechanical properties Calculations:

Use Vienna *Ab initio* Simulation Package (**VASP**) for relaxation, a stress-strain analysis of under linear elastic theory to first obtain elastic coefficients C_{ij} . Then the RVH approximation for poly-crystals the bulk modulus (K), Shear modulus (G), Young's modulus (E) and Poisson's ratio (η), Pugh ratio G/K.

Electronic structure characterization:

Use First-principles orthogonalized linear combination of atomic orbitals (**OLCAO**) method for electronic structure calculation. OLCAO is a Density Functional Theory (DFT) based using LDA and atomic orbitals for basis expansion.

Effective Charge Q^* on each atom, **Bond Order values** $\rho_{\alpha\beta}$ for each pair of atoms according to:

$$Q_{\alpha}^* = \sum_i \sum_{n,occ.} \sum_{j,\beta} C_{i\alpha}^{m*} C_{j\beta}^m \langle b_{i\alpha}(\vec{k}, \vec{r}) | b_{j\beta}(\vec{k}, \vec{r}) \rangle$$

$$\rho_{\alpha\beta} = \sum_{n,occ.} \sum_{j,\beta} C_{i\alpha}^{n*} C_{j\beta}^n \langle b_{i\alpha}(\vec{k}, \vec{r}) | b_{j\beta}(\vec{k}, \vec{r}) \rangle$$

V. Analysis of results

Strategy: Test calculations on 20 MAX phases. (Phase I tasks)

- ♠ Select **20** MAX phases of different components and compositions.
- ♠ Calculate the electronic structure, bonding & optical conductivities of these 20 MAX phases. (Done!)

Yuxiang Mo, Paul Rulis, W.Y. Ching, “Electronic Structure and Optical Conductivities of 20 MAX-Phase Compounds”, Phys. Rev. B86, 165122-1-10 (2012).

- ♠ Calculate the elastic and mechanical properties of the same 20 MAX phases. (Done!)

*W.Y. Ching, Yuxiang Mo, Sitaram Aryal and Paul Rulis, “Intrinsic mechanical properties of 20 MAX phase compounds”, J. Amer. Ceram. Soc. 1-6 (2013)
DOI:10.1111/jace.12376*

- ♠ Expand to all MAX phases. Find the property **trends** among them and explore the **correlations** between properties, compositions and structures. (**Phases II tasks. This presentation!**)

Elastic coefficients and mechanical properties of 20 MAX phases

Crystals	C_{11}	C_{12}	C_{13}	C_{33}	C_{44}	C_{66}	K	G	E	η	G/K=k
Ti ₃ AlC ₂	355.8	81.4	75.3	293.4	120.3	137.2	162.5	126.7	301.7	0.191	0.78
Ti ₃ SiC ₂	369.6	96.2	107.6	358.3	155.0	136.7	191.1	141.3	340.0	0.204	0.74
Ti ₃ GeC ₂	362.0	97.2	97.7	332.0	137.3	132.4	182.2	132.2	319.3	0.208	0.73
Ti ₂ AlC	301.9	68.0	63.0	267.9	105.1	117.0	139.7	110.5	262.3	0.187	0.79
Ti ₂ GaC	300.8	79.2	63.8	246.5	92.4	110.8	139.3	101.4	244.9	0.207	0.73
Ti ₂ InC	284.4	69.3	55.2	235.5	83.9	107.5	128.6	96.0	230.5	0.201	0.75
Ti ₂ SiC	312.9	82.1	110.4	329.2	149.6	115.4	173.0	124.9	302.0	0.209	0.72
Ti ₂ GeC	296.6	85.7	96.8	297.1	121.5	105.5	161.0	110.0	268.8	0.222	0.68
Ti ₂ SnC	262.6	88.6	73.1	255.2	96.8	87.0	138.8	92.4	226.8	0.228	0.67
Ti₂PC	256.8	144.8	155.0	339.5	166.3	56.0	191.8	93.1	240.4	0.291	0.49
Ti₂AsC	212.9	180.4	123.7	289.5	146.3	16.2	150.7	57.2	152.3	0.332	0.38
Ti ₂ SC	339.8	101.4	109.7	361.9	159.5	119.2	186.8	134.4	325.2	0.210	0.72
Ti ₂ AlN	312.9	73.0	95.5	290.7	126.1	120.0	160.5	117.4	283.1	0.206	0.73
V ₂ AlC	334.4	71.5	106.0	320.8	149.8	131.5	172.9	132.1	315.9	0.196	0.76
Nb ₂ AlC	316.6	86.3	117.0	288.6	137.6	115.2	173.6	116.4	285.5	0.226	0.67
Cr ₂ AlC	366.3	85.8	111.3	356.9	142.9	140.2	189.6	137.0	331.2	0.209	0.72
Ta ₂ AlC	344.5	112.2	137.1	327.9	152.3	116.1	198.8	124.1	308.1	0.242	0.62
α -Ta ₃ AlC ₂	453.6	130.5	135.6	388.4	175.0	161.5	232.8	161.1	392.8	0.219	0.69
α -Ta ₄ AlC ₃	459.2	149.1	148.7	383.1	170.5	155.0	243.0	155.3	384.1	0.237	0.64
Ta ₅ AlC ₄	481.5	149.6	158.1	423.6	188.8	165.9	257.2	169.1	416.0	0.231	0.66

Anisotropic ratio C_{33}/C_{11} correlates with G/K. Note: **Ti₂PC** and **Ti₂AsC** are outliers.

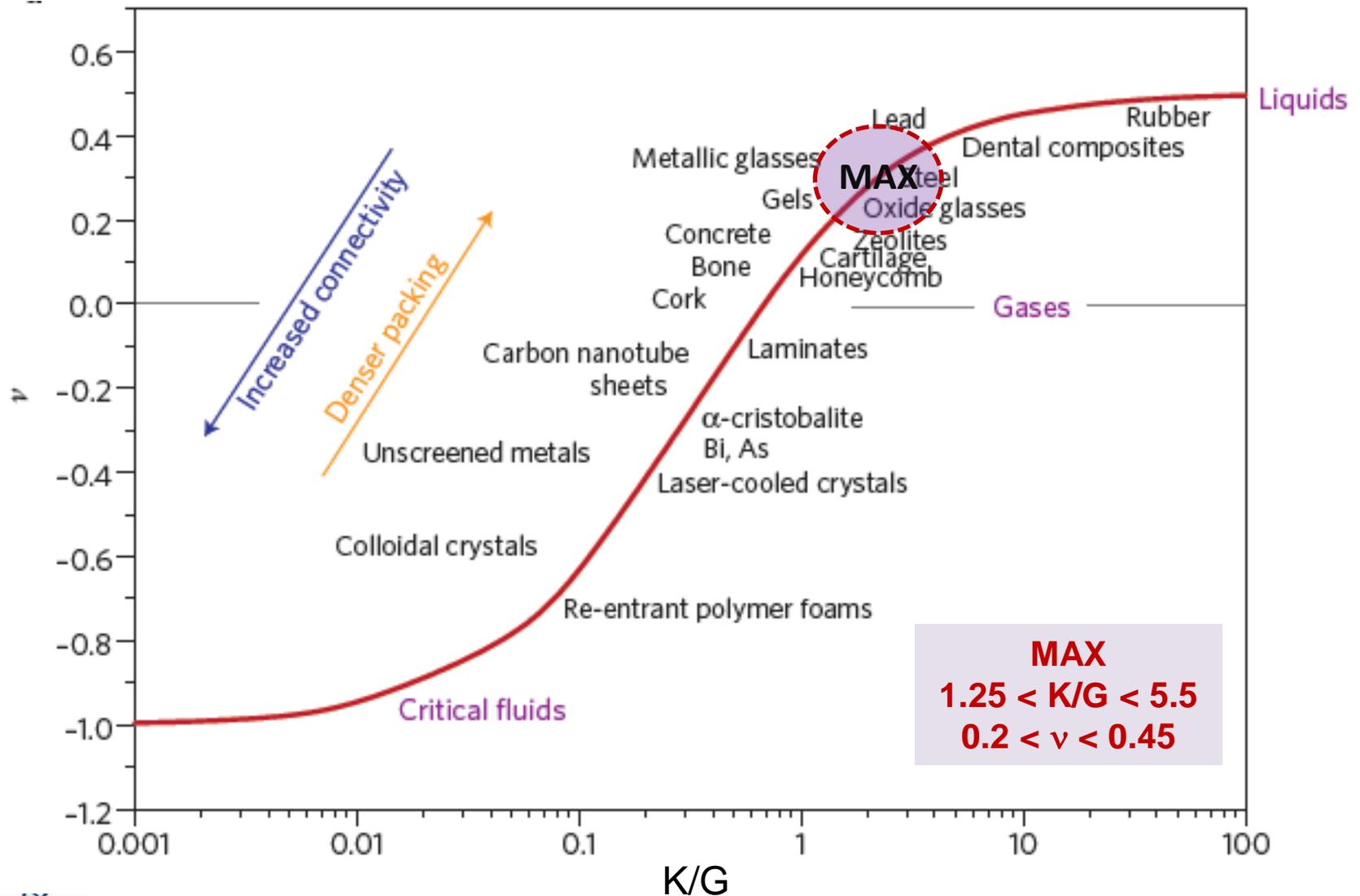
Electronic structure and bonding in the same 20 MAX phases

MAX	$\Delta Q^*(M)$	$\Delta Q^*(X)$	$\Delta Q^*(A)$	TBO	BO(M-X)	BO(M-M)	BO(M-A)	BO(A-A)	$N(E_F)$
Ti ₂ AlC	-0.330	-0.043	0.703	23.510	10.258	4.512	7.231	1.508	11.052
Ti ₂ GaC	-0.485	0.269	0.701	22.680	10.289	4.060	6.986	1.340	10.572
Ti ₂ InC	-0.424	0.148	0.700	22.750	10.238	4.396	6.482	1.636	9.260
Ti ₂ SiC	-0.393	0.097	0.688	22.820	10.344	3.583	8.153	0.742	12.921
Ti ₂ GeC	-0.509	0.324	0.694	21.750	10.337	3.541	7.111	0.758	14.720
Ti ₂ SnC	-0.381	0.069	0.693	22.320	10.294	3.926	7.110	0.993	15.084
Ti ₂ PC	-0.454	0.210	0.699	22.740	10.366	2.802	9.571	0.000	21.762
Ti ₂ AsC	-0.505	0.316	0.695	21.360	10.382	2.893	8.086	0.000	19.697
Ti ₂ SC	-0.447	0.189	0.705	21.340	10.380	2.944	8.018	0.000	7.301
Ti ₂ AlN	-0.295	-0.087	0.679	22.150	8.702	4.646	7.217	1.585	15.502
V ₂ AlC	-0.277	-0.101	0.655	22.820	10.017	4.192	6.905	1.704	21.663
Nb ₂ AlC	-0.493	0.245	0.741	15.410	7.319	1.253	5.354	1.399	13.338
Cr ₂ AlC	-0.098	-0.324	0.521	21.250	9.559	2.837	7.080	1.769	24.384
Ta ₂ AlC	-0.324	-0.044	0.692	24.810	10.130	5.724	7.561	1.397	11.126

We now have such data Table for **ALL** MAX phases.

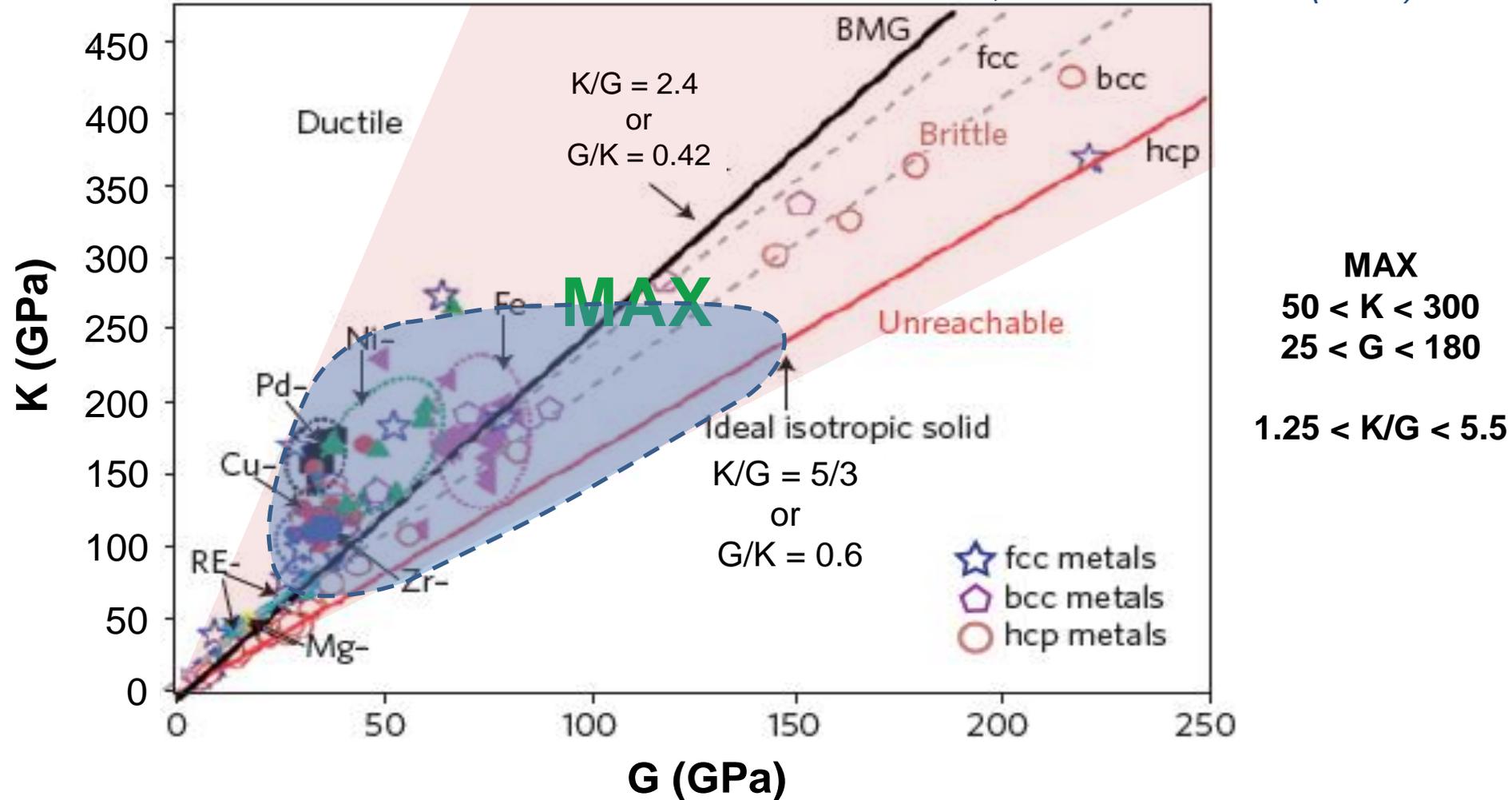
Poisson's ratio ν vs. (Bulk modulus B /Shear modulus G)

G.N. Greaves et. al. Poisson's ratio and modern materials, Nature Materials (2011).



Bulk modulus vs. Shear modulus for metallic glasses, polycrystalline metals. Note: G/K = Pugh ratio

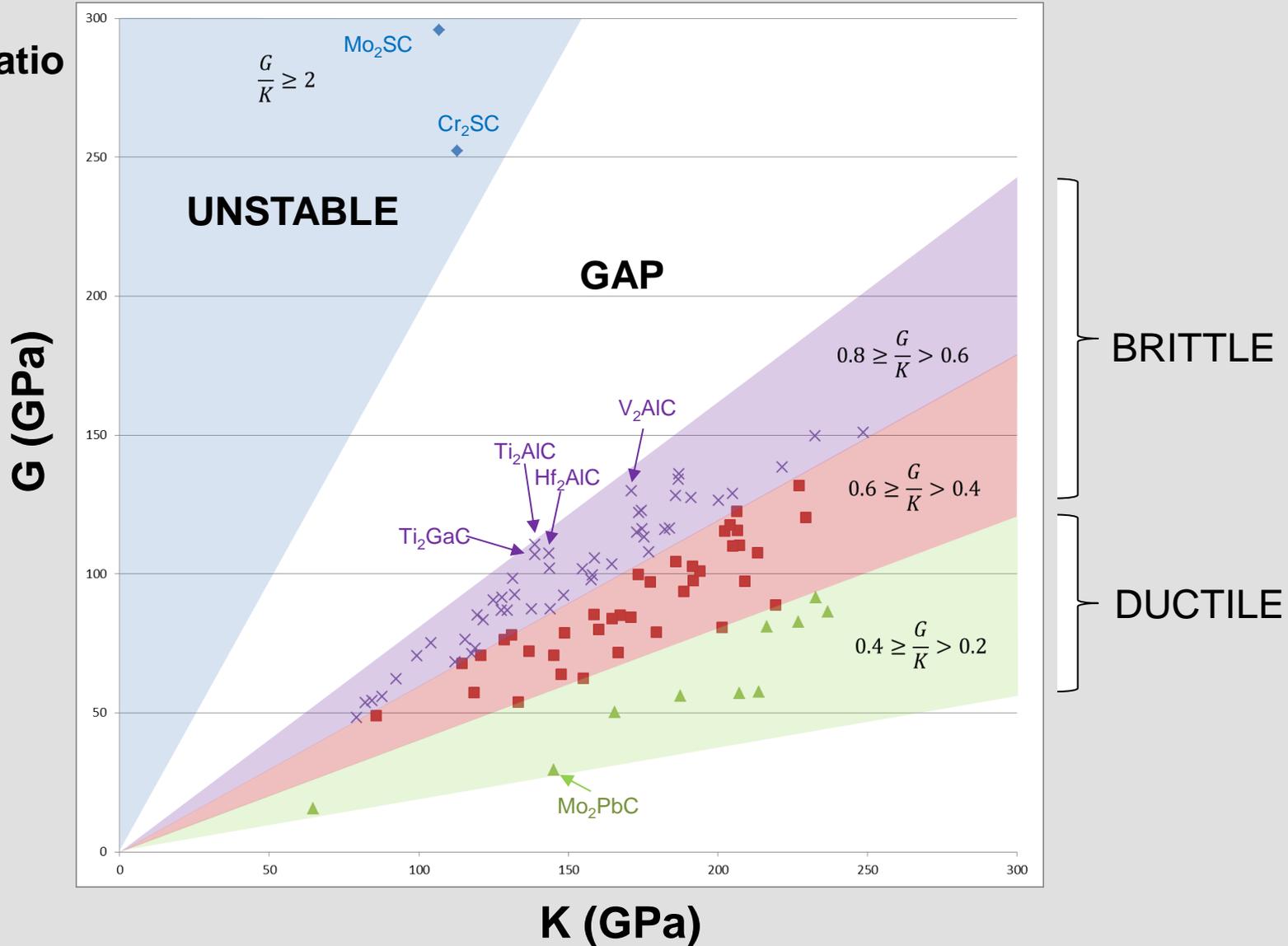
G.N. Greaves et. al. Poisson's ratio and modern materials, Nature Materials (2011).



MAX phases cover a wide range of K/G (1.25 – 5.5) or G/K (0.8 – 0.18) covering both ductile ($G/K > 0.42$) and brittle ($G/K < 0.42$) criteria

G/K of MAX's 211 Carbides

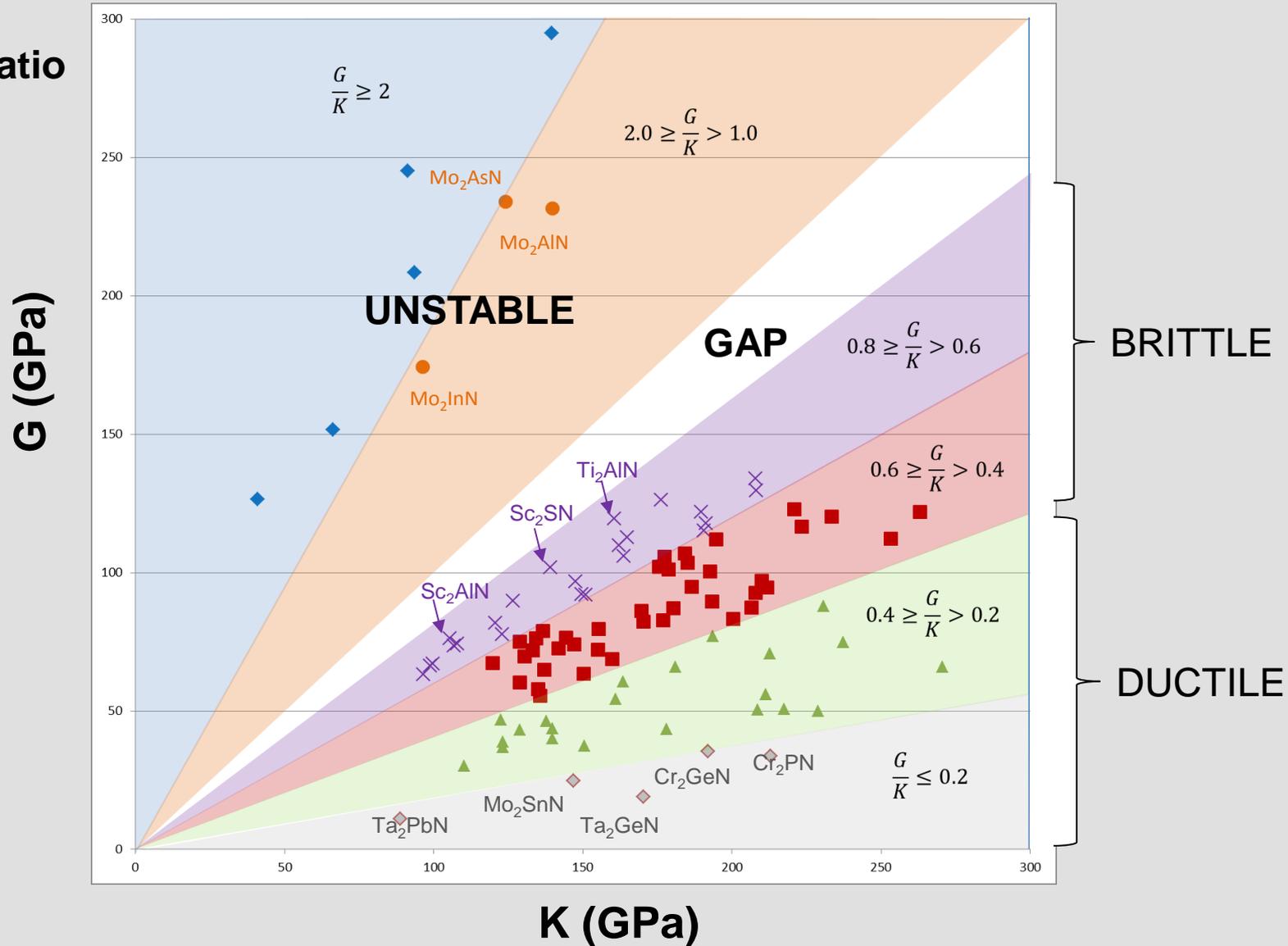
G/K = Pugh ratio



- Range of $G/K > 2$ is most likely unstable and there is a clear GAP dividing stable versus unstable MAX phases
 - A number of high G/K MAX phases identified with the Ti-based MAX phases being the highest.
 - Large number of ductile MAX phases with $G/K < 0.42$ (green regions) with the lowest G/K belongs to Mo₂PbC

G/K of MAX's 211 Nitrides

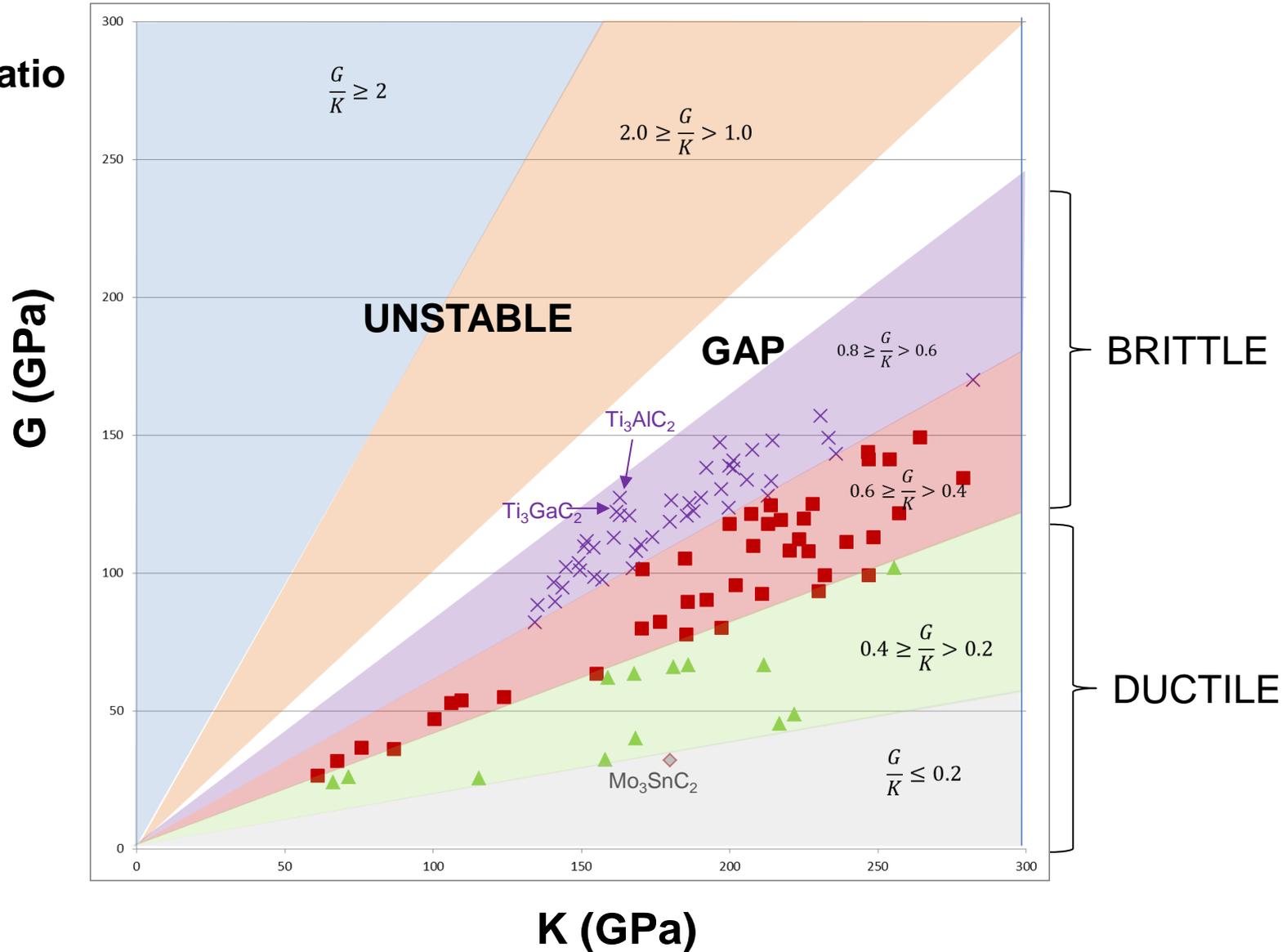
G/K = Pugh ratio



- Range of G/K is more wide-spread (0.11 – 3.0) – Unstable phases identified with $G/K > 1$
- 22 MAX phases with G/K between 0.2 – 0.4 and 5 MAX phases below 0.2 are identified
- Change of X from C to N increases ductility (low G/K ratio).

G/K of MAX's 312 Carbides

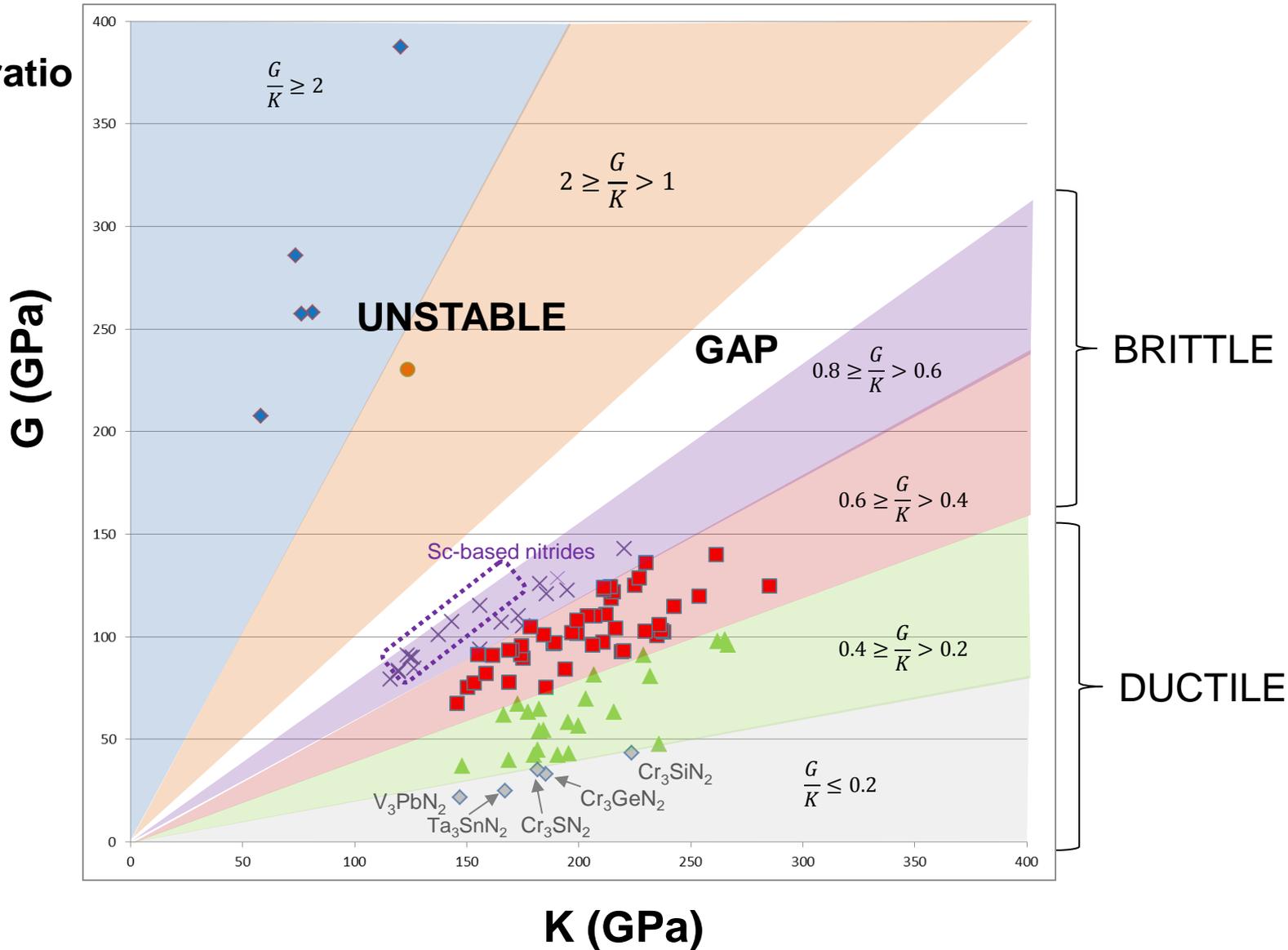
G/K = Pugh ratio



- G/K is similar to 211 carbides with Ti-based MAX having the highest G/K.
- Only one 312 phase with G/K range at or below 0.2 i.e. Mo_3SnC_2 .
- Change from 211 → 312 may also improve the ductility of MAX phases.

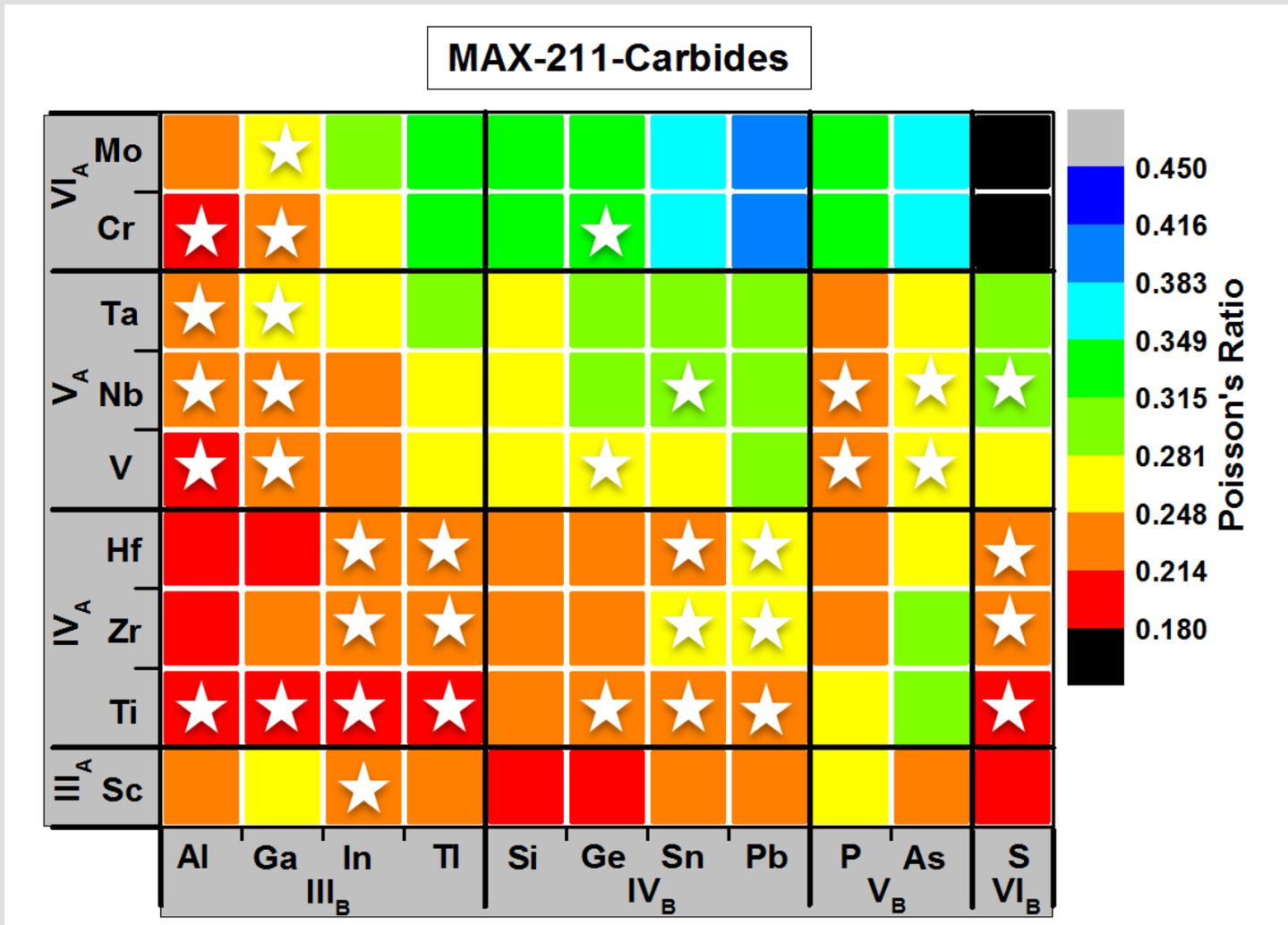
G/K of MAX's 312 Nitrides

G/K = Pugh ratio



- The maximum G/K are not Ti-based, rather they are Sc-based MAX phases.
- Compared to 312 MAX Carbides, more MAX phases (5) with G/K at or below 0.2.
- Same as for 211 phases, the change of X from C to N => better ductility (low G/K ratio)

Poisson's Ratio Map



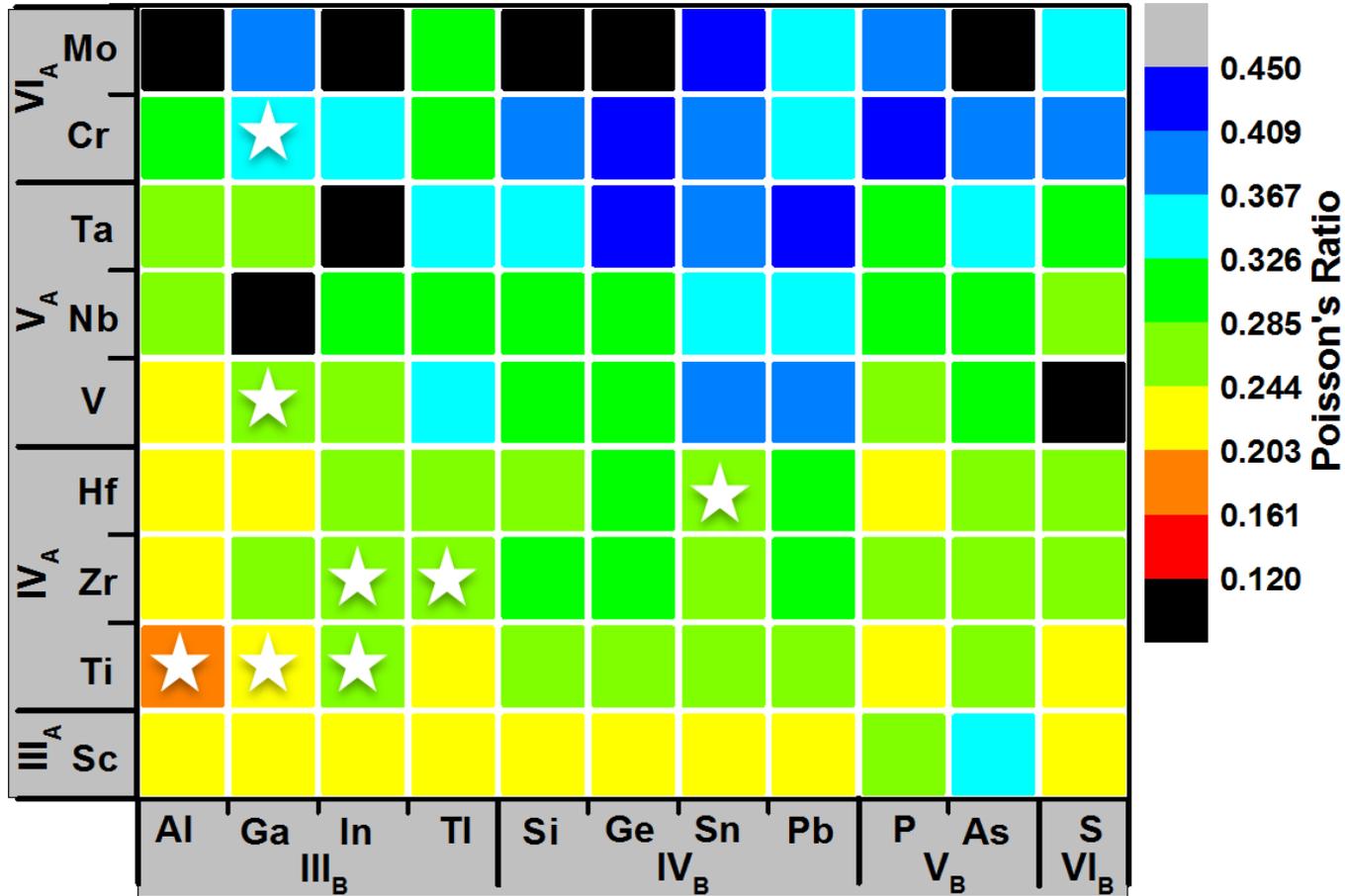
♠ The experimentally reported 211 phases (highlighted as stars) concentrate on regions with relatively low Poisson's ratio (more ceramics-like) , presumably due to the preservation of M-C (binary) covalent bonding in MAX phases.

♠ High Poisson's ratio MAX phase exist. they may offer a better ductility (more metal-like behavior). Two blacked out ones are unstable (screened out).

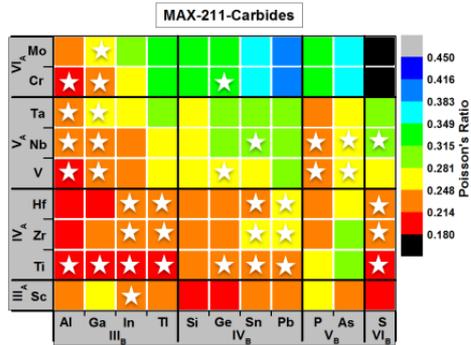
♠ More discoveries of 'ductile' MAX phases are highly desirable.

MAX-211-Nitrides

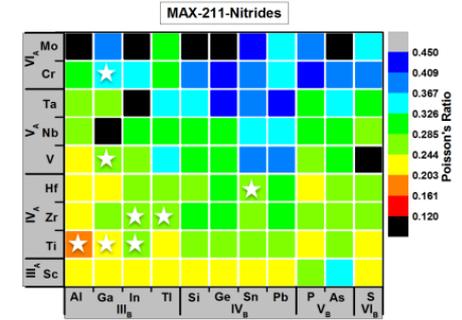
Poisson's
Ratio Map



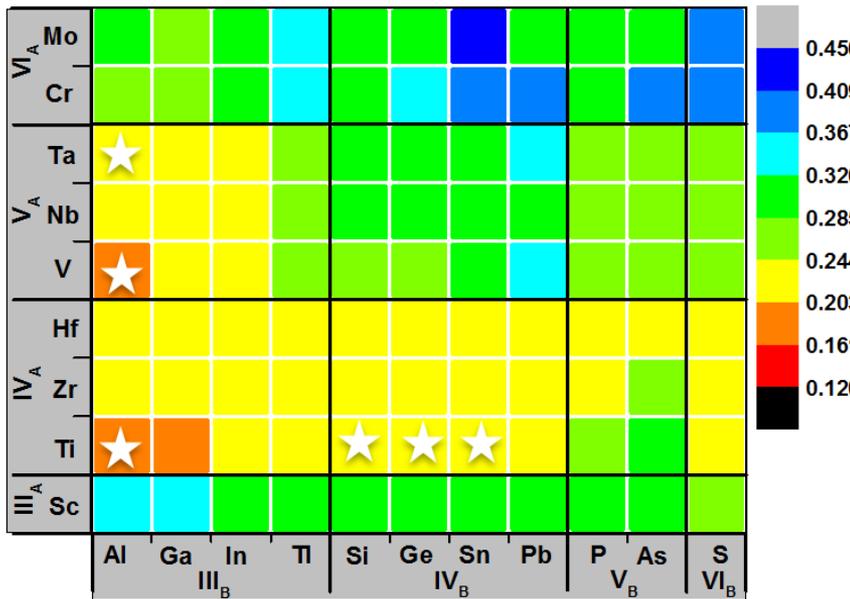
- ♠ Poisson's ratio of MAX nitrides are higher than those of MAX carbide phases.
- ♠ The C → N replacement makes the MAX phases becomes more metal-like.
- ♠ Much fewer MAX nitrides have been experimentally reported (stars).
- ♠ More possibilities of discovering new and ductile MAX phases.



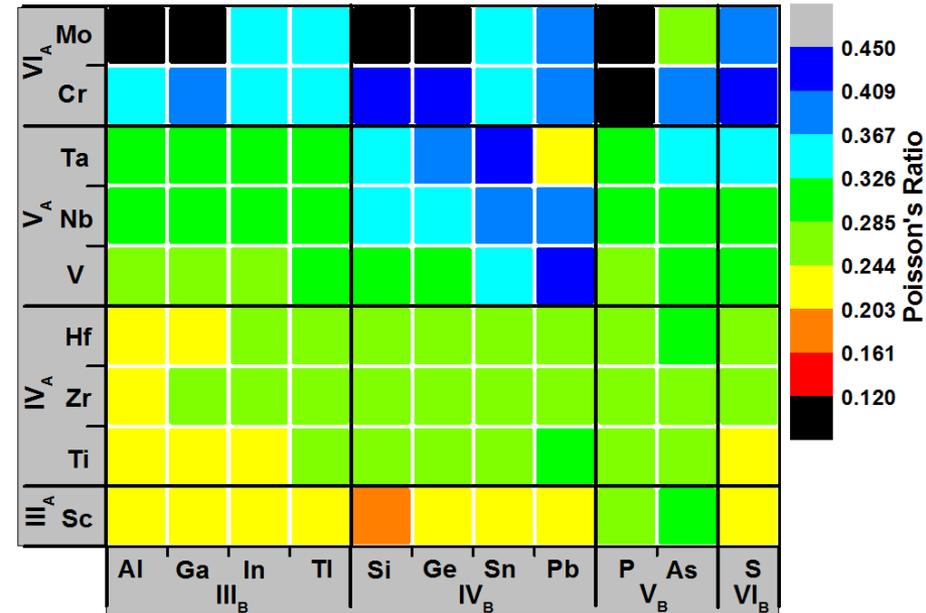
Similar plots for the **(312)** carbides and nitrides



MAX-312-Carbides

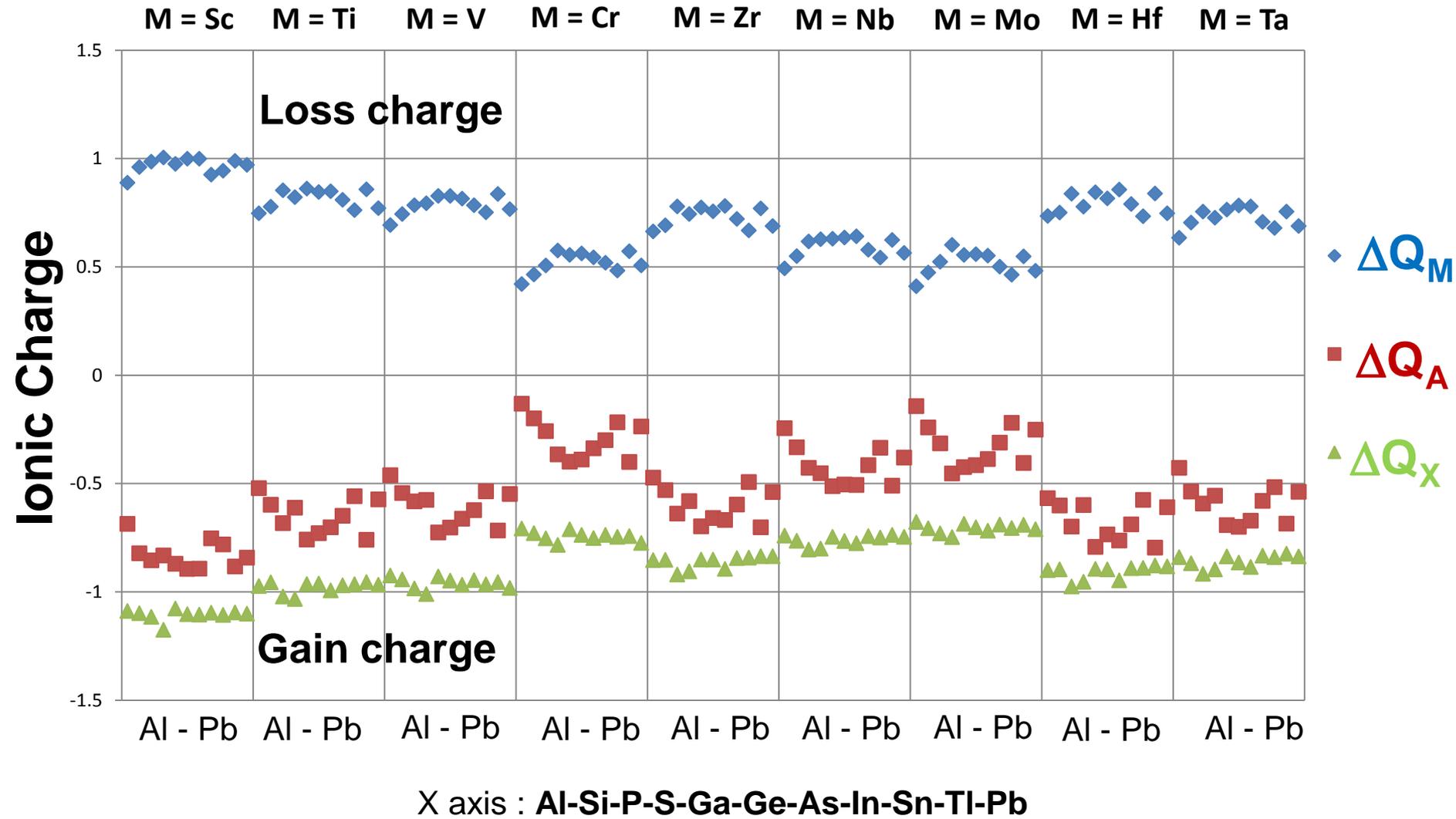


MAX-312-Nitrides



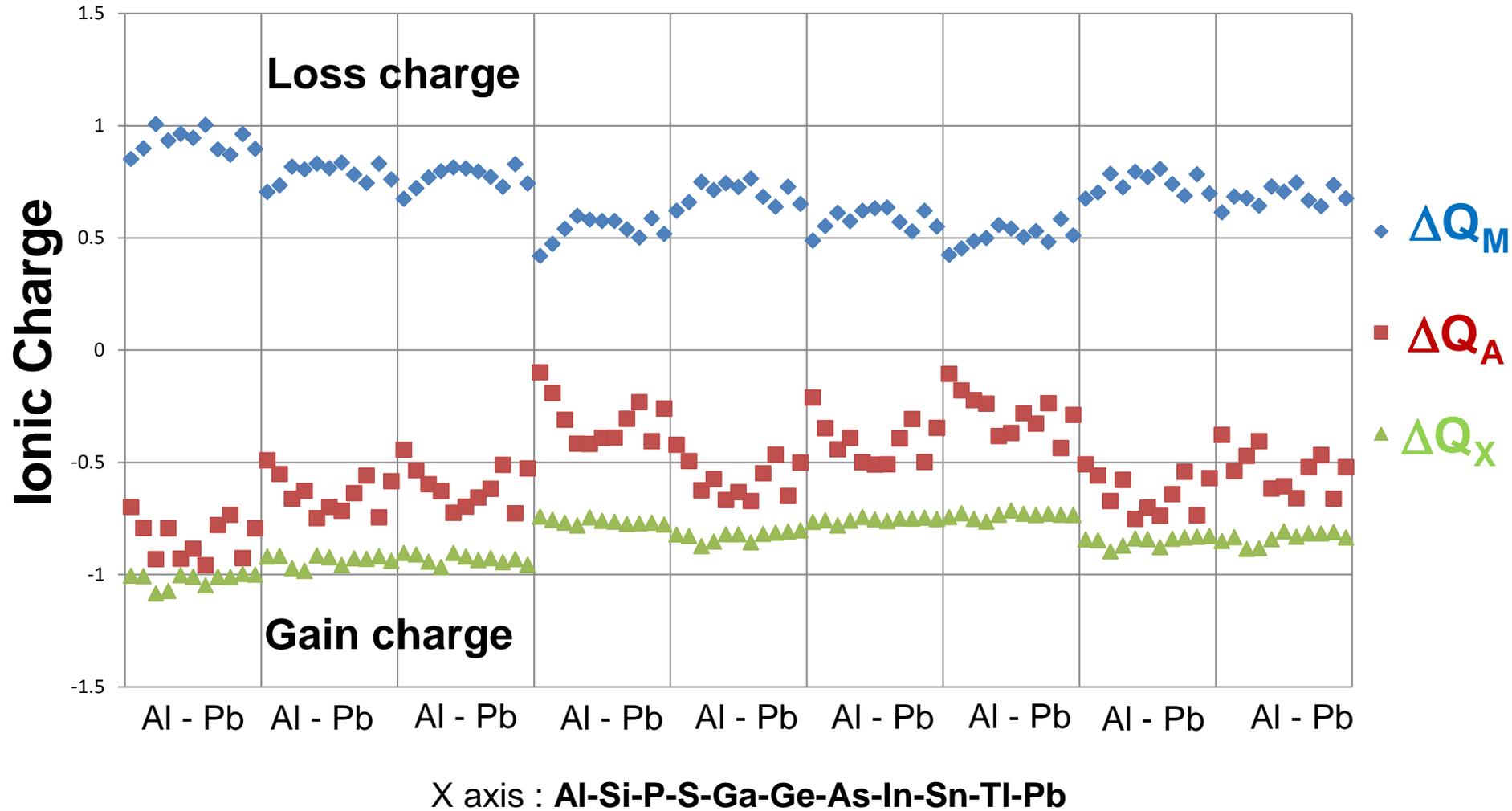
- ♠ An even smaller set of experimental database available for **MAX 312 Carbides**
- ♠ However, that there are more opportunities for achieving higher Poisson's ratio in 312 vs. 211 phases in general.
- ♠ Similar to the case of 211 nitrides, the 312 nitrides posses higher Poisson's ratio.

Ionic Charge in MAX 211 carbide phases

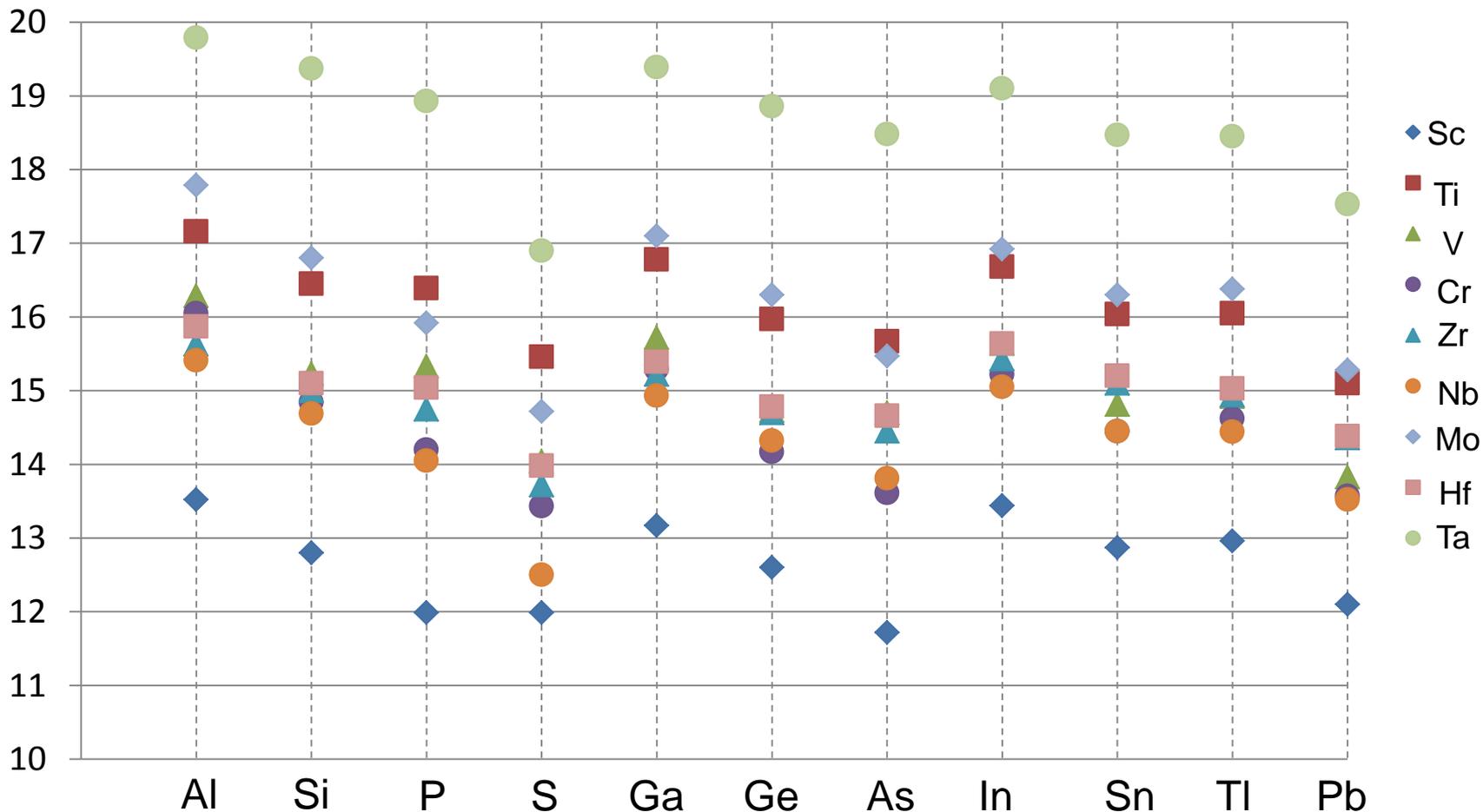


Ionic Charge in MAX 211 nitride phases

M = Sc M = Ti M = V M = Cr M = Zr M = Nb M = Mo M = Hf M = Ta

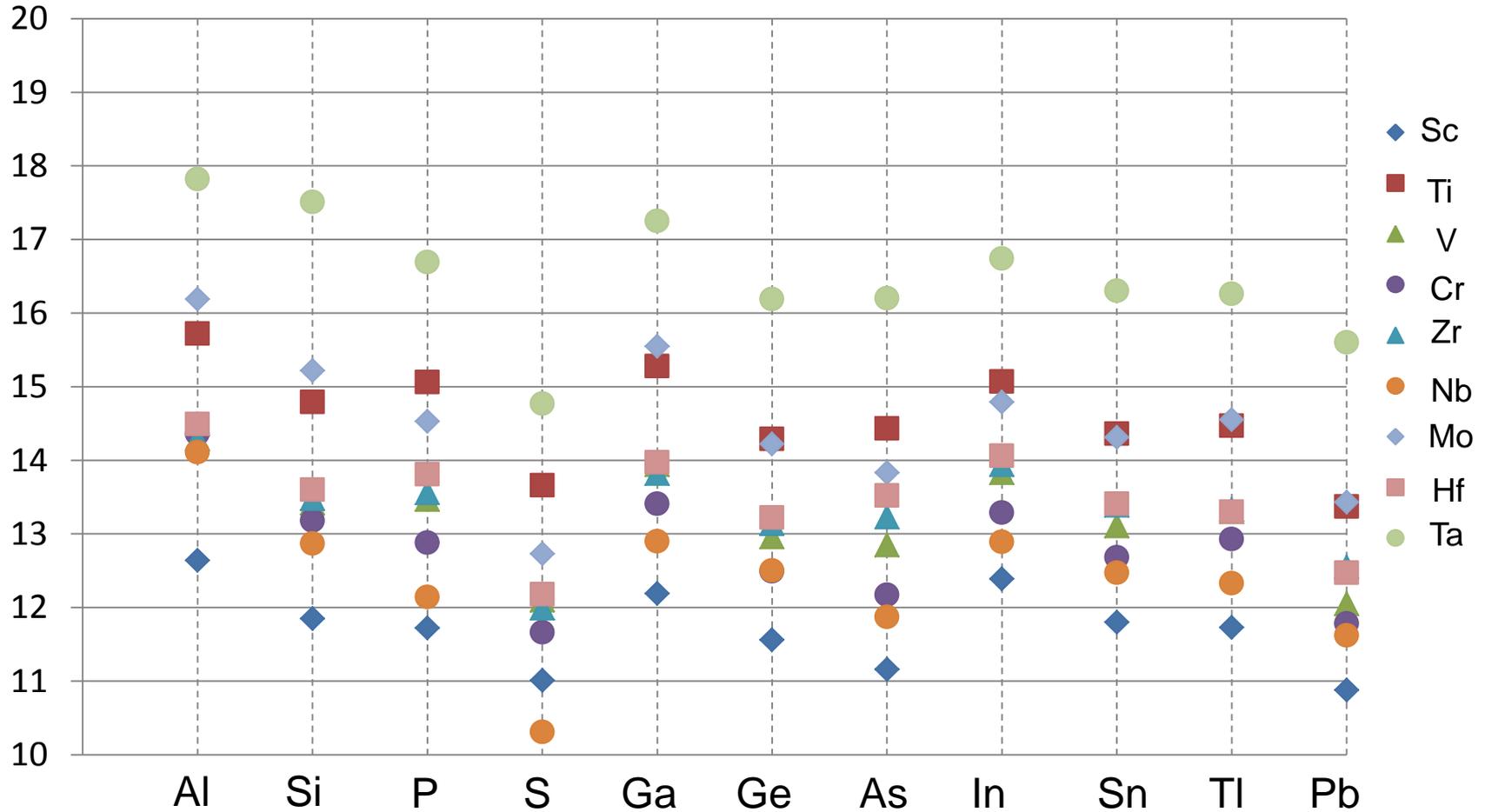


Total Bond Order in MAX 211 carbide phases



Highest BO: M=Ta, Lowest BO M= Sc

Total Bond Order in MAX 211 nitride phases



Similar pattern as in carbides: Highest BO: M=Ta, Lowest BO M= Sc (in most cases)

Genome Approach on MAX phase

Ab-initio-data–Based Machine Learning and Data Mining

Raw Data
generated from
Ab-initio Calculations
on MAX Phases

List of attributes

1. M's group #
2. M's periodic #
3. A's group #
4. X's types (C/N)
5. C_{ij}
6. Bulk Modulus
7. Shear Modulus
8. Poisson's Ratio
9. G/K
- 10....

Data Mining

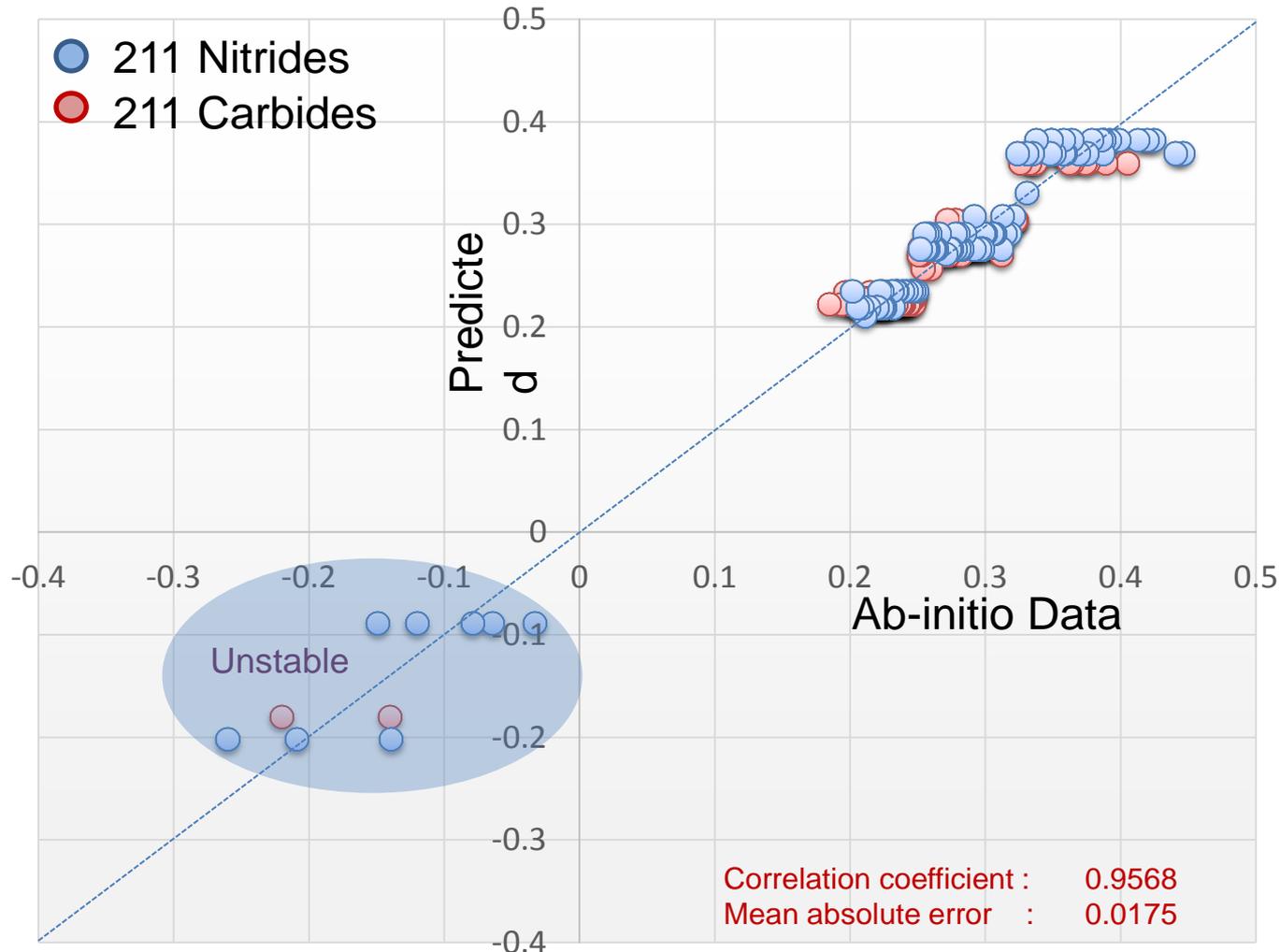
Validation

Prediction of new
MAX compositions
with desired set of
properties

Feedback to ab initio calculations for further materials optimization

Genome Approach on MAX phase: **Concept validation**

Poisson's Ratio (211 MAX Carbides & Nitrides)
Ab initio Data versus **Predicted** from Data Mining Method

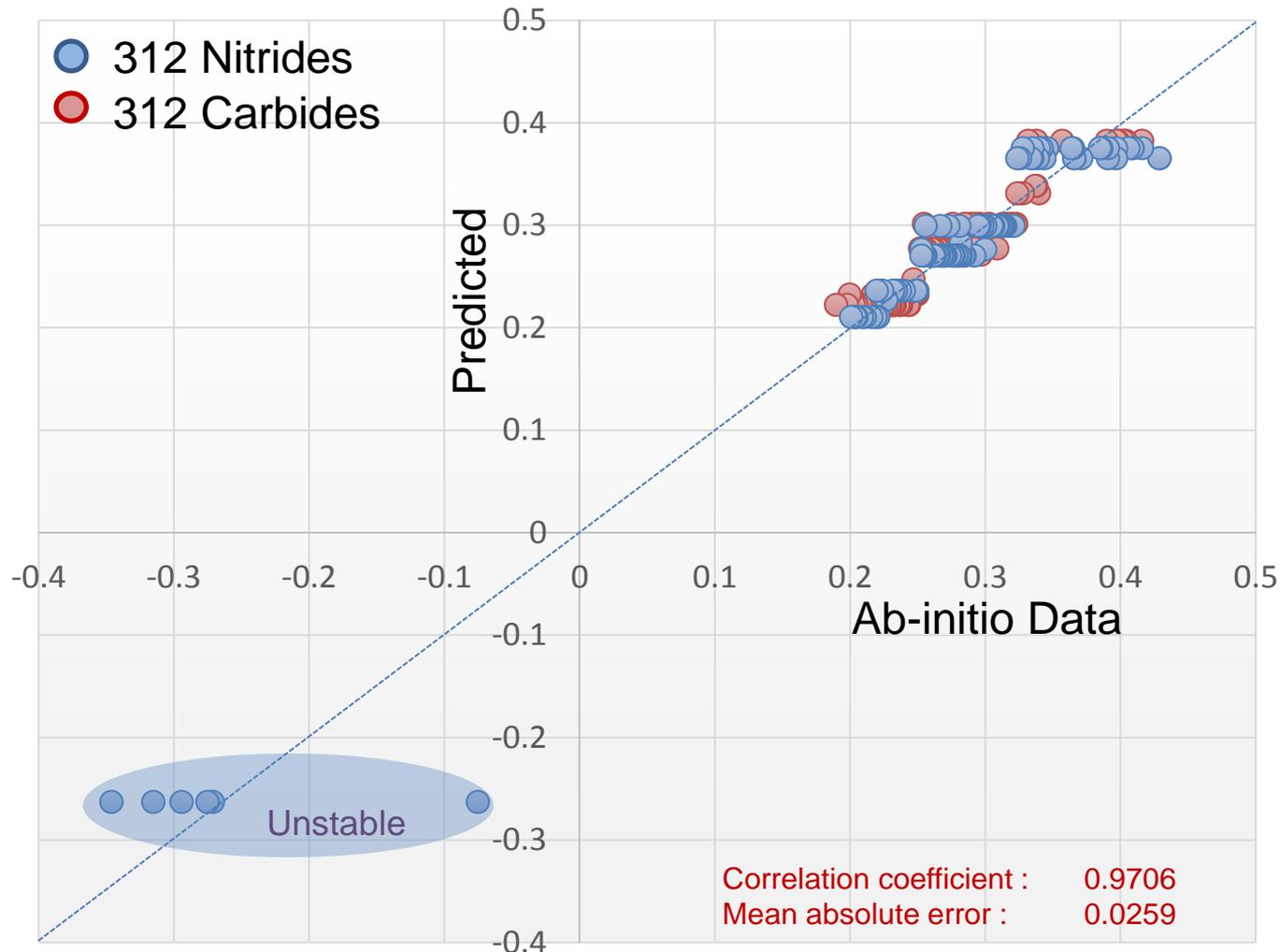


Open Source Data Mining Code : <http://sourceforge.net/projects/weka>

Genome Approach on MAX phase: **Concept validation**

Poisson's Ratio (312 MAX Carbides & Nitrides)

Ab-initio Data versus **Predicted** from Data Mining Method



Open Source Data Mining Code : <http://sourceforge.net/projects/weka>

Summary

- ♠ Massive data base has been constructed for **all** MAX phases. These include both the mechanical parameters and electronic structures.
- ♠ Results totally consistent with experimentally available information.
- ♠ The screened out phases identified and shown to be non-existent.
- ♠ There are noticeable trends in the nature of the mechanical properties based on their positions in the Periodic Table.
- ♠ Correlations to the electronic structure and bonding has yet to be fully analyzed and identified.
- ♠ These data base will be extremely valuable to experimentalists who try to synthesize new MAX phases in laboratories.
- ♠ This complete set of data can be used to test the algorithms for data mining and machine learning informatics in materials research.

Future work

- ♠ Additional analysis of massive data in seeking correlations.
- ♠ Will extend to solid solutions and composites in MAX phases.
- ♠ Can the elements **M**, **A**, **X** in MAX phases be extended?
- ♠ Extension of the genomic approach to other class of materials such as: Ni-based super-critical alloys, multi-component bulk metallic glasses, light weight high entropy alloys, nano-particle inclusion in α -SiO₂ matrix, crystallite (M₂₃C₆, γ') inclusion in metal matrix composites. etc.
- ♠ Extension to other properties such as chemical composition, corrosion resistance, thermoconductivity, optical properties, failure behavior, mechanical properties at high temperature etc. will be actively pursued.

Thank you!