TENTATIVE LECTURE SCHEDULE

		Date	Topic
1.	Wed	07.09.	Course Introduction & Short Review of the Elements
2.	Fri	09.09.	Periodic Properties & Periodic Table & Main Group Elements (starts)
3.	Mon	12.09.	Short Survey of the Chemistry of Main Group Elements (continues)
4.	Fri	16.09.	Zn + Ti, Zr, Hf & Atomic Layer Deposition (ALD)
5.	Mon	19.09.	Transition Metals: General Aspects & Pigments
6.	Wed	21.09.	Redox Chemistry
7.	Fri	23.09.	Crystal Field Theory (Linda Sederholm)
8.	Mon	26.09.	V, Nb, Ta & Metal Complexes & MOFs
9.	Wed	28.09.	Cr, Mo, W & 2D materials
10.	Fri	30.09.	Mn, Fe, Co, Ni, Cu & Magnetism & Superconductivity
10.	Mon	03.10.	Ag, Au, Pt, Pd & Catalysis (Antti Karttunen)
11.	Fri	07.10.	Lanthanoids + Actinoids & Luminescence
12.	Mon	10.10.	EXTRA
14.	Wed	12.10.	Resources of Elements & Rare/Critical Elements & Element Substitutions
15.	Fri	14.10.	Inorganic Materials Chemistry Research

EXAM: Oct. 18, 9:00-12:00

INSTRUCTIONS for SEMINAR PRESENTATIONS

- Presentation (~20 min) is given in a group of (two or) three persons
- It is evaluated in the scale: 15 ~ 25 points
- Presentation is given in English, and the slides are put up in MyCourses afterwards
- Content of the presentation:

- ELEMENT: discovery, origin of name, abundancy, world production, special features if any, etc.

- CHEMISTRY:, electronic configuration, oxidation states, metal and ionic sizes, reactivity, etc., **regarding the position in Periodic Table**

- COMPOUNDS: examples of important compounds, their properties and applications, etc.

- SPECIFIC FUNCTIONALITIES/APPLICATIONS: Two or three examples of exciting functionalities/applications of the element or its compounds. Here the meaning is to discuss why this specific element is needed in each selected application. **You will be given one or two scientific articles for a reference, and you should search for couple of more (recent) articles to be discussed in the presentation**.

PRESENTATION TOPICS/SCHEDULE

Fri	16.09.	Zn:	Rautakorpi, Stenbrink & Hyvärinen
Mon	26.09.	Nb:	Souza, Rahikka & Tong
Wed	28.09.	Mo:	Alimbekova & Tran (Nhi)
		(Ti:	Mäki & Israr)
Fri	30.09.	Mn:	Tao & Song (Zonghang)
		Cu:	Marechal, Weppe & Ishtiaq
		Ru:	Järvinen & Verkama
Fri	07.10.	Eu:	Bardiau, Wolfsberger & Klingerhöfer
		Nd:	Helminen & Keskimaula
		U:	Airas & Holopainen
Wed	12.10.	Co:	Song (Yutong) & Wang
		In:	Antila & Wallius
		Te:	Peussa & Heylen

QUESTIONS: Lecture 5

- Give plausible explanations for the following melting point (^oC) comparisons:

  Cu 1083 & Zn 420

  Cr 1860 & Mn 1245 & Fe 1535

  Fe 1535 & Ru 2282 & Os 3045

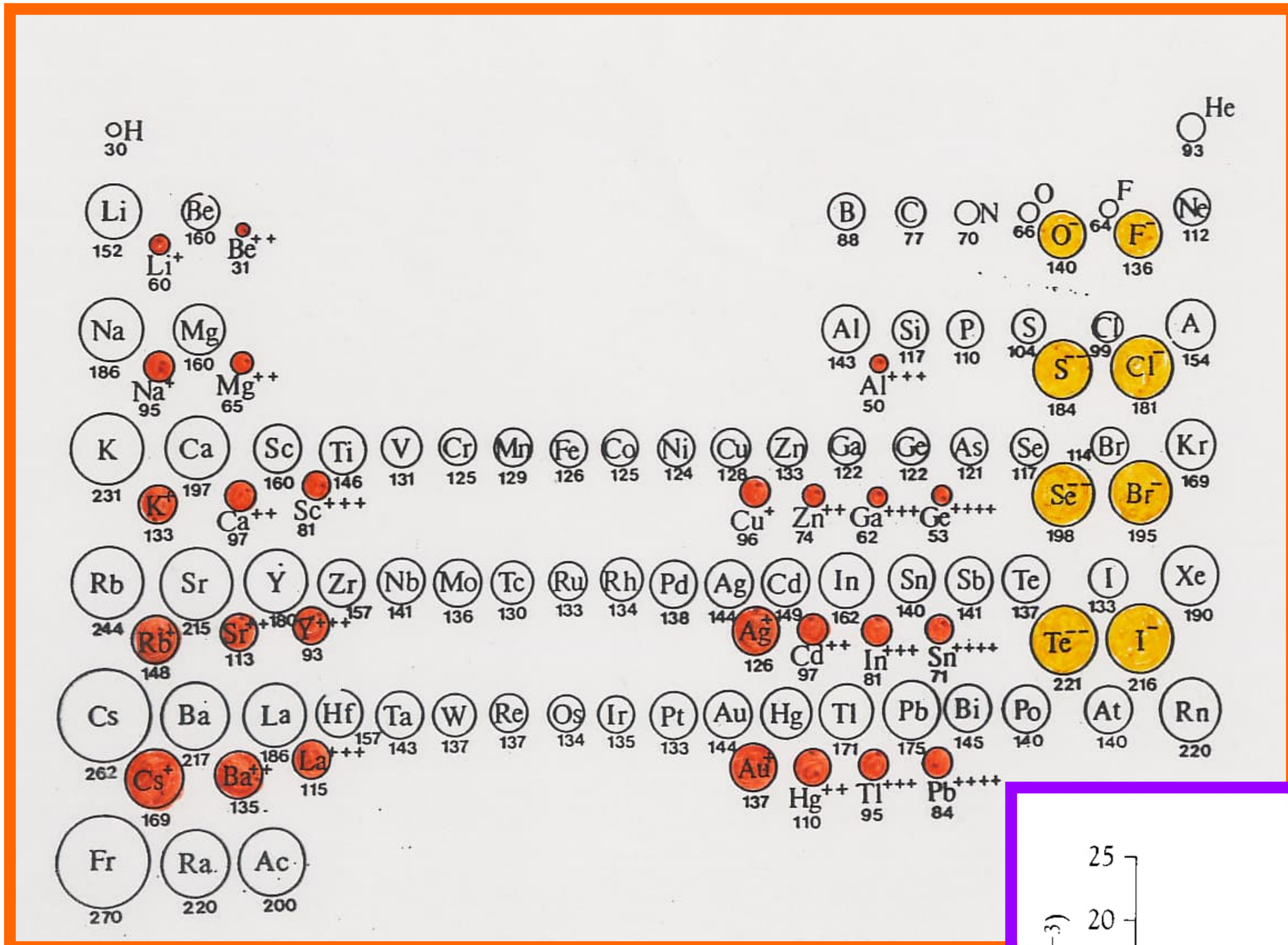
- Select among the following ions those which you assume would be color-less or weakly colored: Ti^{4+}, Ti^{3+}, Mn^{4+}, Mn^{3+}, Mn^{2+}, Fe^{3+}, Fe^{2+}, Co^{2+}, Cu^{2+}, Cu^{+}. Most importantly, motivate your answer with short explanations.

- Why pigments may appear different under sunlight and under fluorescent lighting?

d-BLOCK ELEMENTS

GENERAL FEATURES

- All are metals
- Relatively small in size (d electrons shield poorly each other)
- Multiple oxidation states $\rightarrow$ richness of chemistry
- Reactivity varies
- More electronegative than alkali and alkaline earth metals
- Both ionic and covalent compounds
- General rule: at lower oxidation states more ionic bond nature (behaves more like a metal)
- General rule: at low oxidation states positive metal ions, at high oxidation states oxoanions (e.g. Mn^{2+} and MnO_4^-)



Atomic/ionic radius

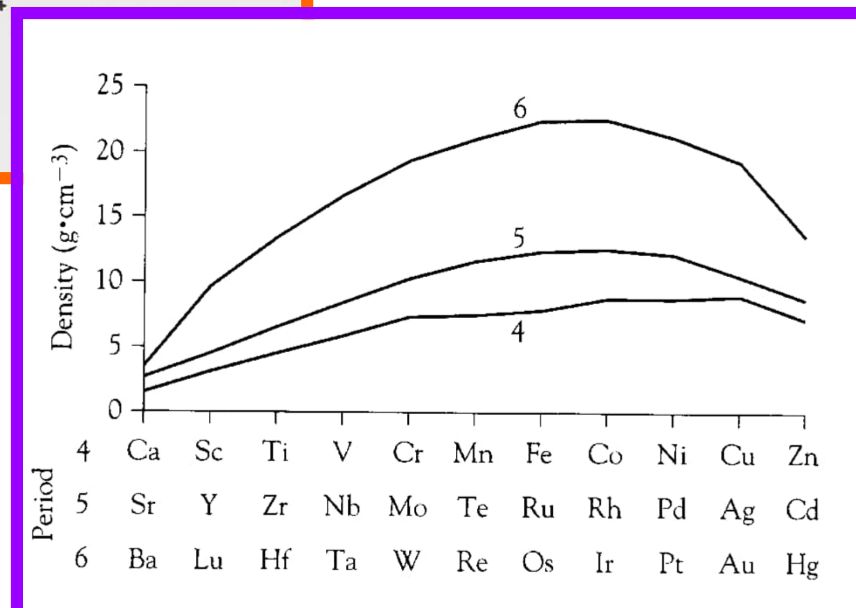
Rank the hydride ion, helium atom and lithium ion in terms of size

Explain the relative sizes.

	Nuclear charge	Number of electrons	Ionic radii (Å)
H^-	1	2	2.08
He	2	2	0.93
Li^+	3	2	0.60

6/15/2015

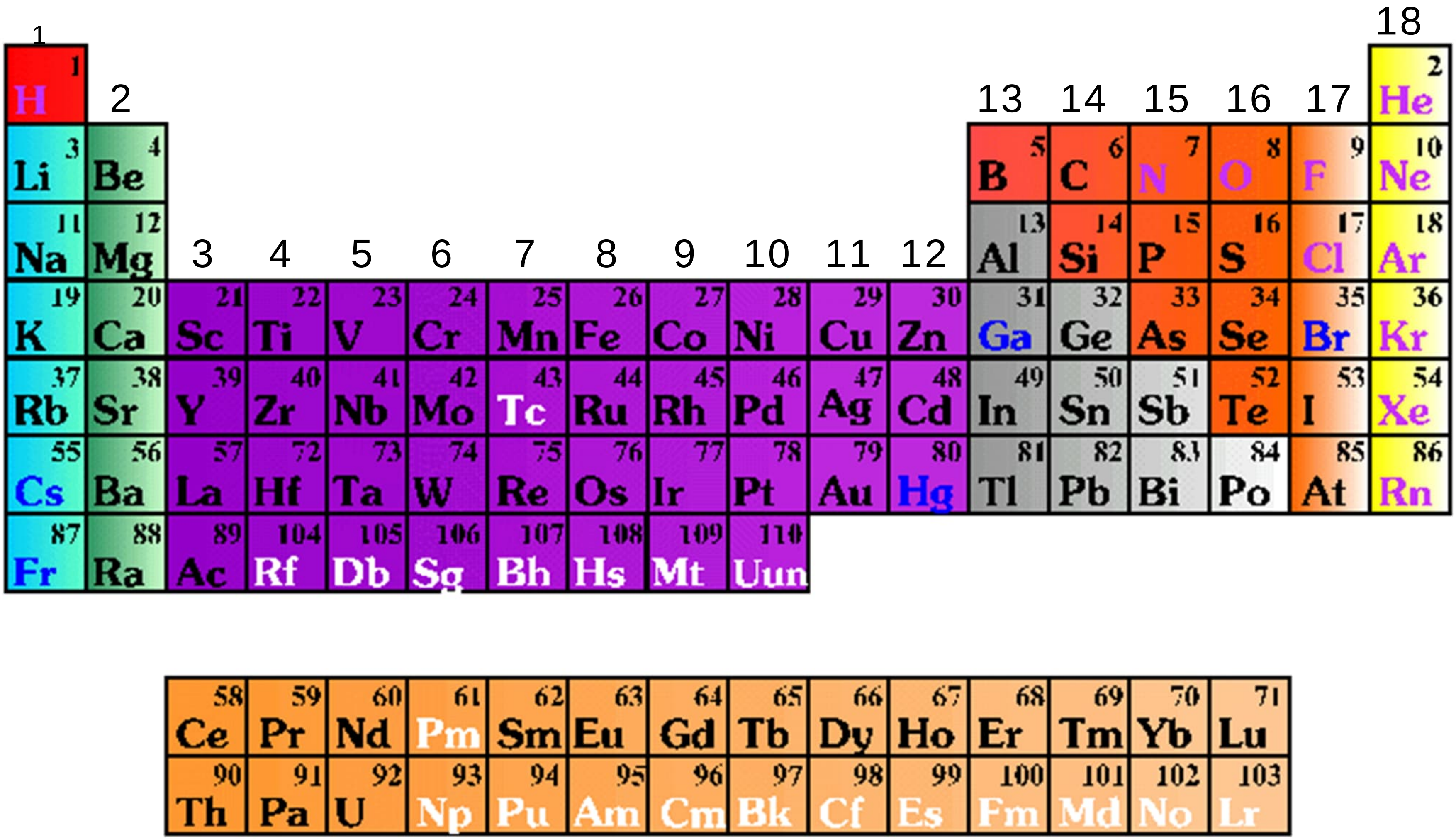
Density



Ionic radii for 3d cations (CN = 6) in Å:

- with increasing oxidation state ionic radius decreases

Ox. state	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
+II	0.86	0.79	0.80	0.83	0.78	0.75	0.69	0.73	0.74
+III	0.67	0.64	0.62	0.65	0.65	0.61	0.60	0.54	-
+IV	0.61	0.58	0.55	0.53	0.59	0.53	0.48	-	-



Alkali metals

Alkaline earth metals

Halogens

Noble gases

Transition metals

Lanthanides

Actinides

OXIDATION STATES

Element	Symbol	Electronic Configuration
Scandium	Sc	$[Ar]3d^1 4s^2$
Titanium	Ti	$[Ar]3d^2 4s^2$
Vanadium	V	$[Ar]3d^3 4s^2$
Chromium	Cr	$[Ar]3d^5 4s^1$
Manganese	Mn	$[Ar]3d^5 4s^2$
Iron	Fe	$[Ar]3d^6 4s^2$
Cobalt	Co	$[Ar]3d^7 4s^2$
Nickel	Ni	$[Ar]3d^8 4s^2$
Copper	Cu	$[Ar]3d^{10} 4s^1$
Zinc	Zn	$[Ar]3d^{10} 4s^2$

Element							
Sc			**+3**				
Ti		+2	+3	**+4**			
V		+2	+3	**+4**	**+5**		
Cr		+2	**+3**	+4	+5	+6	
Mn		**+2**	+3	+4	+5	+6	+7
Fe		**+2**	**+3**	+4	+5	+6	
Co		**+2**	**+3**	+4	+5		
Ni		**+2**	+3	+4			
Cu	+1	**+2**	+3				
Zn		**+2**					

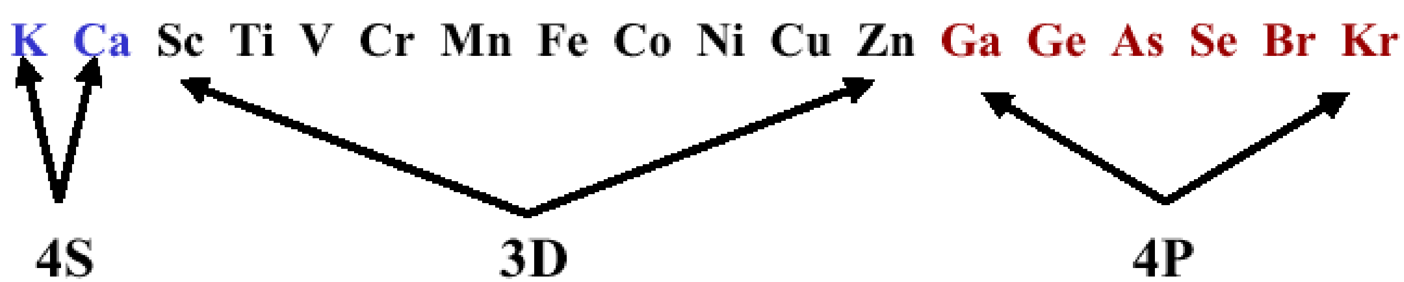


Figure 1. The 4th row of the periodic table. The transition metals are the elements that range from Sc (Scandium) to Zn (Zinc).

	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	(Zn)
+VIII										
+VII					•					
+VI				•	o	o				
+V			•		•					
+IV		•	o		o			o		
+III	•	•	•	•	o	•	•			
+II		o	o	o	•	•	•	•	•	•
+I									•	

	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	(Cd)
+VIII						o				
+VII					•					
+VI				•	o	o				
+V			•	o						
+IV		•	o	o	o	•	o	o		
+III	•	o	o	o	o	o	•		o	
+II			o	o		o	o	•		•
+I						o	o		•	

	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	(Hg)
+VIII						•				
+VII					•					
+VI				•	o	•				
+V			•	o	o					
+IV		•	o	o	o	o	•	•		
+III	•		o	o	o		•		•	
+II			o	o				•		•
+I									o	•

$ns^2(n-1)d^x$

• : most stable
o : possible

MELTING POINTS (°C)

Ti	1668	Zr	1852	Hf	2220
V	1890	Nb	1470	Ta	3000
Cr	1860	Mo	2620	W	3410
Mn	1245	Tc	2140	Re	3180
Fe	1535	Ru	2282	Os	3045
Co	1492	Rh	1960	Ir	2443
Ni	1452	Pd	1552	Pt	1769
Cu	1083	Ag	961	Au	1063

- **many valence electrons**
  → many electrons per atom in the metal bond
  → good electrical conductors
  → strong bonds
  → high melting points
  → hard
- **compare to; Zn 420, Cd 321, Hg -38**
- **compare to: alkali metals 179→29, alkaline earth metals 1080 → 725**

Crystal (or ligand) field SPLITTING of d (or f) ORBITAL energies

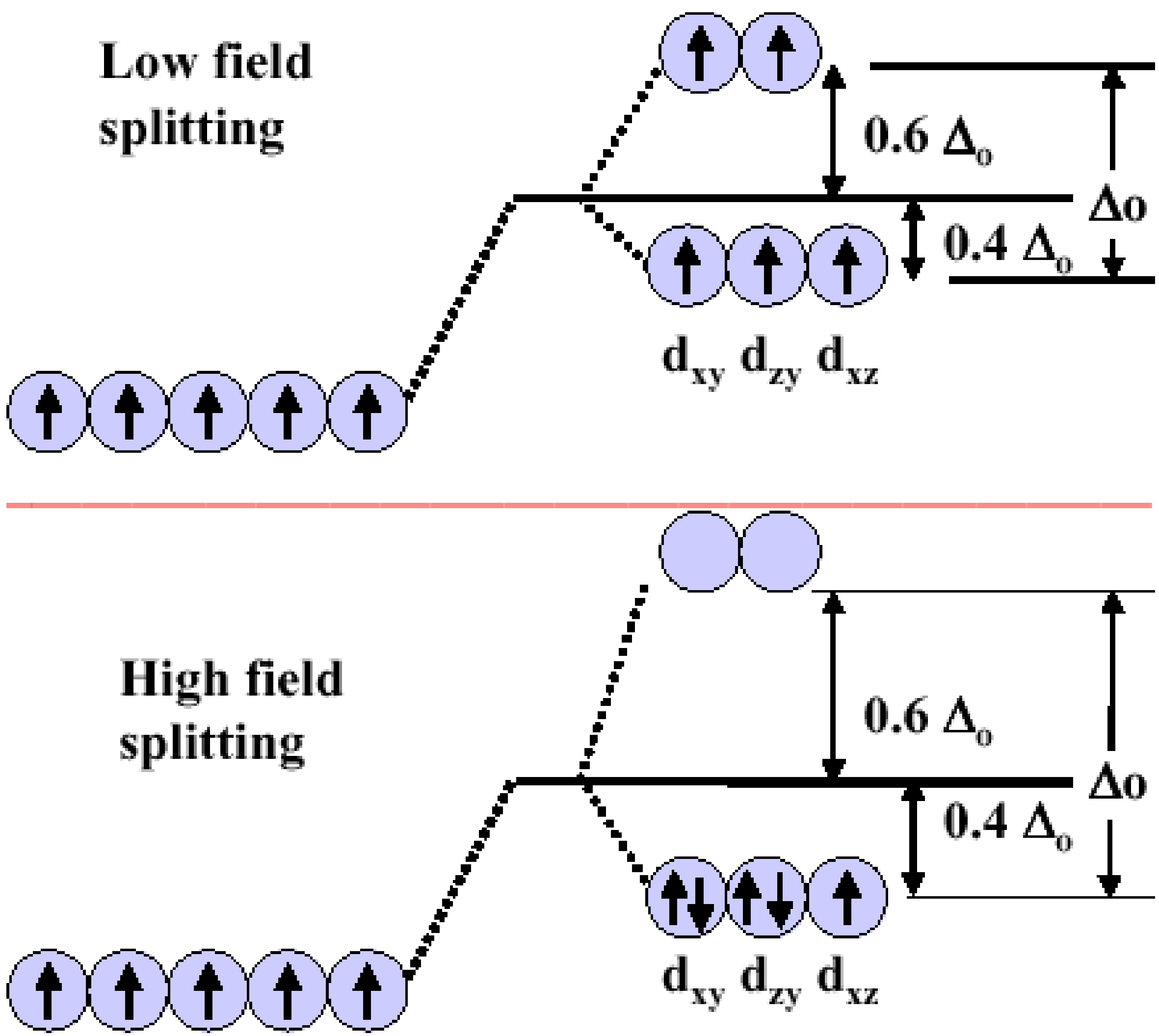
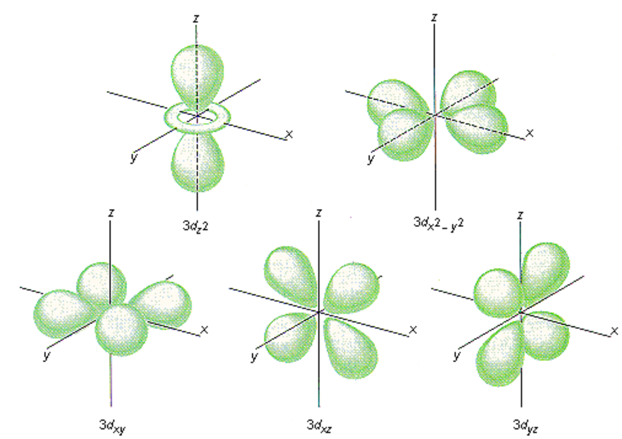


Figure 5. The two cases of crystal field splitting for the octahedral geometry.

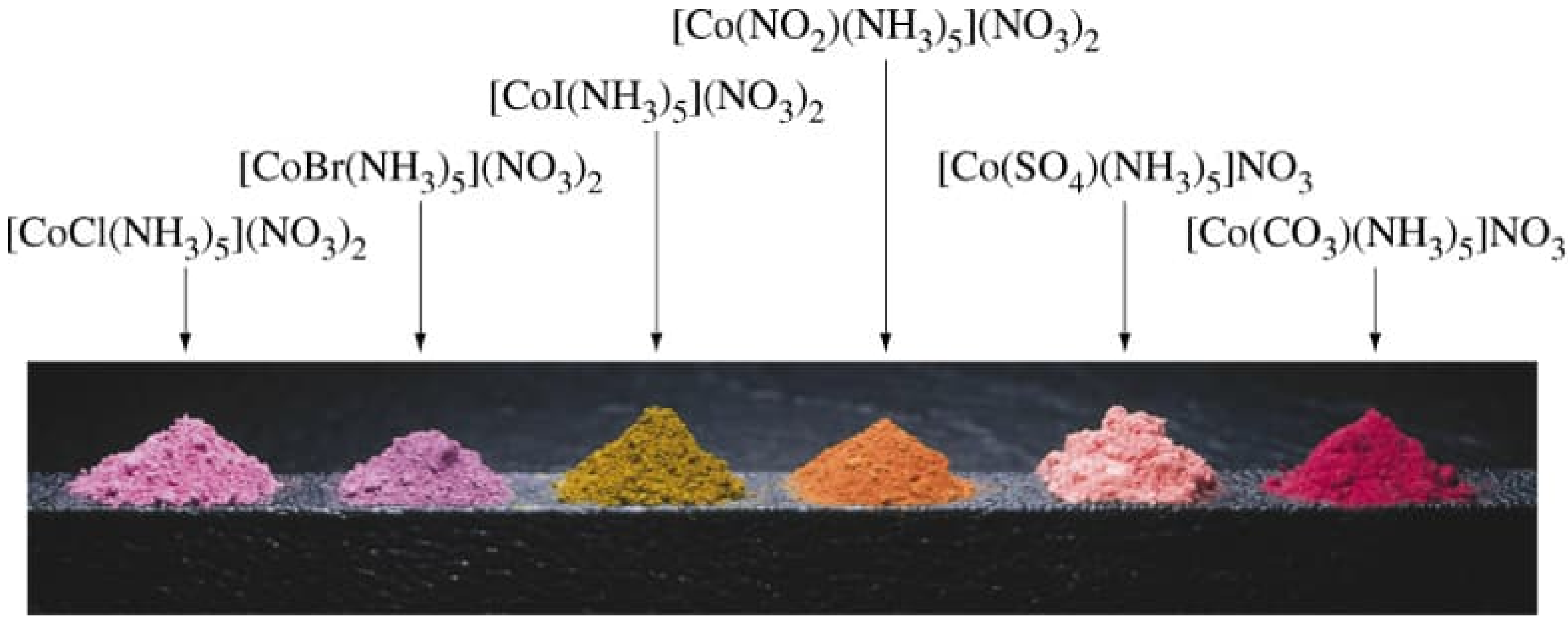
d-orbital energies



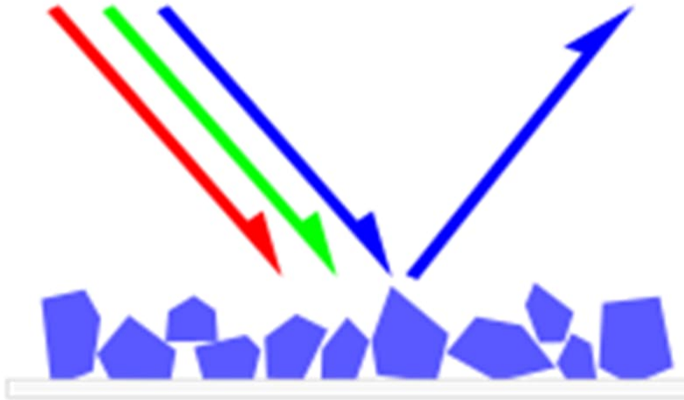
In an isolated atom the different *d*-orbitals of the same shell all have the same energy (but different shapes & orientations)

COLOURS

- **partly filled *d*-orbitals**
- **electrons can transfer from one *d*-orbital to another**
- **energy needed for the transfer is small**
- **corresponds to visible light wavelengths**
- **ions absorb certain wavelengths within the visible light spectrum**
- **if ion absorbs certain colour (e.g. red) the reflected light contains relatively more of the other colours (blue and green), and the ion looks coloured (bluish green)**
- **ions with empty or full orbitals (d^0 ja d^{10}) are color-uless**
- **ions with half-filled orbitals (d^5) are colour-less or faintly coloured**


$[Co(NO_2)(NH_3)_5](NO_3)_2$
$[CoI(NH_3)_5](NO_3)_2$
$[CoBr(NH_3)_5](NO_3)_2$
$[Co(SO_4)(NH_3)_5]NO_3$
$[CoCl(NH_3)_5](NO_3)_2$
$[Co(CO_3)(NH_3)_5]NO_3$

PIGMENTS



- Pigment: material with wavelength-selective absorption
- Practically usable pigment:
  - high tinting strength
  - stable in light and heat
  - insoluble in binder (or water) → suspension (compare to dyes: dissolved in solvent)
  - nonpoisonous, etc.
- Application fields: paints, inks, arts, plastics, fabrics, cosmetics, food, etc.
- Many natural pigments (carbon black, iron-oxide based ochres, etc.) have been used as colorants since prehistoric times
- April 2018 by *Bloomberg Businessweek*:
  - global value of pigment industry $30 billion
  - TiO_2 (white) has the largest share

- **INORGANIC PIGMENTS** more stable than organic pigments
- **Different absorption processes**
  - Conjugated organic molecules: double bonds absorb light
  - Inorganic pigments: different electron transfer processes
- **Note:** pigments are different from luminescent materials (discussed later on in this course)
- **Note:** spectrum of the incident light affects the colour of the pigment, as different wavelength ranges are left to be reflected or scattered

Inorganic BLUE PIGMENTS

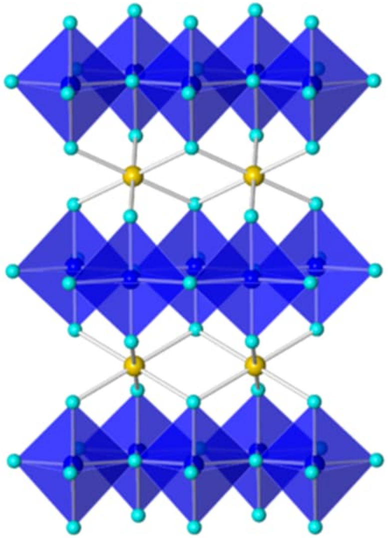
Vermeer 1665

- Very rare in nature/unstable/poisonous
- **6 000 years ago, *Ultramarine*: expensive** !!
  “beyond the sea” made from *lapis lazuli*
  (= semiprecious gemstone mined in Afghanistan)
- **4 000 years ago, *Egyptian Blue*:**
  “turquoise”, $CaCuSi_4O_{10}$
  first synthetic pigment: sand & copper & heat

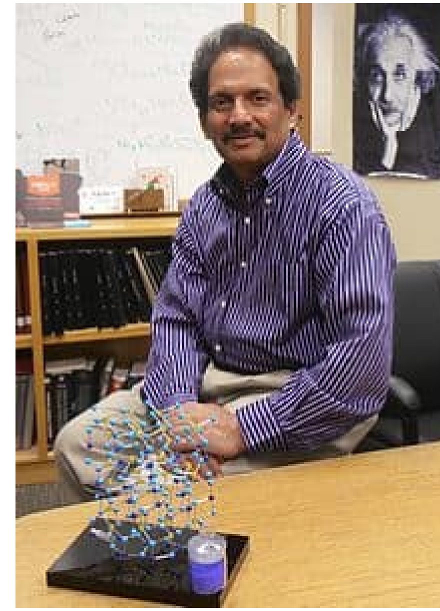
- **2 000 years ago, Chinese Han Blue:**
  $BaCuSi_4O_{10}$
- **1826 *French Ultramarine*:** synthetic

- **1704 *Prussian Blue*:** $Fe_4[Fe(CN)_6]_3$
  (also called: Berlin, Turnbull or midnight blue)
- **1802 *Cobalt Blue*:** $CoAl_2O_4$
- **2009 *Mas Blue*:** $Y(In,Mn)O_3$

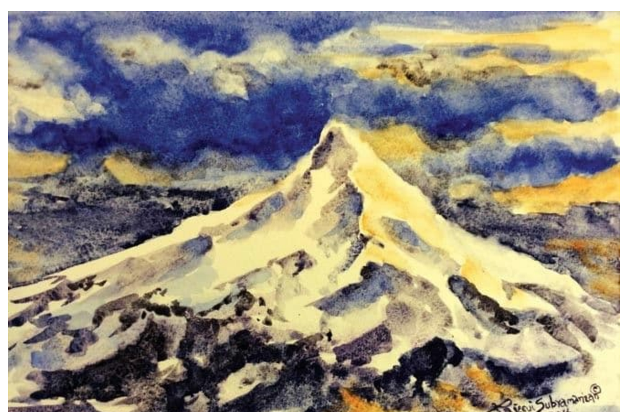
- **Prof. Mas Subramanian** received 2008 National Science Foundation grant to explore **novel materials for electronics applications**
- Research aim: **multiferroic (FM + FE)** materials
- He directed his PhD student Andrew Smith to synthesize a mixture of two oxides: $YInO_3$ (ferroelectric; white) $YMnO_3$ (antiferromagnetic; black)
- The result was NOT multiferroics, but blue material
- Subramanian has experience in chemical industry (DuPont) and recognized the value of the new **blue pigment** (filed a patent)
- Color adjusted by In/Mn ratio **(Crystal Field Engineering)**: $Y(In_{0.8}Mn_{0.2})O_3$ strongest
- **Huge Public interest:**
  - industry: Nike, Crayola, etc.
  - media: New York Times, Time Magazine, National Geographic, Businessweek, etc.
  - arts: Harward Art Museum, etc.



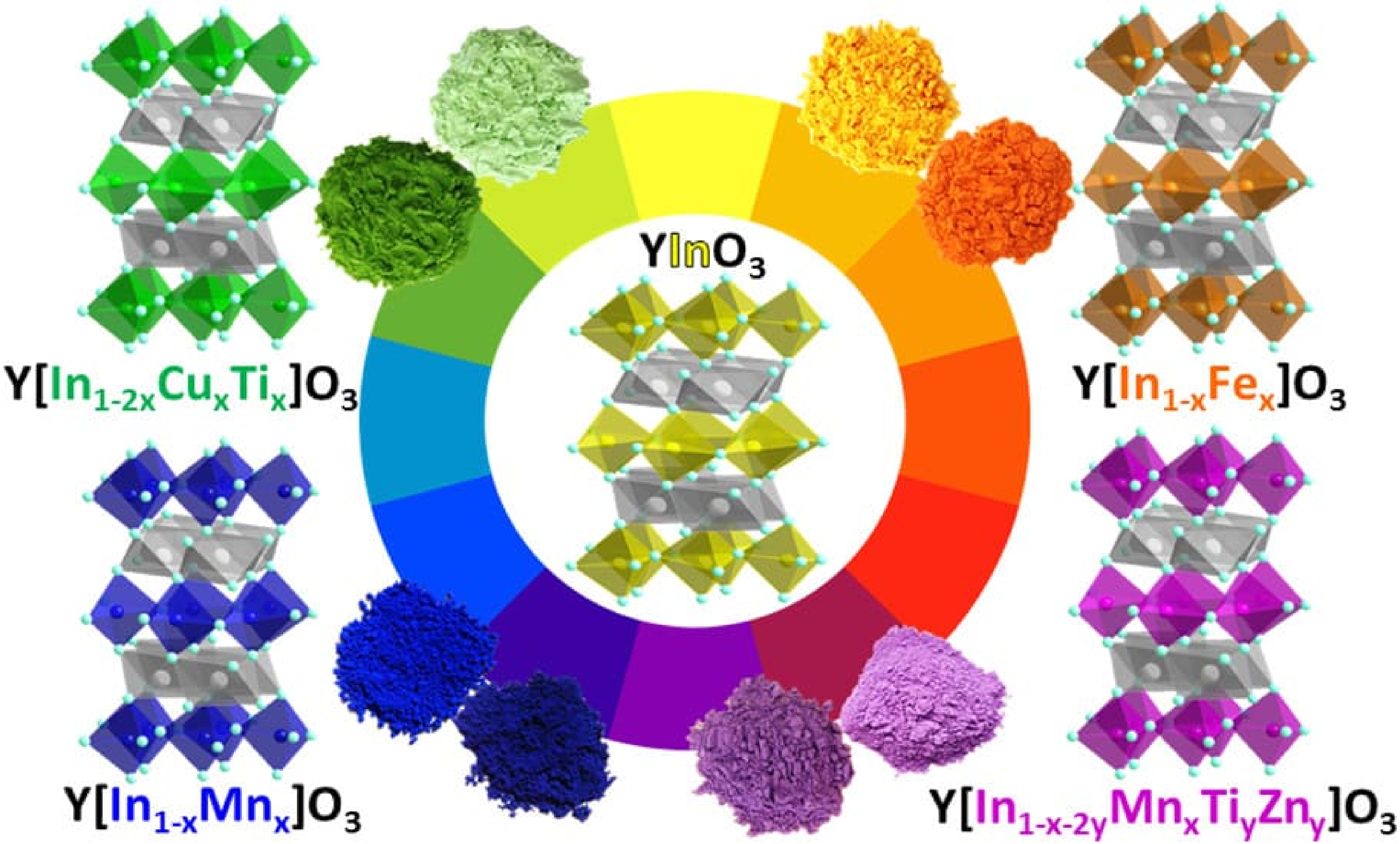
Mas Subramanian



- Born: 1954, Chennai, India
- MSc. 1977 (Inorganic Chemistry: clays and minerals)
  University of Madras 1977
- PhD 1982 (Solid State Chemistry: pyrochlore oxides)
  Indian Institute of Technology, Madras
- 1982-1984 PostDoc, Texas A&M University, USA
- 1984-2006 DuPont, USA:
  - ceramics, superconductors, dielectrics, catalysis, thermoelectrics, multiferroics, ionic conductors, etc.
- **2006-now Professor at Oregon State University**:
  design and synthesis of novel functional materials for emerging applications in energy, environment & electronics
- 2009: novel durable blue pigment: **$(Y,In)MnO_3$ or "Mas Blue"**



Mount Hood (Oregon)
by Aquarelles de Mas Blue
by Ms. Rajeevi Subramanian

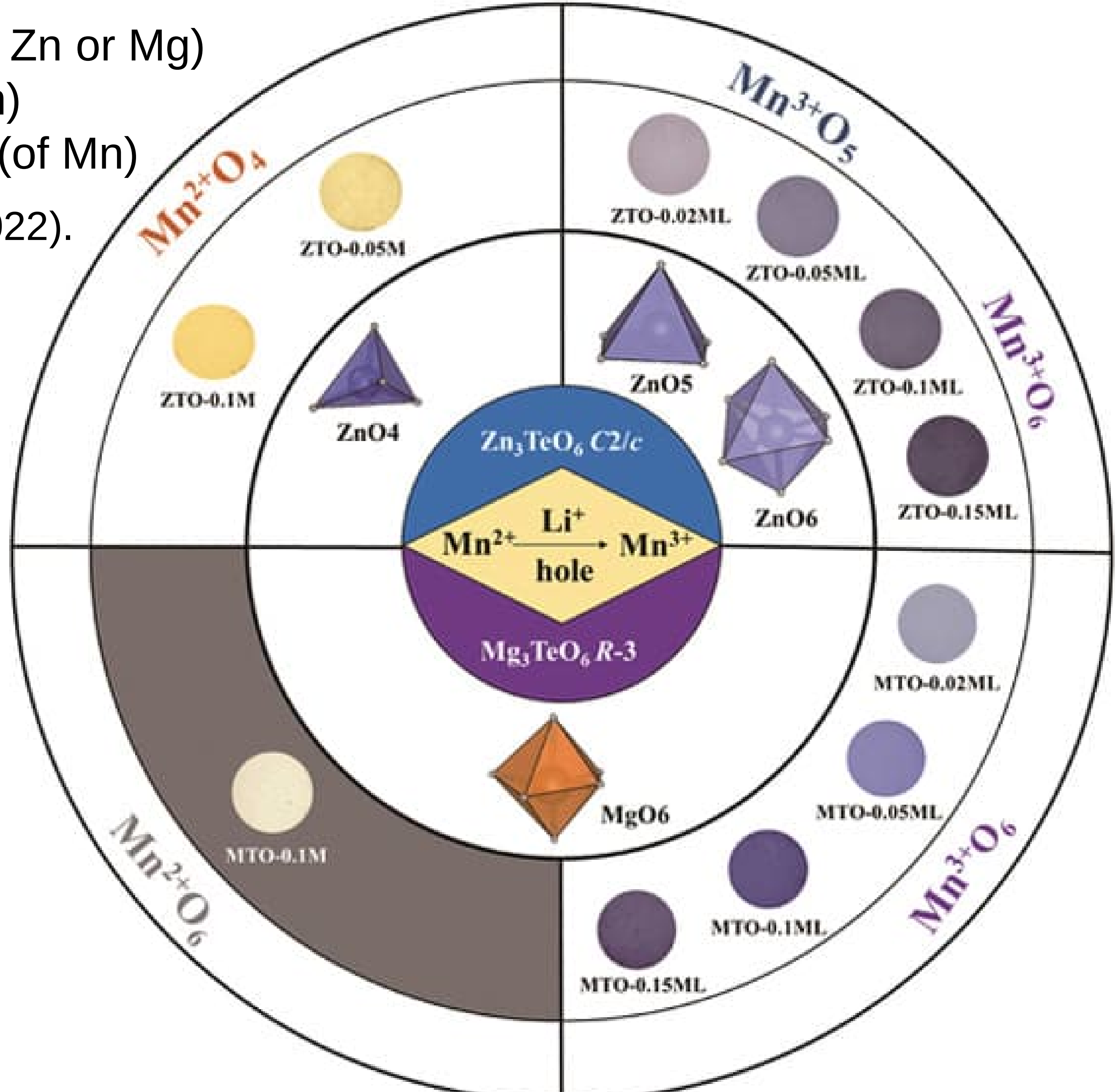


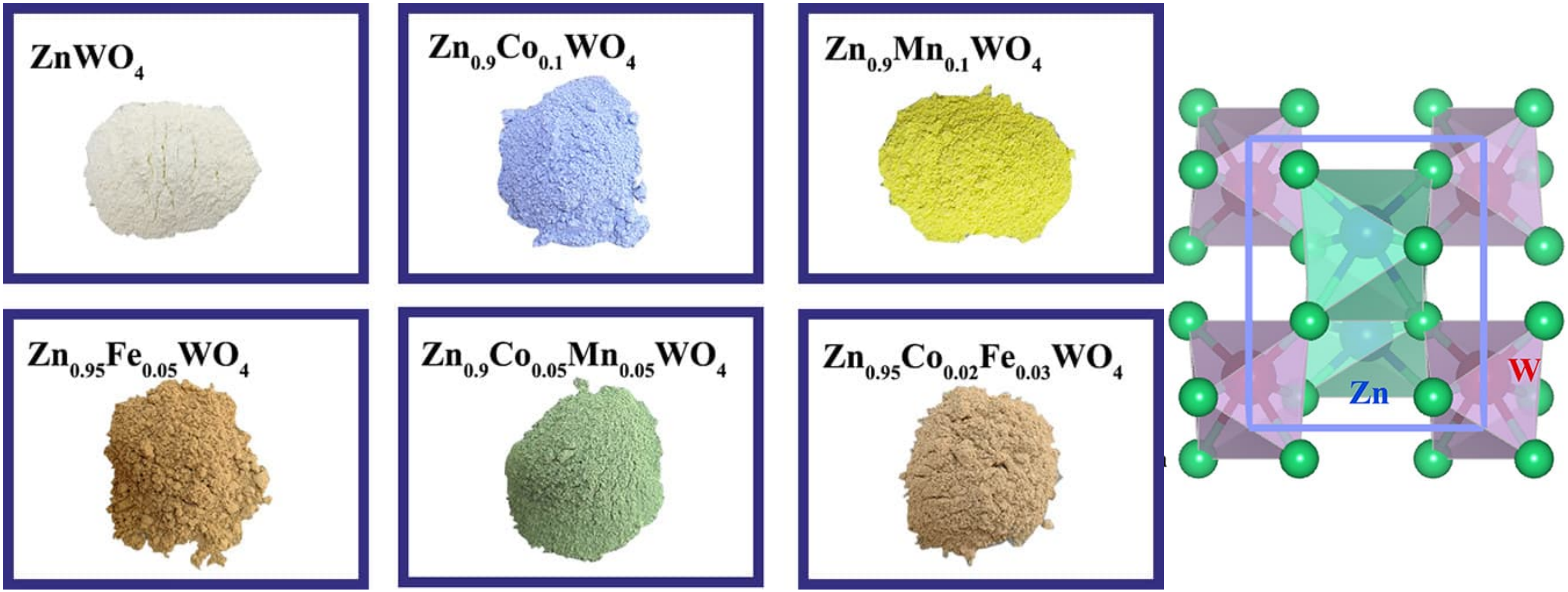
J. Li, S. Lorger, J.K. Stalick, A.W. Sleight & M.A. Subramanian,
From serendipity to rational design: tuning the blue **trigonal bipyramidal Mn^{+3}** chromophore to violet and purple through application of **chemical pressure**,
Inorganic Chemistry 55, 9798 (2016).

RATIONAL DESIGN of INORGANIC PIGMENTS

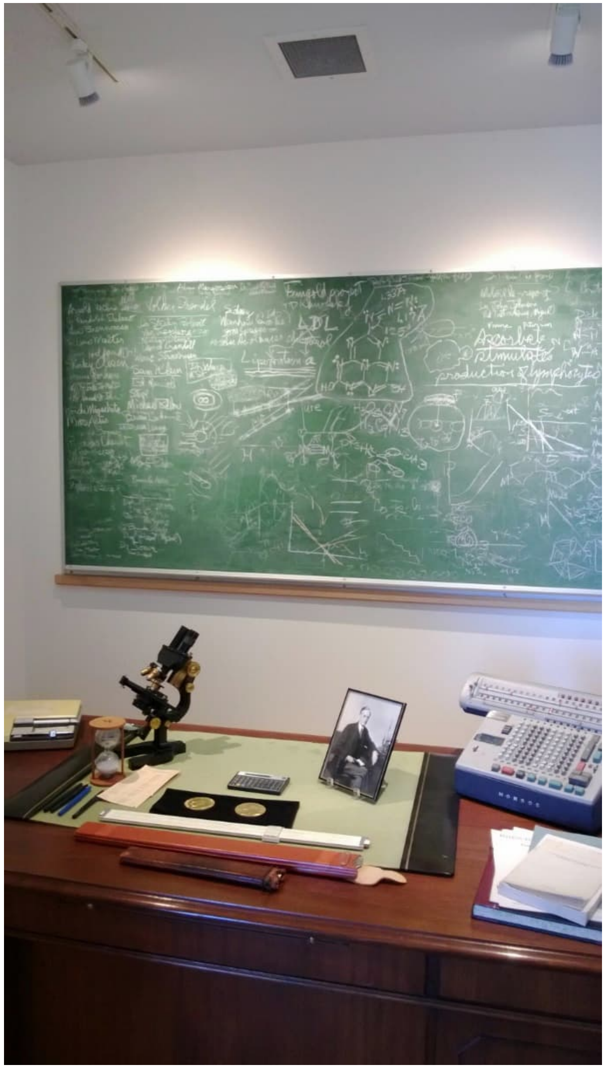
- $(A,\mathbf{Mn},Li)_3TeO_6$ (A = Zn or Mg)
- Ionic valence (of Mn)
- Local surroundings (of Mn)

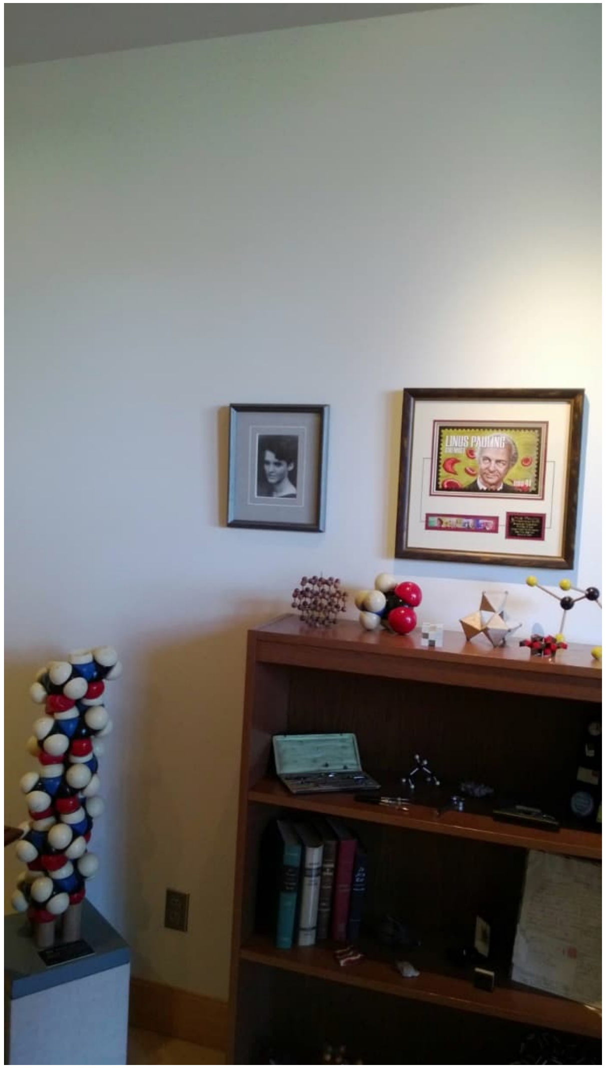
Inorg. Chem. 61, 693 (2022).





W. Zhou, J. Ye, Z. Liu, L. Wang, L. Chen, S. Zhuo, Y. Liu & W. Chen,
High near-infrared reflective **$Zn_{1-x}A_xWO_4$ pigments** with various hues facilely fabricated by **tuning doped transition metal ions (A = Co, Mn, and Fe),** *Inorganic Chemistry* 61, 693 (2022).





Linus Carl Pauling (1901–1994) was an American chemist, biochemist, peace activist, author, and educator, graduated at **Oregon State University**. He published more than 1200 papers and books, 850 on scientific topics.
New Scientist rated him in 2000 the 16th most important scientist in history.
Pauling was one of the founders of the fields of quantum chemistry and molecular biology.
For his scientific work, Pauling was awarded the Nobel Prize in Chemistry in 1954.
In 1962, for his peace activism, he was awarded the Nobel Peace Prize.
Pauling is one of only two people who have received Nobel Prizes in different fields, the other being Marie Curie.