

LECTURE SCHEDULE

Mon (Pt) 12.15 – 14.00
Wed (Ke2) 10.15 – 12.00
Fri (Pt) 10.15 – 12.00

	Date	Topic
1.	Wed 06.09.	Course Introduction & Short Review on Elements & Periodic Table
2.	Fri 08.09.	Short Survey of Main Group Elements
3.	Mon 11.09.	Zn + Ti, Zr, Hf & Atomic Layer Deposition (ALD)
4.	Wed 13.09.	Transition Metals: General Aspects & Pigments
5.	Fri 15.09.	Redox Chemistry
6.	Mon 18.09.	Crystal Field Theory
7.	Wed 20.09.	V, Nb, Ta & Perovskites & Metal Complexes & MOFs & MLD
8.	Mon 25.09.	Cr, Mo, W & 2D materials & Mxenes & Layer-Engineering
9.	Wed 27.09.	Mn, Fe, Co, Ni, Cu
10.	Fri 29.09.	Cu & Magnetism & Superconductivity
11.	Mon 02.10.	Ag, Au, Pt, Pd & Catalysis (Antti Karttunen)
12.	Wed 04.10.	Lanthanoids + Actinoids & Luminescence
	Fri 06.10.	
13.	Wed 11.10.	Resources of Elements & Rare/Critical Elements & Element Substitutions
14.	Fri 13.10.	Inorganic Materials Chemistry Research

EXAM: Tuesday Oct. 17, 9:00-12:00 in Ke2

PRESENTATION TOPICS/SCHEDULE

Wed	20.09.	Nb:	
Mon	25.09.	Mo:	
Wed	27.09.	Mn:	Naomi Lyle, Sanni Ilmaranta, Tomoki Nakayama
		Ru:	Miklos Nemesszeghy ???
Fri	29.09.	Cu:	Koshila Hiruni, Kaushalya Poonanoo, Roger Peltonen
Wed	04.10.	Eu:	Binglu Wang & Maryam Jafarishiad
		Nd:	Patrich Wiesenfeldt ???
		U:	Miikka Viirto & Ashish Singh
Wed	11.10.	Co:	Gabrielle Laurent & Yan Zheng
		In:	Sonja Alasaukko-oja & Katri Haapalinna
		Te:	Sofia Rantala ???

QUESTIONS: Lecture 2

Name your file Exe-3-Familyname; Return by noon tomorrow into MyCourses drop-box

- 1. Each of the following main group elements is specific/unique among all the elements, regarding at least one chemical or physical feature: B, F, He. Explain which feature.**
- 2. For a hypothetical group of elements (Aa – Ff) in Periodic Table, the following melting points have been reported: Aa 30 °C, Bb 100 °C, Cc 400 °C, Dd 550 °C, Ee 500 °C, Ff 250 °C. Based on this information, predict (with short explanations) the metallic versus non-metallic nature of each element. When combined with OH groups, do you expect Bb to form acidic or basic compound?**

MAIN GROUP ELEMENTS

- Hydrogen: position in Periodic Table, isotopes, hydrides, hydrogen storage
- Alkali metals: group trends, Li-ion battery
- Alkaline earth metals *versus* alkali metals
- Boron group: crystal structures & melting points, boranes, borides, BNCT treatment, MgB₂ superconductor
- Isoelectronic; C-C and B-N, ultrahighpressure
- Nitrogen group: metal character and basicity of oxides (N < P < As < Sb < Bi)
- Multitude of sulphur compounds
- Lightest element *versus* other group members: F – Cl, Br, I
- Ionization energies and compounds of noble gases

Where would you place **hydrogen** in Periodic Table ?

1																	18
H ¹	2														He ²		
Li ³	Be ⁴											B ⁵	C ⁶	N ⁷	O ⁸	F ⁹	Ne ¹⁰
Na ¹¹	Mg ¹²	3	4	5	6	7	8	9	10	11	12	Al ¹³	Si ¹⁴	P ¹⁵	S ¹⁶	Cl ¹⁷	Ar ¹⁸
K ¹⁹	Ca ²⁰	Sc ²¹	Ti ²²	V ²³	Cr ²⁴	Mn ²⁵	Fe ²⁶	Co ²⁷	Ni ²⁸	Cu ²⁹	Zn ³⁰	Ga ³¹	Ge ³²	As ³³	Se ³⁴	Br ³⁵	Kr ³⁶
Rb ³⁷	Sr ³⁸	Y ³⁹	Zr ⁴⁰	Nb ⁴¹	Mo ⁴²	Tc ⁴³	Ru ⁴⁴	Rh ⁴⁵	Pd ⁴⁶	Ag ⁴⁷	Cd ⁴⁸	In ⁴⁹	Sn ⁵⁰	Sb ⁵¹	Te ⁵²	I ⁵³	Xe ⁵⁴
Cs ⁵⁵	Ba ⁵⁶	La ⁵⁷	Hf ⁷²	Ta ⁷³	W ⁷⁴	Re ⁷⁵	Os ⁷⁶	Ir ⁷⁷	Pt ⁷⁸	Au ⁷⁹	Hg ⁸⁰	Tl ⁸¹	Pb ⁸²	Bi ⁸³	Po ⁸⁴	At ⁸⁵	Rn ⁸⁶
Fr ⁸⁷	Ra ⁸⁸	Ac ⁸⁹	Rf ¹⁰⁴	Db ¹⁰⁵	Sg ¹⁰⁶	Bh ¹⁰⁷	Hs ¹⁰⁸	Mt ¹⁰⁹	Uun ¹¹⁰								

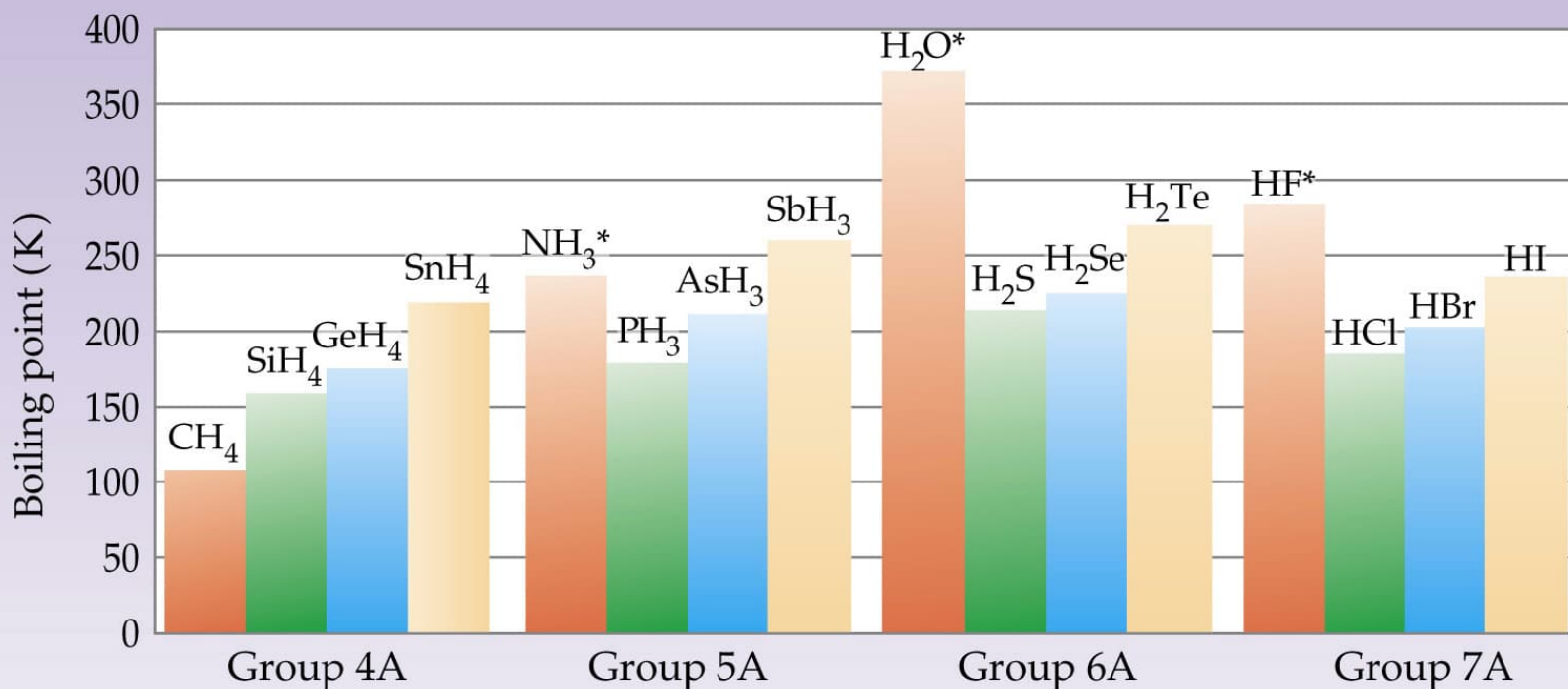
58	59	60	61	62	63	64	65	66	67	68	69	70	71
Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
90	91	92	93	94	95	96	97	98	99	100	101	102	103
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

HYDRIDES

- Binary compounds of hydrogen
- Hydrogen forms hydrides with most of the elements
- Electronegativity of hydrogen only little higher than the average electronegativity of elements → many of the "hydrides" do not contain the H^- hydride ion
- Hydrides are categorized according to the type of bonding: ionic, covalent or metallic
- **IONIC HYDRIDES**
 - with alkali and alkaline earth metals (except Be, Mg)
 - metal cation and H^- ion
 - crystal structures similar to those of halides (Cl^- replaced by H^-)
 - very reactive, e.g.: $\text{LiH} + \text{H}_2\text{O} \rightarrow \text{LiOH} + \text{H}_2$
(used as reductants)

■ COVALENT HYDRIDES (not correct name for all these compounds)

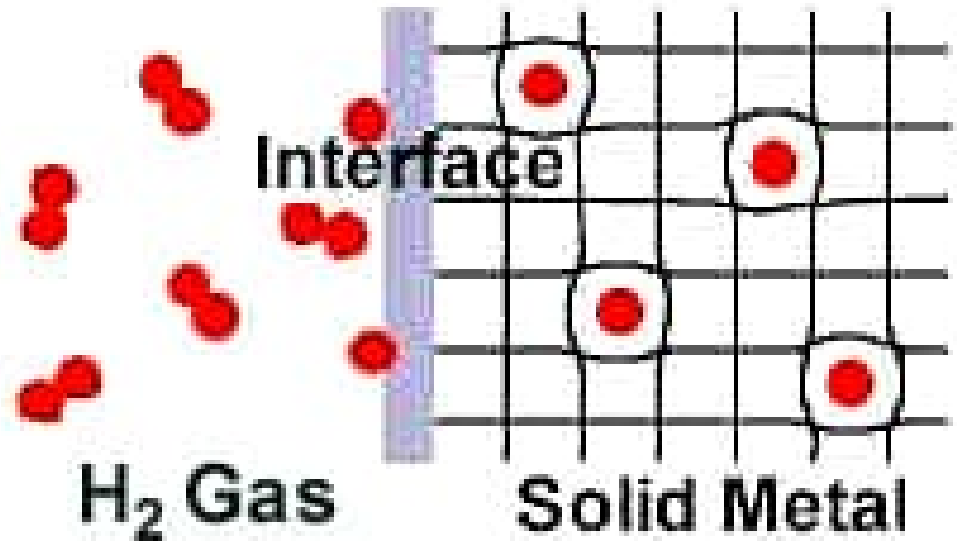
- with all nonmetals (except noble gases) and the most electro-negative metals (Sn,Ga)
- most of these hydrides are gaseous at room temperature



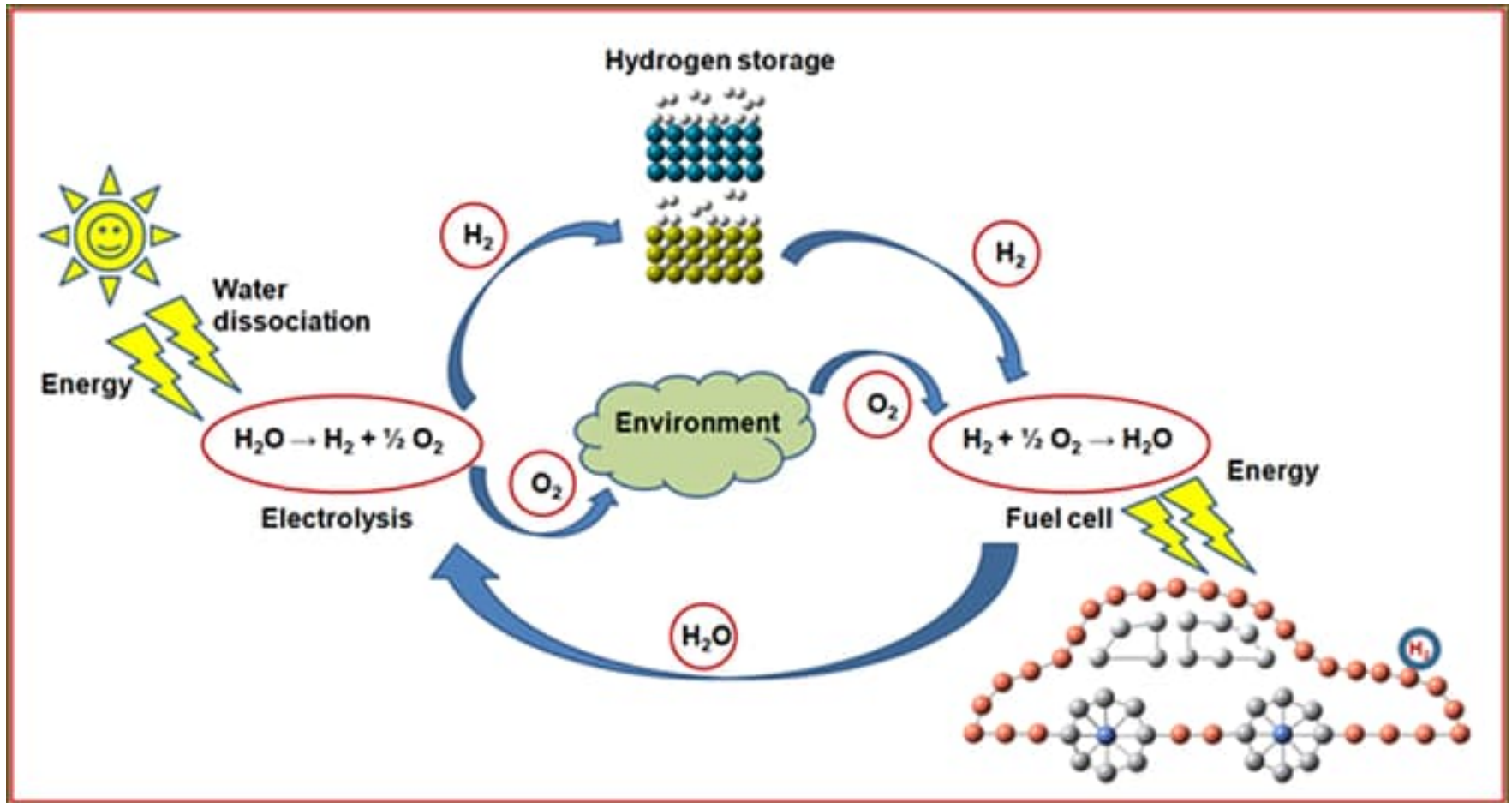
*The boiling points generally increase with increasing molecular mass down a group of the periodic table, but the hydrides of nitrogen (NH₃), oxygen (H₂O), and fluorine (HF) have abnormally high boiling points because these molecules form hydrogen bonds.

METALLIC (TRANSITION METAL) HYDRIDES

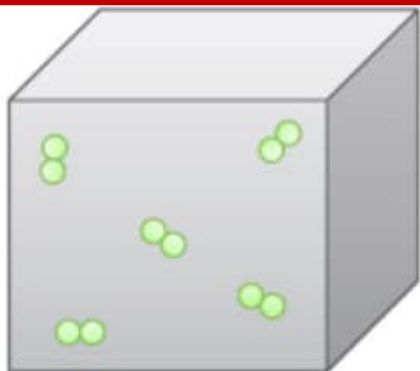
- solid materials
- hydrogen in interstitial positions
- often nonstoichiometric, e.g. $\text{TiH}_{1.9}$
- volume increases upon hydrogen intercalation
→ no strong bonding (attraction)
- used for **HYDROGEN STORAGE**
 - $\text{Ti} + \text{H}_2 + \text{little heating/pressure} \rightarrow \text{TiH}_{1.9}$
 - $\text{TiH}_{1.9} + \text{higher temp.} \rightarrow \text{Ti} + \text{H}_2$



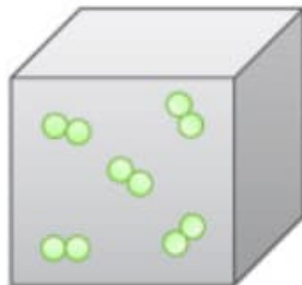
HYDROGEN STORAGE !!!



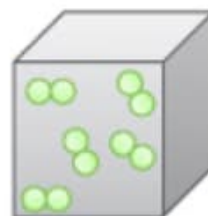
Physical Storage



1 bar
normal
0.3 g/L



150 bar
lab cylinders
10 g/L



350 bar
Gen 1 vehicles
28 g/L

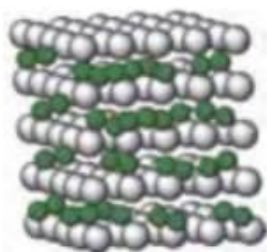


700 bar
Gen 2 vehicles
40g/L

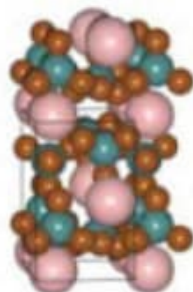


liquid H₂
71 g H₂/L
@ 20 K

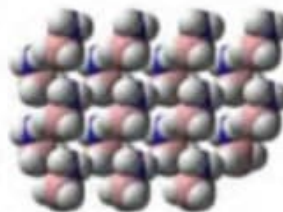
Materials-based Storage



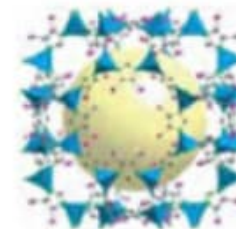
interstitial hydrides
~100-150 g H₂/L



complex hydrides
~70-150 g H₂/L



chemical storage
~70-150 g H₂/L



sorbents
≤ 70 g H₂/L

Reference



water
111 g H₂/L




MOF (Metal-Organic Framework):
- Highly porous materials

When going **from metals to non-metals** (from left to right in Periodic Table):
A gradual change in **acid-base character** (seen for the OH compounds)

- In compounds with OH groups (E-O-H) electronegativity of the cation (E) defines whether the compound is an oxoacid or a base
- small electronegativity: $E-O-H \rightarrow E^+ + OH^-$ (base)
- large electronegativity: $E-O-H \rightarrow E-O^- + H^+$ (acid)
- For example: elements of the third period:

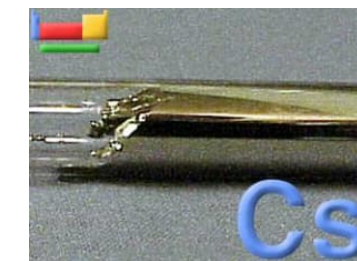
NaOH	strong base
Mg(OH) ₂	base
Al(OH) ₃	amfolyte
Si(OH) ₄	weak acid [H ₄ SiO ₄]
OP(OH) ₃	acid [H ₃ PO ₄]
O ₂ S(OH) ₂	strong acid [H ₂ SO ₄]
O ₃ Cl(OH)	strong acid [HClO ₄]



Electro-
negativity
increases

ALKALI METALS

- Chemically highly coherent group, but lithium somewhat more different (diagonal relationship Li-Mg)
- Metal radius (Å):
Li 1.52 (Mg 1.60), Na 1.86, K 2.27, Rb 2.48, Cs 2.65
- Ionic radius (Å):
Li 0.76 (Mg 0.72), Na 1.02, K 1.38, Rb 1.52, Cs 1.67
- Charge/ionic radius:
Li 1.40, Na 0.88, K 0.66, Rb 0.60, Cs 0.55
- Melting point (°C): Li 180, Na 98, K 64, Rb 39, Cs 29
- Oxidation product: Li_2O , $\text{Na}_2\text{O}/\text{Na}_2\text{O}_2$, K_2O_2 , KO_2 , RbO_2 , CsO_2
- Li compounds more covalent than others
- Li compounds dissolve more easily into nonpolar solvents, and less into water
- Only Li forms the nitride, Li_3N (ref. Mg_3N_2)
- Li salts often contain water of crystallization, e.g. $\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$ (ref. $\text{MgClO}_4 \cdot 6\text{H}_2\text{O}$)



ALKALI *VERSUS* ALKALINE EARTH METALS

- Alkaline earth metals have larger Z_{eff} than alkali metals
 - smaller
 - denser
 - harder
- Alkaline earth metals have two valence electrons per atom
 - metal bonds stronger
 - better electrical conductivity
 - higher melting and boiling points

	Li/Be	Na/Mg	K/Ca	Rb/Sr	Cs/Ba
Electronegativity	1.0/1.5	0.9/1.2	0.8/1.0	0.8/1.0	0.7/0.9
Metal radius (Å)	1.52/1.12	1.86/1.60	2.27/1.97	2.48/2.15	2.65/2.22
Density (g/cm ³)	0.53/1.85	0.97/1.74	0.86/1.55	1.53/2.63	1.87/3.59
Melting point (°C)	181/1289	98/650	64/842	40/769	28/729
RT-resistivity (μohm cm)	9.47/3.70	4.89/4.48	7.39/3.42	13.1/13.4	

LITHIUM-ION BATTERY

- **WHY Lithium:** the lightest of all metals & the greatest electrochemical potential & the largest energy density per weight & small and easy/fast to move
- Charging: Li-ions from cathode to anode; Discharging: Li-ions from anode to cathode
- Commercialization: Sony 1991
- Used: portable electronics

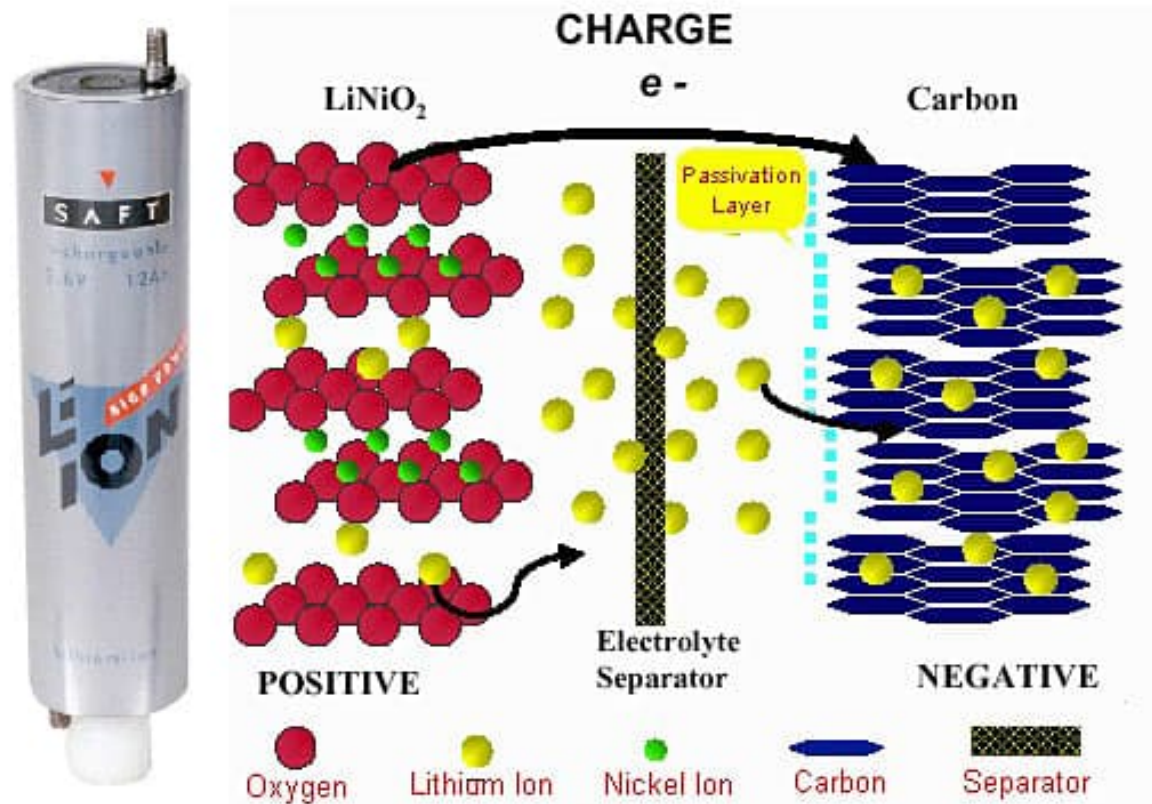
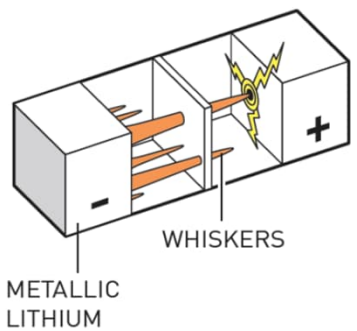
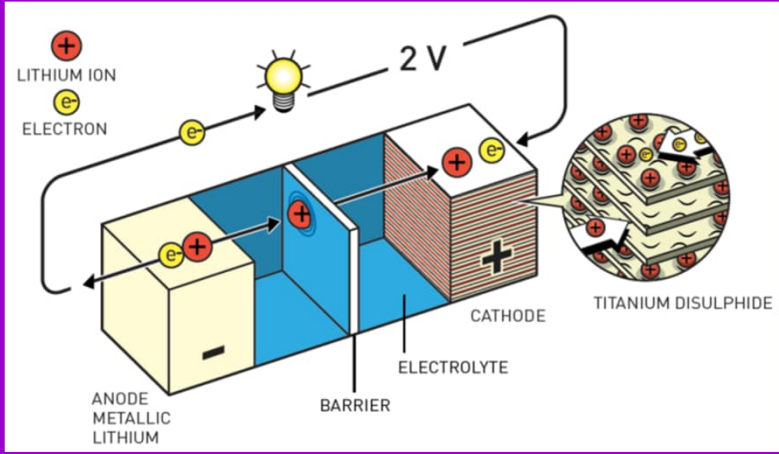
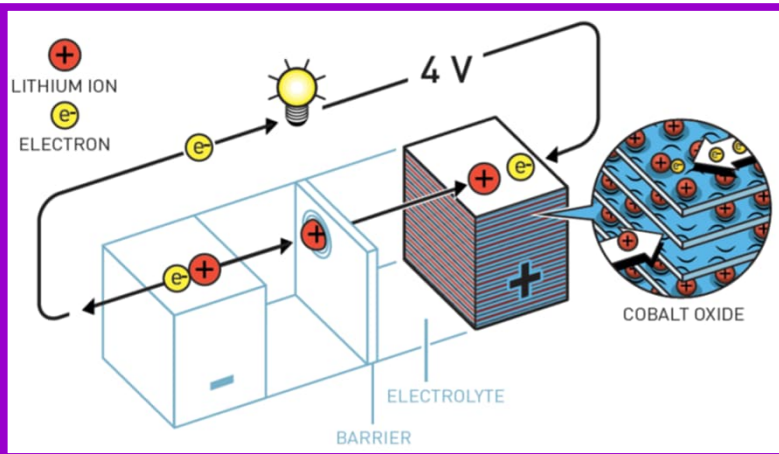


Photo Courtesy of SAFT America



Chemistry Nobel 2019



Stanley Whittingham (born 1941 UK):

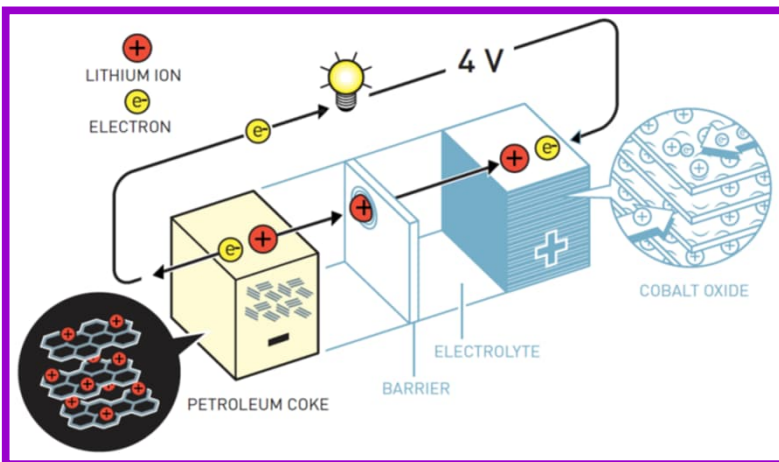
- Exxon: TiS_2 cathode 1976

John Goodenough (born 1922 USA):

- Univ. Oxford: LiCoO_2 cathode 1980

Akira Yoshino (born 1948 Jpn):

- Asahi Kasei: carbon-based anode 1985



Commercialization: Sony 1991

Current Li-ion battery materials / new alternatives

CATHODE:

LiCoO₂

Li(Co_{1/3}Mn_{1/3}Ni_{1/3})O₂, LiMn₂O₄, LiFePO₄

ANODE:

Grafite

Si, Li₄Ti₅O₁₂

ELECTROLYTE:

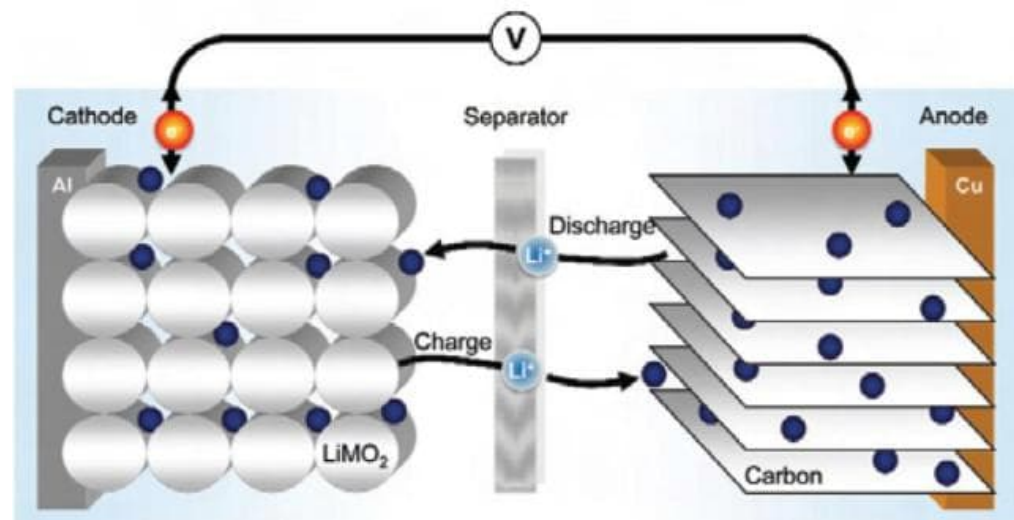
LiPF₆ + ethylene carbonate solvent

Solid electrolyte materials

BINDERS:

PVDF (polyvinylidene fluoride) + NMP (N-methylpyrrolidone)



Water-soluble binders

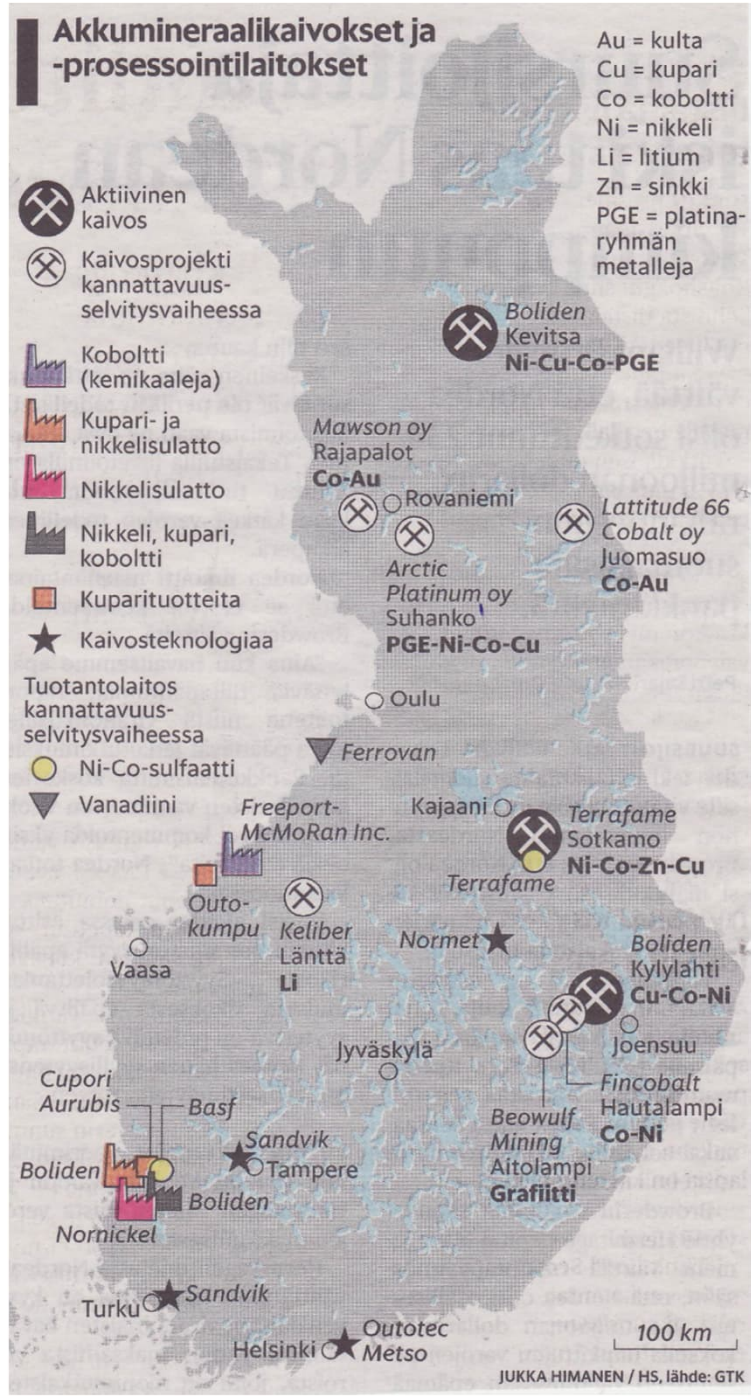


Akkumineraalikaivokset ja -prosessointilaitokset

Au = kulta
 Cu = kupari
 Co = koboltti
 Ni = nikkeli
 Li = litium
 Zn = sinkki
 PGE = platina-ryhmän metalleja

-  Aktiivinen kaivos
-  Kaivosprojekti kannattavuus-selvitysvaiheessa
-  Koboltti (kemikaaleja)
-  Kupari- ja nikkelisulatto
-  Nikkelisulatto
-  Nikkeli, kupari, koboltti
-  Kuparituotteita
-  Kaivosteknologiaa

- Tuotantolaitos kannattavuus-selvitysvaiheessa
-  Ni-Co-sulfaatti
 -  Vanadiini



100 km

p-BLOCK

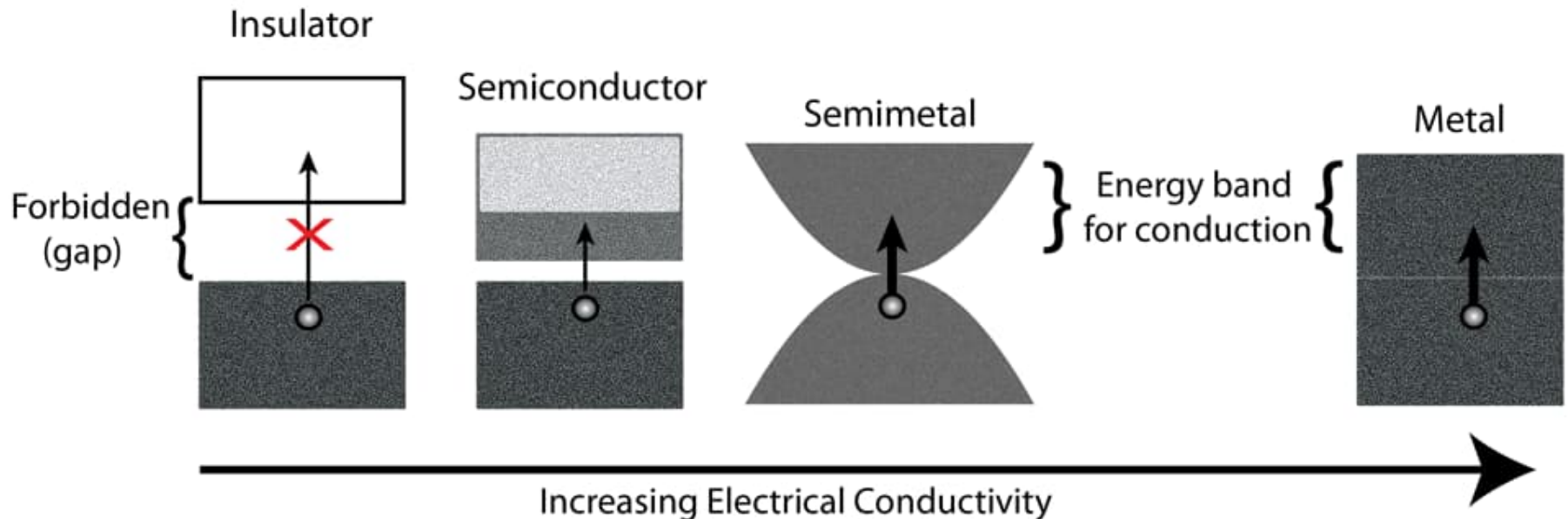
Metals Metalloids Nonmetals

1 H	2 He																
3 Li	4 Be	5 B	6 C	7 N	8 O	9 F	10 Ne										
11 Na	12 Mg	13 Al	14 Si	15 P	16 S	17 Cl	18 Ar										
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	71 Lu	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	103 Lr	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Uub	113	114	115	116	117	118

57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb
89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No

Metalloids

- Element with properties intermediate between those of typical metals and nonmetals: boron, silicon, germanium, arsenic, antimony, tellurium & polonium
- Named *metalloid* (original meaning: metalloid = nonmetal) since 1950s
- In physics (when referring to the band structure): metalloid \approx semimetal
- Semimetal should not be confused with semiconductor (or halfmetal)
- Typical properties of metalloids: brittle and somewhat shiny solids
- Important industrial materials (e.g. transistors, other semiconductor devices, ceramics, solar cells)





BORON GROUP: MELTING POINTS

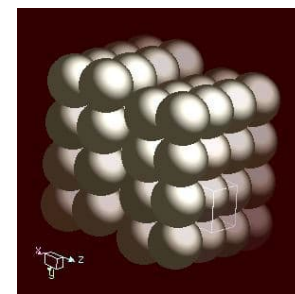
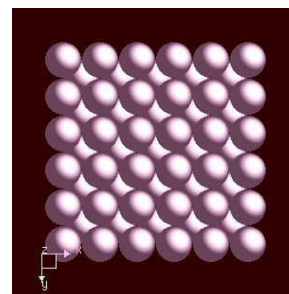
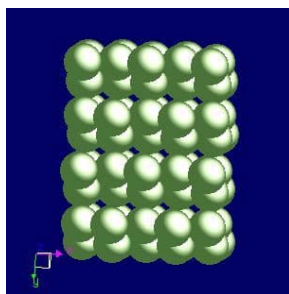
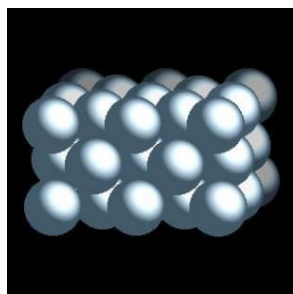
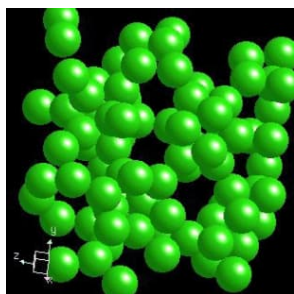
2180 °C

660 °C

30 °C

157 °C

303 °C



Boron

Aluminum

Gallium

Indium

Thallium

Rhombohedral

CCP

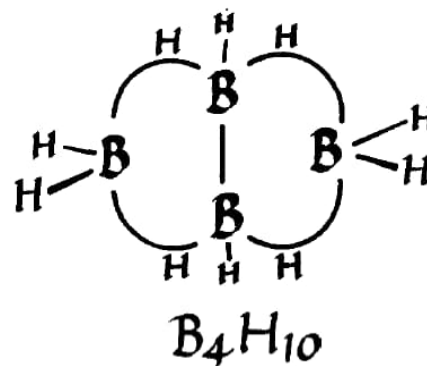
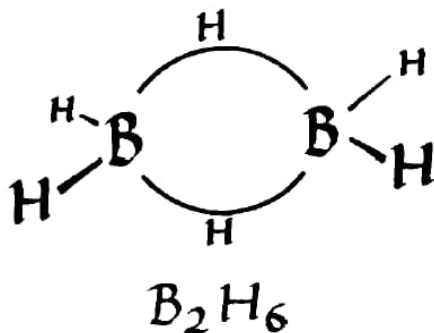
Orthorhombic

Tetragonal

HCP

BORON: ELECTRON DEFICIENT COMPOUNDS

- B: $1s^2 2s^2 2p^1$
 - 3 valence electrons → octet not possible with covalent bonds
 - electronegativity 2.0 → ionic bonds not possible
- Difficult to achieve electron octet → *electron deficient* compounds
- Normal single bond: 2 atoms and 2 bond electrons (2c-2e)
- Electron deficient compound: 3 atoms and 2 bond electrons (3c-2e)
- Boranes $B_n H_{n+4}$ or $B_n H_{n+6}$: typical electron deficient compounds
- Also Al, Ga, Be and Li form electron deficient compounds:
 $(AlH_3)_n$, $Al_2(CH_3)_6$, $[Be(CH_3)_2]_n$, $[Li(CH_3)]_4$



BORIDES

- Binary compounds of boron with metals
 - more than 200 different compounds
 - stoichiometry varies $M_5B \dots MB_{66}$
(e.g. M_2B , MB , MB_2 , MB_4 , MB_6)
 - M-rich typical for *d*-block transition metals,
B-rich for main group metals, lanthanoids and actinoids
 - known are also nonstoichiometric and mixed borides
 - **extremely hard, high-temperature resistive, chemically inert**
 - uses: coatings, electrodes,
nuclear technology (protection, neutron counter: $^1_0n + ^{10}_5B \rightarrow ^7_3Li + ^4_2He$)



- Boron carbide

- “ B_4C ” = $B_{12}C_3$
- one of the hardest materials
- uses: armor material, bicycles

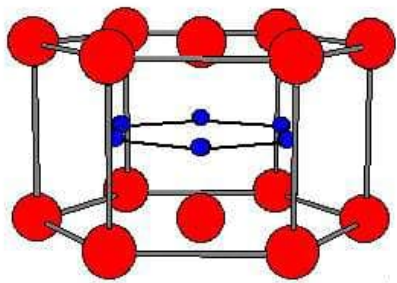


BORIDE STRUCTURES

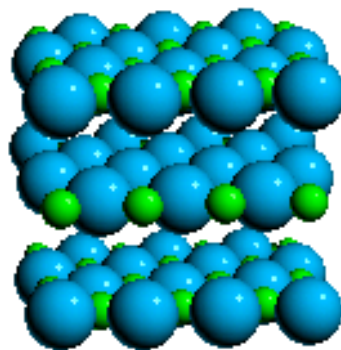
- **M-rich:**
 - (1) separate B atoms
 - (2) separate B₂ atom pairs
 - (3) B_n chains
 - (4) double chains
 - (5) planes (MB₂)

(**catenation** tendency of B atoms increases with increasing B content)
- **B-rich:**
 - (1) planes
 - (2) 3D nets
 - (3) clusters (e.g. B₆ octahedra and B₁₂ icosahedra)

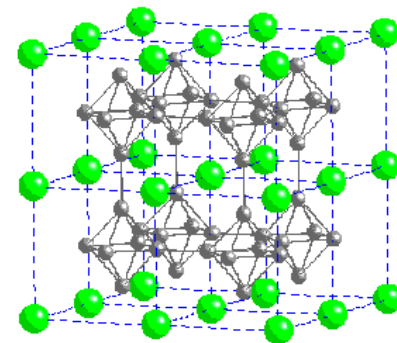
MgB₂



TiB₂

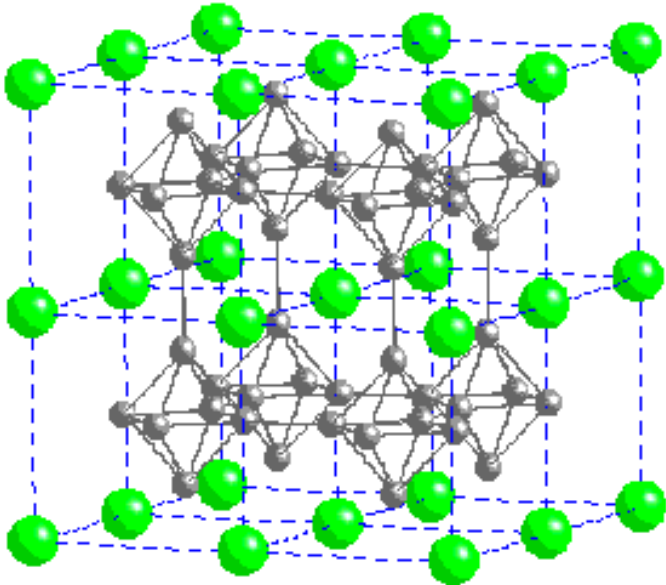


LaB₆



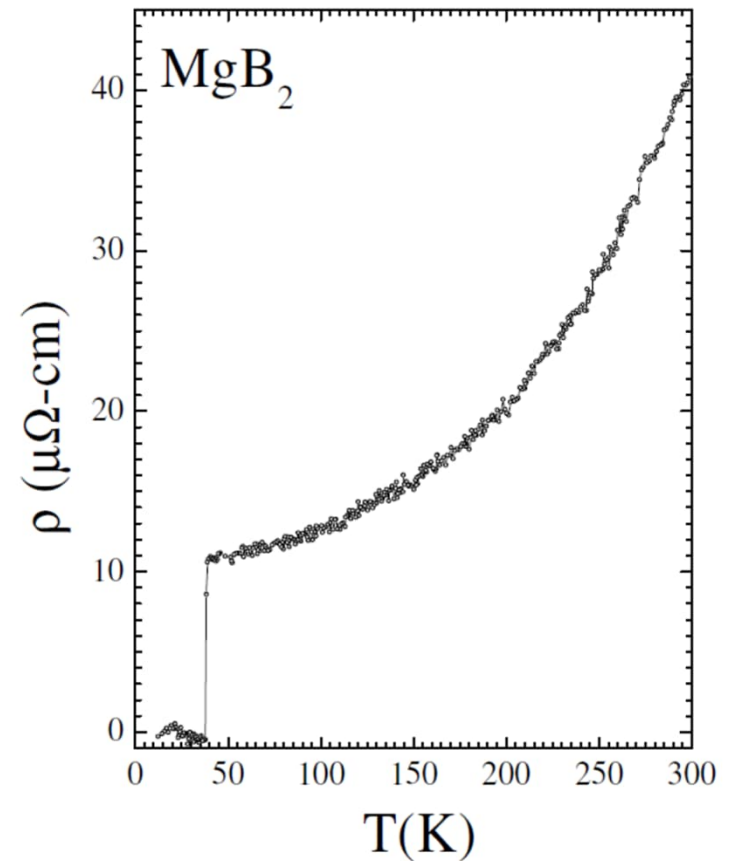
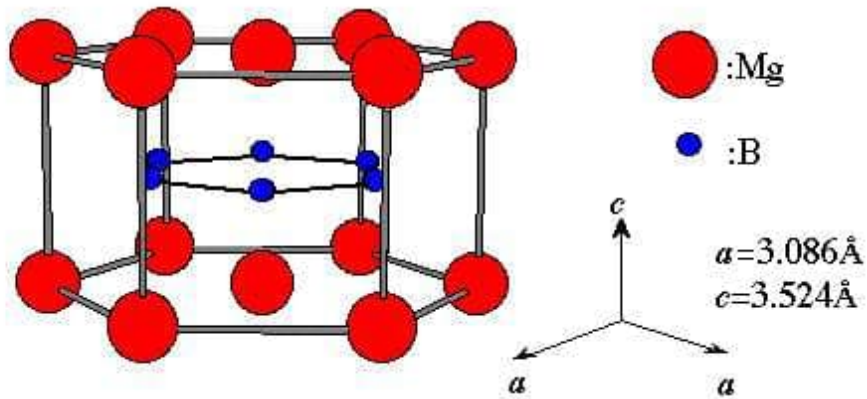
BONDING in BORIDES

- The simple ionic / covalent / metal bond concepts fail
- **LaB₆**:
 - in B₆ clusters electron-deficient (multicenter-2e) bonds
 - between clusters covalent (2c-2e) B-B bonds
 - move of two electrons from **La** to B₆ cluster
 - La²⁺-B₆²⁻ ionic bond
 - third valence electron of La is delocalized (metal bond)
 - good electrical conductivity, good electron emission
 - use: electron guns in electron microscopes



Akimitsu 2001: Superconductivity with $T_c = 39$ K

Akimitsu_fig2



BORON-NEUTRON-CAPTURE-THERAPY (BNCT)

- Treatment of inoperable brain tumors/cancer
- Boron (^{10}B) absorbs efficiently neutrons (large absorption cross section)
→ radioactive ^{11}B :a
- Radioactive radiation destroys tumor cells
- Challenge: to deliver high concentrations of a boron compound specifically to tumor cells
- Some boron compounds such as $(\text{B}_{12}\text{H}_{11}\text{SH})^{2-}$ ion based ones have a tendency to accumulate in cancer cells



Isotope	Hydrogen-1	Boron-10	Carbon-12	Nitrogen-14	Oxygen-16
Neutron-abs. cross-section (barn)	0.33	3.8×10^3	3.4×10^{-3}	1.8	1.8×10^{-4}

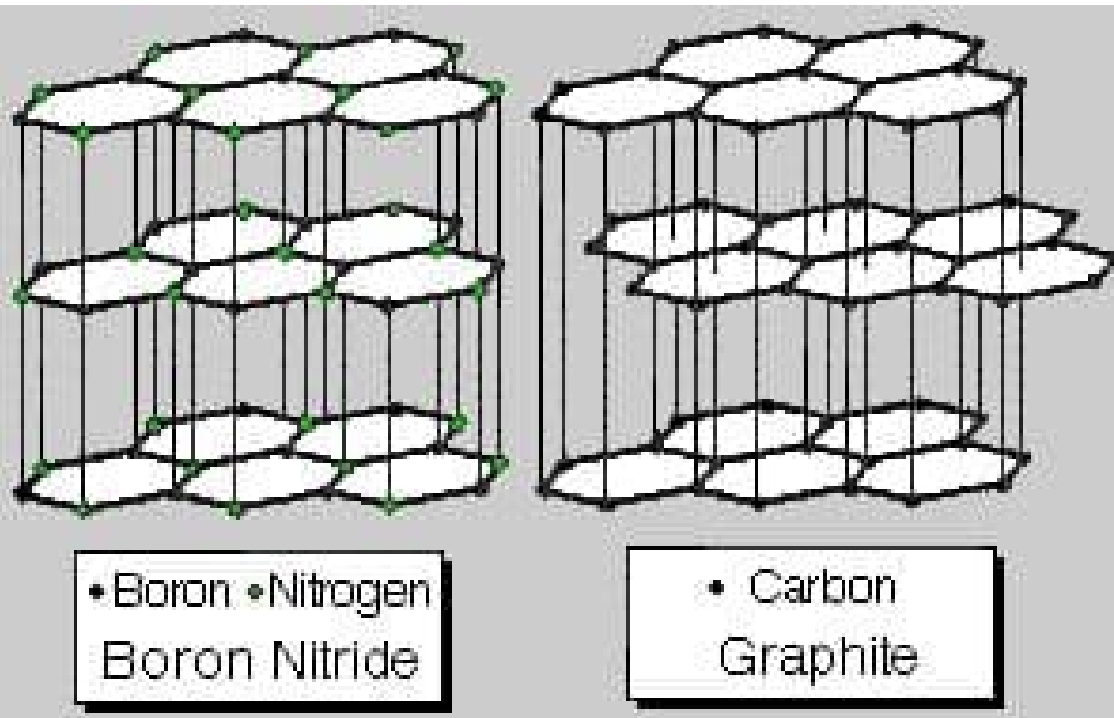
1 barn = 10^{-24} cm²

ISOELECTRONIC: C-C and B-N

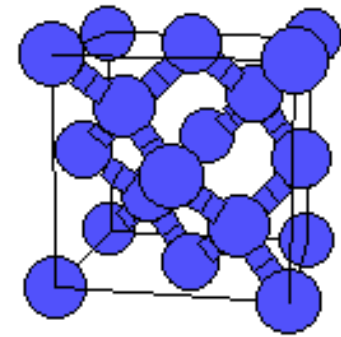
- Boron has one valence electron less and nitrogen one valence electron more than carbon → **Boron nitride BN** has in average the same number of valence electrons per atom as carbon → C ja BN isoelectronic → resemble each other
- BN forms similar assemblies as those in different carbon allotropes: graphite, diamond, fullerenes, nanotubes and graphene

GRAPHITE STRUCTURE: C and BN

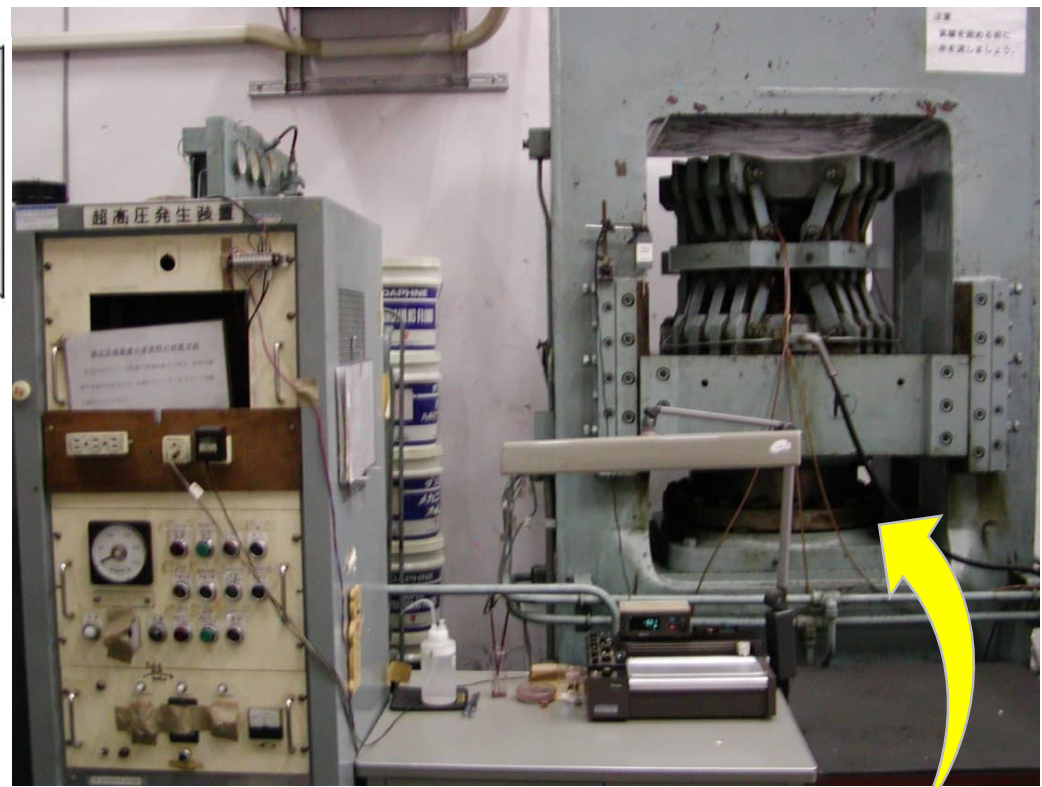
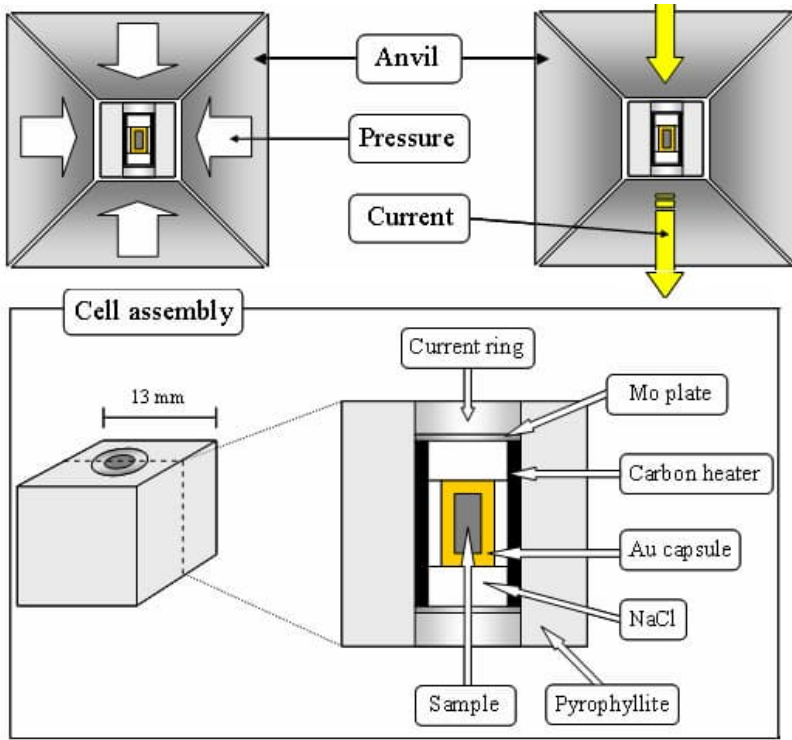
- C: the fourth valence electron loosely bound → good electrical conductivity → black
- BN: Polar bond between the layers → no electrical conductivity → white



DIAMOND



- Diamond and graphite known for thousands of years
- The fact that they are different forms of the same element was understood much later
- The critical combustion experiments were made in the end of 18th century: diamond and graphite produce the same amount of CO₂ (per same mass)
- In nature diamonds have been formed slowly from graphite under high-pressure high-temperature conditions
- The first synthetic diamonds were made in 1953 in Sweden under 7 GPa (= 70 000 atm) and at high temperature using molten Ni as a catalyst (nowadays most of the diamonds are man-made)
- In diamond the C atoms are packed much denser (3.5 g/cm³) compared to the graphite (2.3 g/cm³); this is the reason why the high-pressure conditions promotes the formation of diamonds
- For high-tech applications diamond thin films are needed; these are synthesized using hydrocarbons as precursors (methanol, ethanol) (Note: the same tetrahedral *sp*³ hybridization as in diamond)

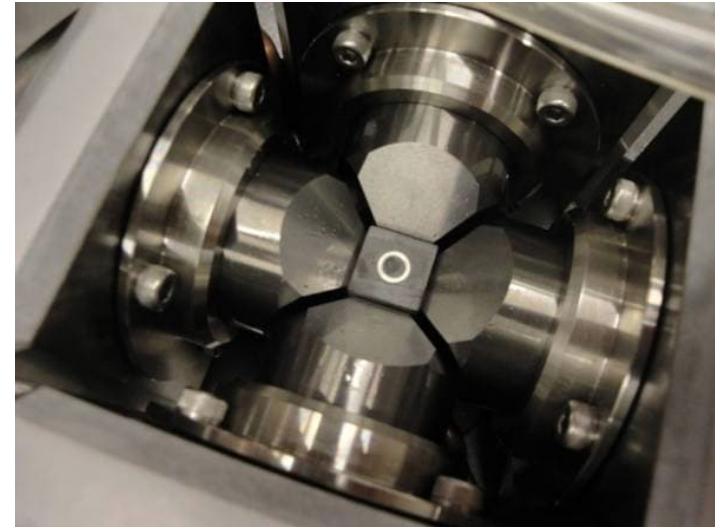
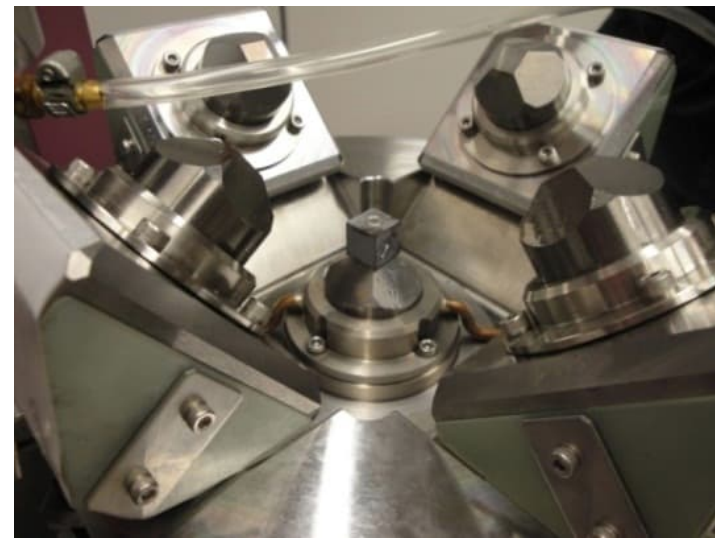
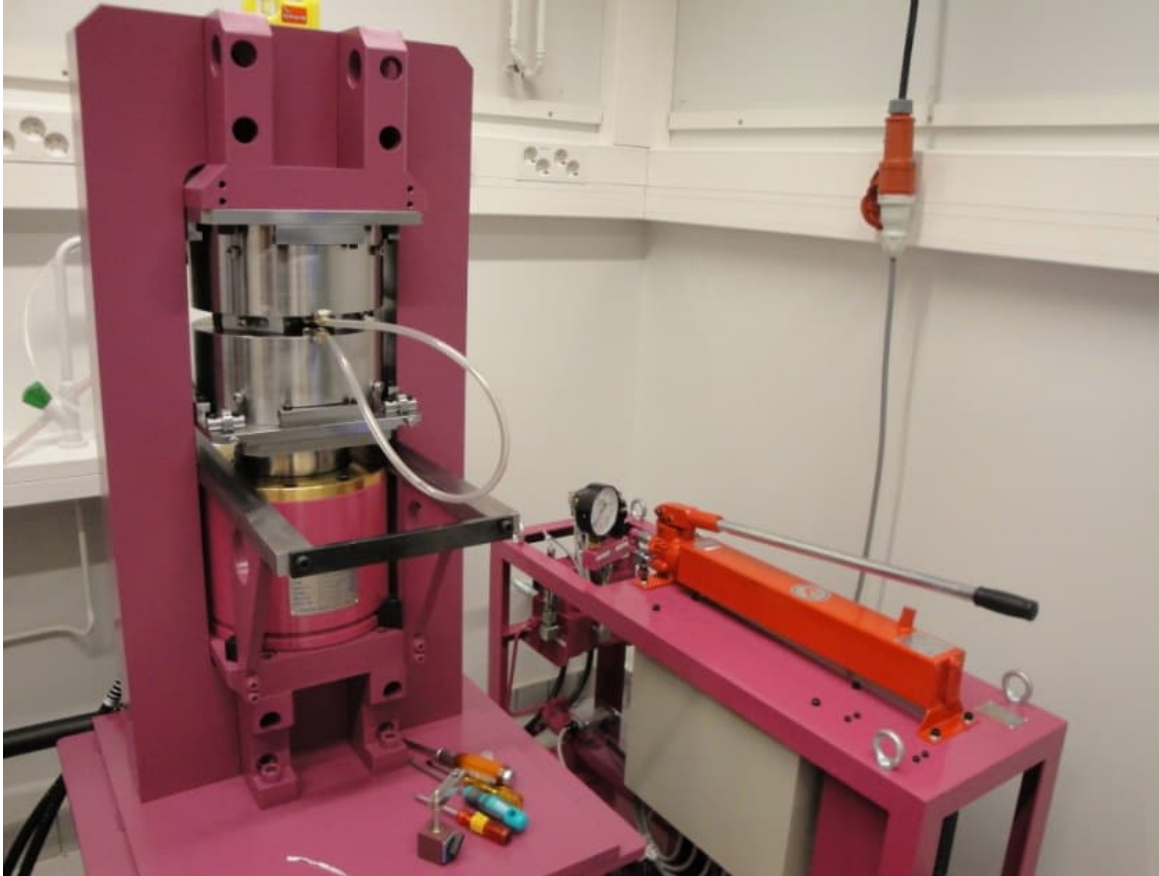


HIGH-PRESSURE SYNTHESIS

- 5 GPa = 50 000 atm
- 400 – 1200 °C
- 10 – 120 min
- 50 – 100 mg

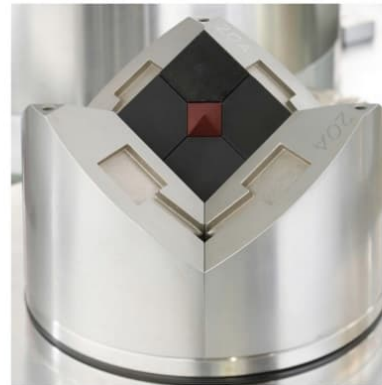
HP equipment
at Tokyo Tech

H. Yamauchi & M. Karppinen, *Supercond. Sci. Technol.* 13, R33 (2000).



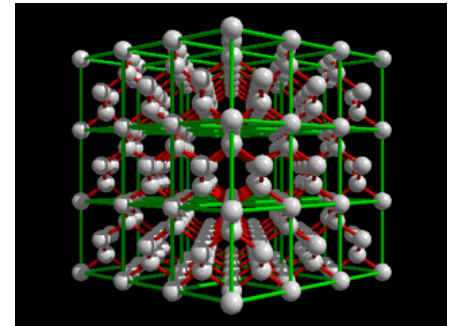
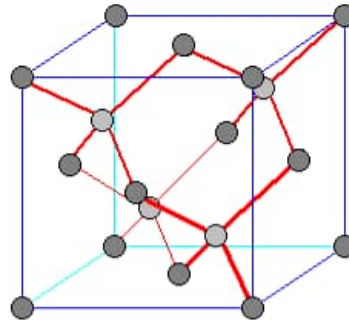
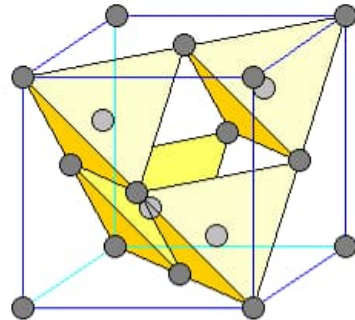
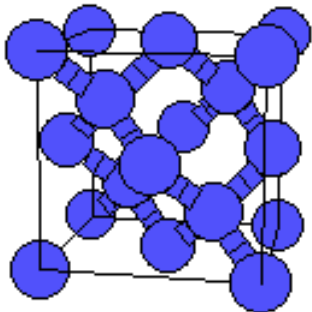
HP equipment at Aalto

- 4 GPa & 25 GPa



DIAMOND STRUCTURE: C and BN

- Each C atom (or B and N atom) bonded with strong covalent bonds to tetrahedrally surrounding neighbours
- In the 3D atom lattice each C-C bond is equally long (1.54 Å) and strong
- All four valence electrons of carbon are bound in the four bonds
→ pure diamond is one of the best known electrical insulators
- Strong covalent bonds → diamond is the strongest material known
- Diamond-type BN is the second strongest material (ca. 50 % of the harness of diamond)
- Strong bonds → high melting point (4100 °C)



DIAMOND AS THERMAL CONDUCTOR & SEMICONDUCTOR

- Diamond is the best thermal conductor among the known materials
(ca. 5-times better than the best metals)
- In diamond thermal conduction happens via phonons (vibrations of C atoms)
[in metals heat (like electricity) transport occurs via moving valence electrons]
- C atoms are light and the C-C bond is strong
→ efficient heat conduction
(impurities and lattice imperfections depress thermal conductivity)
- BN \approx “impure C”
→ diamond-type BN is not as good thermal conductor as diamond
- Pure diamond is electrical insulator (used as heatsink for semiconductor laser diodes)
- B-doping of diamond → p-type semiconductor
- Diamond-type BN:
 - slight B excess → p-type semiconductor
 - slight N excess → n-type semiconductor

METALLIC CHARACTER and BASICITY OF OXIDE: $N < P < As < Sb < Bi$

■ N, P nonmetals, As, Sb semimetals, Bi metal

■ However: resistivity increases $As < Sb < Bi$

■ N (g), P (s; mp. 44 °C), As (s), Sb (s), Bi (s)

■ N₂ gas (:N ≡ N:) but C solid (4 x C-C)

■ Melting points (°C):

N -210, P 44, As subl. 615, Sb 631, Bi 271

For metals/nonmetals m.p. decreases/increases in a group from up to down

■ Oxidation states: N: -III ... +V

P: -III, +III, +IV, +V

As, Sb, Bi: +III, +V (Bi: inert-pair effect)

■ Acid-base nature of oxide reflects the (non)metal character of the element

- N oxides (+I ... +V), P₂O₃ and P₂O₅ acidic

- As₂O₃, As₂O₅ and Sb₂O₃ amfoteric

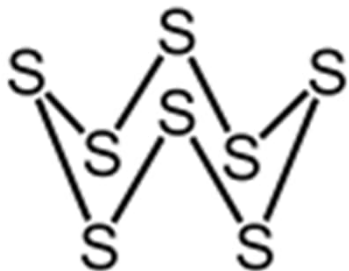
- Bi₂O₃ basic

The periodic table is color-coded to show the trend of metallic character and basicity of oxides. The legend indicates: Metals (yellow), Metalloids (purple), and Nonmetals (green). The elements N, P, As, Sb, and Bi are highlighted in purple, indicating they are metalloids. The elements H, He, Li, Be, B, C, Si, Ge, Sn, Pb, Bi, and Po are highlighted in green, indicating they are nonmetals. The elements Na, Mg, Al, Ga, In, Tl, Fr, Ra, and the lanthanide and actinide series are highlighted in yellow, indicating they are metals. The trend shows that metallic character increases from top-left to bottom-right, and the basicity of oxides increases in the same direction.

1	2											13	14	15	16	17	18
H	He											B	C	N	O	F	Ne
3	4											5	6	7	8	9	10
Li	Be											Al	Si	P	S	Cl	Ar
11	12	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Na	Mg	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
55	56	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86
Cs	Ba	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
87	88	103	104	105	106	107	108	109	110	111	112	113	114	115	116	117	118
Fr	Ra	Lr	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Uub						
		57	58	59	60	61	62	63	64	65	66	67	68	69	70		
		La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb		
		89	90	91	92	93	94	95	96	97	98	99	100	101	102		
		Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No		

MULTITUDE OF SULPHUR COMPOUNDS

- Several stable oxidation states
- Allotropy of S: tens of allotropes (ref. O 2, Se 6, Te 3, Po 2)
- Various S-chains and S-rings, where other atoms can bond
- Most common: S₈-ring "crown" (different polymorfs)
- Polycations S_n²⁺ (*n*=4 yellow, *n*=8 blue, *n*=19 red)
- Polysulfides S_n²⁻ (*n*=2-6; strongly colourful)
- Thio-compounds
- Sulphur is also one of the basic elements in organic compounds



HALOGENS

Chemically very homogeneous group, except fluorine which differs from the rest of the group members in many ways

Element	Melting Point (°C)	Boiling Point (°C)
F ₂	-219	-188
Cl ₂	-101	-34
Br ₂	-7	+60
I ₂	+114	+185
As (rad. act)	+320	+337

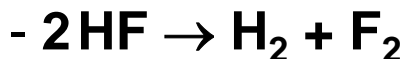


FLUORINE *VERSUS* OTHER HALOGENS

- Atomic radius (Å): **F 0.71**, Cl 0.99, Br 1.14, I 1.33
- F₂: small F atoms with many outer electrons → large electron-electron repulsion → small bond energy → Fluorine is **HIGHLY REACTIVE**
- Electronegativity: **F 4.0**, Cl 3.0, Br 2.8, I 2.5, At 2.2
- Oxidation states:

F:	-I
Cl:	-I, +I, (+II), +III, (+IV), +V, (+VI), +VIII
Br:	-I, +I, +III, (+IV), +V, (+VI), +VIII
I:	-I, +I, +III, +V, +VIII

Preparation of fluorine (from fluorite CaF₂) Moissan 1886 (Nobel 1906):



- problem: F₂ and HF gases highly reactive and poisonous

- electrolysis in KF melt, Pt cell, Pt-Ir electrodes, -50 °C

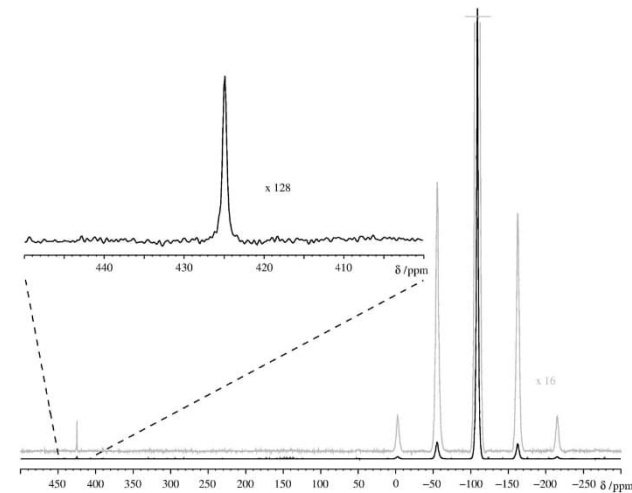
- **HOWEVER:** sometimes metals exist in their highest oxidation states in oxides rather than in fluorides, e.g. OsO₄ possible, but not OsF₈

- Reason: 8 F⁻ ions around the small Os⁸⁺ cation not possible !



Antozonite (Stink Spar)

- The CaF_2 mineral “Stink Spar” in Wölsendorf contains minute amounts of radioactive uranium inclusions
- Uranium constantly emits ionizing radiation which splits CaF_2 into calcium and elemental fluorine
- The thus formed fluorine remains in tiny inclusions
- It however slowly reacts with atmospheric oxygen and water vapour, producing ozone
- The characteristic smell of ozone gave the name for the mineral



2012: First proof of F_2 on Earth by ^{19}F -MAS-NMR

J. Schmedt auf der Günne, M. Mangstl & **F. Kraus**, *Angew. Chem. Int. Ed.* **51**, 7847 (2012).

NOBLE GASES: BASIC PROPERTIES

- Helium has the lowest known boiling point (-269 °C)
- Ionization energies (kJ/mol):
He 2269, Ne 2079, Ar 1519, Kr 1349, Xe 1169, Rn 1036

COMPOUNDS

- Bartlett 1962: $\text{O}_2(g) + \text{PtF}_6(g) \rightarrow [\text{O}_2^+][\text{PtF}_6^-](s)$
- Ionization energy of O_2 1180 kJ/mol \approx IE(Xe)
→ “[Xe][PtF₆]” → Ar, Kr, Xe form compounds with the most electronegative elements
- Oxidation states: +II, +IV, +VI, +VIII
- Bond strengths (kJ/mol): Xe-F 130, Xe-O 84, Kr-F 50
- KMXeNaO_6 double perovskite !
[S.N. Britvin et al., Angew. Chem. 127, 1 (2015)]

SUPERFLUIDS

- Under normal pressure He stays in liquid state down to 0 K
- ^3He and ^4He superfluids at low temperatures
- Viscosity zero \rightarrow continuous movement \rightarrow escape from the container
- Laws of classical mechanics do not work \rightarrow quantum mechanics
- Ultrahigh thermal conductivity

