

M. Sc. Bionics Engineering



UNIVERSITÀ DI PISA



Sant'Anna
Scuola Universitaria Superiore Pisa



SCUOLA
ALTI STUDI
LUCCA

ADVANCED MATERIALS FOR BIONICS

LECTURE 6: CERAMICS

Prof. Francesco Greco

AY 2024-25

L6 - 14.10.2024

QUESTIONS

- How do the crystal structures of ceramic materials differ from those for metals?
- How are defects, impurities accommodated in the ceramic lattice?
- What are glasses?
- Why some ceramics exhibit piezoelectricity? What are uses of piezoceramics?
- What are bioceramics?
- Why is silicon carbide becoming important in electronics and biomedicine?

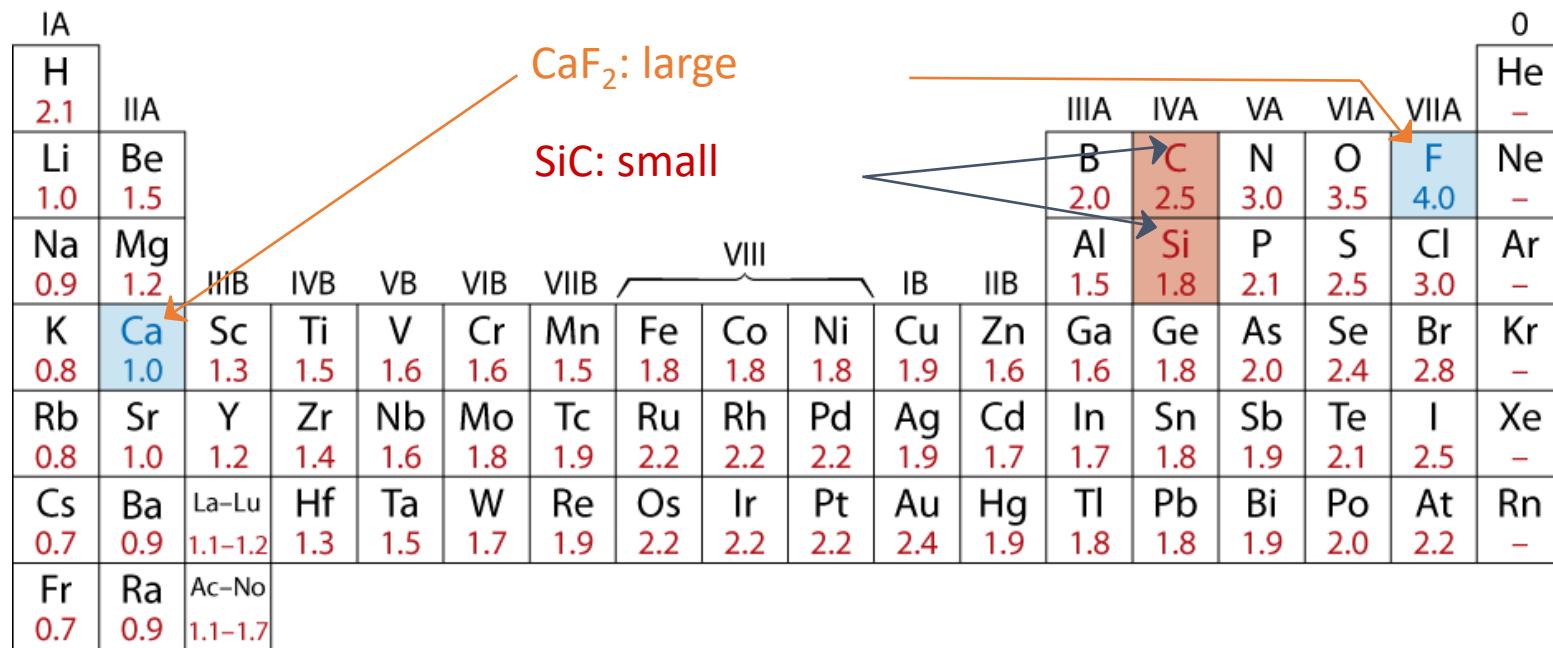


L6.1

STRUCTURE AND PROPERTIES OF CERAMICS

ATOMIC BONDING IN CERAMICS

- two or more elements involved: generally more complex struct than metals
- Bonding:
 - Can be **ionic and/or covalent** in character
 - % ionic character increases with difference in electronegativity of atoms
- Degree of ionic character: large or small



BOND HYBRIDIZATION

Bond Hybridization is possible when there is significant covalent bonding

- hybrid electron orbitals form

example: SiC

$$X_{\text{Si}} = 1.8 \text{ and } X_{\text{C}} = 2.5$$

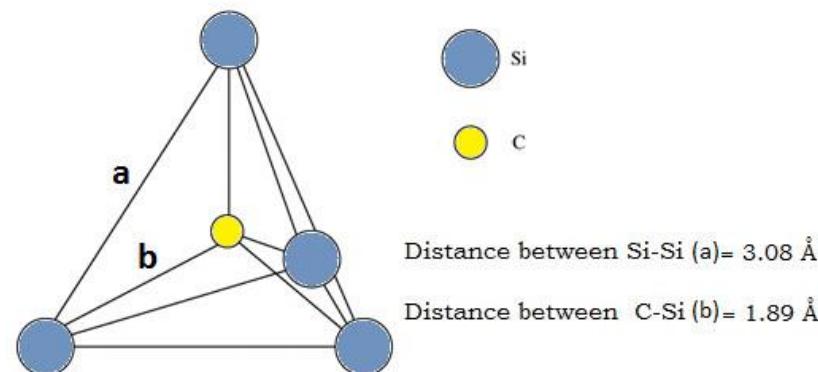
$$\% \text{ ionic character} = 100 \{1 - \exp[-0.25(X_{\text{Si}} - X_{\text{C}})^2]\} = 11.5\%$$

~ 89% covalent bonding

Both Si and C prefer sp^3 hybridization



Si atoms occupy tetrahedral sites



IONIC CHARACTER

% Ionic Character of interatomic bonds for several ceramic materials

Material	Percent Ionic Character
CaF ₂	89
MgO	73
NaCl	67
Al ₂ O ₃	63
SiO ₂	51
Si ₃ N ₄	30
ZnS	18
SiC	12

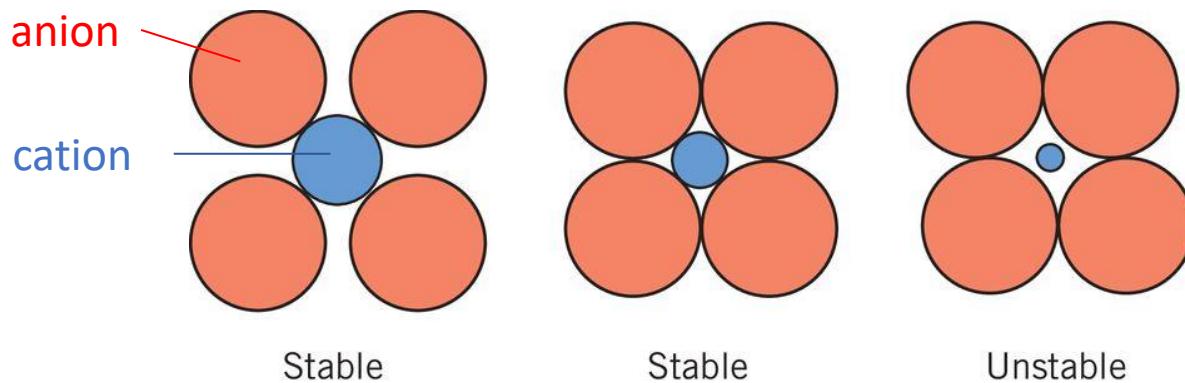
FACTORS DETERMINING CRYSTAL STRUCTURE

1. Maintenance of Charge Neutrality :

- net charge should be zero

2. Relative sizes of ions – Formation of stable structures:

- maximize the # of oppositely charged ion neighbors.



r_c : ionic radius cation
 r_a : ionic radius anion

important:

$$r_c / r_a$$

IONIC RADII AND COORDINATION NUMBERS

r_c : ionic radius cation

r_a : ionic radius anion

Cation	Ionic Radius (nm)	Anion	Ionic Radius (nm)
Al ³⁺	0.053	Br ⁻	0.196
Ba ²⁺	0.136	Cl ⁻	0.181
Ca ²⁺	0.100	F ⁻	0.133
Cs ⁺	0.170	I ⁻	0.220
Fe ²⁺	0.077	O ²⁻	0.140
Fe ³⁺	0.069	S ²⁻	0.184
K ⁺	0.138		
Mg ²⁺	0.072		
Mn ²⁺	0.067		
Na ⁺	0.102		
Ni ²⁺	0.069		
Si ⁴⁺	0.040		
Ti ⁴⁺	0.061		

most common in ceramics

Coordination n.	r_c / r_a	Geometry
2	< 0.155	
3	0.155 – 0.255	
4	0.255 – 0.414	
6	0.414 – 0.732	
8	0.732 – 1.0	

CRYSTAL STRUCTURES OF CERAMICS

Module Menu

- Unit Cells
 - NaCl
 - CsCl
 - ZnS
 - Diamond
 - Graphite
 - CaF₂
 - BaTiO₃
- Spinel/Inverse Spinel
- Close-packed Structures
- Molecule Definition Utility

Ceramic Crystal Structures

CsCl

- Rotate (click-and-drag) the 3-D unit cell.
- Click on the listed Atomic Packing arrangements to view and rotate the plane.

Change to FULL-SPHERE representation

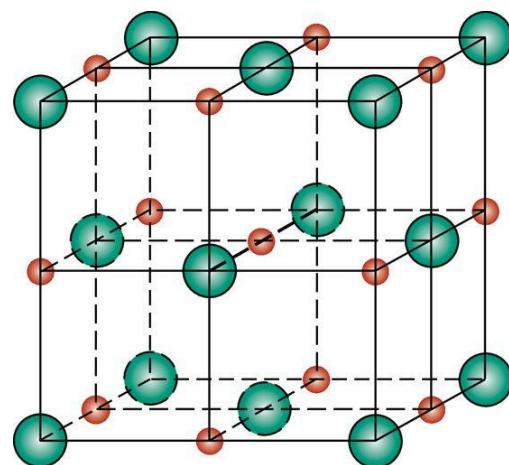
(100)
(110)
(111)
(112)
(122)
(123)
Reset

[Wiley - VMSE \(drbuc2jl8158i.cloudfront.net\)](http://drbuc2jl8158i.cloudfront.net)

AX STRUCTURES

- A: cation, X: anion same charge

NaCl type



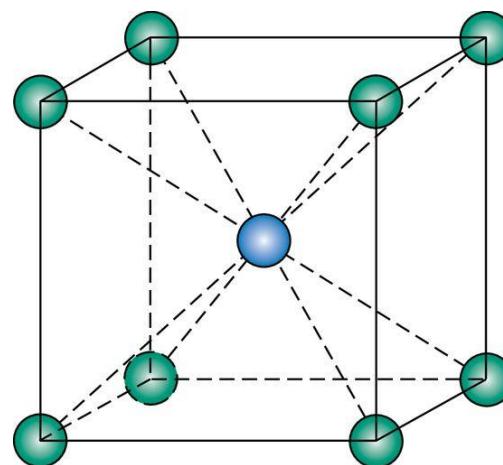
● Na⁺

● Cl⁻

CN: 6 - fcc, 2 atoms basis

NaCl, MgO, MnS, LiF, FeO

CsCl type

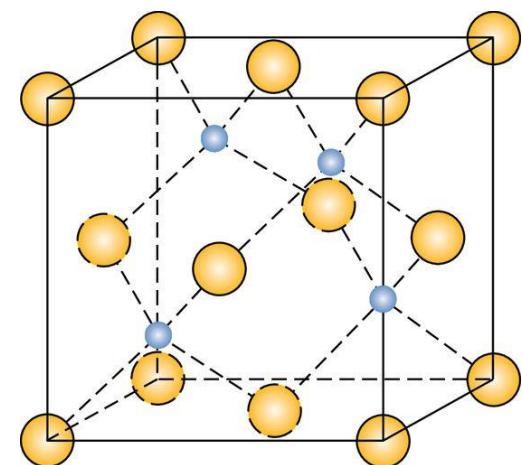


● Cs⁺

● Cl⁻

CN: 8 - sc, 2 atoms basis

Blend (ZnS) type



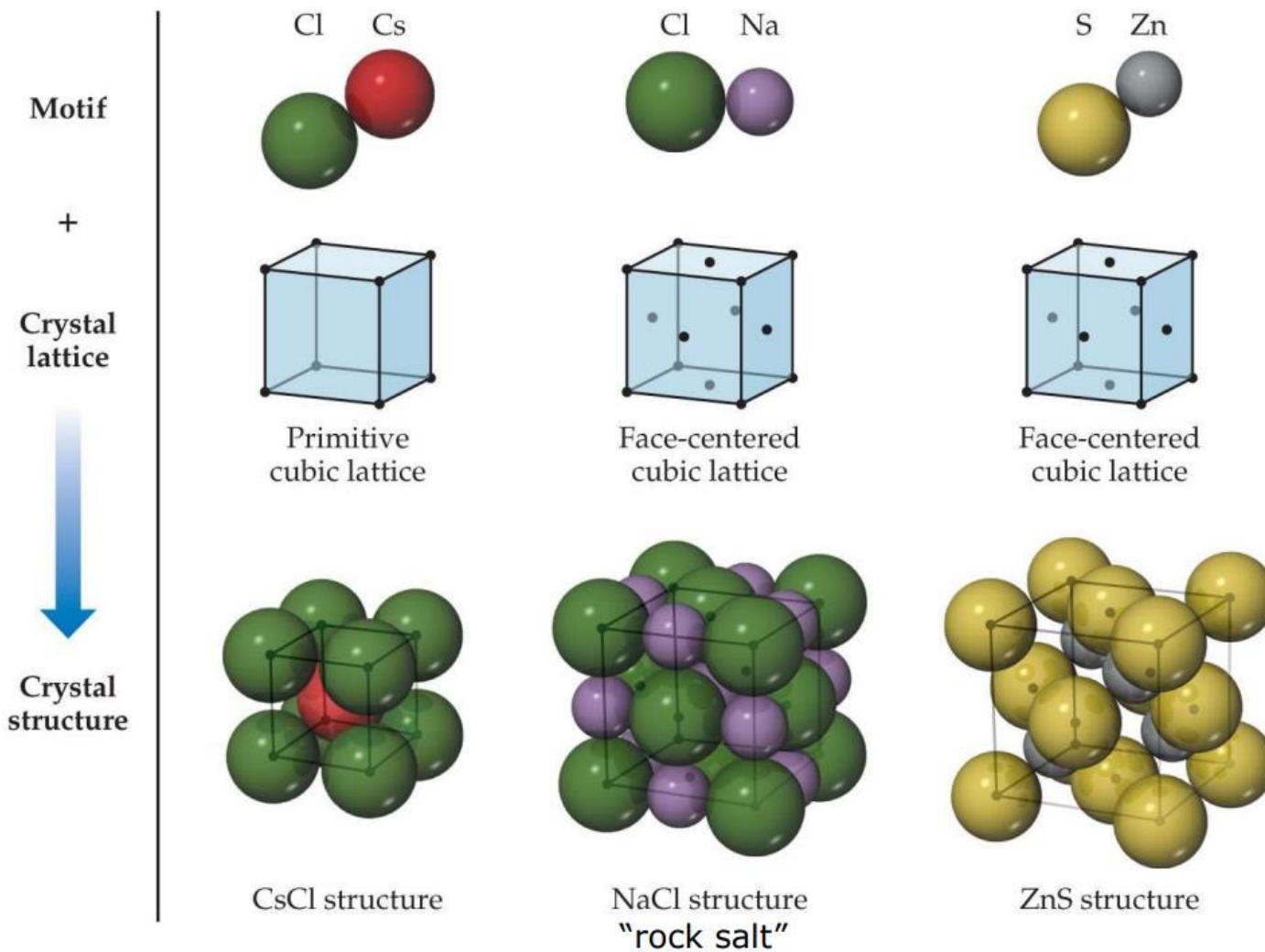
● Zn

● S

CN: 4 - fcc, 2 atoms basis

ZnS, ZnTe, SiC

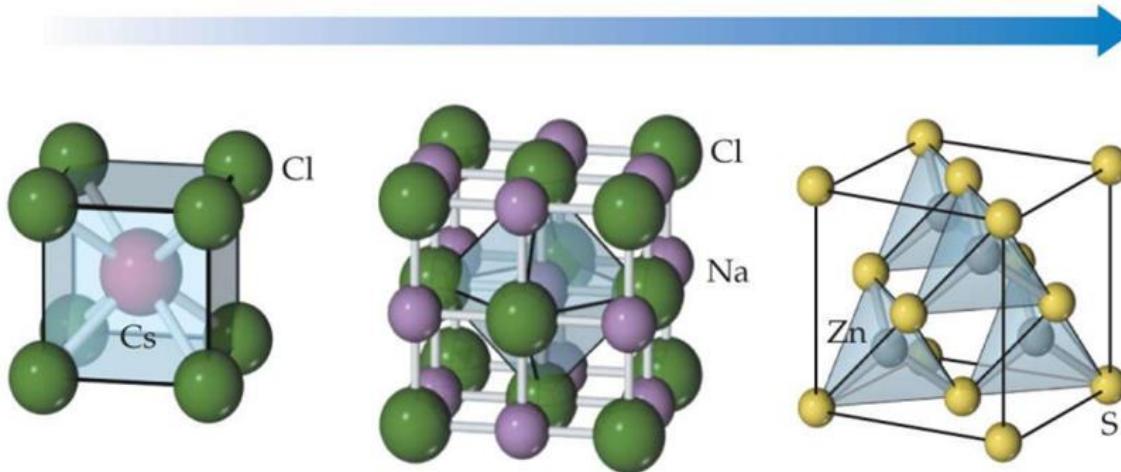
AX STRUCTURES – MOTIF+LATTICE



Source: <https://www.unf.edu/~michael.lufaso/chem204>

AX STRUCTURES – IONIC RADII & CN

Decreasing r_+ / r_-

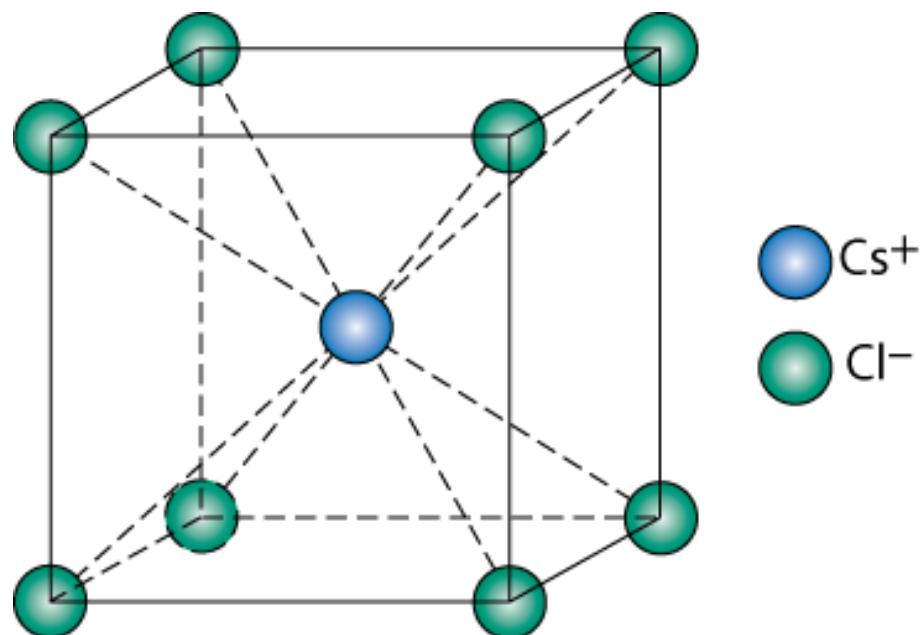


	CsCl	NaCl	ZnS
Cation radius, r_+ (Å)	1.74	1.02	0.74
Anion radius, r_- (Å)	1.81	1.81	1.84
r_+ / r_-	0.96	0.56	0.40
Cation coordination number	8	6	4
Anion coordination number	8	6	4

Source: <https://www.unf.edu/~michael.lufaso/chem204>

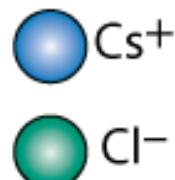
CsCl STRUCTURES

Cesium Chloride structure:



$$\text{Cs}^+ \ r_{\text{Cs}^+} = 0.174 \text{ nm}$$

$$\text{Cl}^- \ r_{\text{Cl}^-} = 0.181 \text{ nm}$$



$$r_c/r_a = 0.961 \approx 1$$

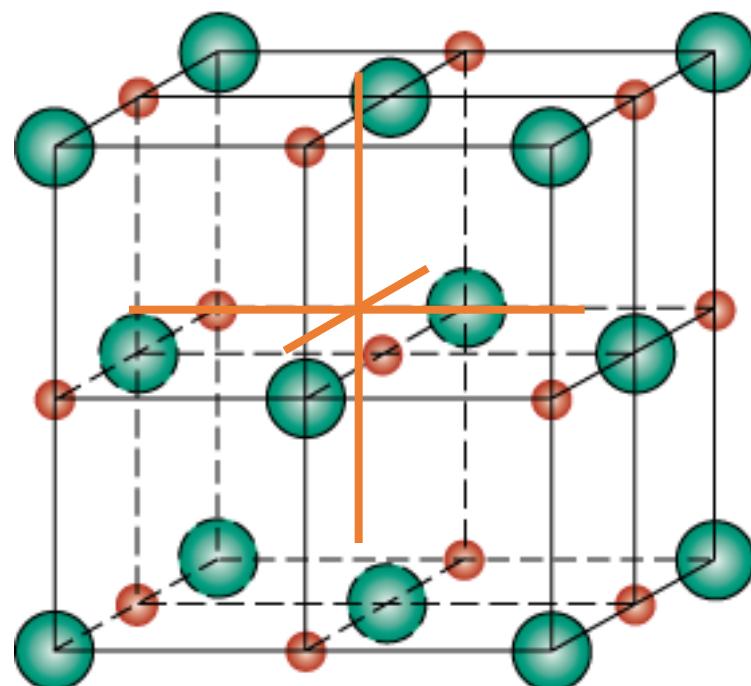
∴ cubic sites preferred

each Cs^+ has 8 neighbor Cl^-

ROCK SALT STRUCTURE

Same concepts can be applied to ionic solids in general

Example: NaCl (rock salt) structure



$$\bullet \text{ Na}^+ \quad r_{\text{Na}} = 0.102 \text{ nm}$$

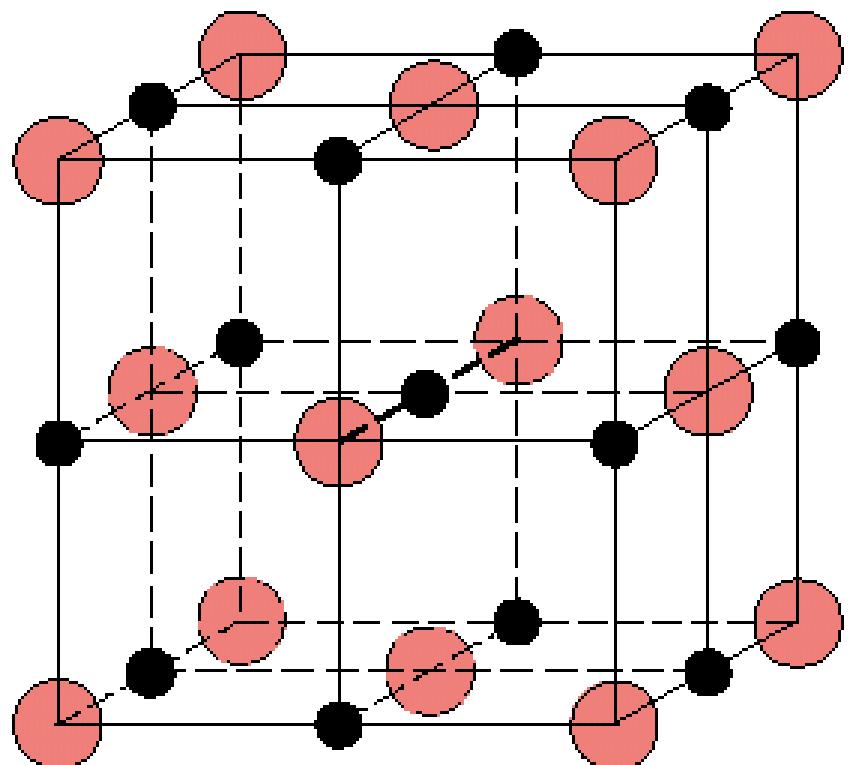
$$\bullet \text{ Cl}^- \quad r_{\text{Cl}} = 0.181 \text{ nm}$$

$$r_{\text{Na}}/r_{\text{Cl}} = 0.564$$

∴ octahedral sites preferred

MgO AND FeO

MgO and FeO also have the NaCl structure



● O²⁻ $r_O = 0.140 \text{ nm}$

● Mg²⁺ $r_{\text{Mg}} = 0.072 \text{ nm}$

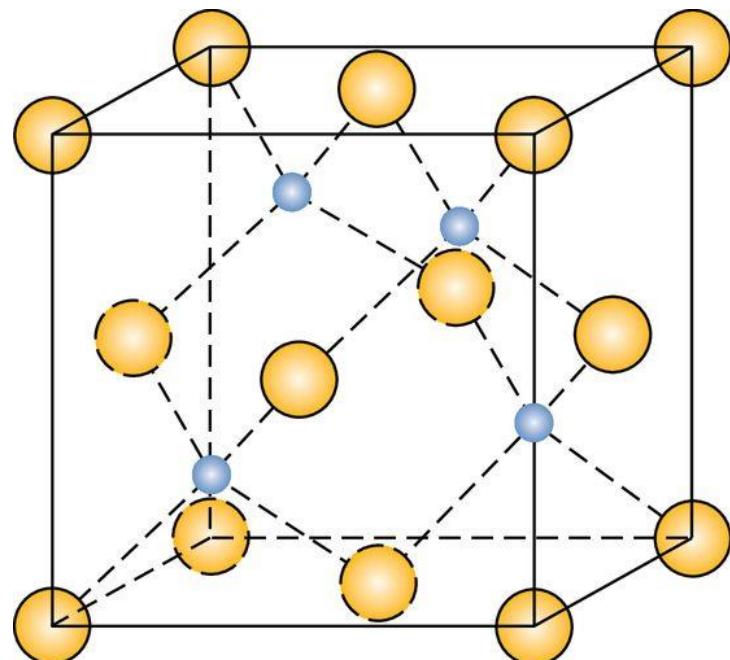
$$r_{\text{Mg}}/r_O = 0.514$$

∴ octahedral sites preferred

each Mg²⁺ (or Fe²⁺) has 6 neighbor oxygen atoms

ZnS STRUCTURES

ZnS (blend) structure:



● Zn

○ S

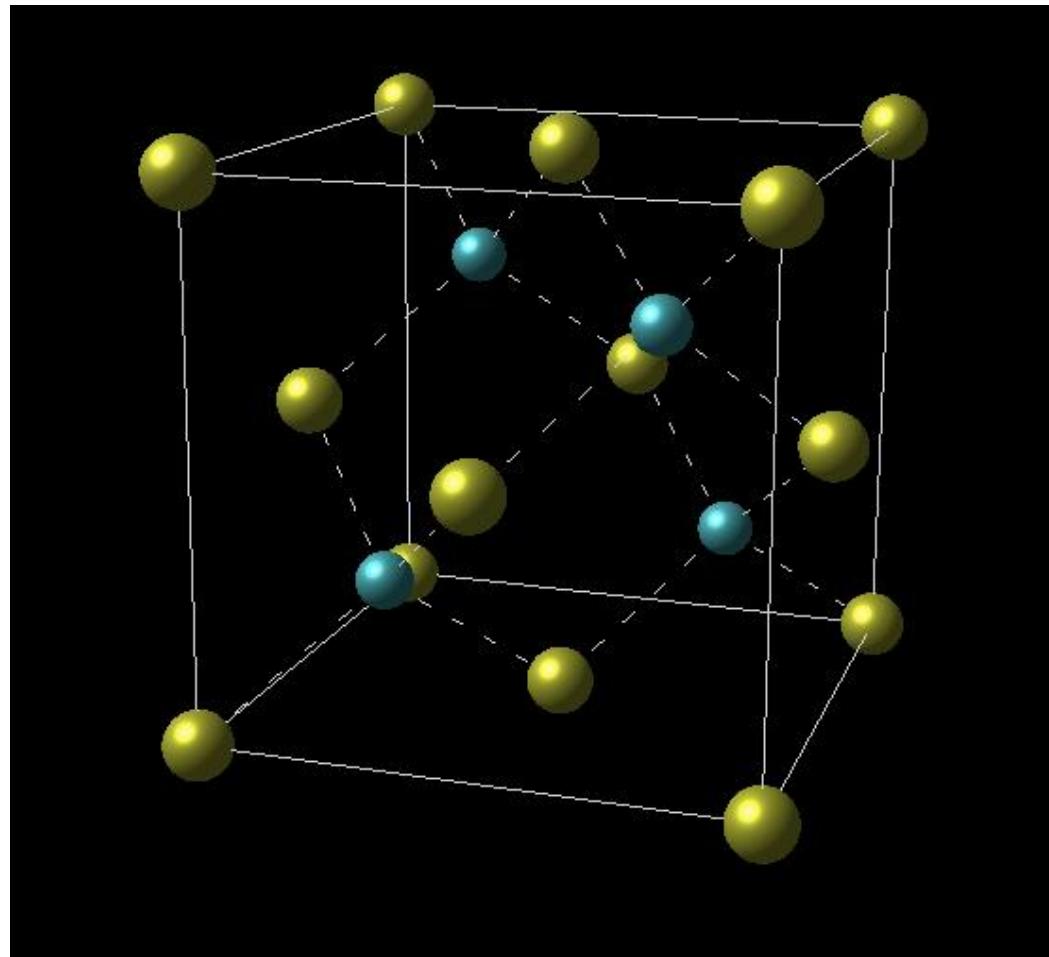
$$\text{Zn}^{2+} \quad r_{\text{Zn}^{2+}} = 0.074 \text{ nm}$$

$$\text{S}^{2-} \quad r_{\text{S}^{2-}} = 0.184 \text{ nm}$$

$$r_c/r_a = 0.40$$

∴ tetrahedral sites preferred

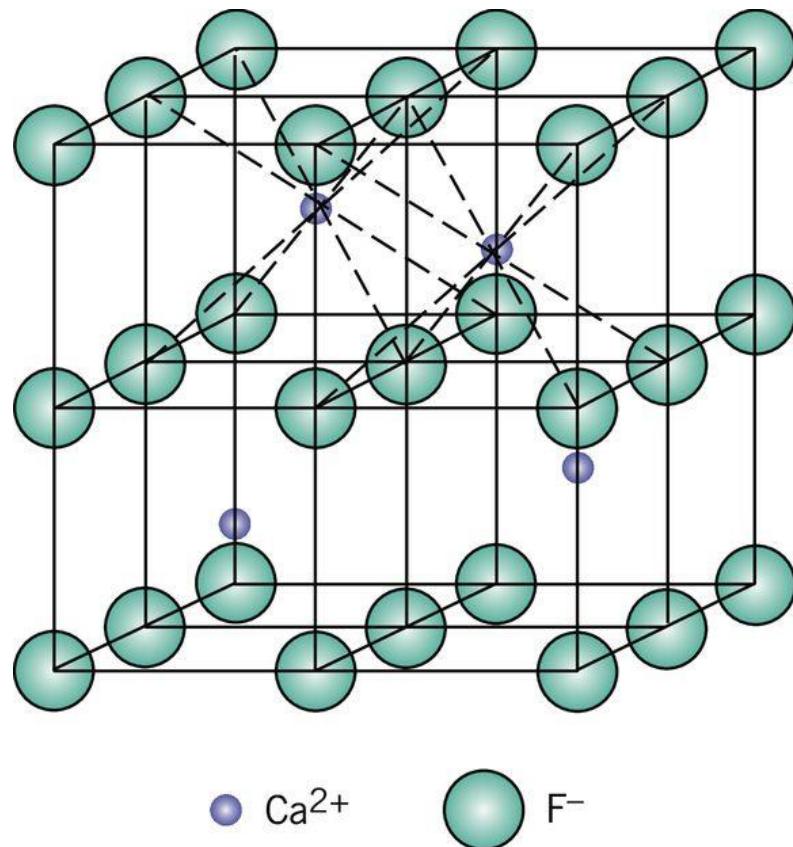
VMSE Screenshot – ZINC BLENDE UNIT CELL



[Wiley - VMSE \(drbuc2jl8158i.cloudfront.net\)](http://Wiley - VMSE (drbuc2jl8158i.cloudfront.net))

$A_m X_p$ STRUCTURES

A: cation, X: anion different charges



CaF_2
fluorite

similar to CsCl BUT only half of central position occupied by Ca^{2+} ions

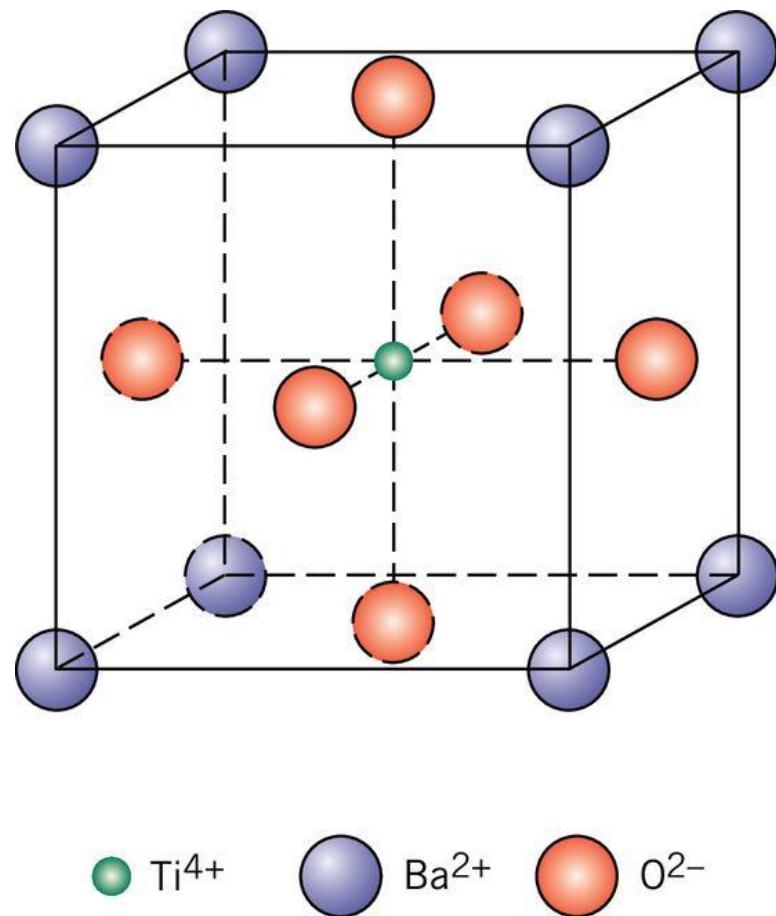
CN: 8 (cations), 4 (anions)
structure: sc, 2 atoms basis

$\text{CaF}_2, \text{ZrO}_2, \text{UO}_2, \text{PuO}_2, \text{ThO}_2$

$A_m B_n X_p$ STRUCTURES

- A: cation, B: cation, X: anion

different charges



example

$BaTiO_3$

barium titanate

perovskite structure

[Barium Titanate](#)

[BaTiO₃](#)

[\(chemtube3d.com\)](#)

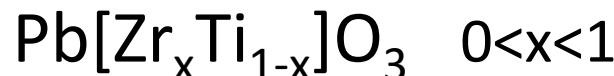
CN: 12 (A), 6 (B), 6 (X)

structure: simple cubic

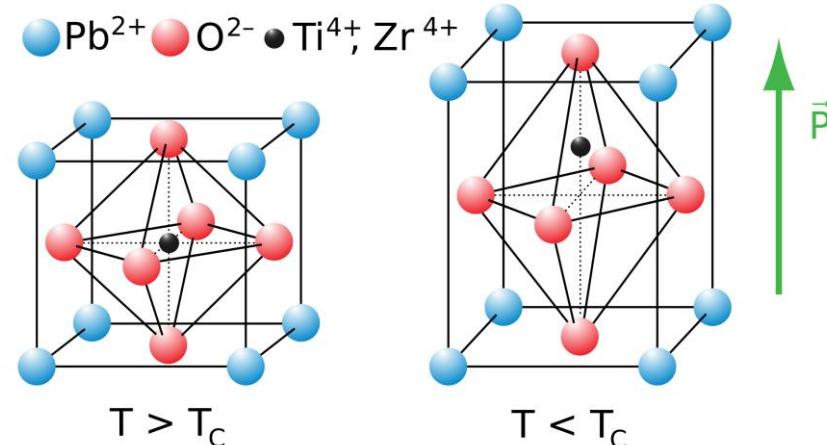
Perovskites exhibit many interesting and useful properties: **piezoelectricity**, **pyroelectricity**, **ferroelectricity**, **electro-optical effects**, **magneto-optical effects**, and **superconductivity**.

PEROVSKITES EXAMPLES

PZT: Lead Zirconate Titanate



In PZT, a fraction x of the B sites in the crystal are occupied by Zr atoms and a fraction $(1 - x)$ of the B sites are occupied by Ti atoms.



Piezoelectric material: the crystal expands when a voltage is applied across it

actuators in scanning tunneling/atomic force microscopes, inkjet printers, fuel injectors, etc..

pressure sensors: when stress is applied to a crystal, a voltage appears accross it



L6.2

PIEZOCERAMICS

PIEZOELECTRICITY



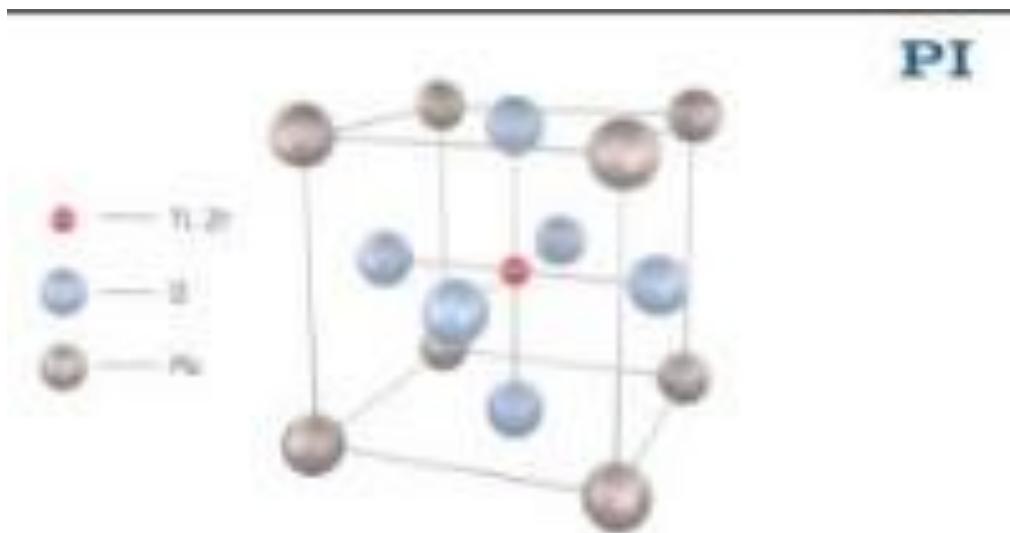
YOUTUBE VIDEO (channel «Steve Mould»)

[Piezoelectricity - why hitting crystals makes electricity - YouTube](#)

(09:20)

PIEZOELECTRIC CERAMICS

- natural monocrystalline materials - quartz, tourmaline:
piezoelectric effect is relatively small
- Polycrystalline ferroelectric ceramics - barium titanate (BaTiO_3)
and **lead zirconate titanate (PZT)**:
exhibit larger displacements or induce larger electric voltages



[Fundamentals of Piezo Technology](#)
www.picericamic.com

PIEZOELECTRIC TRANSDUCERS



YOUTUBE VIDEO (channel «Physik Instrument») (03:19)

<https://youtu.be/DeZGc4wufN0>

EXAMPLES OF USES OF PIEZOCERAMICS

VIDEO RESOURCES

PICERAMIC – Virtual Trade SHOWS: Medical Technology

- Contactless Patient Monitoring With Ultrasound
- Incisionless Surgery Using Therapeutic Ultrasound
- Miniaturized Tools for Minimally Invasive Medical Procedures
- Ultrafast Liquid Handling in Small Spaces

PICERAMIC – Virtual Trade SHOWS: Industrial Ultrasonics

- Smart Metering for Intelligent Data Acquisition
- Ultrasound for Industrial Automation
- Hydroacoustics in Underwater Communication

PICERAMIC – Virtual Trade SHOWS: Industrial Precision Dosing

- Digital printing – Drop on Demand Inkjet
- Precise Dosing of Highly Viscous Media

PIEZOELECTRIC CERAMIC TRANSDUCERS

HOME ASSIGNMENT

visit Physik Instrumente (PI) website:

PI – Solutions for Precision Motion and Positioning
(physikinstrumente.com)

PI

MENU =

Piezo Technology
Piezoceramic Components & Actuators

PI Ceramic offers a wealth of experience in the manufacturing of piezoceramic materials, components, and actuators. The piezoceramic materials can be adapted individually to perfectly fit the later use of the piezo components. Lead-free piezo ceramics are available for the construction of sensor components. Actuators made of piezo crystals provide a hysteresis-free linear displacement.

 Fundamentals of Piezo Technology	 Properties of Piezo Actuators	 Generating Ultrasound	 Piezoceramic Materials
 Manufacturing Technology	 PICMA® Technology	 Integrated Piezo Actuators	 DuraAct Patch Transducer Technology

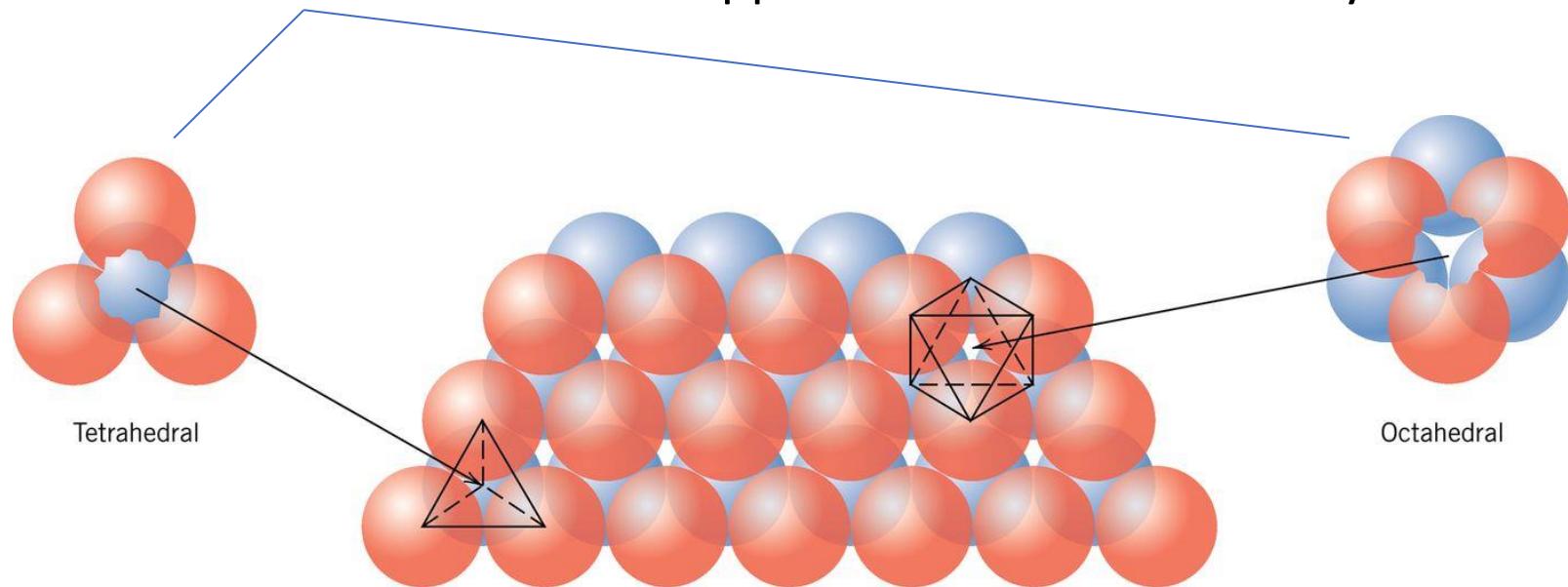


L6.3

OXIDE STRUCTURES, PACKING OF ANIONS, GLASS

CLOSE PACKING OF ANIONS

- similar as in metals (FCC, HCP), close-packed planes of ions: large anions
- small interstitial sites** between cpp in which the cations may reside



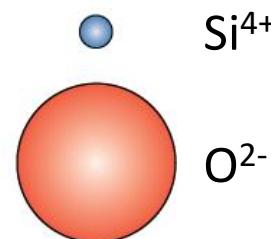
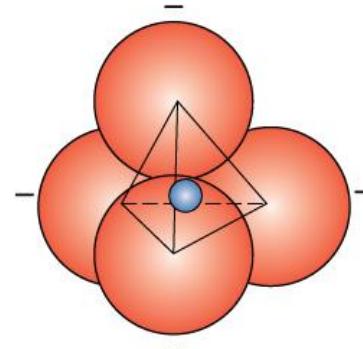
Adapted from W. G. Moffatt, G. W. Pearsall, and J. Wulff, *The Structure and Properties of Materials*, Vol. I, *Structure*, John Wiley & Sons, 1964. Reproduced with permission of Janet M. Moffatt.

3D VIEW – VMSE Ceramic Close Packed Structures

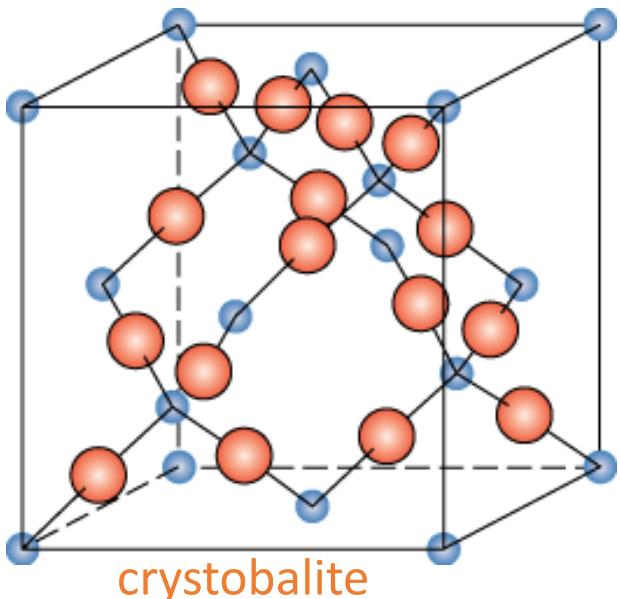
SILICATE CERAMICS

Most common elements on earth are Si & O

basic unit of all silicates: tetrahedron $(\text{SiO}_4)^{4-}$



Figs. 12.9 & 12.10, Callister & Rethwisch
10e



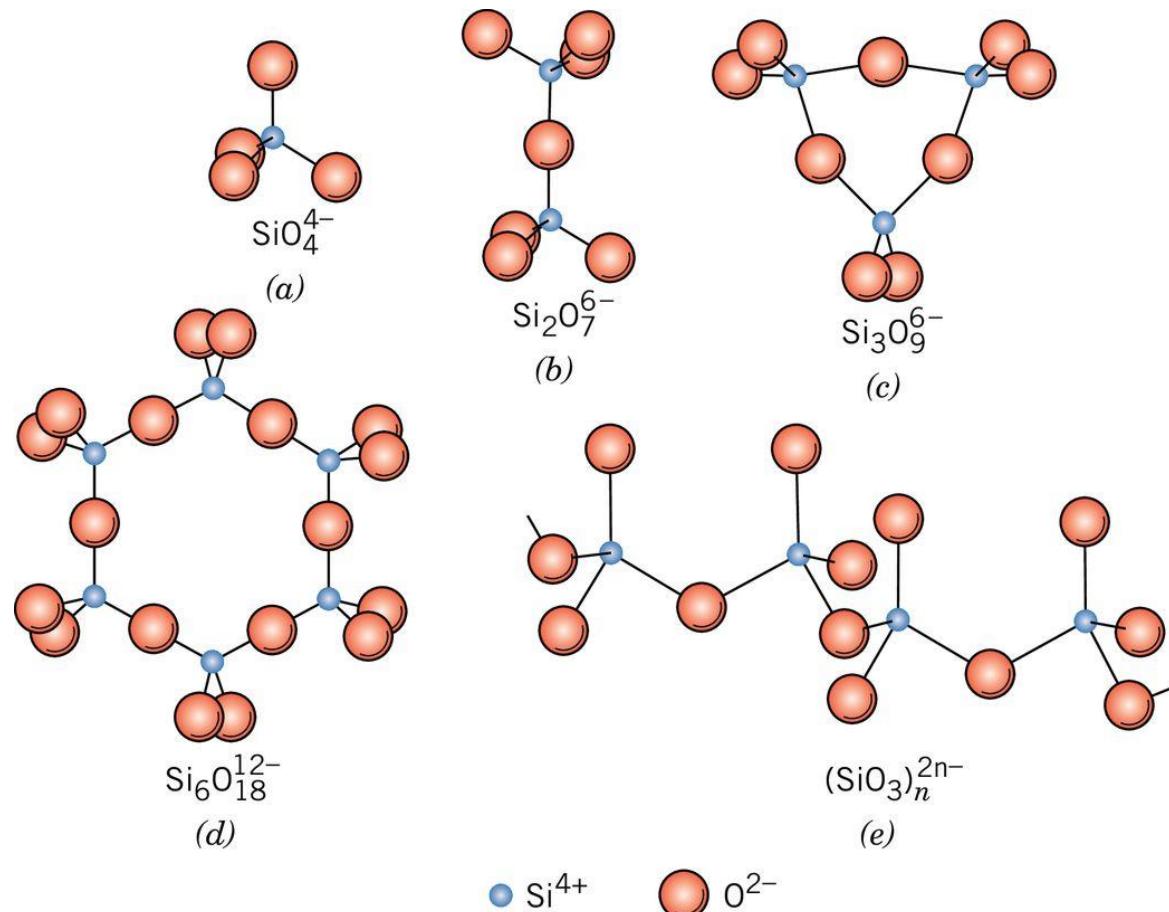
SiO_2 (silica) **polymorphic** forms are quartz, crystobalite, & tridymite

“open” structures: relatively low density (e.g. quartz 2.65 g/cm³)

The strong Si-O bonds lead to a high melting temperature (1710°C) for this material

SILICATES

Bonding of adjacent SiO_4^{4-} : sharing of common corners, edges, or faces



Presence of cations such as Ca^{2+} , Mg^{2+} , & Al^{3+} :

1. maintain charge neutrality,
2. ionically bond SiO_4^{4-} to one another

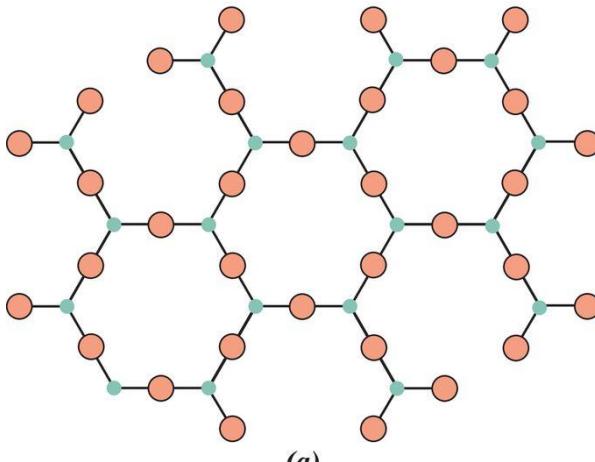
e.g.



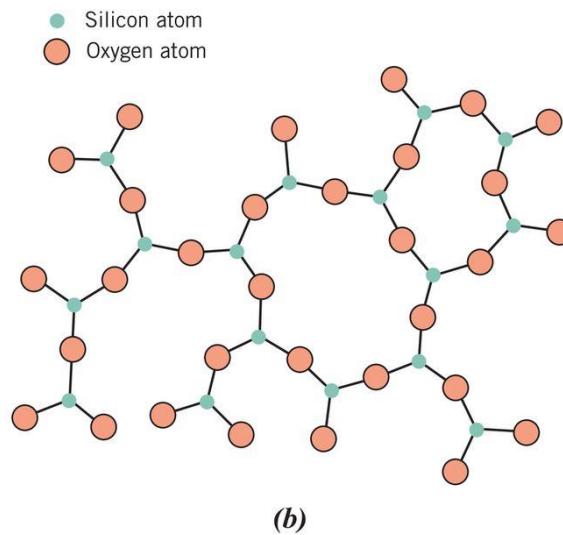
GLASS STRUCTURE

Glass is noncrystalline (**amorphous**)

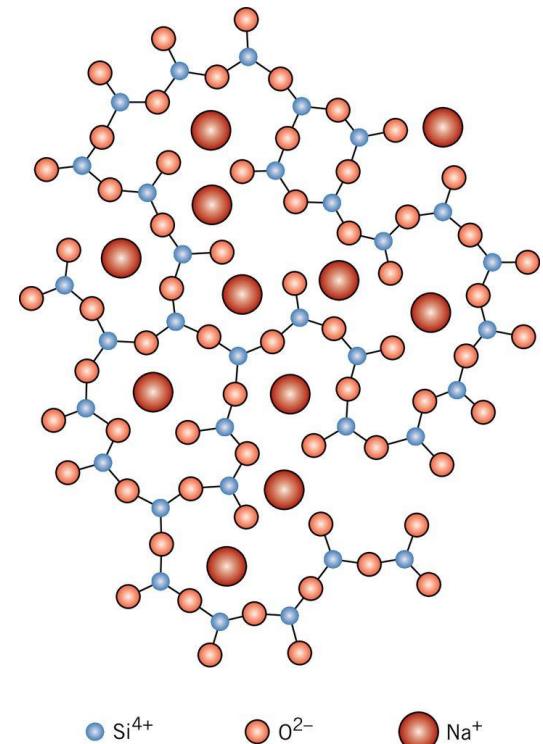
- Fused silica is SiO_2 to which no impurities have been added
- Other common glasses contain impurity ions such as Na^+ , Ca^{2+} , Al^{3+} , and B^{3+}



Crystalline silica
(quartz)



Non-Crystalline silica



(soda glass)

OXIDE GLASSES

oxides of elements from groups III, IV, V & mixtures with metallic oxides form glasses

window glass: 70% SiO_2 , + 20% Na_2O , 10% CaO

ions preventing crystallisation: Na, Mg, Ca, ...different number of bonds to O

1	H	Hydrogen	1.00794
3	Li	Lithium	6.941
4	Be	Beryllium	9.012182
11	Na	Sodium	22.989770
12	Mg	Magnesium	24.3050

C

O

C

19	K	Potassium	39.0983
20	Ca	Calcium	40.078
21	Sc	Scandium	44.955910
22	Ti	Titanium	47.867
23	V	Vanadium	50.9415
24	Cr	Chromium	51.9961
25	Mn	Manganese	54.938049
26	Fe	Iron	55.845
27	Co	Cobalt	58.933200
28	Ni	Nickel	58.6934
29	Cu	Copper	63.546
30	Zn	Zinc	65.39
31	Ga	Gallium	69.723
32	Ge	Germanium	72.61
33	As	Arsenic	74.92160
34	Se	Selenium	78.96
35	Br	Bromine	79.904
36	Kr	Krypton	83.80
37	Rb	Rubidium	85.4678
38	Sr	Strontrium	87.62
39	Y	Yttrium	88.90585
40	Zr	Zirconium	91.224
41	Nb	Nobium	92.90638
42	Mo	Molybdenum	95.94
43	Tc	Technetium	(98)
44	Ru	Ruthenium	101.07
45	Rh	Rhodium	102.90550
46	Pd	Palladium	106.42
47	Ag	Silver	107.8682
48	Cd	Cadmium	112.411
49	In	Indium	114.818
50	Tl	Tin	118.710
51	Sb	Antimony	121.760
52	Te	Tellurium	127.60
53	I	Iodine	126.90447
54	Xe	Xenon	131.29
55	Cs	Cesium	132.90545
56	Ba	Barium	137.327
57	La	Lanthanum	138.9055
72	Hf	Hafnium	178.49
73	Ta	Tantalum	180.9479
74	W	Tungsten	183.84
75	Re	Rhenium	186.207
76	Os	Osmium	190.23
77	Ir	Irindium	192.217
78	Pt	Platinum	195.078
79	Au	Gold	196.96655
80	Hg	Mercury	200.59
81	Tl	Thallium	204.3833
82	Pb	Lead	207.2
83	Bi	Bismuth	208.98038
84	Po	Poisonium	(209)
85	At	Actatina	(210)
86	Rn	Radon	(222)

- ✓ Glass former: high valence state, covalent bonding with O
- ✓ Modifier: low valence state, ionic bonding with O



1]

ygen ion

- ea
- re



Network modifiers



Glass formers



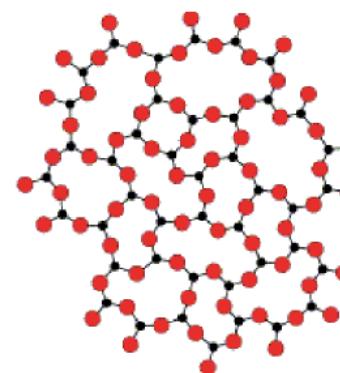
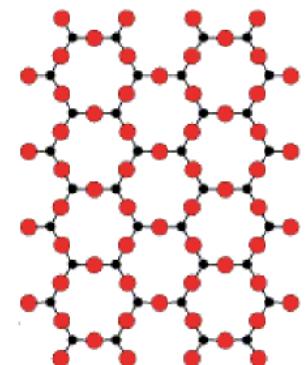
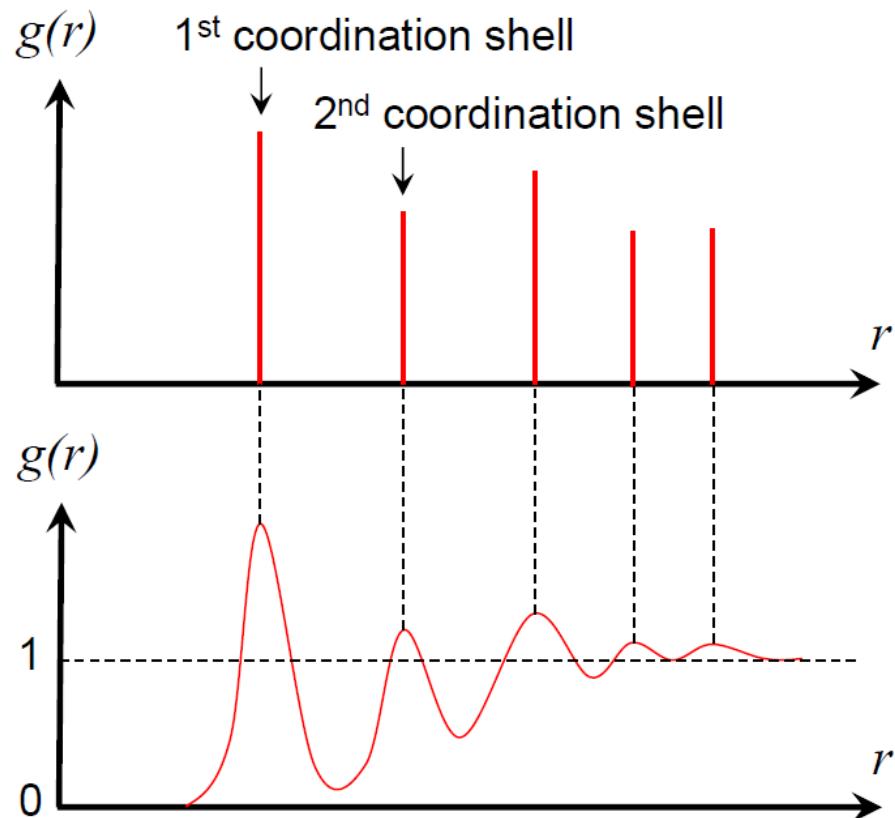
Intermediates

what is a glass state?

MORE ON GLASSES, GLASS TRANSITION
in SECTION 2 of the Course

PDFs of ideal (hard sphere) crystals vs. glasses

radial distribution function



(taken from <https://ocw.mit.edu>; MIT 3.071 Amorphous Materials, Juejun Hu)

IMPERFECTIONS IN CERAMICS

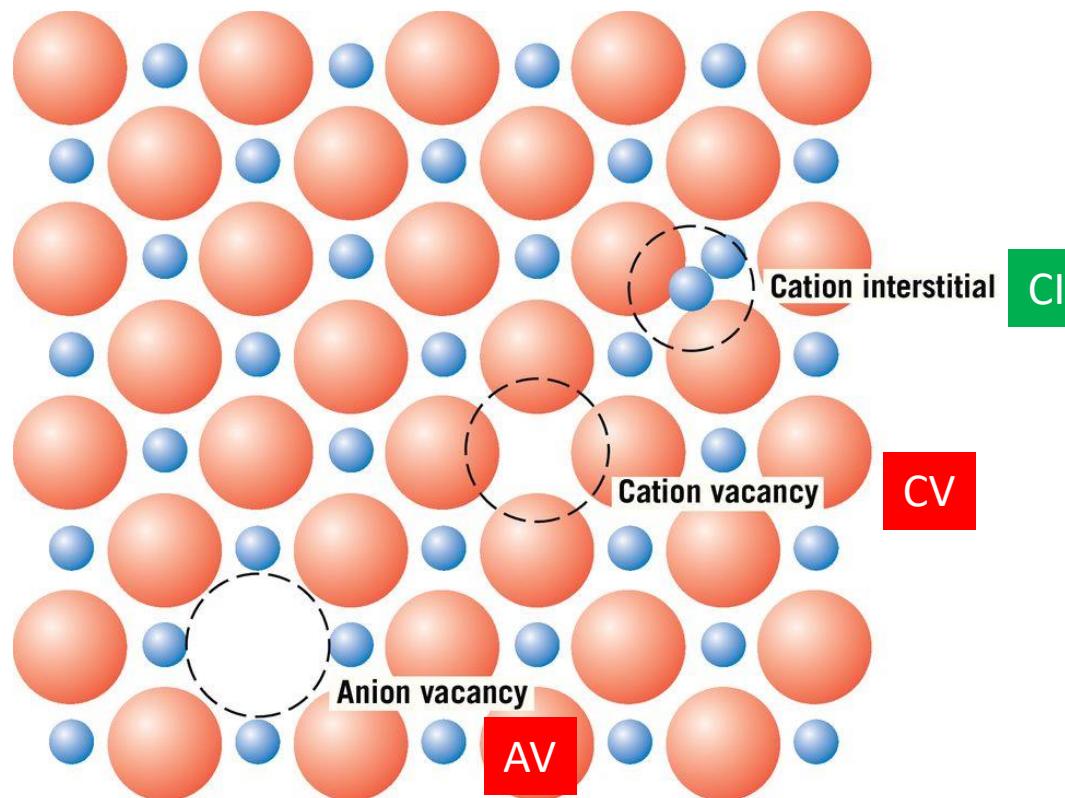
Vacancies

- vacancies exist in ceramics for both cations and anions

Interstitials

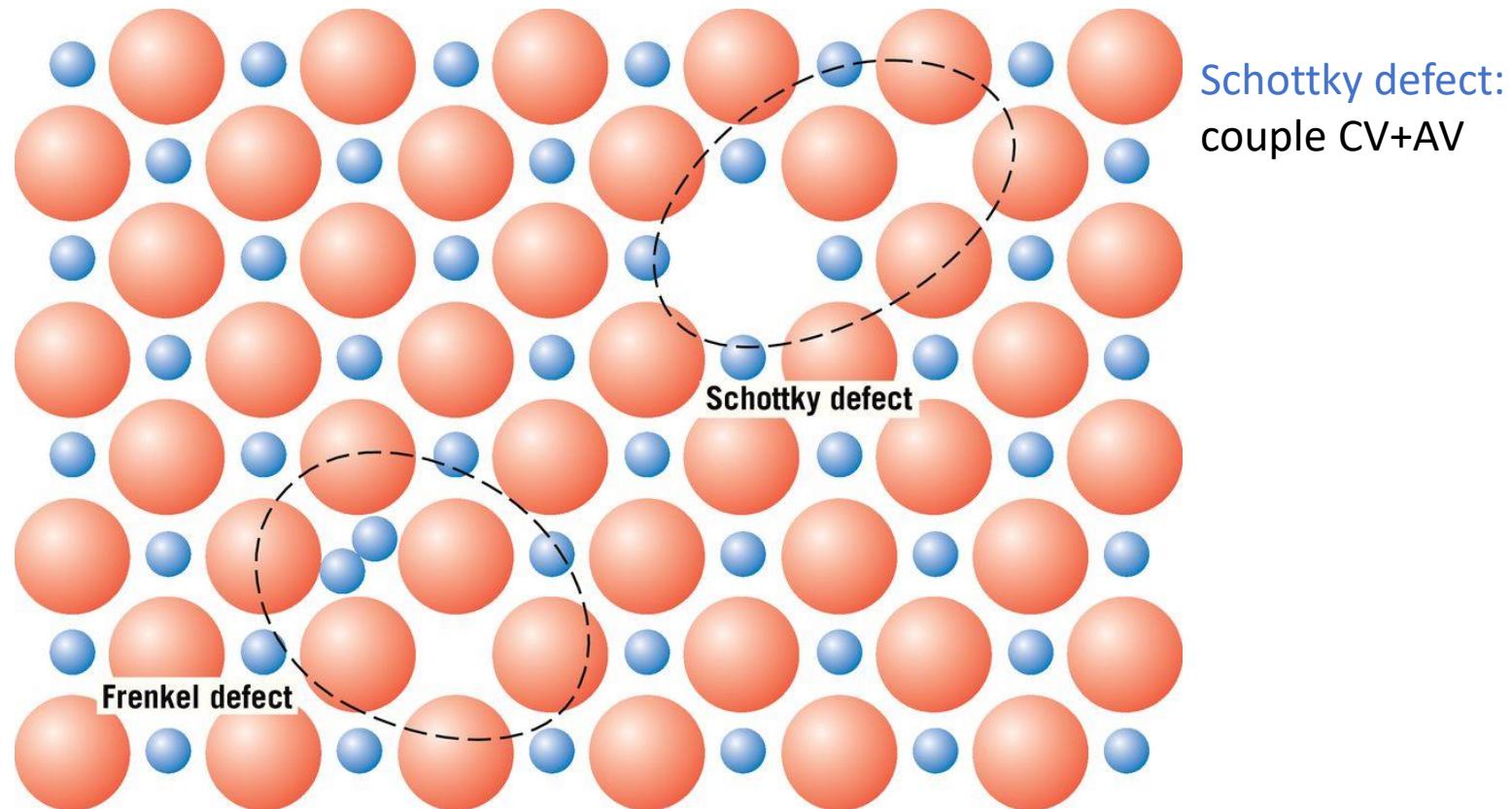
- interstitials exist for cations

not normally observed for anions because anions are large relative to the interstitial sites



IMPERFECTIONS IN CERAMICS

AX type



Frenkel defect:
couple CI +CV

Schottky defect:
couple CV+AV

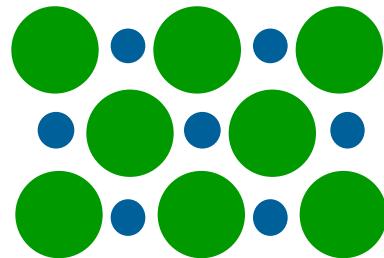
IMPERFECTIONS IN CERAMICS

- Electroneutrality (**charge balance**) must be maintained when impurities are present

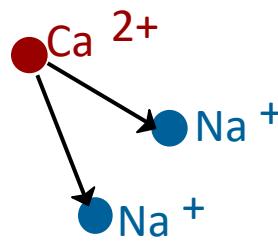
NaCl



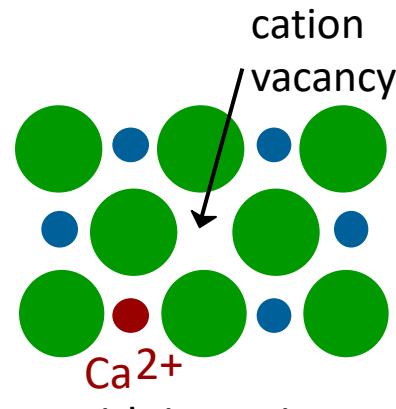
- Substitutional cation impurity



without impurity

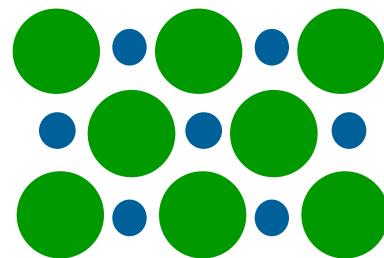


Ca^{2+} impurity

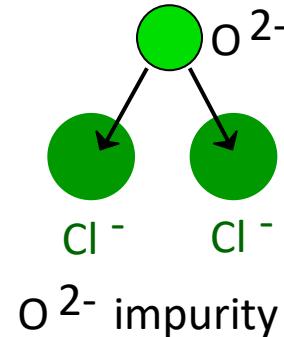


with impurity

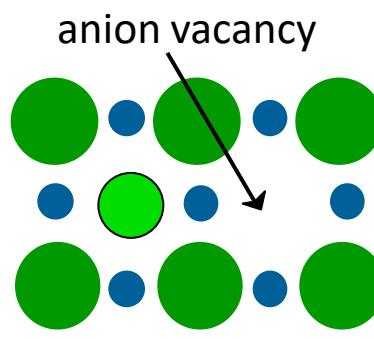
- Substitutional anion impurity



without impurity



O^{2-} impurity



with impurity



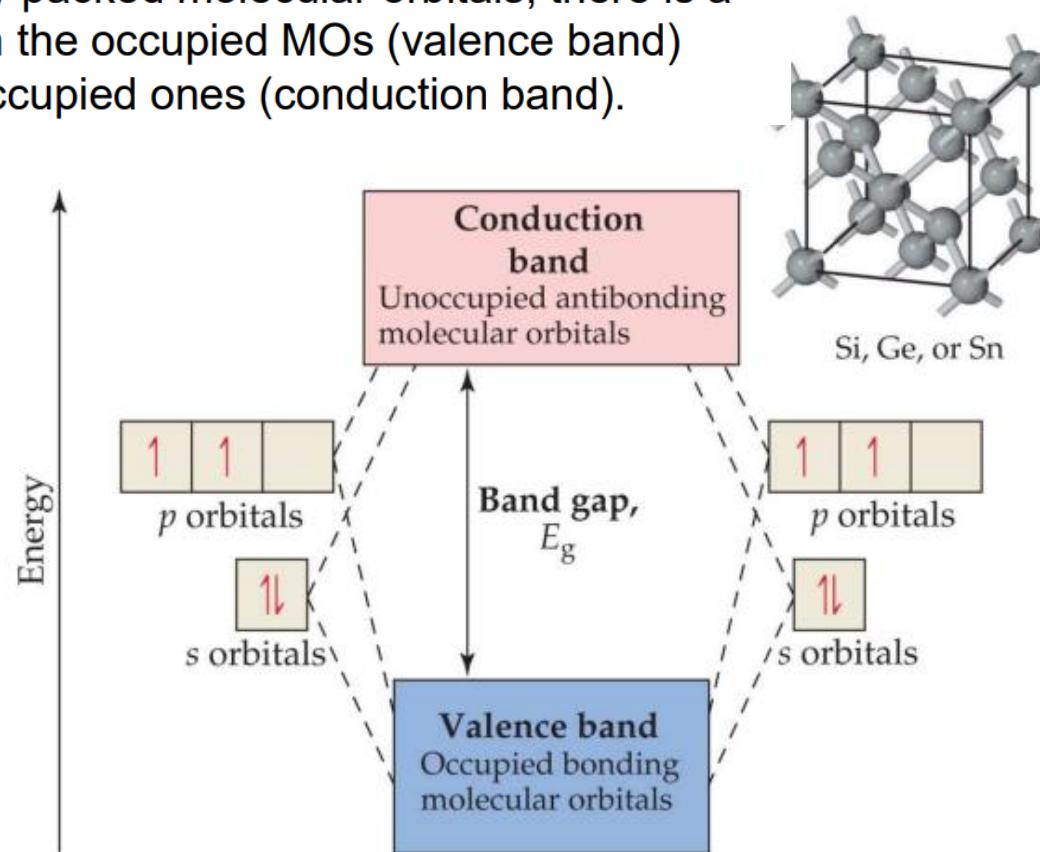
L6.4

PILLS ON SEMICONDUCTORS, SILICON CARBIDE

SHORT NOTES: SEMICONDUCTORS

impossible to recap here, please make ref to previous courses!

In the closely packed molecular orbitals, there is a gap between the occupied MOs (valence band) and the unoccupied ones (conduction band).



SHORT NOTES: SEMICONDUCTORS

- Band gaps decrease as one proceeds down a group.
- Band gaps greater than 3.5 eV are so large that material is an insulator, not a semiconductor.

TABLE 12.4 Band Gaps of Select Elemental and Compound Semiconductors

Material	Structure Type	E_g , eV [†]					
Si	Diamond	1.11		13 Al	14 Si	15 P	
AlP	Zinc blende	2.43		30 Zn	31 Ga	32 Ge	33 As
Ge	Diamond	0.67		34 Se			
GaAs	Zinc blende	1.43		48 Cd	49 In	50 Sn	51 Sb
ZnSe	Zinc blende	2.58		52 Te			
Sn [‡]	Diamond	0.08					
InSb	Zinc blende	0.18					
CdTe	Zinc blende	1.50					

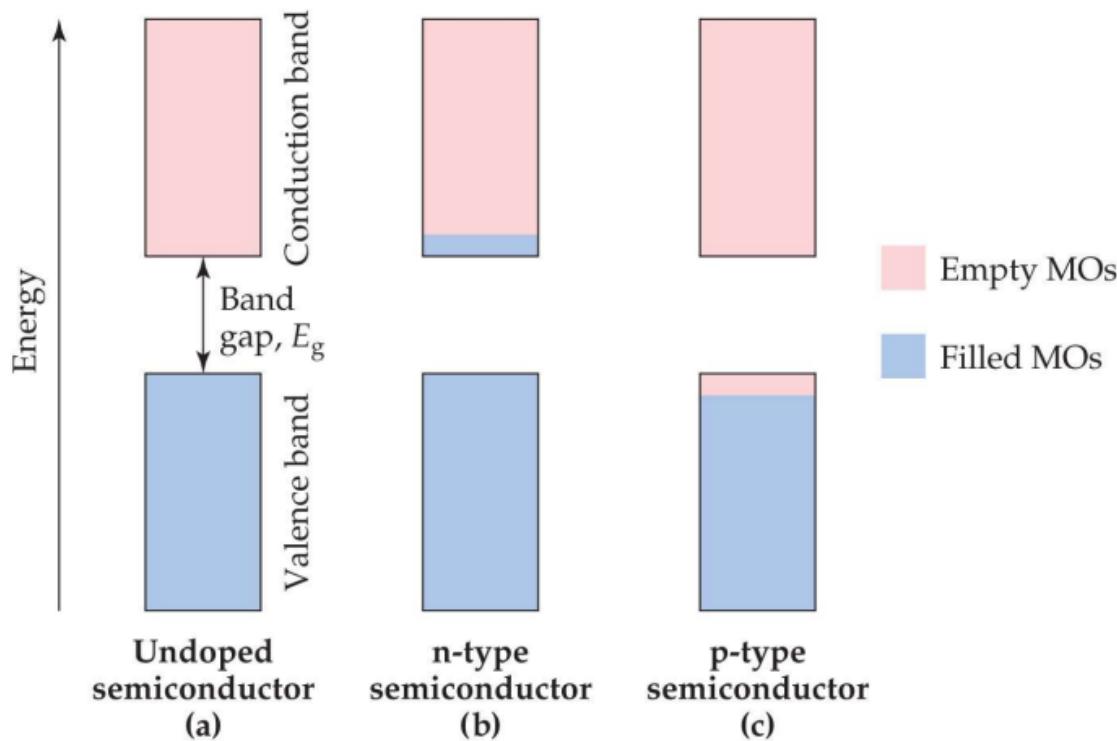
[†] Band gap energies are room temperature values, $1 \text{ eV} = 1.602 \times 10^{-19} \text{ J}$.

[‡] These data are for gray tin, the semiconducting allotrope of tin. The other allotrope, white tin, is a metal.

SHORT NOTES: SEMICONDUCTORS

Doped semiconductors

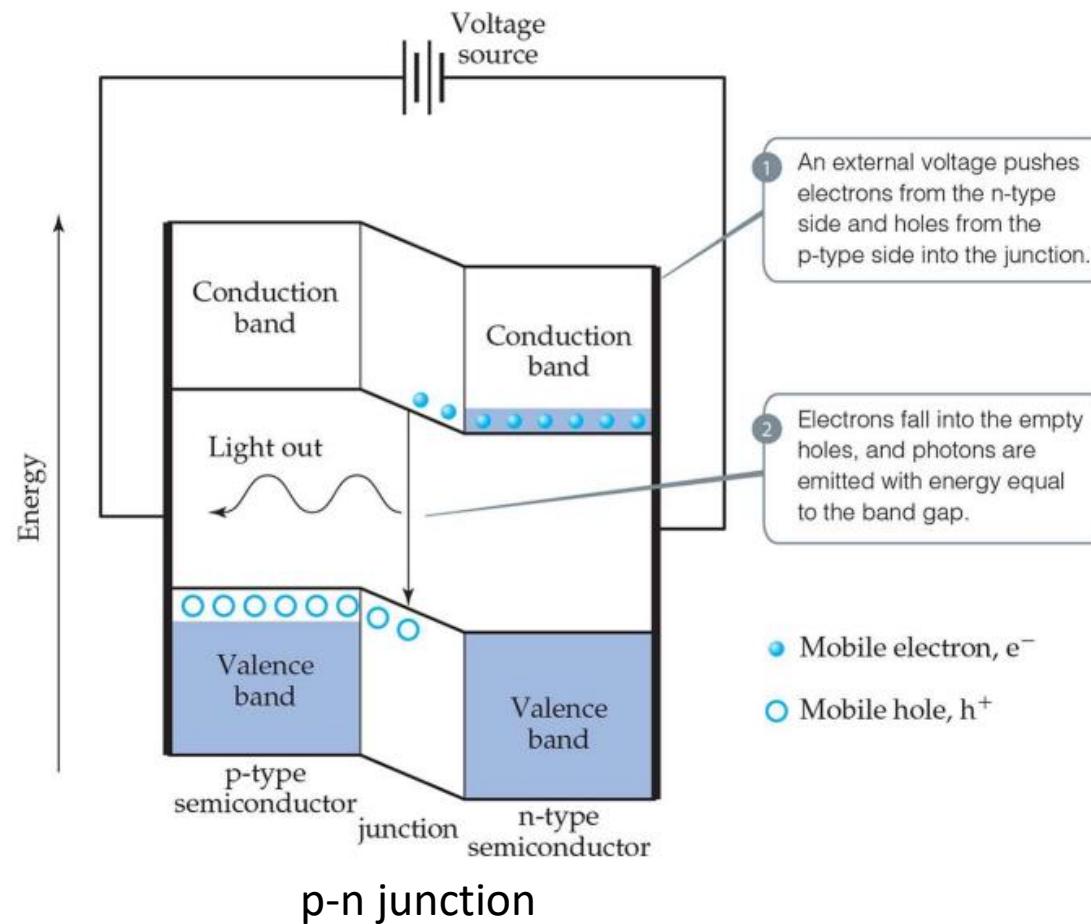
By introducing very small amounts of impurities that have more (*n*-type) or fewer (*p*-type) valence electrons, one can increase the conductivity of a semiconductor.



for Si (val 4):
p-type imp. B (val 3)
n-type imp. P (val. 5)

SHORT NOTES: SEMICONDUCTORS

SOLID-STATE LIGHTING: Light Emitting Diodes (LED)



FROM SAND TO SEMICONDUCTORS – CHIP MANUFACTURING



YOUTUBE VIDEO (channel «Infineon»)

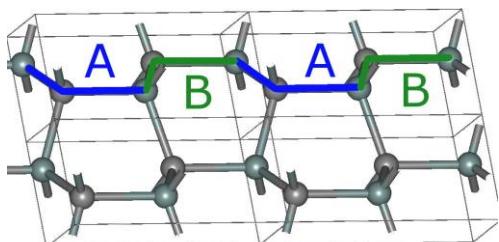
(13:32)

<https://youtu.be/bor0qLifjz4>

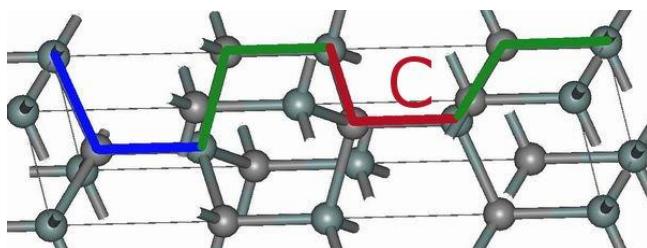
SILICON CARBIDE

>250 polymorphs of SiC had been identified !

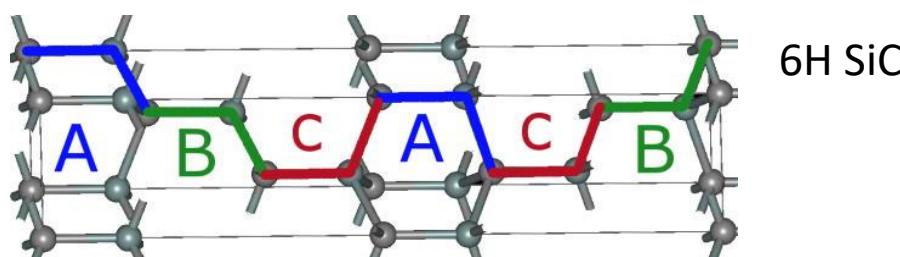
Hexagonal structures



2H SiC



4H SiC



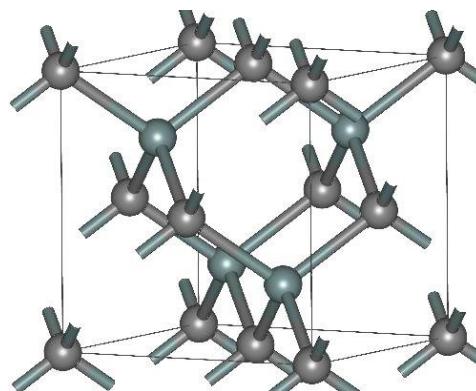
6H SiC



[3D view JSMol SiC 4H \(tugraz.at\)](#)

Cubic structure

3C SiC



SILICON CARBIDE

- low thermal expansion coefficient, high hardness, rigidity, thermal conductivity, resistance to wear, high T stability

Properties of major SiC polytypes^{[5][27]}

Polytype	3C (β)	4H	6H (α)
Crystal structure	Zinc blende (cubic)	Hexagonal	Hexagonal
Space group	$T_d^2\bar{F}43m$	$C_{6v}^4-P6_3mc$	$C_{6v}^4-P6_3mc$
Pearson symbol	cF8	hP8	hP12
Lattice constants (Å)	4.3596	3.0730; 10.053	3.0810; 15.12
Density (g/cm ³)	3.21	3.21	3.21
Bandgap (eV)	2.36	3.23	3.05
Bulk modulus (GPa)	250	220	220
Thermal conductivity (W·m ⁻¹ ·K ⁻¹) @ 300 K (see [36] for temp. dependence)	360	370	490

MAIN FIELDS of APPLICATIONS

- abrasives, cutting tools
- automotive: high perf. brake disks
- important semiconductor: power electronics

SiC – SILICON CARBIDE



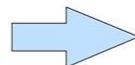
YOUTUBE VIDEO (channel «Subject Zero Science»)

(06:51)

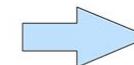
[Silicon Carbide - The subtle REVOLUTION - YouTube](#)

SiC GROWTH AND BIOCOMPATIBILITY

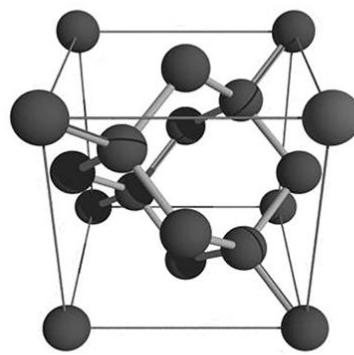
Silicon Substrate



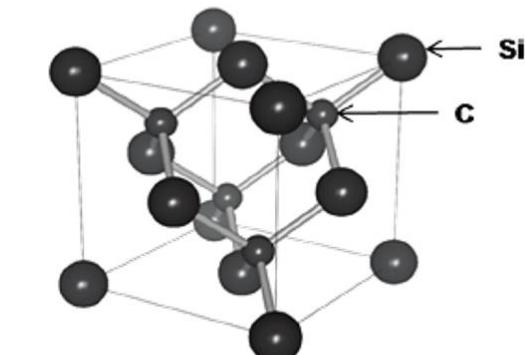
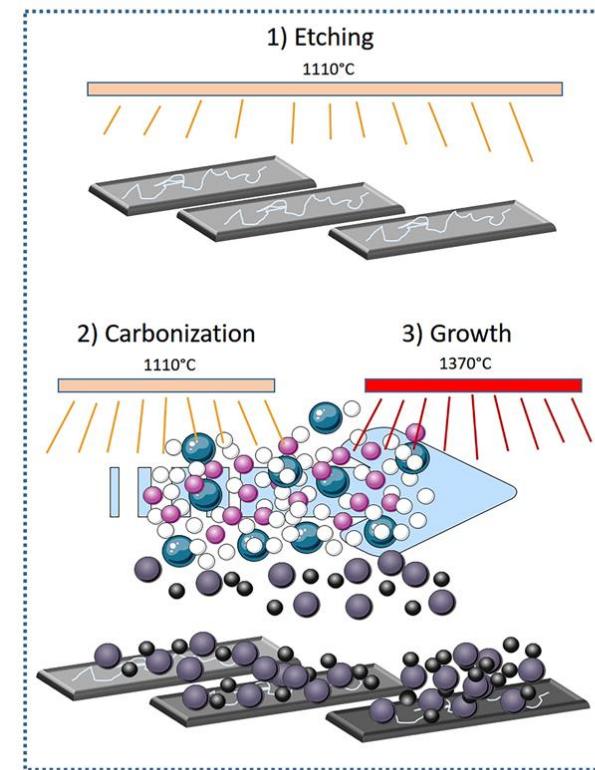
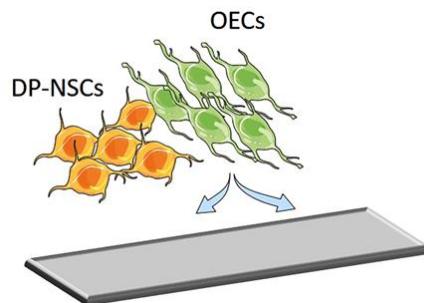
Chemical Vapour Deposition Process



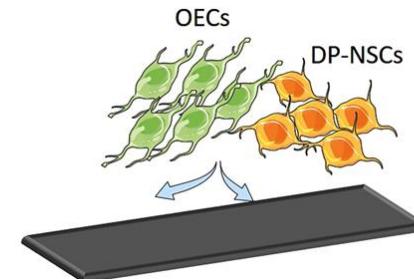
Cubic Silicon Carbide



Biocompatibility evaluations

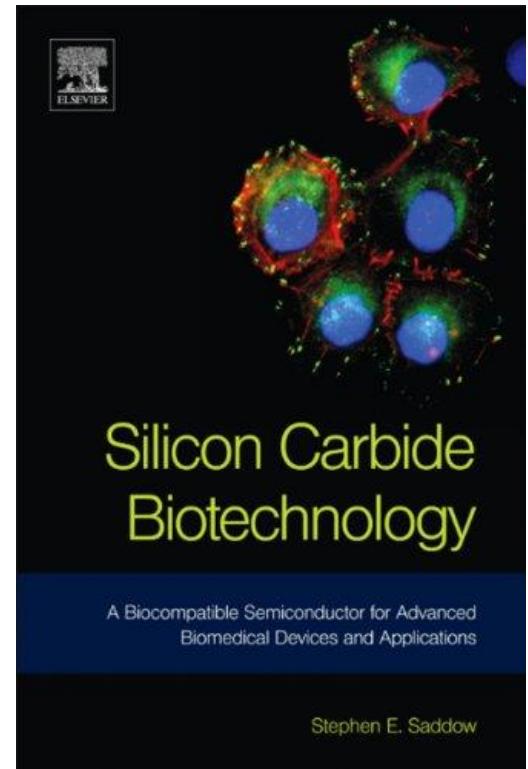


Biocompatibility evaluations

CVD: Trichlorosilane ● and ethylene ● used as Si ● and C ● precursors carried by H₂ ○Bonaventura, G., et al. *Sci Rep* 9, 11540 (2019). <https://doi.org/10.1038/s41598-019-48041-3>

SiC – SILICON CARBIDE

- biocompatibility, hemocompatibility
- heart stent coatings and bone implant scaffolds, neurological implants and sensors
- proposed as alternative to Si-based electronics for long term use,
- permanent implanted devices: glucose sensors, brain-machine-interface devices, smart bone and organ implants)



SEMINAR
TOPIC

**SiC applications in Biomedicine
and Bionics**



L6.5

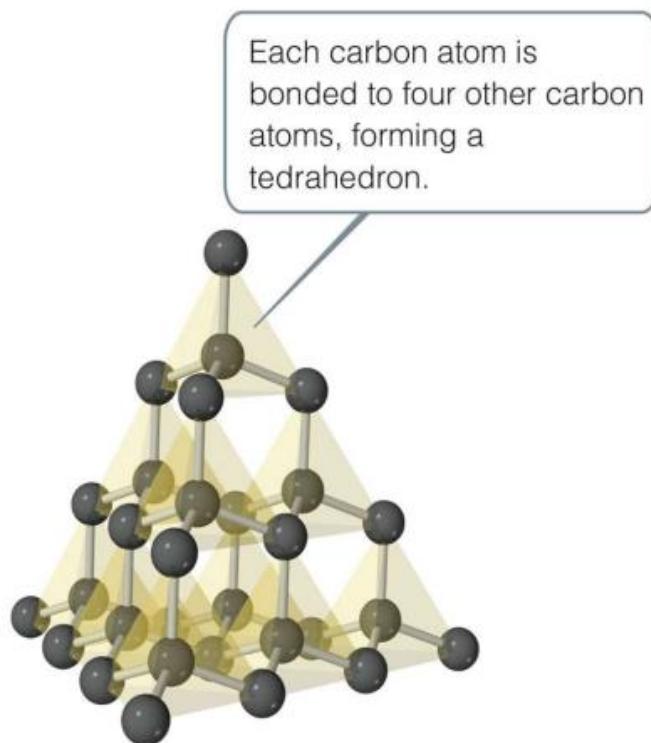
CARBON POLYMORPHS

Classwork 2 Question 5

what is the difference btw.: I) a carbon nanotube, II) a fullerene, III) graphene, IV) graphite? sketch the chem structure of graphene (see instructions for sending sketches)

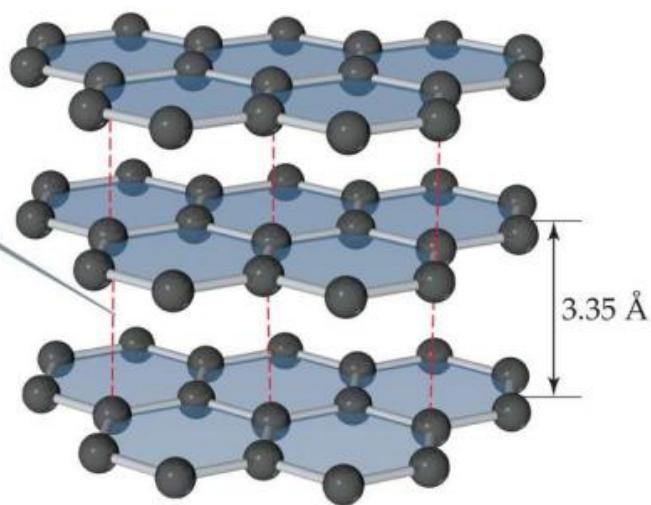
POLYMORPHS OF CARBON

- covalent network solids



(a) Diamond

Sheets are held together by dispersion forces.



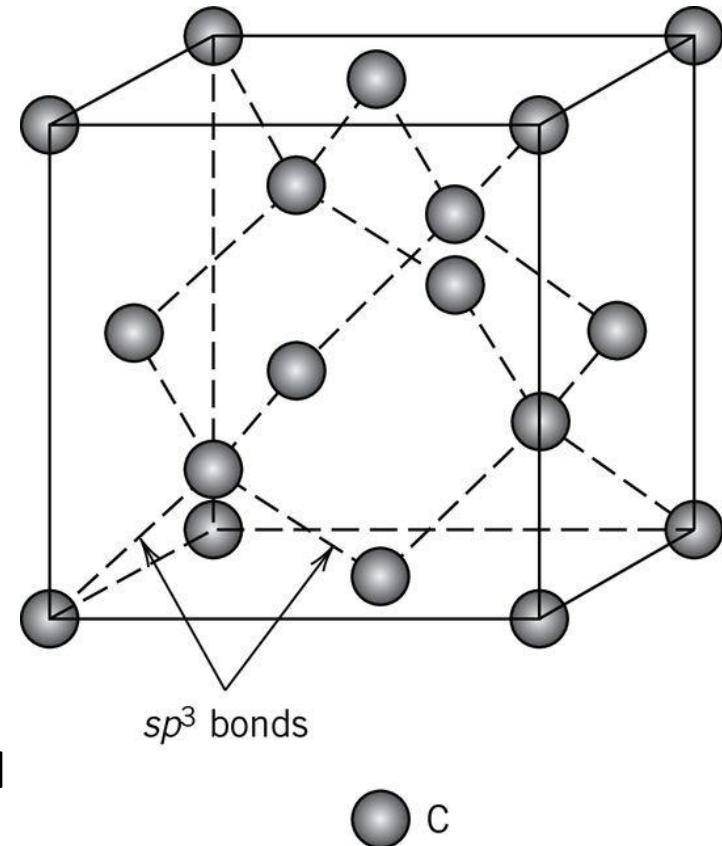
(b) Graphite

Source: <https://www.unf.edu/~michael.lufaso/chem204>

POLYMORPHS OF CARBON - DIAMOND

Diamond

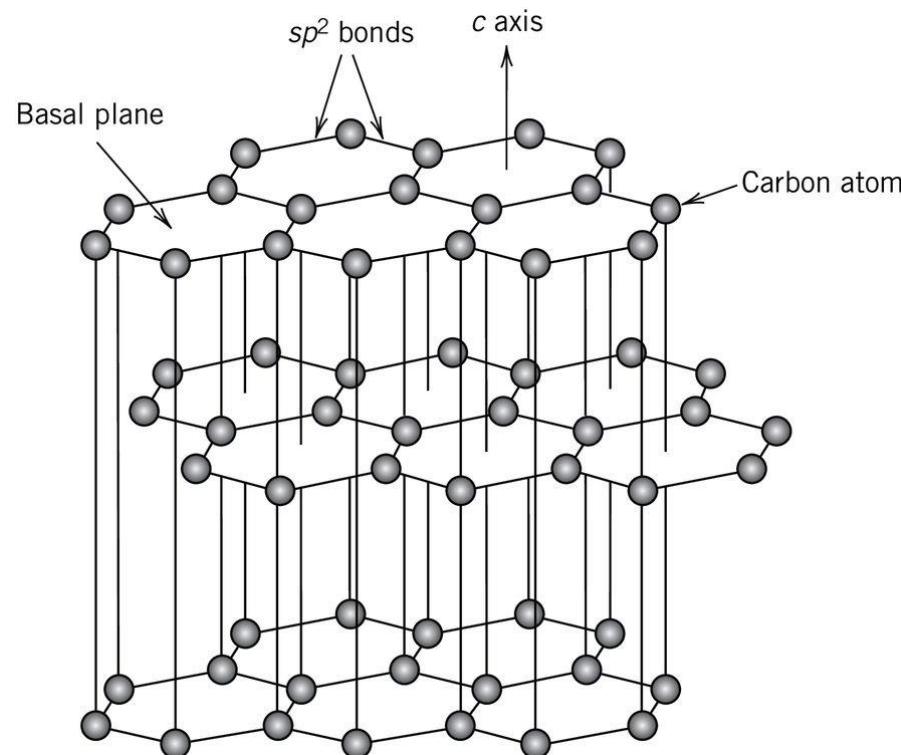
- tetrahedral bonding of carbon
hardest material known
very high thermal conductivity
- large single crystals – gemstones
- small crystals – used to grind/cut other materials
- diamond thin films
hard surface coatings – used for cutting tools, medical devices, etc.
- transparent in the VIS and IR: widest spectral transmission range of all materials



POLYMORPHS OF CARBON - GRAPHITE

Graphite

- layered structure – parallel hexagonal arrays of carbon atoms
- weak VdW forces between layers
- planes slide easily over one another -- good lubricant

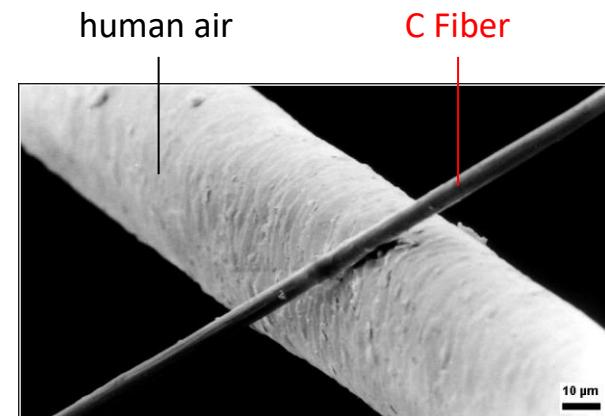


CARBON FIBERS

- small-diameter, high-strength, and high-modulus fibers
- used as reinforcements in polymer-matrix composites
- various arrangements of graphene layers.

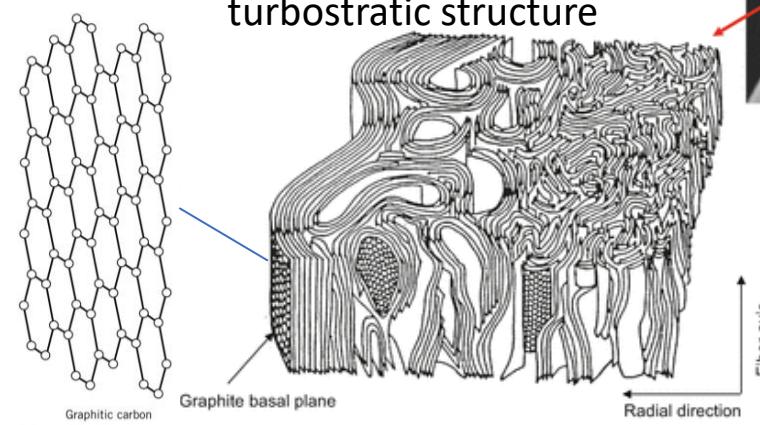
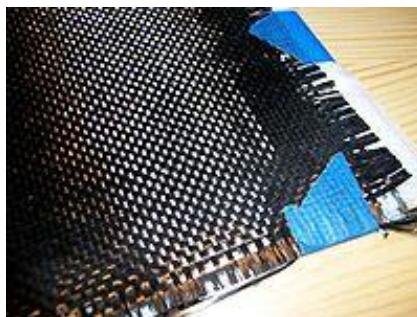
1. graphitic carbon fibers: high Elastic Modulus

ordered structure of graphite—planes parallel to one another; weak van der Waals interplanar bonds.



2. disordered structure: high Strength

graphene sheets randomly folded, tilted, and crumpled to form **turbostratic carbon**.



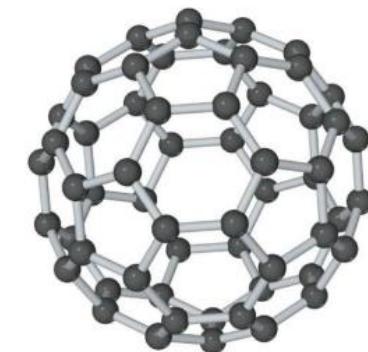
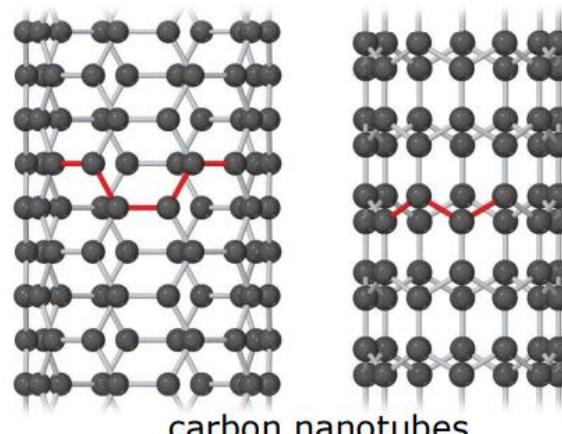
CARBON MATERIALS PROPERTIES

Table 13.3 Properties of Diamond, Graphite, and Carbon (for Fibers)

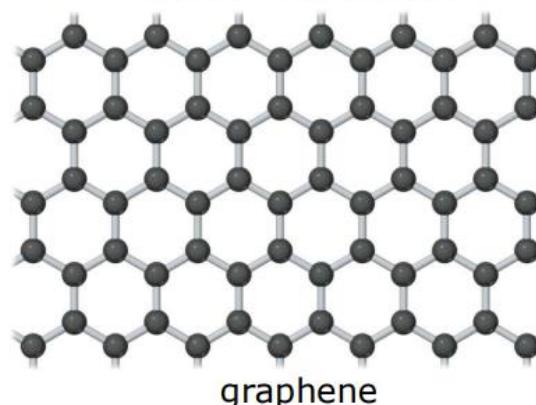
Property	Material				
	Diamond	In-Plane		Out-of-Plane	Carbon (Fibers)
Density (g/cm ³)	3.51		2.26		1.78–2.15
Modulus of elasticity (GPa)	700–1200	350		36.5	230–725 ^a
Strength (MPa)	1050	2500		—	1500–4500 ^a
Thermal Conductivity (W/m·K)	2000–2500	1960		6.0	11–70 ^a
Coefficient, Thermal Expansion (10 ⁻⁶ K ⁻¹)	0.11–1.2	–1		+29	–0.5––0.6 ^a 7–10 ^b
Electrical Resistivity (Ω·m)	10 ¹¹ – 10 ¹⁴	1.4 × 10 ^{−5}		1 × 10 ^{−2}	9.5 × 10 ^{−6} –17 × 10 ^{−6}

^a Longitudinal fiber direction.

^b Transverse (radial) fiber direction.

Buckminsterfullerene (C_{60})

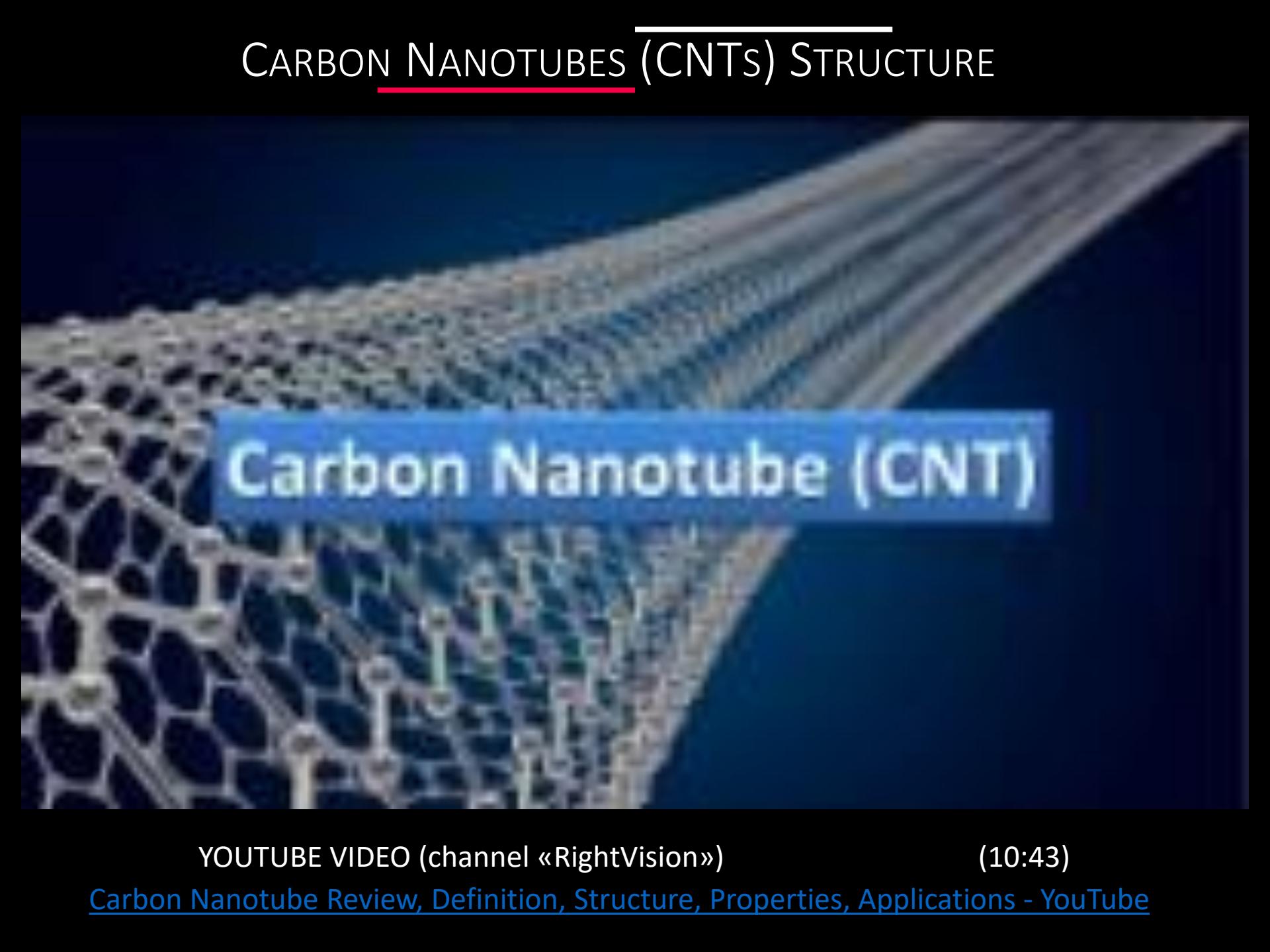
carbon nanotubes



graphene

MORE ON NANOSCALE
POLYMORPHS in SECT 2:
Graphene
Fullerene
Carbon Nanotubes

CARBON NANOTUBES (CNTs) STRUCTURE



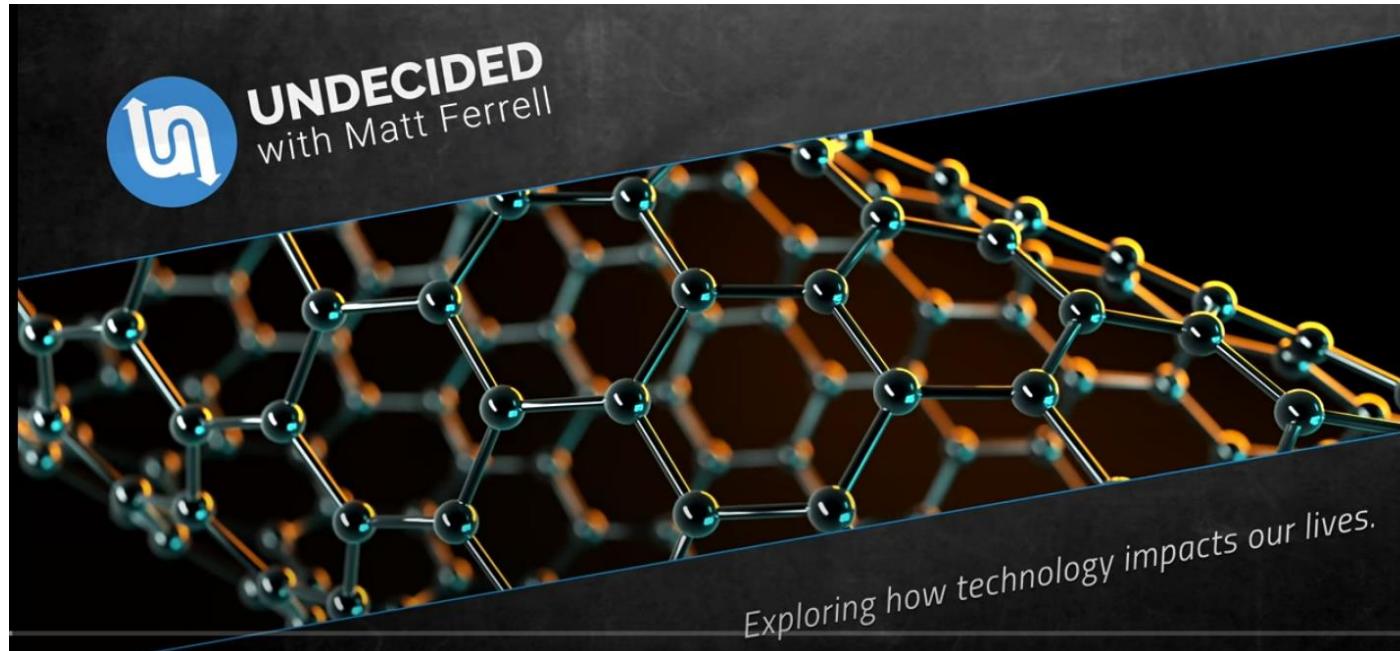
Carbon Nanotube (CNT)

YOUTUBE VIDEO (channel «RightVision»)

(10:43)

[Carbon Nanotube Review, Definition, Structure, Properties, Applications - YouTube](#)

CNTS AND RENEWABLE ENERGY



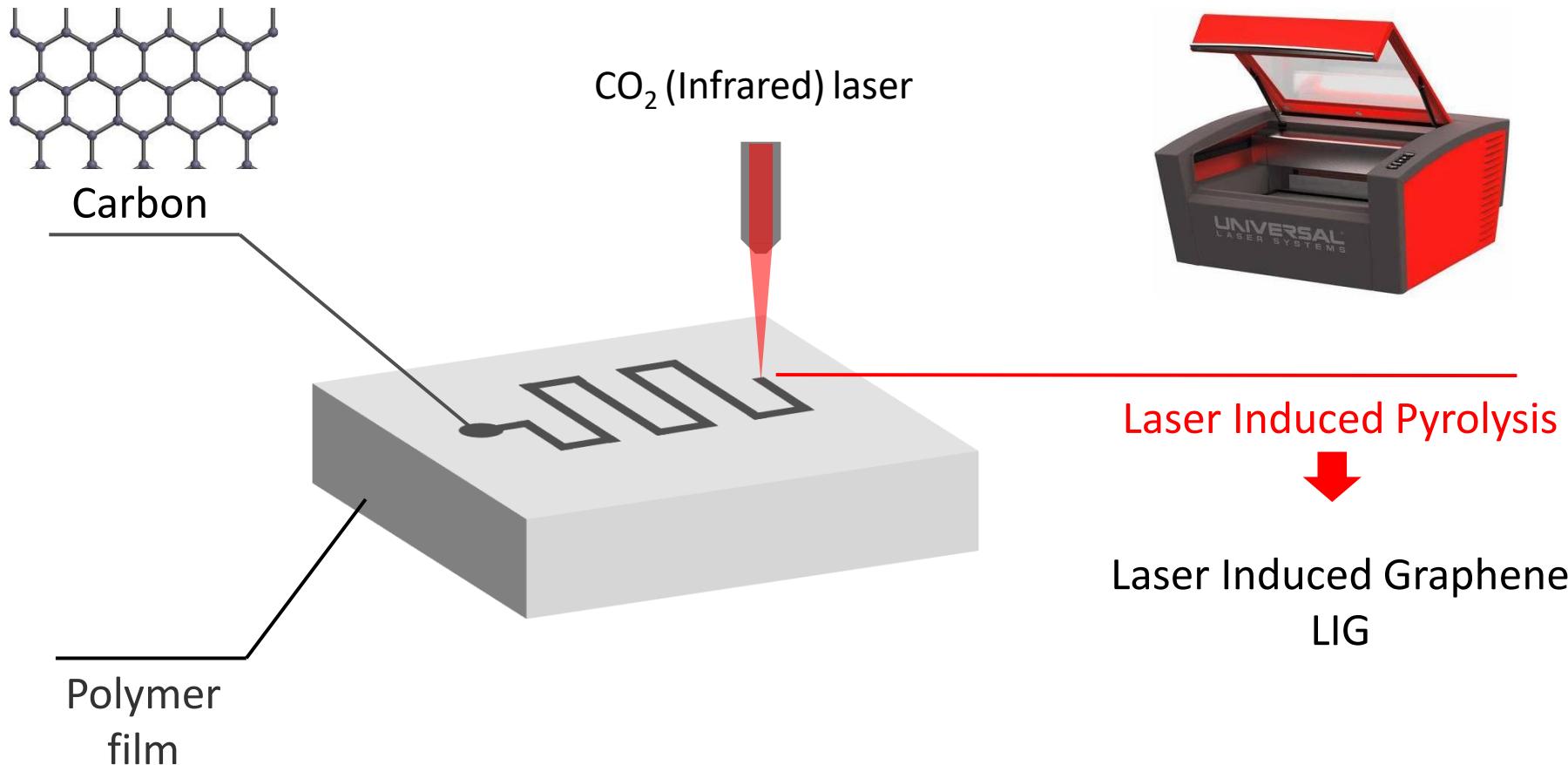
Revisiting How Carbon Nanotubes Will Change Renewable Energy

YOUTUBE VIDEO (Undecided_Matt Ferrell)

<https://youtu.be/QEAmTvan0EU>

NEW APPROACH: LASER INDUCED GRAPHENE (LIG)

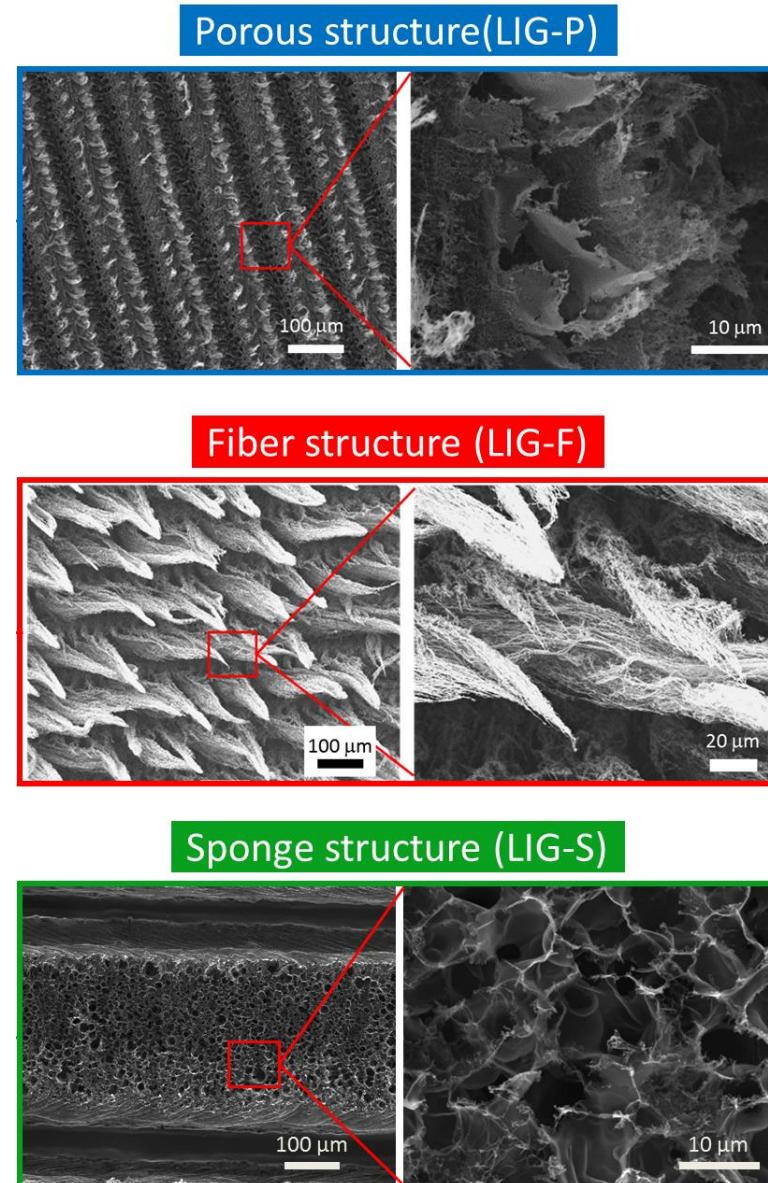
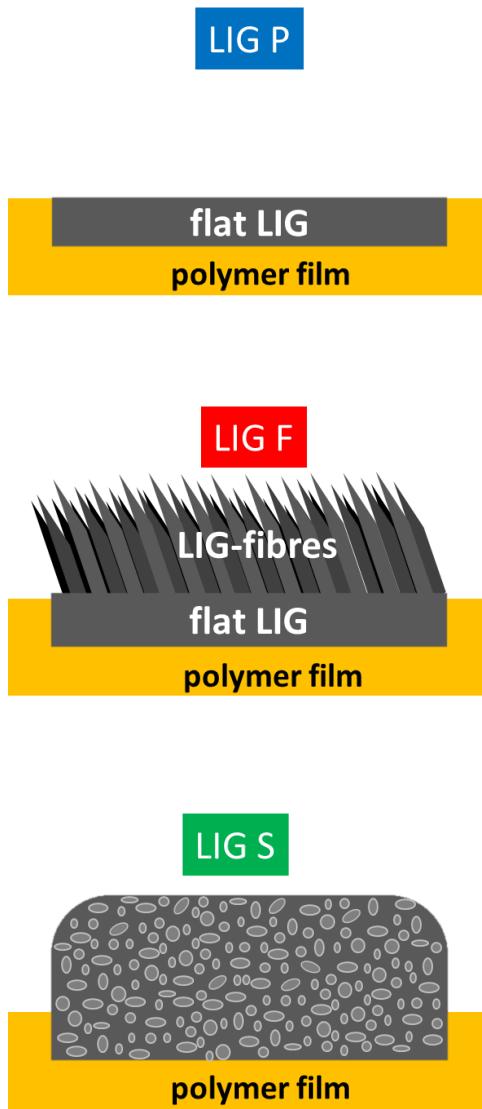
laser-scribing graphene conductors into polymer precursors



J. Lin, J. M. Tour, et al., *Nature Commun.* 5, 5714 2014

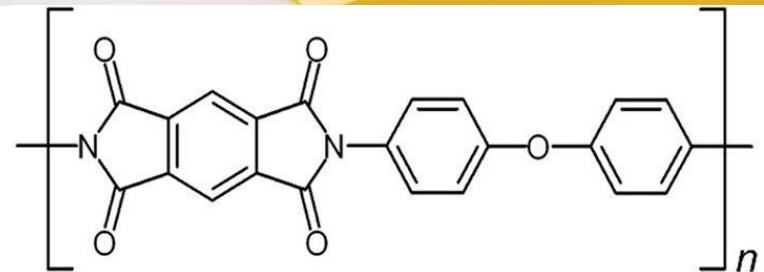
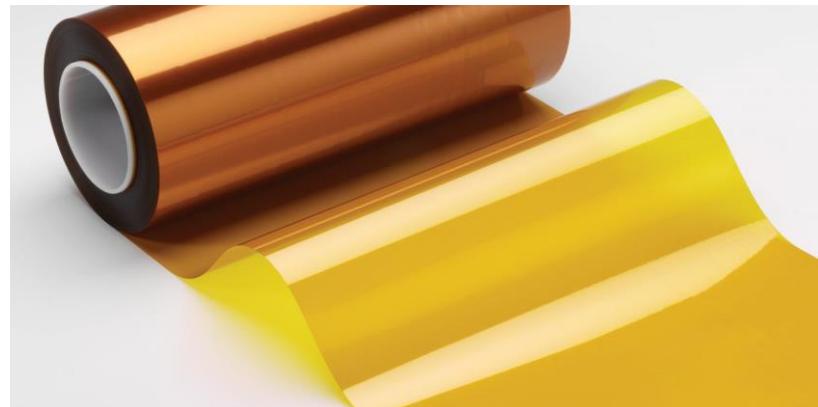


TUNING LASER INDUCED GRAPHENE (LIG)



Standard LIG precursor

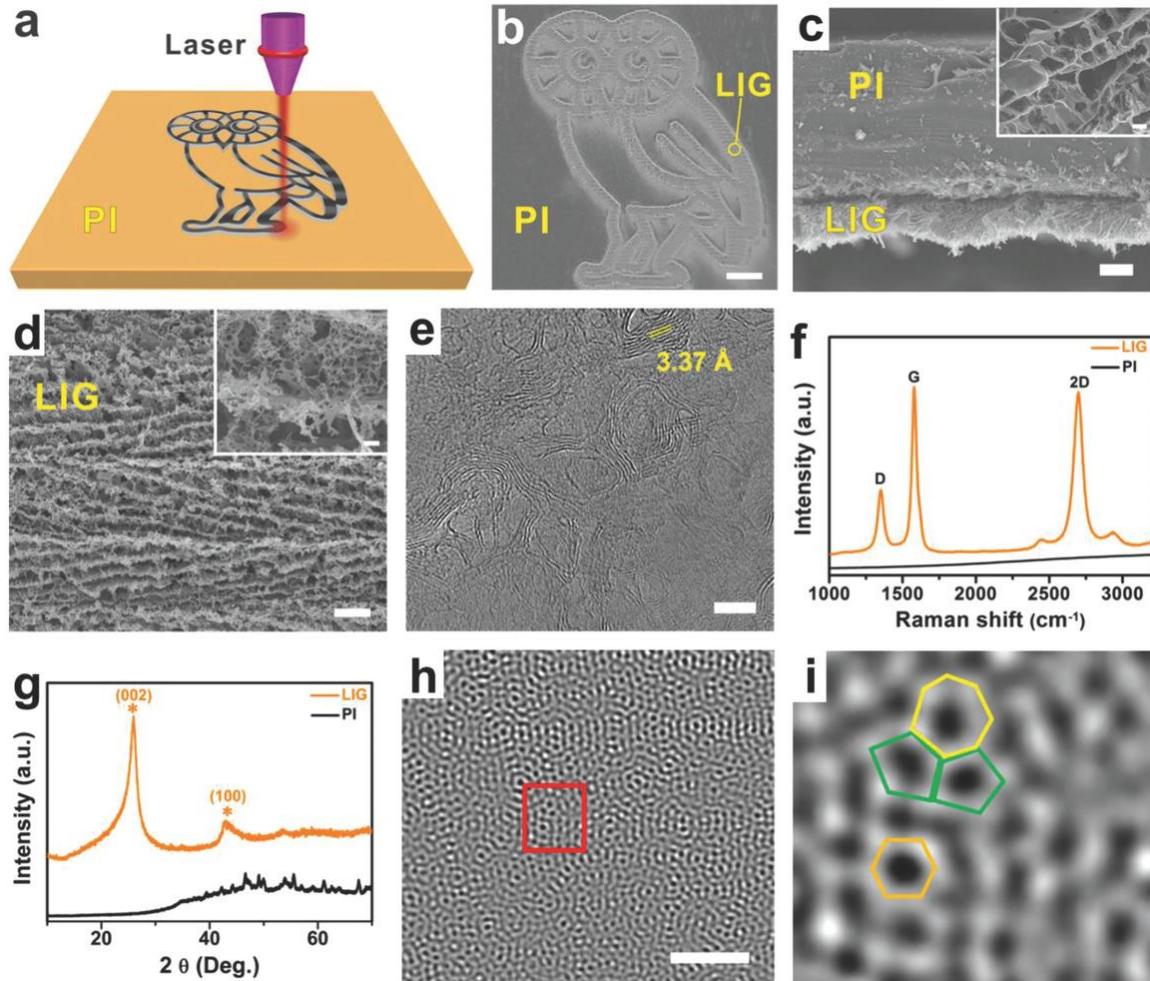
- Polyimide film
 - Kapton ®



- Other synthetic and bio-derived precursors:
BUT in some cases require inert atmosphere, or addition of flame/retardants, catalysts (e.g. Fe(NO₃)₃)

LASER INDUCED GRAPHENE (LIG)

- LIG from polyimide (PI)
- accidental discovery! Tour Group, Rice Univ. 2014



MORE ON LIG
& soft LIG-based
sensors/actuators
in following lectures !

CARBON



YOUTUBE & TEDED VIDEO (Periodic Videos-Univ Nottingham) (10:03)
[Carbon - Periodic Table of Videos - YouTube](#)



L6.6

BIOCERAMICS

BIOCERAMICS

- biomedical applications: main use in implants (bones, teeth,..)
- desirable properties: chemical inertness, hardness, wear resistance, and low coefficient of friction;
- crystalline oxide materials, glasses, and glass-ceramics

Al_2O_3 : alumina

YSZ: Yttria Stabilized- Zirconia (ZrO_2)

Calcium Phosphate materials

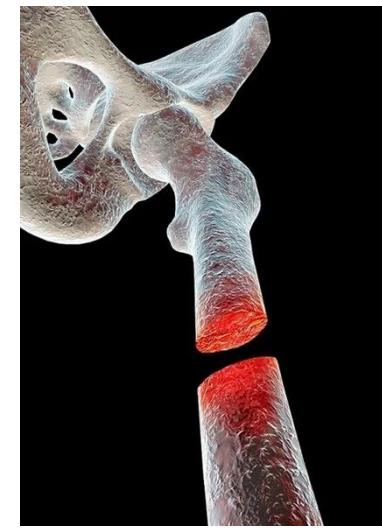
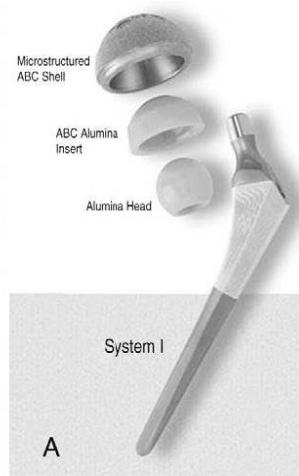


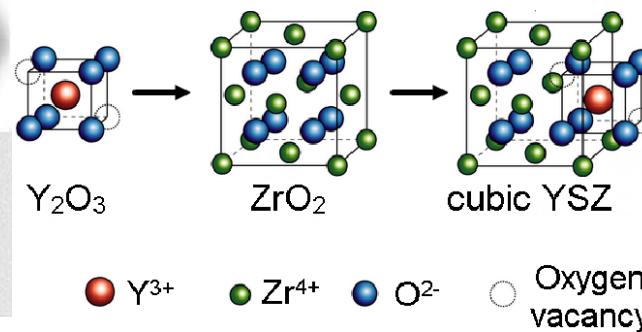
Image Credits: Naeblis/shutterstock.com



<https://doi.org/10.1016/j.arth.2008.06.003>

SEMINAR
TOPIC 10

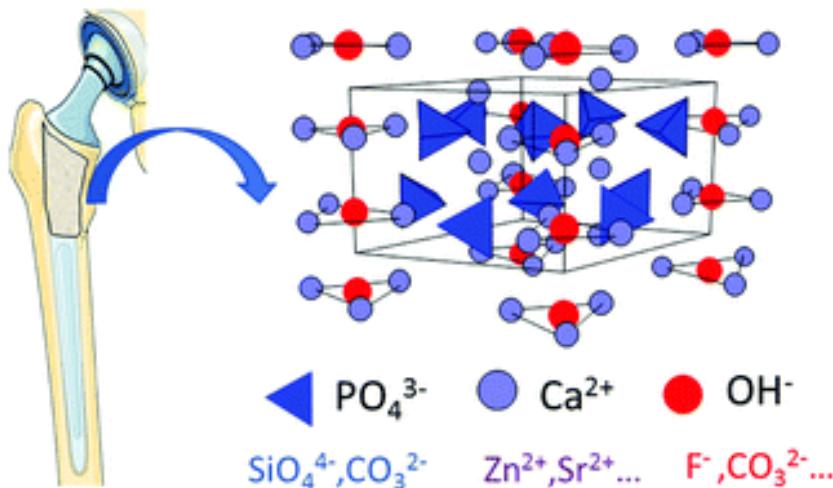
Zirconia and Alumina ceramics
in Biomedicine/Bionics



BIOCERAMICS

CALCIUM PHOSPHATE

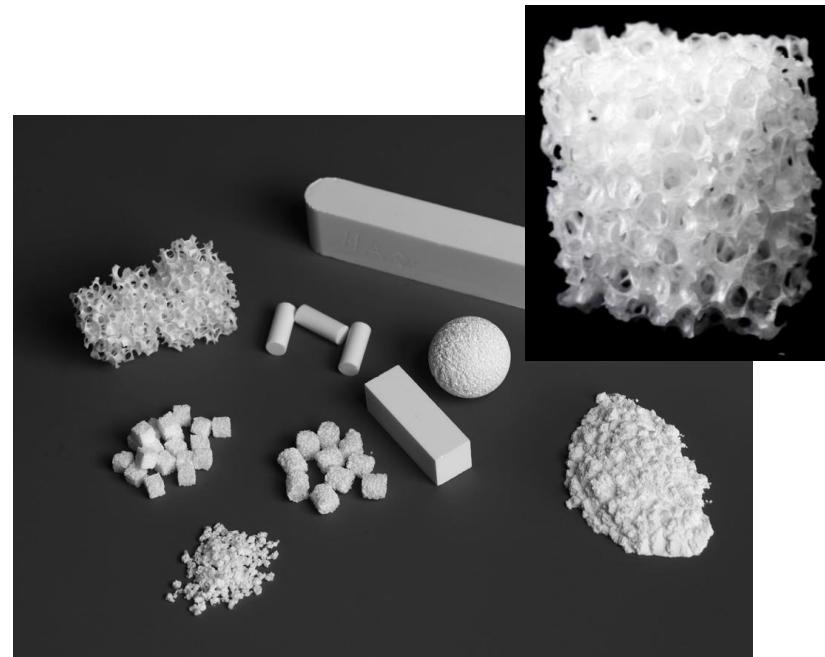
- implant material that is gradually infiltrated with and replaced by natural bone tissue during the healing process
- implant ultimately dissolves into the body of the host.
- Two types of calcium phosphate materials for **resorbable** implants:
TCP - tricalcium phosphate $\text{Ca}_3(\text{PO}_4)_2$ **HAP - hydroxyapatite $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$**
- also used for implantable drug-delivery systems.



HAP coating of bone implants

from: D. Arcos et al. J. Mat Chem B, 2020, <https://doi.org/10.1039/C9TB02710F>

Francesco Greco



Source: <https://www.cambioceramics.com/products/#blcks>

Advanced Materials for Bionics



BIOCERAMICS USES

Table 1: Bioceramics Applications^[12]

Devices	Function	Biomaterial
Artificial total hip, knee, shoulder, elbow, wrist	Reconstruct arthritic or fractured joints	High-density alumina, metal bioglass coatings
Bone plates, screws, wires	Repair fractures	Bioglass-metal fibre composite, Polysulphone-carbon fibre composite
Intramedullary nails	Align fractures	Bioglass-metal fibre composite, Polysulphone-carbon fibre composite
Harrington rods	Correct chronic spinal curvature	Bioglass-metal fibre composite, Polysulphone-carbon fibre composite
Permanently implanted artificial limbs	Replace missing extremities	Bioglass-metal fibre composite, Polysulphone-carbon fibre composite
Vertebrae Spacers and extensors	Correct congenital deformity	Al_2O_3
Spinal fusion	Immobilise vertebrae to protect spinal cord	Bioglass
Alveolar bone replacements, mandibular reconstruction	Restore the alveolar ridge to improve denture fit	Polytetra fluoro ethylene (PTFE) - carbon composite, Porous Al_2O_3 , Bioglass, dense-apatite
End osseous tooth replacement implants	Replace diseased, damaged or loosened teeth	Al_2O_3 , Bioglass, dense hydroxyapatite, vitreous carbon
Orthodontic anchors	Provide posts for stress application required to change deformities	Bioglass-coated Al_2O_3 , Bioglass coated vitallium

Source: Wikipedia,
data taken from: Thamaraiselvi, T., and S. Rajeswari. "Biological evaluation of bioceramic materials-a review." *Carbon* 24.31 (2004): 172.



BIOCERAMIC PROPERTIES

Table 2: Mechanical Properties of Ceramic Biomaterials^[12]

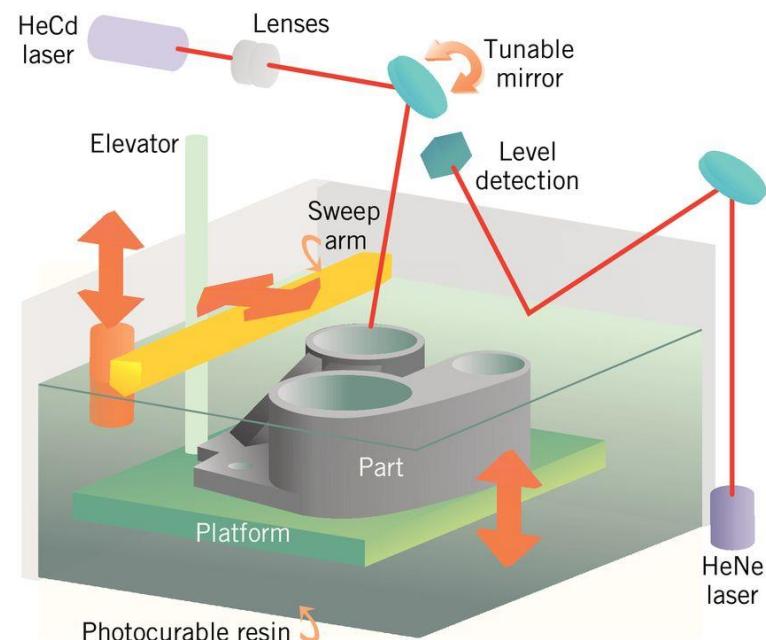
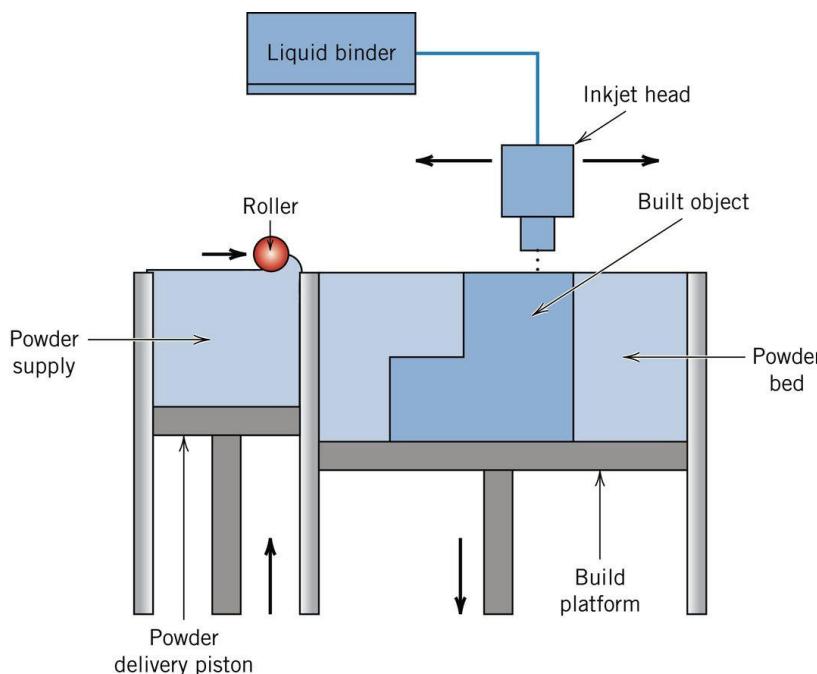
Material	Young's Modulus (GPa)	Compressive Strength (MPa)	Bond strength (GPa)	Hardness	Density (g/cm ³)
Inert Al ₂ O ₃	380	4000	300-400	2000-3000(HV)	>3.9
ZrO ₂ (PS)	150-200	2000	200-500	1000-3000(HV)	≈6.0
Graphite	20-25	138	NA	NA	1.5-1.9
(LTI)Pyrolytic Carbon	17-28	900	270-500	NA	1.7-2.2
Vitreous Carbon	24-31	172	70-207	150-200(DPH)	1.4-1.6
Bioactive HAP	73-117	600	120	350	3.1
Bioglass	≈75	1000	50	NA	2.5
AW Glass Ceramic	118	1080	215	680	2.8
Bone	3-30	130-180	60-160	NA	NA

The variation in Young's Modulus noted for some of the materials listed is due to variation in density of test specimens.
PS - Partially Stabilized; HA - Hydroxyapatite; NA - Not Available; AW - Apatite-Wallastonite; HV - Vickers Hardness;
DPH - Diamond Pyramid Hardness

Source: Wikipedia,
data taken from: Thamaraiselvi, T., and S. Rajeswari. "Biological evaluation of bioceramic materials-a review." *Carbon* 24.31 (2004): 172.

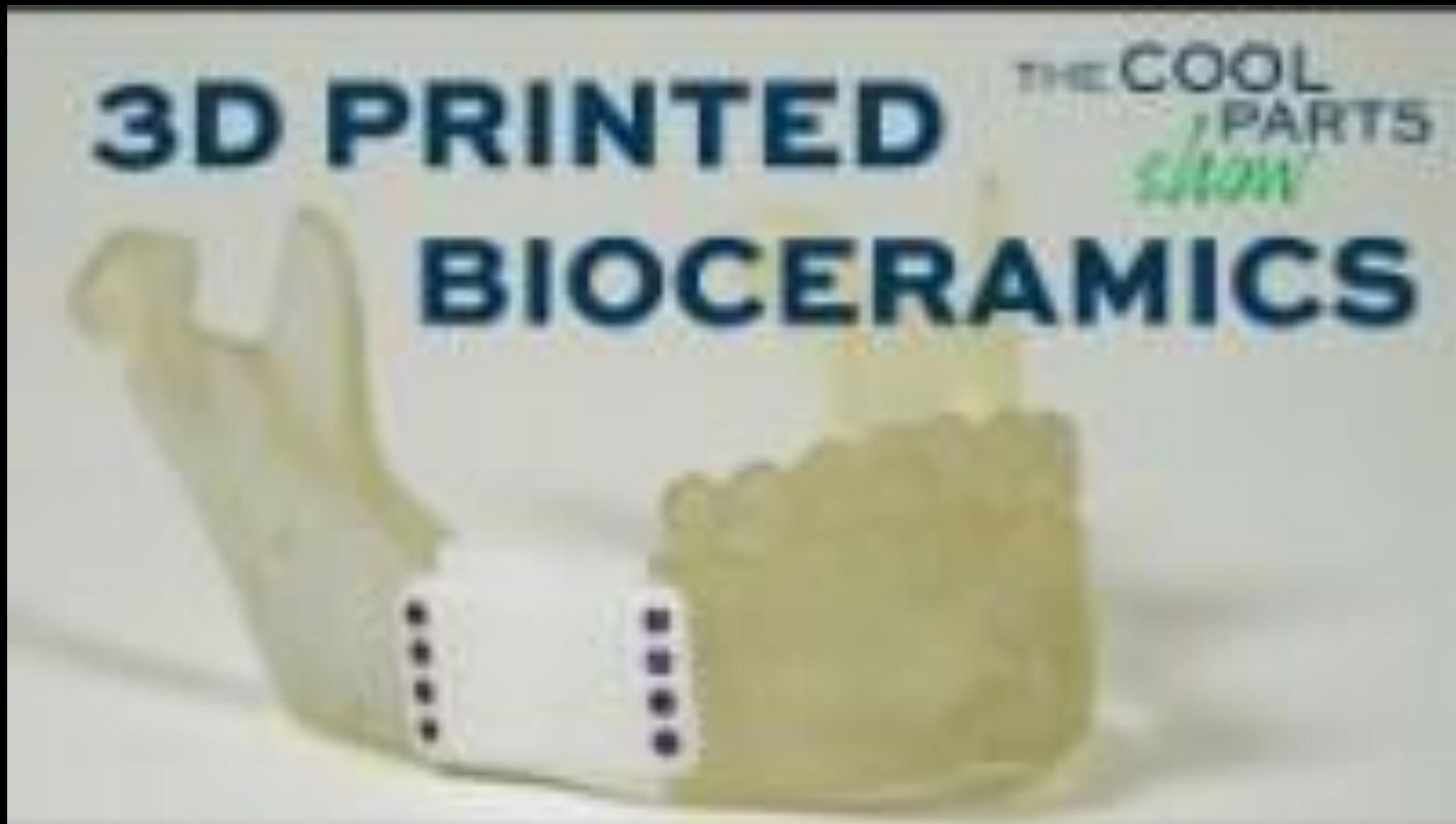
3D PRINTING OF CERAMICS

- more about this (and other 3d printing/additive manufacturing techniques) in a dedicated **LESSON**



© I. A. Aksay, R. Garg, and D. M. Dabbs, Princeton University.

3D PRINTED BIOCERAMICS



YOUTUBE VIDEO (channel «Additive Manufacturing»)

(12:57)

[3D Printed Bioceramics for Bone Replacement: The Cool Parts Show S3E2 - YouTube](#)

Y-STABILIZED ZIRCONIA

HOME ASSIGNMENT

- how can you tell the difference between a real and a fake diamond?



YOUTUBE VIDEO (channel «Mat Sci Guy»)

(08:24)

[The Story of Cubic Zirconia: Far More than just Fake Diamond - YouTube](#)



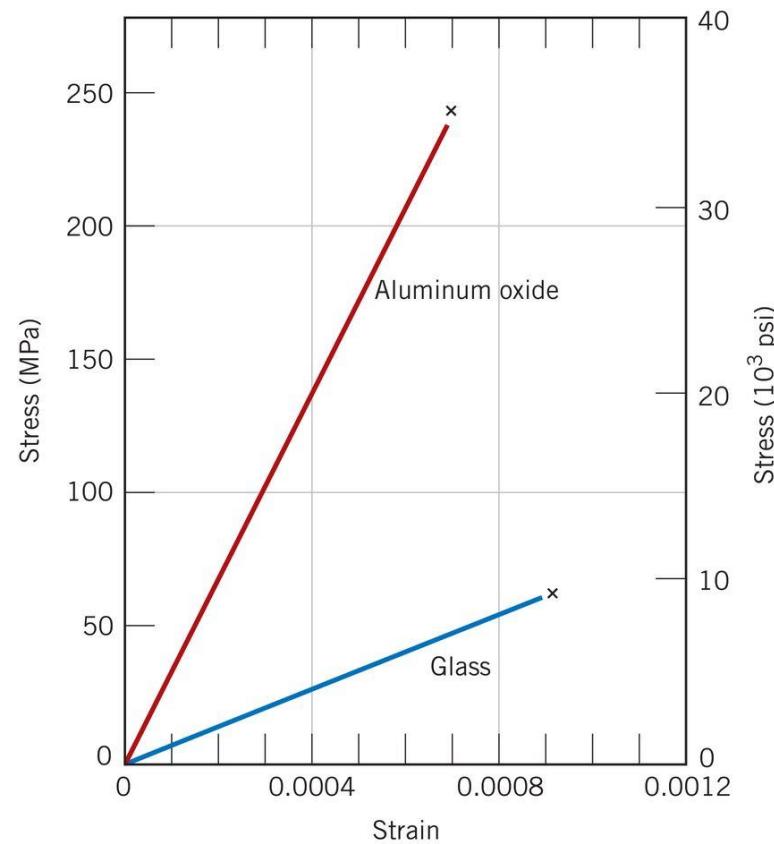
L6.7

MECH PROPERTIES OF CERAMICS

MECHANICAL PROPERTIES

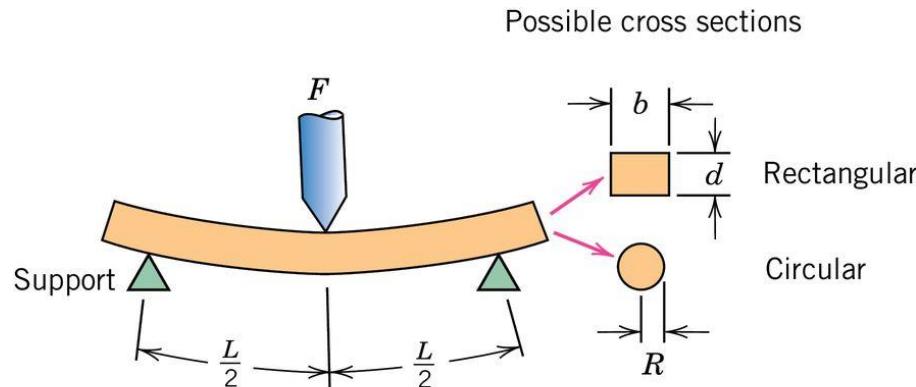
- more brittle than metals: break at $\epsilon \approx 0.1\%$
- $E = 70 - 500 \text{ GPa}$

elastic
behaviour



FLEXURAL TESTS – MEASUREMENT OF ELASTIC MODULUS

- RT behavior is usually elastic, with brittle failure
- 3-Point Bend Testing often used - tensile tests are difficult for brittle materials



$$\sigma = \text{stress} = \frac{Mc}{I}$$

where M = maximum bending moment

c = distance from center of specimen
to outer fibers

I = moment of inertia of cross section

F = applied load

	\underline{M}	\underline{c}	\underline{I}	$\underline{\sigma}$
Rectangular	$\frac{FL}{4}$	$\frac{d}{2}$	$\frac{bd^3}{12}$	$\frac{3FL}{2bd^2}$
Circular	$\frac{FL}{4}$	R	$\frac{\pi R^4}{4}$	$\frac{FL}{\pi R^3}$



MECHANICAL PROPERTIES

Table 12.5 Tabulation of Flexural Strength (Modulus of Rupture) and Modulus of Elasticity for Ten Common Ceramic Materials

Material	Flexural Strength		Modulus of Elasticity	
	MPa	ksi	GPa	10^6 psi
Silicon nitride (Si_3N_4)	250–1000	35–145	304	44
Zirconia ^a (ZrO_2)	800–1500	115–215	205	30
Silicon carbide (SiC)	100–820	15–120	345	50
Aluminum oxide (Al_2O_3)	275–700	40–100	393	57
Glass-ceramic (Pyroceram)	247	36	120	17
Mullite ($3\text{Al}_2\text{O}_3\text{--}2\text{SiO}_2$)	185	27	145	21
Spinel (MgAl_2O_4)	110–245	16–35.5	260	38
Magnesium oxide (MgO)	105 ^b	15 ^b	225	33
Fused silica (SiO_2)	110	16	73	11
Soda-lime glass	69	10	69	10

^a Partially stabilized with 3 mol% Y_2O_3 .

^b Sintered and containing approximately 5% porosity.

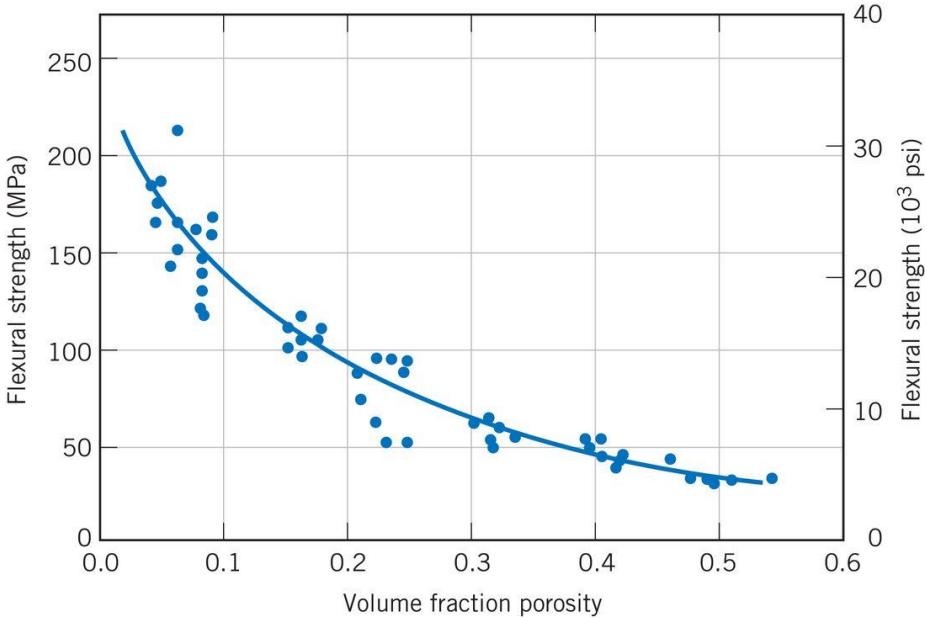
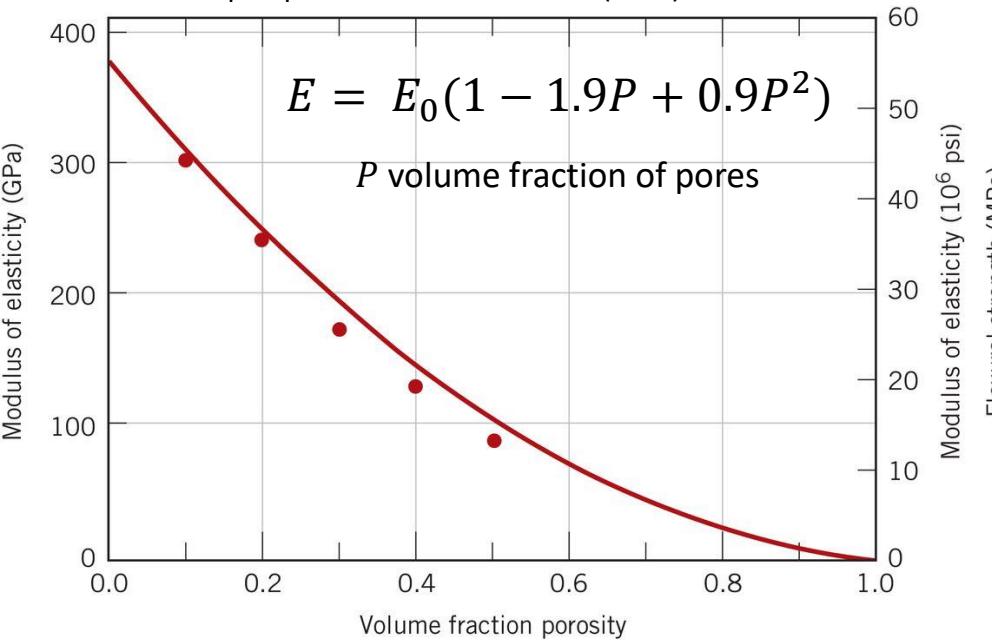
MECHANICAL PROPERTIES

Porous ceramics

Pores

- reduction of real section resistant to load
- stress concentrators

example: porous Aluminum oxide (@RT)



SUMMARY L6

- L6.1 • Structures and properties of ceramics
- L6.2 • Piezoceramics
- L6.3 • Oxide Structures, Packing of Anions, Glass
- L6.4 • Semiconductors, SiC
- L6.5 • Carbon Polymorphs
- L6.6 • Bioceramics
- L6.7 • Mech Properties of Ceramics



READINGS

READINGS:

- Callister Rethwisch – Chapters 12, 13



NETWORK COVALENT SOLIDS



Network Covalent solids

JoVE VIDEO

<https://www.jove.com/it/science-education/11358/network-covalent-solids>

ADDITIONAL RESOURCES

- connected to video about piezoelectricity and piezoelectric crystals

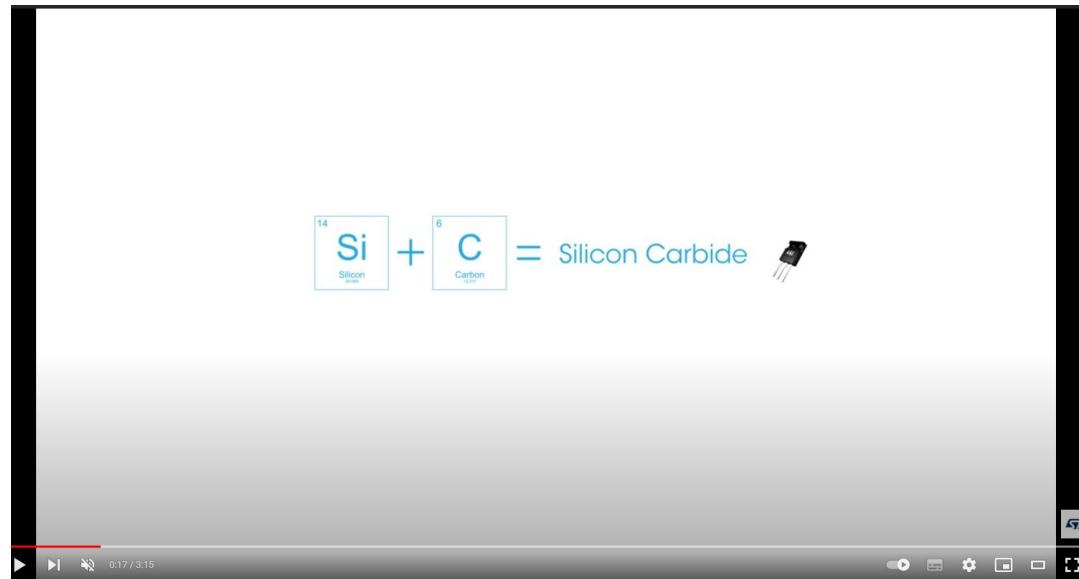


How a quartz watch works - its heart beats 32,768 times a second

YOUTUBE VIDEO (Steve Mould channel)

https://youtu.be/_2By2ane2I4

ADDITIONAL RESOURCES

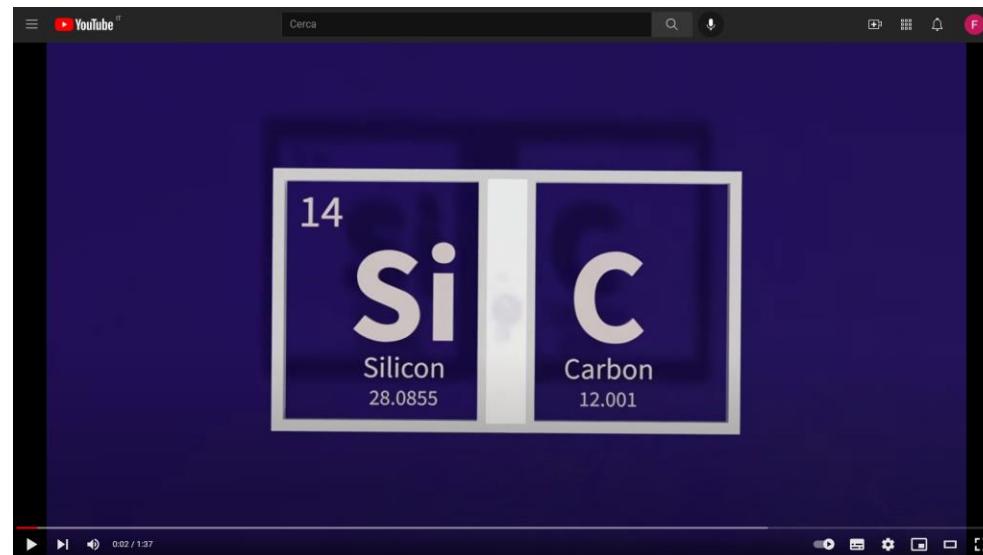


Silicon Carbide, it's all about the Bandgap!

YOUTUBE VIDEO (ST Microelectronics)

<https://youtu.be/hV5mqmuozIA>

ADDITIONAL RESOURCES



Wolfspeed Silicon Carbide 101

YOUTUBE VIDEO (Wolfspeed Inc.)

<https://youtu.be/kcWKDYmk5qY>

ADDITIONAL RESOURCES

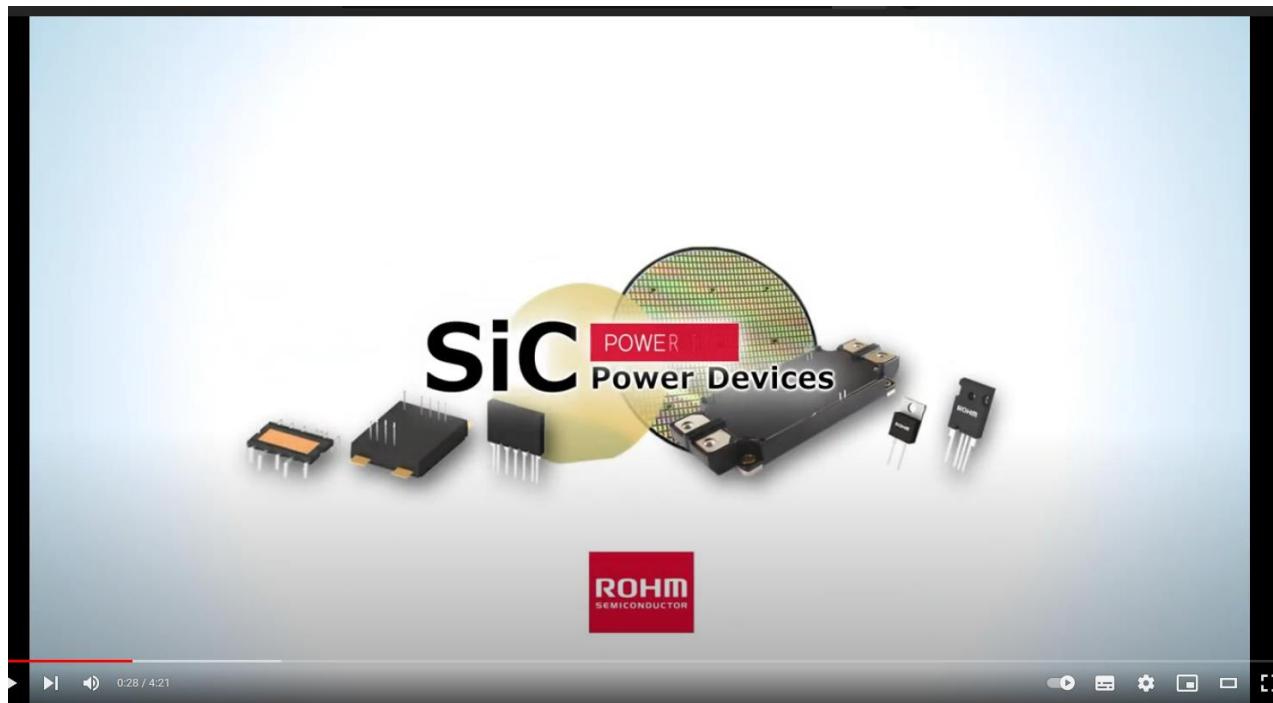


Growth of SiC crystals

YOUTUBE VIDEO (ROHM Semiconductors Europe)

<https://youtu.be/LeHE-7KmVvE>

ADDITIONAL RESOURCES



Power the Future with ROHM's SiC Power Devices

YOUTUBE VIDEO (ROHM Semiconductors Europe)

<https://youtu.be/r6FLeK8QRss>

ADDITIONAL RESOURCES



How Carbon Nanotubes will change the world

YOUTUBE VIDEO (Real Engineering)

<https://youtu.be/Slif11QOsRI>

(19:34)

ADDITIONAL RESOURCES

The screenshot shows a presentation slide titled "Material Portfolio" from LITHOZ. The slide displays a variety of ceramic materials, each with a small image and a label: Piezoceramics, Silica-based, Tricalciumphosphate, Porcelain, Regolith, Magnesia, Cordierite, Hydroxyapatite, Glass-ceramics (transparent ceramics), Zirconia, Alumina, and Bioglass. Below the slide is a video player interface showing a video of Johannes Homa. To the right of the video is a "CAPSULE AV" panel with a list of participants and their messages. At the bottom is a ClickMeeting control bar.

Webinar | The Benefits of Ceramics for AM Applications

YOUTUBE VIDEO (LITHOZ)

<https://youtu.be/CVLWb6JnH4E>

52 min !!!