Crystalline materials: structures and properties

Igor Stolichnov

Nanolab, STI-IEM (Nanoelectronic Devices laboratory), ELB 334
igor.stolitchnov@epfl.ch

Assistants: Vanessa Conti, Riccardo Bosio

Mon: 16:15 -18:00, 2h
Tue: 9:15 12:00, 3h

Organization & practical aspects -1

Course: 5h/week:

- lectures 3.5h/week (average); exercises 1.5h/weeks (Tuesdays)
- your regular homework - finishing up exercises in class, reading
- corrections appear online before the next lecture

- test in class (near the end of course, April-May, will be announced in advance) – must be returned
- test = full mark is 1, counted as 1/6 of the exam grade
- demonstrations & experiments (depending on time available)
- discussions based on your questions & feedback

Organization & practical aspects -2

Access to the teaching material - Moodle

Teaching materials on moodle:

- copies of slides and presentations
- scripts (extracts from books, written explanations of some topics)
- regular exercises + solutions (typically available in 1 week)
- papers for reading (recent results, state of the art in relevant topics)
- other materials

What is obligatory for the exam and what is optional?

-in principle, the information presented in lecture handouts and exercises is required / sufficient to answer all exam questions
-if you understand lectures and can solve exercises – you are good for exam

Organization & practical aspects - 3

Apart from materials on moodle:

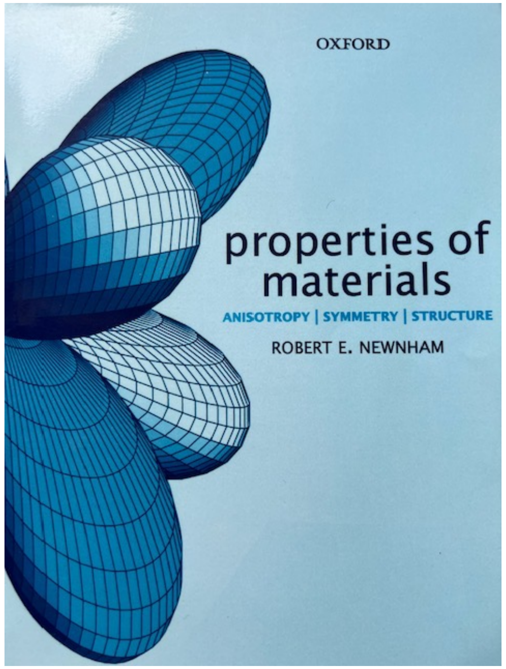
- web resources: open source crystallography data and visualizers
- optional reading (next slide)
- other resources like youtube lectures (can discuss within course)

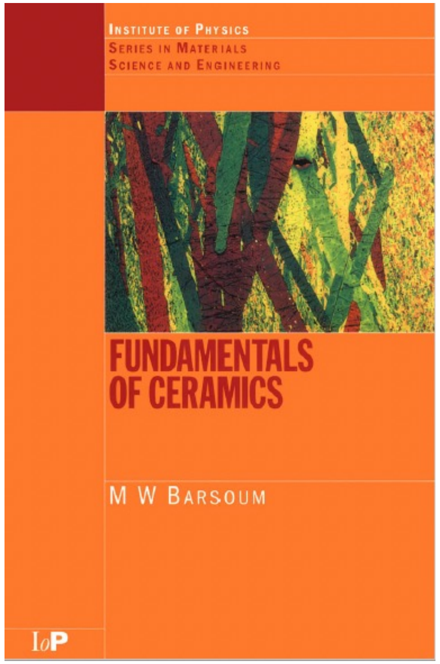
Please download VESTA: http://jp-minerals.org/vesta/en/download.html
(you may have to download an older version if your computer does not support 64 bits)

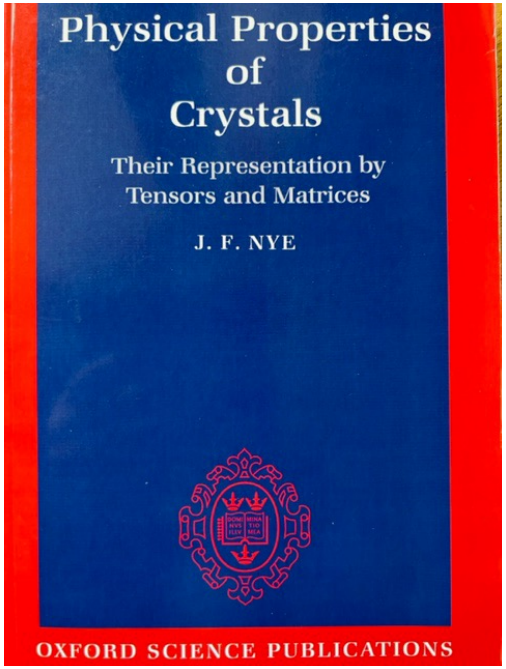
Exam:

- summer session, written exam, 3h
- open book exam: class notes, printed and handwritten materials - OK
- Not permitted: Laptops, ipads, tablettes, smartphones, other gadgets, digital carriers

Recommended books







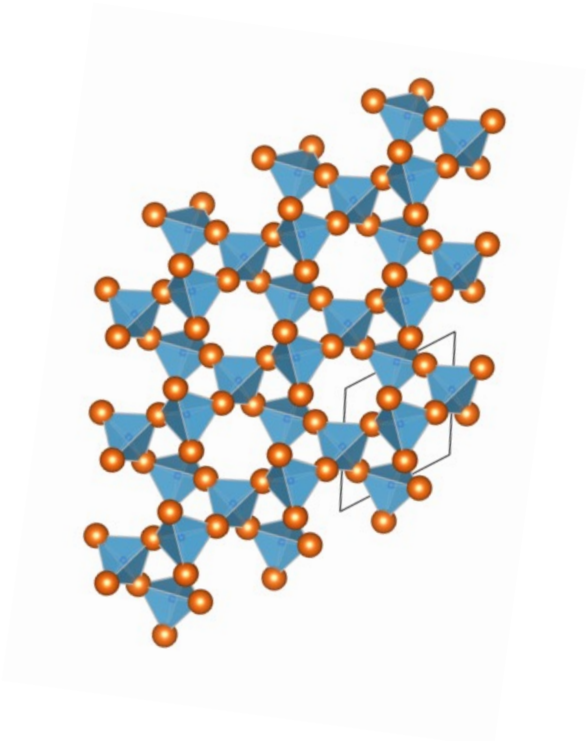
R. E. Newnham: Properties of materials. Anisotropy, symmetry, structure. Oxford University Press 2005

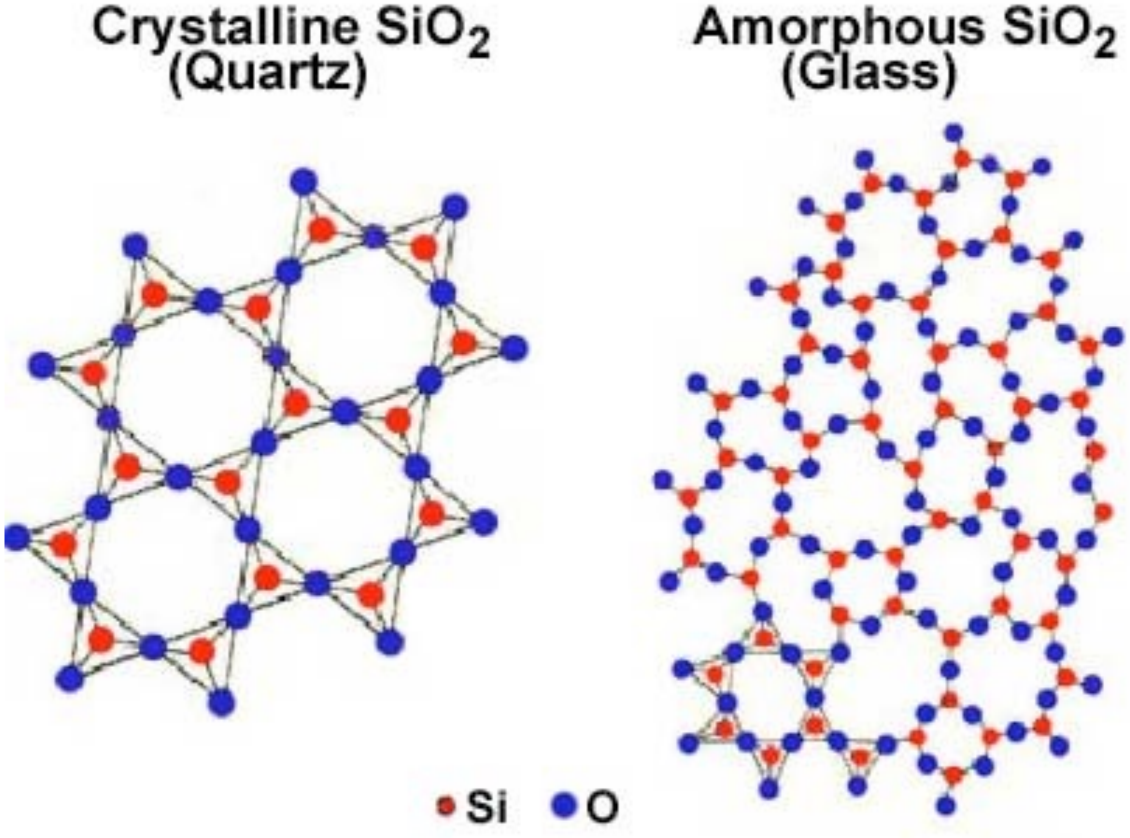
M. Barsoum: Fundamentals of Ceramics, Taylor&Francis, 2nd edition 2019

J. F. Nye: Physical Properties of Crystals. Oxford University Press 1985 + later reprints

This course: crystalline materials: structures and properties

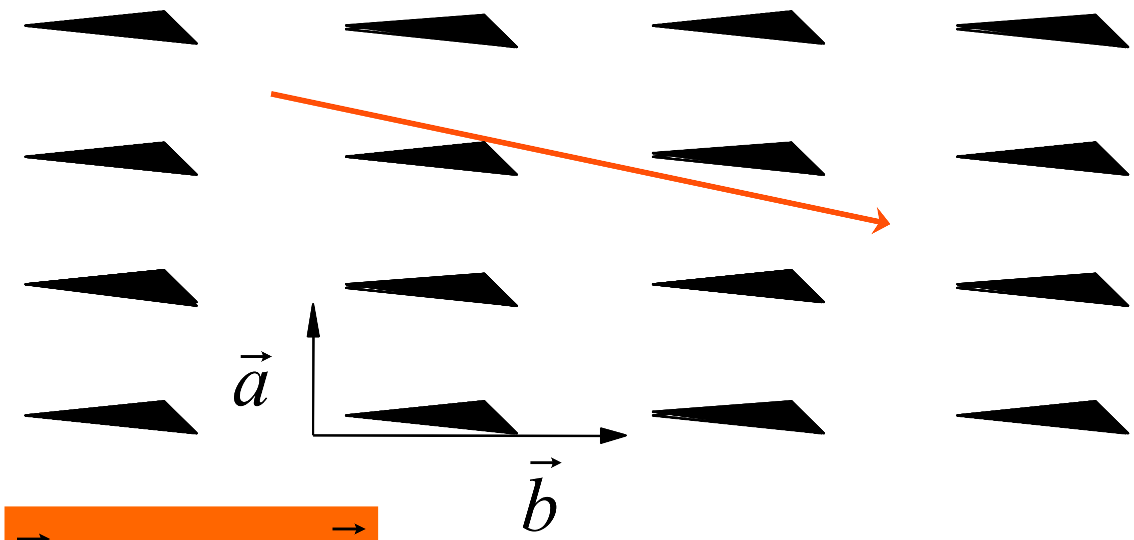
What means crystalline? Example: SiO_2 crystal vs amorphous





Crystalline Symmetry

Translational symmetry



$$\vec{t} = -\vec{a} + 2\vec{b}$$

$$\vec{t} = n\vec{a} + m\vec{b}$$

translation vector → $\vec{t}$

fundamental translation vectors → $\vec{a}$, $\vec{b}$

Symmetry is the property of an object to remain unchanged under application of certain operations

Type od symmetry:
- Translations
- Rotations
- Inversions
- Others…

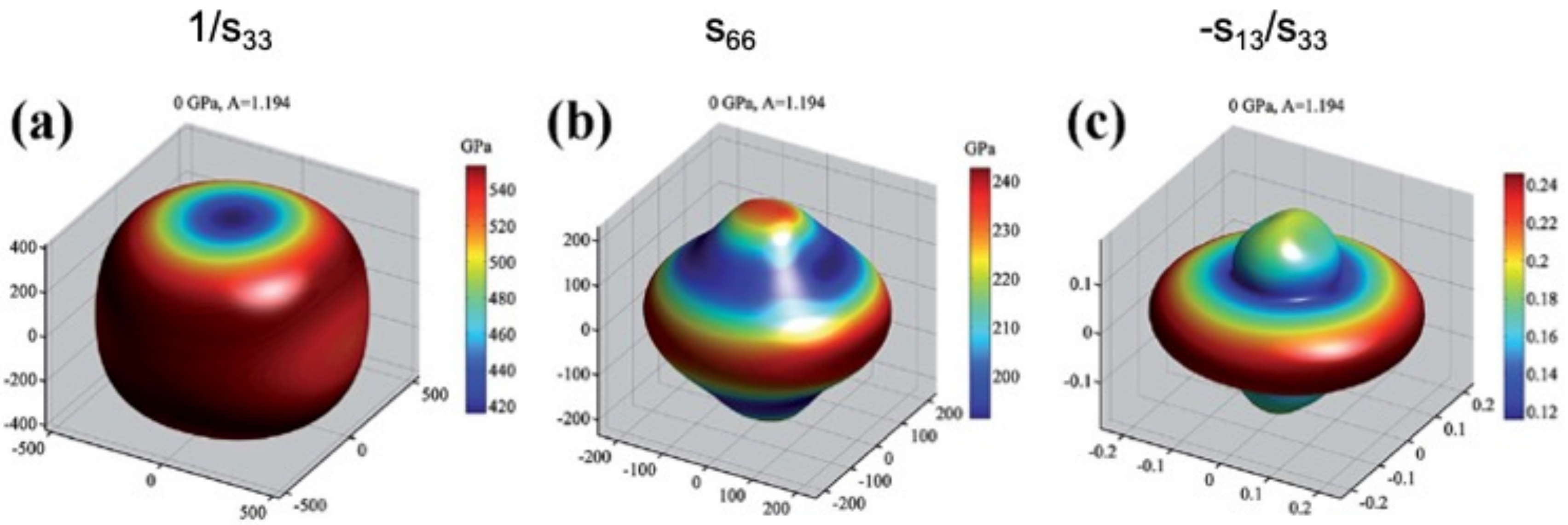
Crystalline Symmetry: properties

Crystalline physics: symmetry - properties

- **Anisotropy**
- **Symmetry of properties**
- **Limitations by symmetry (forbidden properties)**

Example: direction dependence of longitudinal piezoelectric module for orthorhombic crystals

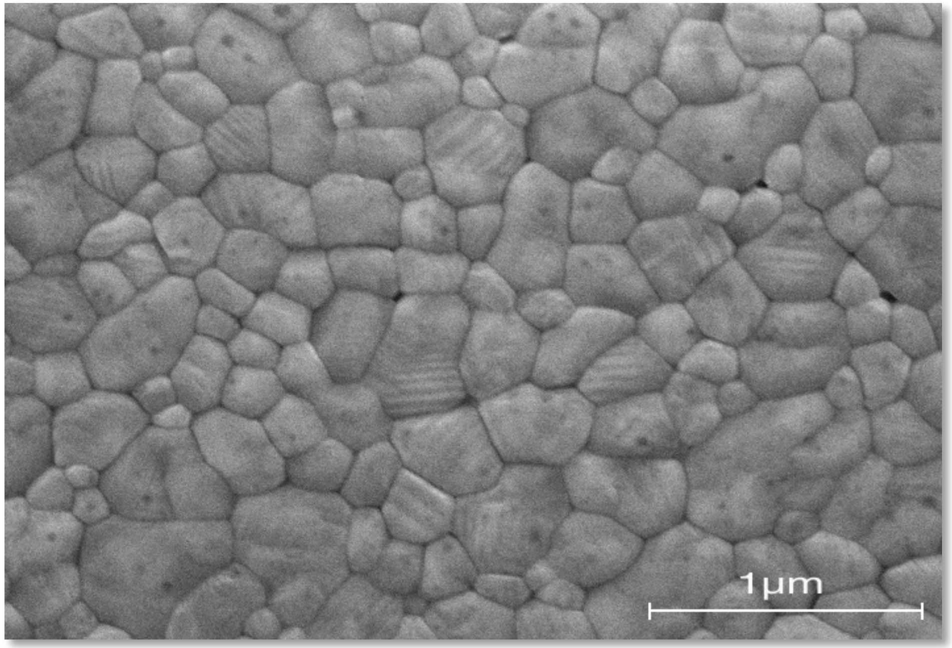
Example: Direction dependence of elastic moduli for orthorhombic ZrB_4



Crystalline materials: single crystals, polycrystalline (ceramics)

- Single crystals: electronics (Si, GaAs…), optics, electromechanics

- Polycrystalline materials, ceramics
- Usually formed at high temperature by sintering (but sintering can also take place at temperatures as low as 200°C)
- Ceramics: Inorganic and nonmetalic

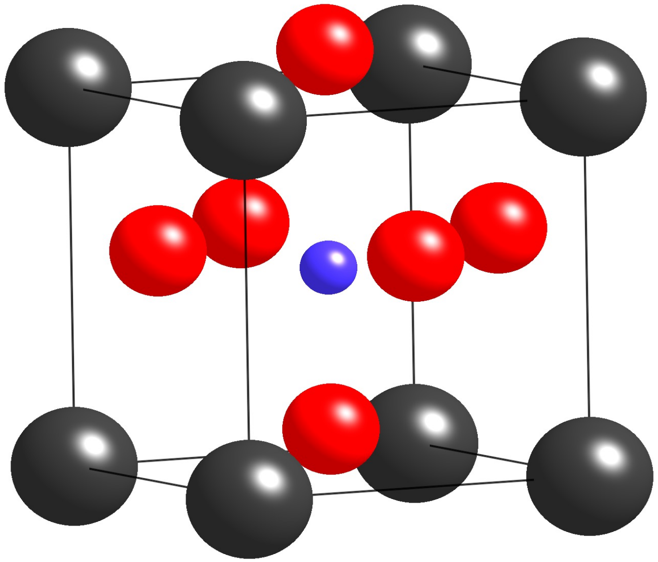


$PbTiO_3$

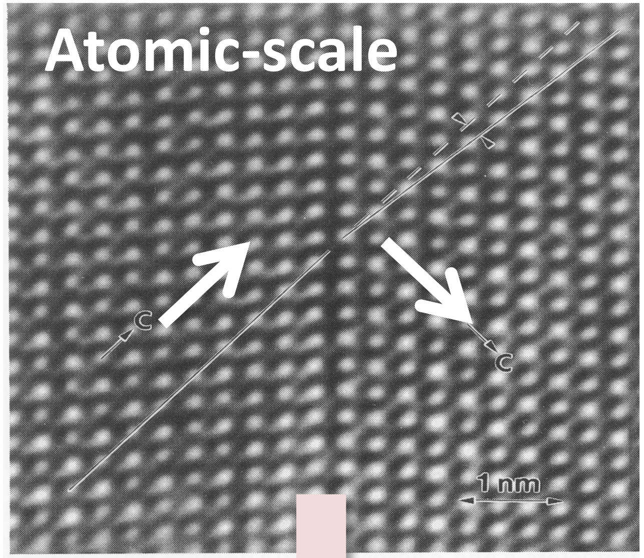
Ceramics is more than just a big amount of microcrystals:

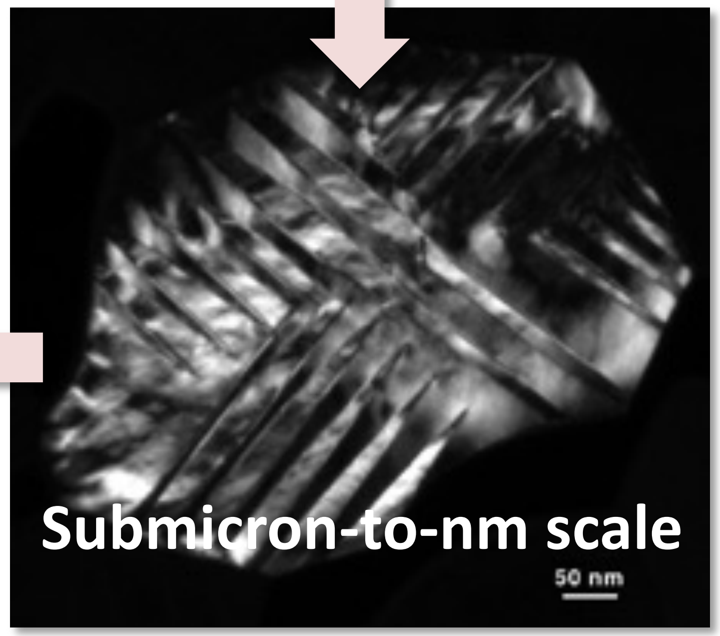
- Bulk vs thin films
- Grains and grain boundaries
- Nano-size crystals – new properties
- Pores
- Defects engineering

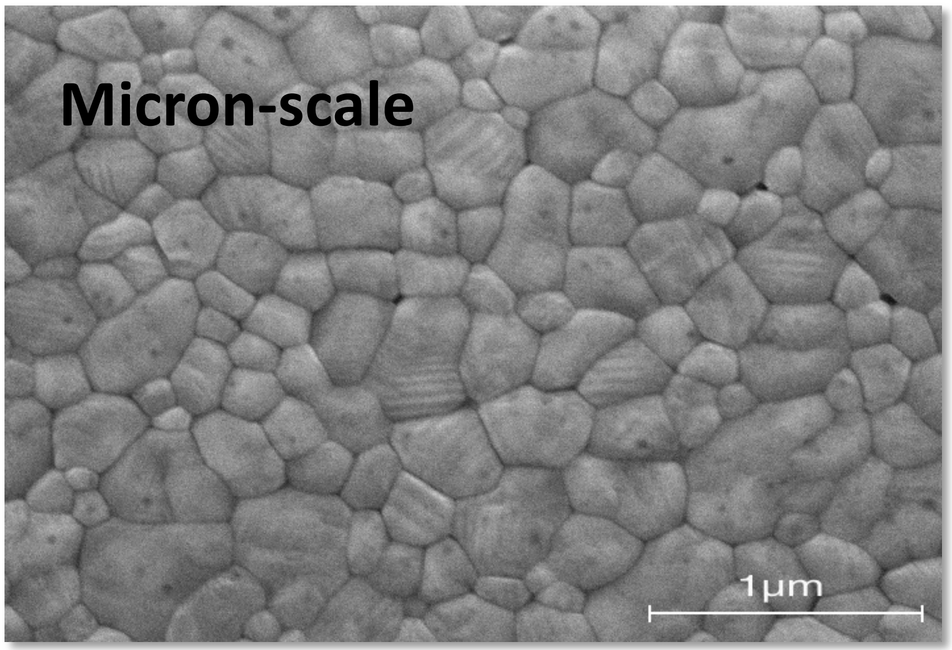
Crystalline materials: structure – property relations, scales



$PbTiO_3$







Ceramics since early time

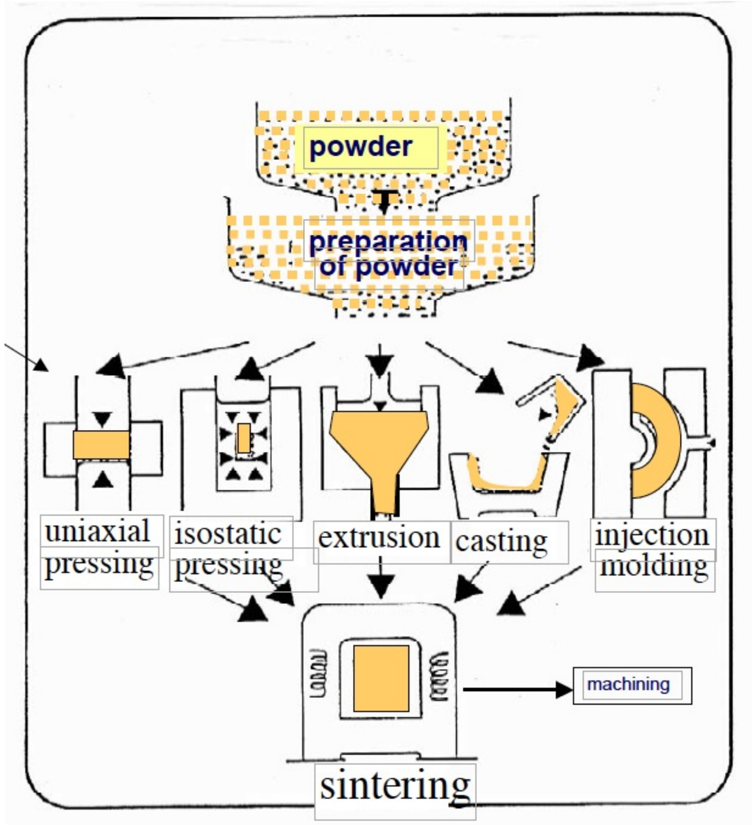
- Used since very early time
- • 26 000 y – first figurine
- • 11 000 y – storage of cereals
- • 3 500 y - glass

Terracotta Army, Xian, 210–209 BCE

How are ceramics made?

Main steps for classical ceramics:

Choice of composition
Powder preparation
Formation of “body”
Sintering
Machining

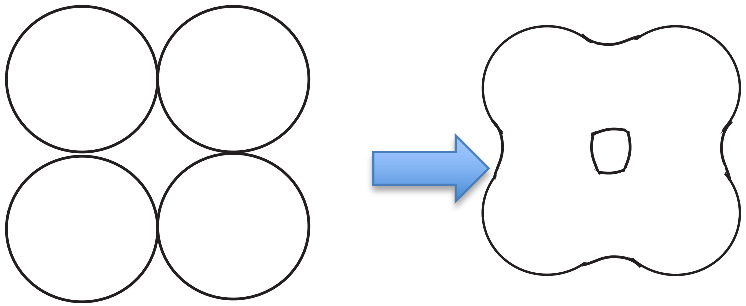


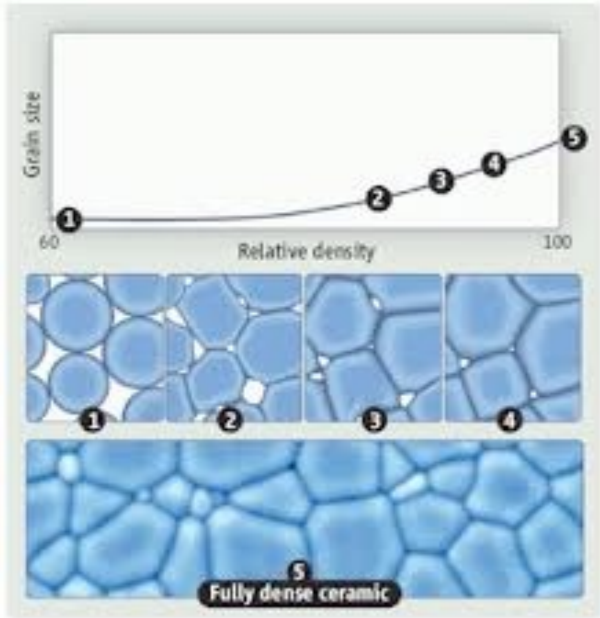
Modern Ceramics

Refractory and insulating ceramics
Structural ceramics
Electrical, optical ceramics
Magnetic, piezoelectric, ferroelectric, superconducting ceramics,….

Sintering: ceramics is more than just microcrystals

-main mechanism is diffusion at high temperature
-other types of mass transport are possible at low temperatures

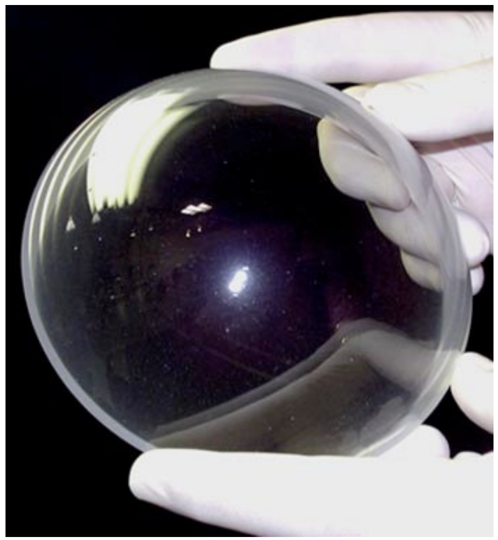




Shrinkage, densification, grain growth

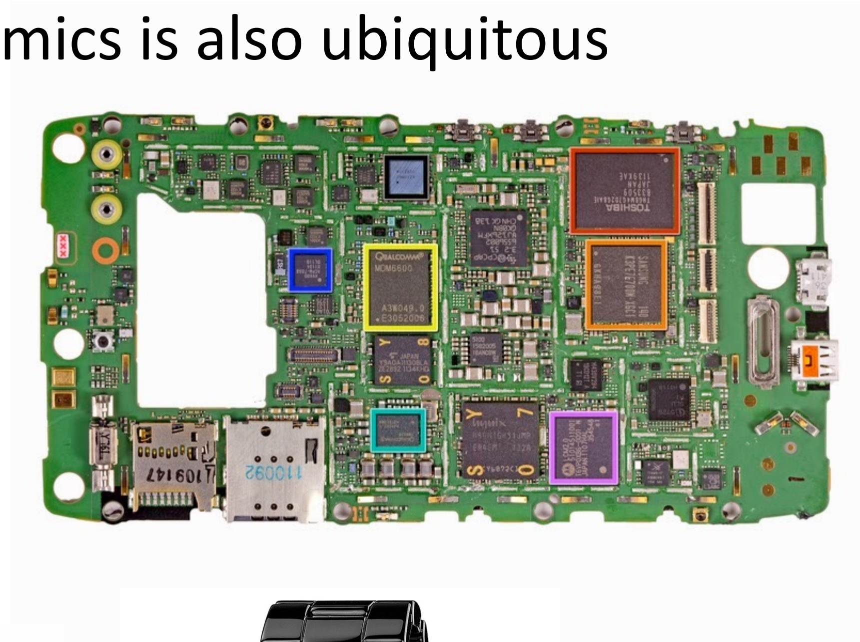
Properties are affected by:

- Defects (stationary or mobile)
- Grain boundaries, grain size
- Geometry, thickness …



Ceramics in our everyday lives

- Structural ceramics is most visible
- Functional ceramics is also ubiquitous



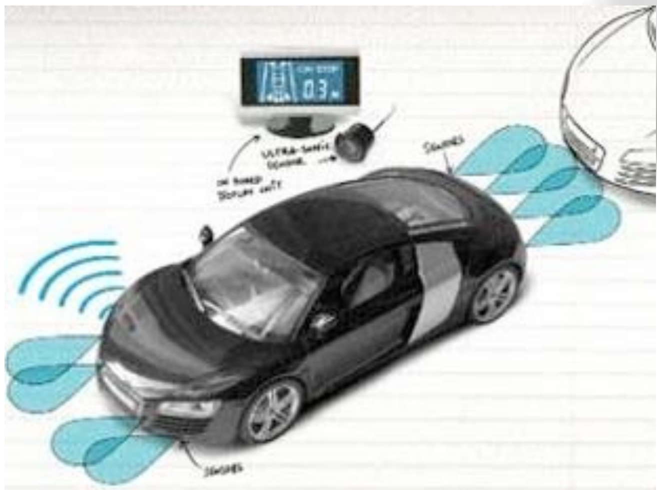
Ball bearings

turbines

Si_3N_4

Acoustic applications

- Medical ultrasonic imaging- $Pb(Zr,Ti)O_3$ and composites
- Nondestructive testing-$Pb(Zr,Ti)O_3$
- SONAR –$Pb(Zr,Ti)O_3$ and composites
- Parking sensors-$Pb(Zr,Ti)O_3$
- Acoustic tomography- $Pb(Zr,Ti)O_3$

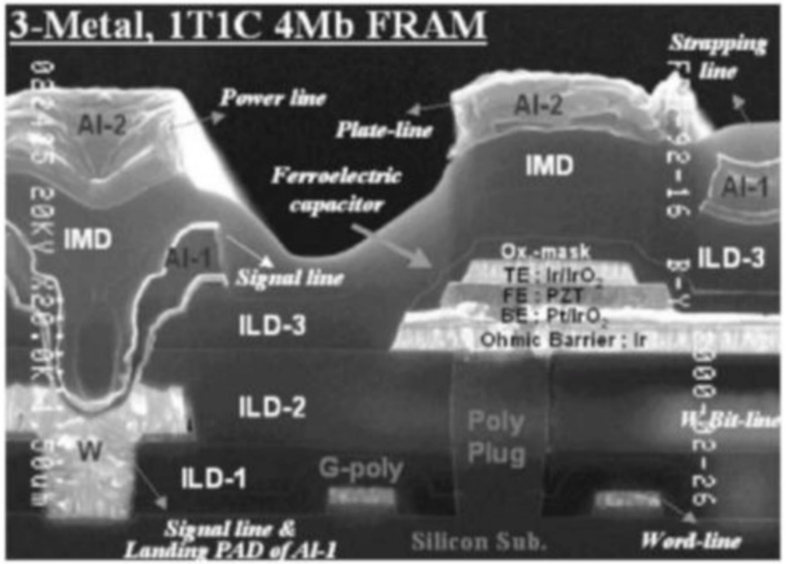


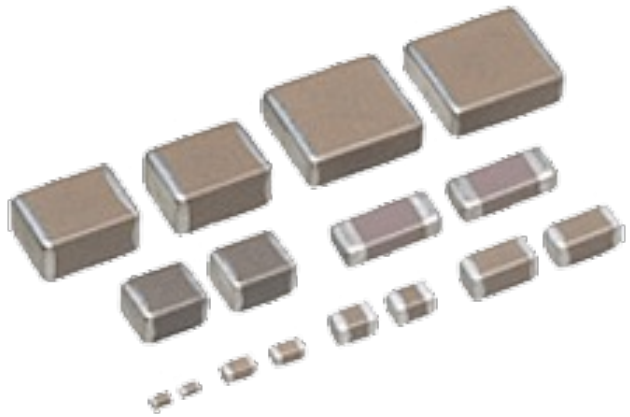
Ceramics in electronics and microelectronics

- Barrier layers:
  - Si3N4, SiO2, SiC, TiO2…..
- Functional layers:
  - AlN, Ta_2O_5, $BaTiO_3$, $Pb(Zr,Ti)O_3$, ...
- Bulk materials:
  - $BaTiO_3$, $Pb(Zr,Ti)O_3$,barium ferrite

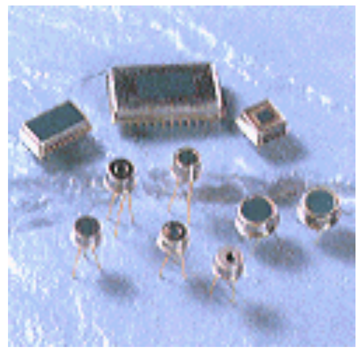
- Properties:
  - Electrical insulation (substrates)
  - Semi-conductivity (gas sensors)
  - Ionic conductivity (fuel cells)
  - Superconductivity
  - Dielectric permittivity (capacitors)
  - Piezoelectricity (actuators and sensors)
  - Ferroelectricity (memories)
  - Magnetisation and magnetostriction (actuators, sensors, inductors)

FRAM (emerging Ferroelectric Random Access Memory)





capacitors



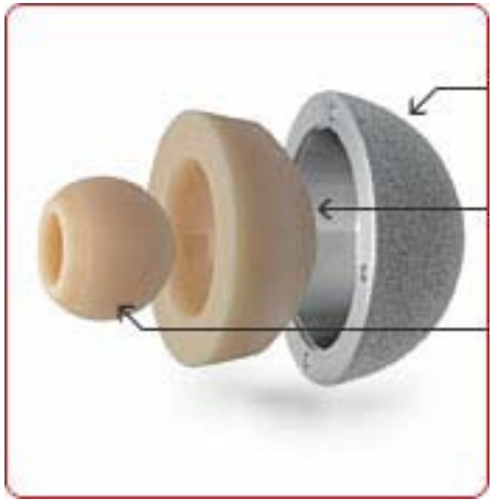
sensors

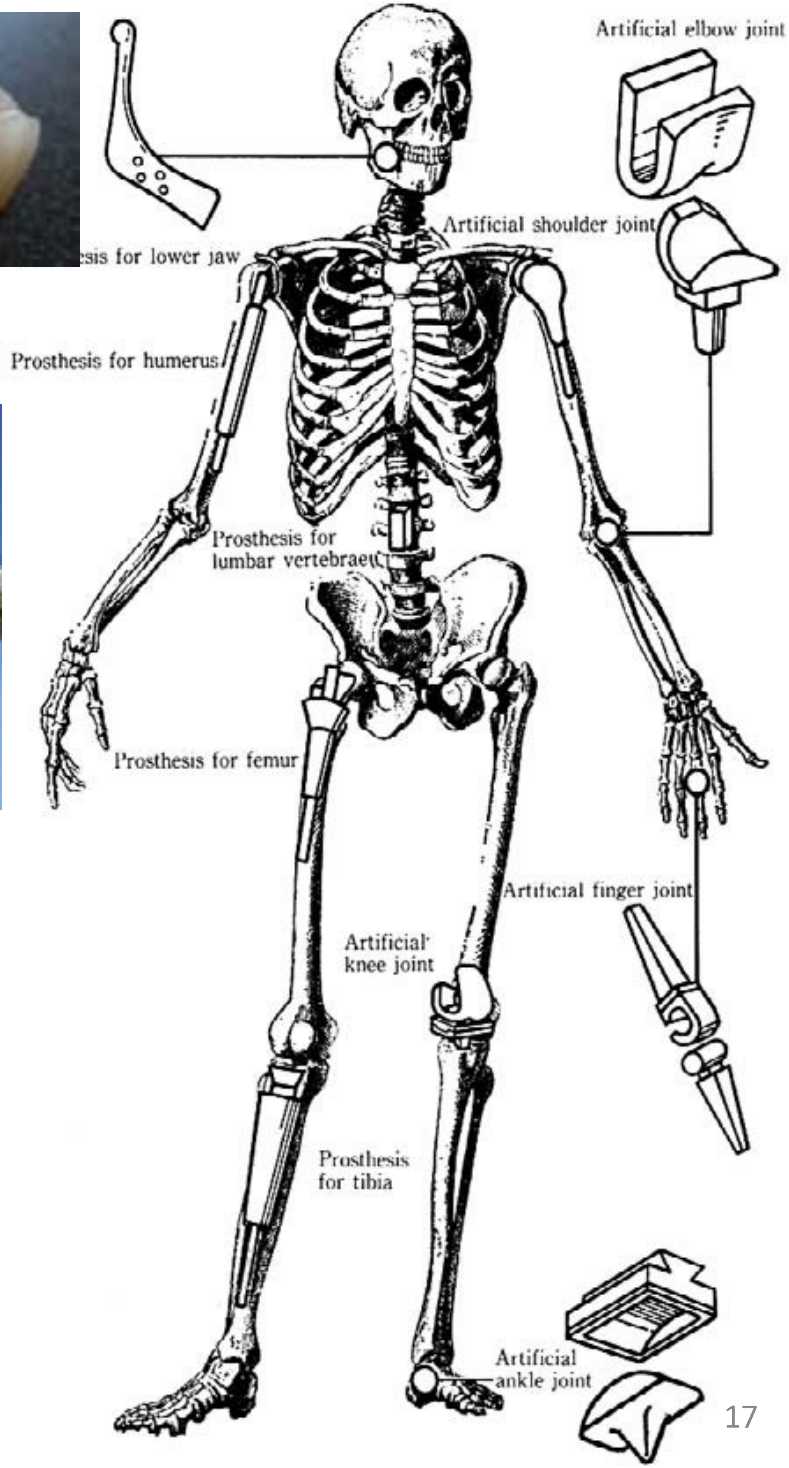
700 in a smart phone

Biomedical applications

Objectives: “permanent” replacement of “mechanical” parts of human body

- Materials :
  - Zirconia
  - Alumina
  - Hydroxyapatite





Essential properties:
- biocompatibility
- chemical stability (inert)
- resistance to corrosion

Diversity of ceramic materials

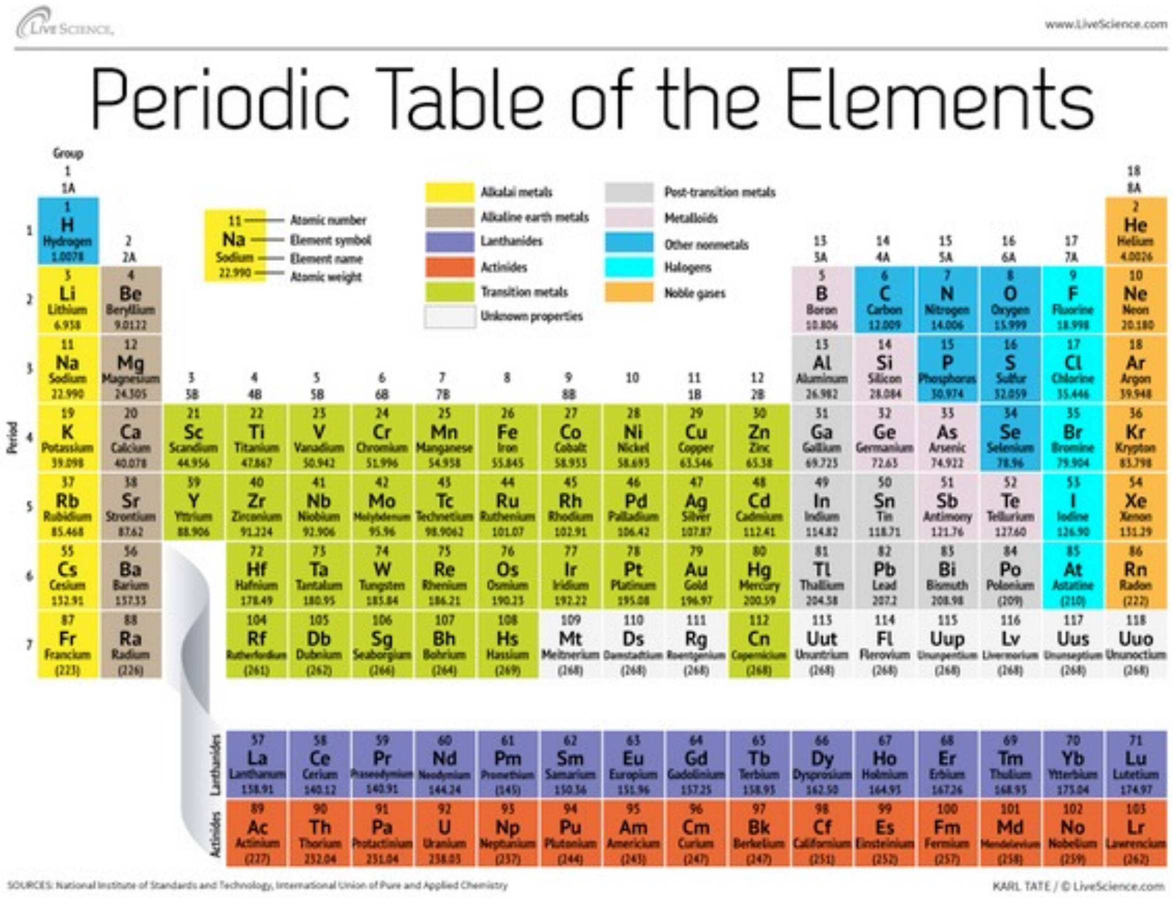
-ancient vs modern
(bricks vs multilayer capacitors)

-varied composition
(MgO to $YBaCuO_7$, $Pb(Mg,Nb)TiO_3$,
$(K, Na,Li)(Nb,Ta)O_3$)

-structural vs functional
(Al_2O_3 vs $La_{1-x}Sr_xMnO_3$)

-bulk vs films and nano –size
($Pb(Zr,Ti)O_3$, AlN)

-applications:
- -optical (Al_2O_3, Y_2O_3)
- -electronics ($BaTiO_3$)
- -acoustic ($Pb(Zr,Ti)O_3$)
- -structural (ZrO_2)
- -thermic (alumina-silica-borosilicate fibers)
- -biomedical (alumina, calcium phosphate)
- -magnetic ($BaFe_2O_4$)



Application-relevant concerns: cost, toxicity, environment

Quest for new ceramic materials

- Application-relevant properties:
  - Hardness, fracture resistance, temperature stability
  - Thermal conductivity and electrical insulation
  - High electro-mechanical coupling
  - Electrical resistance and magnetic properties
  - Biocompatibility

  And

  …cost, availability of materials, environmental compatibility,…

Abundance of elements in Earth's crust

Element	Approximate % by weight
Oxygen	46.6
Silicon	27.7
Aluminum	8.1
Iron	5.0
Calcium	3.6
Sodium	2.8
Potassium	2.6
Magnesium	2.1
All others	1.5

Element	Symbol	Atomic Number	Percent in Universe	Percent in Earth	Percent in Human Body
Hydrogen	H	1	91	0.14	9.5
Helium	He	2	9	Trace	Trace
Carbon	C	6	0.02	0.03	18.5
Nitrogen	N	7	0.04	Trace	3.3
Oxygen	O	8	0.06	47	65
Sodium	Na	11	Trace	2.8	0.2
Magnesium	Mg	12	Trace	2.1	0.1
Phosphorus	P	15	Trace	0.07	1
Sulfur	S	16	Trace	0.03	0.3
Chlorine	Cl	17	Trace	0.01	0.2
Potassium	K	19	Trace	2.6	0.4
Calcium	Ca	20	Trace	3.6	1.5
Iron	Fe	26	Trace	5	Trace

% by mass)

Do we have enough mass of elements to build stuff?

Feldspars ($KAlSi_3O_8$ - $NaAlSi_3O_8$ - $CaAl_2Si_2O_8$) are a group of rockforming tectosilicate minerals which make up as much as 60% of the Earth's crust.
Silicate perovskite$(Mg,Fe)SiO_3$ may form up to 93% of the lower mantle
Magnesium iron silicate perovskite is considered to be the most abundant mineral in the Earth, making up 38% of its volume

Gold mining in Indonesia

NatGeo / 1-2009

1 oz (30 grams) of Au = 250 tons of earth

Crystalline materials: structures and properties - topics

- Crystalline structures, basics of crystallography, bonds, symmetry
- Symmetry + Tensors + Thermodynamics = powerful description of properties of crystalline solids
- Application-relevant properties: dielectric, mechanical, thermal and electrical transport
- Cross-coupled application-relevant properties: electro-mechanical and thermo-electro-mechanical properties
- Practical aspects: suitable instruments, methods and techniques for measurements and analysis of properties

Crystalline materials: structures and properties – goals, knowledge and skills to be acquired

- Understand structures, symmetry and properties of crystalline materials

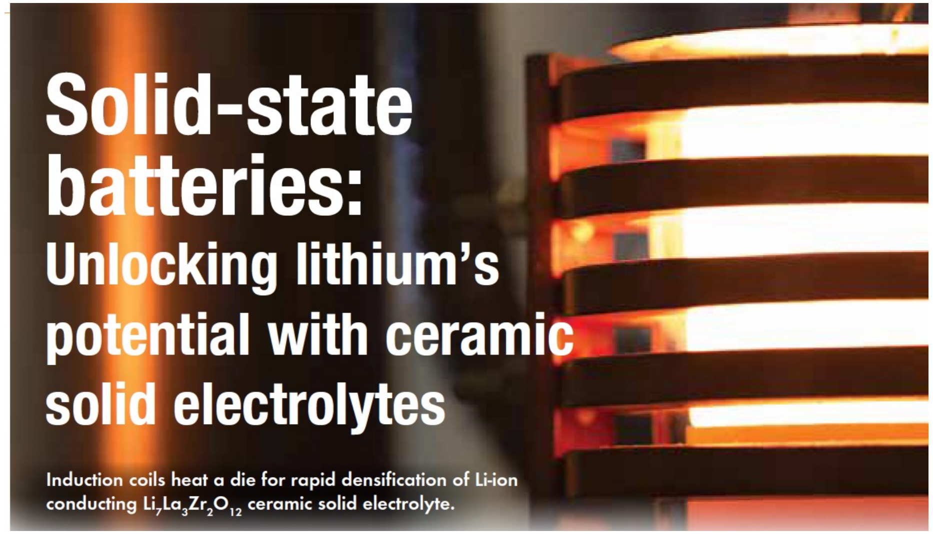
- Ability to understand application-relevant properties and ways of engineering/tailoring/oprimizing properties for applications

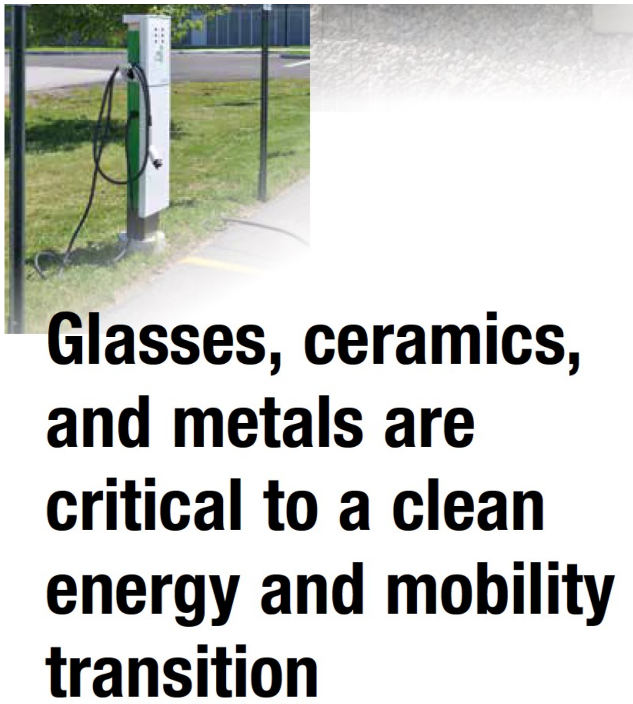
- Ability to predict properties based on structures

- Understanding basic experimental techniques and approaches

- Ability to apply this knowledge to solving problems in materials science and engineering

Additional reading: modern functional ceramics (optional)





Downloadable from Moodle