Dental ceramics

Classification, structure and properties

Pavel Bradna, Antonin Tichy

pavel.bradna@lf1.cuni.cz, antonin.tichy@lf1.cuni.cz

Institute of Medical Biochemistry and Laboratory Diagnostics,
Institute of Dental Medicine

First Faculty of Medicine ,
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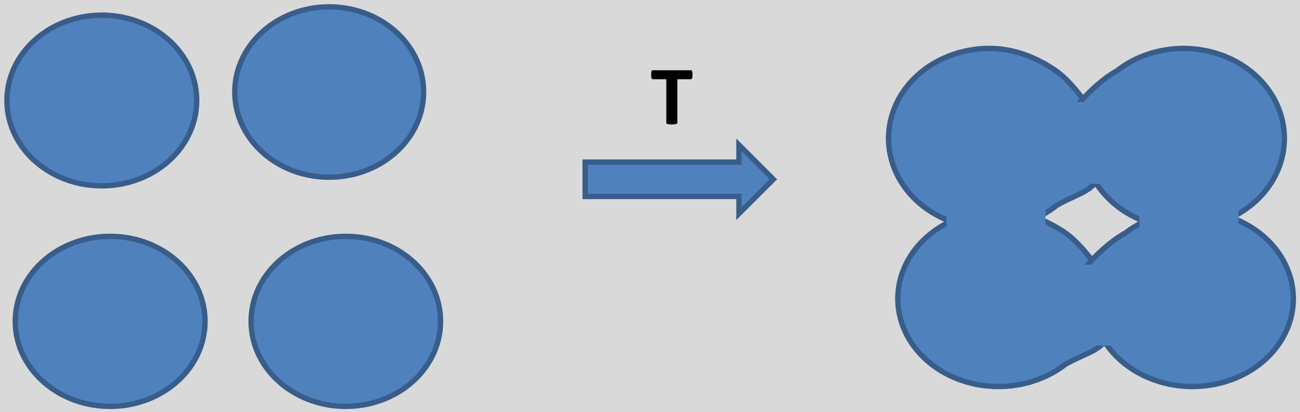
Definition of ceramics:

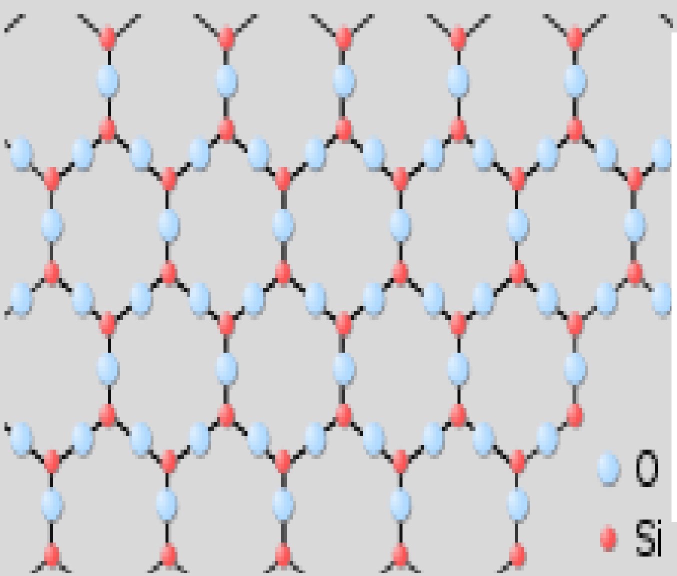
Inorganic, **non-metallic heterogeneous** materials **containing** >30 % of **crystalline particles** and prepared by particle **sintering** at high temperatures.

Sintering (firing) – process of strengthening and densifying (lowering porosity) of powder materials at high temperatures (below their melting point) due to interdiffusion at their boundaries leading to their mutual bonding.

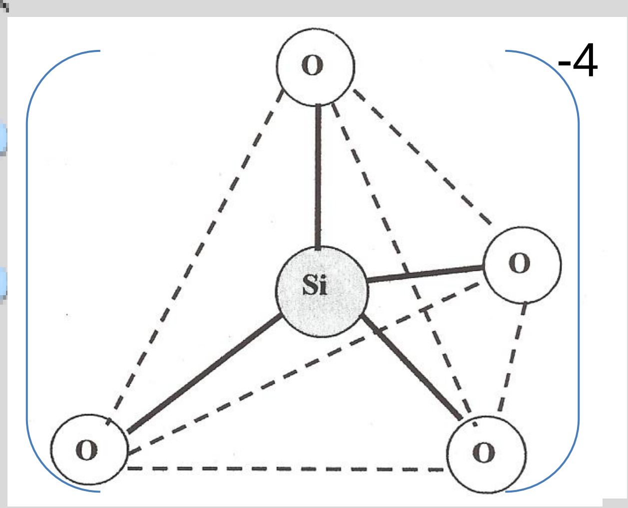


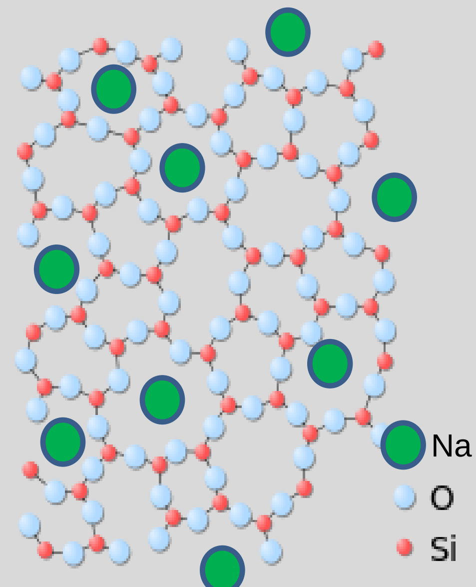
Definition of glass:

Glass is amorphous (non-crystalline) solid material with the structure „resembling liquid", characterized by transitition at T_g (glass transitition temperature) from a hard and brittle to molten plastic state on heating. This process is reversible.



Regular network of crystalline SiO_2





Random network of amorphous glassy sodium SiO_2

Dental ceramics:

Contains various amount of potassium/sodium **feldspar** ($KAlSi_3O_8$,$NaAlSi_3O_8$), crystals of **leucite** ($KAlSi_2O_6$), **quartz**, **Al_2O_3, ZrO_2, lithium disilicate** ($Li_2Si_2O_5$)**, spinel** ($MgAl_2O_4$)**, etc.**

Note to the terminology of ceramics:

In some literature a term porcelain is often used for ceramic materials. Porcelains, however, contain **> 40 wt.% of kaolin which is** in dental ceramics in much lower quantity. For that reason a more general term **dental ceramics should be preferred.**

However, traditional name porcelain can be also used mainly for feldspathic ceramics/e.g. porcelain fused to metal.

Dental ceramics indications:

In denture prothesis manufacturing ceramic materials are processed using various methods: **sintering**, **casting**, **pressing**, **CAD/CAM**, **copy-milling,** etc:

- Inlays and onlays,
- Veneering material for metal-ceramic crowns and bridges,
- Aesthetic veneering over natural teeth,
- Single **all-ceramic** crowns and short (typically 3-unit) bridges,
- Artificial teeth, orthodontic brackets, implant abutments.

Properties of dental ceramics

- **Highly aesthetic**,
- **Biocompatible** – non-toxic, chemically inert,
- **Stable – resistant to oral cavity environment**,
- Low adherence of bacteria,
- **High strength in compression but low tensile strength, brittle**, some rather abrasive to opposing teeth,
- Thermal conductivity similar to enamel and dentin,

- Requires skilled technician, special expensive equipment,
- High price.

Classification of dental ceramics

There are several classification systems, according to e.g:

- Indication (veneers, crowns, bridges, inlays…),
- Type of restoration (metal-ceramic, all-ceramic),
- Processing (sintering, casting, pressing, infiltration, machinable - CAD/CAM, copy milling),
- Type of crystalline phase (leucite, spinel, lithium disilicate…),
- Chemical composition.

Why classification system is needed?

- To orient in the broad range of ceramic materials.
- To understand their structure - properties relationships and physical principles behind.

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To understand which and why various ceramic materials can be used under specific clinical conditions?

Examples of classification systems

Anusavice KJ: Phillips´ Science of Dental Materials, 11th. edition, 2002:

- Silicate ceramics – characterized by an **amorphous** SiO_2 **glass phase** and small amount of Al_2O_3, MgO, ZrO_2 (include *dental porcelains*),
- Oxide ceramics – contain principal crystalline phase of Al_2O_3, MgO, ZrO_2 with no or a **small content of glass phase**,
- Nonoxide ceramics – nitrides, carbides – **not used in dentistry** (dark colours, processing at high temperatures),
- Glass-ceramics – **partially crystallized glasses** produced by nucleation and growth of crystals in the glass matrix.

McLaren AD et al: Ceramics in Dentistry-Part I: Classes of Materials.

http://www.insidedentistry.net

Microstructural classification:

- Glass-based systems (mainly silica),
- Glass-based systems with fillers (leucite, lithium disilicate),
- Crystalline-based systems with glass fillers (mainly alumina),
- Polycrystalline solids (alumina and zirconia).

Craig´s: Restorative Dental Materials, Mosby, 12th. Edition, 2006:

Classification according to the type of restoration or processing method

Application	Processing	Crystalline phase
All-ceramic	Machined (CAD/CAM, copy-milling)	ZrO_2, alumina Al_2O_3, feldspar ($KAlSi_3O_8$), mica, leucite ($KAlSi_2O_6$)
	Slip-cast	ZrO_2, Al_2O_3, spinel ($MgAl_2O_4$)
	Heat-pressed	Leucite, lithiumdisilicate ($Li_2Si_2O_5$)
	Sintered	Leucite, Al_2O_3
Ceramic-metal	Sintered	Leucite
Denture teeth	Manufactured	Feldspar

Classification according to firing temperature

High fusing ceramics >1300^{o}C

Medium fusing ceramics 1100-1250^{o}C

Low fusing ceramics 870-1050^{o}C

Ultra low fusing ceramics <850^{o}C

Result:

students are confused and do not understand principles of ceramic´s properties and their clinical use.

Classification system based on the phase structure:

Kelly JR: Dental ceramics: current thinking and trends. Dent. Clin. N. Am. 48, 2004, str. 513-515.

Any ceramic material can be considered as a **composite material** consisting of two distinct phases:

Continuous – amorphous, forming predominantly **glass matrix,**

Dispersed – composed of crystalline filler particles, which reinforce a matrix, increasing the strength and resistance to fracture.

Types of dental ceramics according to Kelly:

1. Predominantly glassy (feldspathic) ceramics

   glassy **amorphous** material with a low content of crystalline filler particles, resistant to crystallization (devitrification),

2. Particle filled glassy ceramics,

3. Polycrystalline ceramics.

Type of ceramics	Main components	Uses
Predominantly glassy ceramics (Feldspathic ceramics)	Feldspathic glass colorants high-melting glass particles	Veneer for all-ceramic substructures, inlays, onlays

Type of ceramics		Main components	Uses	
Particle filled glassy ceramics	**Moderately filled glassy ceramics**	**Feldspathic glass** *Particles of crystalline **leucite*** *(17-25 wt.%)*	Veneer for metal substructures, inlays, onlays	
	Highly filled glassy ceramics	**Feldspatic glass** Al_2O_3 *(app 55 wt. %)*	Single-unit crowns, ceramic substructures	
		Feldspathic glass *Particles of **leucite** (40-55 wt.%) of fluoromica flakes (55 vol. %)*	Single-unit crowns, inlays, onlays	Glass-ceramics
		Feldspathic glass (modified) *Lithium disilicate whiskers (app 70 vol.%)*	Single-unit crowns, **anterior** three-unit bridges	Glass-ceramics
		Lanthan glass Al_2O_3 *(app 70 vol %) or* Al_2O_3 *and MgO*	Single-unit crowns, **anterior** three-unit bridges	Glass-infiltrated
		Aluminoborosilicate glass Al_2O_3*(app 50 vol. %) and* ZrO_2 *(app 20 vol. %)*	Single-unit crowns, three-unit bridges	Glass-infiltrated

Type of ceramics	Main components	Uses
Polycrystaline ceramics	***Aluminium oxide*** *Al_2O_3, dopants (<0.5 wt .%)*	Single-unit crowns, three-unit bridges
	Zirconium oxide *(3-5 wt. % ytrium oxide Y_2O_3…)*	

Higher filler content **increases mechanical resistance** of dental ceramics, such as **compressive strength, flexural, tensile strength** and **fracture toughness.**

On the other hand, fillers increase opacity - compromised aesthetic properties.

1. Prediminantly glassy ceramics

More glass than ceramics

Main raw materials in feldspathic ceramics

Feldspar – naturally occurring crystalline potassium or sodium (less often) aluminium silicate $KAlSi_3O_8/(K_2O\text{-}Al_2O_3\text{-}6SiO_2)$

In dental ceramics high purity feldspar is used.

Fusing temperature 1150 – 1300°C

it acts as a **flux** – substances **decreasing the firing temperature** of the ceramics.

Quartz (crystalline SiO_2)

Colorless and transparent mineral of hight melting point (1700°C), but in the presence of feldspar or alkali it **melts at lower temp**. In dental ceramics it stabilizes the shape of ceramic material and provide its transparency,

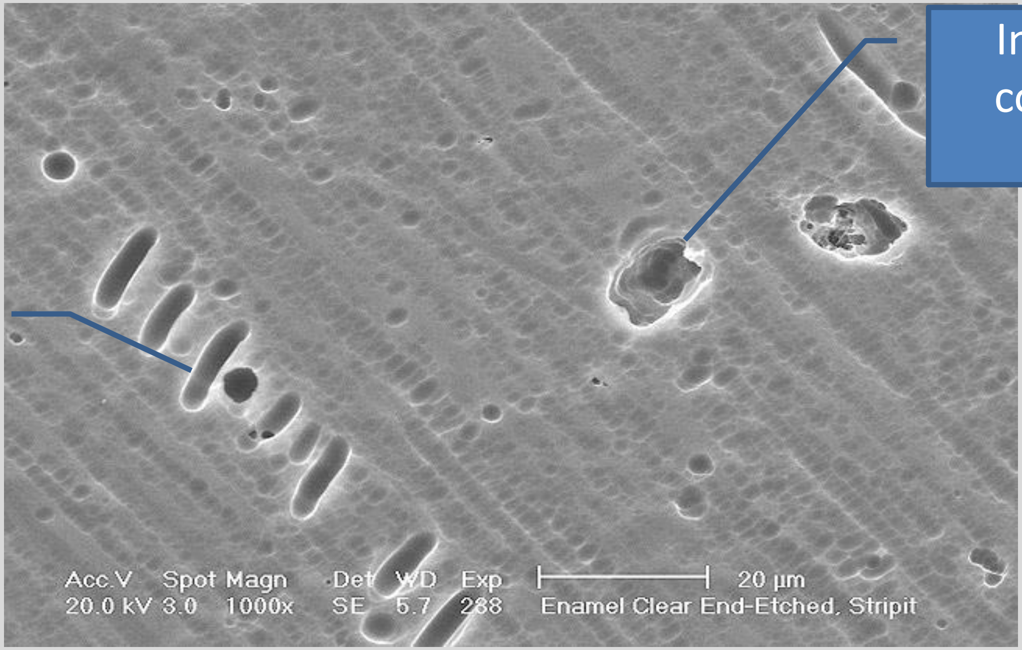
Kaolin (Al_2O_3-$2SiO_2$-$2H_2O$)

White crystalline clay mineral with the high melting point 1750°C, used to stabilize the shape of ceramics during drying and firing (to bind the loosely held ceramic particles together), added in **small amount,**

Glass modifiers – alkaline Na, K carbonates to lower fusion temperature (however, decrease chemical

Components are ground, melted, quenched and ground to a powder to be mixed with water and condensed on a die

Microstructure of predominantly glassy ceramics



Microstructure of glassy veneering ceramics
Russell Giordano, Edward A. McLaren, 2010

Increased resistance to crystallization

Low flexural strength (60 – 70) MPa;
Indications – e.g. veneering metallic or ceramic constructions,

2. Filled ceramics

a) Moderately filled glassy ceramics – leucite ceramics

Feldspathic glass:

Problem No. 1: superior aestehetic properties but **low mechanical strength**.

Solution – to prepare mechanicaly resis-tant metal/framework/construction and to fuse feldspatic ceramics on its surface.

Problem No. 2: smaller **coefficient of thermal expansion** of ceramics than metals causing **chiping or cracking of the ceramic veneers**.

Solution – invention of glass filled with **leucite** crystals of higher thermal expansion coefficient **and alloys with decreased coefficient of thermal expansion.**

Problem No. 3: **weak bond** between the alloy and ceramics.

Solution – addition of In, Sn, Fe forming oxides on the **alloy surface to bond chemi-cally with the glass.**

Problem of thermal expansion coefficients mismatch:

Incorporation of leucite crystals ($KAlSi_2O_6$) of much **higher** coefficient of thermal expansion **(CTE) than feldspathic glass** and having very similar refractive indices as the feldspathic glass – its presence **doesn´t increase opacity.**

Coefficient of thermal expansion :

feldspathic glass 8x10^{-6} K^{-1},

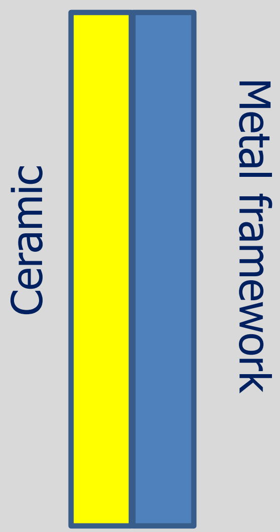
metals (**12-18**)x10^{-6} K^{-1},

leucite $KAlSi_2O_6$ (**20-26**x10^{-6})K^{-1}.

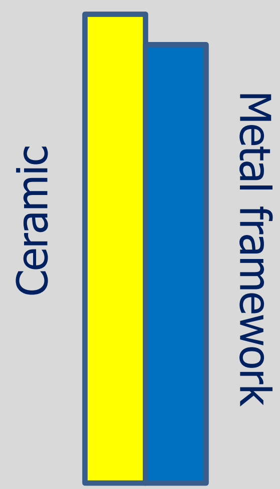
At **(17-25) wt. % of leucite crystals** CTE is **slightly lower, e.g.**: $14 \times 10^{-6}\ K^{-1}$, **than of metal substructure** with the coefficient of thermal expansion $14.5 \times 10^{-6}\ K^{-1}$.

Under these conditions the ceramic is in slight compression after cooling – resists cracks propagation in the ceramics.

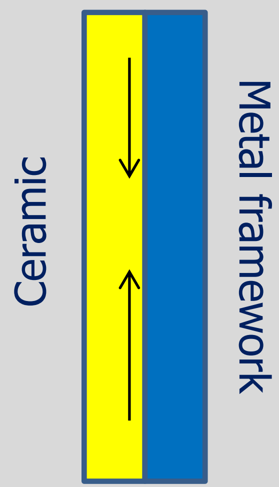
Dimensions on firing



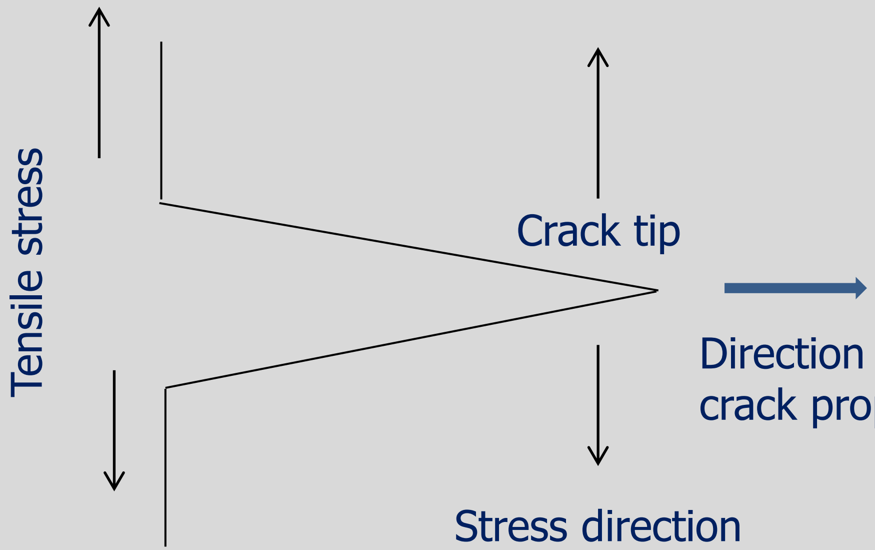
Dimensions during cooling. **No bond** between ceramic and the metal, **mismatch** between **their CTE** Metal shrinks more



Dimensions on cooling – Ceramic and the metal bonds, CTE optimized

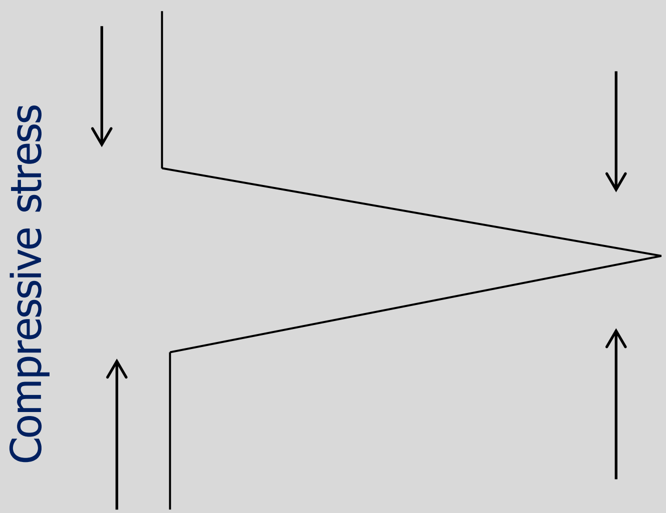


Crack initiated by flaws, voids, inhomogeneities under tensile stress opens, growths and propagates to a critical size – a catastrofic fracture



Ideal conditions for a brittle fracture

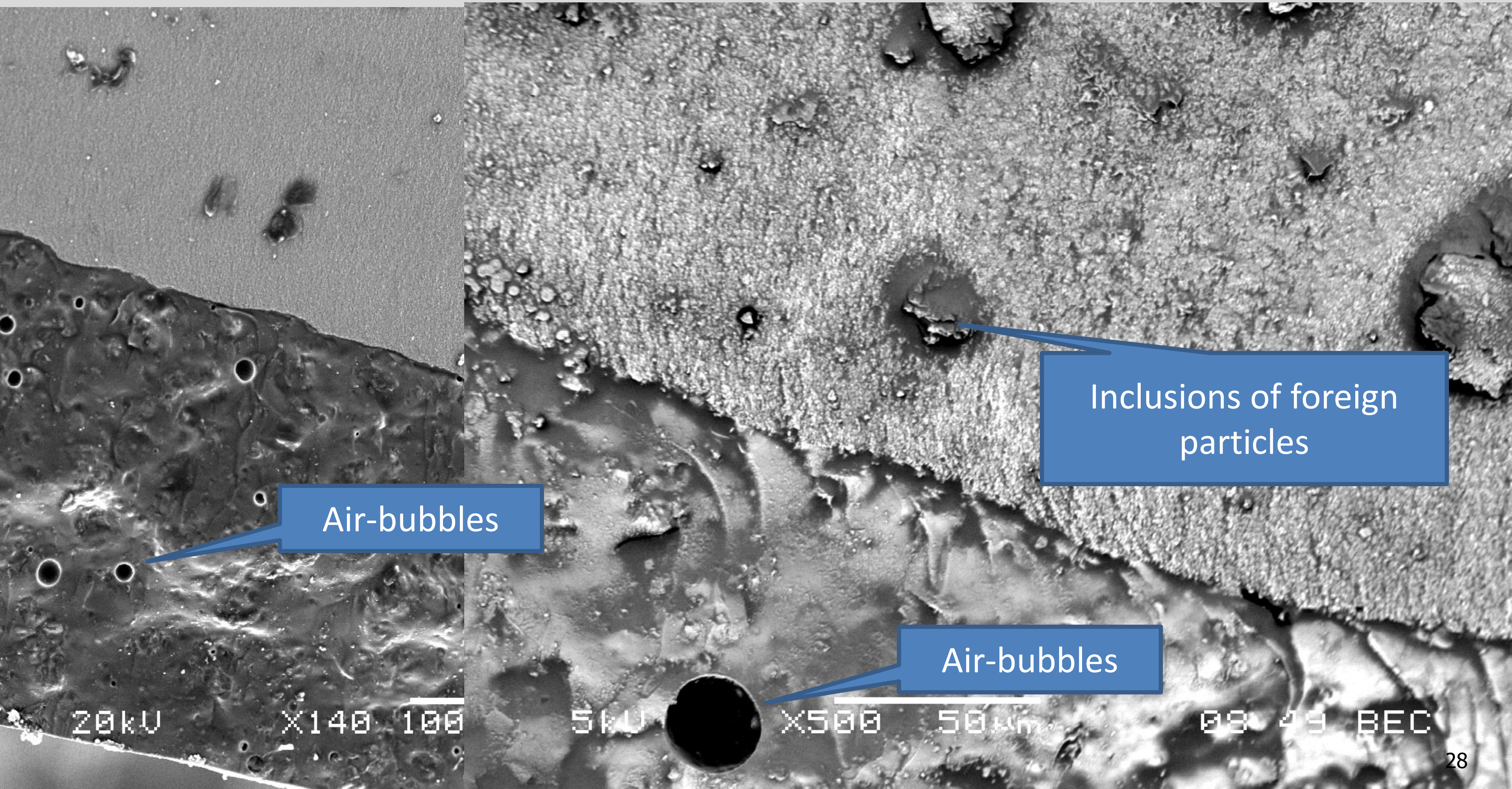
Crack under compressive strength – the crack is closed



Flaws, defects do not play a significant role – **increased flexural/tensile strength**

Problems of flaws or defects in the ceramics structure

Defects in the structure (voids/porosity, inclusions of contaminants, not properly sintered particles)



b) Highly filled ceramics

How to **improve mechanical resistance** of filled dental ceramics?

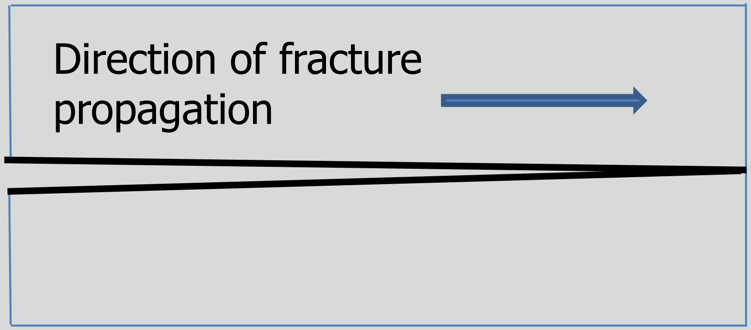
Posibilities:

1. To increase **percentage** of crystalline phase or use **fibrous** fillers which will retard cracks propagation,

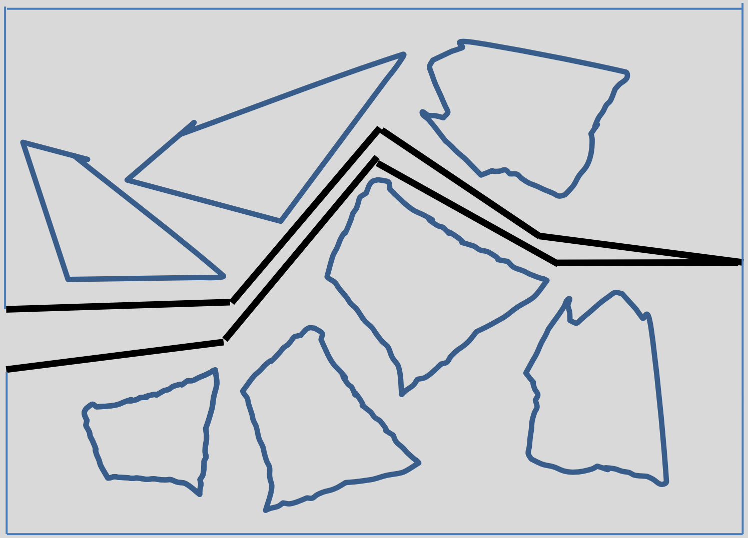
2. To interconect crystalline particles to stress resistant network.

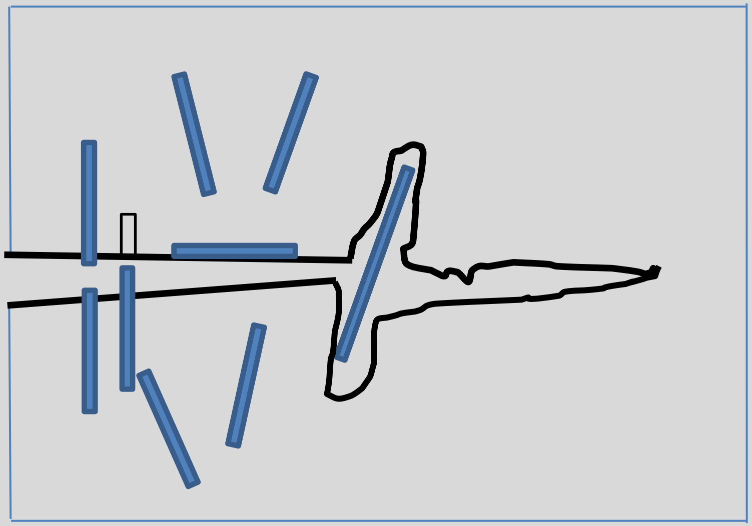
How to increase toughness of brittle materials

Homogeneous brittle material



Heterogeneous material reinforced with fillers





Examples of fracture toughness improvement: a) deflection of a fracture by filler particles (deflection toughening), b) energy consumption by fracture of reinforcing fibres or their debonding from a matrix

However:

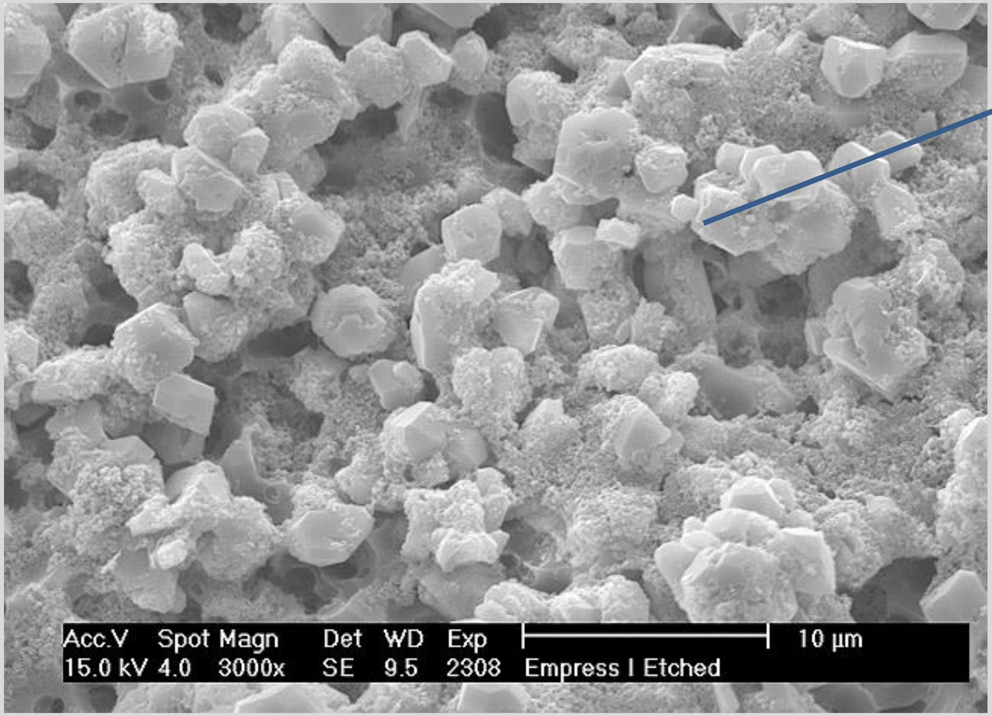
1. Too **high viscosity** of molten glass **acts against** the incorporation of increased amount of crystalline phase,

2. **Differences in refractive indices** of glass and crystalline phase **enlarge the opacity** of a ceramics.

Solution:

1. Highly filled leucite ceramics,
2. Lithium disilicate ceramics,
3. Infiltrated ceramics.

1. Highly filled leucite ceramics (40-55 wt. %) leucite – growth of leucite crystals is enhanced by their **controlled nucleation and crystallization** (ceraming) in a glassy feldspathic matrix

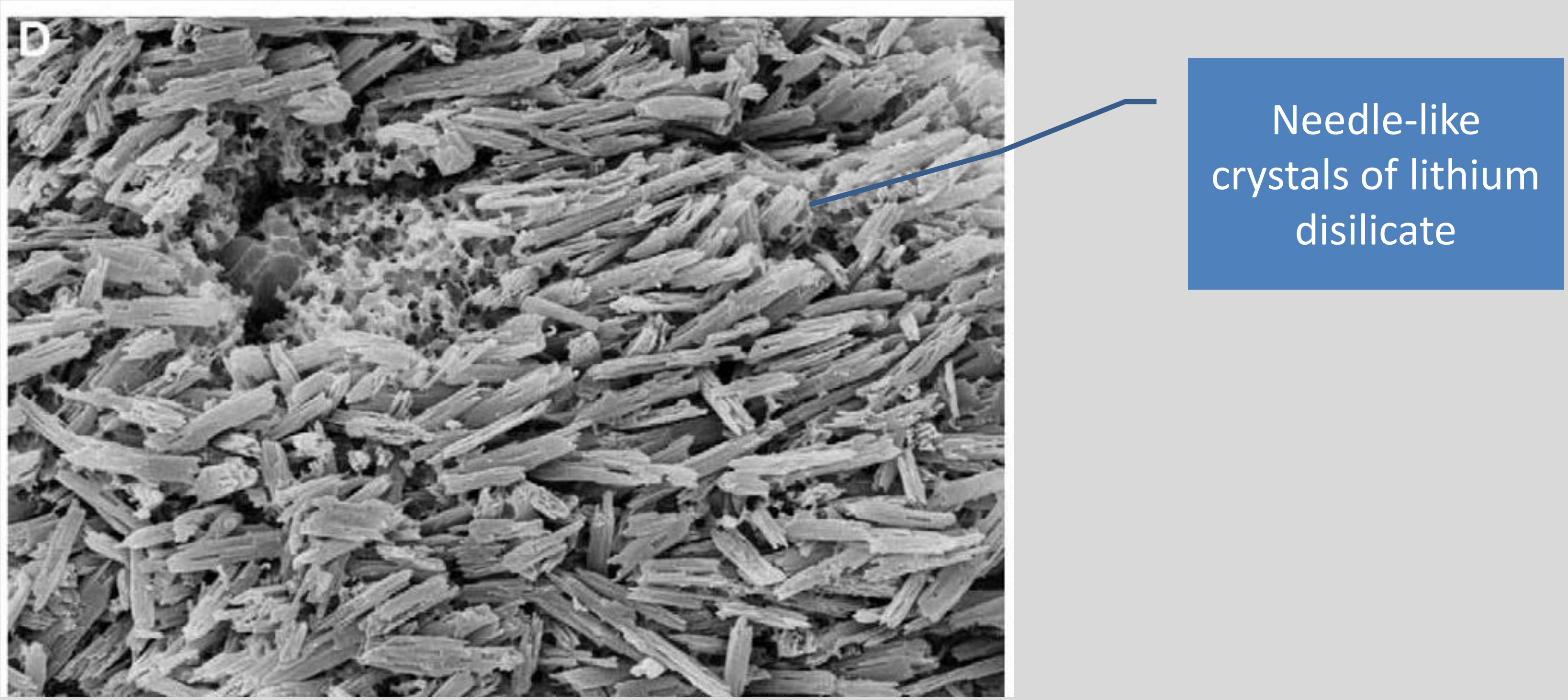


Leucite crystals reinforcing structure of feldspathic matrix

Microstructure of a leucite pressing ceramics after dissolution of its glassy matrix

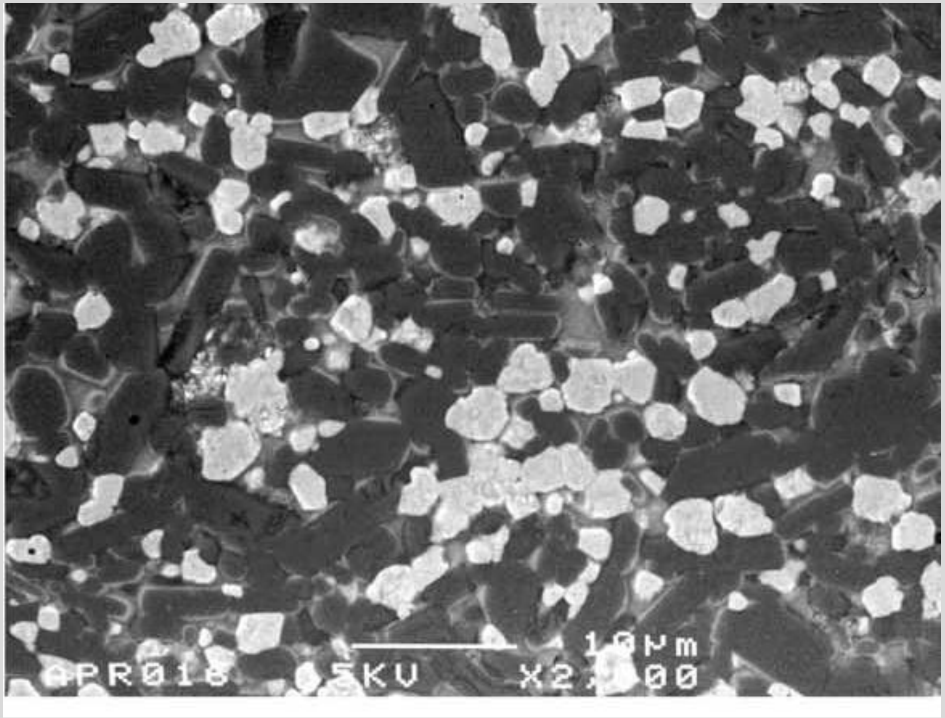
Russell Giordano; Edward A. McLaren, 2010

2. Lithium disilicate ceramics – needle-like crystals ($Li_2Si_2O_5$) filling app. 70 vol. % significantly improve strength and fracture toughness of the ceramics.



Microstructure of lithium disilicate ceramics. The matrix removed by its selective dissolution.
Borges, Sophr, de Goes, Sobrinho, Chan. 2003.

3. Infiltrated ceramics – sintered crystals of **Al_2O_3, Al_2O_3-ZrO_2** form mechanically strong network, voids among the crystals are infiltrated with a **low-viscosity glass (La in the case of alumina).**

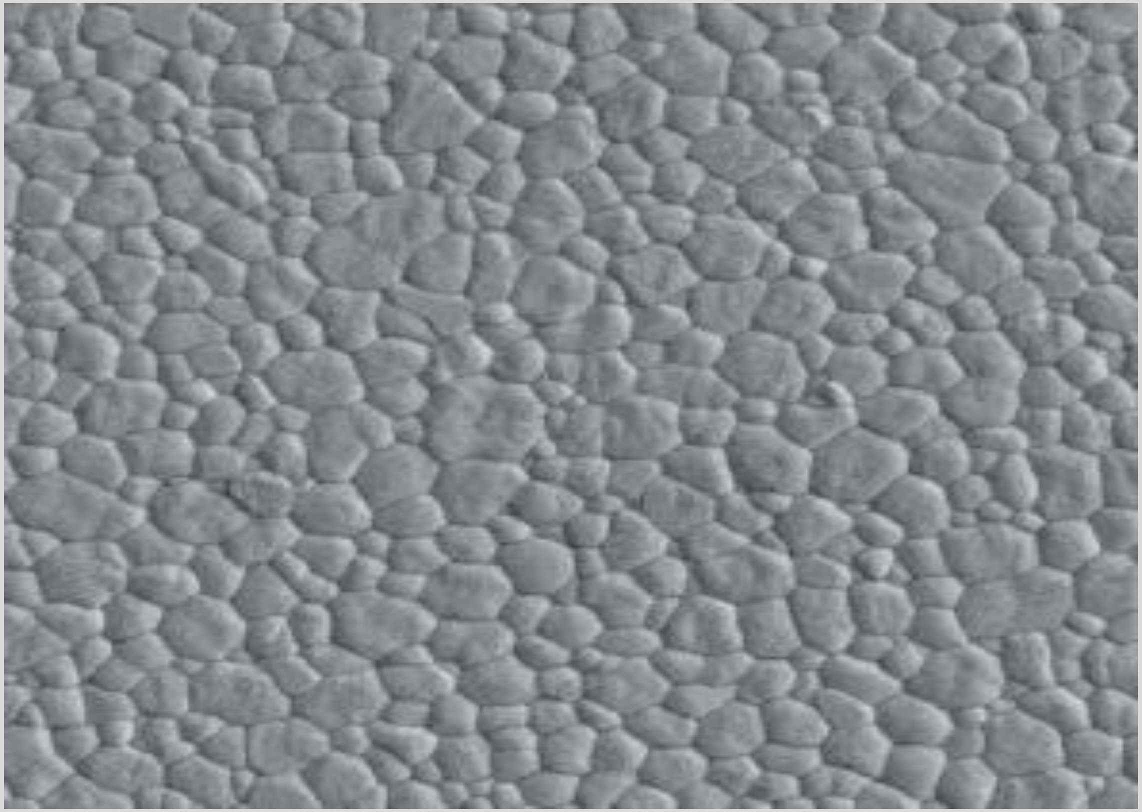


Crystals:
white - ZrO_2
dark - Al_2O_3

Microstructure of infiltrated Al_2O_3-ZrO_2 ceramics.
Guazzatoa, Albakrya, Ringerb, Swain, et al: 2004.

3. Polycrystalline ceramics

Even higher strength of a ceramics – to form a ceramic material consisting of **closely packed** ZrO_2, or Al_2O_3 crystals with a very low **content of a glassy phase** and free of porosity.



Microstructure of a zirconium ceramics.

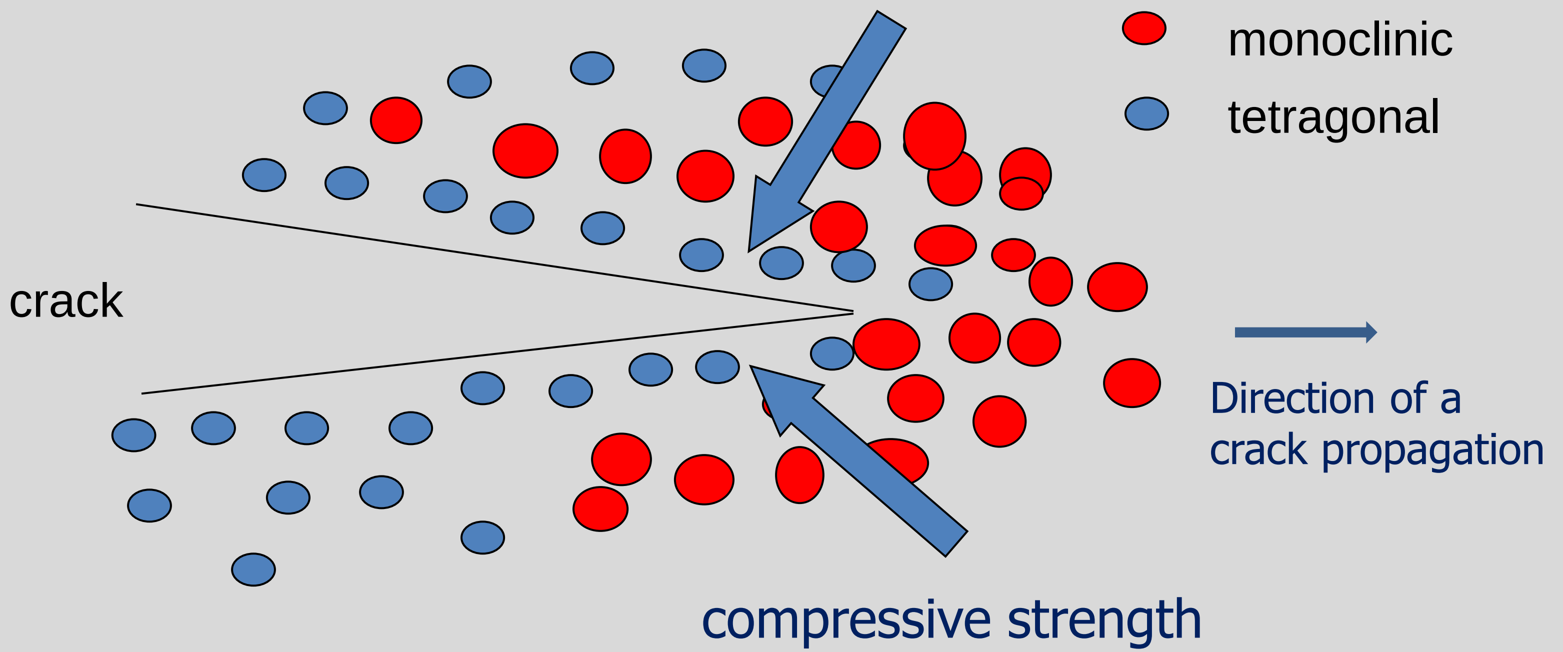
McLaren, Cao. 2009.

Zirconia ceramics – complicated crystal-line structure and its phase transformation under stress:

ZrO_2 – monoclinic (m) - up to 1170°C
tetragonal (t) - up to 2370°C
cubic - at higher temperature

During transformation **tetragonal – monoclinic** (t-m) the volume increases by app. **4.5 %** - **stabilization of cracks growth. t-modification is stabilized at the ambient temperature by Y, Mg, Ca, Ce oxides.**

Transformation t-m is also initiated by a **stress field** at the crack tip. It generates a compressive stress field which closes the cracks and and **stops their growth**.



Problem: transformation t-m is also initiated due to mechanical stresses acting during **grinding**, **air-abrasion** and at the presence of water (**low temperature aging**) leading to **decreased mechanical strength** of the ceramics.

Typical flexural strength and a fracture toughness of ceramics. Fracture toughness characterizes resistance of to brittle fracture (compare with metallic materials 60-150 [MPa.m$^{1/2}$]).

Ceramics		Flexural strength [MPa]	Fracture toughness [MPa.m$^{1/2}$]
Predominantly glassy ceramics	Feldspathic ceramics	60-80	<1.0
Moderately filled ceramics	Leucite ceramics	100-150	1.2
Highly filled ceramics	Lithium disilicate ceramics	300-500	3.0
	Infiltrated ceramics	300-600	4-5
Polycrystalline ceramics	Zirconium ceramics	800-1000	7-10

Guazzato, Albakry, Ringer, Swein. Strength, fracture toughness and microstructure of a selection of all-ceramic materials. Part I and II. Dental Materials 2004.