International Spring School on Forefront Alloys and Advanced Materials for Extreme Conditions

15 – 17 May 2017

Sardinia, Italy

Materials consolidation by high pressure in solid and liquid medium for extreme conditions

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Engineer- CNRS

« Crystal Growth, High pressure, Sintering, Thin Films »

+

« Metallurgy and functional materials »

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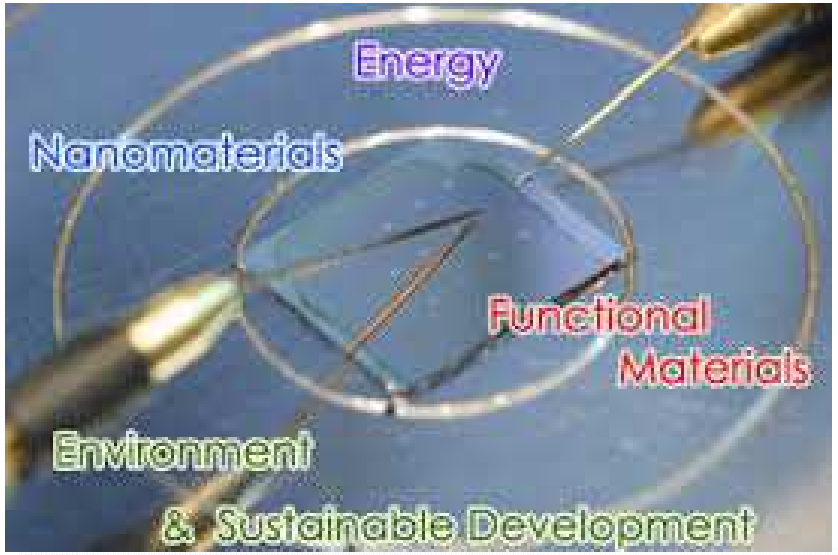

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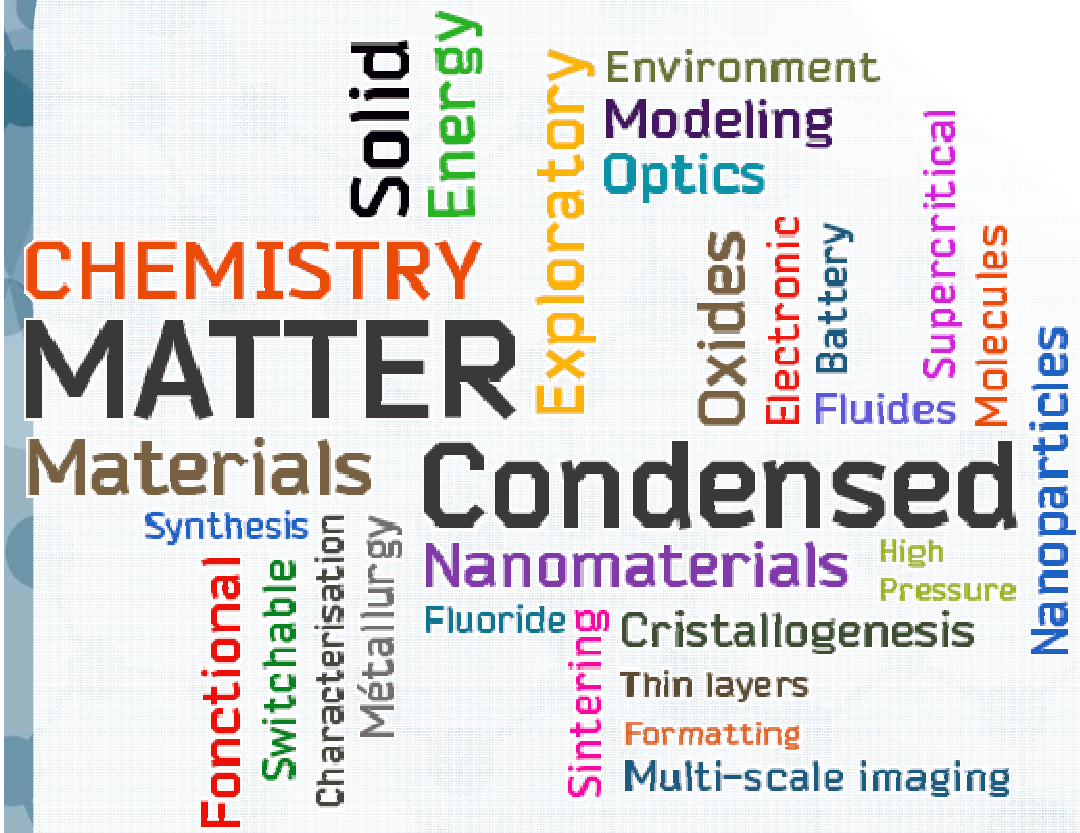
Solid
Energy
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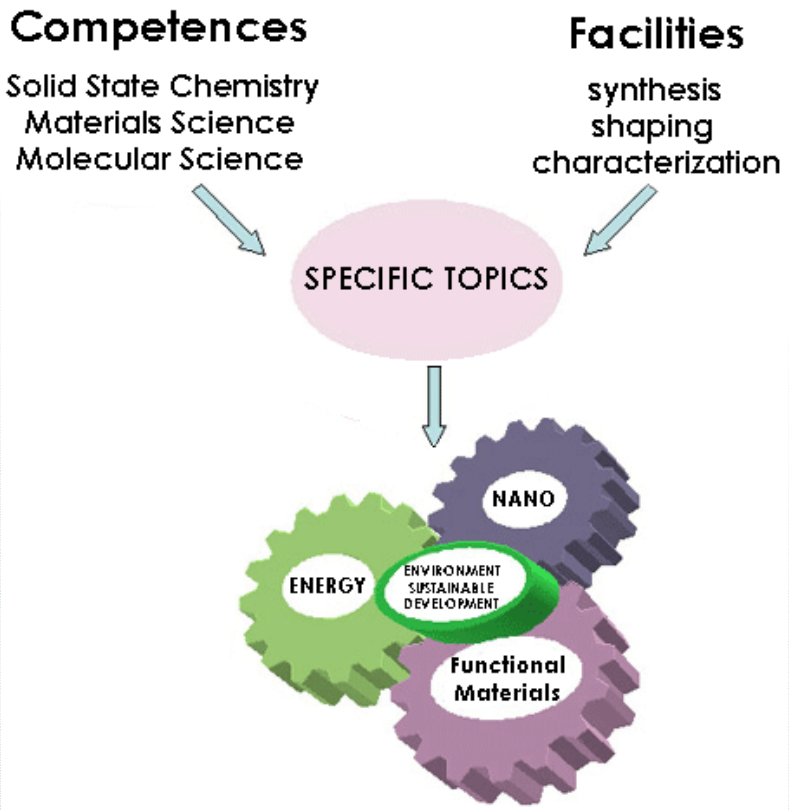
Oxides
Electronic
Battery
Supercritical
Molecules
Fluides
Nanoparticles
CHEMISTRY
MATTER
Materials
Condensed
Synthesis
Nanomaterials
High
Pressure
Fluoride
Cristallogenesis
Thin layers
Formatting
Multi-scale imaging
Sintering
Fonctional
Switchable
Characterisation
Métallurgy


Competences
Solid State Chemistry
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Molecular Science
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shaping
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NANO
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CELLULE PROJETS

GROUPES DE RECHERCHE

GROUPE 1
Oxydes et électro-céramiques architecturées pour l'énergie et l'électronique

GROUPE 2
Energie : matériaux et batteries

GROUPE 3
Chimie et photonique des matériaux oxydes et fluorures

GROUPE 4
Métallurgie et matériaux fonctionnels

GROUPE 5
Chimie des nanomatériaux

GROUPE 6
Molécules et matériaux commutables

GROUPE 7
Fluides supercritiques

CENTRE DE RESSOURCES

Cristallogenèse, hautes pressions, frittage, couches minces et interfaces

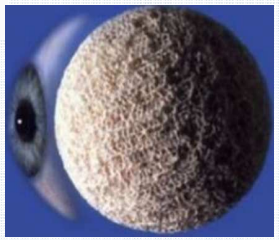
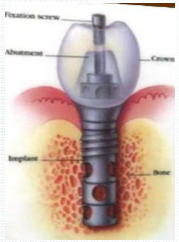
AXES TRANSVERSES

SERVICES COLLECTIFS

Commission des services collectifs

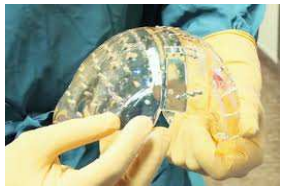
- Diffraction des rayons X
- Analyses chimiques/ Mesures thermiques
- Granulométrie/BET
- Bibliothèque/ Documentation
- Atelier de mécanique
- Instrumentation/ Electronique
- Mesures optiques
- Mesures électriques
- Mesures magnétiques
- Spectroscopies de résonance Mössbauer/RMN/RPE
- Distribution des fluides spéciaux (liquides cryogéniques, gaz et solvants) gestion des déchets

Biocéramics



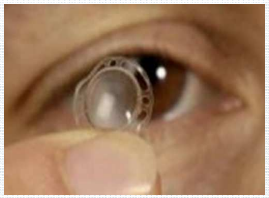










Materials and devices for various medical applications

Nose cone- heat seeking missiles

Night vision devices

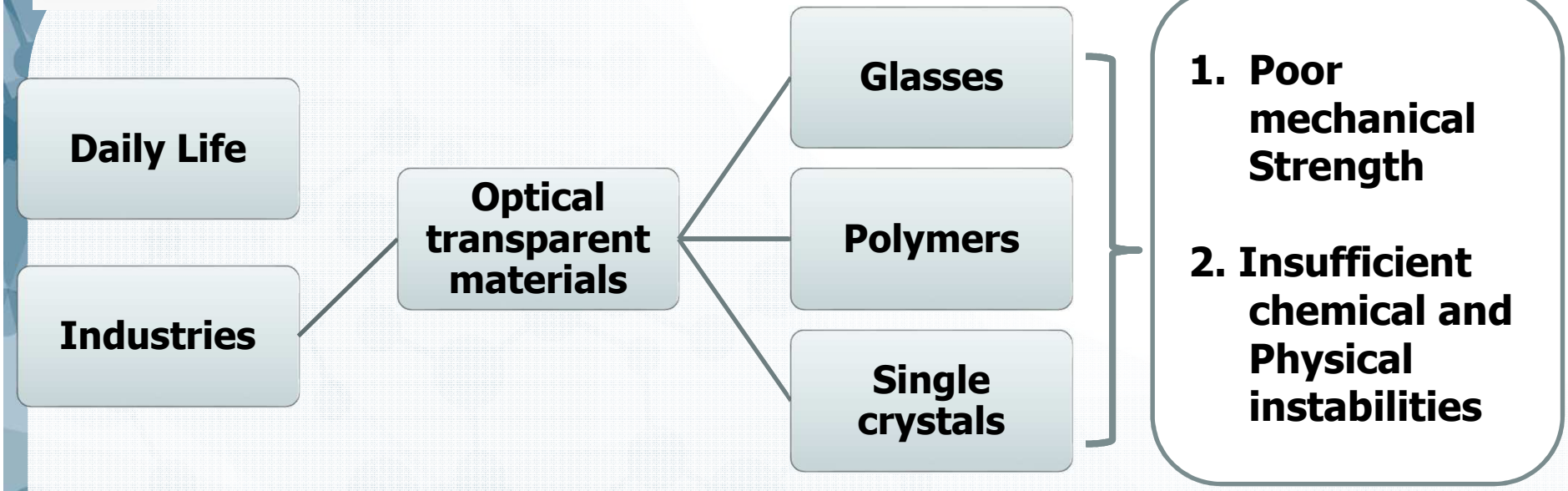
Laser cutting tools

Transparent ceramics applications

Armor/ window

Bullet shields

1. Introduction on optical transparent materials

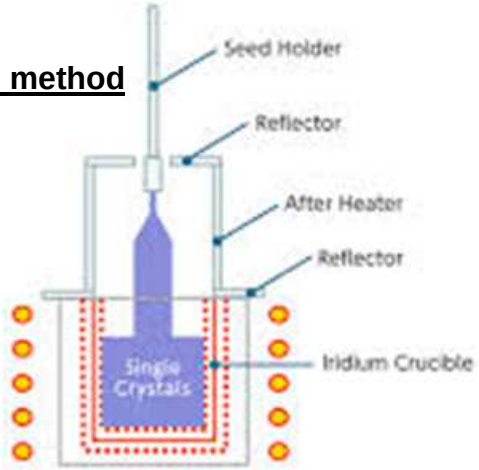


- Conventional transparent materials have a strong absorption in the IR range and usually possess melting points < 600°C- inhibits usage at higher temperatures

- Hence it was essential to develop new transparent materials that can be used for applications operating in harsh and extreme conditions

Conventional crystal growth techniques

Czochralski method



Bridgman method

1. Requires melting
2. May induce decomposition/phase changes in some compositions
3. Lengthy experiments

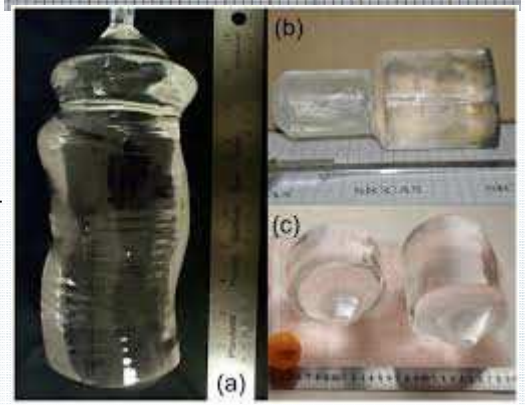
Expensive components

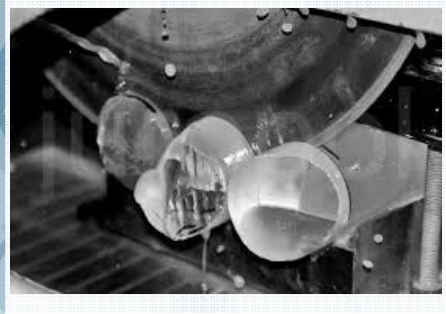
Iridium and Platinum crucibles

→ **Grown crystals are restricted by crucibles**

1. Grown crystals are prone to defects and thermal stresses
2. Inhomogenous/ segregation of dopants
3. Grown crystal predetermined by its crystalline structure

←





→

1. Additional cutting and processing
Required for fabrication of devices in required shapes
2. Wastage of material during cutting and polishing

Introduction on optical transparent materials

Traditionally used single crystals		
Sapphire (Al_2O_3) IR Windows	YAG ($Y_3Al_5O_{12}$) Lasers	PZN-PT ($PbZn_{1/3}Nb_{2/3}O_3$-$PbTiO_3$) Electro-optics

Growth of single crystals

- Sophisticated facilities
- Time consuming
- Expensive

Additional drawbacks of single crystals:

1. Shapes determined by lattice structures
2. Has shape of processing container and processing conditions
3. Machining of single crystals to meet specific applications is a difficult task
4. Difficulty of large scale production
5. Mechanical brittleness of some materials

Could transparent ceramics be advantageous over single crystals?

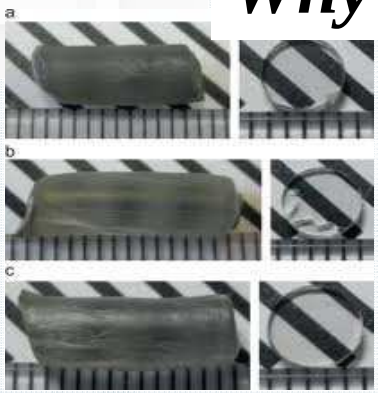
Advantages of transparent ceramics over single crystals

- ❑ Cost-effectiveness
- ❑ Large scale production
- ❑ Feasibility of shape controlling
- ❑ Better Mechanical properties

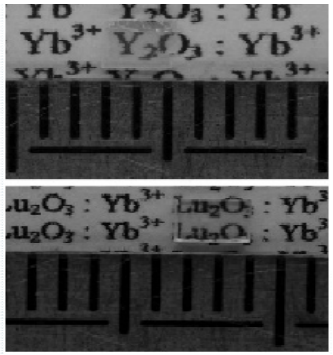
Ceramics: Densified polycrystalline grains with grain boundaries

Vital difference of single crystals and ceramics are various sites to scatter light

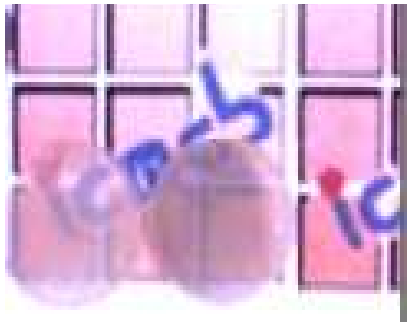
Why transparent ceramics over single crystals?



YAG crystal grown @ 1950°C

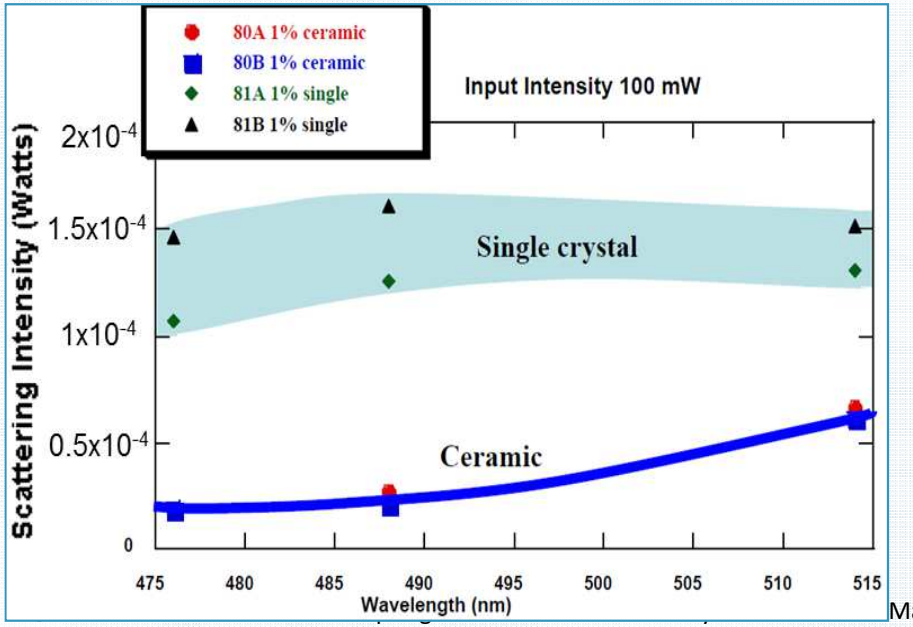


Sesquioxide crystal grown @ 1200°C by flux method

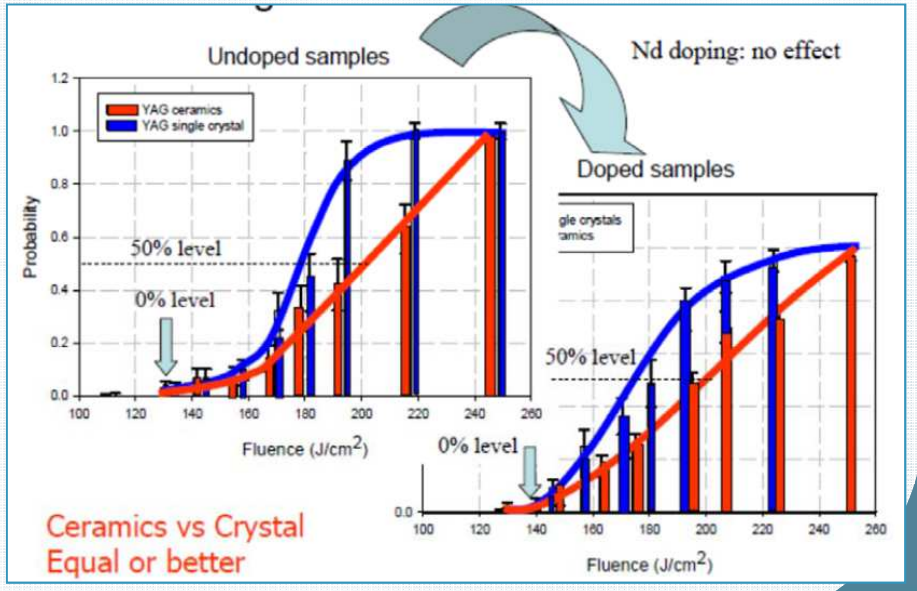


Yb:Lu_2O_3 ceramics -1400°C- 20 min

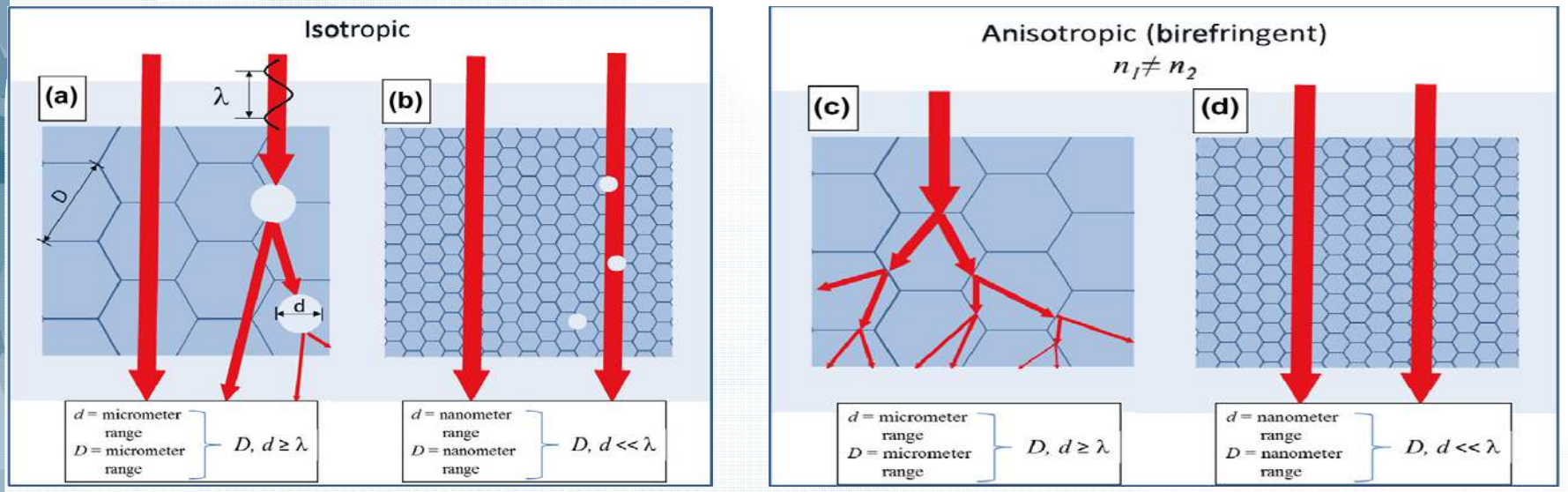
Demonstration of lower scattering loss in ceramic Nd:YAG



Laser damage threshold



Role of microstructure on optical properties

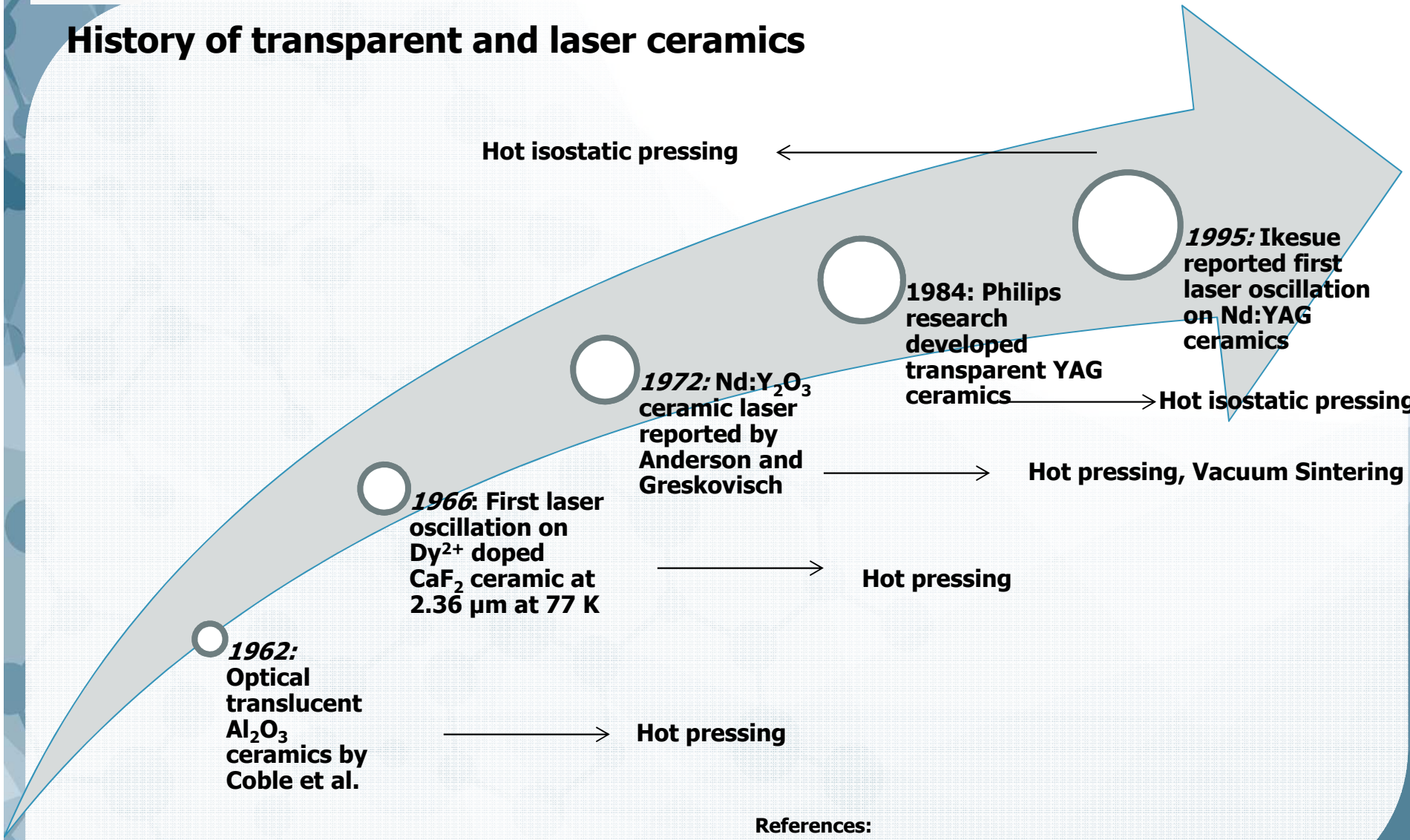


Schematic representations of the interaction of light with polycrystalline ceramics.

- ***Materials with cubic symmetry- refractive index 'n' similar in all directions- Isotropic***
  - **Isotropic material- Pore scattering efficiency depends on pore size**
    - **pore size ~ µm (i.e., Comparable to wavelength of light)- High scattering**
    - **pore size < 100 nm, Interaction with visible light is minimal & optical transmittance increases**

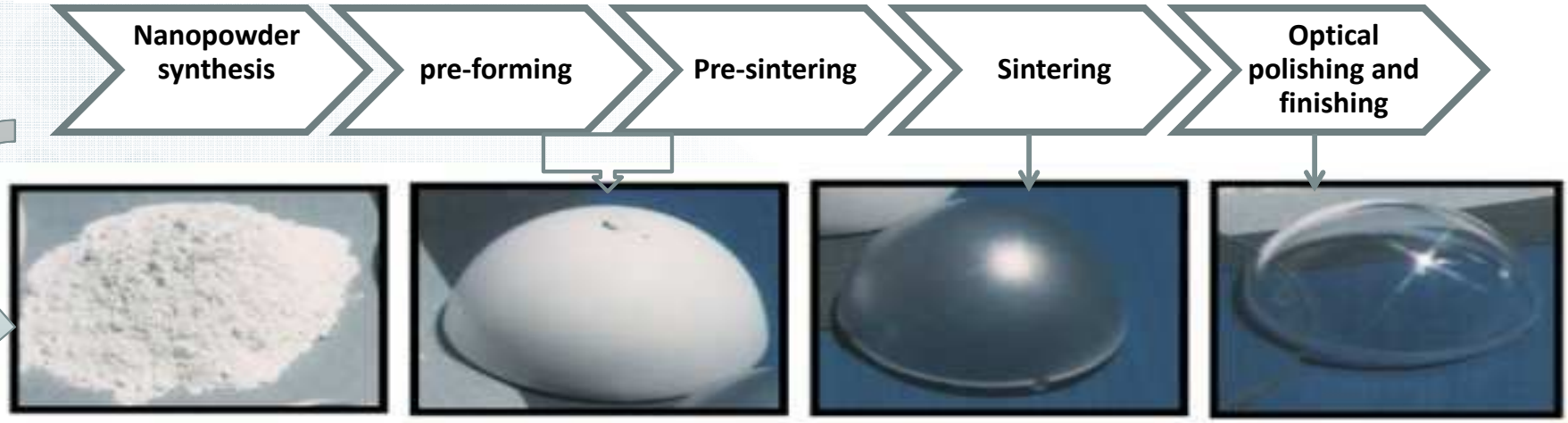
- ***Materials with non-cubic symmetry- anisotropic/ birefringent***
  - **Grain size plays a more significant role**
    - **Light is scattered at each grain boundary**
    - **A strategy to improve transparency of an anisotropic material is to ensure nanometric grain sizes**

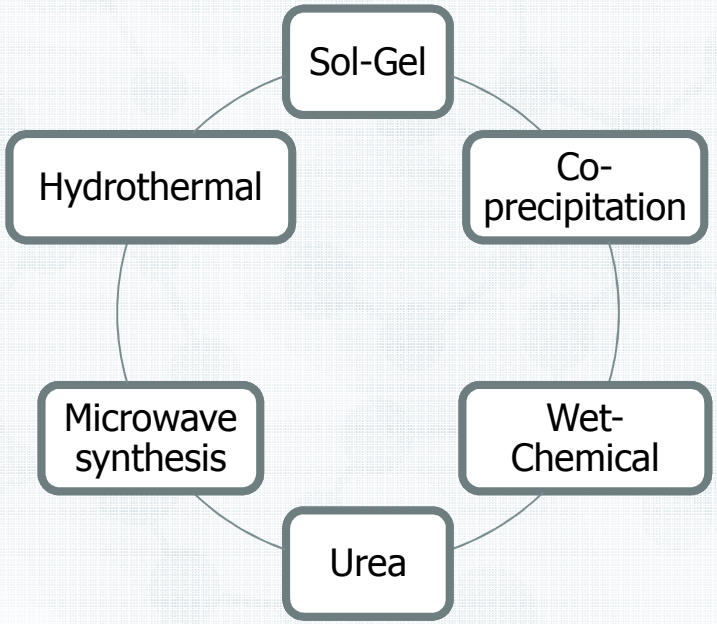
History of transparent and laser ceramics



References:
Carnall, E ., et al Mater. Sci. Res., Vol. 3, pp. 165&173, 1966.
Coble, R.L., 1961, *J. Appl. Phys., vol. 32 (5), pp. 787-99.*

Essential steps involved in fabrication of transparent ceramics





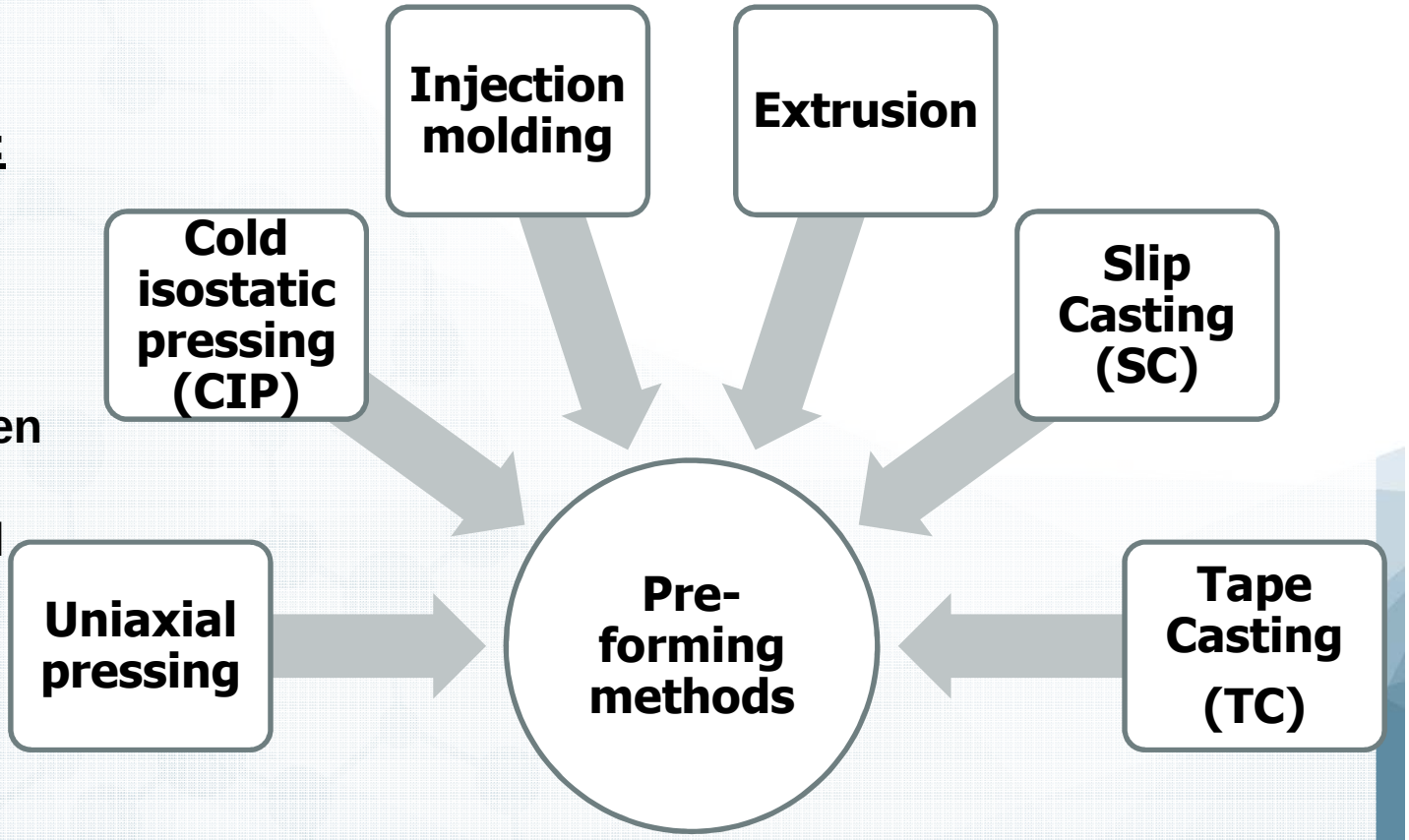
Various methods of nanopowder syntheses used for transparent ceramics

1. **Nanopowders of the range 20 - 200 nm**
2. **Non-aggromelation of nanopowders**
3. **Free flowing powder**
4. **High purity**

Pre-forming methods used for fabrication of transparent ceramics

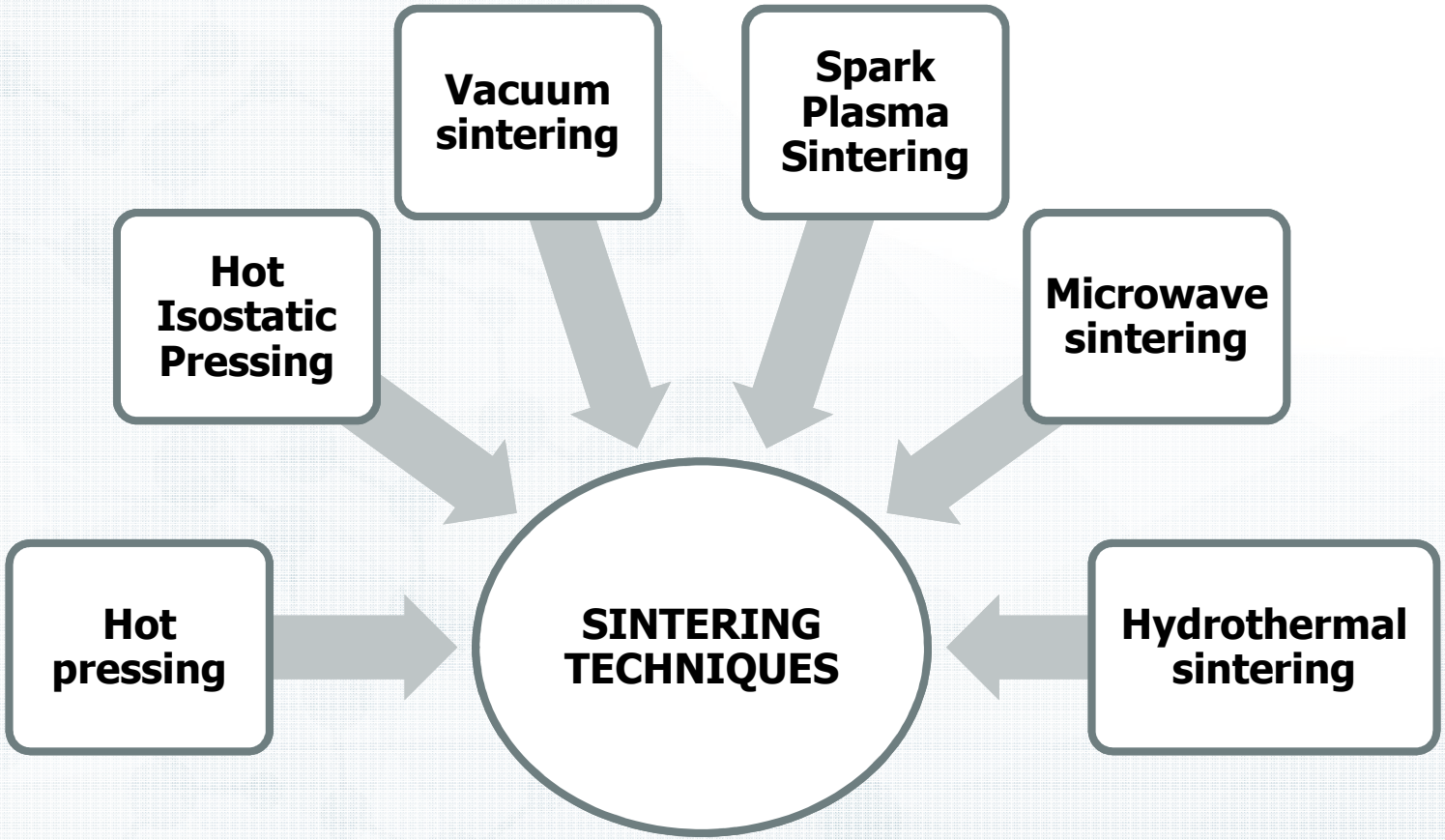
Advantages of pre-forming methods:

1. No pores formation,
2. Uniform/ homogenous green body
3. Easy pore removal

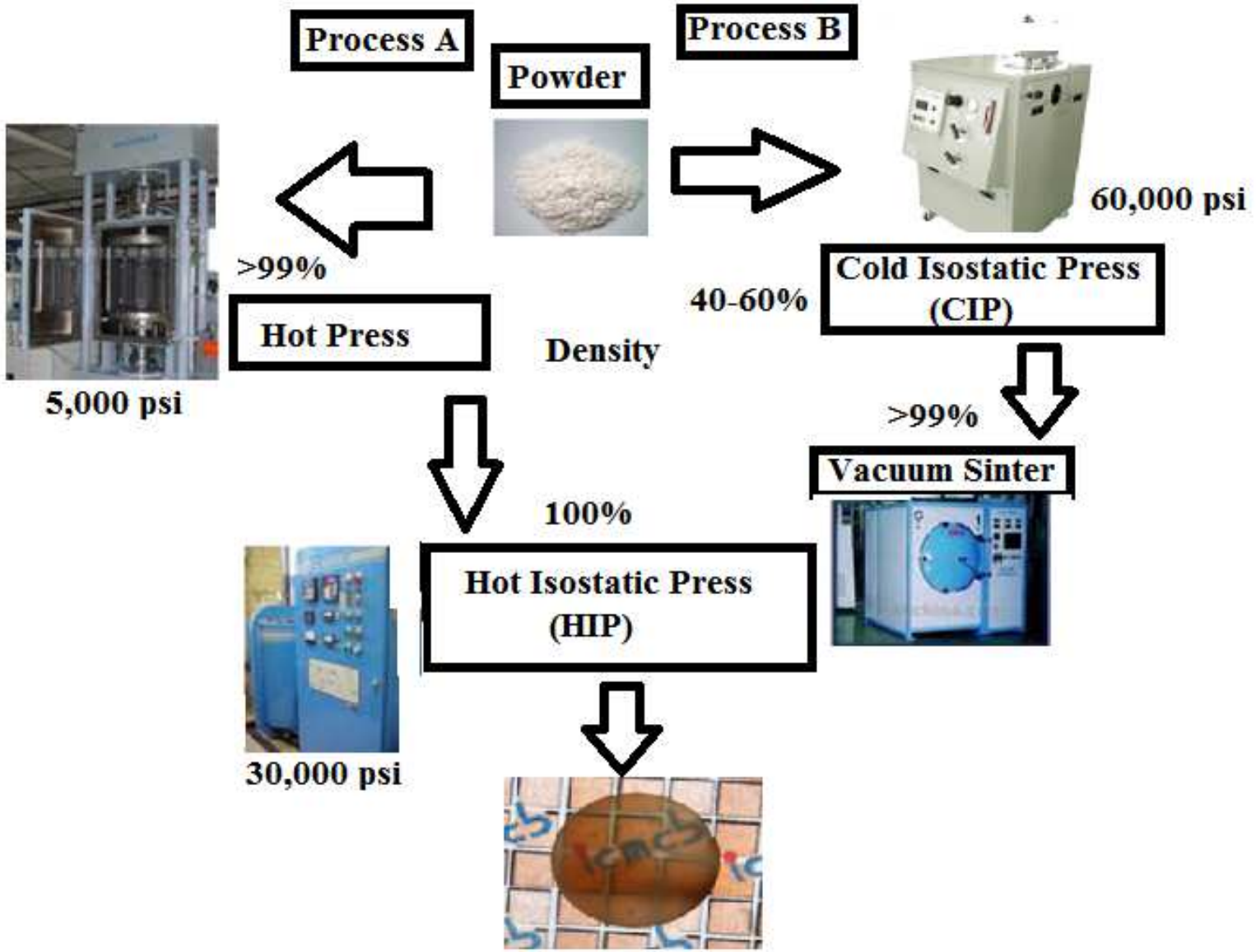


MOST FREQUENTLY USED PRE-FORMING METHODS : CIP, SC and TC.

Different sintering techniques employed to obtain transparent ceramics



General procedure for fabrication of transparent ceramics



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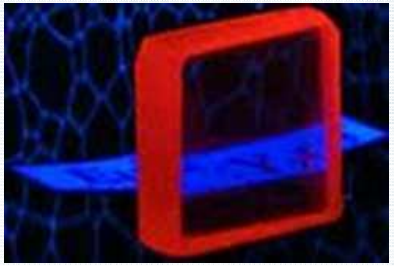
Arc tube lamp

Electro-optics

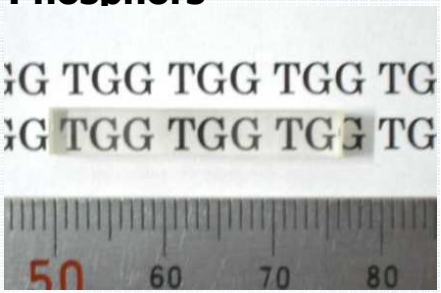
Laser ceramics



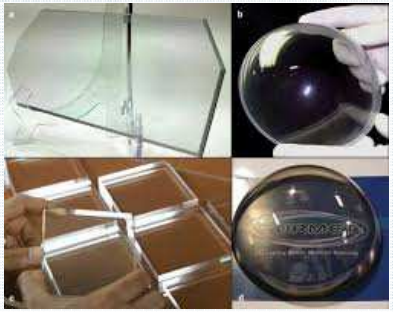
Scintillators and Phosphors

Applications of transparent ceramics

Armor applications



Faraday rotators

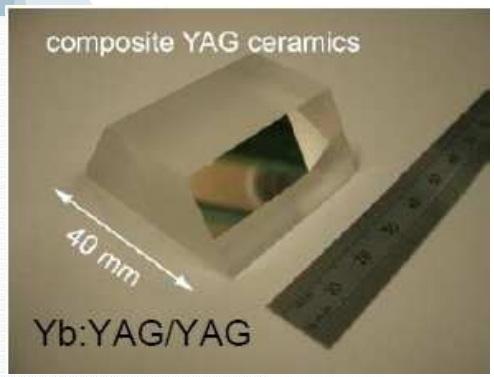


Domes and windows applications

Infrared optic and lens

Small optical parts with complex structure

Composite material with different gradients of doping in Nd:Yb:YAG



Yb:YAG composite ceramic laser with a total reflection active mirror

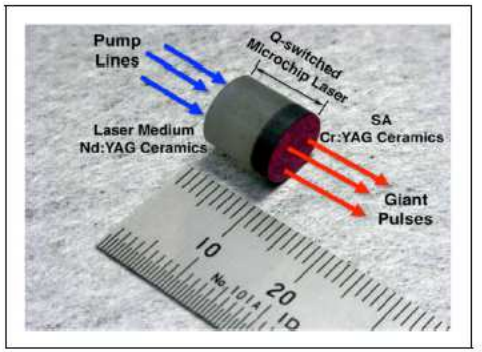
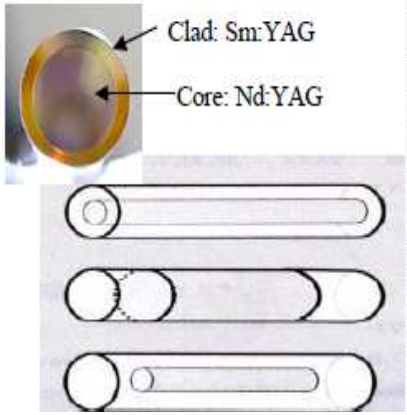


Photo of monolithic Nd:YAG/ Cr: YAG Composite ceramic chip

Devices realized with transparent ceramics

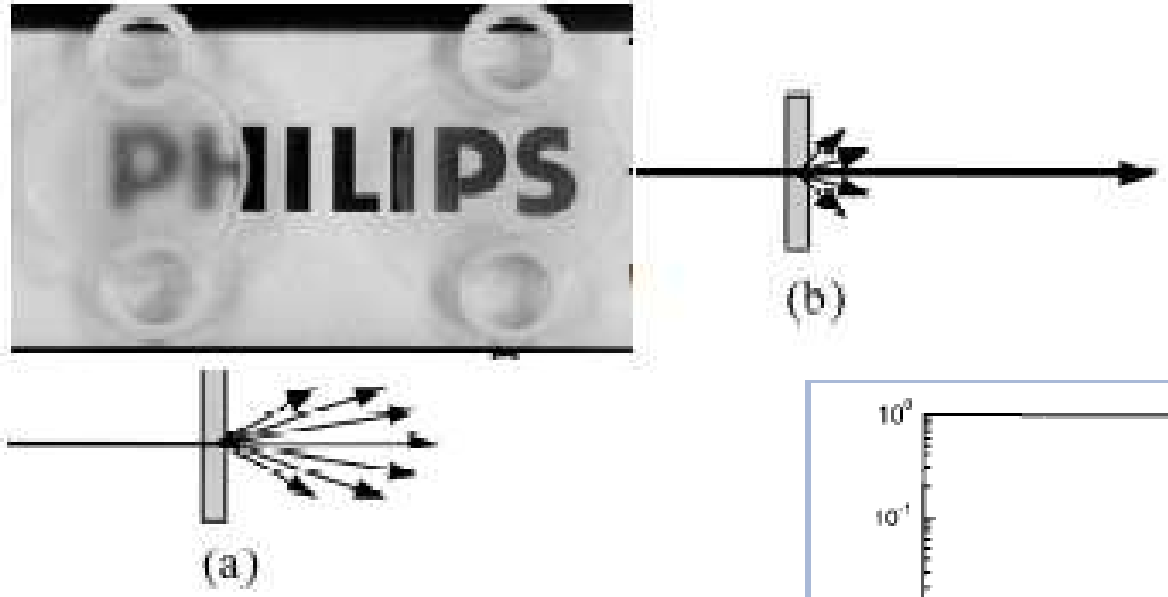


Composite Ceramic laser

Plate bonding – Composite materials

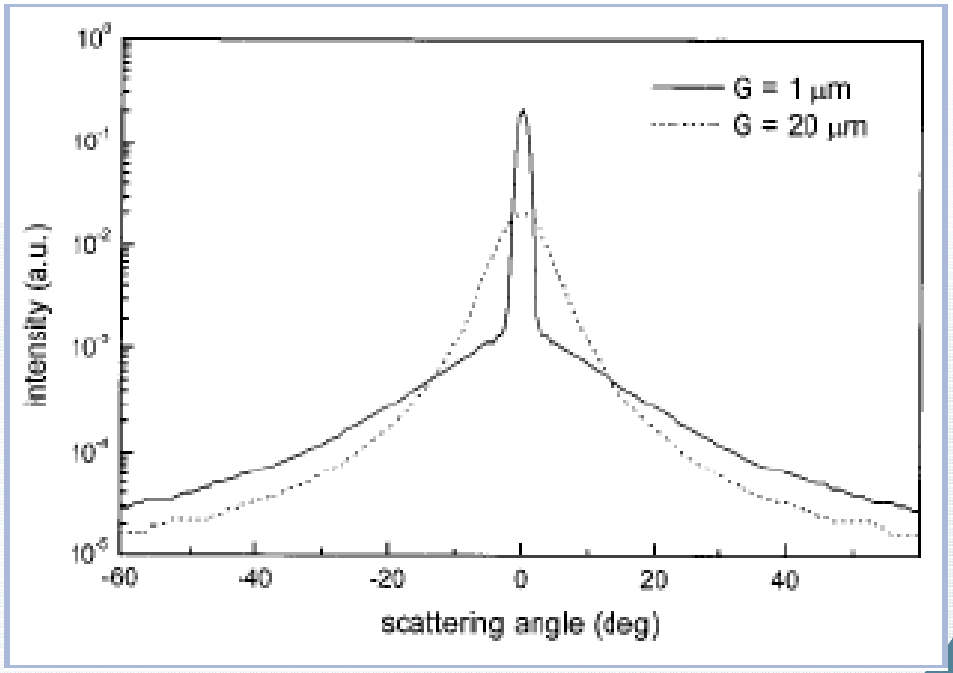
Photo of the composite, all ceramics passively Q-switched Nd: YAG/Cr:YAG with three beam output

Dependence of transparency of grain size

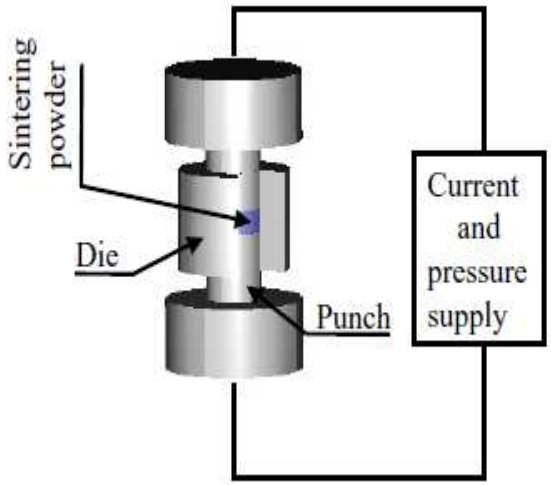


Optical transparency are highly influenced by grain size.

Large grain sizes create diffuse/ multi scattering.



SPARK PLASMA SINTERING (SPS)

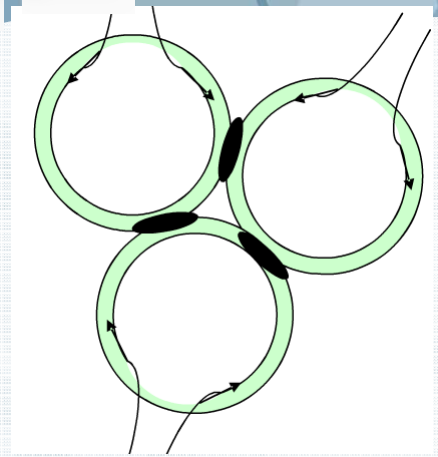


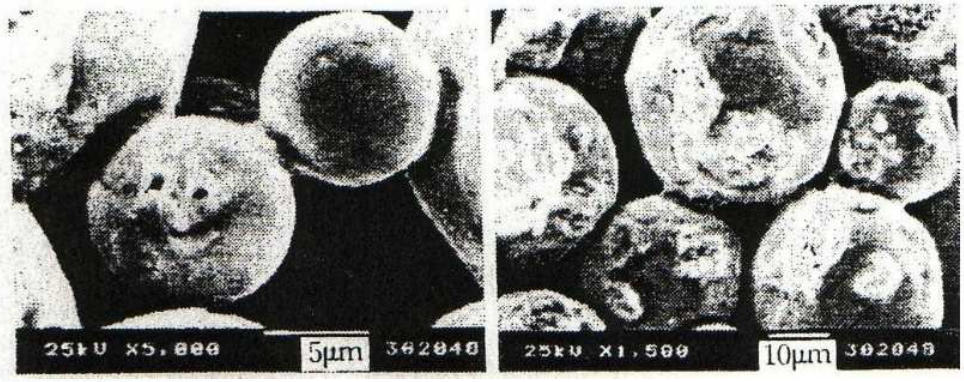
- Method developed to obtain fully dense and fine-grained transparent ceramics at low temperatures within short duration of time
- Also known as field assisted sintering or pulsed electric current sintering.
- SPS uses a high density current flux through the sample and the die to cause Joule heating within the sample.
- High heating rate is another important highlight of SPS.

Disadvantages: Carbon contamination from the die set-up

Few examples of transparent ceramics fabricated by SPS:
Rare earth doped Sesquioxides, Garnet, YAG, Al_2O_3, ZnO, ZrO_2, PMN-PT

Detailed mechanisms involved in SPS is presented in the preceding slides



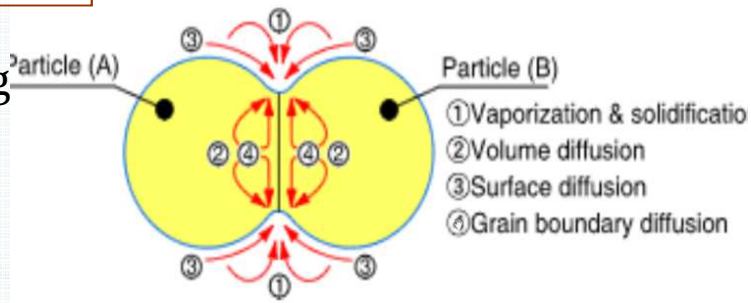


Neck formation due to localized heating

Groza et al., UC Davis

Joule's heating: localized temperature increment → Sintering activated

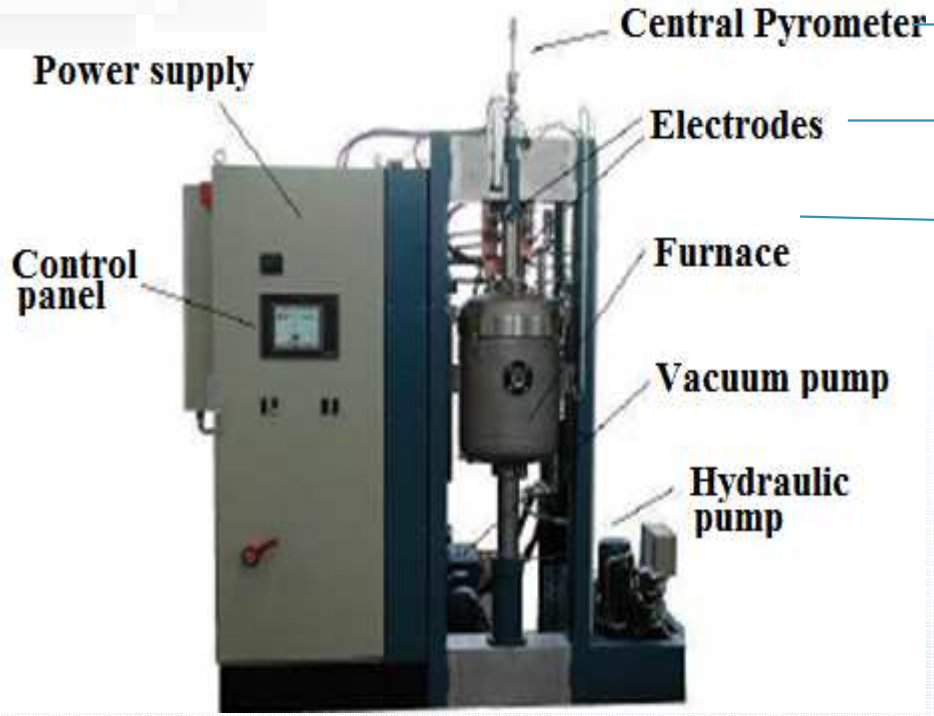
Three mechanisms that contributes to spark plasma sintering
(a) Activation of powder particles by pulsed current
(b) Resistance sintering
(c) Pressure application



❑ In the presence of Pressure and electric current, localized necking occurs faster due to Joule heating.

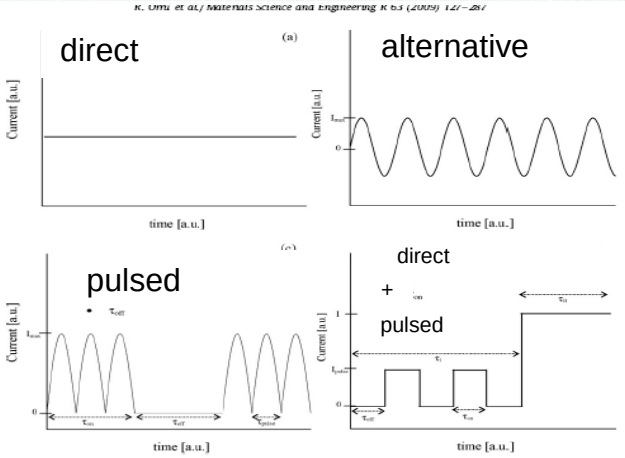
❑ Consequently temperature raises very fast (faster than conventional sintering and hot pressing) and the densification is completed within few minutes.

hot pressing / Spark plasma sintering



hot pressing

Spark plasma sintering

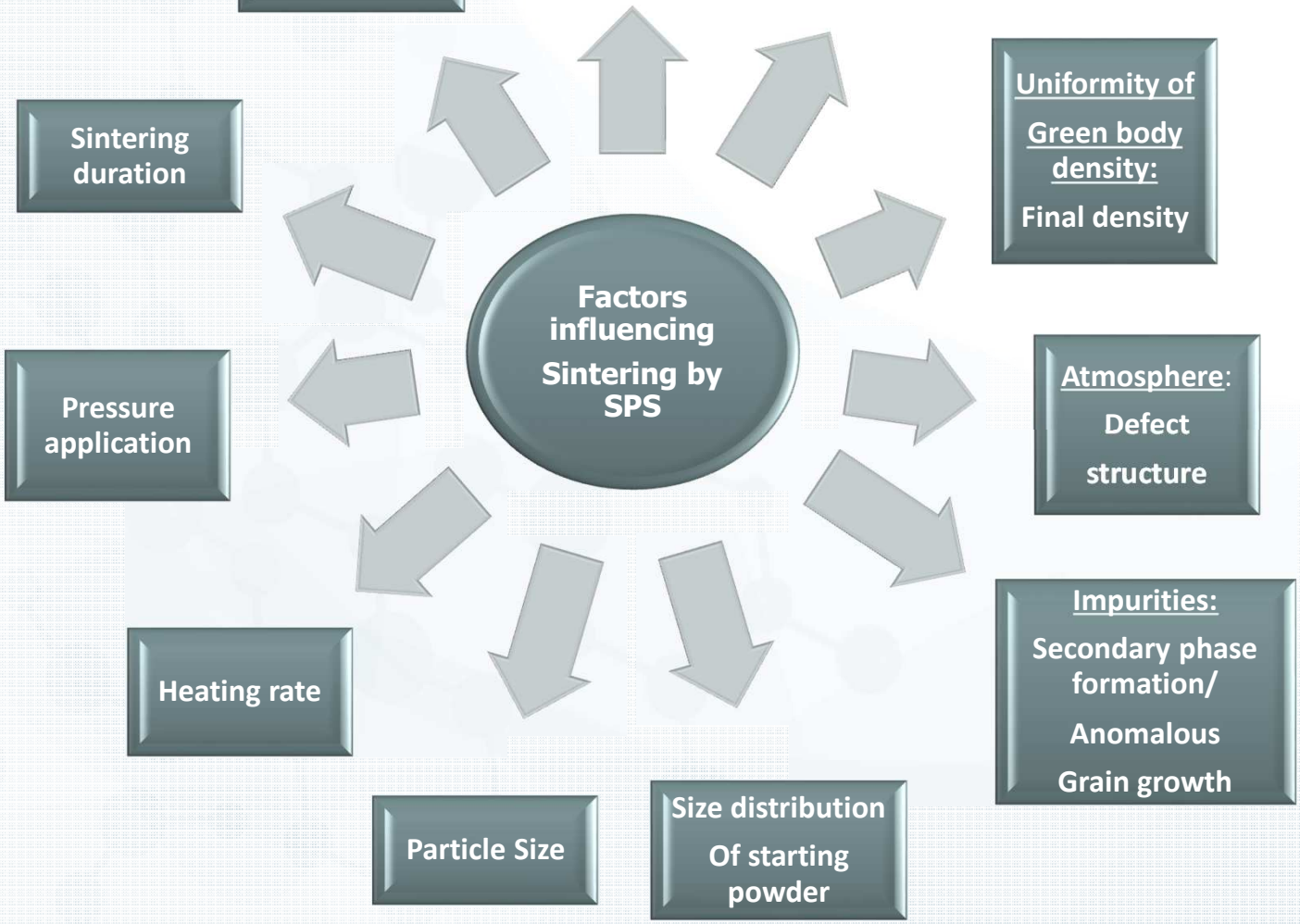


Main differences:

1. Heating modes and heating rates

- ❑ **SPS: Joule effect -→ 1000°C/min (250°C/min)**
- ❑ **Hot pressing: a) Inductive heating: 150°C/min (100°C/min)**
  b) Resistive heating: 50°C/min (10°C/min)

2. Pulses (3.3ms) or continuous current


Factors influencing Sintering by SPS
Temperature: Densification, sintering rate
Green density: Final density of sintered body
Uniformity of Green body density: Final density
Atmosphere: Defect structure
Impurities: Secondary phase formation/ Anomalous Grain growth
Size distribution Of starting powder
Particle Size
Heating rate
Pressure application
Sintering duration
Pulses (ON/OFF) during heating/ cooling

FEW EXAMPLES FROM RESEARCH WORK ON TRANSPARENT CERAMICS BY SPS AT ICMCB

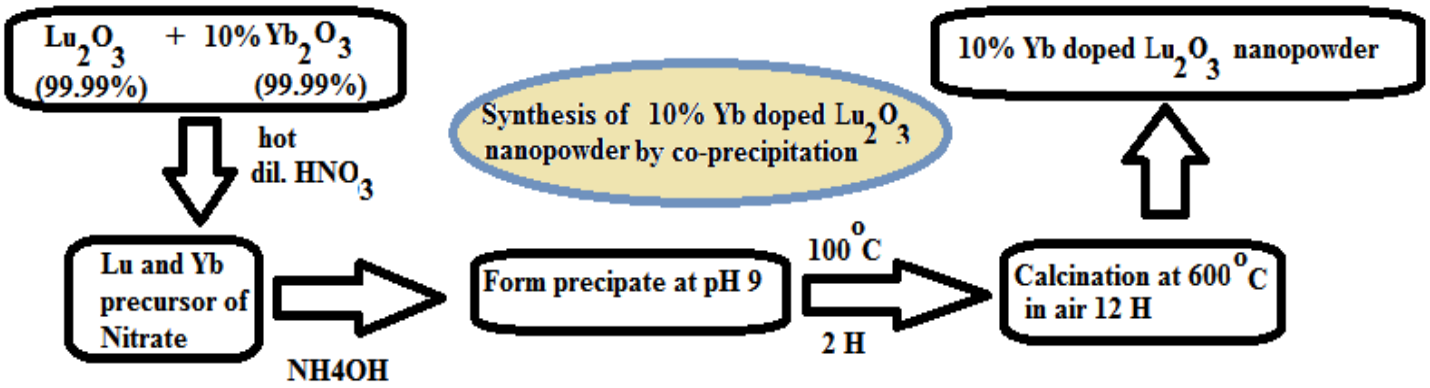
1. Cubic / isotropic Crystalline structured materials: Sesquioxides

2. Non cubic / anisotropic Crystalline structured materials: Alumina

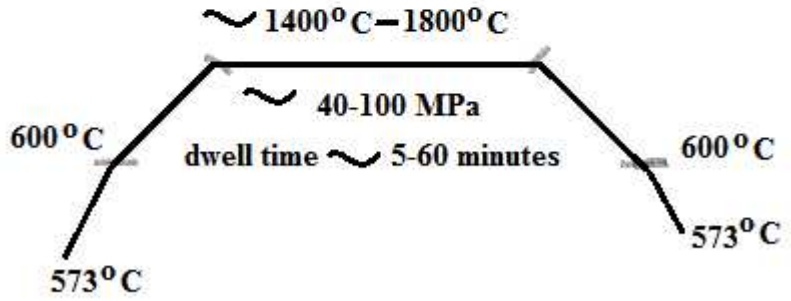
How the sintered parameters could help us to control the microstructure and then the final properties

Cubic / isotropic Crystalline structured materials

10% Yb doped Lu_2O_3 – Cubic system- our experimental studies

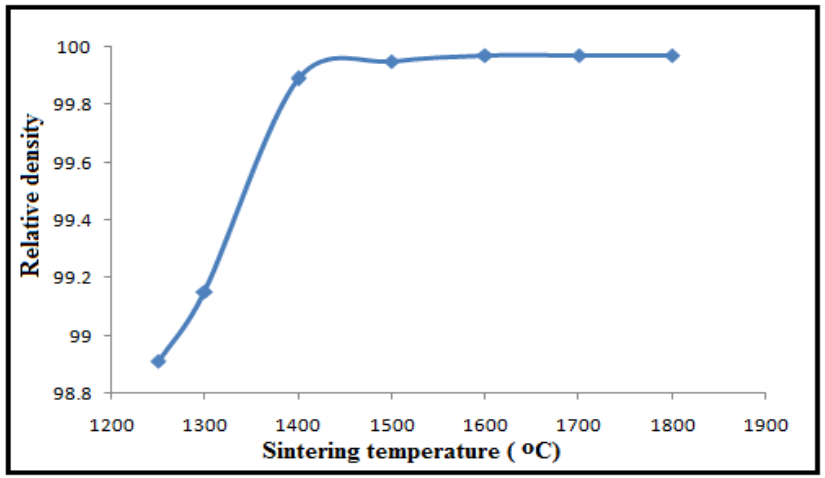


Dr. Sinter lab Spark Plasma Sintering system,
model SPS-511S/SPS-515S
Vacuum= 10^-3 torr
Pulse sequence for SPS
applied voltage = 12: 2
Heating rate & cooling rate = 5 °C/minute- 200 °C/minute
Pressure= 40 -100 MPa
Dwell time= 5- 60 minutes



Cubic / isotropic Crystalline structured materials

Dependence of relative density on sintering temperature at P_s = 100 MPa, t_s = 5 min



❑ **Effect of Pressure**

➢ Sintering curves of YLO bodies strongly dependent on the preload pressure (P_o) :
1) by applying constant maximum pressure (P_s) in the entire process. 2) by applying P_s only during the dwell time (t_s): best result

❑ **Effect of sintering temperature**

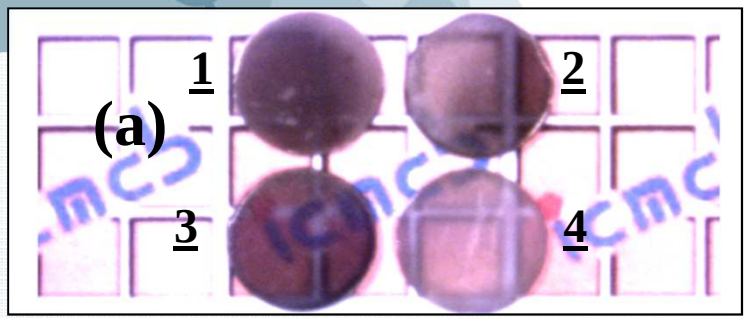
➢ **Ma**ximum densification was reached at 1350°C, above this temperature, the densification increases very little

❑ **Effect of heating rate**

➢ **A**verage size of the grain increases rapidly with increasing heating rate (R_H), leading to inhomogeneous grain size distribution inhibiting transparency of the ceramic : optimal R_H to yield transparent YLO ceramics determined to be R_H = 50°C/min.

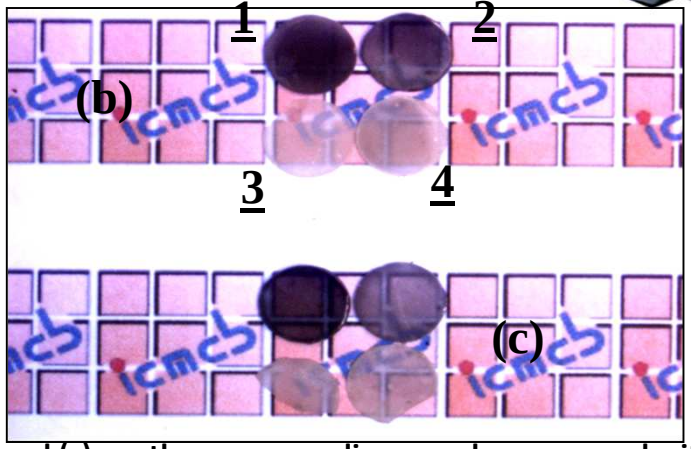
(M. Prakasam et al. / Ceramics International 39 (2013) 1307–1313)

Cubic / isotropic Crystalline structured materials



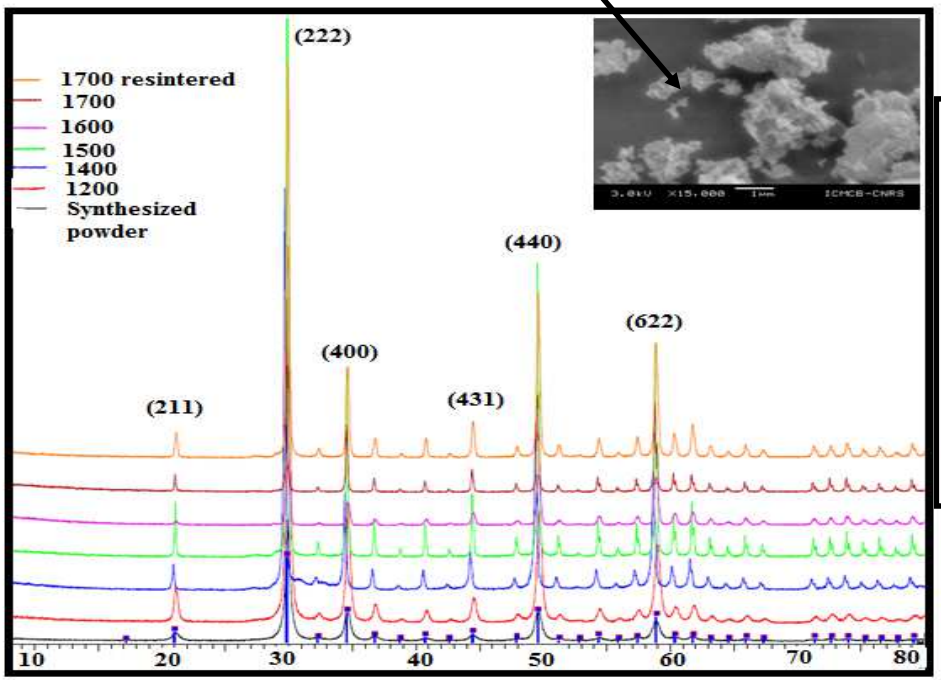
$10\%Yb_2O_3$ doped Lu_2O_3 ceramics sinetred at 1700°C Ps=100MPa

(a) 1. R_H= 10°C/min t_s= 20 min
2. R_H= 10°C/min t_s= 5 min
3. R_H= 50°C/min t_s= 20 min
4. R_H= 50°C/min t_s= 5 min



(b) and (c) are the corresponding samples compared with annealed samples at 1200°C for 12 h (oxygen vacancies, C)

Starting powder: $\phi \approx$ 10 nm

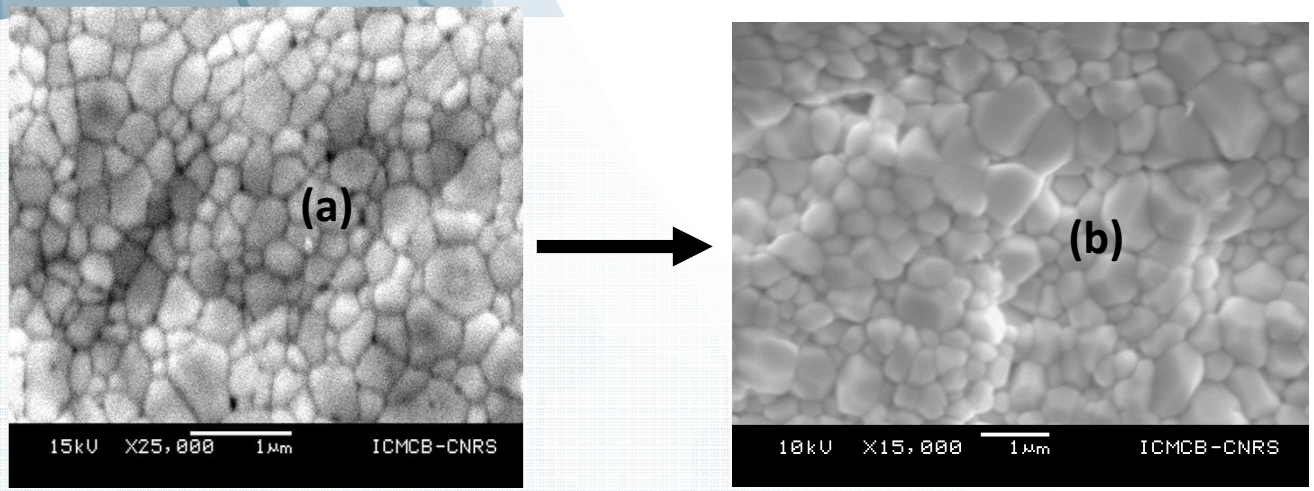


❑ Unit cell parameter for YLO : a = 10.402 Å ⇒ slight increase than the value of Lu_2O_3 cell parameter, due to the incorporation of the Yb in the crystal structure of Lu_2O_3

❑ In the whole temperature range (1400°C-1800°C) of analyses chosen for investigation ⇒ no additional phases or decomposition have been observed.

(M. Prakasam et al. / Ceramics International 39 (2013) 1307–1313)

Cubic / isotropic Crystalline structured materials



SEM micrographs of ceramics :

(a) 1700°C, 100MPa, t_s= 5min and R_H=50°C/min

(b) 1700°C, 100MPa, t_s= 5min and R_H=50°C/min, annealed at 1200°C for 12 h

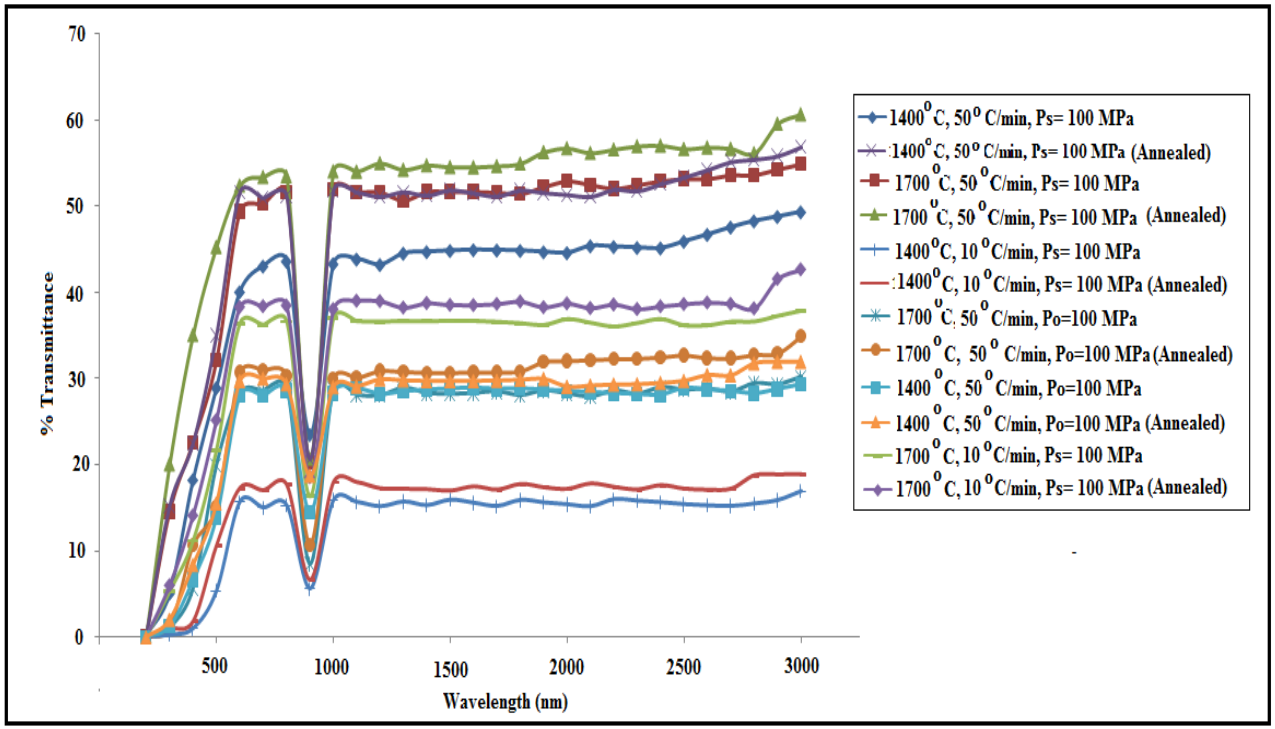
❑ **Over the temperature range of 1400°C-1800°C, with P_S= 100MPa, R_H = 50°C/min and t_s < 20min, the grain grew uniformly, with distinct grain boundaries.**

❑ **Porosity (Archimedes) of YLO ceramics decreases with increasing temperatures and increasing holding time, while the applied pressure has little effect on the porosity.**

(M. Prakasam et al. / Ceramics International 39 (2013) 1307–1313)

Cubic / isotropic Crystalline structured materials

Transmittance spectrum of sinetred transparent ceramics under different sintering conditions by spark plasma sintering



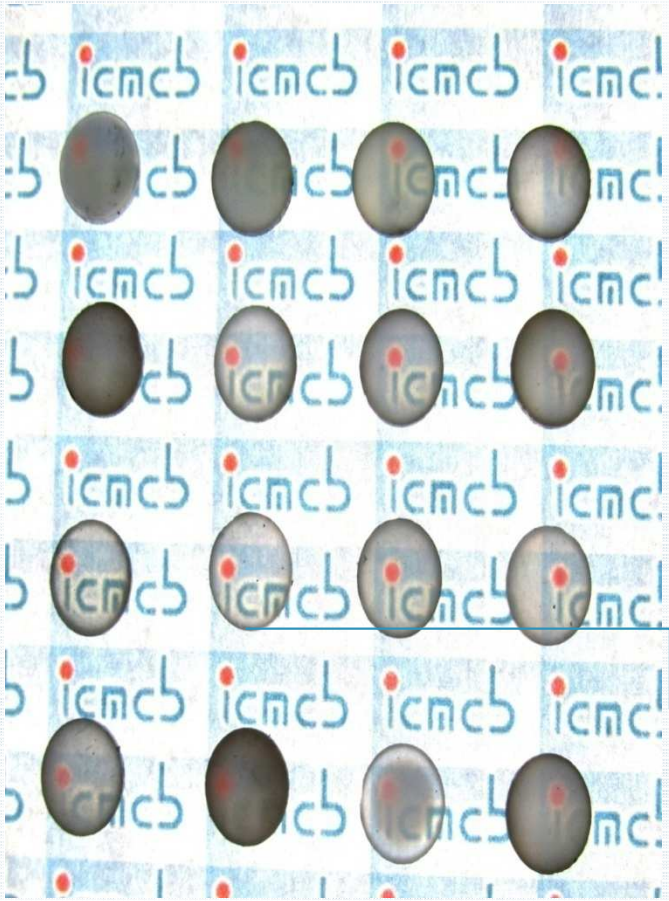
→ **The samples sintered at 1700°C for 5 minutes exhibited higher transparency than that of the ceramics sintered at 1400°C.**

→ **The increasing transmission with sintering temperature may be attributed due to densification.**

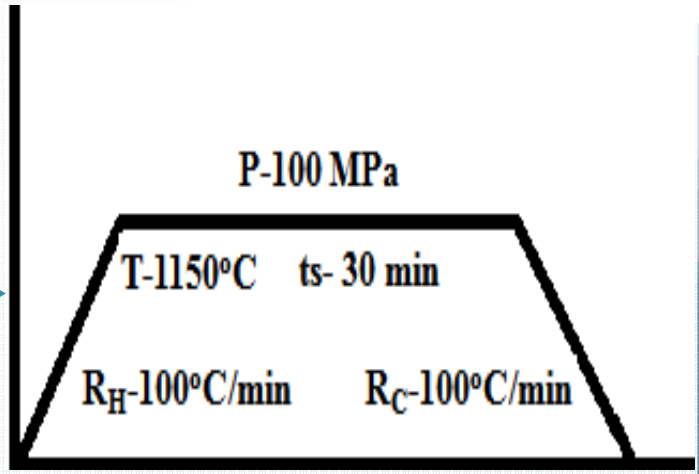
→ **The YLO ceramics fabricated at 1700°C and 1400°C had nearly 5-10% improvement in transmittance upon annealing at 1200°C for 12 h.**

M. Prakasam et al. / Ceramics International 39 (2013) 1307–1313

Noncubic / anisotropic Crystalline structured materials



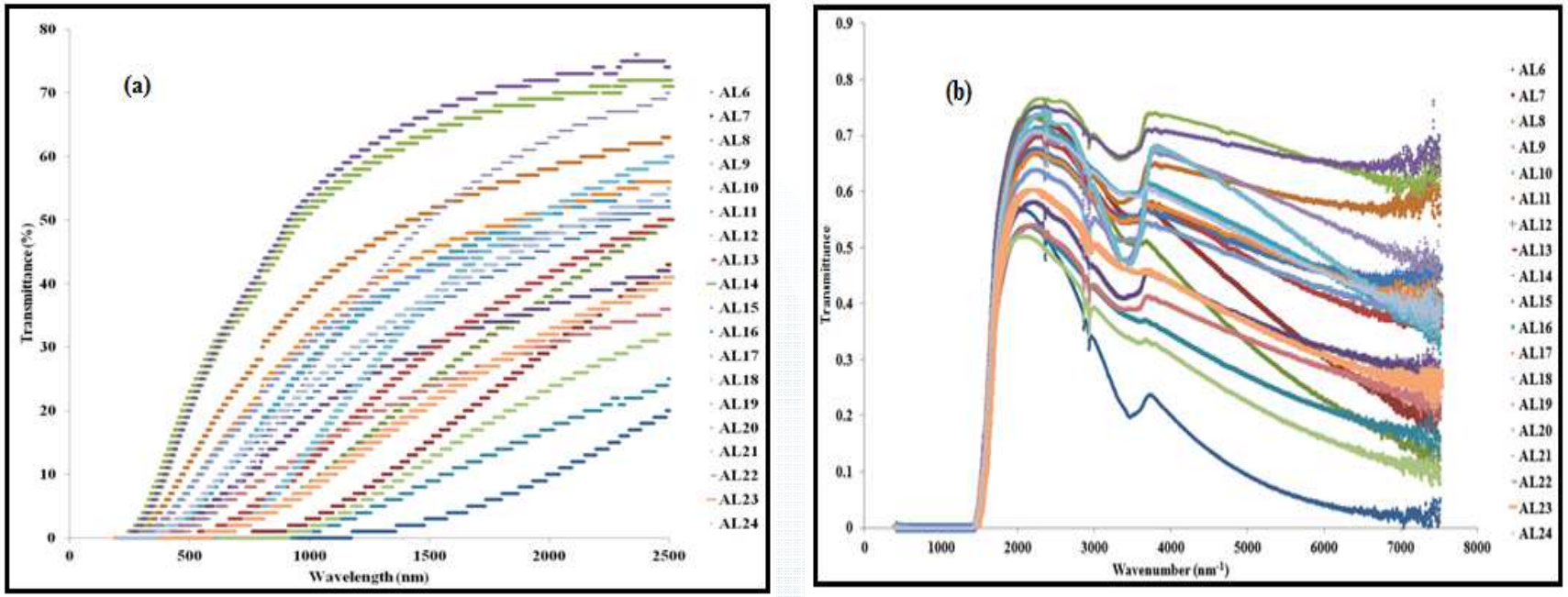
Transparent Al_2O_3 ceramics for Armor and IR applications



M. Prakasam et al. / Journal of European Ceramics society (Accepted) 2014

Noncubic / anisotropic Crystalline structured materials

Optical Characterization of PCA obtained by SPS



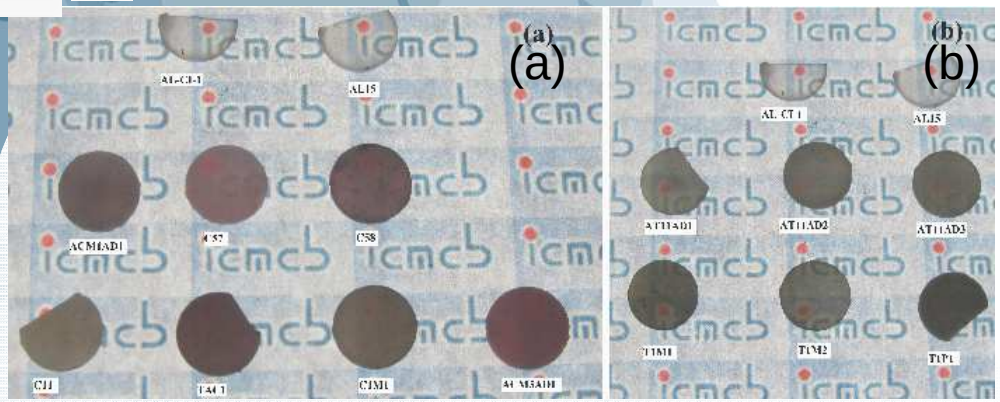
Transmittance spectra of PCA ceramics in (a) UV-Visible region and (b) Infra-red region (thickness 2mm)

→ **Maximum transmission of alumina has been achieved by other techniques such as pressureless sintering, followed by HIP, Its transmission is very close to that of saphir single crystal and remains at 86% in the wavelength range of 3-4.5 µm for a thickness of 1mm.**

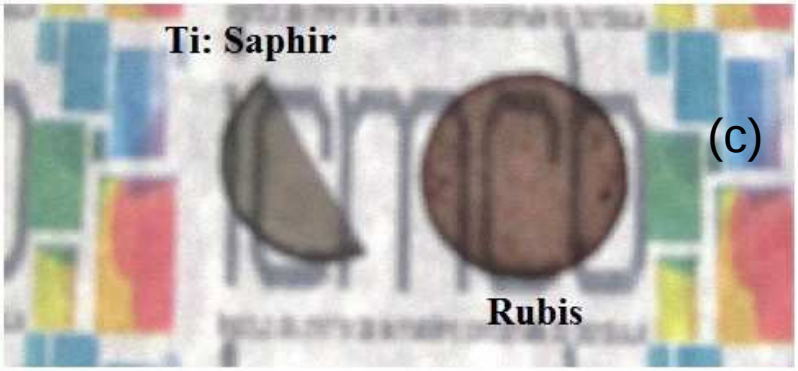
→ **It can be inferred that the transmittance of PCA increases in UV-Visible-NIR and mid-IR with the increasing dwell time, pressure and heating rate.**

→ **Further the application of pressure (100 MPa) at the start of sintering cycle decreases the transmittance of the PCA ceramics to 10% lesser than the application of pressure at the dwell time.**

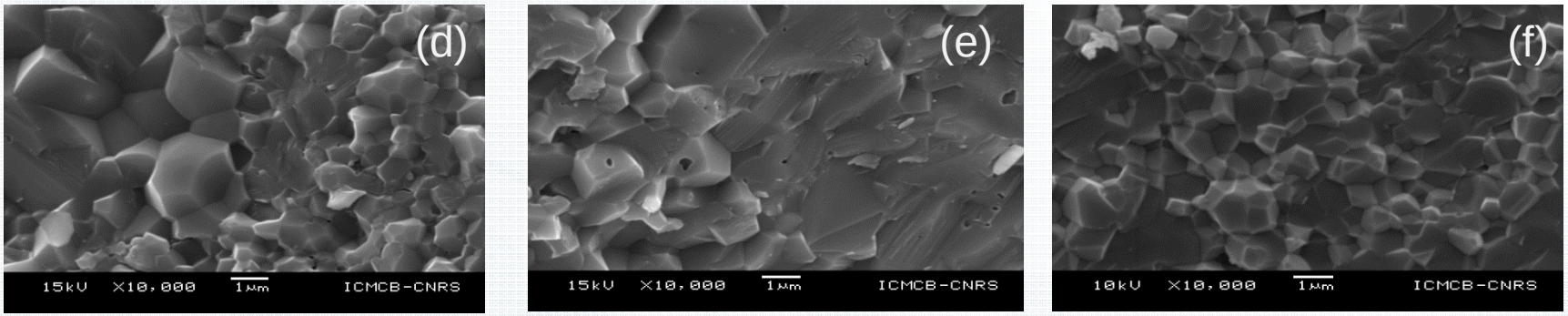
Control of grain growth (Al_2O_3 doped with Cr_2O_3 and Ti_2O_3) by additive to avoid abnormal grain growth upon sintering



(a) Al_2O_3 doped with Cr_2O_3 sintered at different sintering conditions
(b) Al_2O_3 doped with Ti_2O_3 sintered at different sintering conditions



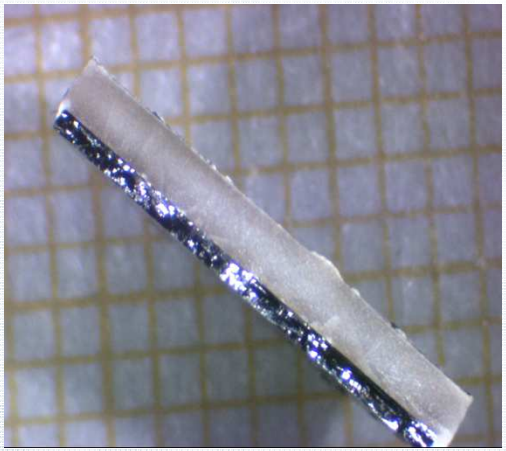
(c) Al_2O_3 doped with Cr_2O_3 and Ti_2O_3 sintered by addition of 0.05 Wt% of MgO



Microstructures of Al_2O_3 doped with Cr_2O_3 at 1300°C with dwell time of 20 minutes (d) heating rate 10°C/min (e) heating rate 100°C/min and (f) heating rate 10°C/min with addition of 0.05 Wt% MgO

- **Effectiveness of the additive to suppress grain growth** is often found to depend on its ability to segregate at the grain boundaries.
- **Inhibition of grain growth** is believed to occur by a mechanism of solute drag. A Strong interaction occurs between the segregated solute and the grain boundary so that the solute must be carried along with the moving boundary.
- Solute diffusion across the boundary is assumed to be slower than that of host atoms and therefore becomes rate controlling.

Transparent ceramics fabricated at ICMCB by SPS



Translucent ZnO ceramics on Silicon substrate by SPS for LED applications
Product developed for company Nanovation, Paris at ICMCB

HAp Sintering temperature = 850°C, Dwell time= 10 min

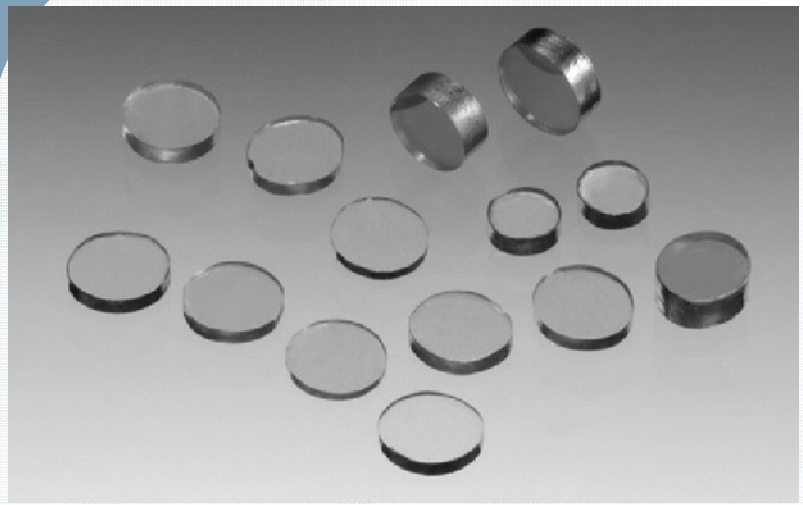
Zirconia Sintering temperature = 1200°C, Dwell time= 20 min

$AgGaGe_5Se_{12}$

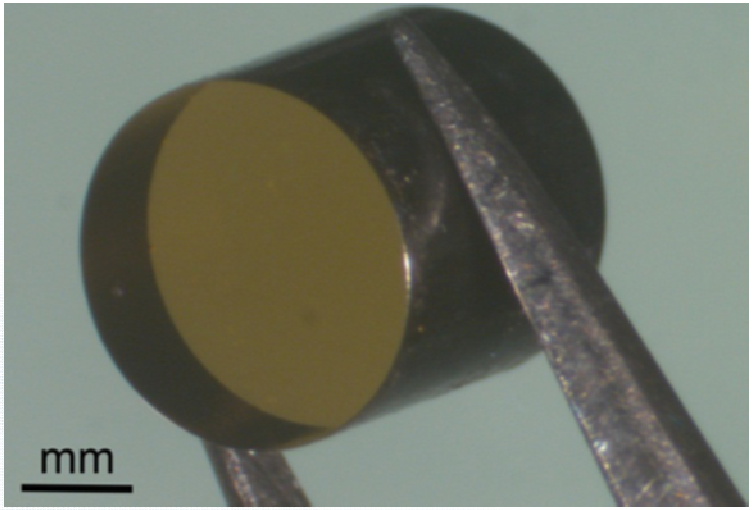
$AgGaGe_3Se_8$

Silver based Chalcogenides for mid-IR applications

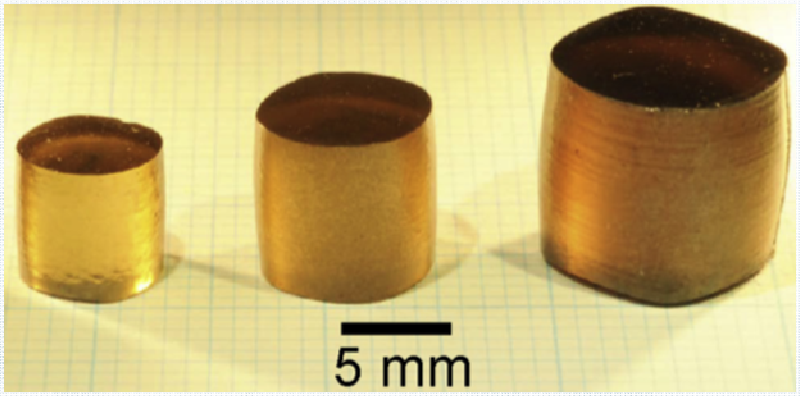
Few examples of transparent PCD to date in literature



K. Harano et al. / Diamond & Related Materials 24 (2012) 78–82



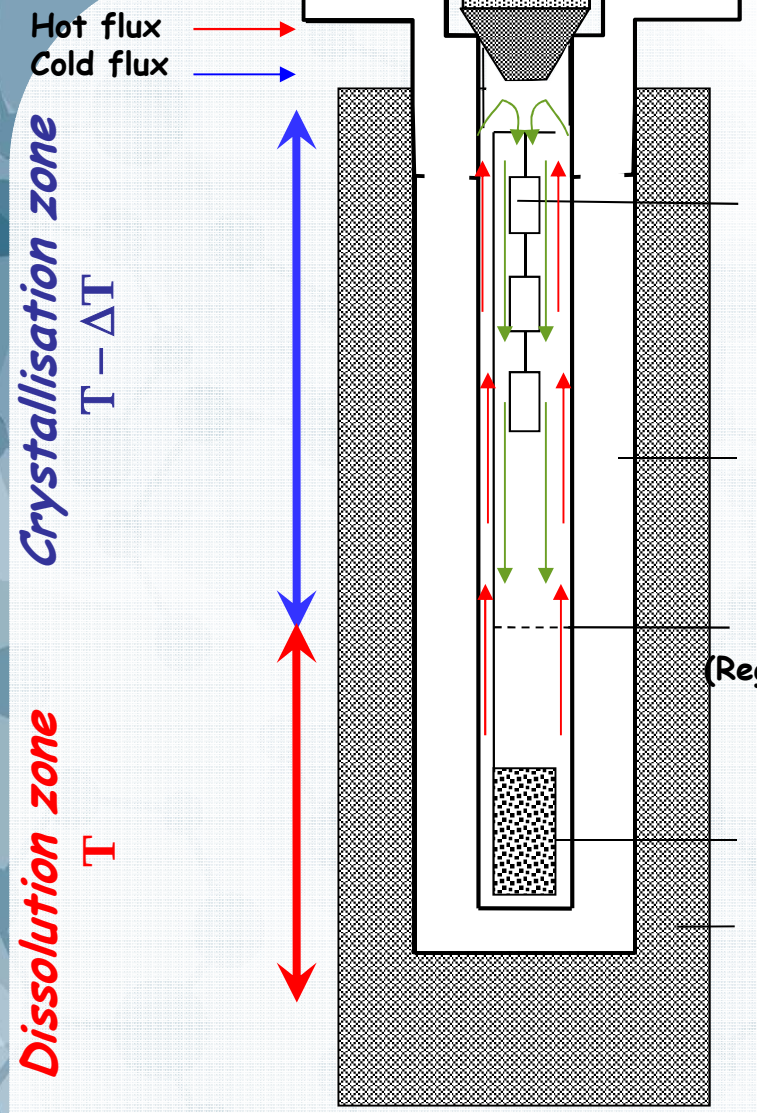
Y.-Y. Chang et al./Physics of the Earth and Planetary Interiors 228 (2014) 47–55



T. Irifune et al./Physics of the Earth and Planetary Interiors 228 (2014) 255–261

Hydrothermal crystal growth of SiO_2

Principle



Dissolution of nutrient by the solvent
in the hot zone (bottom)
($T_{dissolution}$)

↓

Creation of solvated species

↓

Saturation of the solution
In the dissolution zone

↓

Transport (convection) of the solvated species from the hot zone (bottom) to the cold zone (top)

↓

Supersaturation of the solution
in the crystallization zone
($T_{crystallization} < T_{dissolution}$)

↓

Deposition on the seed

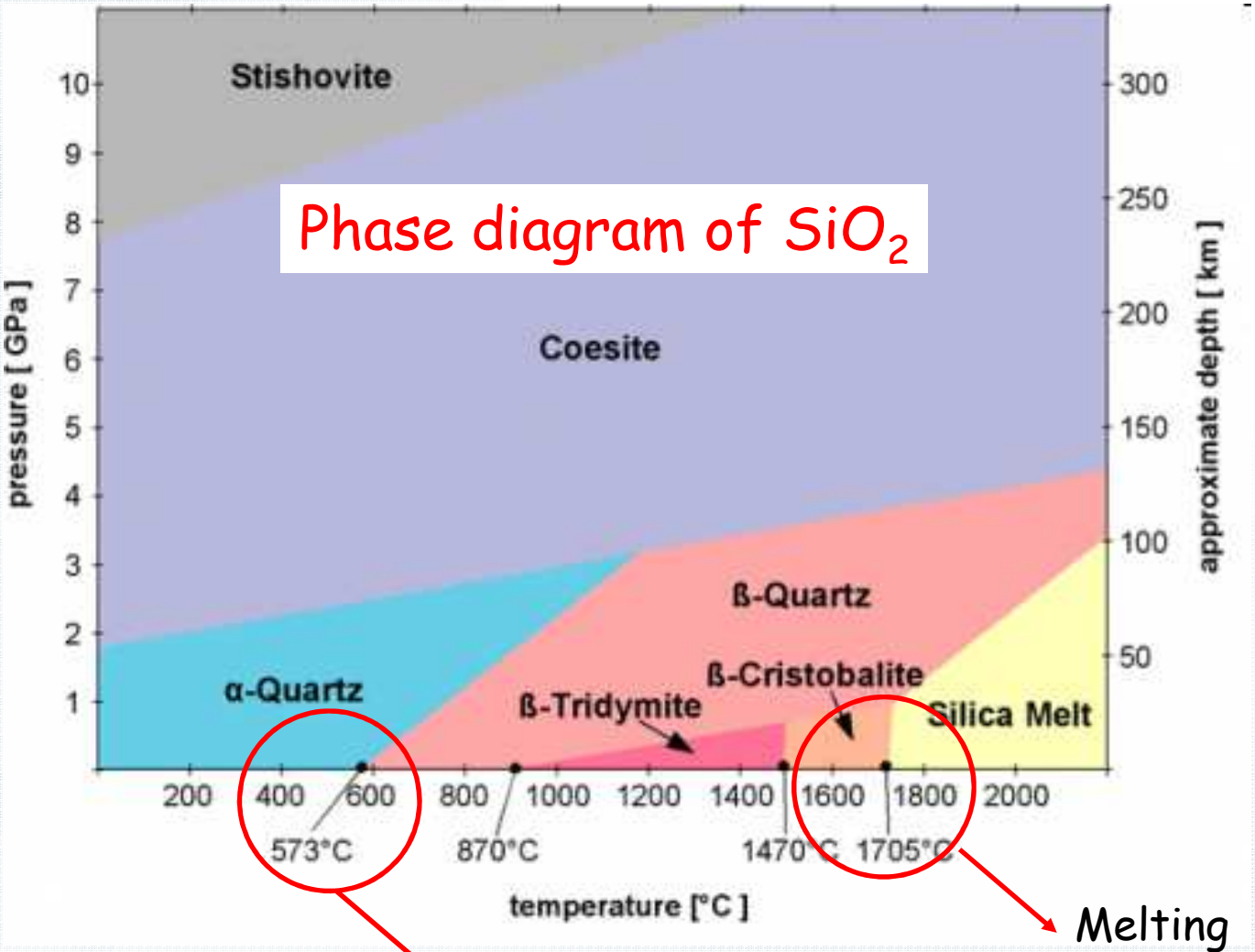
↓

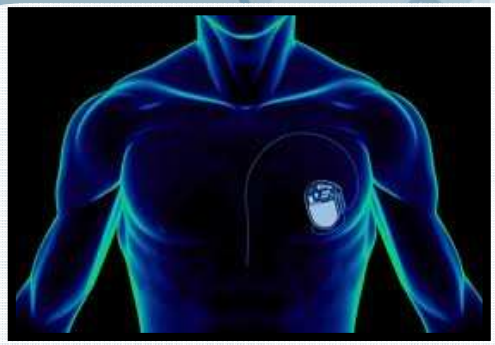
Impoverishment of the solution which descend to the bottom (re-saturated solution) and the cycle re-start

Effect of P = Increase and manage the solubility of precursor « nutrient »

Effect of ΔT = Create a difference of solubility generating a transport of species from hot to cool zone

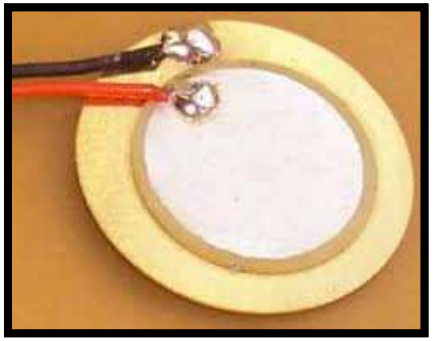
Hydrothermal Crystal Growth and Structural Studies of $Si_{1-x}Ge_xO_2$ Single Crystals



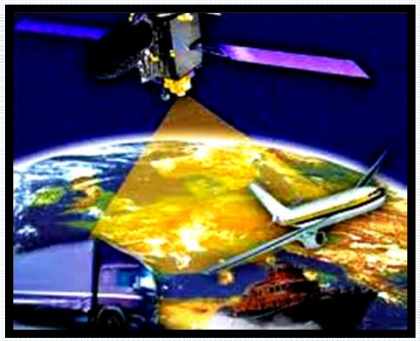


Pacemakers

Celestial navigation

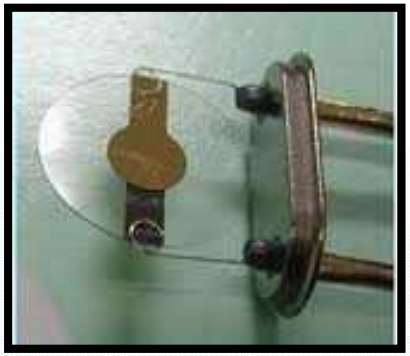


Piezoelectric transducers

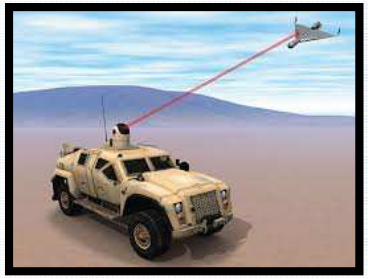


GPS system

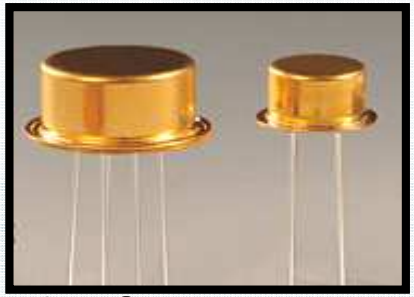
Few examples of Quartz Crystal applications



Quartz crystal microbalance



Military and aerospace navigation



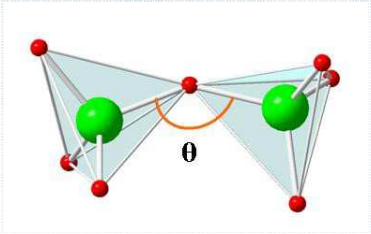
Precise frequency controller

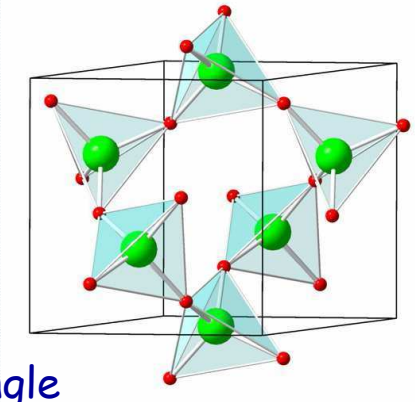
α - Quartz

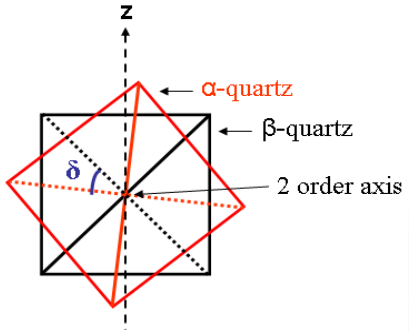
Trigonal system
Space group: $P3_121$ (right) or $P3_221$ (left)

Lattice parameters : a = 4,913Å c = 5,405Å

Helical chain of tetrahedral along the z axis







θ : inter-tetrahedral bridging angle

δ: tetrahedral tilt angle

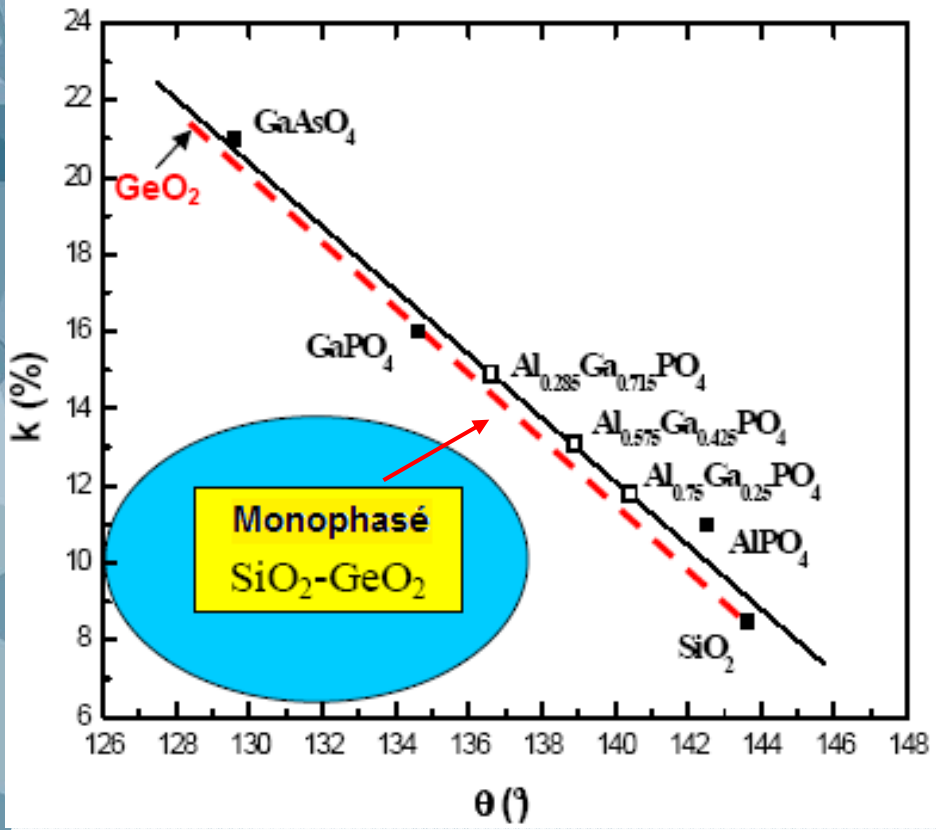
α-quartz: θ = 143.6° and δ = 16.2° ⇒ Electromechanical coupling coefficient k ≈ 8%

β-quartz: θ = 154° and δ = 0° ⇒ Electromechanical coupling coefficient k ≈ 0%

If θ↓ or δ↑ ⇒ distortion (/ β-quartz) ↑

Grimm et al., *J. Ph. Chem. Solids* 1975, 36, 413

Relation between θ (distortion) and k



$AlPO_4$: α-quartz homotype

⇓

Substitution Al / Ga

$Al_{1-x}Ga_xPO_4$

(size: Ga^{3+} >> Al^{3+})

⇓

Θ ↑ (distortion ↑) if at.% Ga ↑

⇓

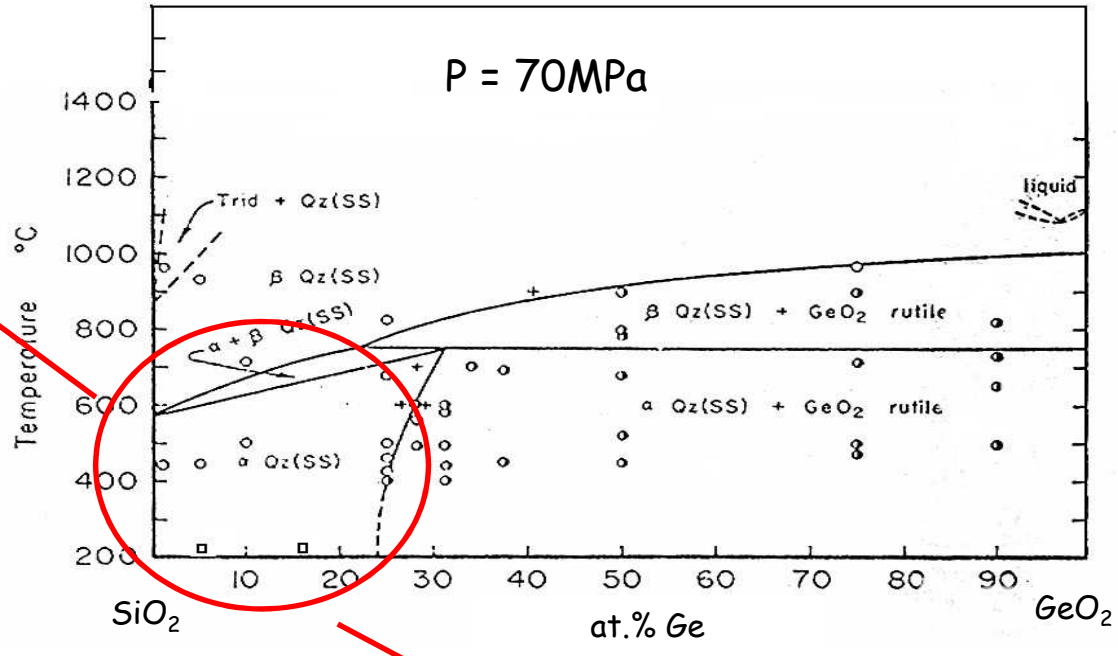
k ↑

E. Philippot et al., *J. solid state chemistry 1996*, 123, 1

SiO_2 : Substitution Si / Ge (size: Ge^{4+} >> Si^{4+}) ⇒ $Si_{1-x}Ge_xO_2$

Existence of SiO_2 – GeO_2 domain

31at.% Ge at 700°C and 70 MPa in SiO_2 α-quartz



GeO_2

Phase rutile like = tetragonal
$P4_2/mnm$

↓ 1033°C ↓

α-quartz like = trigonal
$P3_221$

No information at ambient temperature

Single crystal of $Si_{1-x}Ge_xO_2$

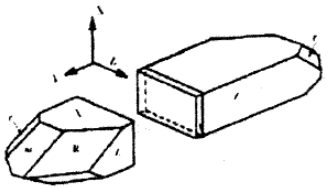
With x (at. %) max ?

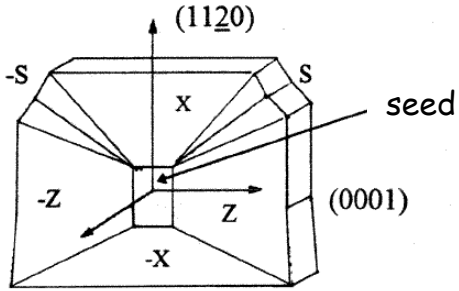
W.S.Miller et al., *Amer. Mineral. 1963,* 48, 1024

SiO_2 α-quartz Hydrothermal Crystal Growth

SiO_2 α-quartz hydrothermal crystal growth

Parameters	**High Pressure**	**Low Pressure**
Temperature	360°C	345°C
Pressure	150 MPa	70-100 MPa
Gradient	25°C	10°C
Solvent	**NaOH 1M**	**Na2CO3 0.8M**
Growth rate (sur Z)	1mm/day	0.4mm/day

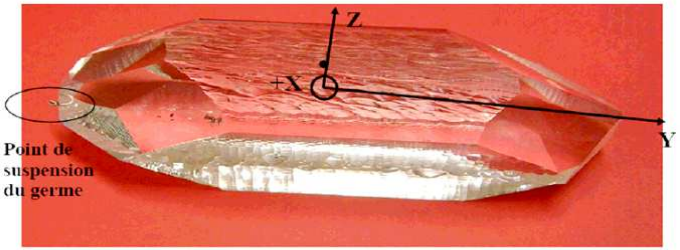




$Si_{1-x}Ge_xO_2$ α-quartz hydrothermal crystal growth

- Seed: SiO_2 α-quartz (no other choice)
- Solvent: NaOH, Na_2CO_3, H_2O, .. (depending of the solubility)
- Nutrient: SiO_2 + GeO_2 (depending of the solubility)
- Pressure: lowest possible
- Temperature : lowest possible

} Industrial application

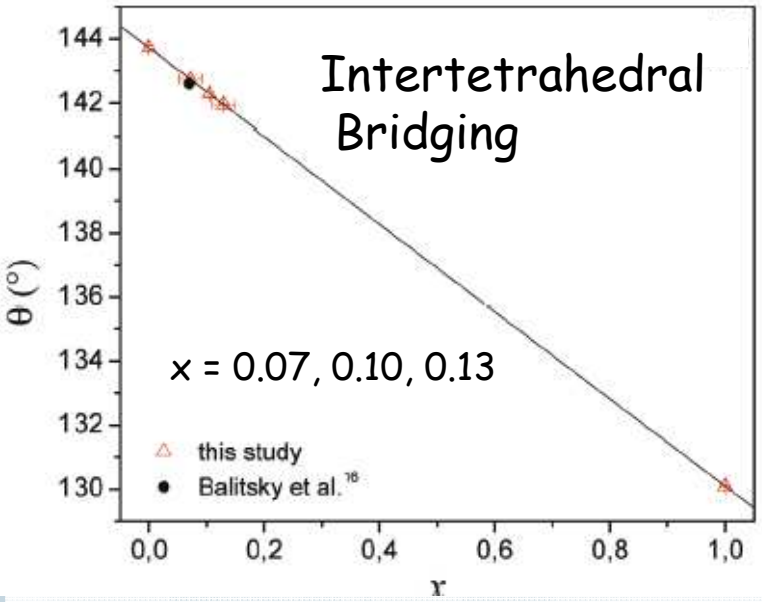


Structural distortion on crystals

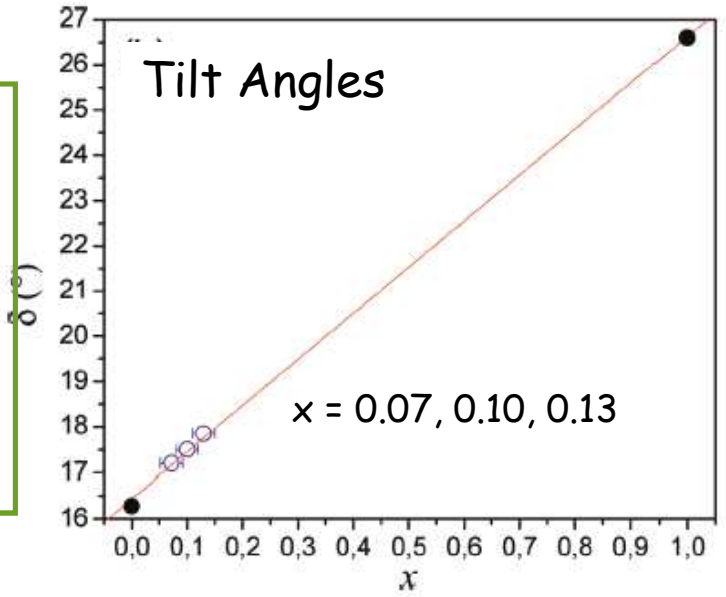
	SiO_2	$Si_{0.93}Ge_{0.07}O_2$	$Si_{0.87}Ge_{0.13}O_2$	GeO_2
a (Å)	4.9137 (8)	4.9200 (2)	4,9222 (2)	4.9853 (1)
c (Å)	5.4047(12)	5.4195 (2)	5,424 (1)	5.6450 (1)
c/a	1.0999	1.1014	1,102	1.1323
V (Å^3)	113.01 (5)	113.61 (1)	113,82 (1)	121.50 (1)
Angle θ (°)	143.6 (1)	142.75 (5)	141,95 (1)	130.05 (4)
Angle δ (°)	16.28 (6)	17.21 (2)	17,85 (3)	26.61 (4)

If x ↗

Inter-tetrahedral Bridging and Tilt Angles in $Si_{1-x}Ge_xO_2$ α-quartz

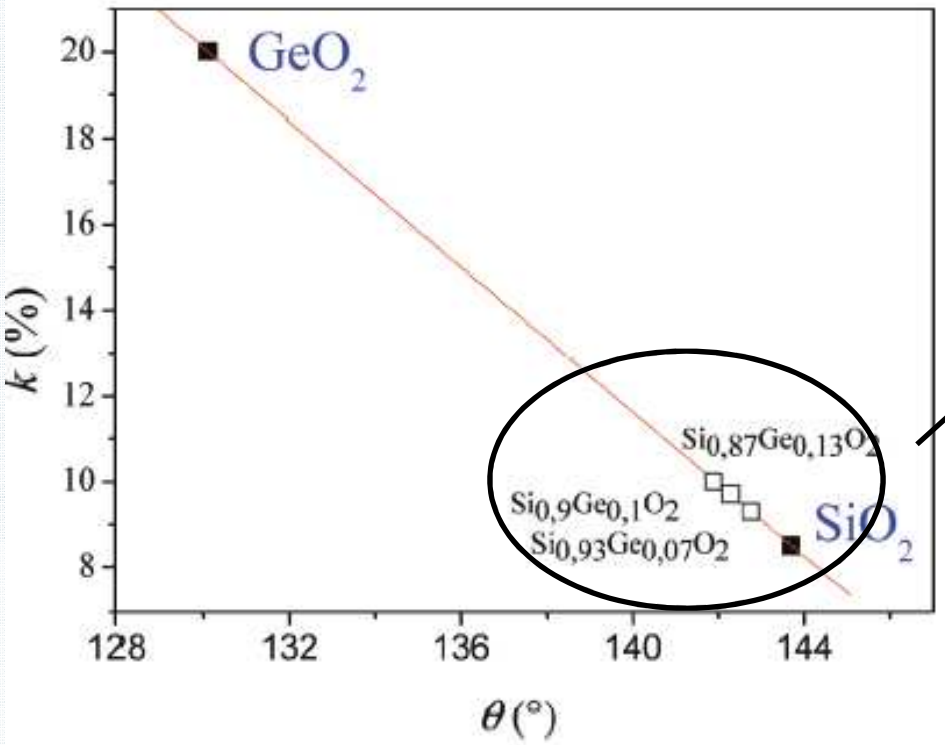


If x↑
⇓
θ↓ and δ↑
⇓
distortion ↑



V. Balitsky et al., *IEEE Int.* 2007, 704

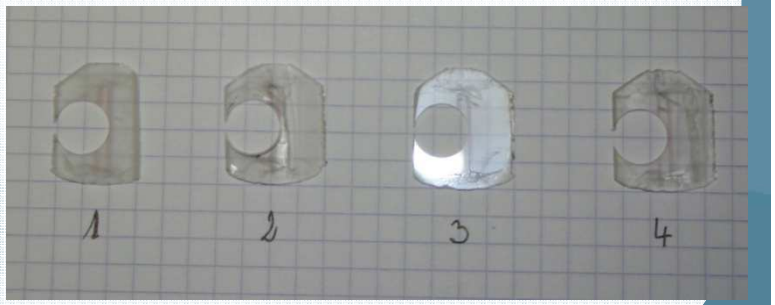
Expected Piezoelectric coupling coefficient k



predicted k values for $Si_{1-x}Ge_xO_2$ crystals with x = 0.07, 0.10, 0.13 function of inter-tetrahedral bridging angle

Next step

discs for resonators



V. Ranieri et al., *Inorg. Chem.* 2011, 50, 4632

Applications of hydro(solvo)thermal crystal growth

- **In industrial scale:**
  - **SiO_2 (α-quartz)** ($NaOH$, Na_2CO_3): piezoelectric properties (oscillators, resonators, transducers) and optics (filters)
  - **ZnO** (KOH, $NaOH$): semi-conductor transparent, dielectric and piezoelectric)
  - **$CaCO_3$** ($NaCl$, $Ca(NO_3)_2$, K_2CO_3.. 150-600°C / 15-200MPa): Optical properties (birefringence and transmission in the large spectral domain)
  - **$KTiOPO_4$ (KTP)**: (K_2HPO_4+KH_2PO_4+H_2O_2/KTP (425-600°C / 70MPa)) : non linear optical properties (lasers)
  - **GaN** (NH_3) : Evaluation of solvothermal crystal growth using mineralizers base ($NaNH_2$ or $LiNH_2$) or acidic (NH_4Cl) (2007-2008) ⇒ Japan
  - **Diamond** (Molten metallic medium) ⇒ Japan

  - **Precious stones: amethyst (purple colored quartz Fe^{3+} + irradiation), citrine (colored quartz Fe^{2+}), blue quartz (doping Co^{2+}), smoky quartz black "morion" (Al^{+} + irradiation), ruby (red Al_2O_3:Cr) , sapphire (Al_2O_3 other colors: Ni, Cr, Co, ..), emerald (Beryl: $Be_3Al_2Si_6O_{18}$:Cr)**

- **In Research scale:**
- piezoelectric materials comparable to α-Quartz
  - Berlinite: α-$AlPO_4$($T\alpha \rightarrow \beta$: 584°C) and $GaPO_4$ ($T\alpha \rightarrow \beta$: 976°C: H_3PO_4, H_2SO_4, HCl, HNO_3)
  - $GaAsO_4$,
  - Langasite
- **GaN**: Nutrient Li_3GaN_2 forming GaN_2^{3-} in NH_3 *(Thèse A. DENIS Univ. Bx 2003)*

Thank you!

The ICARUS project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 713514.

The SUPERMAT project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 692216.