Development and Investigation of Nanocrystalline Composite Materials

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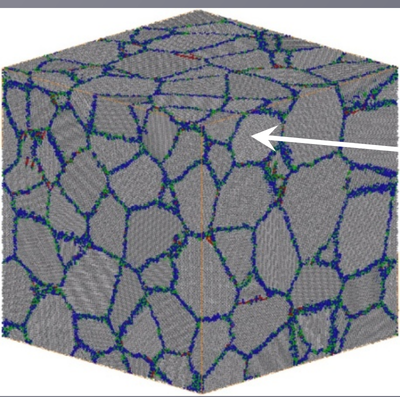
Nanocrystalline Materials

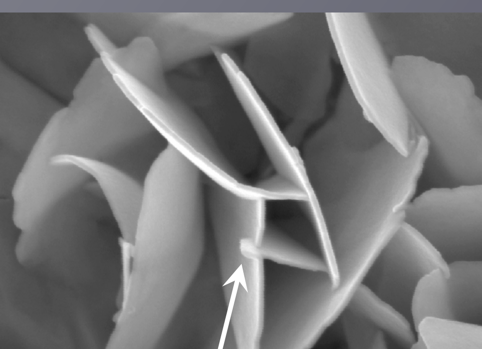
- Nanocrystalline material- is any shaped bulk polycrystalline sample with grain size till 100 nm in at least one dimension

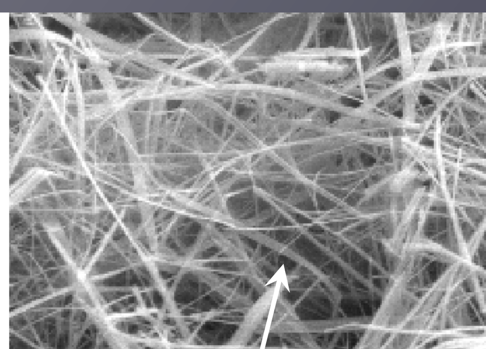


3D Grain no mare 100 nm

- The main techniques for manufacturing nanopowders:
  synthesis by solid-state reaction; spray pyrolysis, pulsed laser deposition thermal synthesis; synthesis in salt melts; hydrothermal synthesis; sol-gel synthesis.

- Standard methods for manufacturing of bulk material;
  cold compaction with further sintering; hot pressing; sintering under high pressure; electric discharge synt.; shock-wave sintering ; gasostate sintering; hot isostatic pressing; Spark Plasma Synthesis (SPS).





1 Dimensional Nanomaterial

$NbSe_2$

2 Dimensional Nanomaterial

The most universal method for manufacturing ;
Nanopowders - sol-gel synthesis
Bulk material - Spark Plasma Synthesis

Materials we are developing

- Scintillating materials:

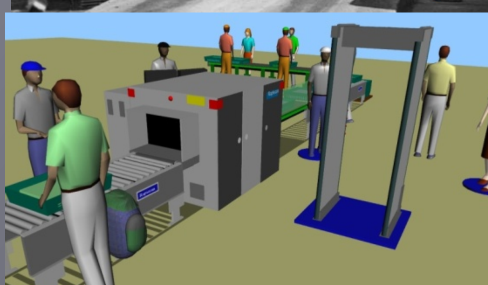
Silicates, LSO, YSO,
Aluminates , LuAP, LuAG
Tungstats: PWO, $CdWO_4$, $CaWO_4$,

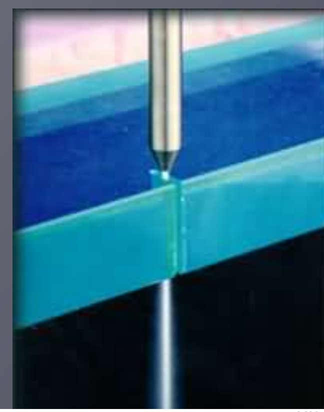
- Hard Metals:

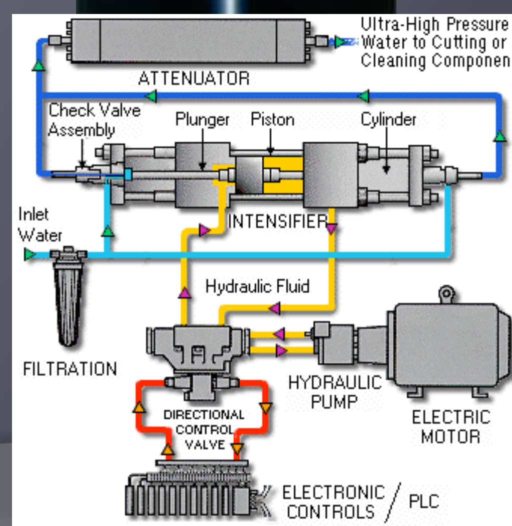
WC-Co
TiC-Ni-Mo-W
TiC-Fe-Ni

- Armor materials:

B_4C
B_4C-Cu-Mn
TiC-Ni-Mo-W
TiB_2 - TiC







Scintillators

Standart:

Silicates - Lu_2SiO_5:Ce (LSO), $Lu_2Si_2O_7$:Ce (LPS), Y_2SiO_5:Ce (YSO)
Aluminates - $LuAlO_3$:Ce (LuAP), $Lu_3Al_5O_{12}$:Ce (LuAG), $Y_3Al_5O_{12}$:Ce (YAG)
Tungstates - $PbWO_4$ (PWO), $ZnWO_4$ (ZWO), $CaWO_4$, $CdWO_4$, Lu_2WO_6

New type scintillators:

Titanites- Lu_2TiO_5:Eu, $Lu_2Ti_2O_7$:Eu,
hafnates- $SrHfO_3$:Ce, Sr_2HfO_4:Ce
phosphates- $LuPO_4$:Ce.

Properties of the Ideal Scintillation Crystal :

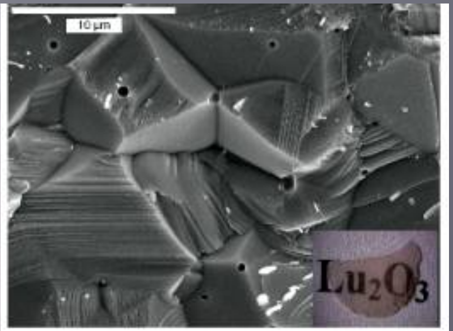
1. High density,
2. Chemical stability and mechanical strength,
3. High atomic number
4. Short decay time
5. High light output
6. Good energy resolution
7. Emission wavelength near 400 nm
8. Transparent at emission wavelength
9. Index of refraction near ~1.5
10. Non hygroscopic
11. Economic growth process

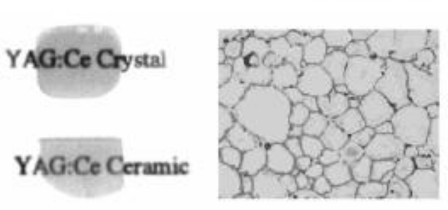
High output of Monocrystals and low obtaining cost.

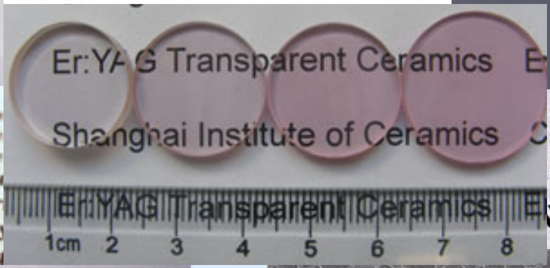
Scintillation ceramics as an alternative of monocrystals

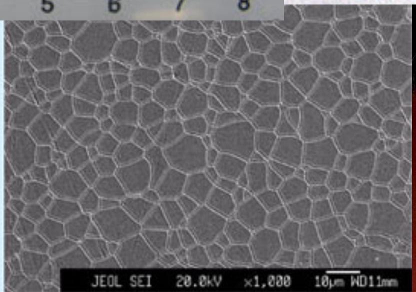
Cubic

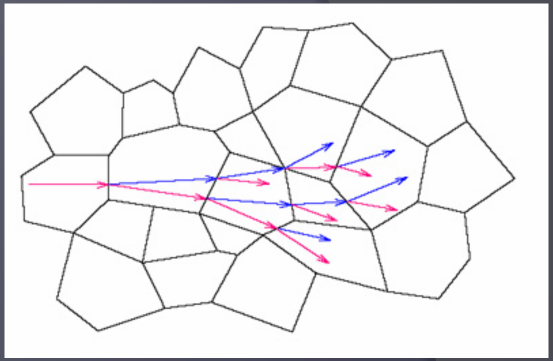
NonCubic







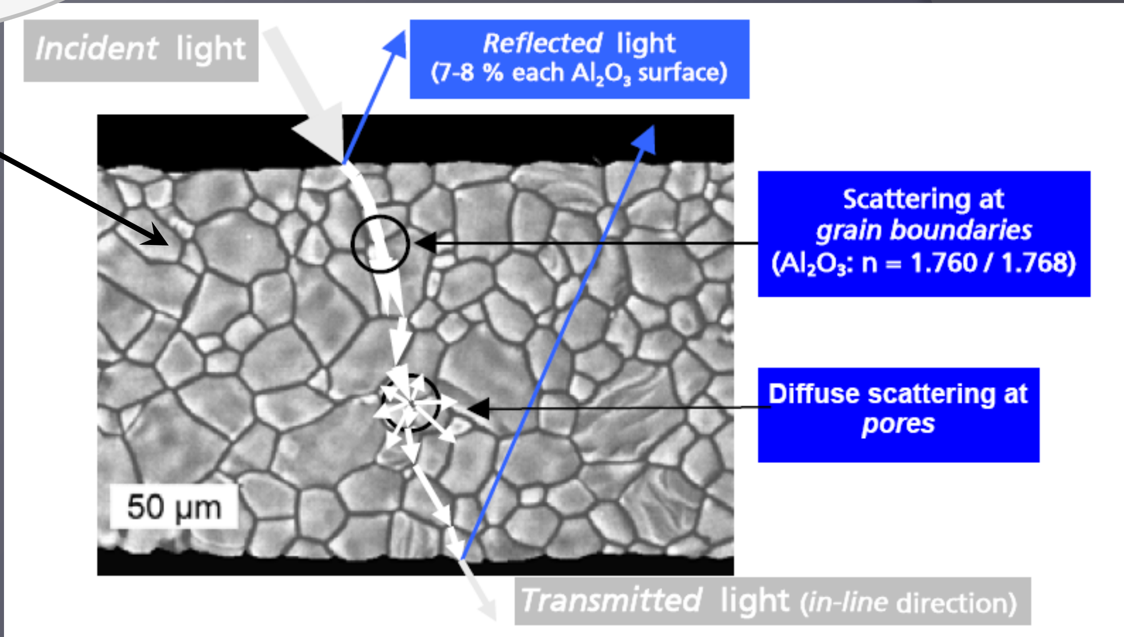




Ceramic with non cubic symmetry have multiple indices of refraction. And therefore leads to multiple scattering of the light.

Scintillation ceramics as an alternative of monocrystals

the material remains transparent if the grain size becomes smaller than the wavelength of light



Light transmission through polycrystalline alumina (Al_2O_3); works of Andreas Krell, Thomas Hutzler, Jens Klimke "Physics and Technology of Transparent Ceramic Armor:"

Technological process of manufacturing nanocrystalline composite materials

Receiving of nanocrystalline powders of composite materials

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XRD, SEM.., investigation of obtained nanocrystalline powders

↓

Compaction of nanocrystalline powder

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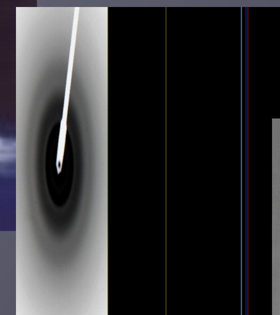
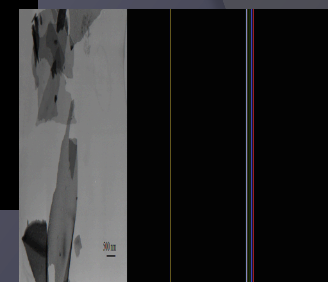
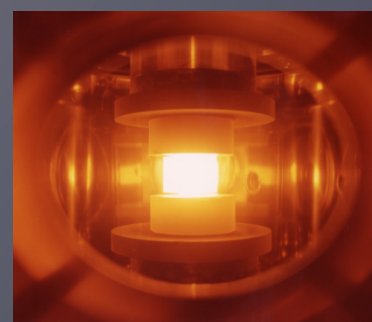
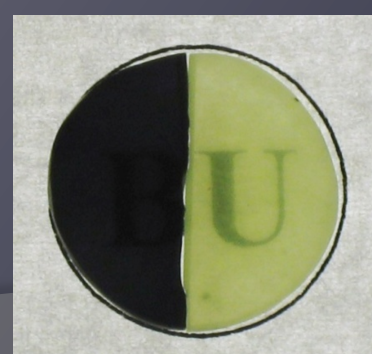
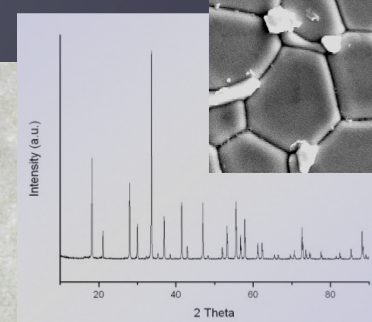
Investigation of properties of obtained bulk sample

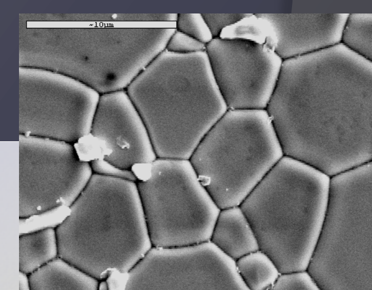




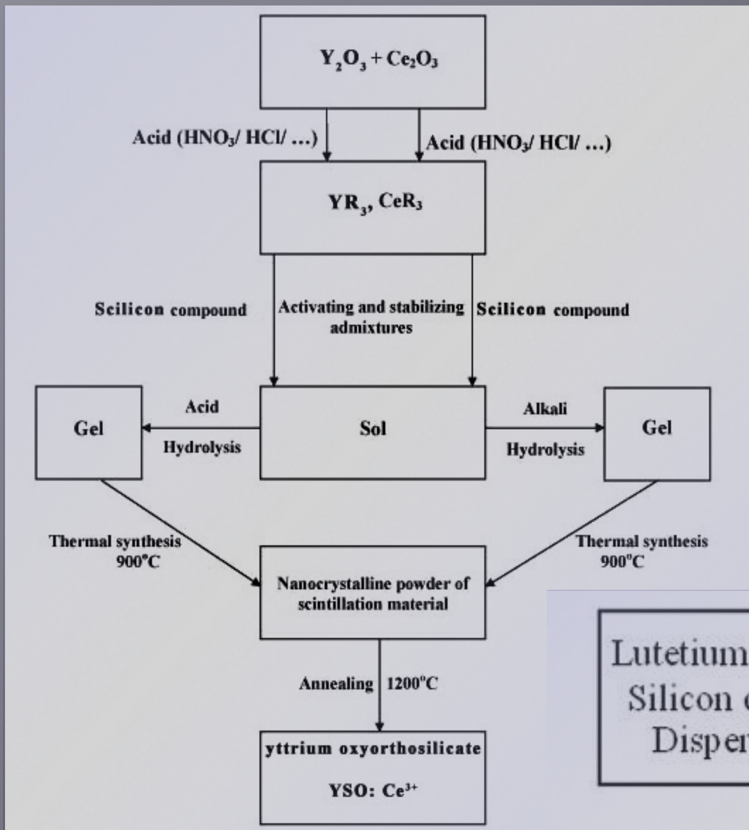


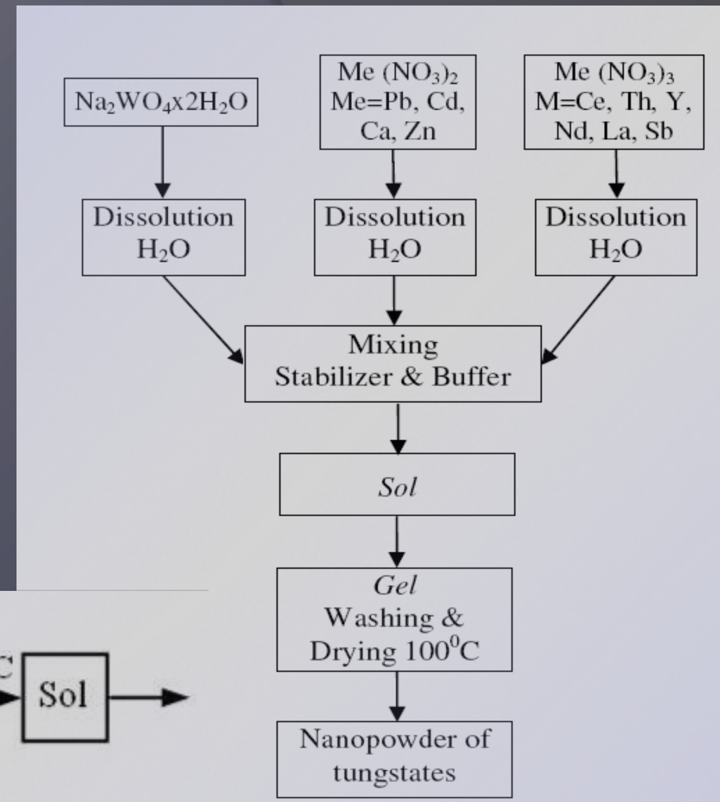


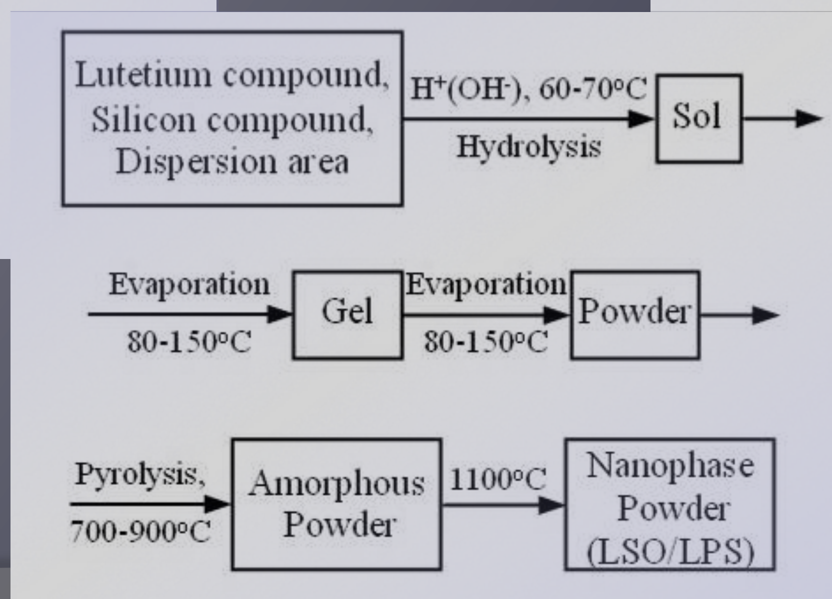




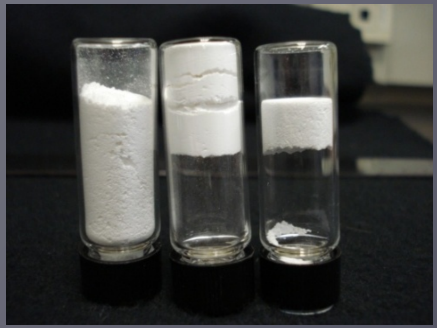
General scheme of the process developed for the synthesis of nanocrystalline powders of scintillating materials







YSO Single Cristal Growth via nanopowder.

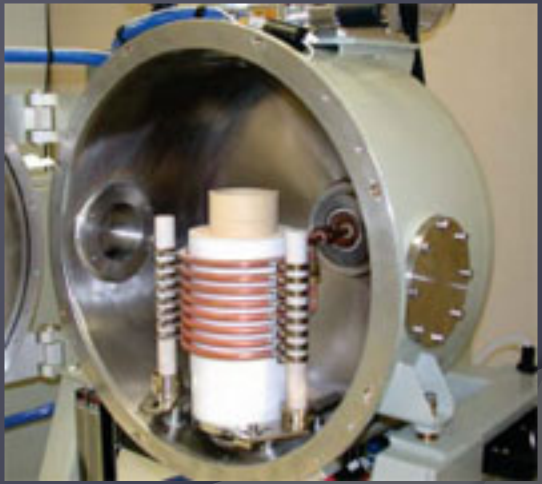


a - Remained nanopowder Y_2SiO_5 after cold loading.

b - Volume comparison between
1- densified Y_2SiO_5, 2-Standard Y_2SiO_5
3- nanopowder Y_2SiO_5

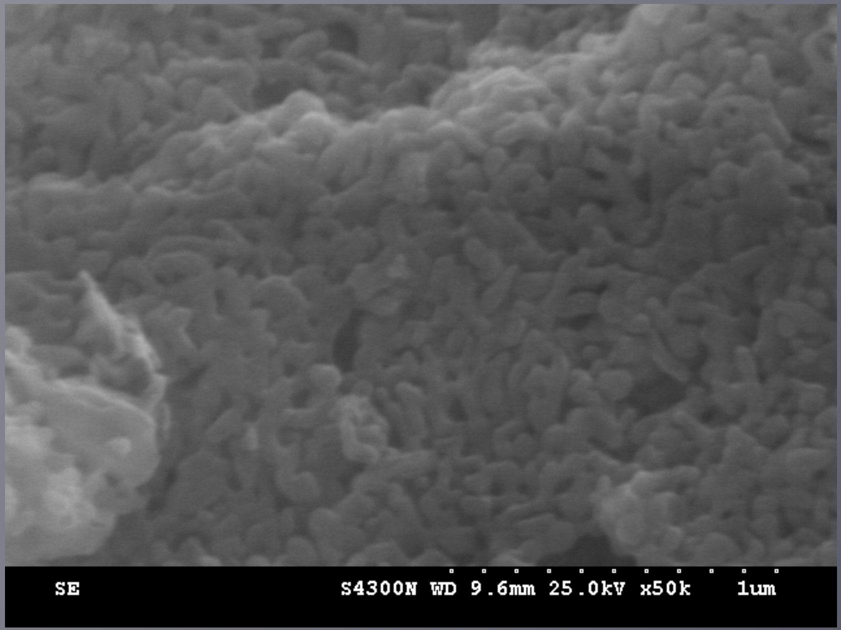
c - Powder charging comparison between
1- densified Y_2SiO_5, 2-Standard Y_2SiO_5
3- nanopowder Y_2SiO_5

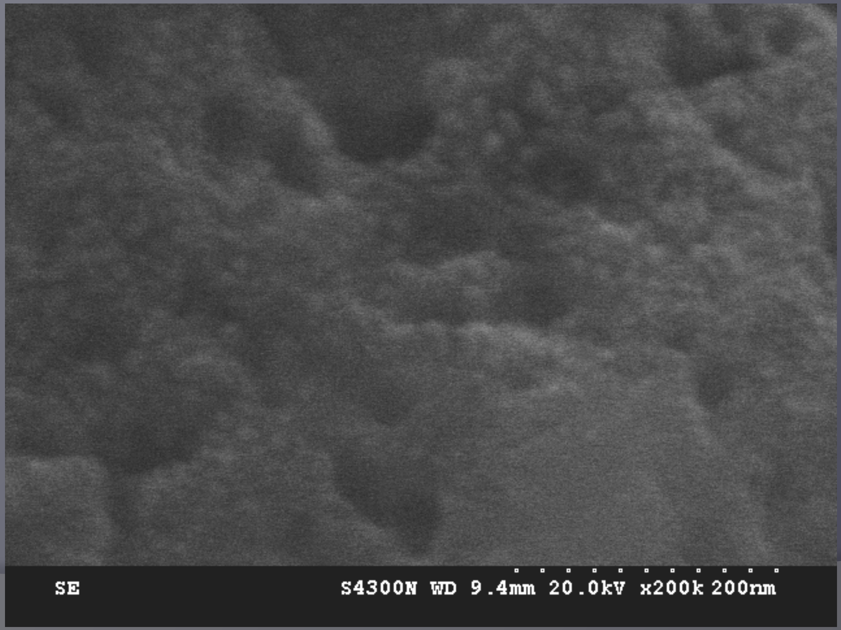
YSO:Ce 0.005% Single Crystal Growth via nanopowder.

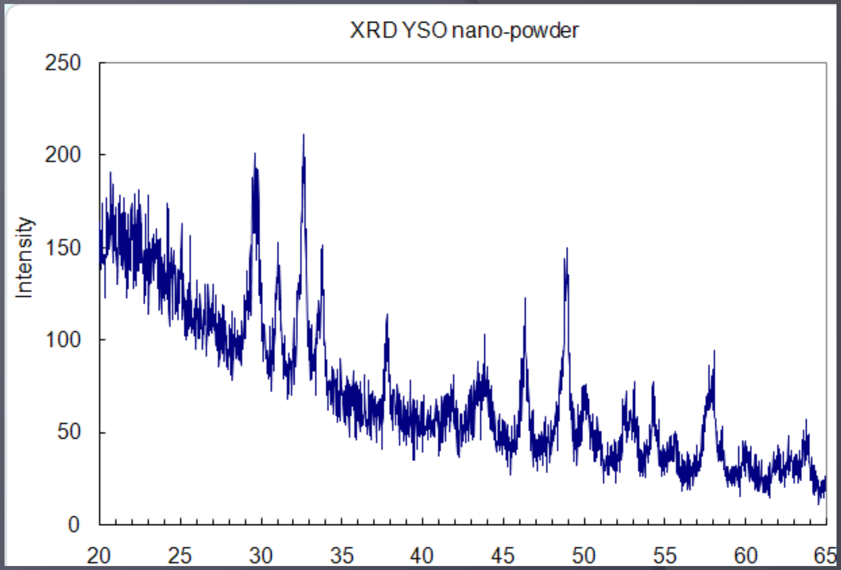


Growth station

Y_2SiO_5 nanopowder used for crystal growth



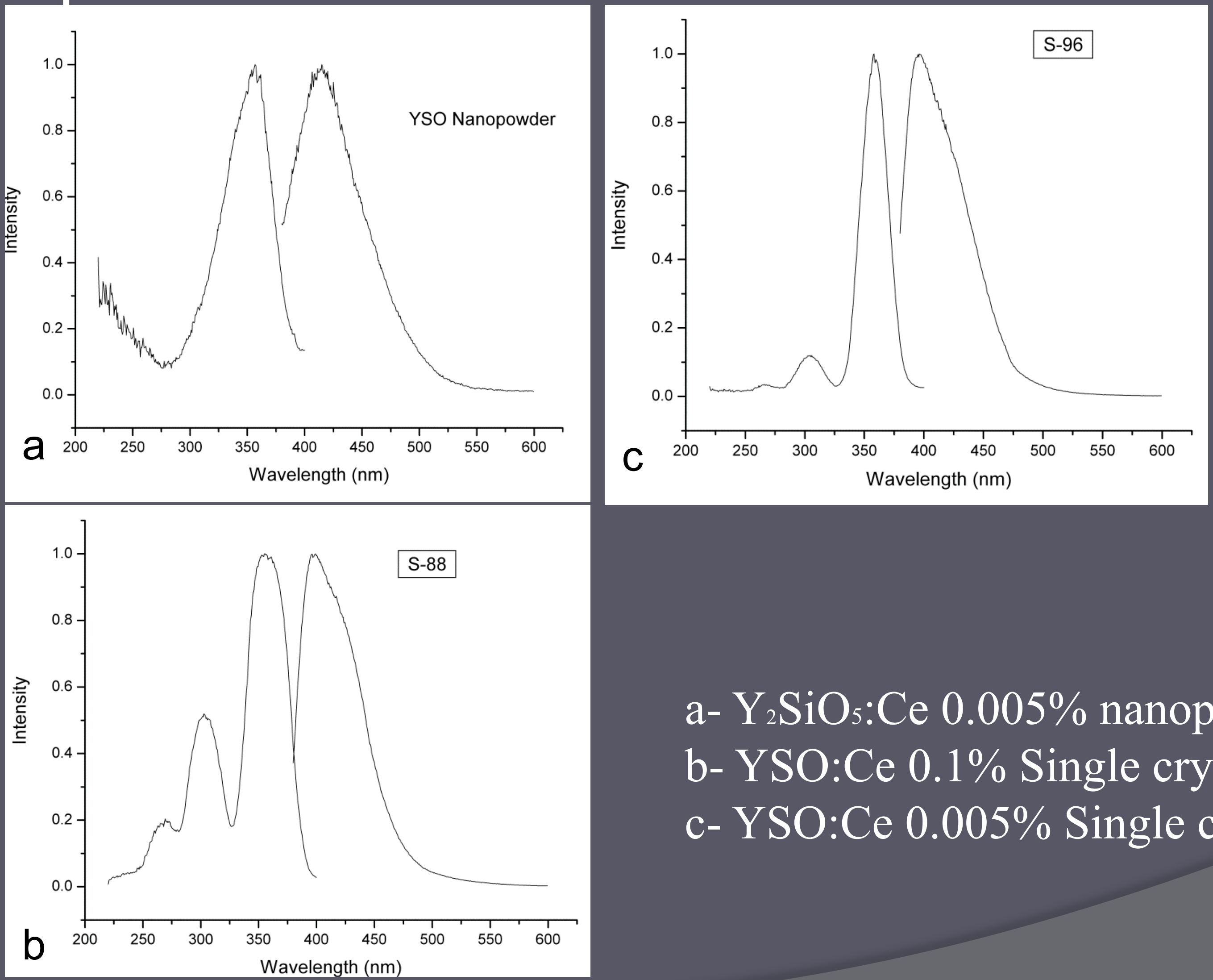




XRD of Nanopowder of Y_2SiO_5

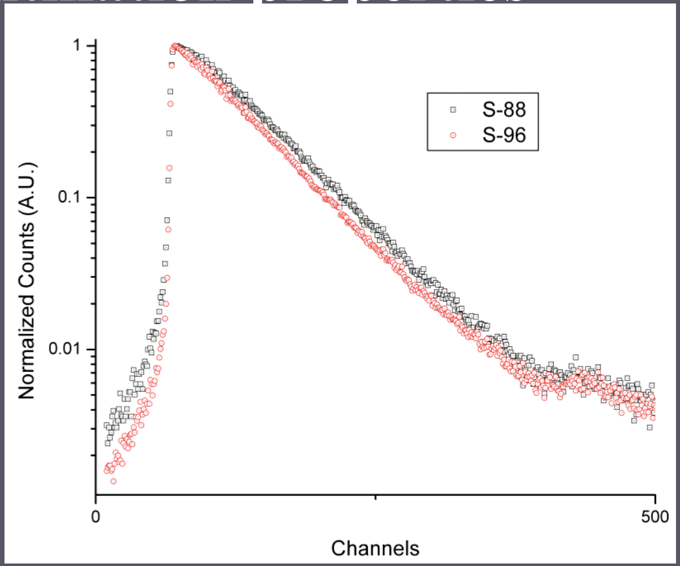
Electron-microscopic images of the Y_2SiO_5 nanopowder, grain size ~ 20-30 nm

Photoluminescence excitation and emission spectra

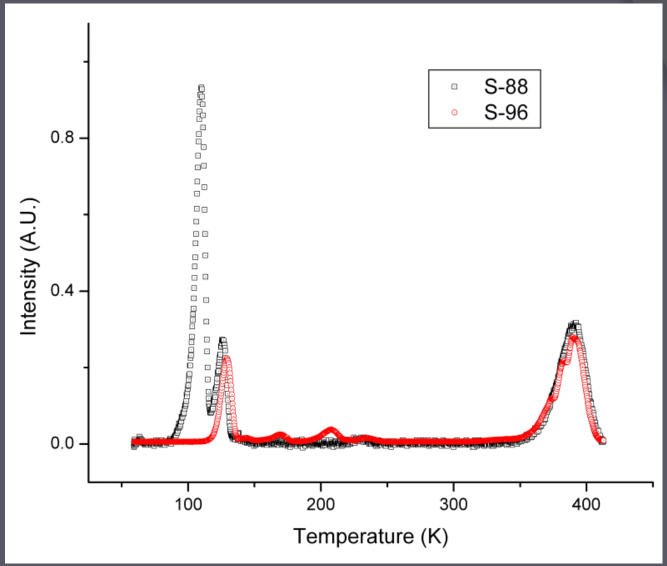


a- Y_2SiO_5:Ce 0.005% nanopowder
b- YSO:Ce 0.1% Single crystal
c- YSO:Ce 0.005% Single crystal

Scintillation properties



Decay time comparison of S-88 - YSO:Ce 0.1% Single crystal and S-96- YSO:Ce 0.005% Single crystal (received from nanopowder)

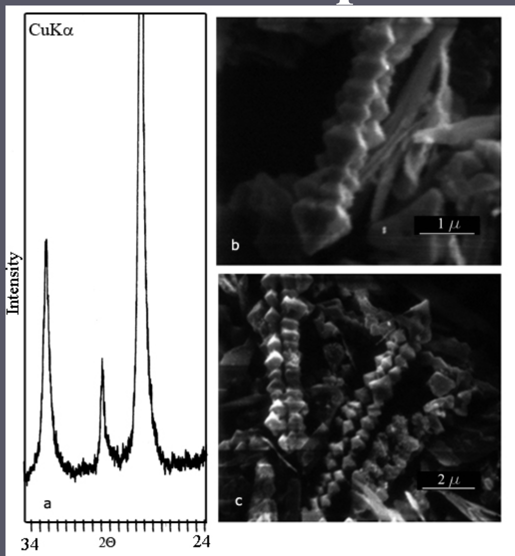


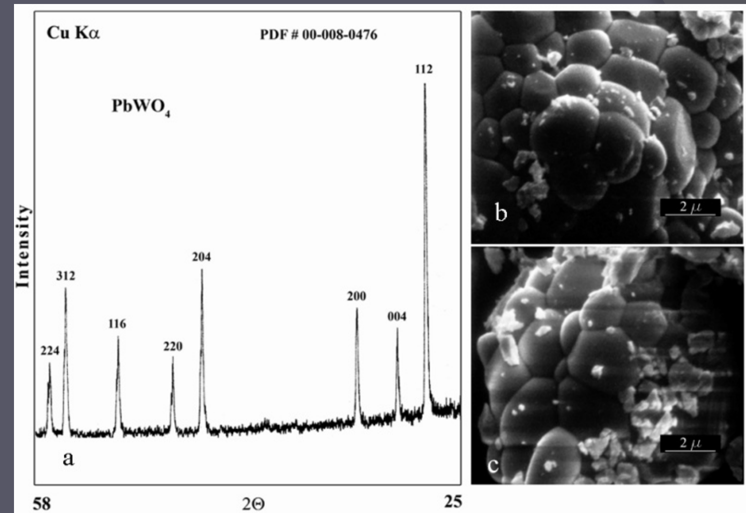
Thermoluminescence Spectrum of YSO:Ce 0.1% and YSO:Ce 0.005%

Results of compression measurements

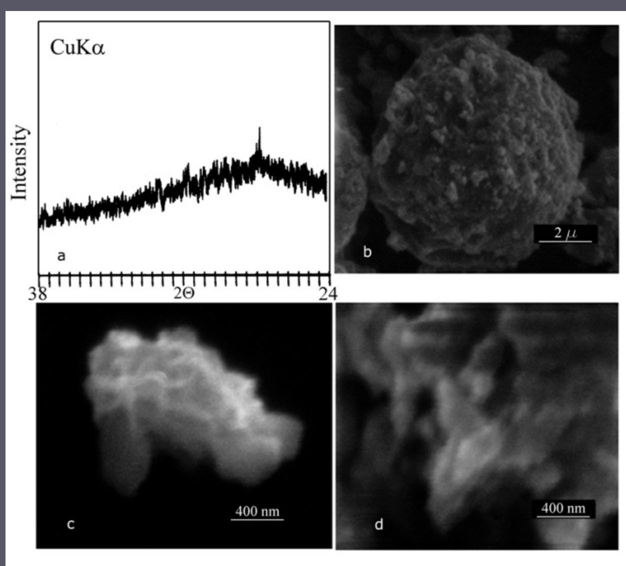
- Shorter decay time 56ns (decay time of ordinary crystal was 76ns);
- increased light yield;
- better energy resolution in respect to uniformity;
- restrain emission in the ~ 300nm range of wavelength;
- increased absorption in the shorter-wavelength ;
- uniformity;
- limited percentage of the powder charge and easier loading process:

PWO nanopowder

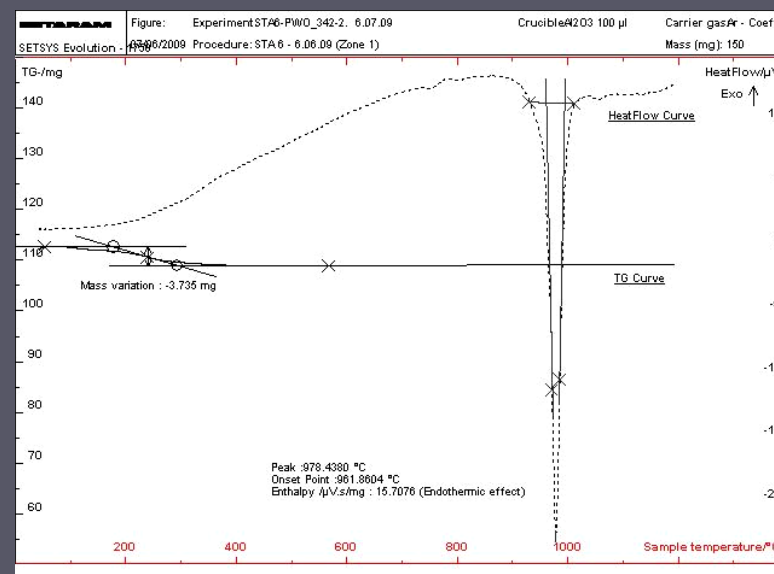




PWO crystalline powder: a- XRD pattern ; b,c, - SEM microg.

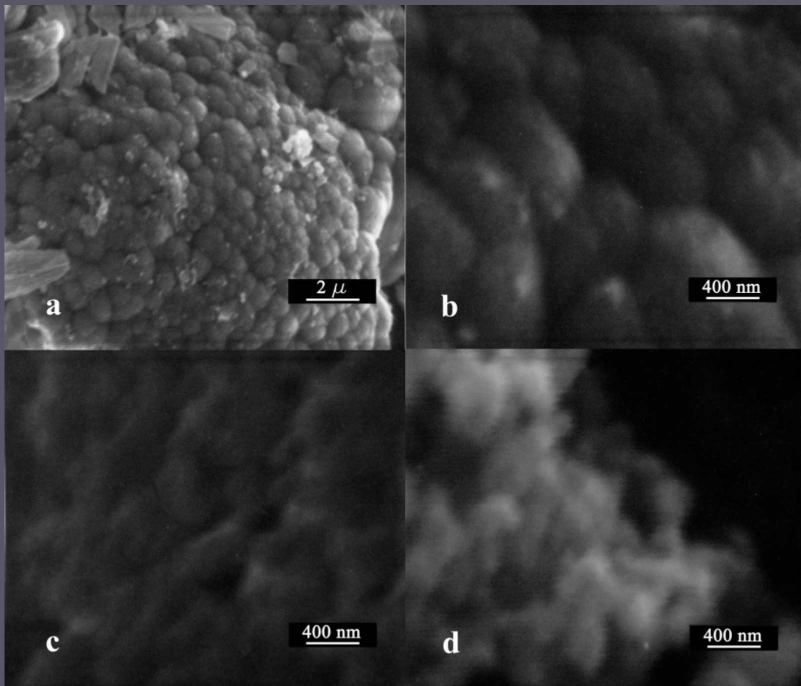


PWO amorphous for X-rays; SEM micrographs at different magnifications

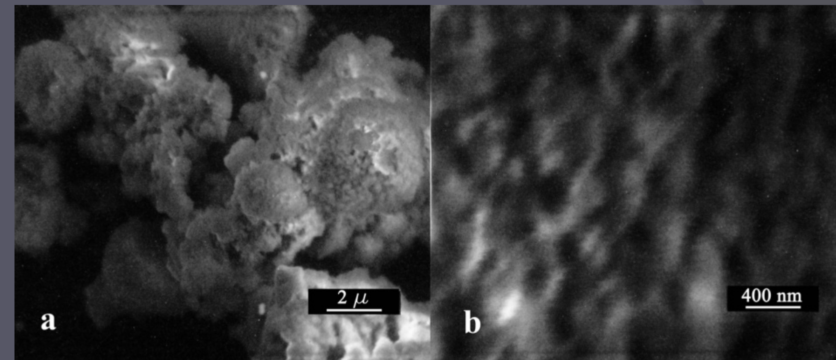


TG and DTA curves of PWO nanopowder
nanocrystalline state provides temperature drop of the melting point of the material almost by 155 °C, the melting point of lead tungstate being 1123°C.

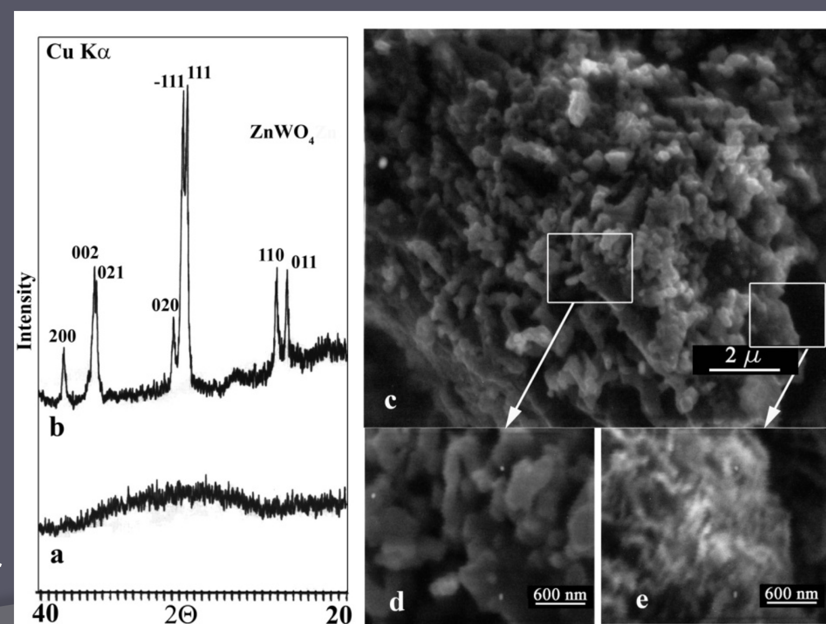
Nanopowder of Tungstates



SEM micrographs of nanocrystalline powders of $CaWO_4$ at different magnification

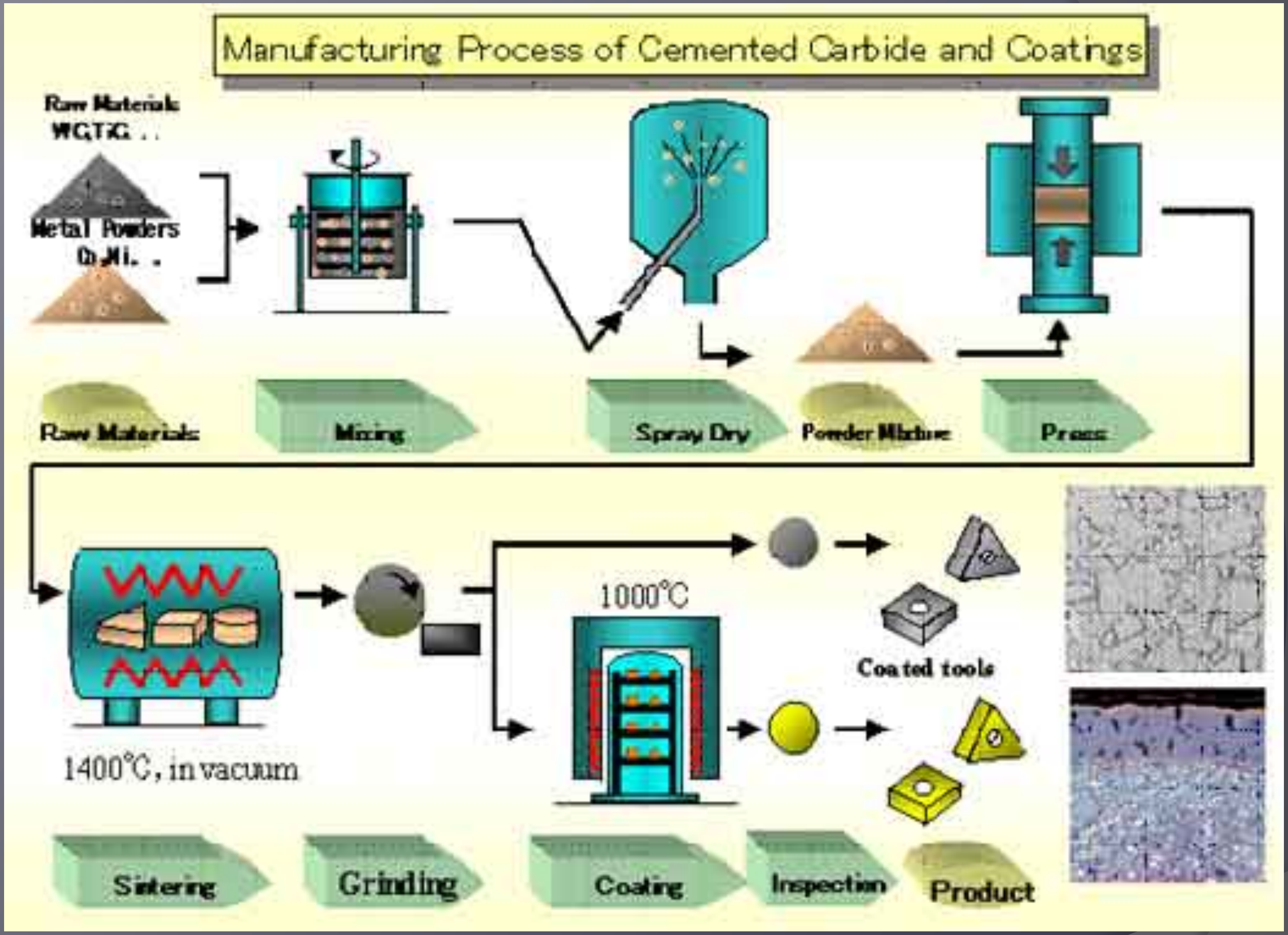


SEM micrographs of nanocrystalline powders of $CdWO_4$ at different magnification



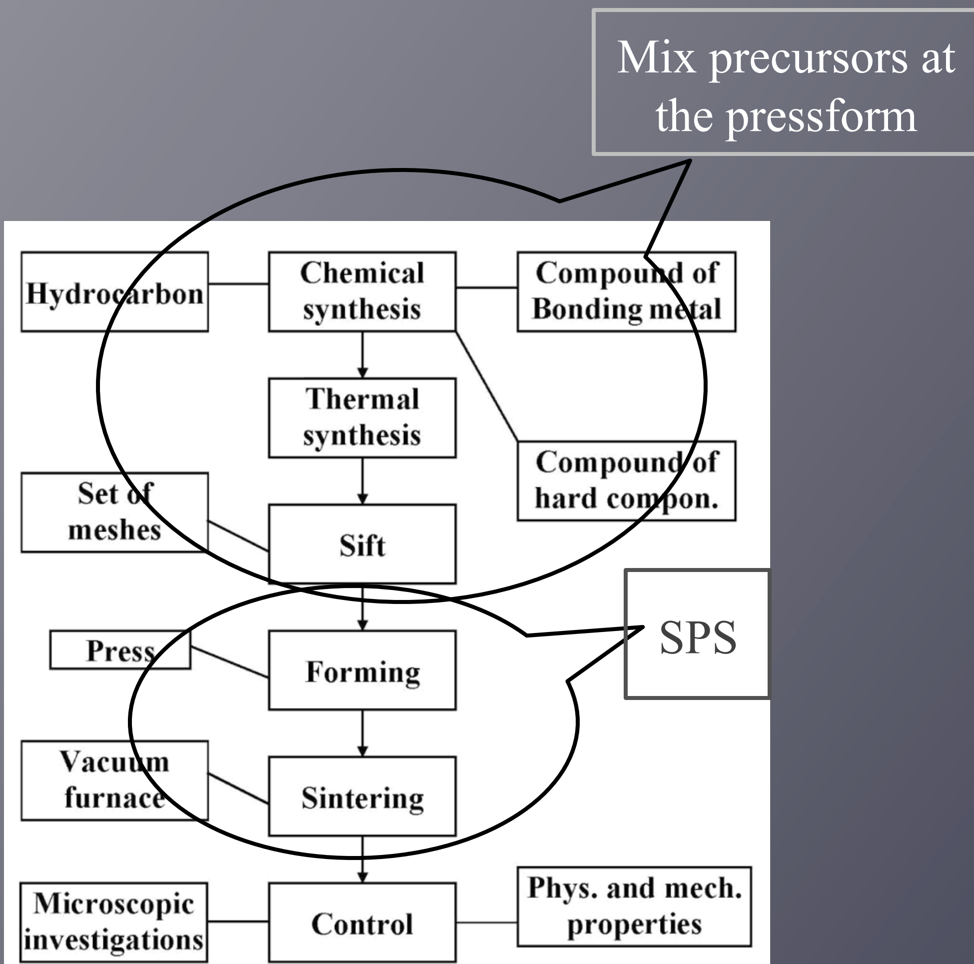
Nanocrystalline powders of $ZnWO_4$: a,b- XRD pattern powders synthesized at room temperature(a) and after annealing at 500°C ;
c,d,e - SEM micrographs at different magnification

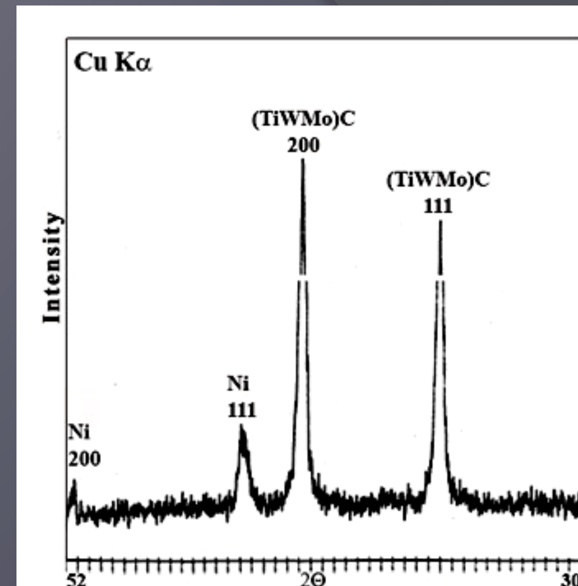
Hard Metals

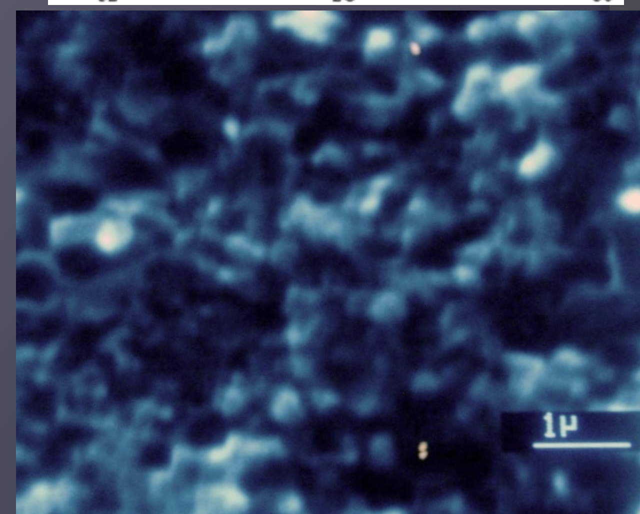


Manufacturing Process of Cemented Carbide and Coatings
Raw Materials
Mixing
Spray Dry
Powder Mixture
Press
1400℃, in vacuum
1000℃
Coated tools
Sintering
Grinding
Coating
Inspection
Product

Hard Metals







XRD pattern of (TiW,Mo)C-Ni system obtained from mixing precursors (TiH_2, $NiCl_2$, MoO_3, WO_3)

Hard Metals

$$TiH_2 \longrightarrow Ti + H_2$$
$$Ti + 3TiCl_4 \longrightarrow 4TiCl_3$$

$$TiCl_3 + C_6H_6 \longrightarrow TiCl_3.C_6H_6$$
$$TiCl_3 + (CH_2)_6N_4 \longrightarrow Ti(CH_2)_6N_4Cl_3$$

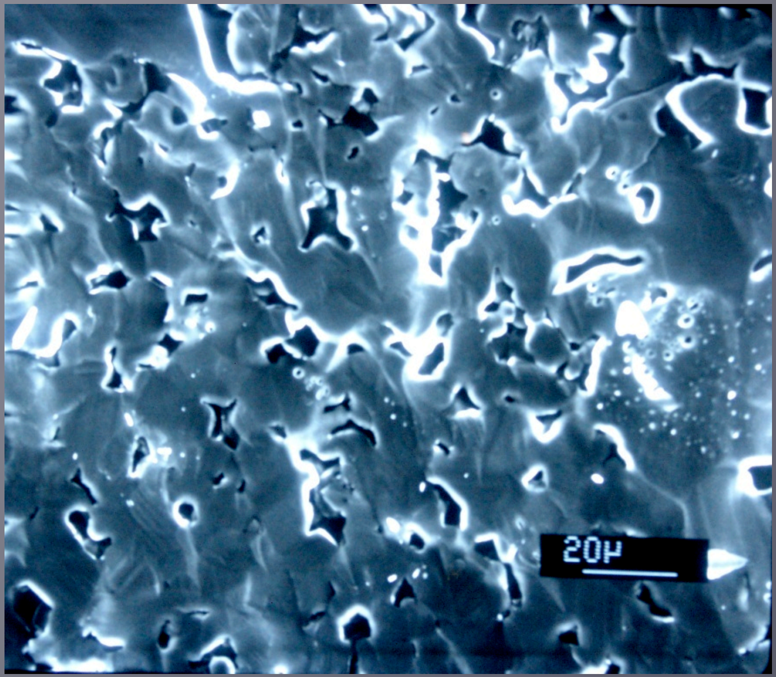
$$(NH_4)_2TiF_6 + NiCl_2 \cdot 6H_2O + 2(CH_2)_6N_4 \longrightarrow 2NH_4Cl + [Ni(H_2O)_6][TiF_6](C_6H_{12}N_4)_2$$

$$TiCl_4 + 4C_6H_5\,NH_2 \longrightarrow NH_2\,Ti(C_6H_5NH_2)_4Cl_4$$
$$TiCl_4 + 2NH_2(CH_2)_6NH_2 \longrightarrow Ti(2NH_2(CH_2)_6NH_2)_2Cl_2$$

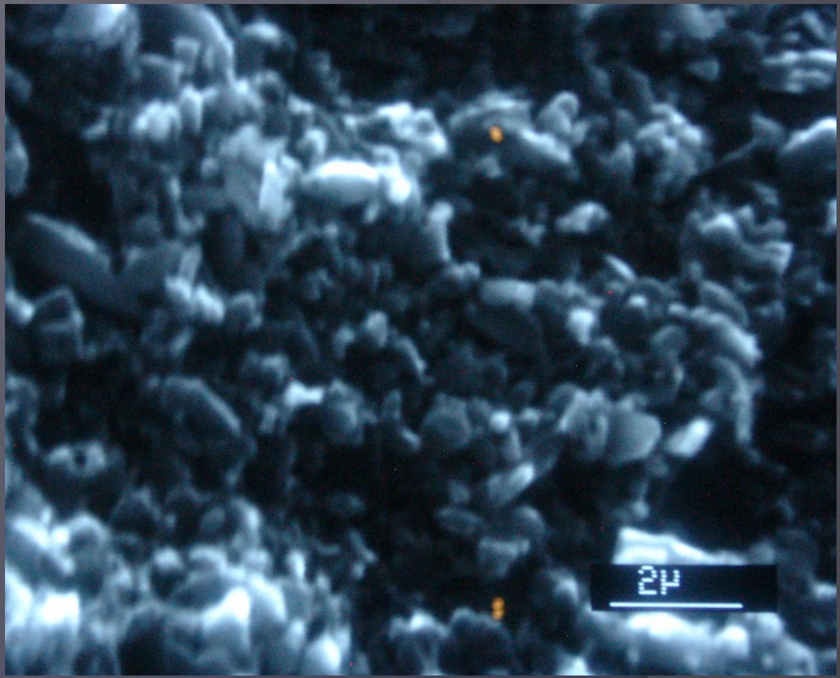
$$NiCl_2 + 4C_6H_5NH_2 \longrightarrow [Ni(C_6H_5NH_2)_4]Cl_2$$
$$MoCl_5 + 5C_6H_5NH_2 \longrightarrow [Mo(C_6H_5NH_2)_5]Cl_5$$
$$WCl_6 + 6C_6H_5NH_2 \longrightarrow [W(C_6H_5NH_2)_6]Cl_6$$

$$CHI_3 + MoCl_5 \longrightarrow [Cl_3Mo = CHI] + I_2 + Cl_2$$
$$CHI_3 + WCl_6 \longrightarrow [Cl_4W = CHI] + I_2 + Cl_2$$

Armor materials

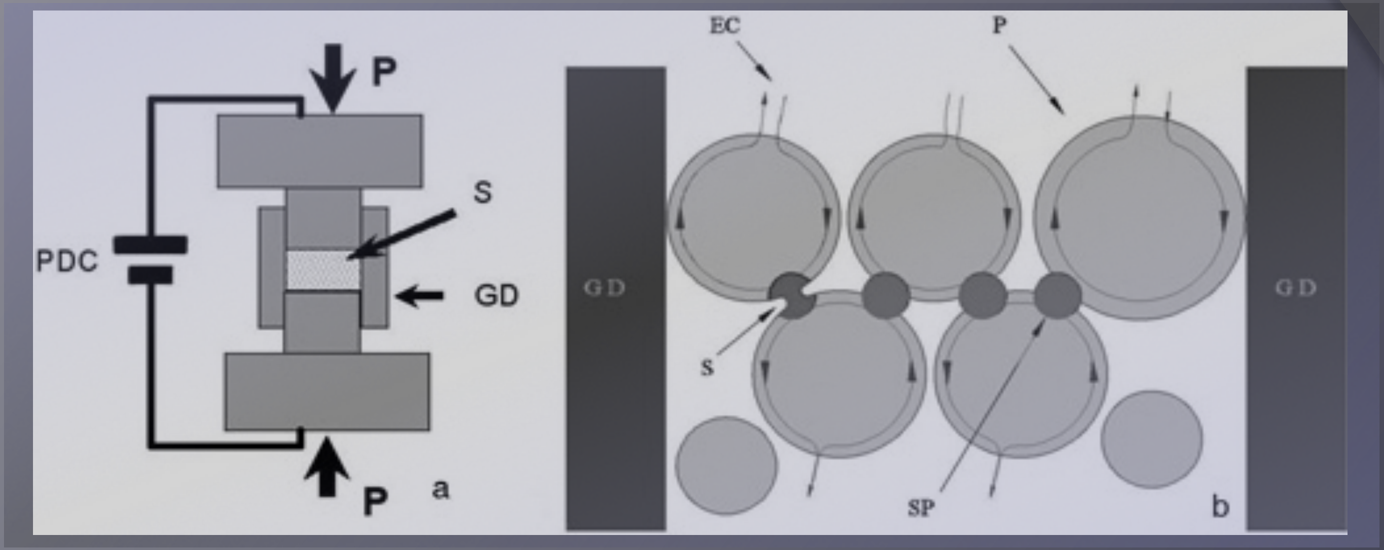


SEM images of BC standard armor material



SEM images of BC armor material sintered via SPS

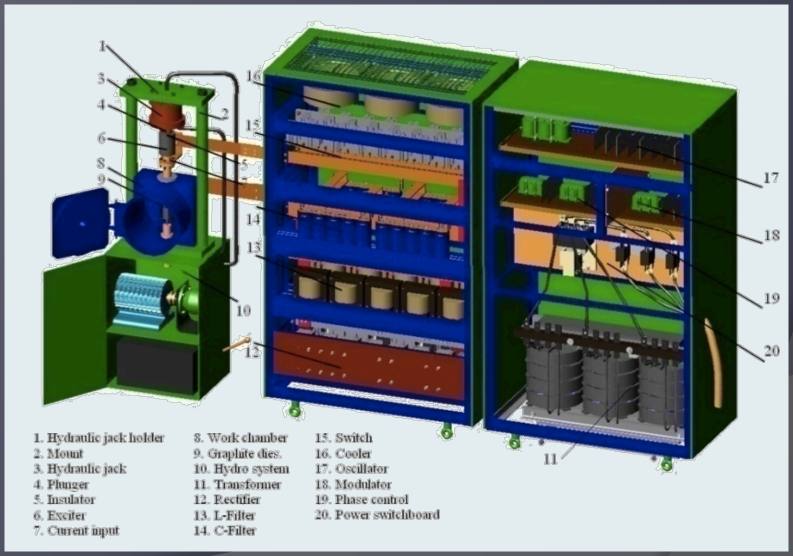
SPS devise for sintering composition materials



Sintering temperature (max 2500^{o}C)

Current (max 5000 A)

Applied pressure (max 200MPa)

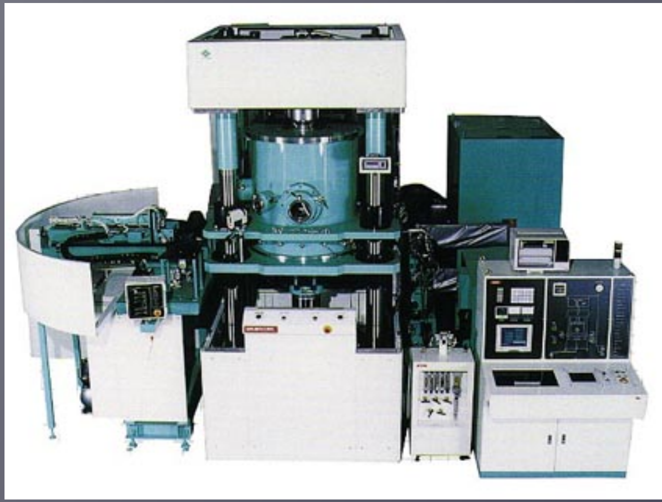


RCSR

Commercial SPS devises for sintering composition materials

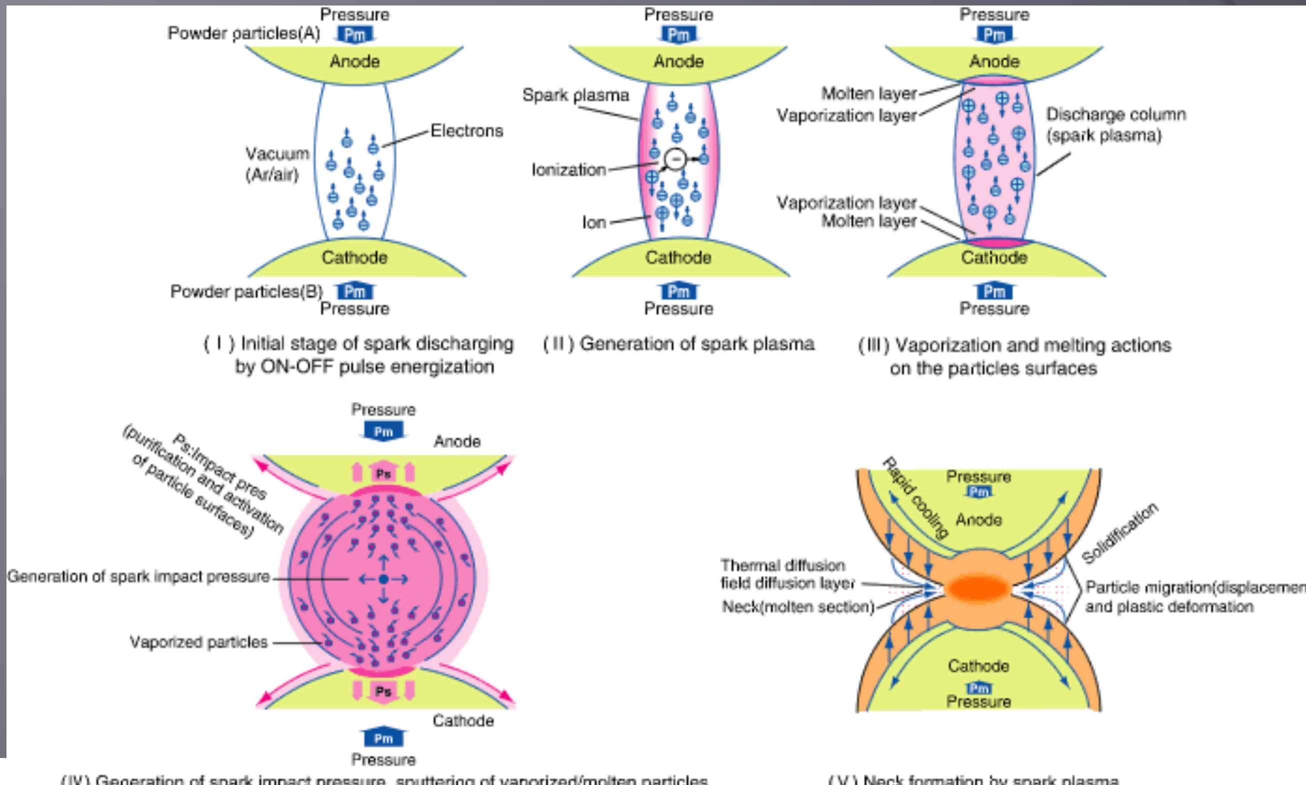
SPS - 511S

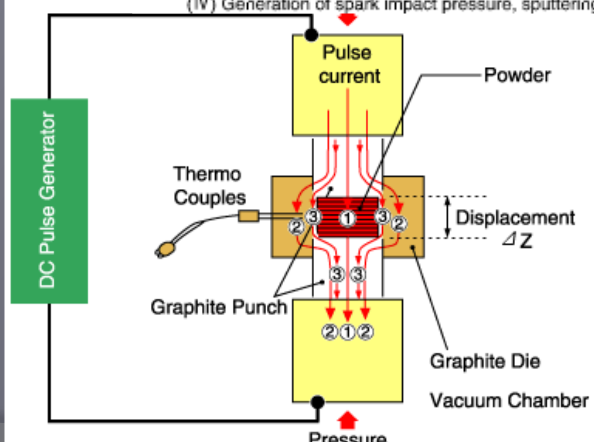
SPS – 2050

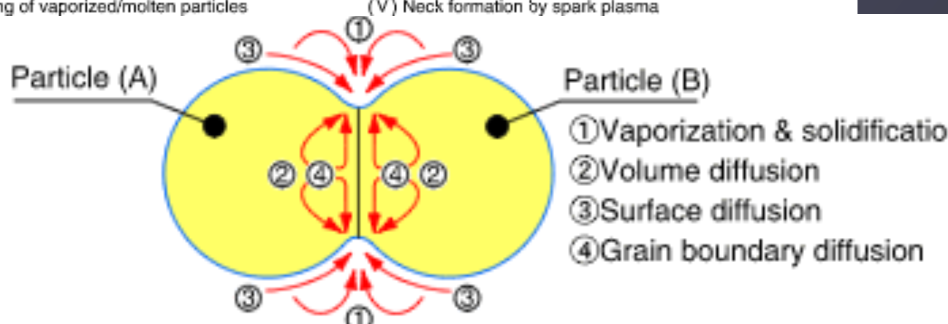


SPS-9.40

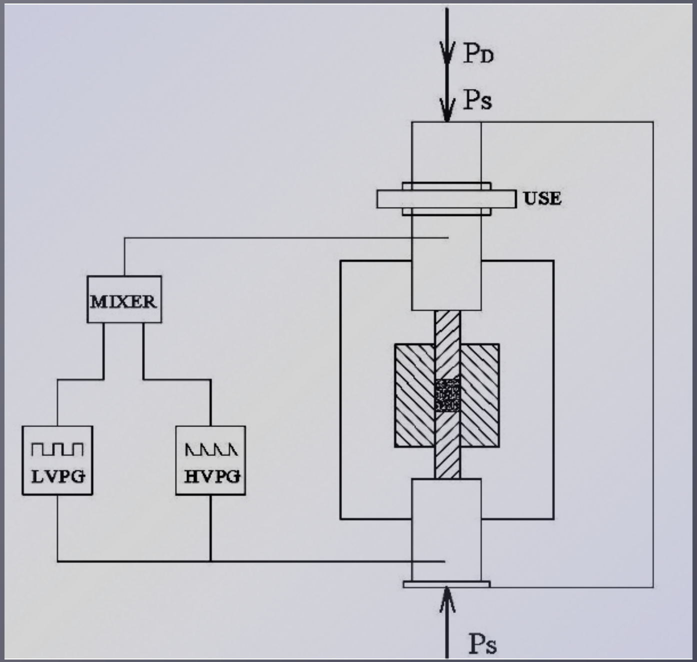
Mechanism of SPS method







Schematic drawing of the modified SPS device that makes possible sintering non-conductive materials by using SPS method;



The device will be additionally equipped with *high voltage pulse generator*. Low voltage will be subjected to regulation and will be changed within the range of 10-20V, force of the current will be 3000-5000A. Magnitude of high voltage will range between 1-2 kv. *Ultrasonic excitation device* with 22-25 kHz frequency will be constructed for providing plasma processes and compaction assistance. The developed device will be equipped with the unit of *Pulsed dynamic loading*. Integral temperature of sintering will range within the interval 1000-1200^{o}C.

Thank you for attention