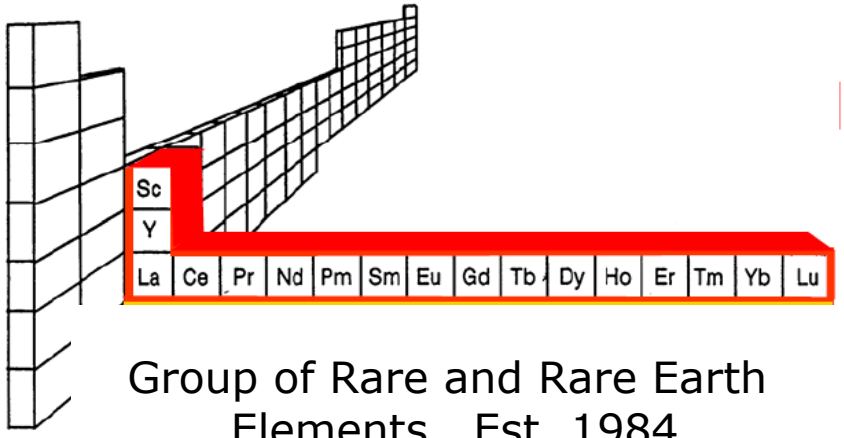


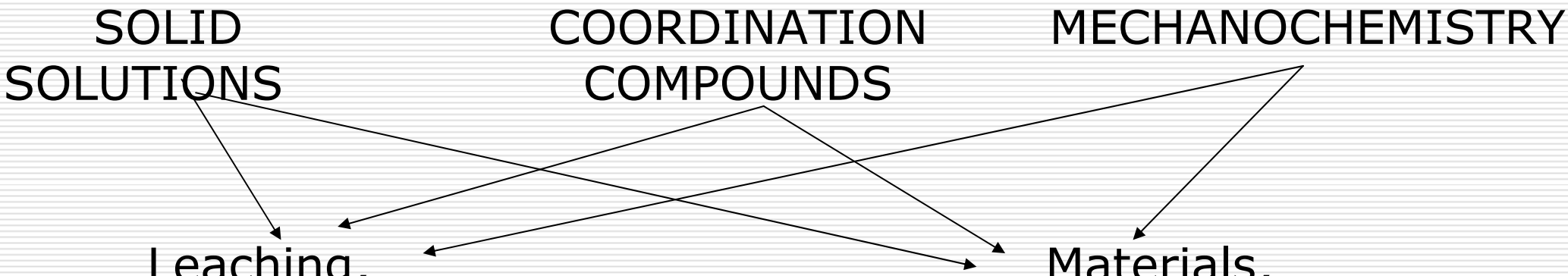
Group of Rare and Rare Earth Elements, Est. 1984

RARE EARTHS CHEMISTRY: SCIENTIFIC, TECHNOLOGICAL AND PRODUCTION ACTIVITIES AT THE DEPARTMENT OF INORGANIC CHEMISTRY, SOFIA UNIVERSITY

M. Milanova, D. Todorovsky, N. Minkova, A. Terziev, M. Getsova, G. Tzvetkov, N. Petrova, M. Uzunova, S. Anastasova, J. Zaharieva, R. Kralchevska, R. Todorovska

Faculty of Chemistry, Sofia University, Bulgaria

Chemistry of rare earth elements



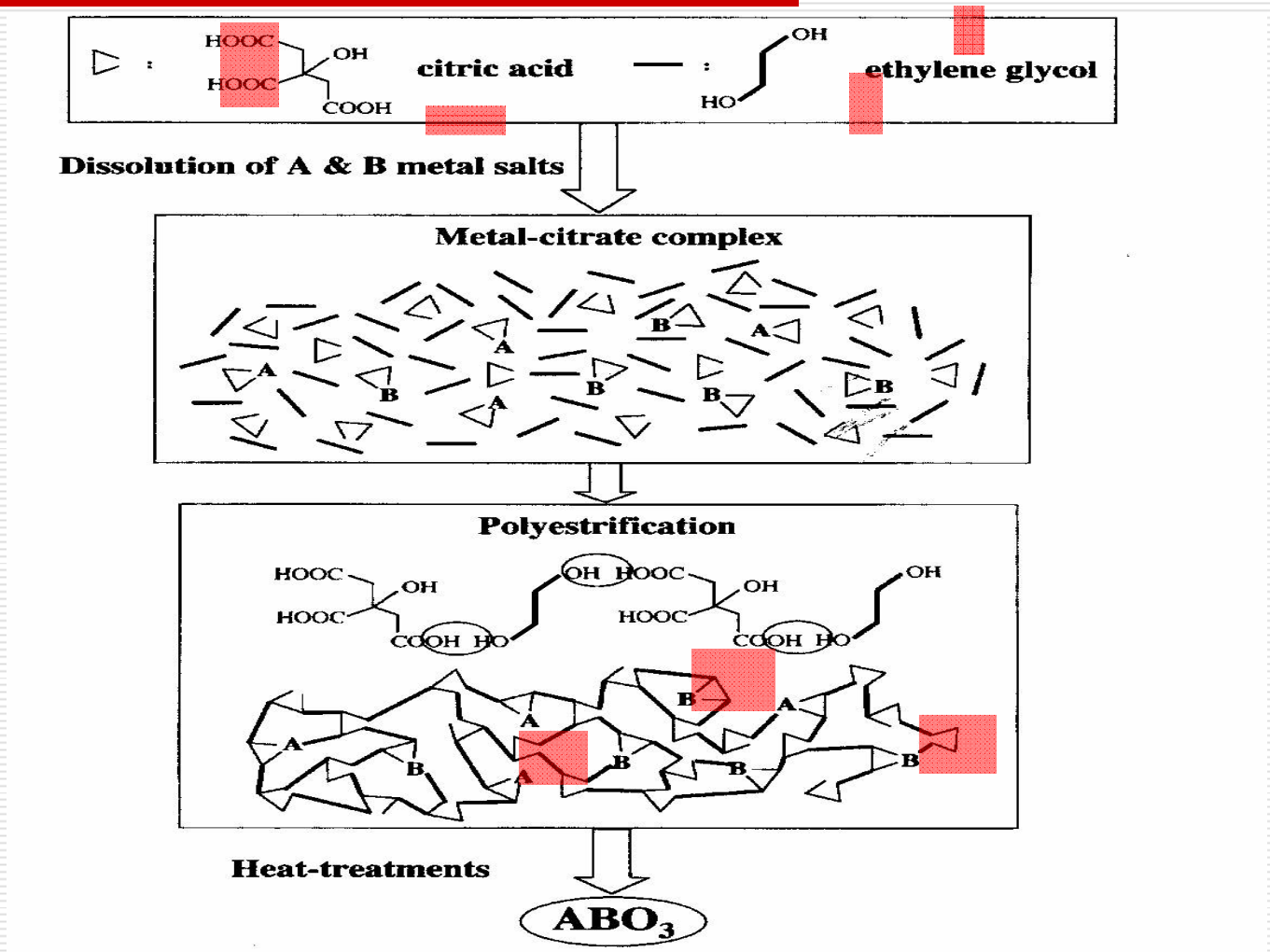
- RE products

- Silicates
- Polymetallic oxides
- Modified photocatalysts
- Thin films
- Optical sensors

Plan

- Materials based on REE
- RE products

Polymerized complex method, PCM



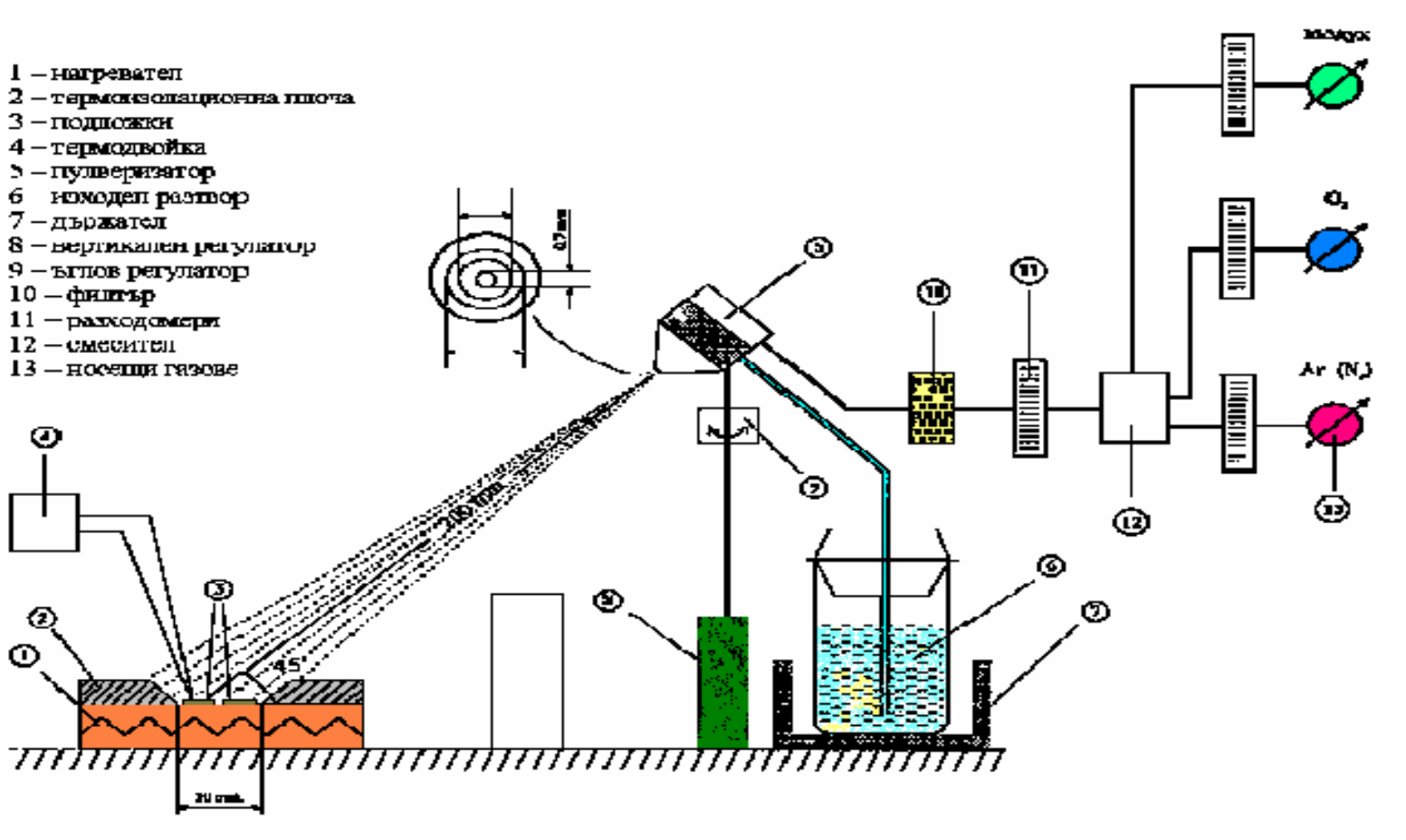
Polymerized complex method
Problems

- Reaction CA /EG
- Factors influencing the complex compositions
- Nature of the complexes in bimetallic systems
- Alcoholic group deprotonation
- Thermochemical behaviour of the complexes; nature of the final precursor
- Application of the solutions of complexes for thin film deposition

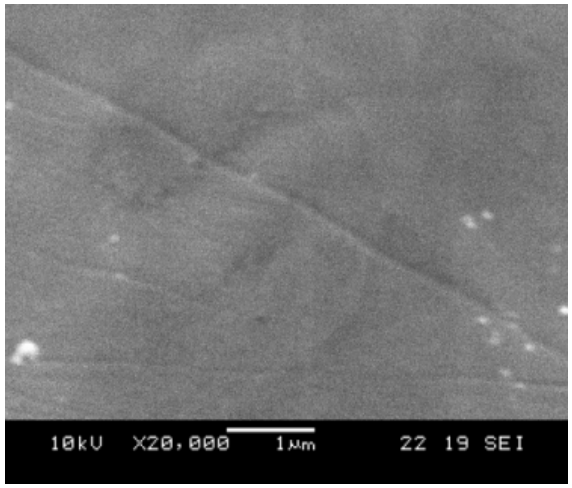
Synthesized and characterised materials

- Buffer layers for high temperature superconductors (Y_2O_3, CeO_2, YSZ)
- Materials of high magnet restriction ($LaMnO_3$, pure/doped with Ca)
- Magnet materials (Fe_2O_3, $Y_3Fe_5O_{12}$,(granite), $YFeO_3$, $Y_3Fe_5O_{12}$ doped with Al or Ce)
- Ferroelectrics ($La_2Ti_2O_7$, $Nd_2Ti_2O_7$)
- Ionic conductors ($Y_2Ti_2O_7$)
- Oxygen sensors based on YSZ, doped with Pt nanoparticles (Assoc. Prof. Dimitrov, Assoc. Prof. Dushkin)
- Optical oxygen sensors
- Photocatalysts based on TiO_2, including modified by doping with La or by mechanochemical treatment (Assoc. Prof. Dimitrov)

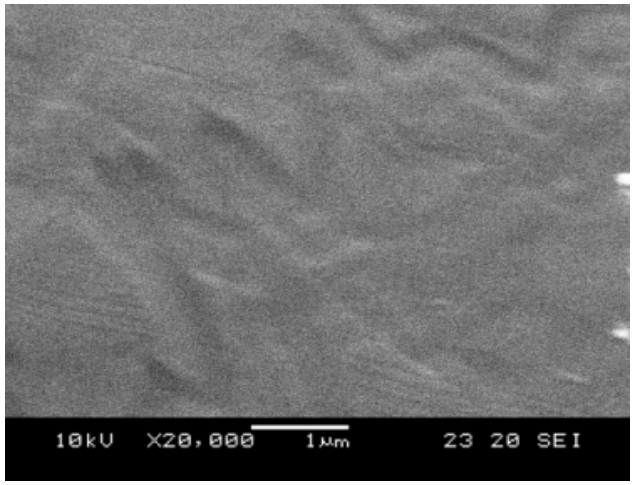
Deposition of thin films
Spray-pyrolysis /PCM (mixed-metal citrates)



Thin films of Y-stabilized ZrO_2
Buffer layers for high temperature superconductors (YBCO)

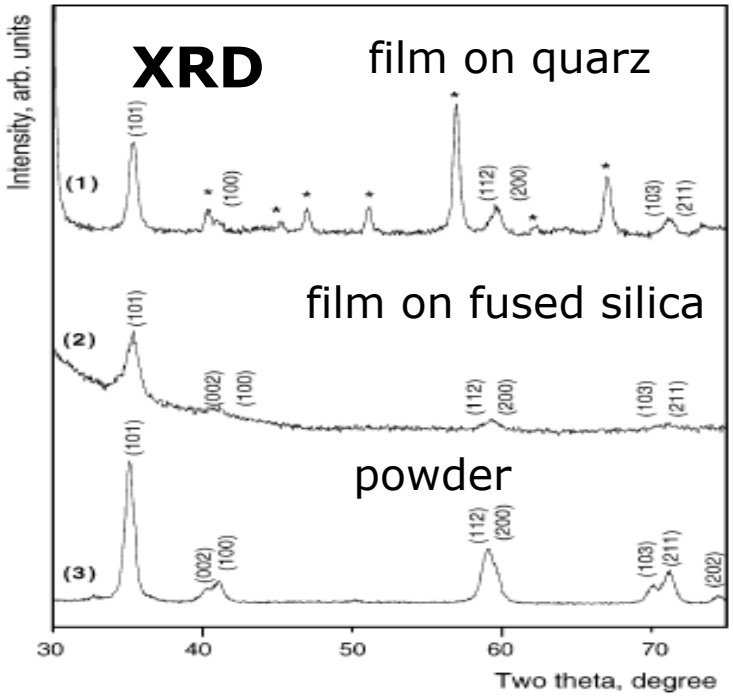


On fused quarz



On glass

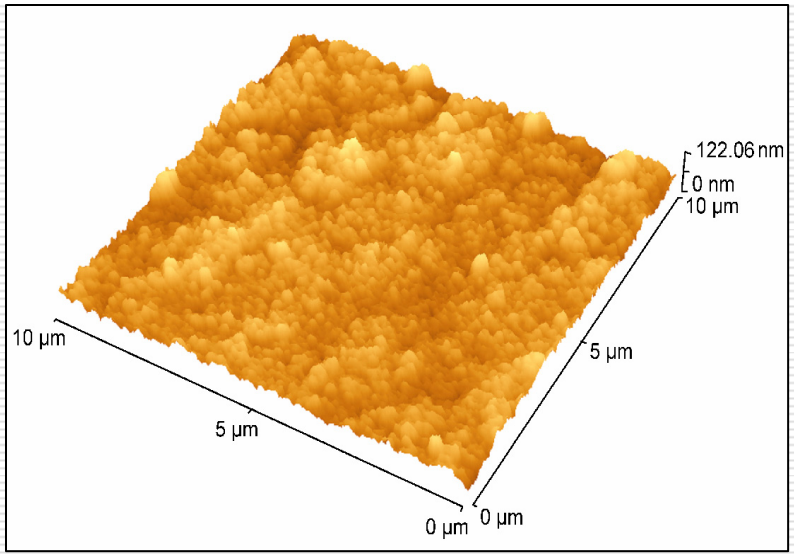
SEM images *(8 mol% Y)*
T substrate 350°C;
additionally annealed at 750°C



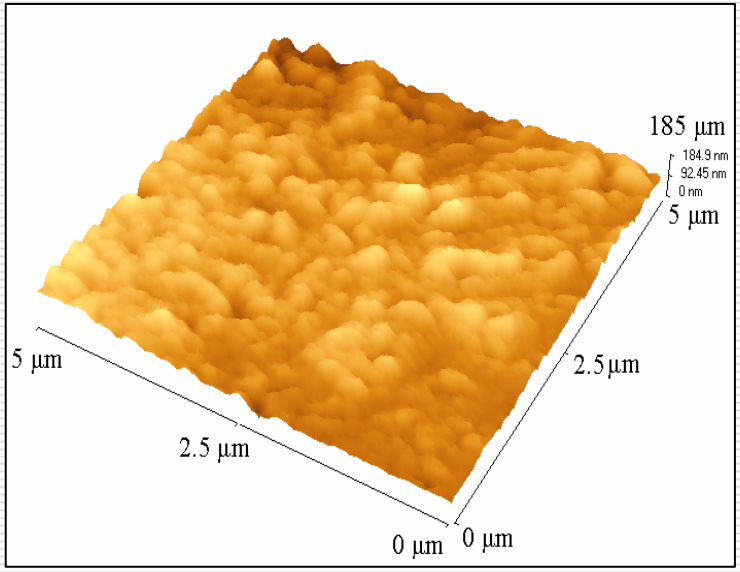
Thin films of CeO_2

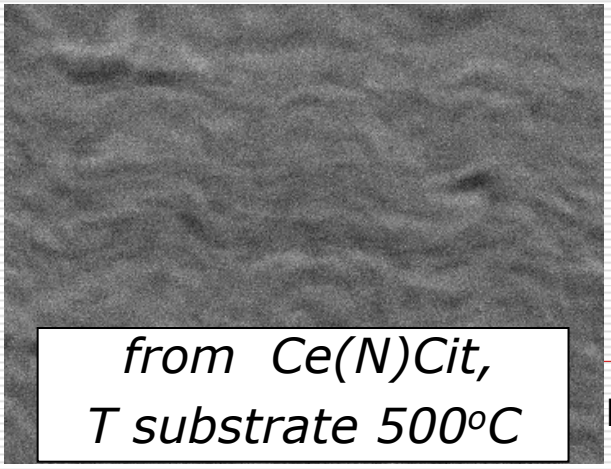
Buffer layers for high temperature superconductors

AFM (10x10 μm), from Ce(N)Cit (fused quarz)

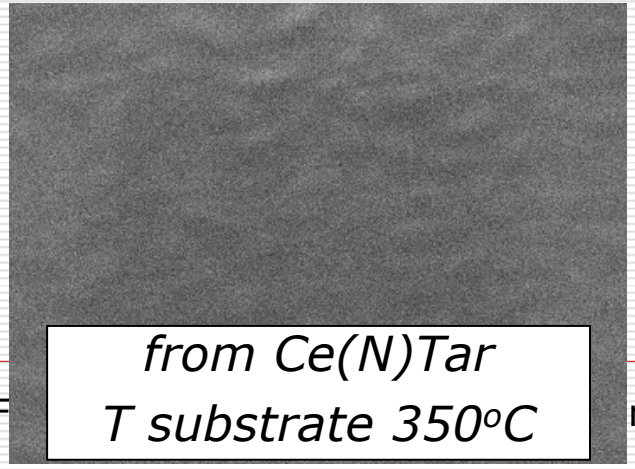


AFM (5x5 μm), from Ce(Cl)Cit (fused quarz)





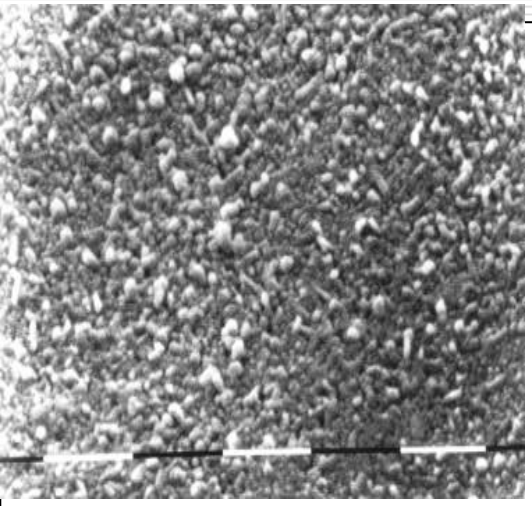
from Ce(N)Cit,
T substrate 500°C



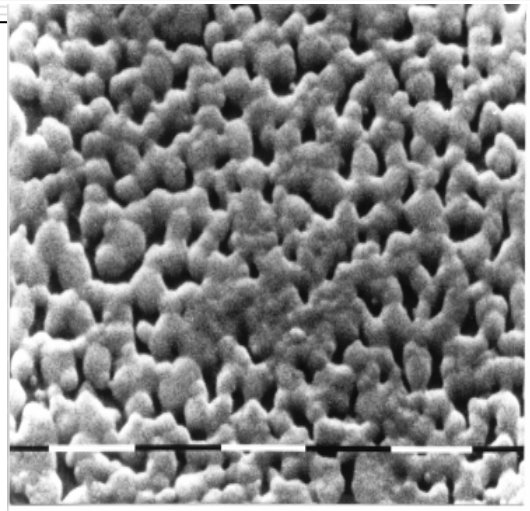
from Ce(N)Tar
T substrate 350°C

size of the grains
(250-400)x(120-240) nm

Thin films of $LaMnO_3$
Materials of high magnet restriction



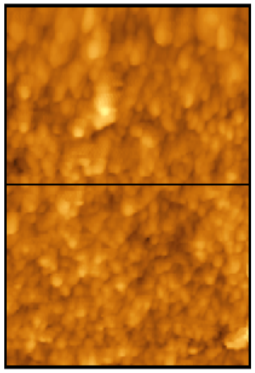
$La_{0,7}Ca_{0,3}MnO_3$

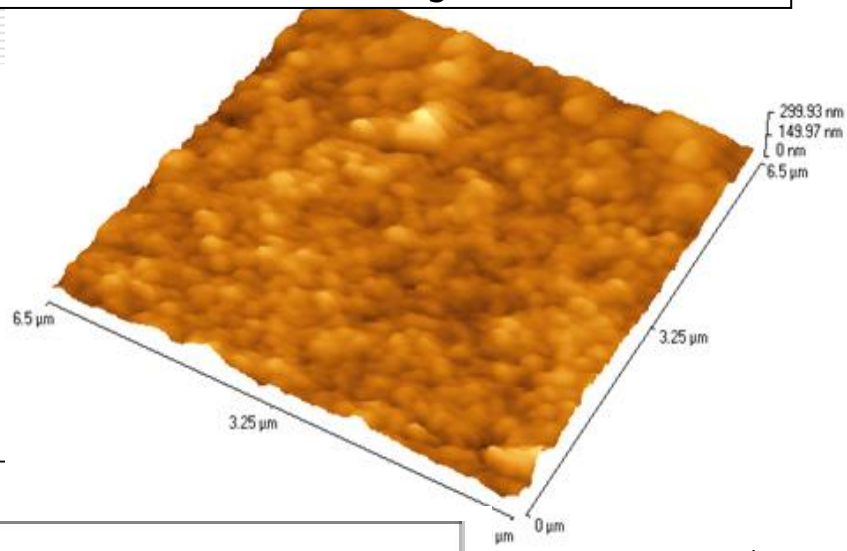


$LaMnO_3$

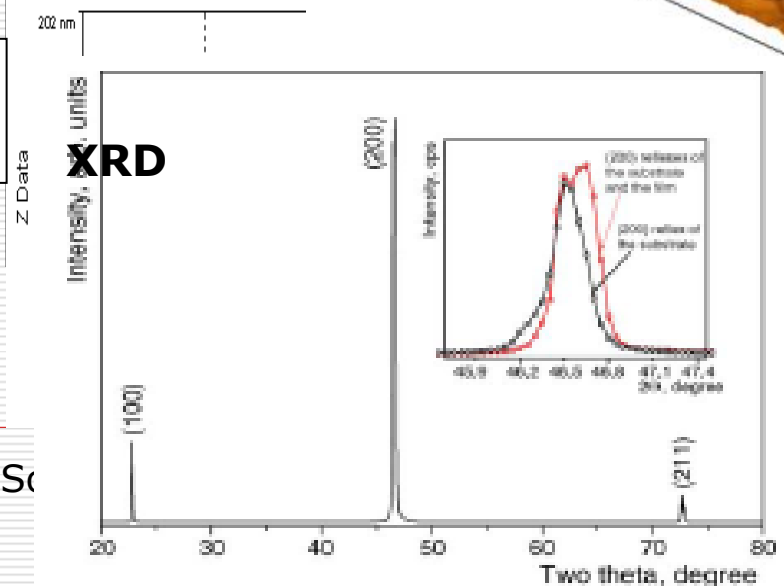
SEM of manganite films *with thickness ~150 nm on* $SrTiO_3$*, x20 000).*

AFM (6,5x6,5 μm) of $LaMnO_3$ film on $SrTiO_3$



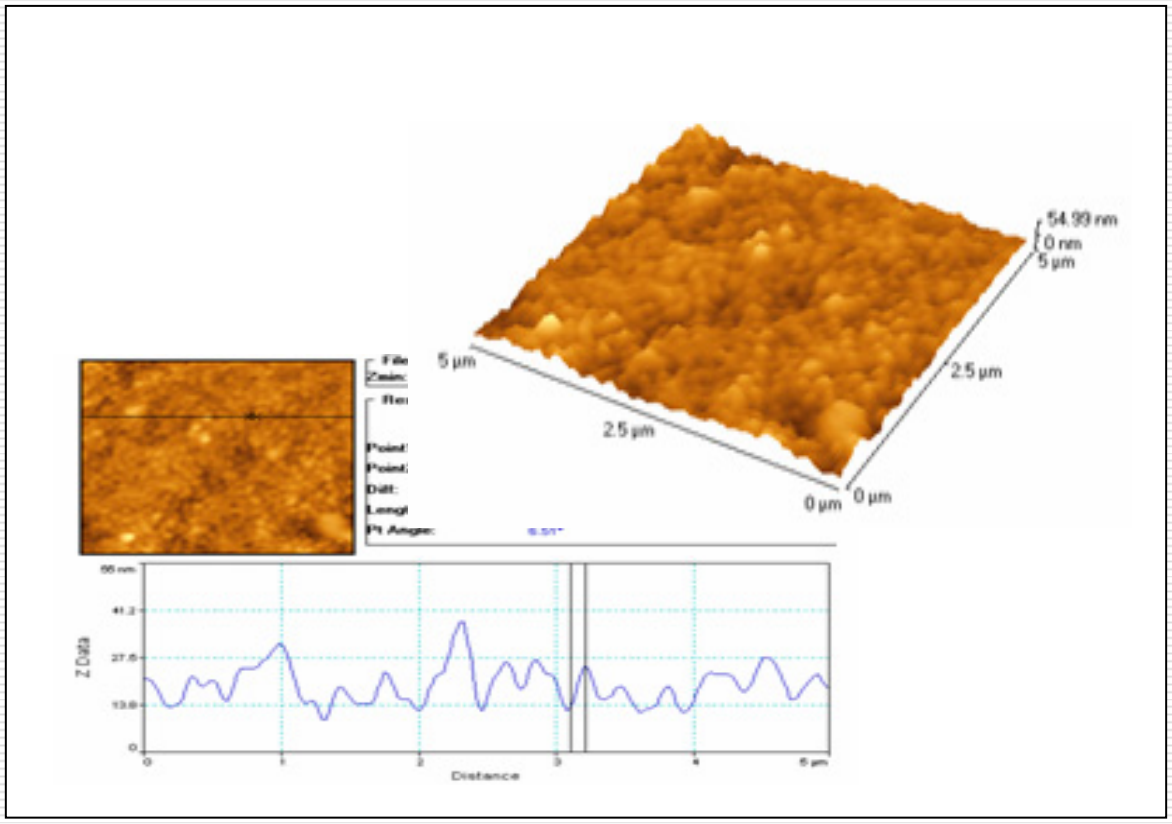


XRD

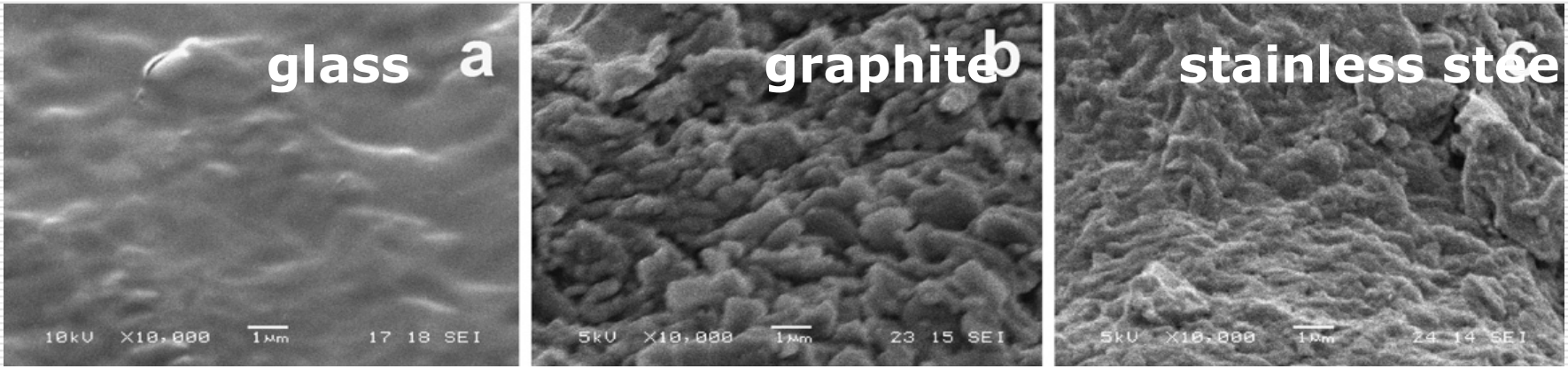


Thin films of $YFeO_3$
Ferromagnetic behaviour, potential UV-Vis photocatalyst

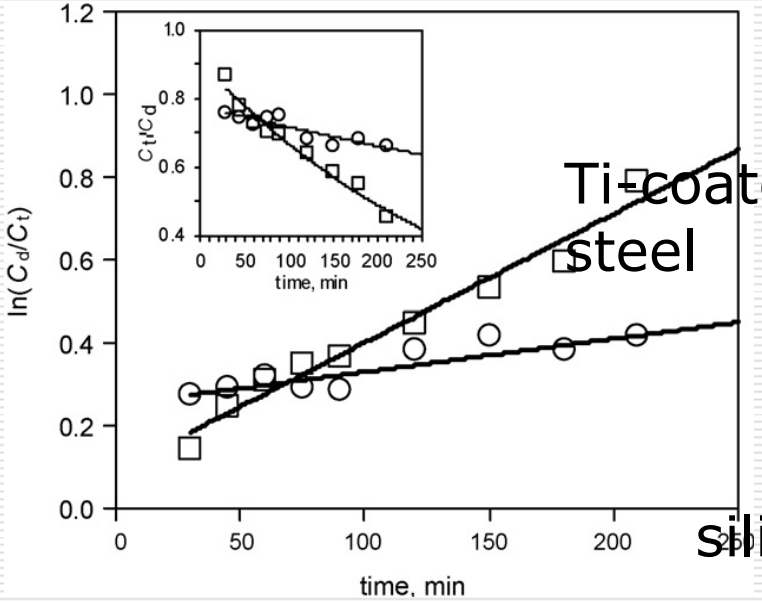
AFM (5x5 μm) of $YFeO_3$ film on $SrTiO_3$



Thin films of La-doped TiO_2
Photocatalysts



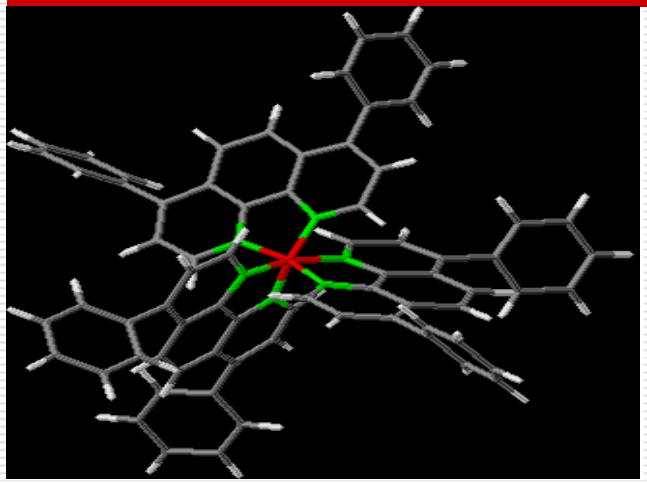
SEM images, post deposition heating at 400ºC (a), 500ºC (b,c).



Degradation of methylene blue, TiO_2:5 mol% La

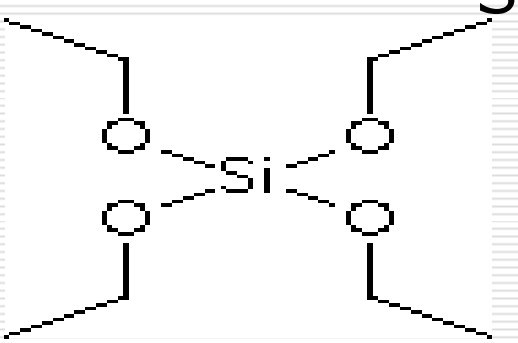
Thin films based on SiO_2

Optical oxygen sensors

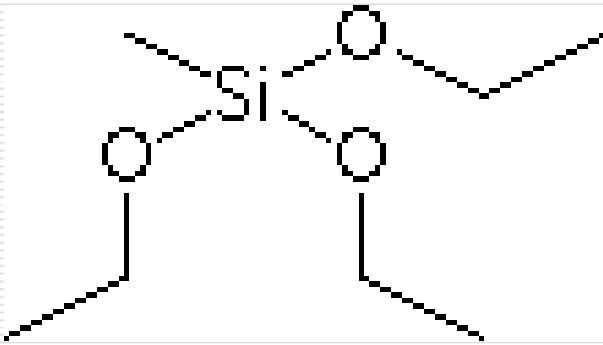


$Ru(dpp)_3^{2+}$

Silanes

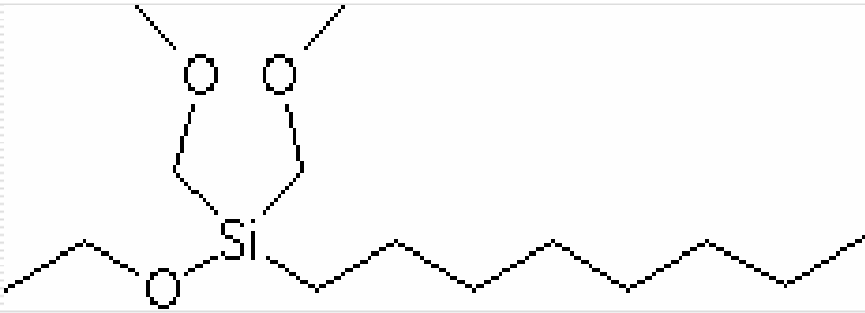


Tetraethoxy silane
(TEOS)



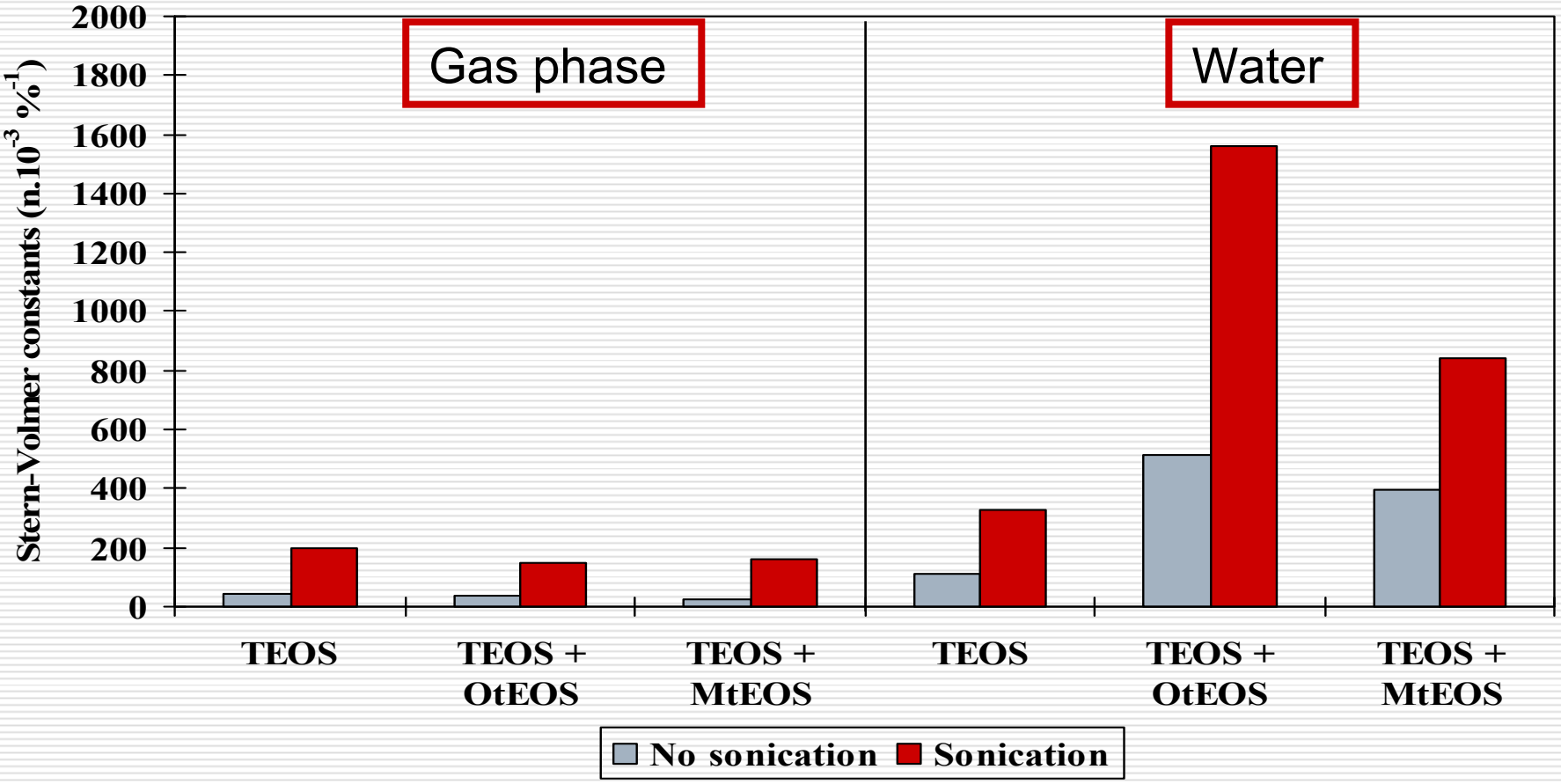
Methyl triethoxysilane
(MTEOS)

$$\frac{I_0}{I} = 1 + K_{SV}[O_2]$$



Octyl-triethoxysilane
(OtEOS)

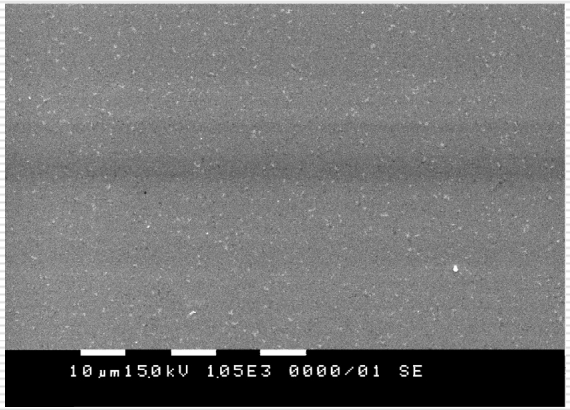
SiO_2-based films
Effect of sonication



PMMA films

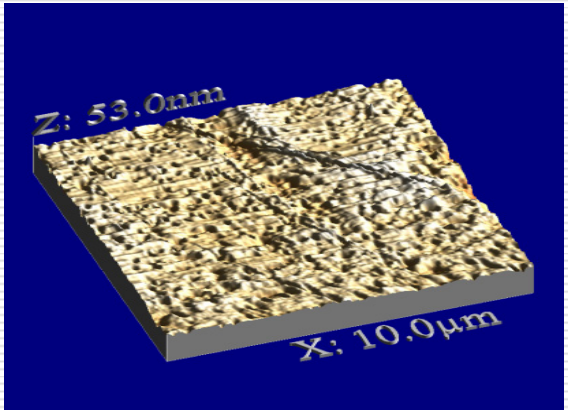
Optical oxygen sensors

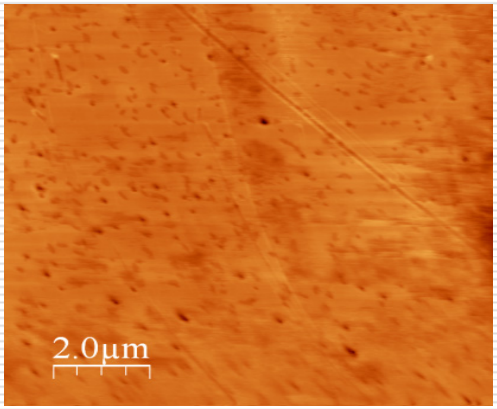
SEM



PMMA solution

AFM



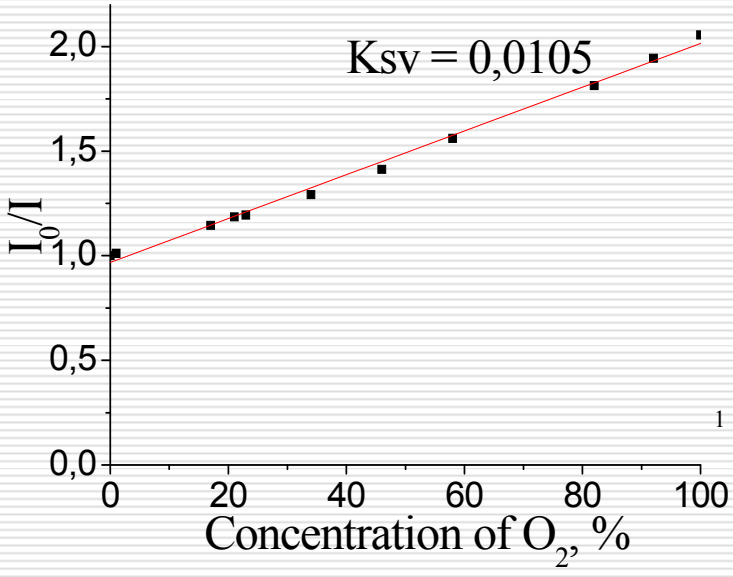


PMMA solution

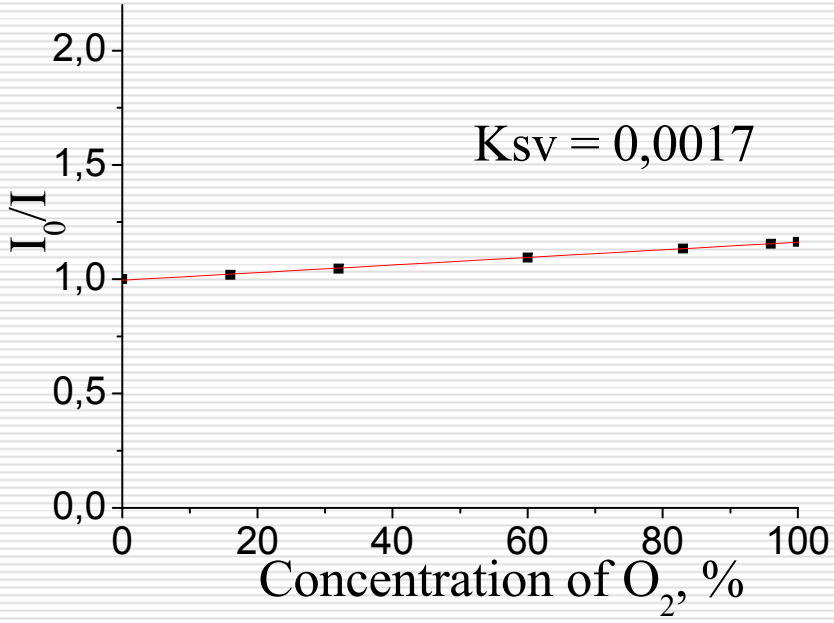
MMA polymerized

PMMA films

Oxygen in the gas phase



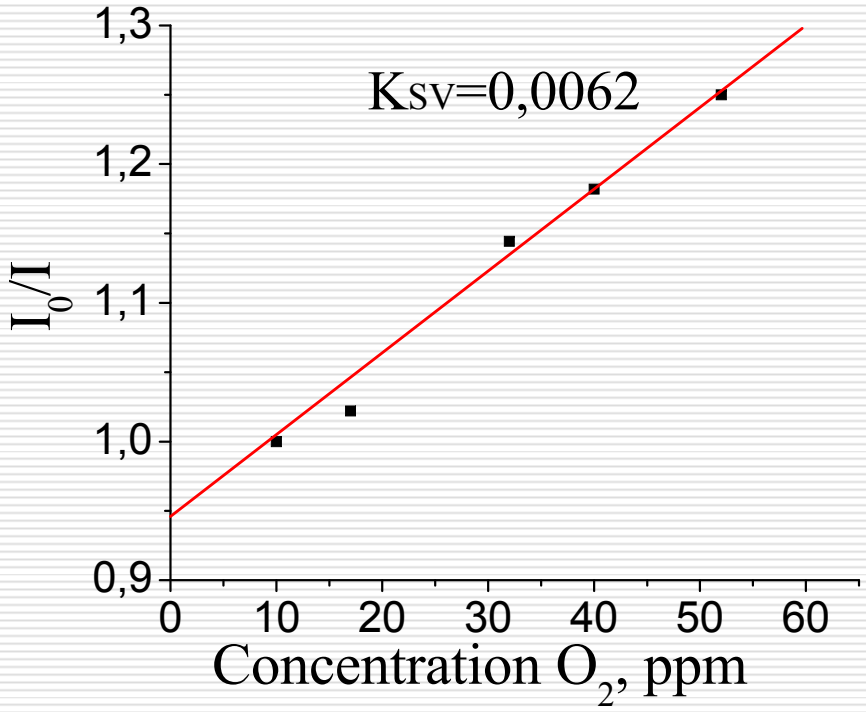
film prepared
via PMMA solution



film prepared *via in situ*
polymerization of MMA

PMMA films

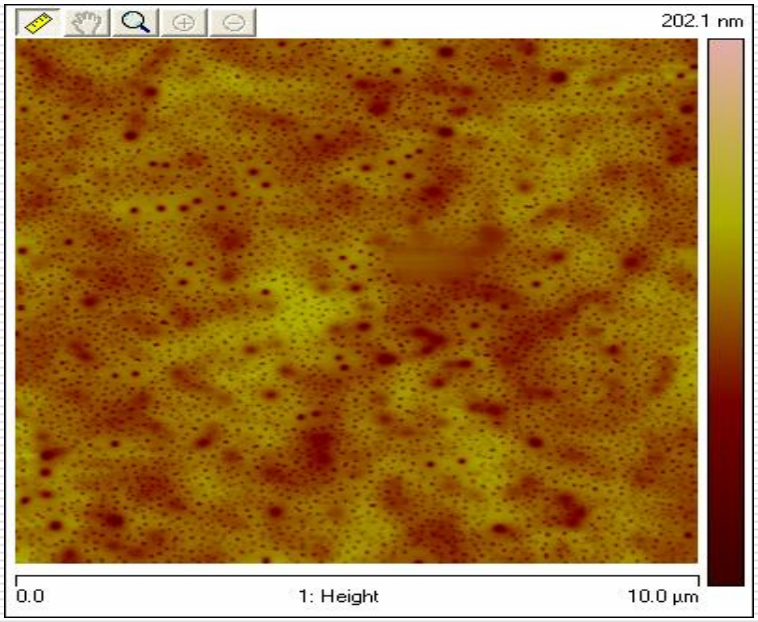
Dissolved oxygen in water

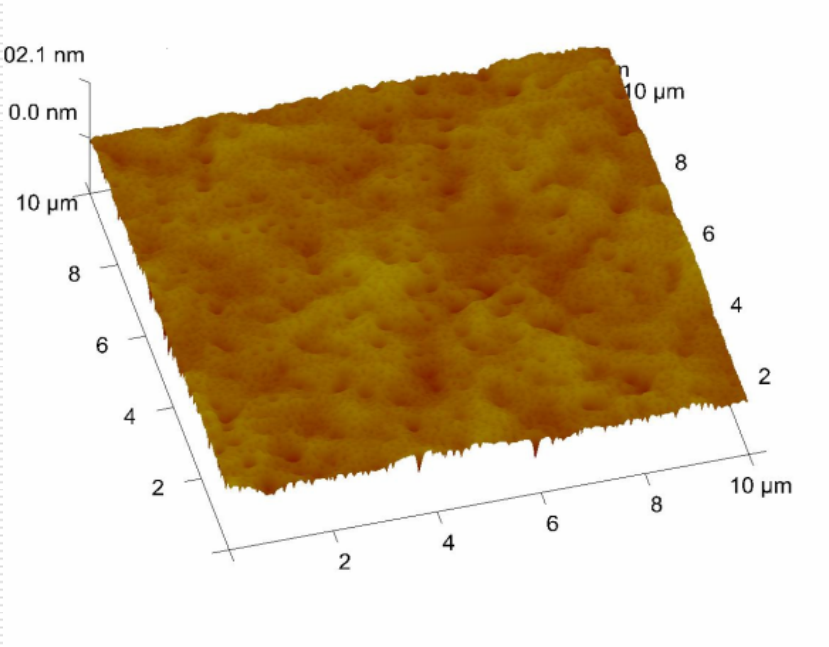


film prepared
via PMMA solution

Hybrid matrix, SiO_2/polyester

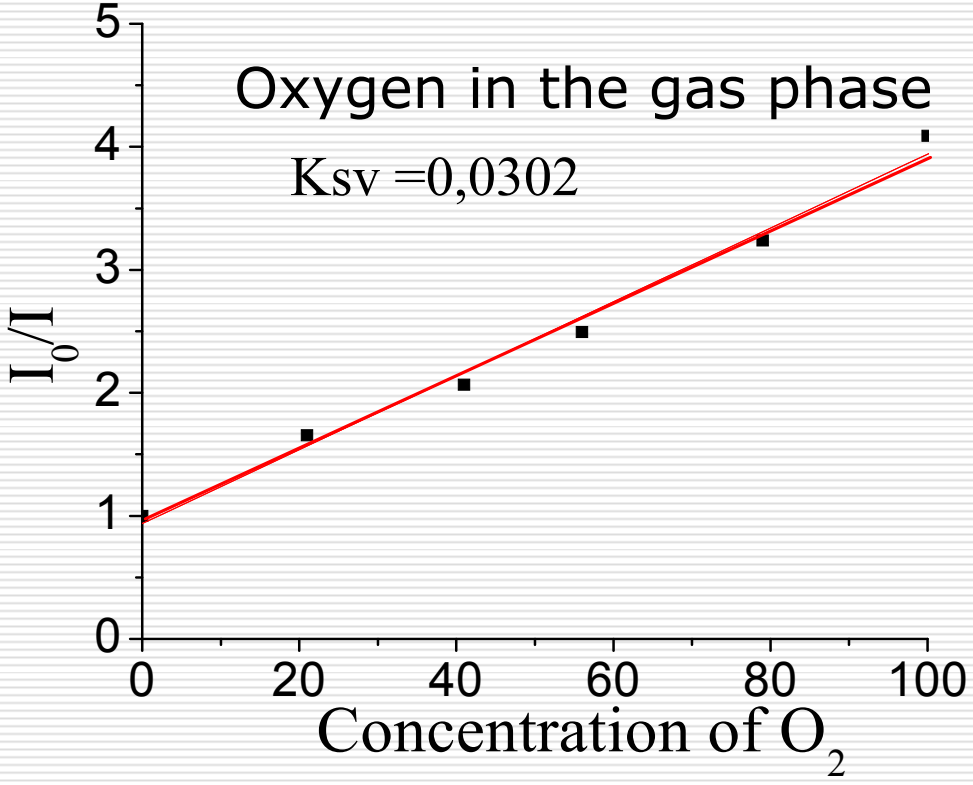
Optical oxygen sensors

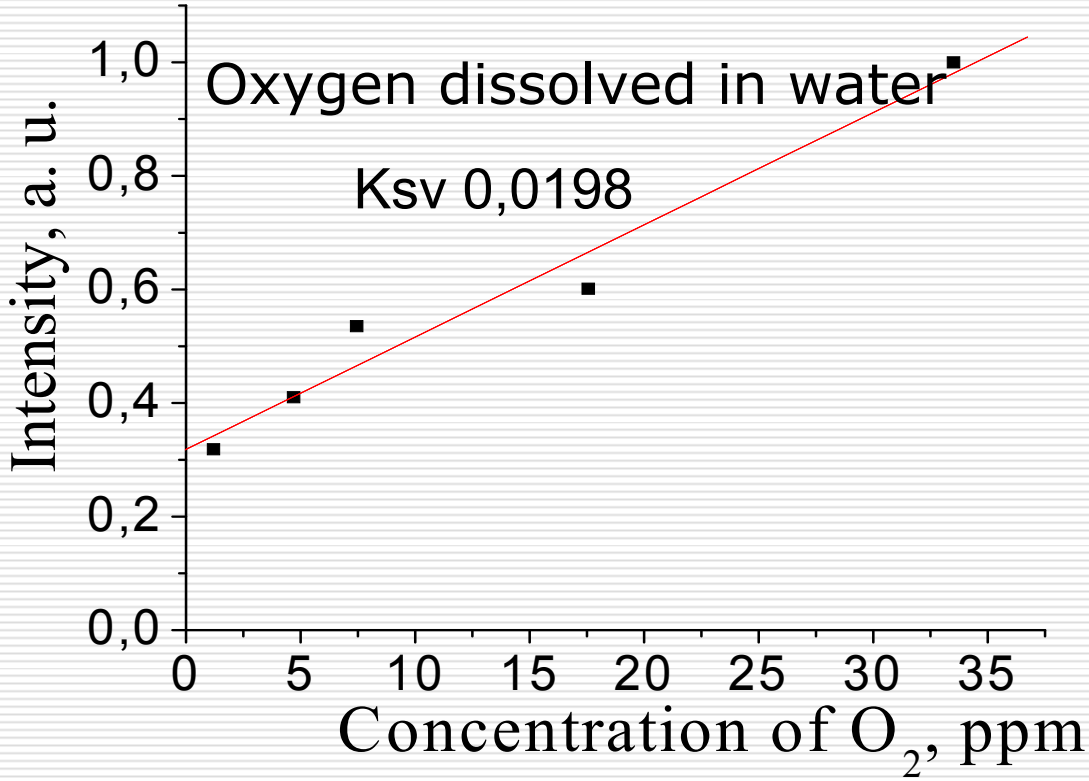




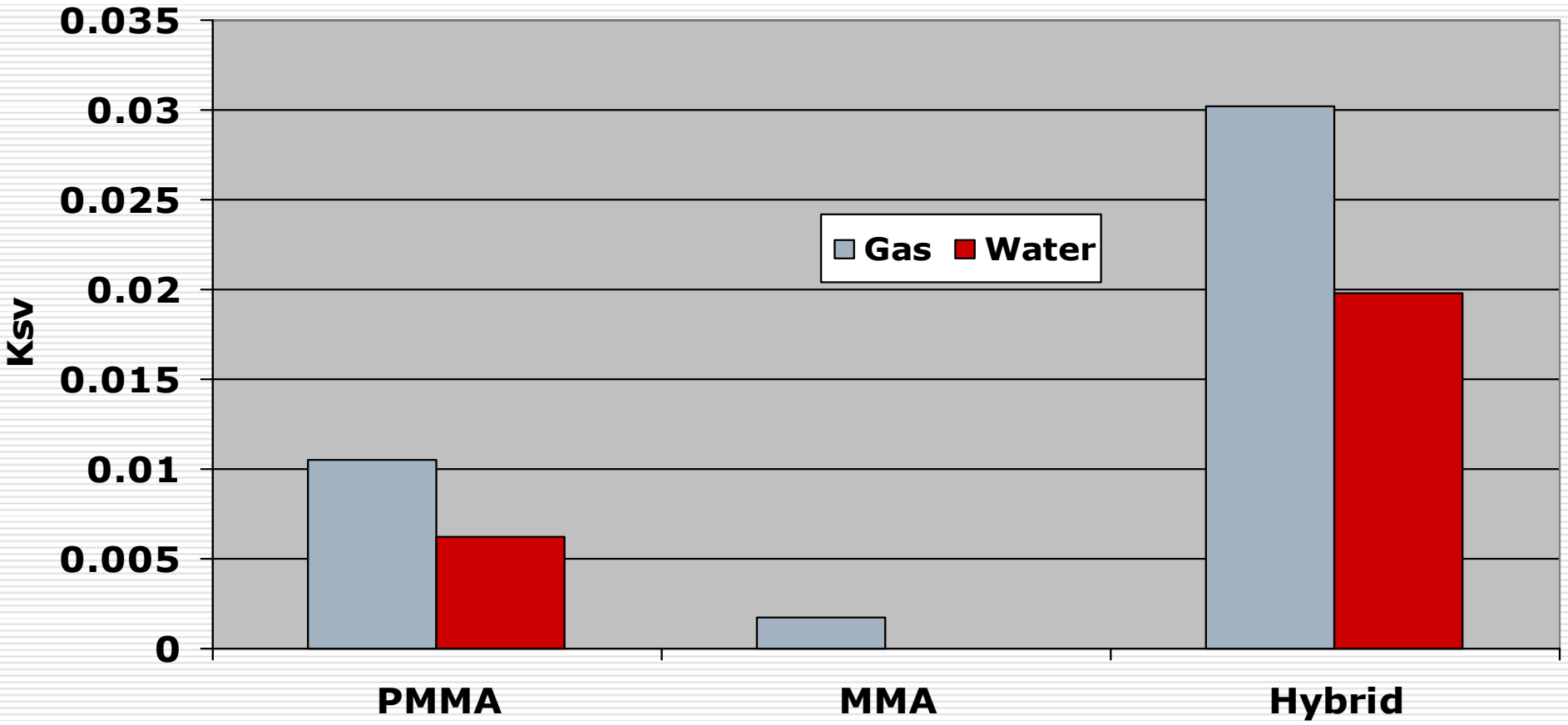
TEOS/CA/EG = 4 : 1 : 1

Hybrid matrix, SiO_2/polyester



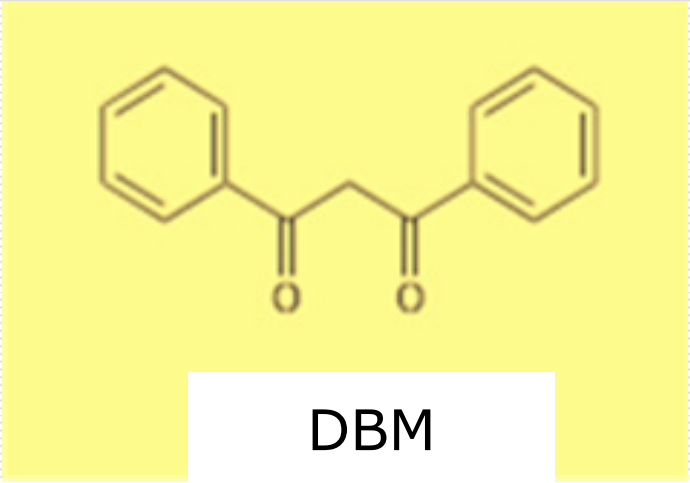


K_{sv}, comparison



Eu β-diketonates

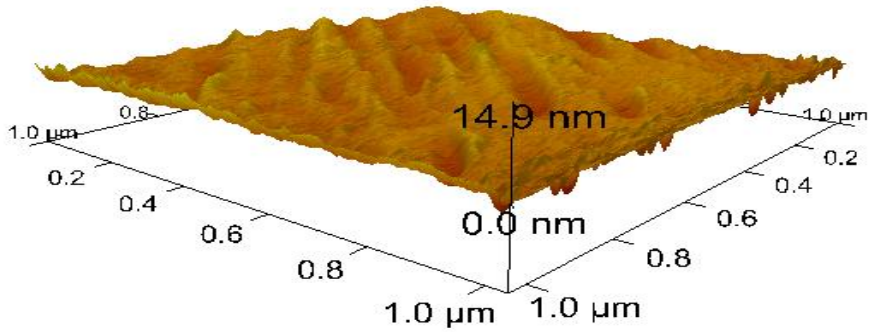
Immobilization in PMMA matrix

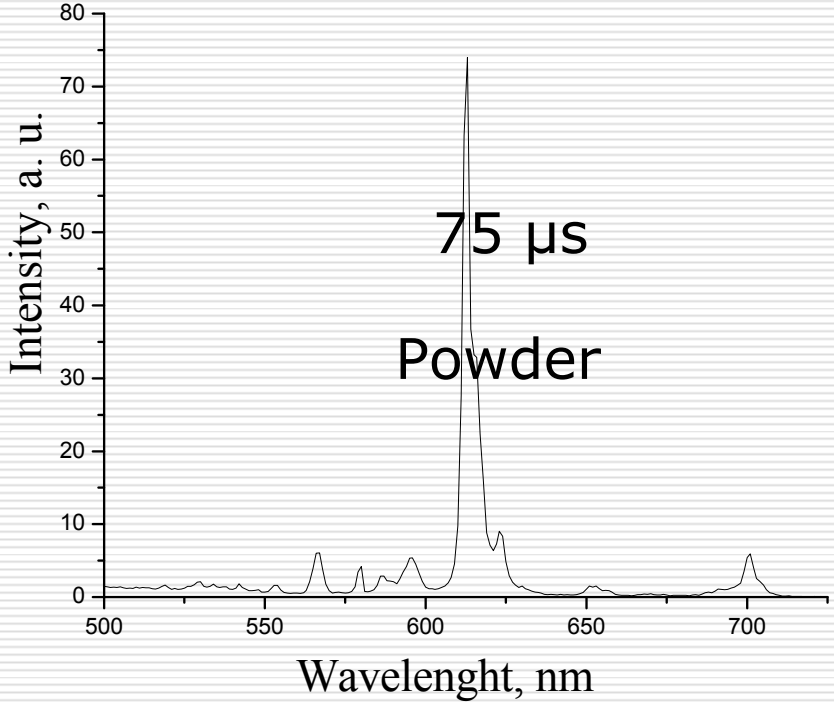


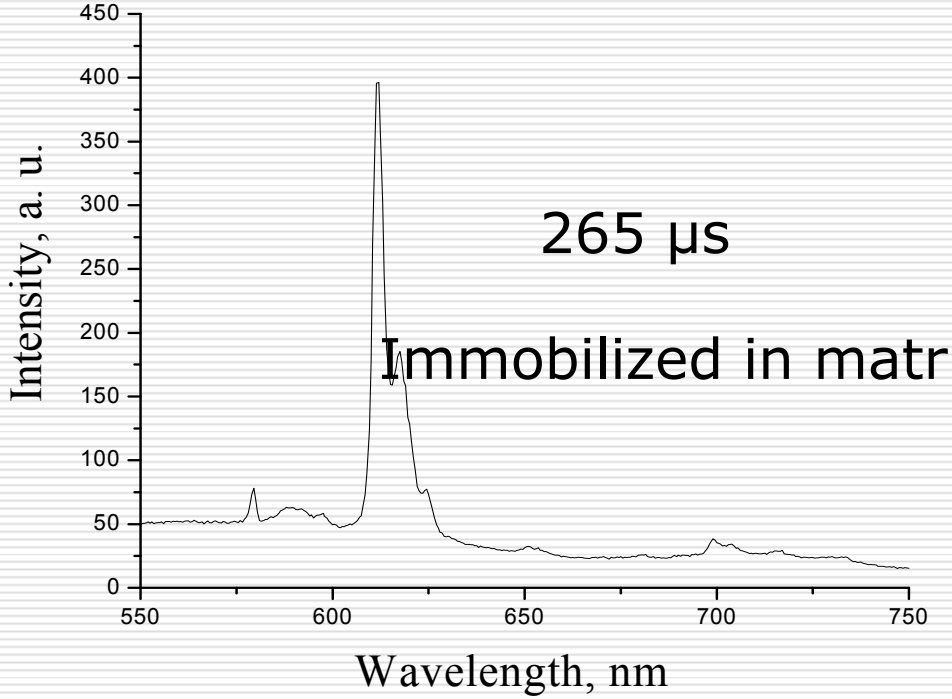
DBM

$Eu(DBM)_3$
oxygen sensitive

AFM ,
$Eu(DBM)_3$ in PMMA



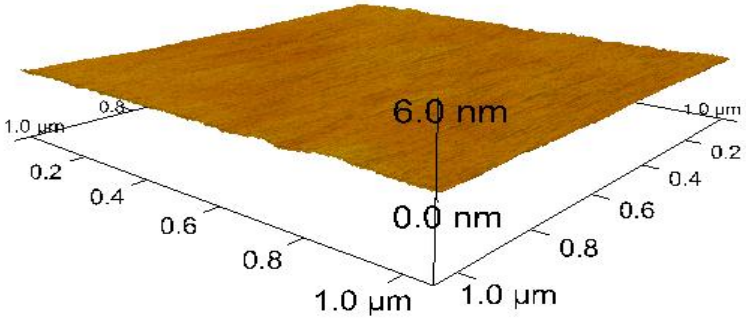


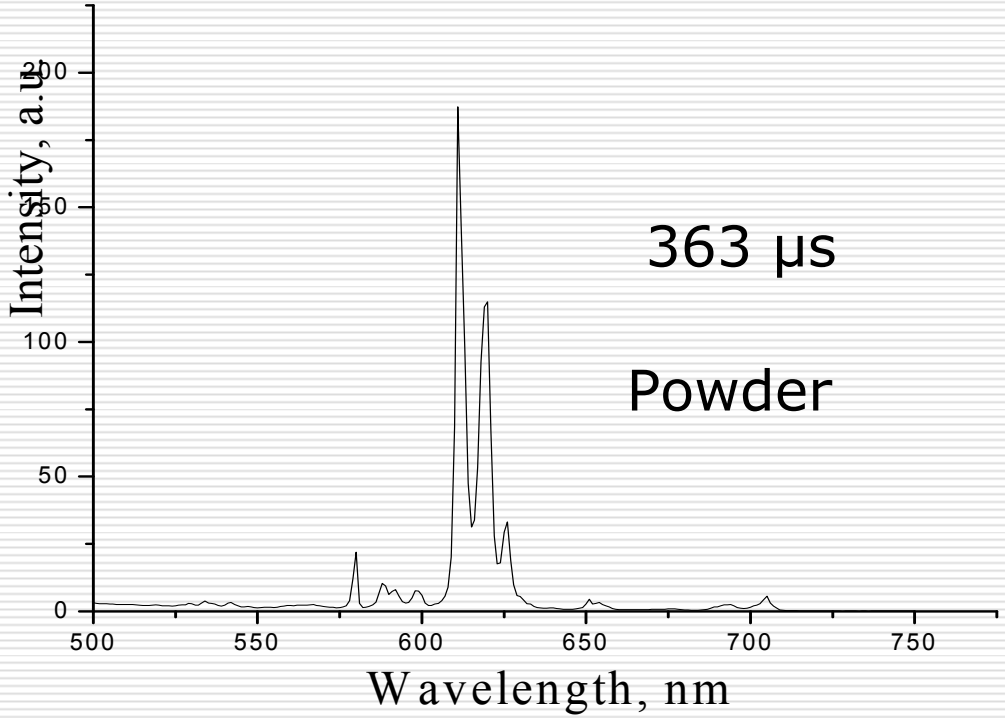


$Eu(DBM)_3.Phen$

Phen – 1,10-phenathroline

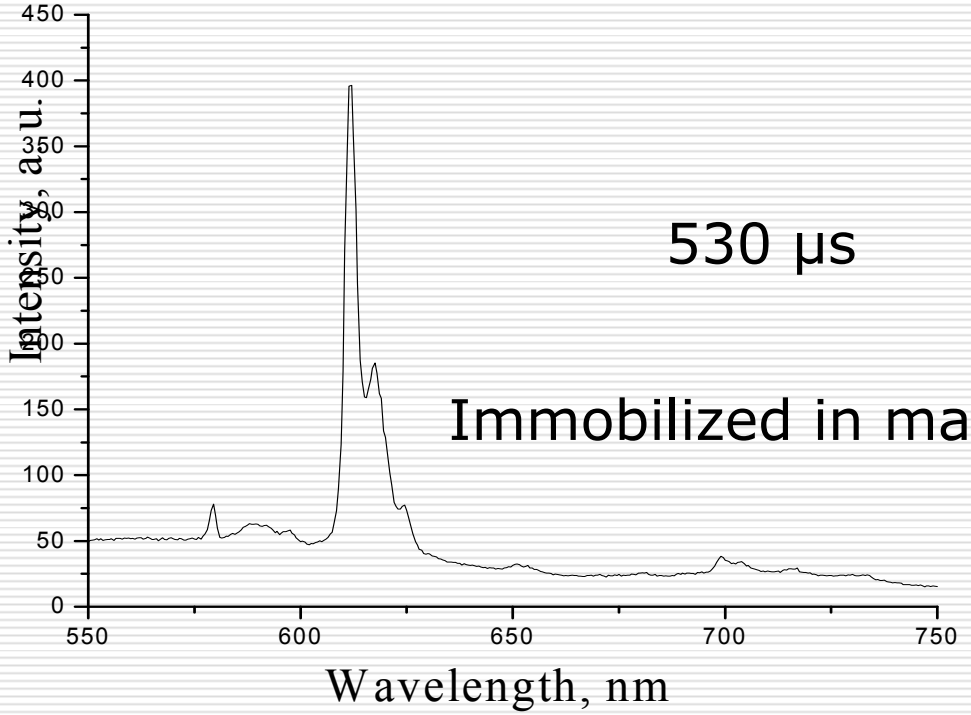
AFM ,
$Eu(DBM)_3$.phen in PMMA





363 µs

Powder



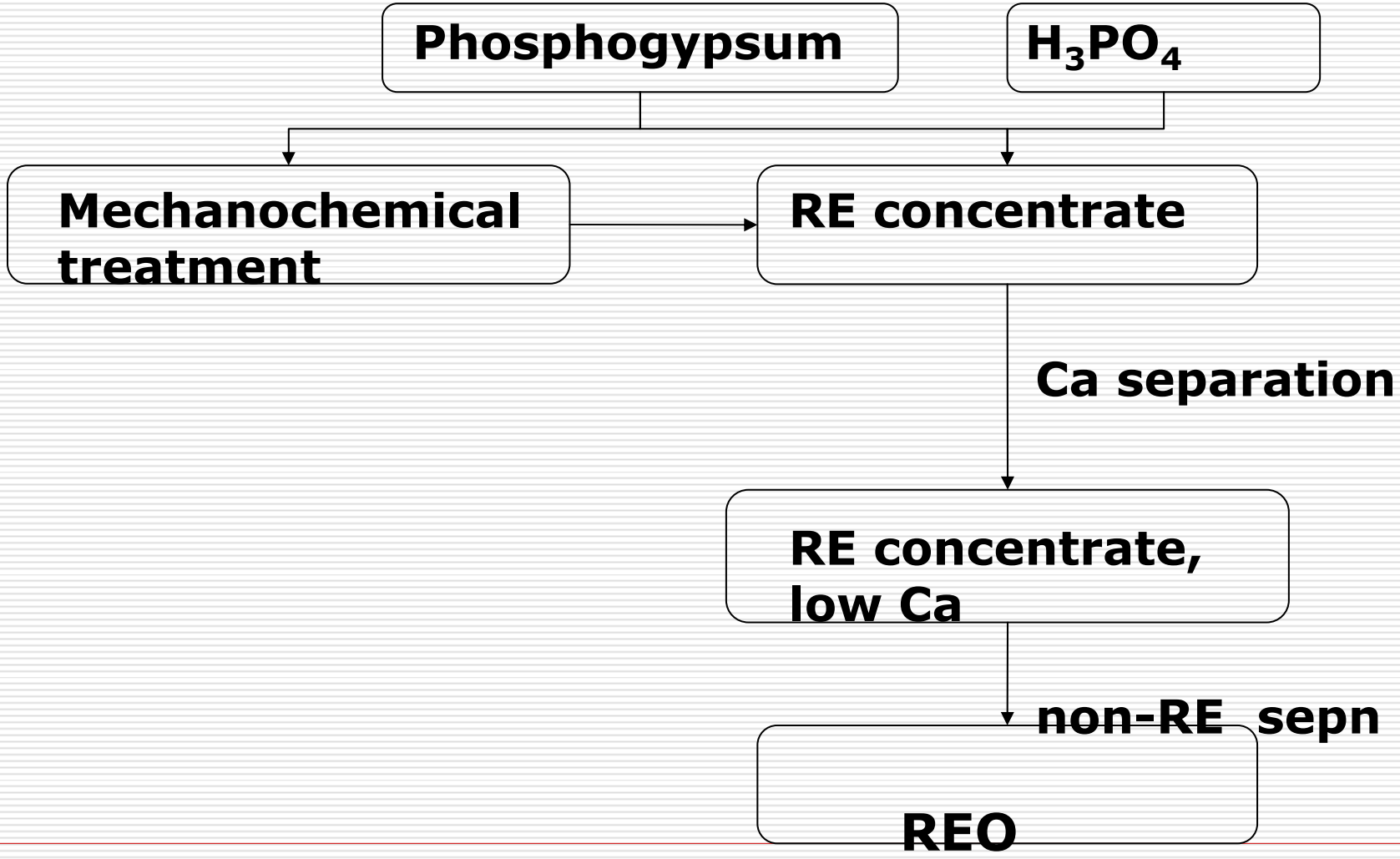
530 µs

Immobilized in matrix

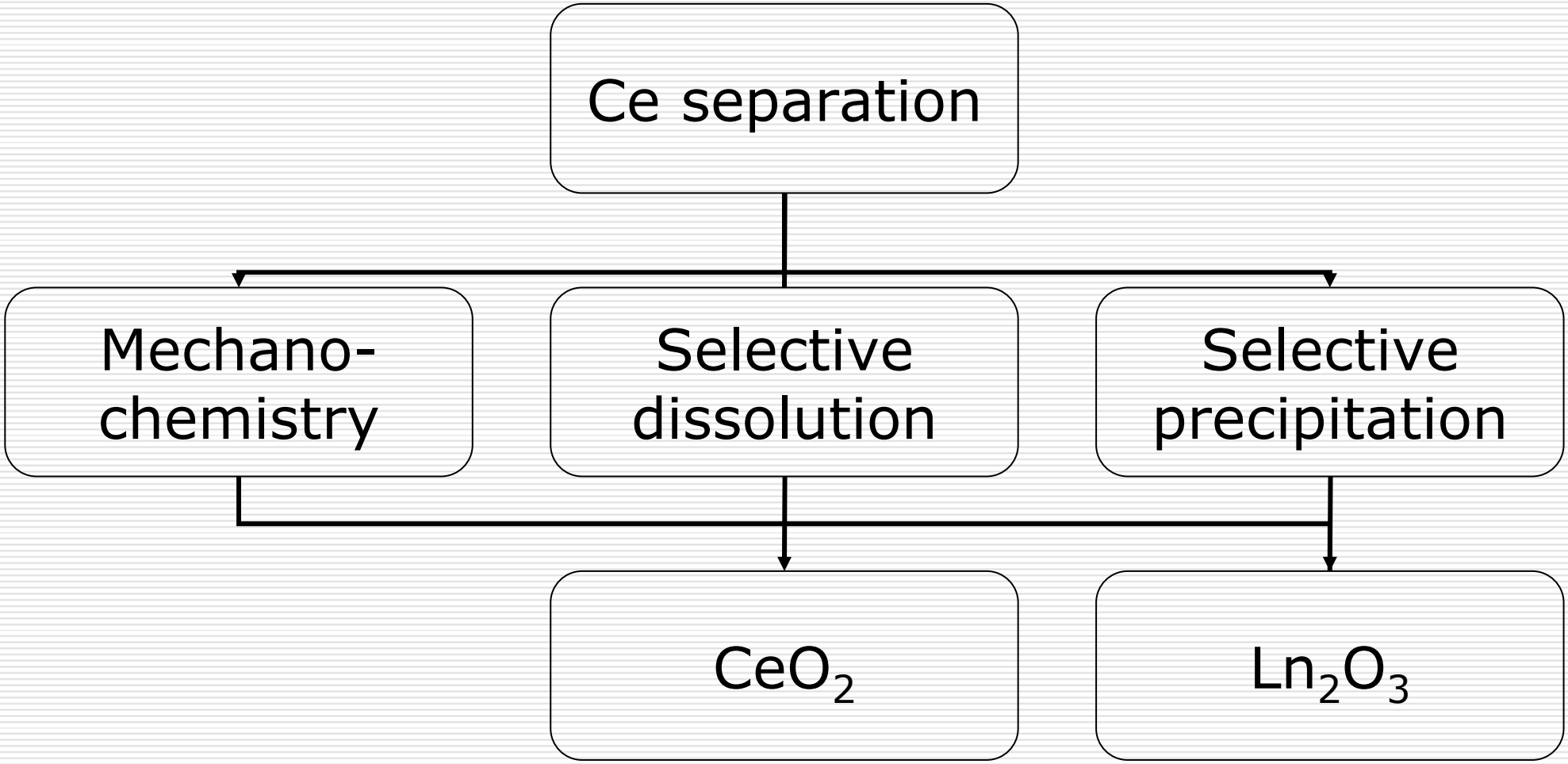
REE products, Technology and production activities

- Methods of RE recovery from waste and by-products
- Production routes for some RE compounds developed and carried out in practice

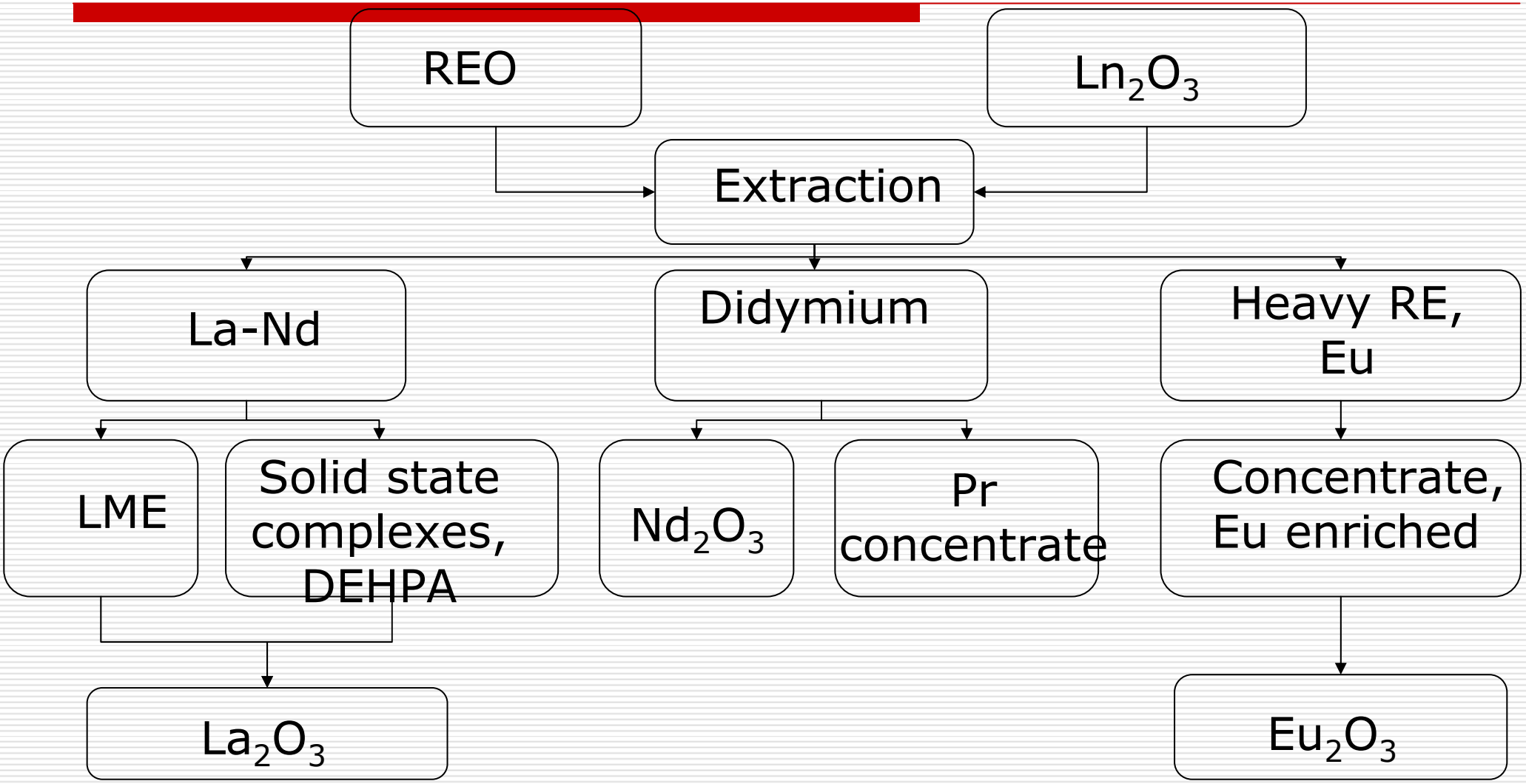
RE sources


Phosphogypsum
H_3PO_4
Mechanochemical treatment
RE concentrate
Ca separation
RE concentrate, low Ca
non-RE sepn
REO

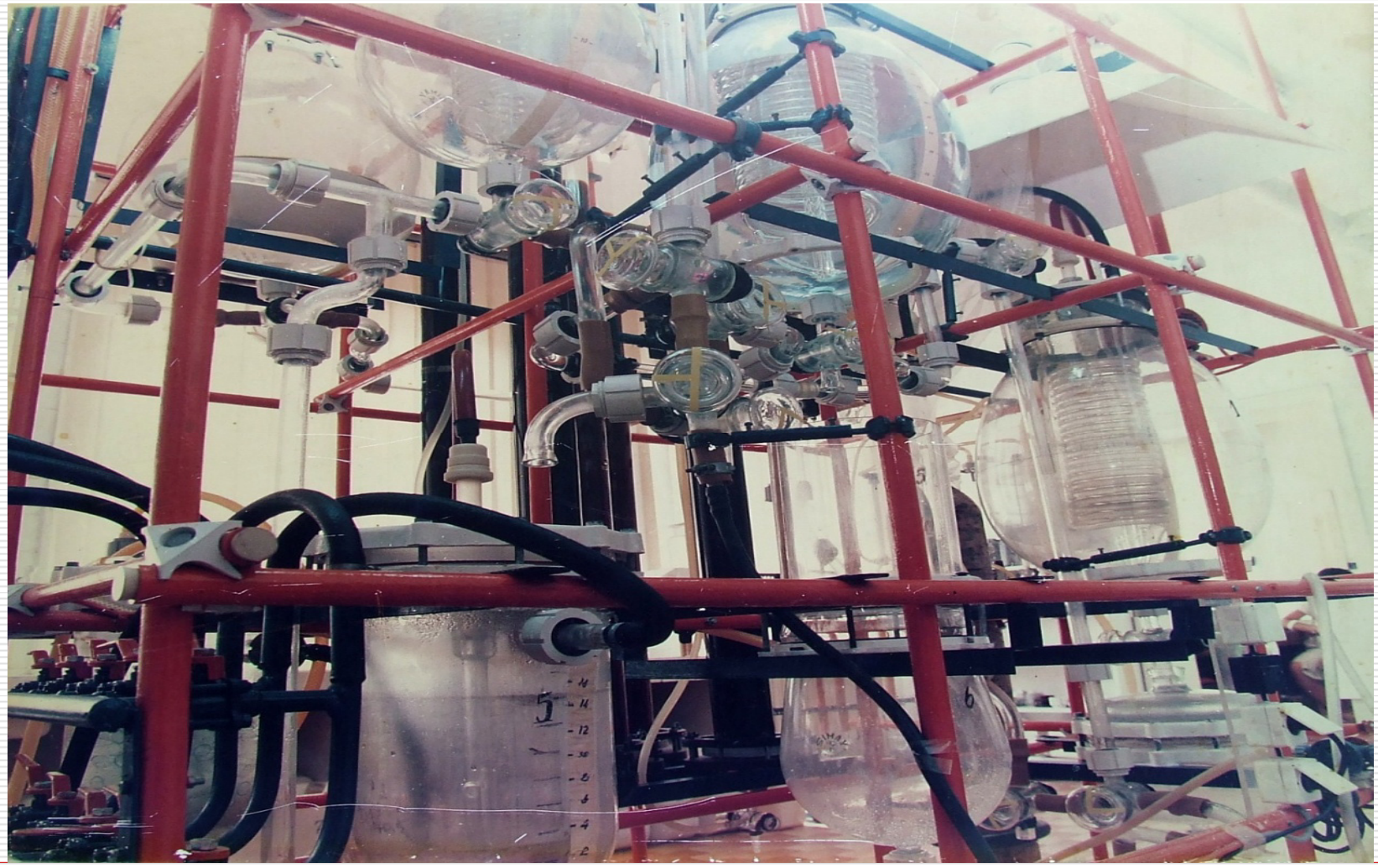
REO treatment



REO/Ln_2O_3


REO
Ln_2O_3
Extraction
La-Nd
Didymium
Heavy RE, Eu
LME
Solid state complexes, DEHPA
Nd_2O_3
Pr concentrate
Concentrate, Eu enriched
La_2O_3
Eu_2O_3

Pilot facilities



Faculty of Chemistry, Sofia University, Bulgaria

Some of the products

Product	REE yield, %	Purity
REE concentrate of low Ca content	99	Ca<1,5%
RE oxide mixture	98	95-99%
CeO_2	94-98	Ln_2O_3: < 10^{-2}%, other impurities: < 0.1%
Oxide mixture, Ce-free		Ce < 1,5%
Nd_2O_3	50	99.5%
	20	99.9%
Eu_2O_3	25	99.8%
	70	98.5%
Y_2O_3	70	99.999%
Y_2O_3 (from YAG)	85	Impurities of Al
Polishing material	85	Cerox quality

Thank you!

Dr. Maria Milanova, Assoc. Prof.,

+ 359-2-8161217

nhmm@wmail.chem.uni-sofia.bg