Optical Properties of Nanocrystalline $Y_2O_3:Eu^{3+}$ Powder Phosphor

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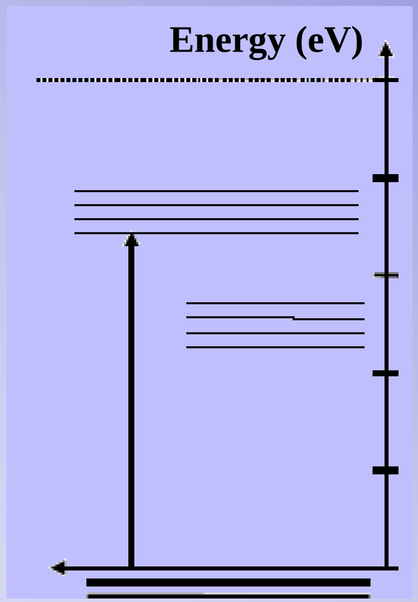
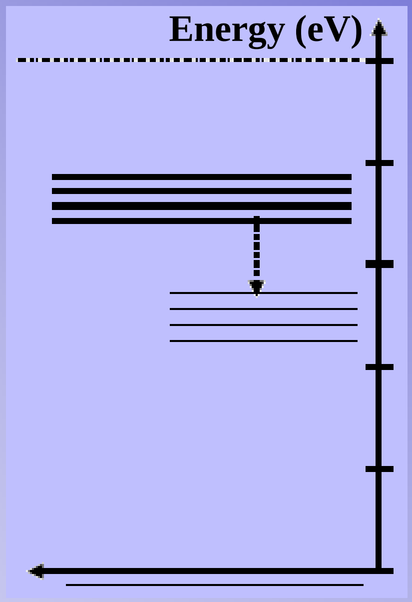
What is a Phosphor?

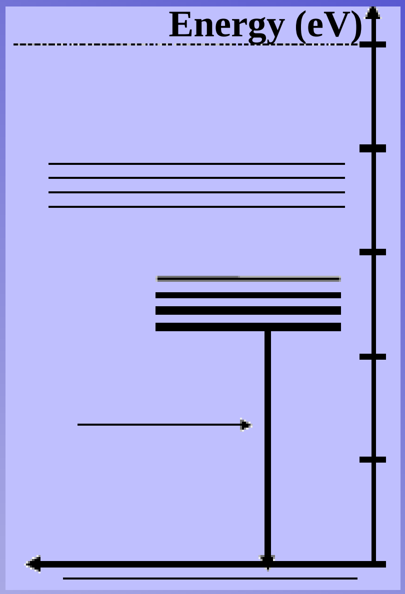
The substance that emits visible light after being energized



1. Electrons absorb energy and go to excited state band



2. Electrons lose its energy to neighbouring atoms and make a transition to impurity state band.



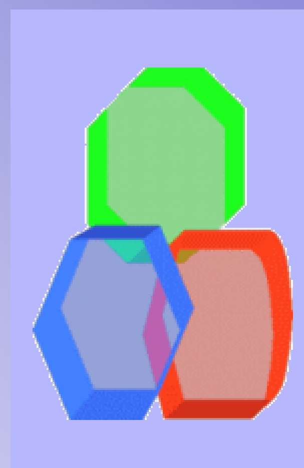
3. Electrons lose energy and make a transition to ground state band

Application of Phosphor

[Excitation]

- Cathode ray
- Ultarviolet ray
- X-ray

[Phosphor]



[Application]

- TV screen
- Computer monitor
- Fluorescent lamp
- Electroluminescence lamp
- Plasma display

Advantage of Powder Phosphors

- **No area limit :**
  can cover a large area of the emissive display
- **Efficiency is higher :**
  light loss through internal reflection etc. is minimized
- **Possibility of having all colours in one plane :**
  required in colour TV display
- **Improved crystallization and uniform distribution of dopant in the host**

Why Nanomaterials?

Particle

- **size**
- **shape**
- **crystallite boundary**

play an important role to control phosphor properties.

Possibility of higher efficiency and narrower emission band in nanocrystalline phosphors

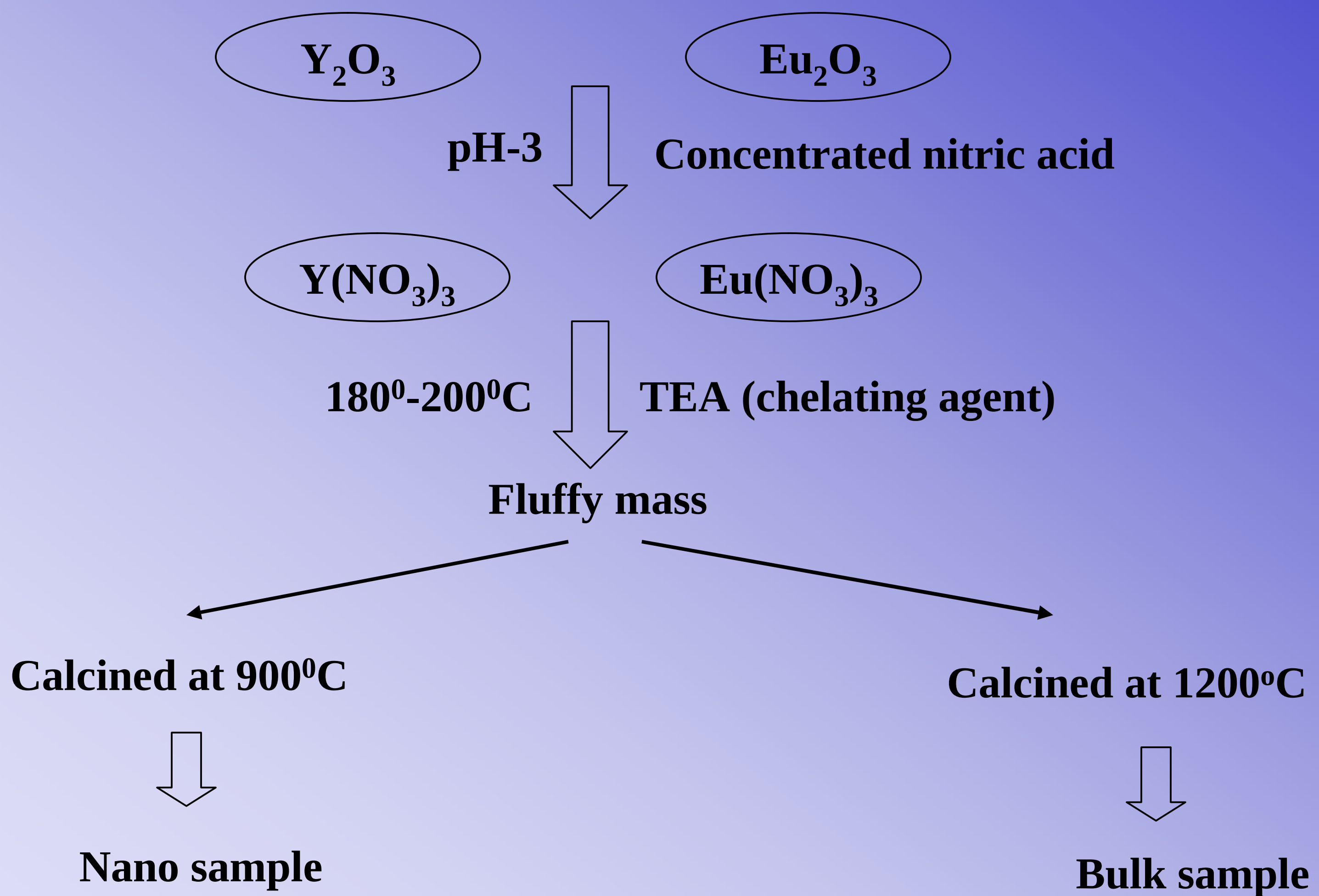
Nanocrystalline $Y_2O_3:Eu^{3+}$ Phosphor

Fundamental and technological importance

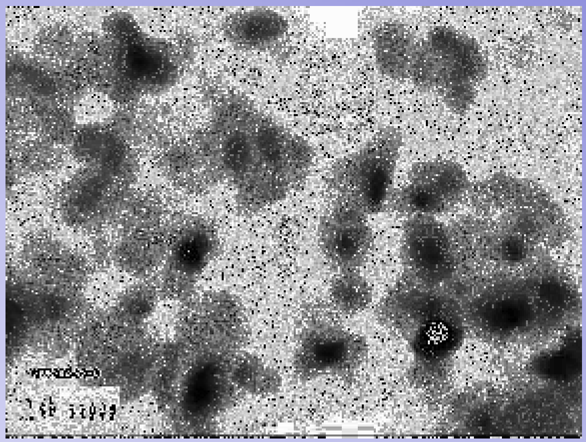
Application

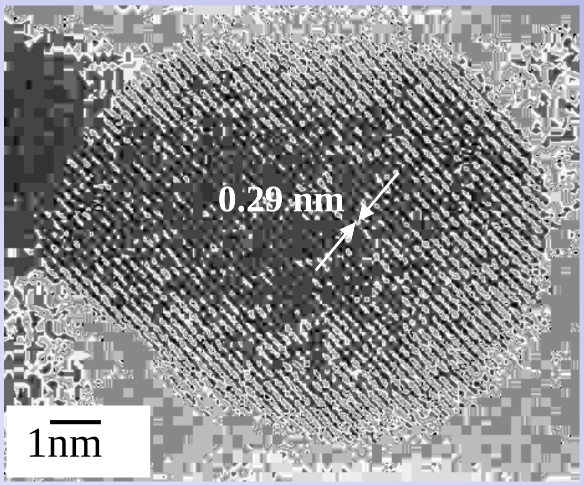
- **Lighting industry**
- **Thermal lensing**
- **Permanent laser based devices**

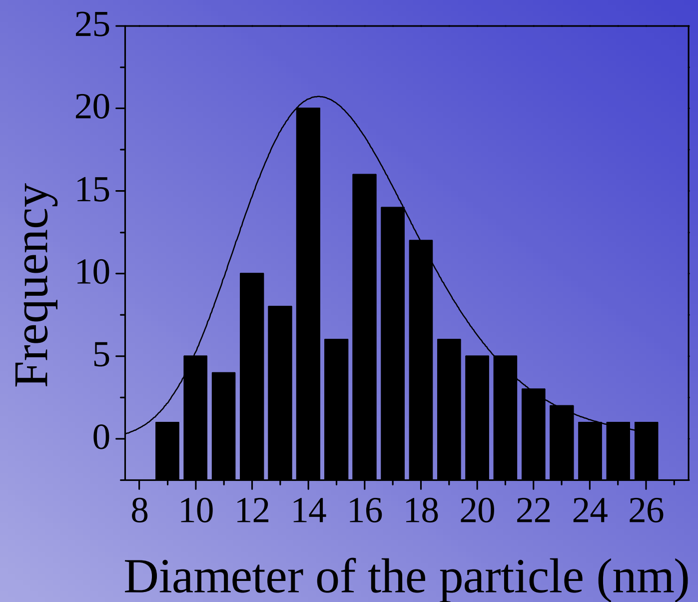
Sample preparation by soft chemical method



Morphology







Assuming log-normal size distribution

$$P(d) = \frac{1}{d\sqrt{2\pi\sigma}} \exp\left(-\frac{\ln(d/\bar{d})}{\sqrt{2}\sigma} \right)^2$$

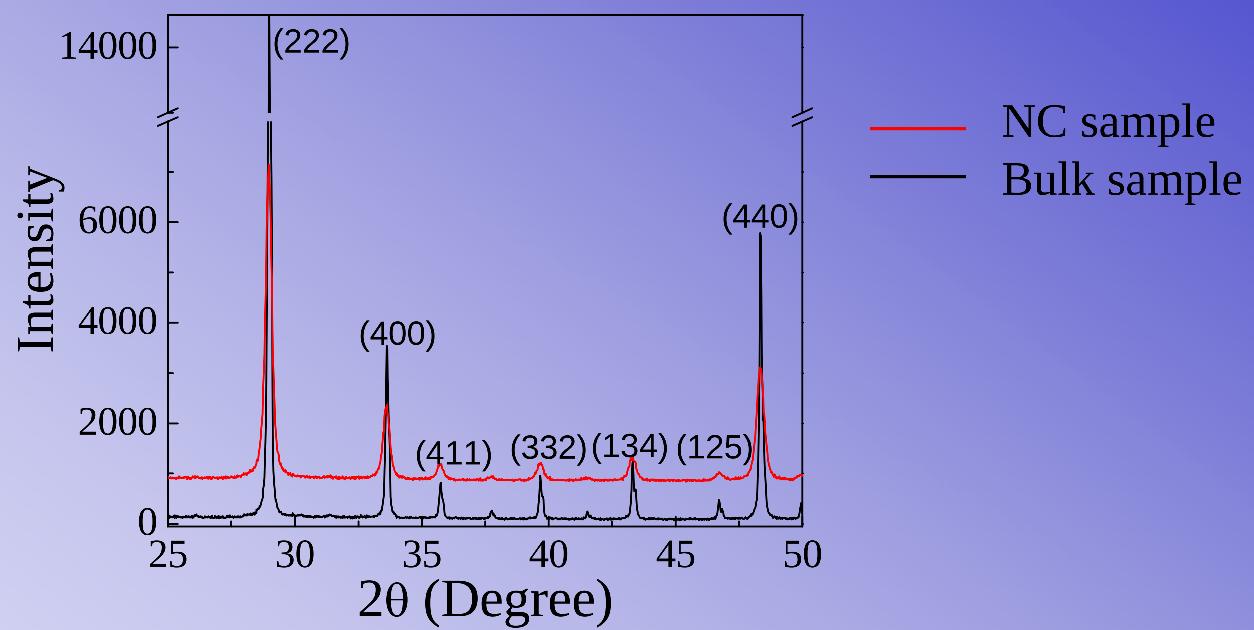
$\bar{d}$: av. Size of the particles

σ : related to size distribution

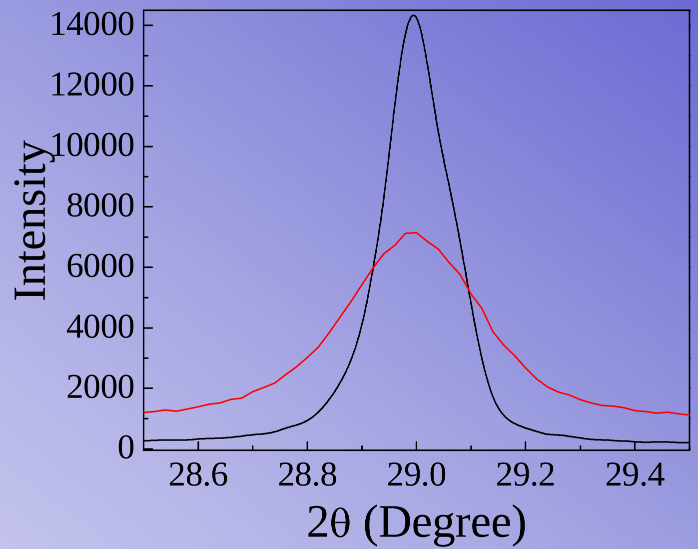
- **Estimated values for nanosample : $\bar{d}$ =15nm**
  σ= 0.14
- **Lattice spacing same as expected in bulk**

X-ray diffraction pattern :

information about formation of the material
impurity content



- **Identical diffraction patterns for nano and bulk samples Cubic (corresponds to space group Ia3)**
- **No distortion in nanocrystalline sample**



We use Sherrer formula

$$\Gamma = \frac{0.94\lambda}{\bar{d}\cos\theta}$$

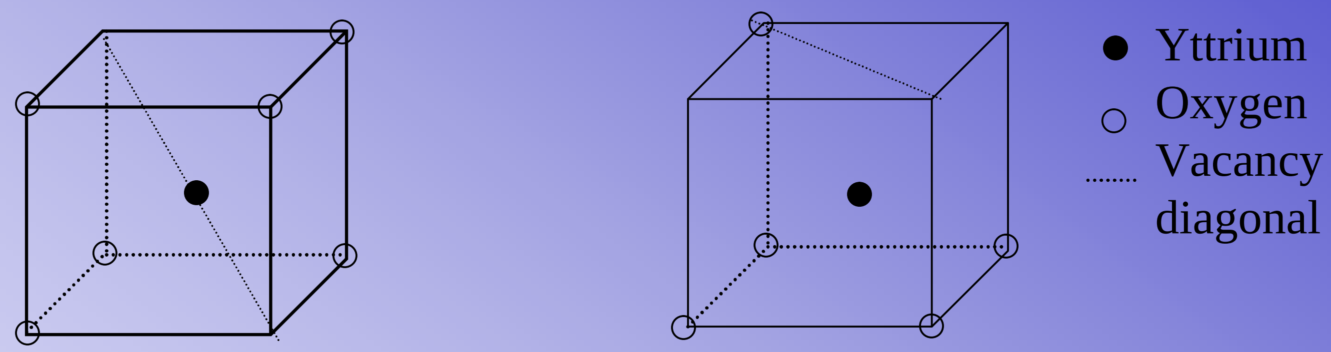
Γ : FWHM of the line

λ : wavelength of copper K_α line

θ : diffraction angle

to estimate the average particle size using broadening of x-ray line (we also take into account the instrumental broadening)

Structure of Y_2O_3



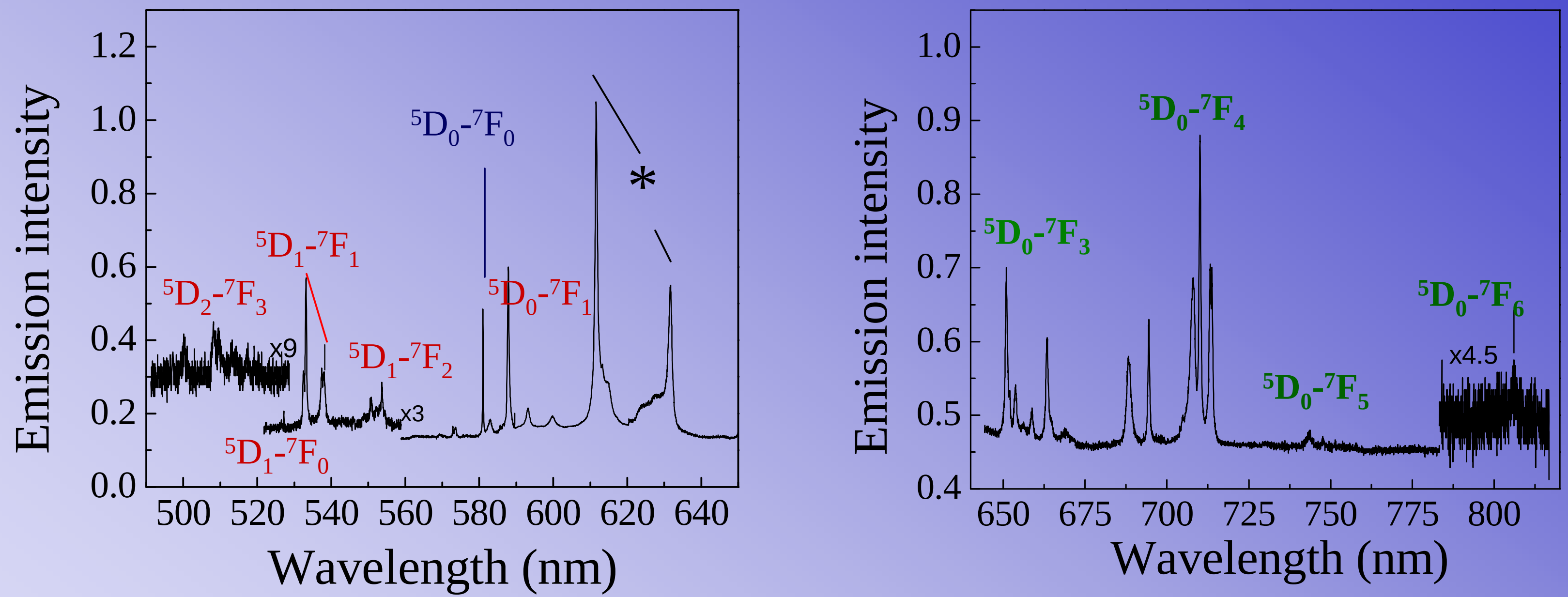
S_6 (25%)
(w/ inversion symmetry)

C_2 (75%)
(w/o inversion symmetry)

N. C. Chang and J.B. Gruber, J. Chem Phys. 41, 3227 (1964).
J. Silver et al, R. J. Phys Chem B, 106, 7200 (2001).

OPTICAL PROPERTIES

Luminescence spectrum



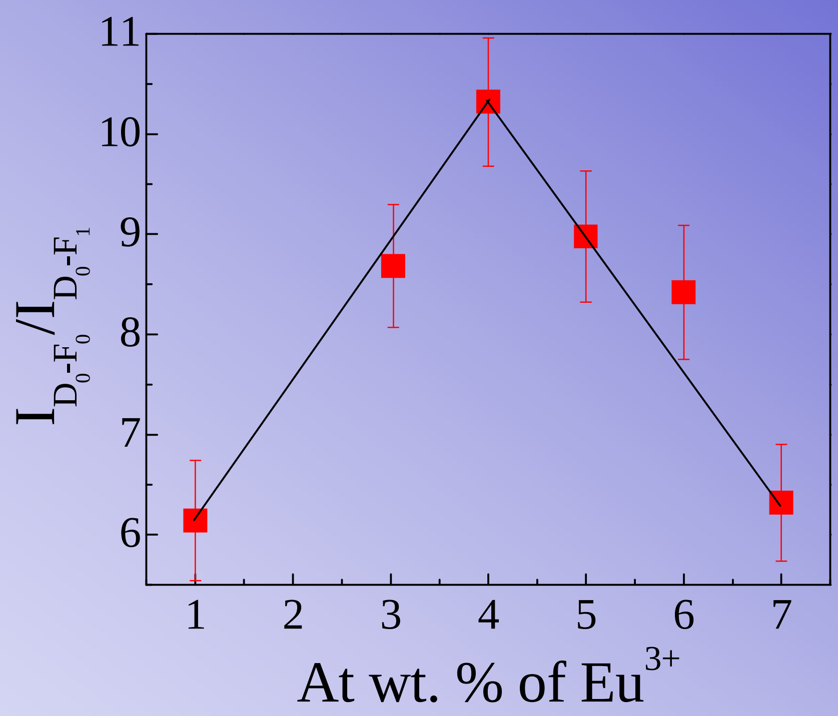
($\Delta J=0, \pm 1$ with $J=0 \not\leftrightarrow J'=0$)
: satisfying magnetic dipole selection rules (S_6 site)

$^5D_0$-$^7F_0$: mixing of odd parity J=1 states into the $^7F_0$ and $^5D_0$ states.

D_0 –$^7F_{4,6}$: Electric dipole in character

$^5D_0$ –$^7F_{3,5}$:First order magnetic dipole transition in the even parity crystal field and the electric dipole transitions to second order

Energy transfer between S_6 to C_2 site



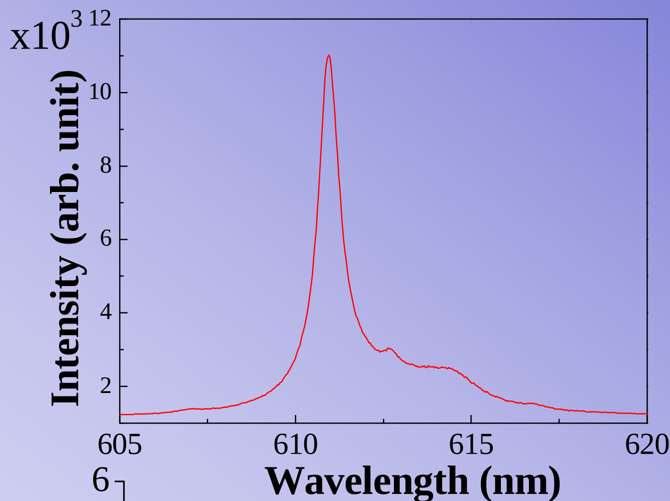
$^5D_0$ – $^7F_1$ (587 nm) originates from S_6 site

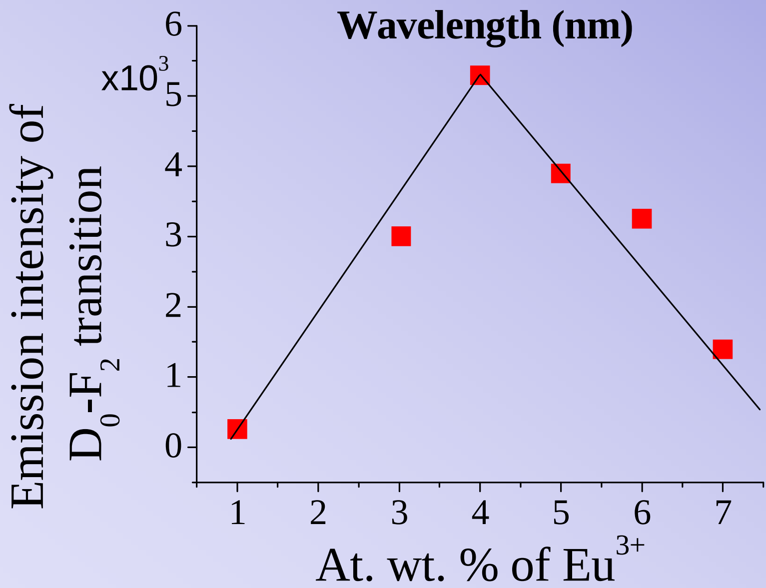
$^5D_0$ – $^7F_0$ (581 nm) originates from C_2site

- **Ratio of emission intensity of S_6 site to the emission intensity of C_2 site decreases with increase in Europium concentration in the sample**

- **Effect of fluorescence quenching after 4 at wt% of Eu^+ doping**

Strongest line at 611 nm due to $^5D_0 - ^7F_2$ transition



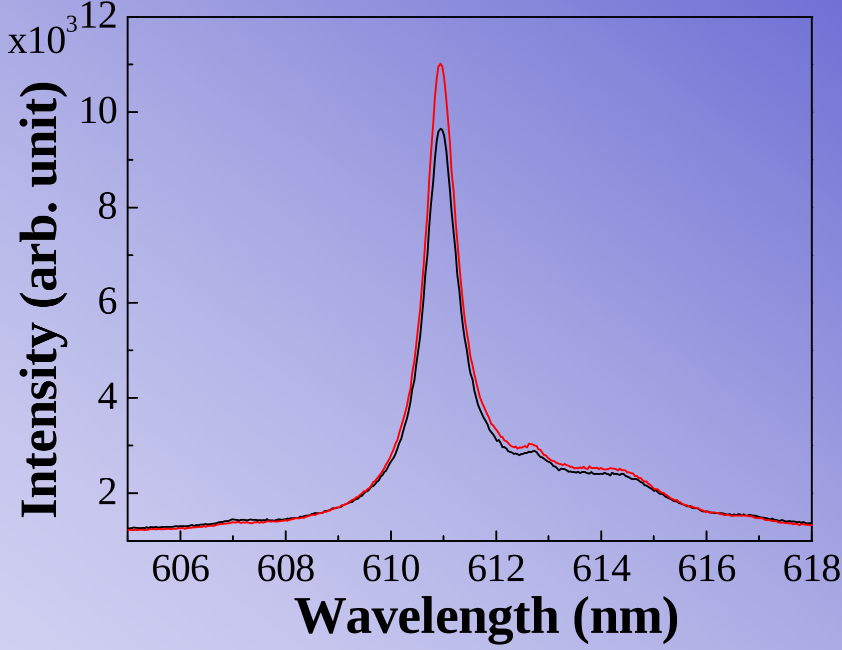


Theory of Judd and Ofelt :
$^5D_0 - ^7F_2$ transition becomes electric dipole type, due to an admixture of opposite parity $4f^{\,n-1}5d$ states by an odd parity crystal field component

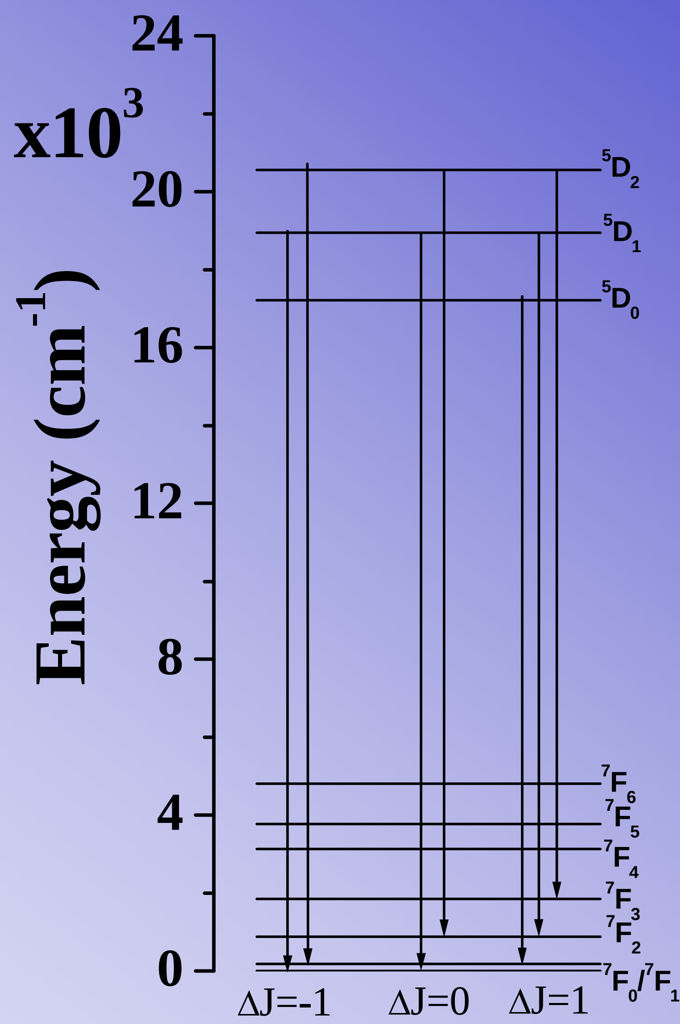
B. R. Judd, Phys. Rev. 127, 750 (1962).
G. S. Ofelt, J. Chem. Phys. 37, 511 (1962).

- **Increase in emission intensity of D_0-F_2 with increase in Europium concentration**
- **Effect of fluorescence quenching after 4 at wt% of Eu^{3+} doping**

16% Increase in luminescence yield for nanocrystalline $Y_2O_3:Eu^{3+}$



Possible cause :
Dramatic shortening of lifetime of the luminescence states
i.e. slower and less efficient surface recombination process.



A schematic diagram of the energy level of Eu^{3+} in nanocrystalline $Y_2O_3:Eu^{3+}$

Crystal field effect

Crystal field Hamiltonian w/o taking into account mixing of different J- state

$$H_{CF} = \sum_{l,m} B_{l,m}^{+} \sum_{i} C_{l,m}(i),$$

Crystal field parameter

$$B_{l,m}^{+} = (-1)^m B_{l,-m}$$

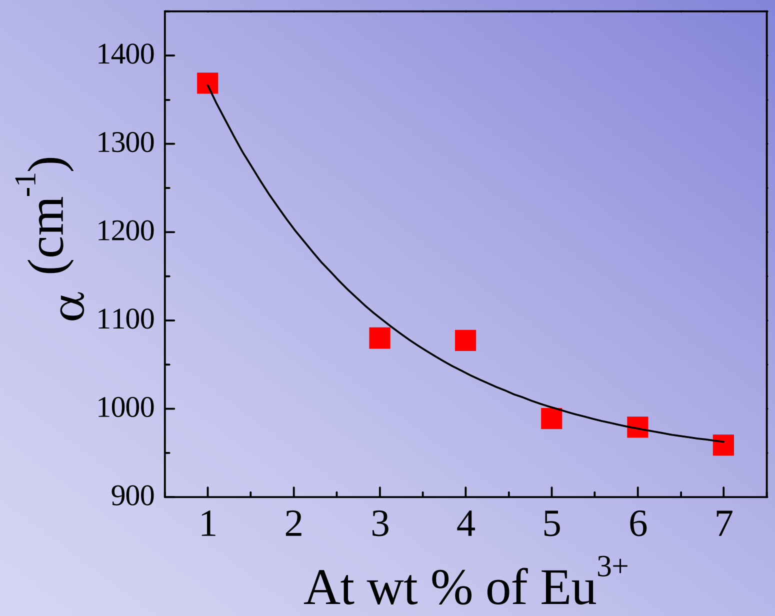
***l*=2,4,6,… and**
***m*=0,±2, ±4…±*l*.**

and $$C_{l,m}(i) = \left(\frac{4\pi}{2l+1} \right)^{1/2} Y_{lm}(\theta_i, \phi_i)$$

- **One needs an extra crystal field term α to include J-mixing**
- **Intensity of $^5D_0$-$^7F_0$ line is proportional to α^2**
  $^5D_0$-$^7F_2$ line is proportional to α

G. Nishimura, M. Tanaka, A. Kurita and T.Kushida, J. Lumin, 48 & 49, 473 (1991).

Crystal field effect in nanocrystalline $Y_2O_3:Eu^{3+}$

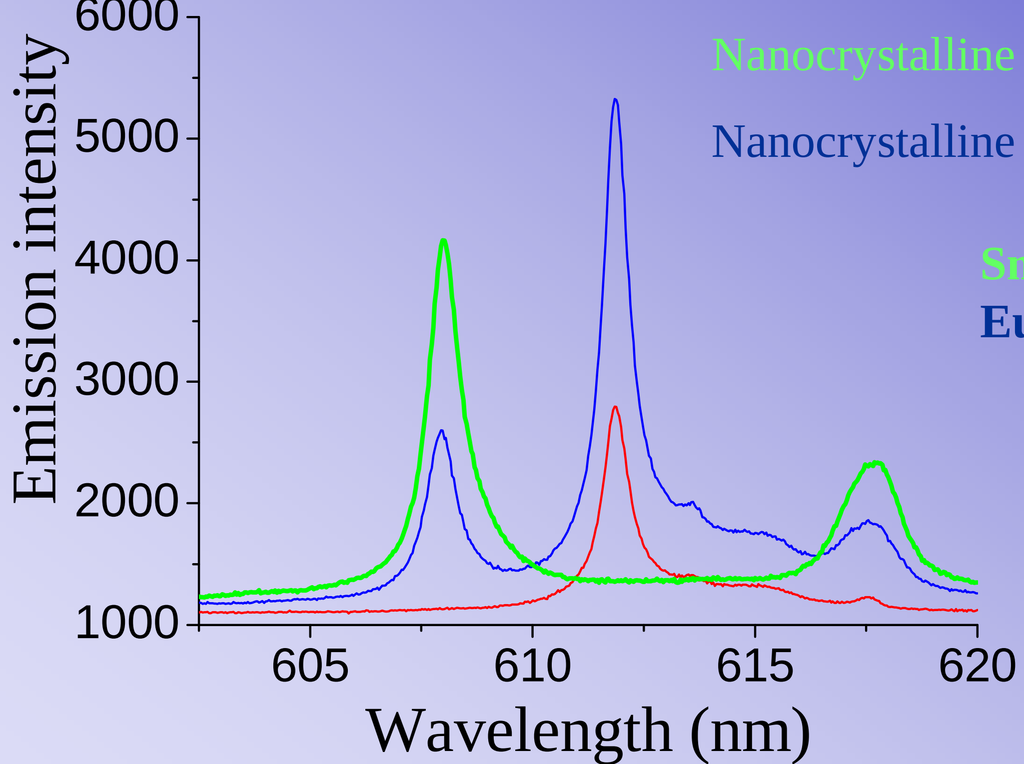


$$\frac{I_{0-0}}{I_{0-2}} = \frac{4\alpha}{75\Delta_{20}}$$

α: crystal field parameter
Δ_{20} : Energy separation between $^7F_2$ and $^7F_0$ levels (900 cm^{-1})

Value of of α for nanocrystalline Y_2O_3 with 4 at wt % Eu^{3+} : 1077 cm^{-1}
for bulk $Y_2O_3:Eu^{3+}$: 995 cm^{-1}

Effect of energy transfer in co-doped sample



Nanocrystalline Y_2O_3:Eu^{3+} (4 At wt%)

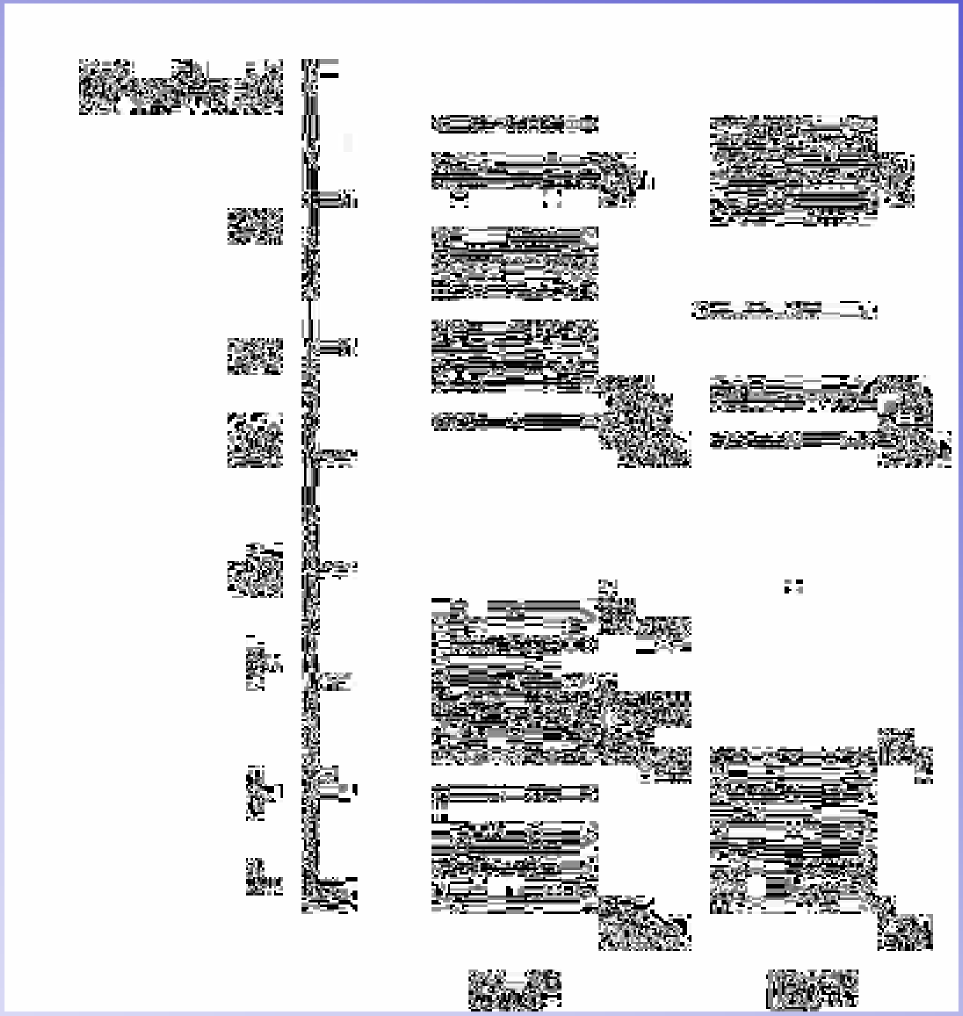
Nanocrystalline Y_2O_3:Sm^{3+} (0.25 At wt %)

Nanocrystalline Y_2O_3:Eu^{3+} :Sm^{3+}

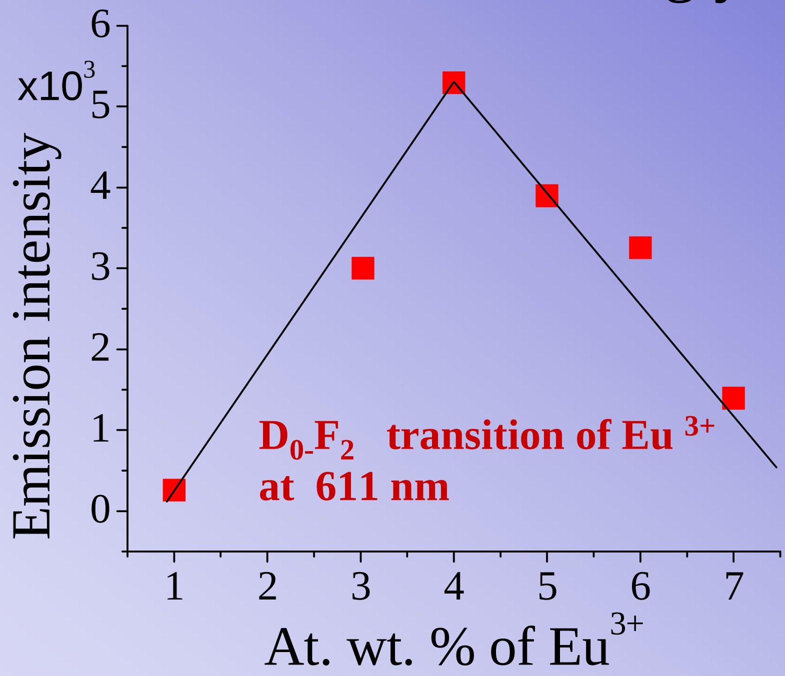
Sm^{3+} : as Donor

Eu^{3+} : as Acceptor

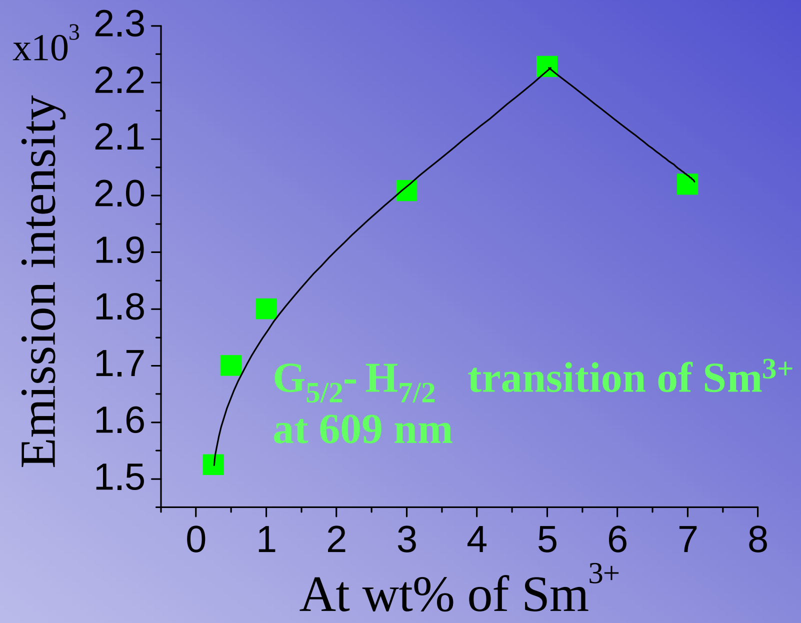
Electronic energy levels for Eu^{3+} and Sm^{3+}



Singly doped sample

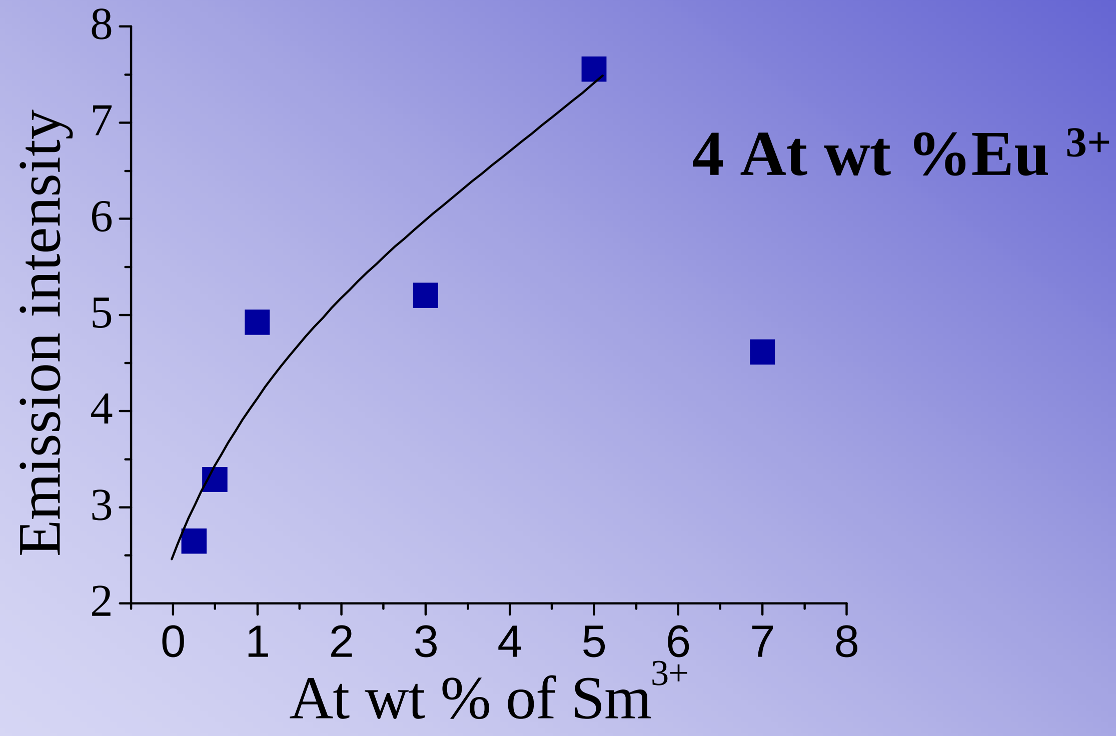


Only acceptor

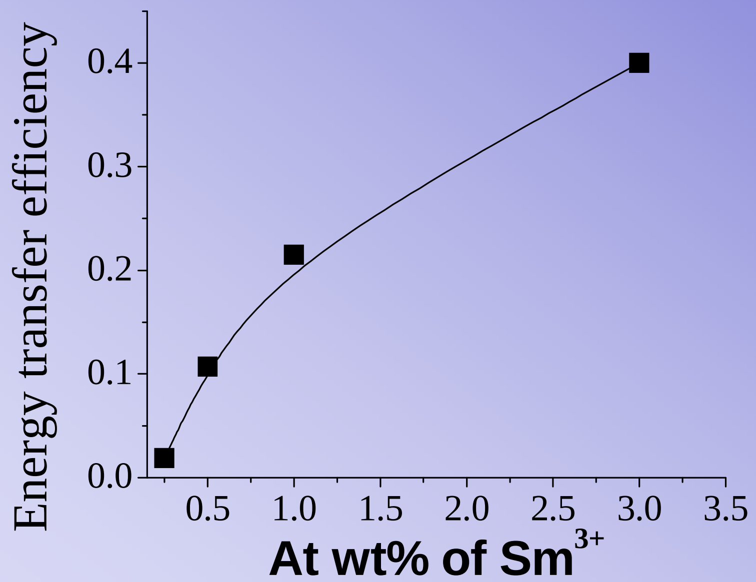


Only donor

Increase in D_{0}-F_{2} transition of 4 At wt %Eu^{3+} in co-doped sample



Energy transfer efficiency with Sm $^{3+}$ concentration



Energy transfer efficiency

$$= 1 - \frac{F_{DA}}{F_D}$$

(neglecting donor-donor transfer)

F_{DA} : Fluorescence inten. of donor (Sm^{3+}) in presence of acceptor (Eu^{3+})

F_D : Fluorescence inten. of donor (Sm^{3+})

- **Increase in energy transfer efficiency with Sm^{3+} concentration for 4 at wt% of Eu^{3+}**

Summary

- **Optical properties of nanocrystalline red-emitting phosphor, Europium doped Yttria ($Y_2O_3:Eu^{3+}$) has been investigated.**

- **Intensity of the strongest emission line at 611 nm of this material doped with 4 at. wt.% of Europium is found to be 16% more than that for the corresponding bulk system.**

- **Narrow electronic emission spectrum suggests a crystalline surrounding in this nanomaterial.**

- **Crystal field parameter and equilibrium thermal energy of the nanocrystalline system has been estimated.**

- **Increase in luminescence efficiency in the nanocrystalline samples in presence of donor has been investigated.**

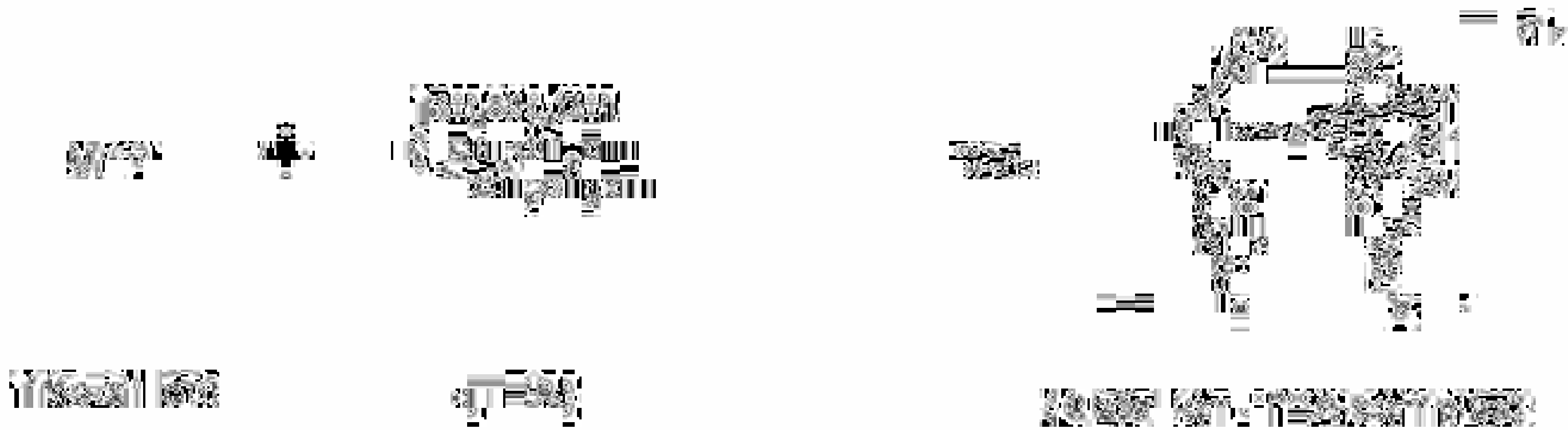
Work in Progress

- Variation of optical properties of the phosphor with the size of the nanoparticles.

- Energy transfer process in more detail by lifetime measurements.

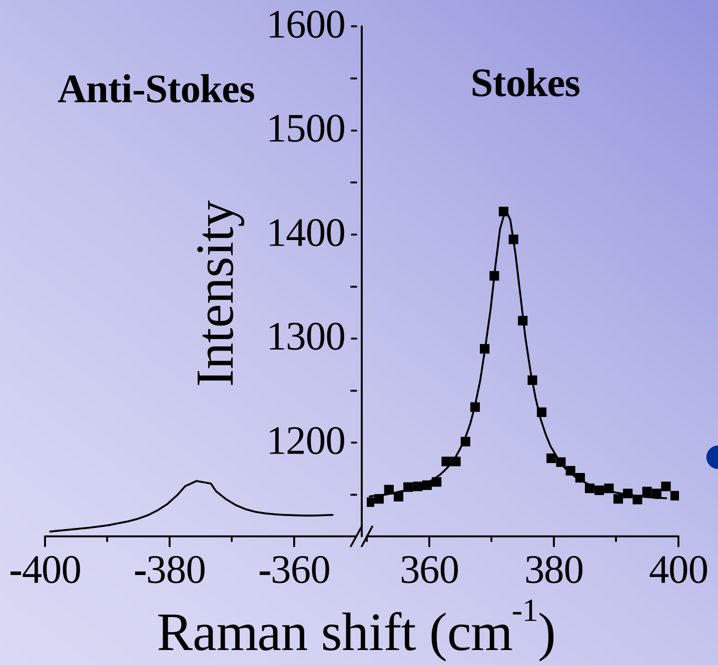
- More accurate estimation of energy transfer efficiency using Dexter-Förster Theory.

THANK YOU



Property	Remark
Size of the particle	15 nm
Size distribution	±5 nm
Phase	Cubic (corresponds to space group Ia3)
Intensity of the strongest emission line at 611 nm	16% more compared to that of bulk system
Linear crystal field parameter	1077 cm^{-1}
Equilibrium energy	57 cm^{-1}

Estimation of equilibrium energy in nanocrystalline $Y_2O_3:Eu^{3+}$ using Raman measurements



Intensity ratio of Stokes and Antistokes Raman scattering

$$\frac{I_s}{I_{AS}} = \exp\left(\frac{\hbar\omega}{kT}\right)$$

- **Equilibrium energies of**
  nanocrystalline sample : 57 cm^{-1}
  bulk sample : 53 cm^{-1}