LMI-ESA 6002

LUMINESCENCE PROPERTIES OPTIMISATION OF PRASEODIUM IN CaTiO3

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INTRODUCTION

The Luminophore

Host Matrix → **$CaTiO_3$**

Activator → **Pr^{3+}**

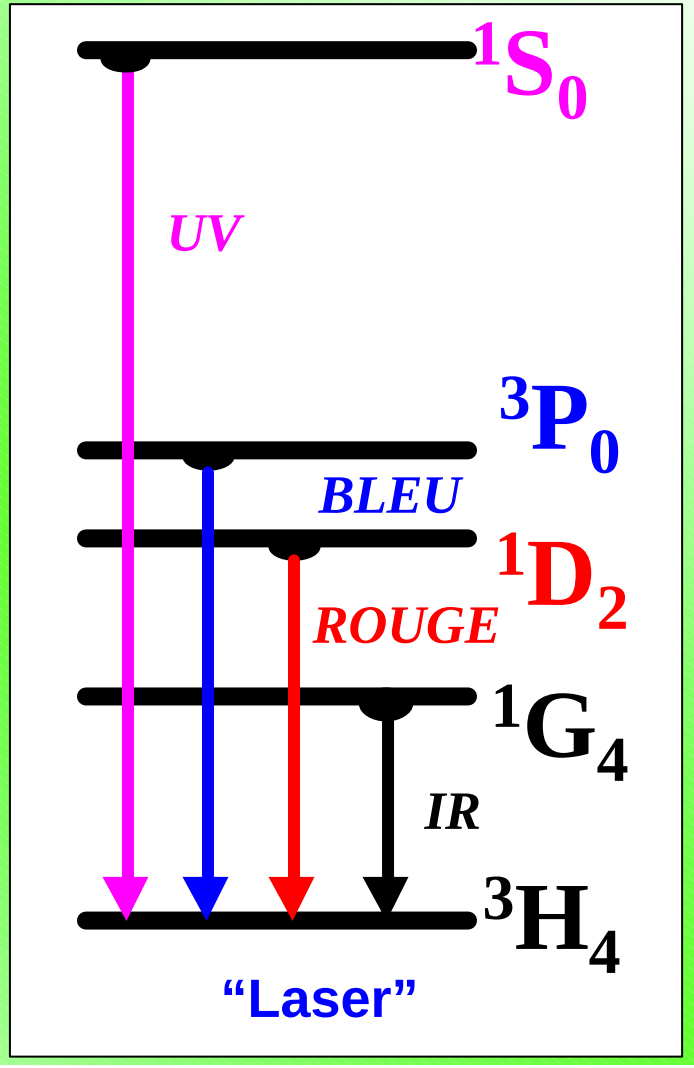
- **Chemistry under control (solid state chemistry, Sol-Gel)**

- **Easy to process (Films)**

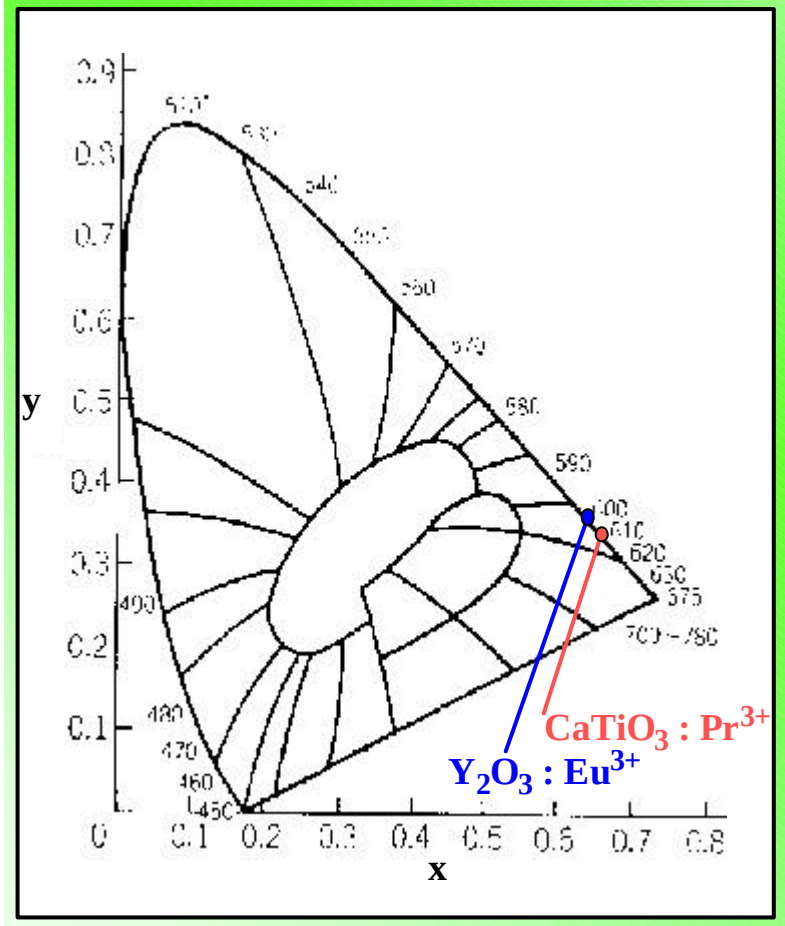
- **Low band gap energy (< 4 eV)**

® ***Intense UV absorption BV ® BC Beneficial to excite the activator.***

® ***Envisioned applications photoluminescence and cathodoluminescence.***



(S. S. Chadha, D. W. Smith, A. Vecht et C. S. Gibbons, SID 94 DIGEST, (1994), 51 -52)



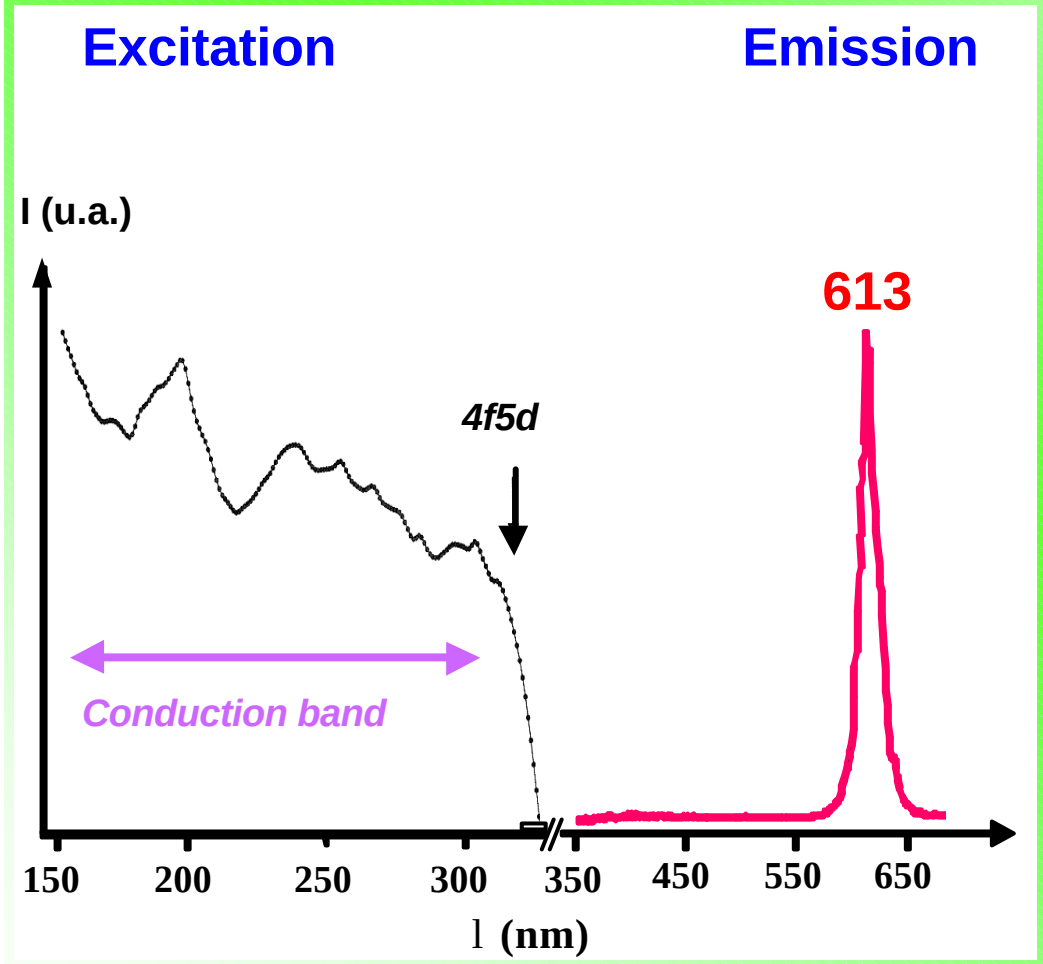
- Chromatic coordinates (CIE)

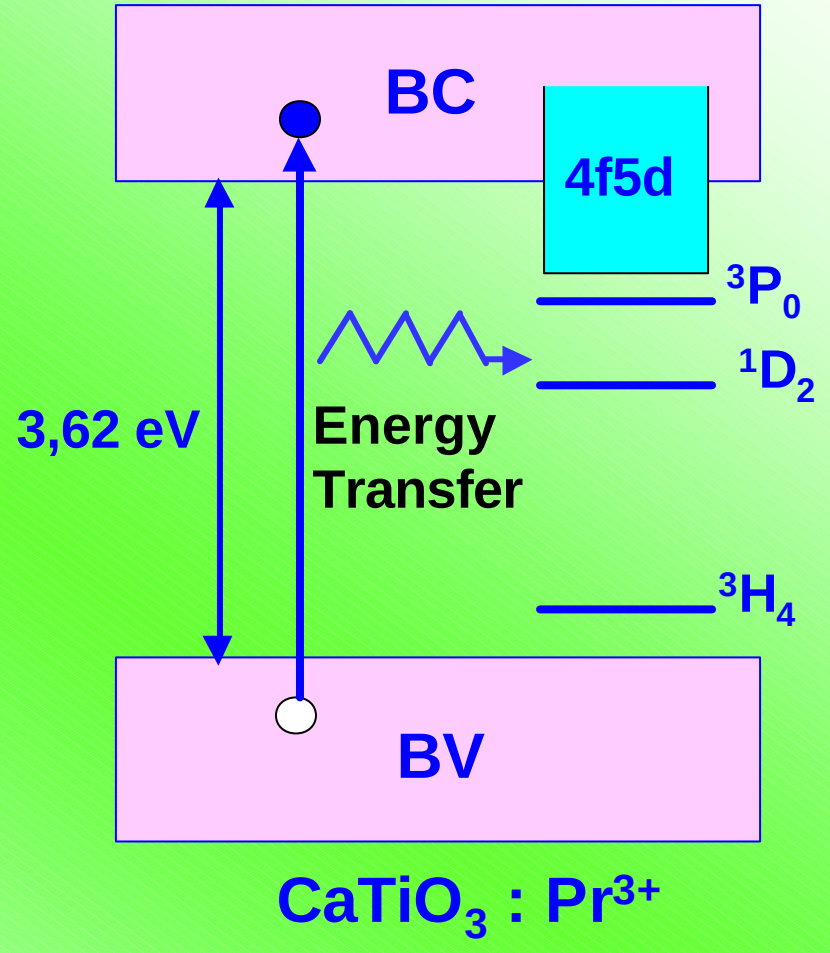
$CaTiO_3 : Pr^{3+}$	x = 0,68 y = 0,31
$Y_2O_3 : Eu^{3+}$	x = 0,65 y = 0,35
Red "Ideal" (NTSC)	x = 0,67 y = 0,33

Advantages of $CaTiO_3 : Pr^{3+}$: Contrast increase in the red at low energetic cost (CaO, TiO_2, Pr^{3+} not expensive).

Problem to be solved : - Determine luminescence mechanisms
- Increase emission yield

PROPERTIES AND MECHANISMS OF LUMINESCENCE OF $CaTiO_3 : Pr^{3+}$



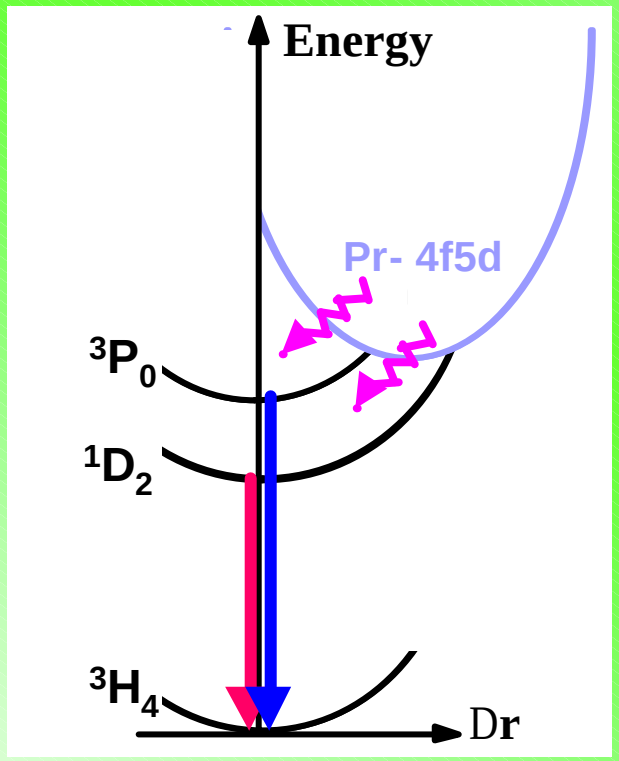


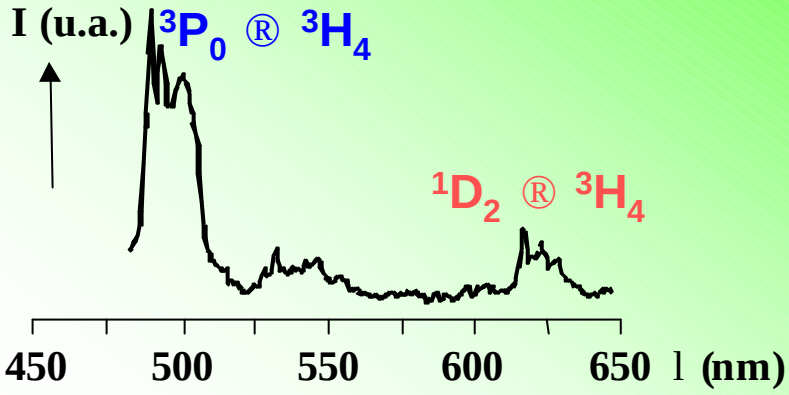
$CaTiO_3 : Pr^{3+}$: Polyvalent activator

Luminescence mechanisms of $CaTiO_3 : Pr^{3+}$

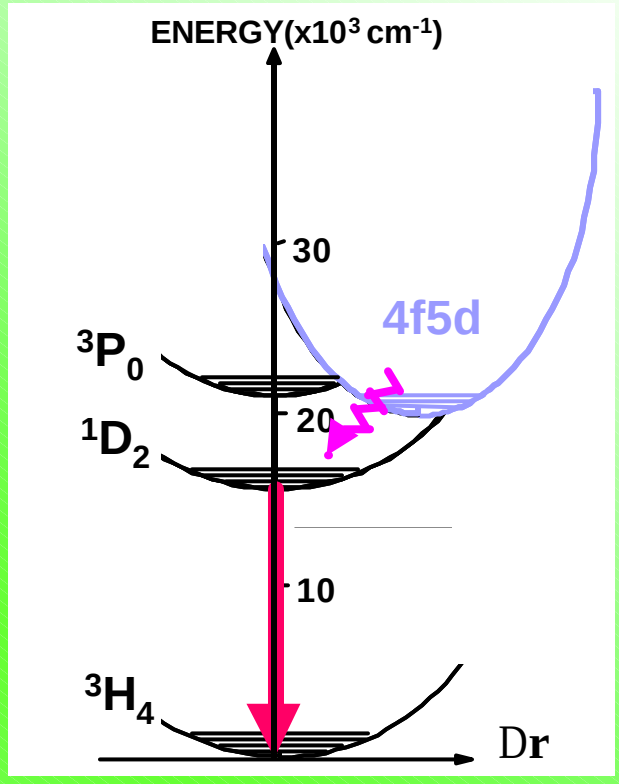
$CaZrO_3 : Pr^{3+}$

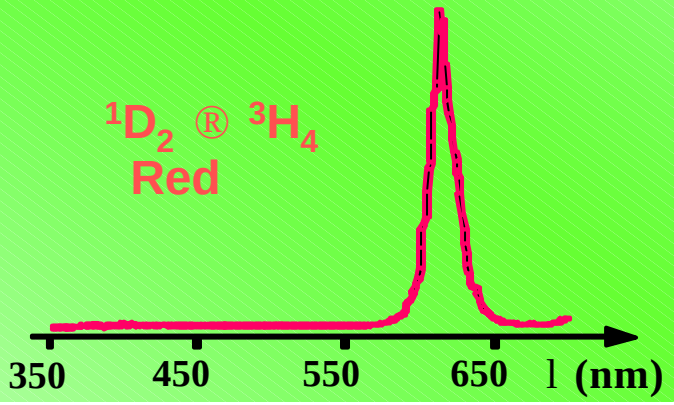
(G. Blasse et H. E. Hœfdraad , Phys. Stat. Sol. (a) 29 , (1975), K95-K97)





$CaTiO_3 : Pr^{3+}$





IMPROVING LUMINESCENCE YIELD

1- Charge Compensation

$Ca^{2+}_{1-x}\ Pr^{3+}_{x} Ti^{4+}\ O_3$ Not compensate ® $Ca^{2+}_{1-x}\ Pr^{3+}_{x} Ti^{4+}_{1-x} Ti^{3+}_{x}\ O_3$

$Ca^{2+}_{1-2x}\ Pr^{3+}_{x}\ Na^{+}_{x}\ Ti^{4+}\ O_3$ ® $(2Ca^{2+}$ ® $1Pr^{3+} + 1Na^{+})$

$Ca^{2+}_{1-2x}\ Pr^{3+}_{x}\ Ag^{+}_{x}\ Ti^{4+}\ O_3$ ® $(2Ca^{2+}$ ® $1Pr^{3+} + 1Ag^{+})$

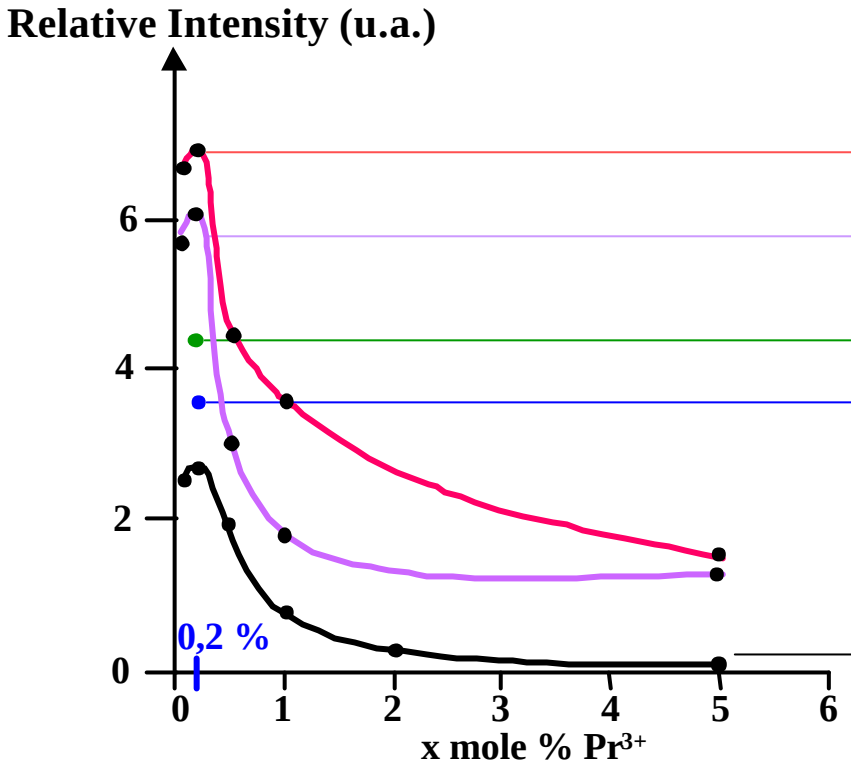
$Ca^{2+}_{1-x}\ Pr^{3+}_{x}\ Ti^{4+}_{\ 1-x}\ Al^{3+}_{x}\ O_3$ ® $(1Ca^{2+}+1Ti^{4+}$ ® $1Pr^{3+}+1Al^{3+})$

$Ca^{2+}_{1-3x/2}\ (\square)_{x/2}\ Pr^{3+}_{x}\ Ti^{4+}\ O_3$ ® Lacunar Perovskite

Solid State Reaction : T = 1200 °C , 4 hours / Air

Variation of the intensity of the Red emission

Exc. : 345 nm
T = 300 K



$Ca^{2+}_{1-3x/2}(\square)_{x/2}\,Pr^{3+}_{x}\,Ti^{4+}\,O_3$ (gain 150%)

$Ca^{2+}_{1-x}\,Pr^{3+}_{x}\,Ti^{4+}_{1-x}\,Al^{3+}_{x}\,O_3$ (gain 120%)

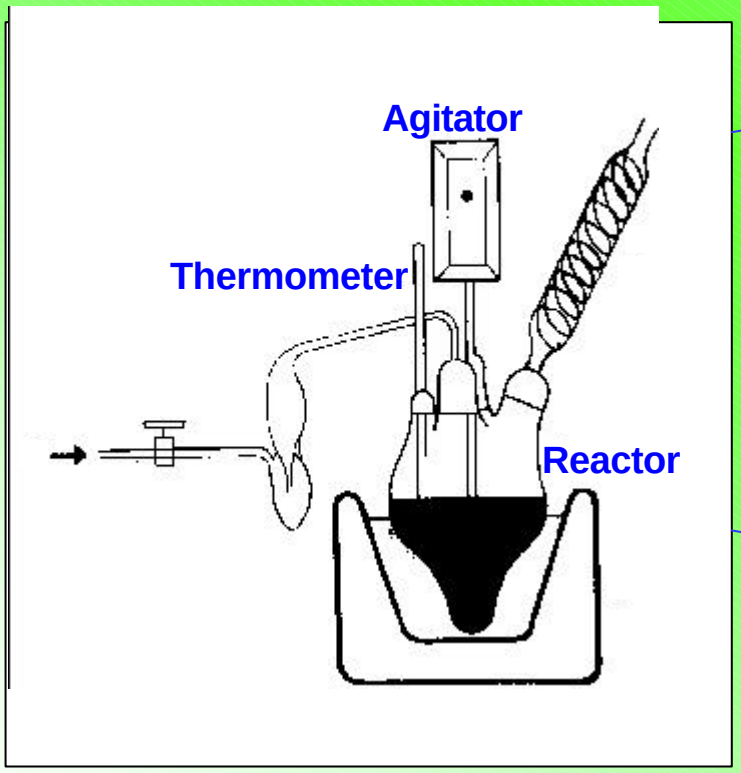
$Ca^{2+}_{1-2x}\,Pr^{3+}_{x}\,Ag^{+}_{x}\,Ti^{4+}\,O_3$ (gain 60%)

$Ca^{2+}_{1-2x}\,Pr^{3+}_{x}\,Na^{+}_{x}\,Ti^{4+}\,O_3$ (gain 30%)

$Ca^{2+}_{1-x}\,Pr^{3+}_{x}Ti^{4+}\,O_3$
(Not compensate)

IMPROVING LUMINESCENCE YIELD

2- Sol-Gel method



Acid Sol-gel

(pH = 3, solvent methanol)

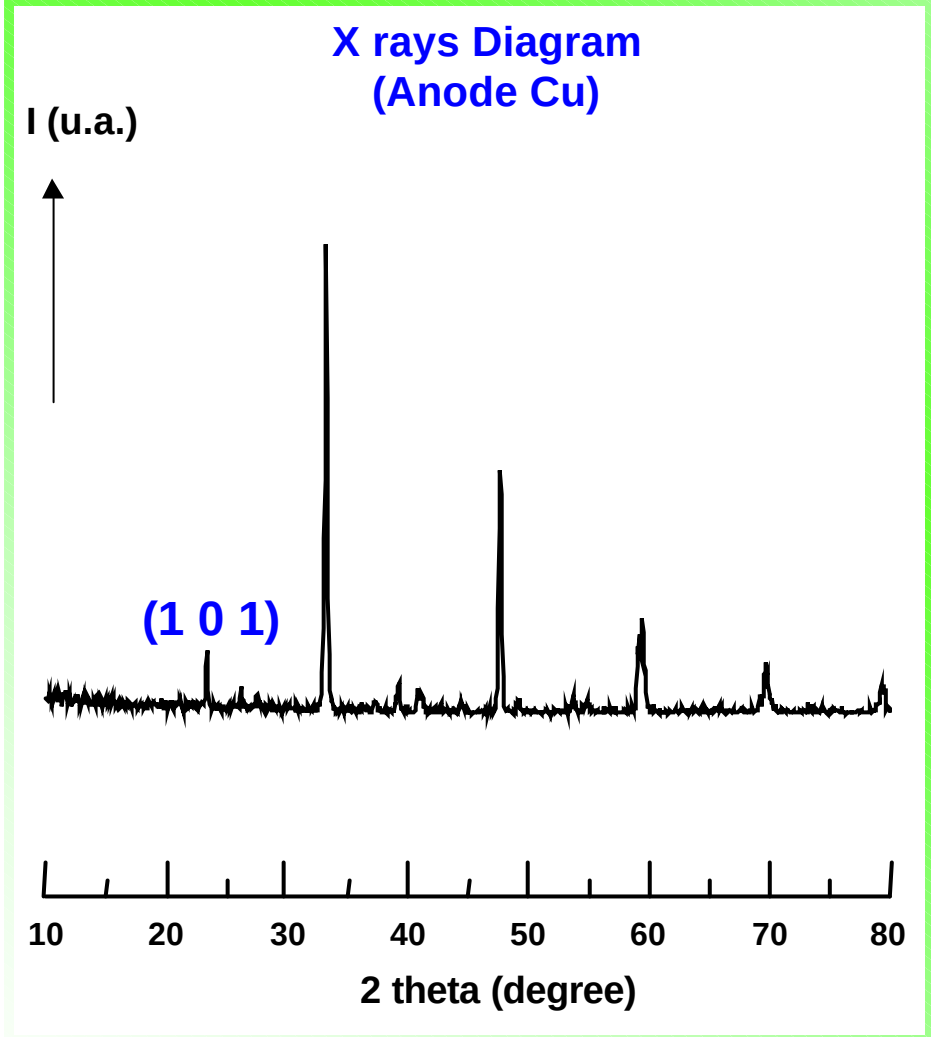
$$(1\text{-}x)CaO + xPrCl_3.7H_2O + Ti(OC_3H_7)_4 \rightarrow Ca_{1-x}Pr_xTiO_3 + 4C_3H_7OH$$

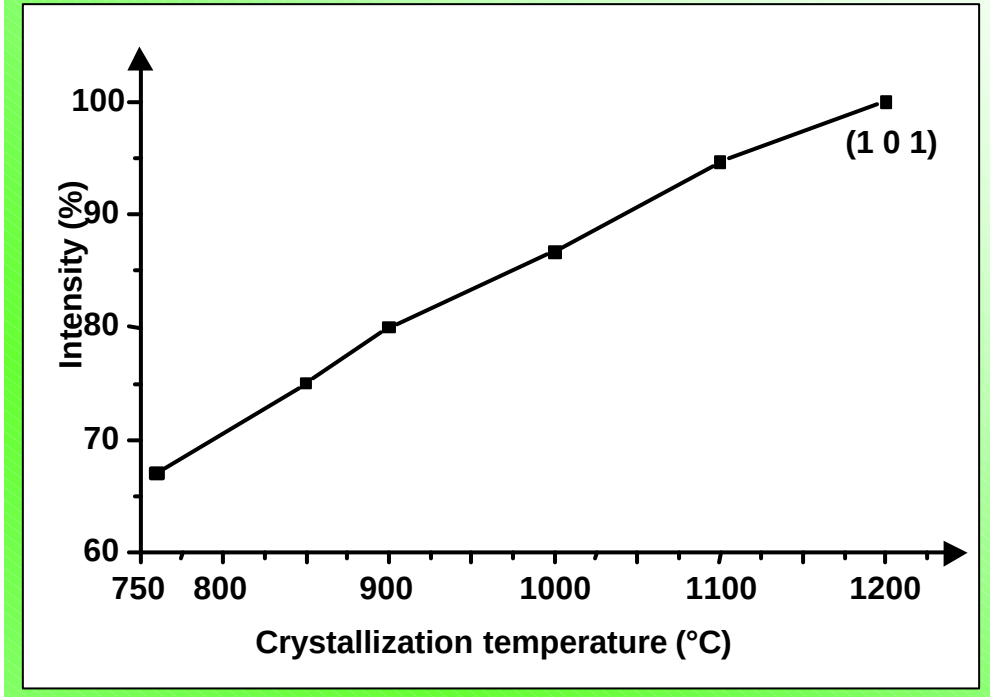
Basic Sol-gel

(pH = 10, solvent isopropanol)

$$(1\text{-}x)CaCl_2.2H_2O + xPrCl_3.7H_2O + Ti(OC_3H_7)_4 \rightarrow Ca_{1-x}Pr_xTiO_3 + 4C_3H_7OH$$

Crystallization



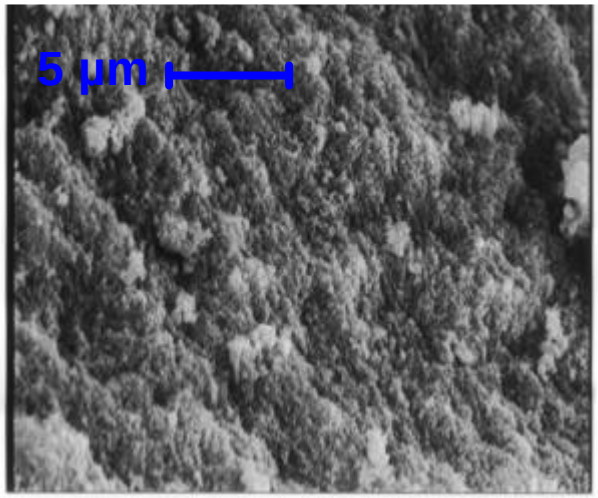


Crystalline phase of interest formed above 760 °C

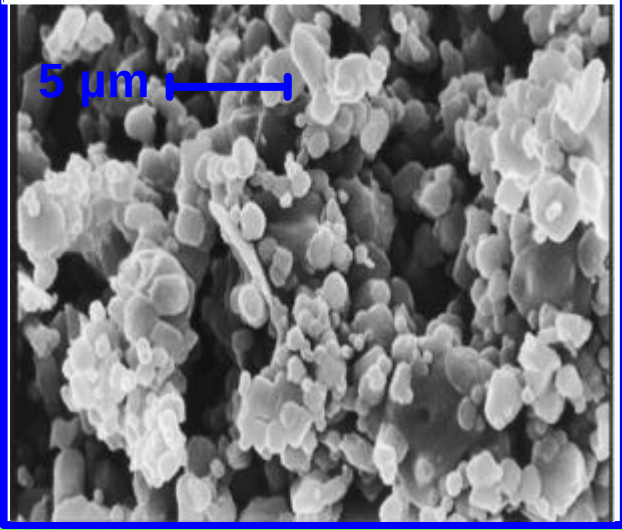
Morphologie

$Ca^{2+}_{1-x} Pr^{3+}_{x} Ti^{4+}_{1-x} Al^{3+}_{x} O_3$

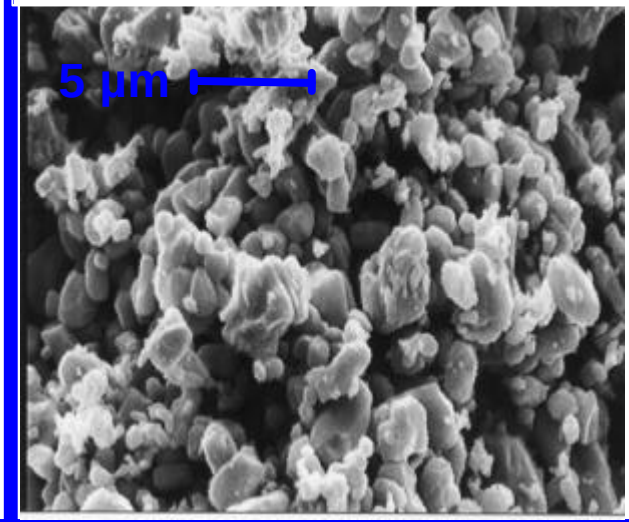
T = 760 °C



T = 1000 °C

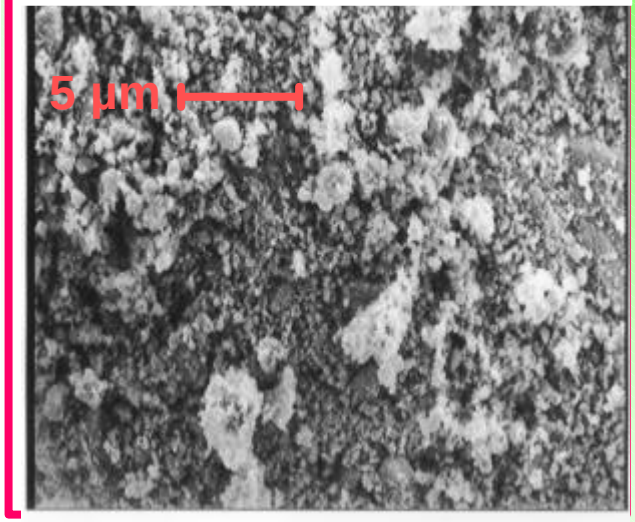


T = 1200 °C

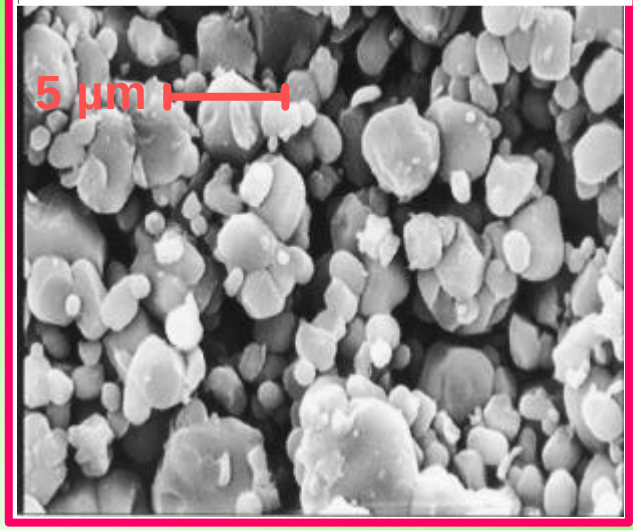


$Ca^{2+}_{1-3x/2} (\square)_{x/2} Pr^{3+}_{x} Ti^{4+} O_3$

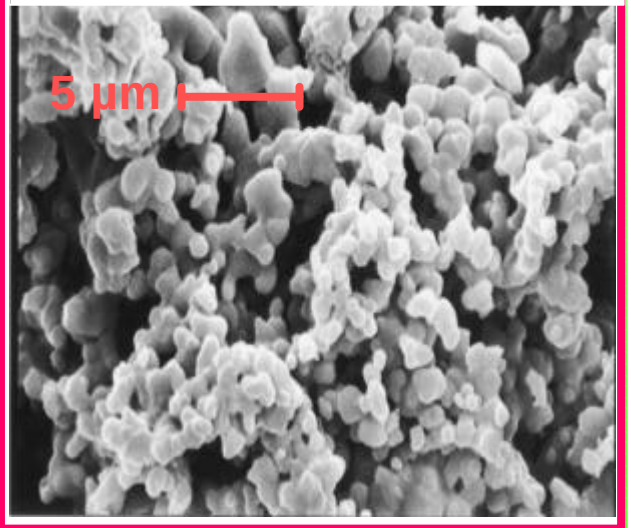
T = 760 °C



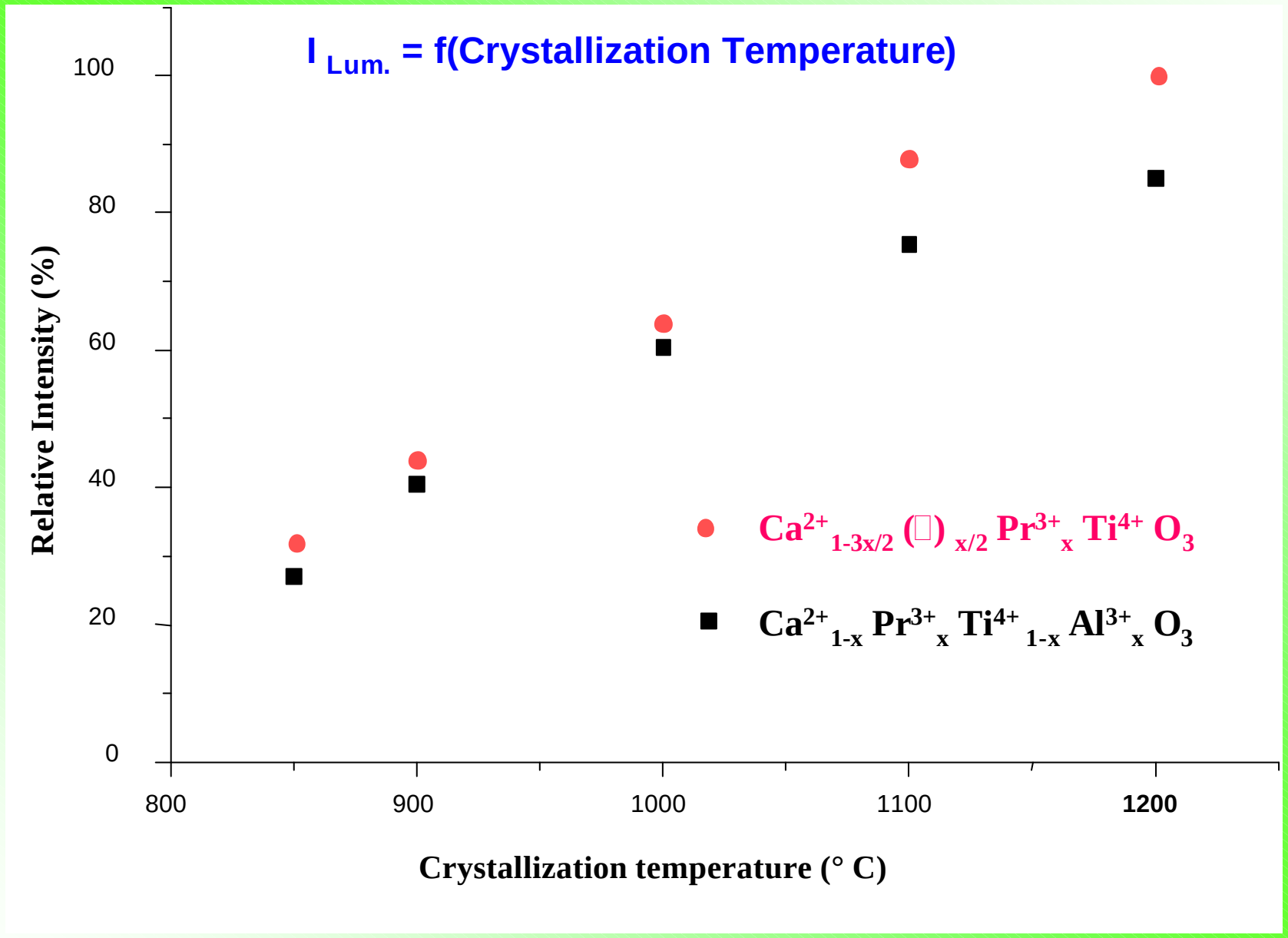
T = 1000 °C



T = 1200 °C

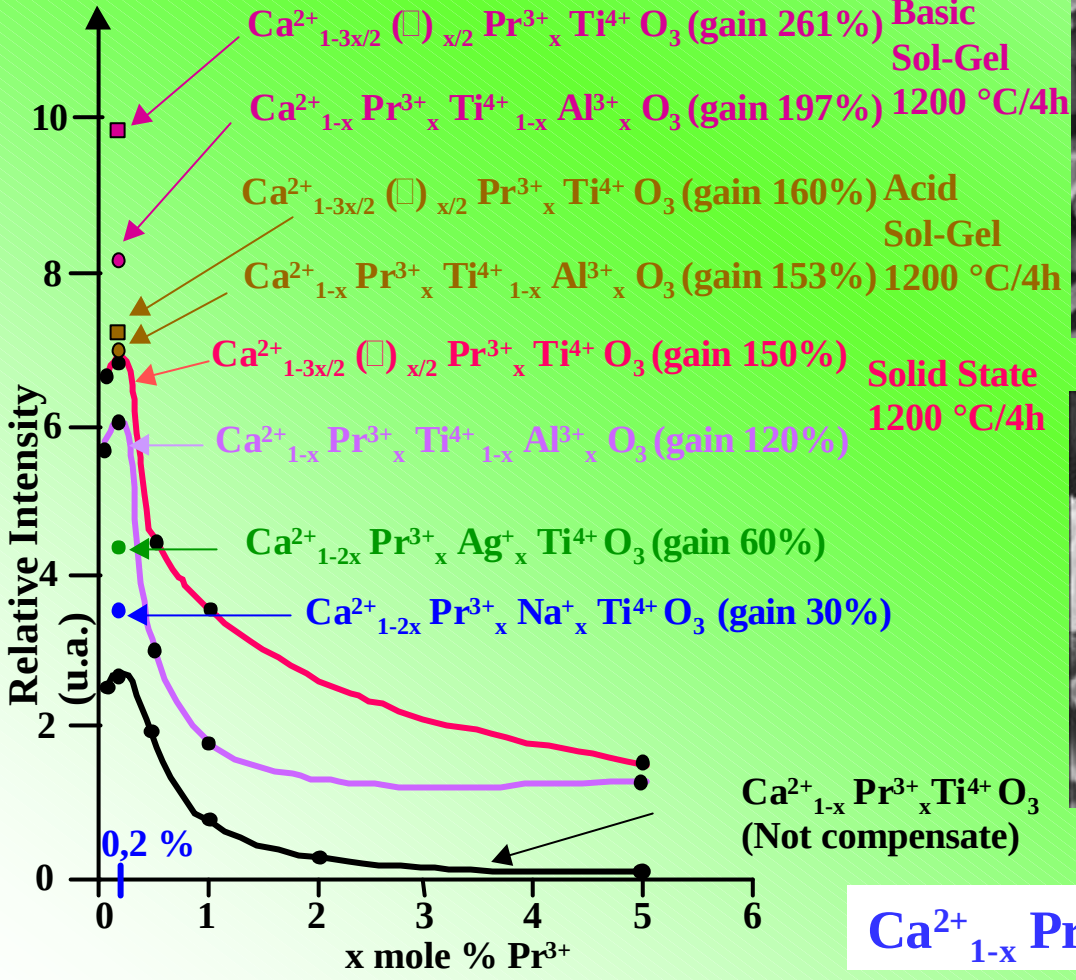


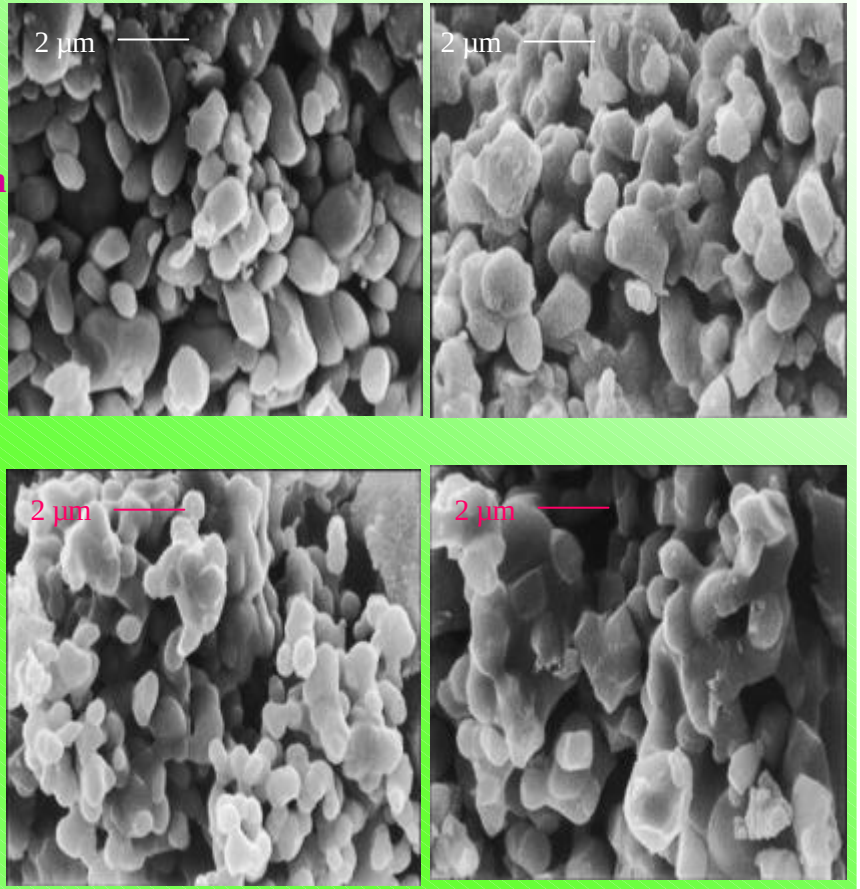
Variation of Red Luminescence



Luminescence properties optimization of praseodymium doped $CaTiO_3$

Exc. : 345 nm
T = 300 K





$Ca^{2+}_{1-x}Pr^{3+}_{x}Ti^{4+}_{1-x}Al^{3+}_{x}O_3$

$Ca^{2+}_{1-3x/2}(\square)_{x/2}Pr^{3+}_{x}Ti^{4+}O_3$

CONCLUSIONS

- Basic Sol-Gel Synthesis
- Crystallization state
- Materials densification

→ Red luminescence Intensity Increases

$Ca_{0,997}Pr_{0,002}TiO_3$ Prepared by Sol-Gel method under basic conditions and heat treated at 1200 °C is a promising polyvalent Red luminophore.