

Structural and Optical Properties of Ce³⁺ Doped YPO₄: Nanophosphors Synthesis by Sol Gel Method

B. Kahouadji, L. Guerbous, L. Lamiri, A. Mendoud

Abstract—Recently, nanomaterials are developed in the form of nano-films, nano-crystals and nano-pores. Lanthanide phosphates as a material find extensive application as laser, ceramic, sensor, phosphor, and also in optoelectronics, medical and biological labels, solar cells and light sources. Among the different kinds of rare-earth orthophosphates, yttrium orthophosphate has been shown to be an efficient host lattice for rare earth activator ions, which have become a research focus because of their important role in the field of light display systems, lasers, and optoelectronic devices. It is in this context that the $4f^n \leftrightarrow 4f^{n-1} 5d$ transitions of rare earth in insulating materials, lying in the UV and VUV, are the aim of large number of studies. Though there has been a few reports on Eu³⁺, Nd³⁺, Pr³⁺, Er³⁺, Ce³⁺, Tm³⁺ doped YPO₄. The $4f^n \leftrightarrow 4f^{n-1} 5d$ transitions of the rare earth dependent to the host-matrix, several matrices ions were used to study these transitions, in this work we are suggesting to study on a very specific class of inorganic material that are orthophosphate doped with rare earth ions. This study focused on the effect of Ce³⁺ concentration on the structural and optical properties of Ce³⁺ doped YPO₄ yttrium orthophosphate with powder form prepared by the Sol Gel method.

Keywords—YPO₄:Ce³⁺, $4f^n \leftrightarrow 4f^{n-1} 5d$ transitions, scintillator.

I. INTRODUCTION

RECENT reports demonstrate that the doped rare earth ions RE³⁺ could be the promising scintillator materials [1],[2]. Rare earth doped orthophosphates (LnPO₄: Ln=La, Ce, Gd or Y) have been attracting much attention [3]. Due to the high energy band gap, high thermal and chemical stability, high luminescence quantum yield, and sharp emission bands of orthophosphate host.

Lanthanide phosphates LnPO₄ crystallize in two polymorphs, that is, tetragonal phase with xenotime structure and monoclinic phase with monazite structure.

Yttrium orthophosphate YPO₄ crystallizes with the zircon structure (xenotime type) with a tetragonal symmetry ($a=b=0.6894\text{nm}$ and $c=0.6027\text{nm}$) and space group I₄₁/amd [4]. Where the site symmetry for Y³⁺ ions is D_{2d} point-group [6]. The structure can be described as chains parallel to the c axis of corner-sharing structural units built of (YO₈) dodecahedron and a (PO₄) tetrahedron linked together by an edge [5], [6] (Fig. 1).

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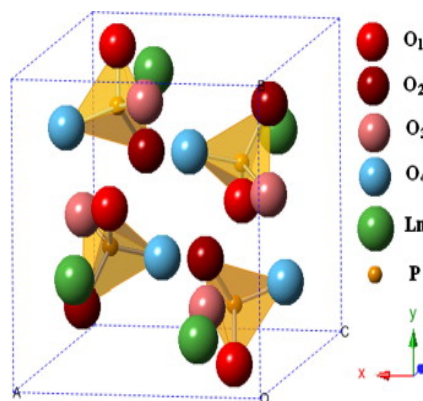


Fig. 1 LnPO₄ Xenotime structure

YPO₄ doped with Ce³⁺ ions attracts increasing interest as a good candidate for manufacturing of scintillators and phosphors because of its cheapness and the fact that its wide bandgap provides enough space for 4f and 5d orbitals of doped lanthanide ions [7].

To enhance luminescence intensity and scintillation efficient in any host doped with rare earth ions, the followings are the main requirements: finding out of optimum concentration of dopant ions (activator) for maximum luminescence in a host material, doping of appropriate sensitizer in the host material so that energy transfer to the activators is maximum, host with low phonon vibrations, host having transparency in visible and near-infrared (NIR) regions, stable in ambient atmosphere chemically and thermally and choose of suitable solvent/reaction medium. [8].

In the present work we have study the concentration effect of Ce³⁺ doped YPO₄ host with powder form on their structural and optical proprieties because there are any study reported Clearly the concentration effect of Ce³⁺ doped YPO₄ synthesis by sol gel method and the mechanism of concentration quenching is discussed in this paper .

II. SAMPLES PREPARATION

For preparation of nanophosphors samples with powder form used in the present work we have adopted the sol gel method, four samples of Ce³⁺ doped YPO₄ prepared with different concentration of Ce:Y_{1-x}Ce_xPO₄ ($x=0.5\%$, 1% , 2% , 5%).

In a typical synthesis process, appropriate amount of Y₂O₃ (99.99%), (NH₄)₂HPO₄ (>99.0%), Ce (NO₃)₃.6H₂O dissolved in appropriate amount of solution (Deionized water + nitric acid) the final mixture obtained stirred for 10h after that a

certain amount of organic additive (ethylene glycol EG) added and stirred for 2h, then the PH of solution was adjusted to 2 by addition of $\text{NH}_3 \cdot \text{H}_2\text{O}$ solution, finally, the colloidal solution was obtained.

The resulting solution dried at 100°C for obtained the samples Ce^{3+} doped YPO_4 samples with powder form.

III. STRUCTURAL CHARACTERIZATION

A. XRD Analysis

All the powder of $\text{YPO}_4:\text{Ce}^{3+}$ nanophosphors annealed at 900°C for 4h with step of $2^\circ/\text{min}$.

The structure of the resulting powder was characterized by X-ray Powder diffraction (X'Pert SW) with $\text{CuK}\alpha$ radiation, $\lambda=0.154056\text{nm}$ employing a scanning step of $2^\circ/\text{min}$ in the 2θ from 10° to 100° range.

The XRD Patterns of $\text{YPO}_4:\text{Ce}^{3+}$ samples prepared with different concentration of Ce^{3+} shows well crystallized tetragonal phase (Xenotime structure) according to JCPDS 09-0377 Fig. 2.

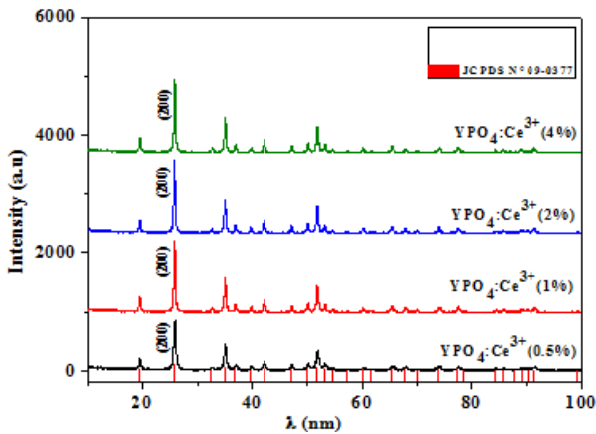


Fig. 2 XRD patterns of $\text{YPO}_4:\text{Ce}^{3+}$ powder annealed at 900°C for 12h

The unit cell volume and lattice parameters of all prepared samples are calculated and summarized in Table I.

TABLE I
UNIT CELL VOLUME AND LATTICE PARAMETERS OF SAMPLES

Concentration (Ce%)	a (Å)	b (Å)	c (Å)	Cell volume (Å ³)
0.5	6.876	6.876	6.010	284.14
1	6.873	6.873	6.02	284.37
2	6.881	6.881	6.0222	285.14
4	6.884	6.884	6.024	285.47

The unit cell volume of the samples increases with increasing concentration of Ce^{3+} in YPO_4 , because the ionic radius of Y^{3+} (0.9 \AA) [9] is less than Ce^{3+} (1.14 \AA) [8]. The increase in the unit cell volume with increasing concentration of Ce^{3+} indicates the quantitative substitution of Ce^{3+} in the lattice site of Y^{3+} in YPO_4 matrix.

B. Grain Size

After that confirmed the pure phase of the powders $\text{YPO}_4:\text{Ce}^{3+}$ prepared with sol gel process we have calculated the grain size of this powders.

The average crystallite size (D) was calculated from Scherrer relation [10]:

$$D = 0.89 \lambda / \beta \cos \theta \quad (1)$$

where D is the effective particle size, β is FWHM, θ is the diffraction angle, λ is the X-ray wavelength, the coefficient 0.89 is used to correct the particle size.

Fig. 3 shows the variation of grain size with Ce concentration.

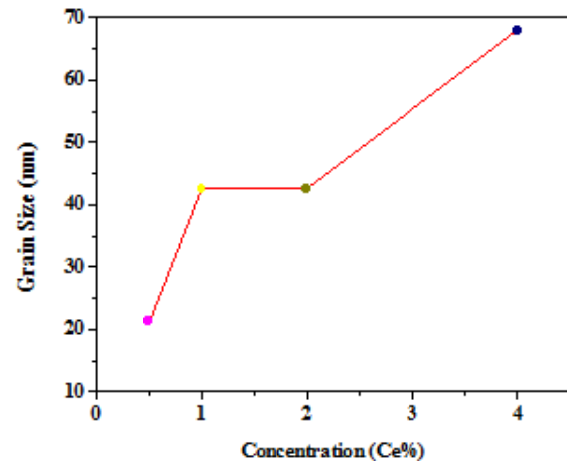


Fig. 3 Grain size of $\text{YPO}_4:\text{Ce}^{3+}$ nanophosphors calculated from Scherrer formula for (200) plane

IV. PHOTOLUMINESCENCE STUDY

The interconfigurational $4f-4f5d$ spectroscopy of the nanopowder $\text{YPO}_4:\text{Ce}^{3+}$ was measured using Perkin Elmer LS 50B luminescence spectrometer equipped with a 150 W Xenon lamp in the range of 200nm-800nm.

A. Ce^{3+} Ion Spectroscopy in YPO_4 Matrix

Fig. 4 shows the $4f$ and $5d$ levels of Ce^{3+} ion in the YPO_4 host [11].

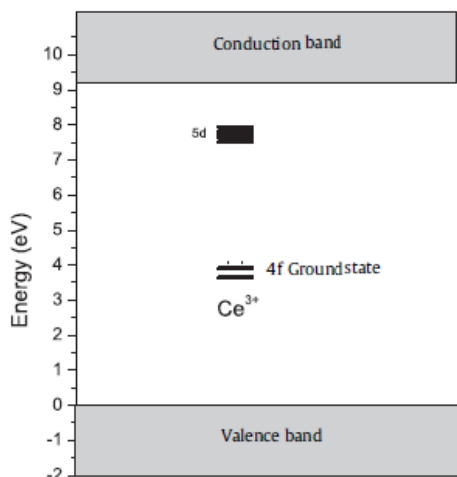


Fig. 4 4f and 5d levels of Ce³⁺ ion in YPO₄ host

It's very clearly that the YPO₄ hosts appropriate to get the good efficient luminescence for Ce³⁺ ion doped YPO₄ because it provides the very large space for 4f and 4d levels of Ce³⁺.

B. Emission Spectra of YPO₄:Ce³⁺ Nanophosphors

The emission spectra of the samples under excitation λ_{EX}= 245nm are shown in Fig. 5.

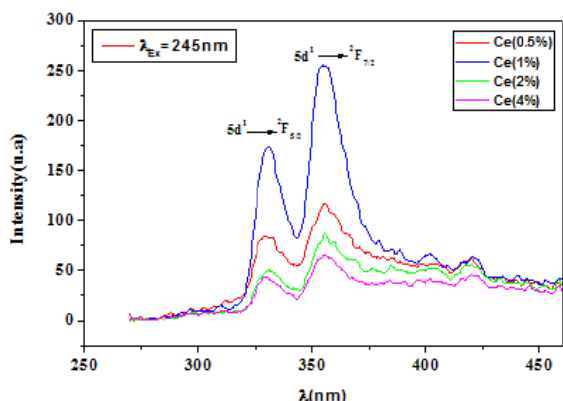


Fig. 5 Emission spectra at room temperature of the YPO₄:Ce³⁺ samples studied under λ_{EX}= 245nm

All spectra emission of nanopowder are studied in the spectra range of 260nm-450nm, The emission spectrum taken at an excitation wave length of 245 nm shows two emission bands centered at 330nm and 355nm, One relatively weak band peaked at 330 nm may be ascribed to the transitions from the excited state levels, which is the lowest crystal-field component of the 5d¹ configuration to the ground state levels ²F_{5/2} of the 4f¹ configuration of dopant Ce³⁺. [12], other band attributed to the 5d¹ - ²F_{7/2} transition.

The intensity of each band increase with increasing of the concentration of Ce³⁺ in the YPO₄ host between 0.5% and 1% after that the intensity of bands decrease with increasing of the concentration of Ce³⁺, Fig. 6 shows the variation of luminescence intensity of 5d¹ - ²F_{7/2} transition with Ce³⁺ concentration.

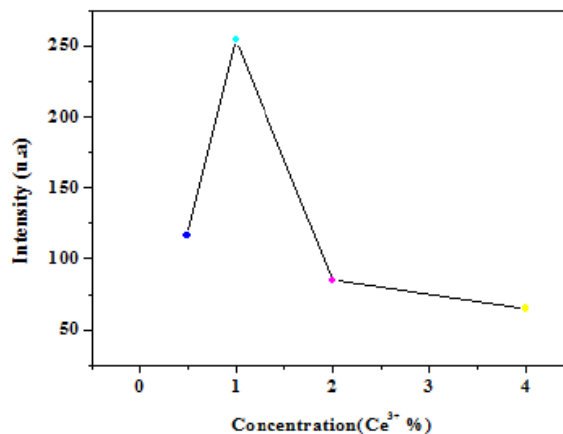


Fig. 6 Effect of Ce³⁺ concentration doped YPO₄ on the luminescence intensity of 5d¹ - ²F_{7/2} transition

The results of luminescence quenching in Fig. 6 show that, for the YPO₄:Ce³⁺ nanopowder, the optimum dopant concentrations of Ce³⁺ ions is 1%.

C. Chromaticity Coordinates

For understand the luminescence color of the Ce³⁺ doped YPO₄ samples after excitation (λ_{EX}= 245nm) we have calculated the chromaticity coordinates.

Table II shows the chromaticity coordinates (x, y) of YPO₄:Ce³⁺ nanophosphors and respective color from CIE diagram.

Concentration (Ce%)	x	y	CIE Color
0.5	0.16309	0.01219	Blue
1	0.163	0.01230	Blue
2	0.1629	0.0123	Blue
4	0.1629	0.0123	Blue

V. CONCLUSION

- YPO₄: Ce³⁺ nanophosphors are successfully synthesized through sol-gel method at moderate temperature (900 °C)
- The prepared YPO₄: Ce³⁺ crystallizes in a single-phase, Tetragonal structure.
- In this study the influence of Ce³⁺ concentration doped YPO₄ host on their structural and optical proprieties is confirmed, So, we have given the emission spectra of Ce³⁺ doped YPO₄ with difference concentration (0.5%, 1%, 2%, 4%) under excitation λ_{EX}= 245nm.
- Finally, the mechanism of luminescence quenching in the YPO₄:Ce³⁺ is studied; the optimum dopant concentration is 1%.

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