Luminescent Properties of Sm^{3+} activated β-$NaYF_4$ Microcrystals

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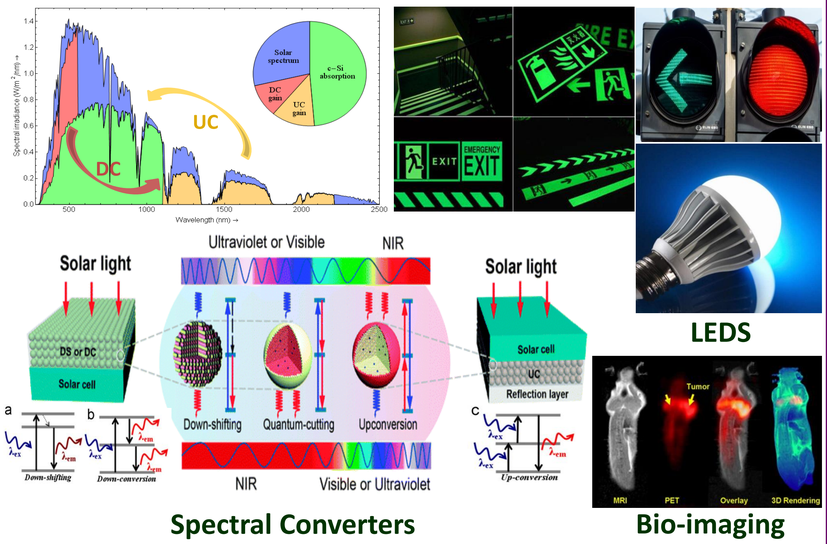
ABSTRACT

Sm^{3+} (1, 3, 5, 7 and 10 at.%) activated β-$NaYF_4$ micro-phosphors were prepared via hydrothermal process at 200^{0}C. X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM), and selected area electron diffraction (SAED) have been used to investigate the morphology and crystal structure of the samples. One interesting outcome of photoluminescence study involved the relative intensity variation of the strongest emission peak at ~600 nm due to $^4G_{5/2}$-$^6H_{7/2}$ transition under the excitation of 400 nm. These results were explained on the basis of multiple energy levels and self concentration quenching associated with the activator ion.

INTRODUCTION

Lanthanide-doped Fluorides have played an outstanding role as phosphors in various fields such as optoelectronic devices (Solar cells, LEDS), solid state lasers, biomedical imaging etc.

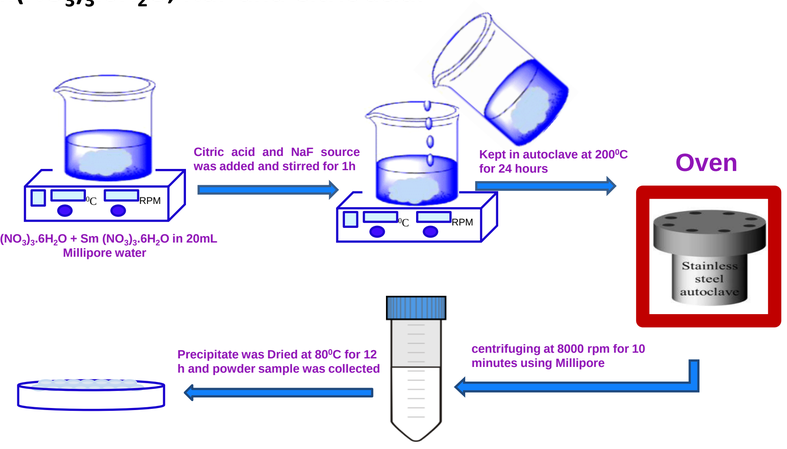


$NaYF_4$ is an ideal host for luminescent lanthanide ions because of their high transparency arising from the low energy phonons and high ionicity.

In this work, an effort is made using simple synthesis procedure to synthesize the microcrystals and studied their luminescence behavior of lanthanide Sm^{3+} doped β-$NaYF_4$ host.

EXPERIMENTAL DETAILS

A series of Hexagonal microcrystals of $NaYF_4$ with 1 - 10 at. % Sm^{3+} were synthesized by a modified hydrothermal synthesis route using high purity (>99.9%) raw powders of $Y(NO_3)_3.6H_2O$, $Sm(NO_3)_3.6H_2O$, NaF and Citric acid.

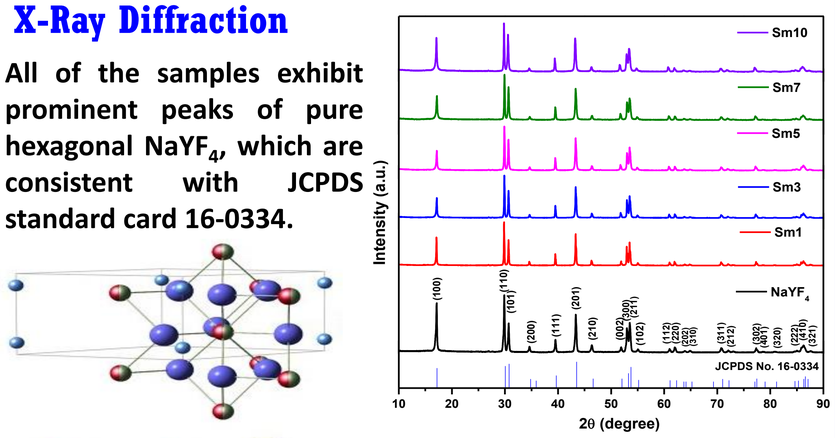


- **The phase purity and structure were characterized through XRD (Rigaku, Japan) with Cu-Kα.**
- **The morphology was examined by FEI, Tecnai G2 TF30-ST TEM and FESEM NOVA NANOSEM450.**
- **The Fourier transform infrared spectroscopy (FTIR) studies have been taken from Shimadzu IR Prestige-21.**
- **Photoluminescence was performed on a PerkinElmer (LS-55).**

RESULTS AND DISCUSSIONS

X-Ray Diffraction

All of the samples exhibit prominent peaks of pure hexagonal $NaYF_4$, which are consistent with JCPDS standard card 16-0334.



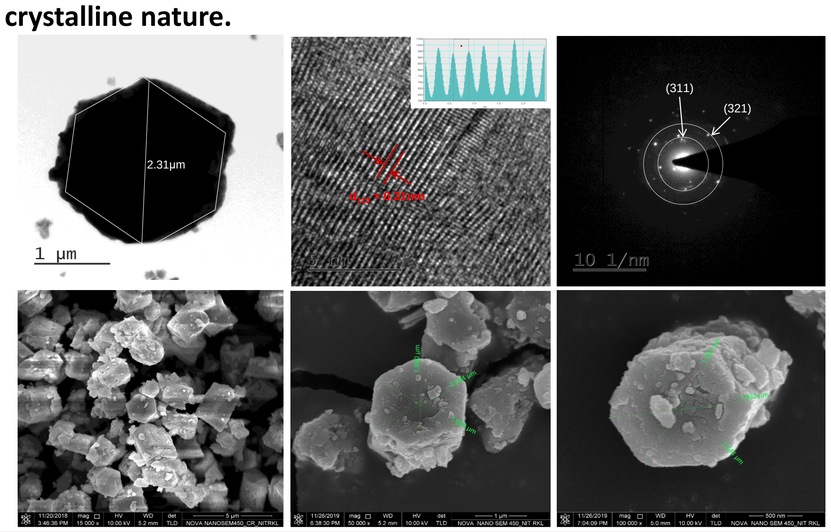
Structure : Hexagonal
Space Group: $P6_3/m$

No detectable secondary phase in the XRD pattern implies that Sm^{3+} has been effectively doped into the respective sites of host lattices β-$NaYF_4$.

FESEM / TEM

B-$NaYF_4$ is found to be regular hexagonal microcrystal with a typical size of 2.31 µm and particle size decreases with doping.

The HRTEM clearly reveals the lattice fringe of 0.31 nm corresponding to (110) plane of β-$NaYF_4$ microcrystal and SAED patterns originate from the planes (311), (321) confirm the crystalline nature.

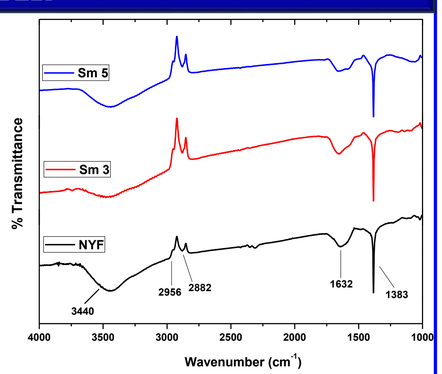


FTIR

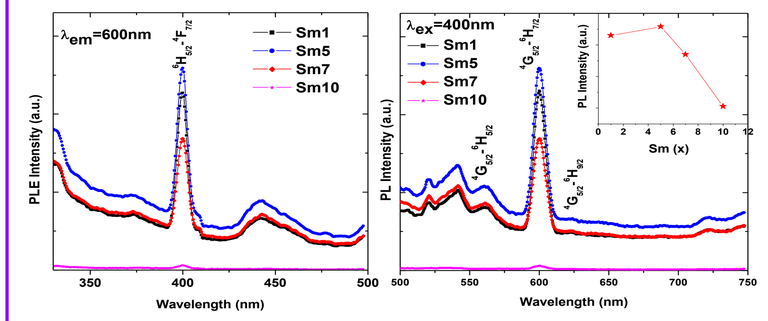
Broad band near 3440 cm^{-1} vibration of the hydroxyl groups (-OH) absorbed on the crystal surface.

2956 cm^{-1}, 2882 cm^{-1} asymmetrical and symmetrical stretching vibration modes of the CH_2 group

1632 and 1383 cm^{-1} vibrations of carboxylate anion ($-COO^-$) indicating the citrate ligands at the surface of crystals.

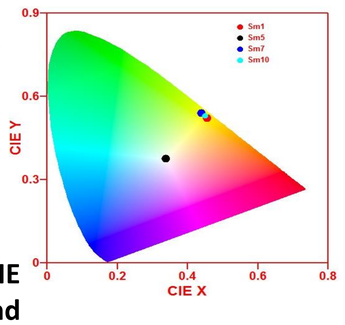


PHOTOLUMINESCENCE



The relative intensity of excitation peak at 400 nm varies with the concentration of the Sm^{3+} is due to the $^6H_{5/2}$-$^4F_{7/2}$ transition.

The emission peak intensity varying with the conc. of Sm^{3+} might be due to self concentration quenching of Sm^{3+}, typically over 5 at. %.



All samples show the CIE chromaticity coordinates around yellow region with higher color purity, while 5 at. % Sm^{3+} doped host matrix shows the coordinates in white region may be due to its higher luminescence property.

Sample	at.% of Sm^{3+} (x)	CIE co-ordinates	
		x	y
$NaYF4:xSm^{3+}$	1	0.45	0.52
	5	0.34	0.38
	7	0.44	0.54
	10	0.45	0.53

CONCLUSIONS

- **A series of hexagonal microcrystals are developed using hydrothermal route. The XRD spectra shows single phase and stoichiometric, implies the activator ions is at Y site.**
- **TEM/FESEM image hexagonal shapes of microcrystals with particle size 2.31 µm .**
- **The HRTEM images reveal the lattice fringes and SAED pattern confirms the crystalline nature of prepared samples.**
- **From the PL, the relative intensity of the emission peak varies with the Sm^{3+} conc. CIE diagram confirms the yellow and white emissions of the microcrystals.**

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