Yb^{3+}/Ho^{3+} DOPED $CePO_4$NANOPHOSPHORS (SYNTHESIS, CHARACTERIZATION, AND ITS LUMINESCENCE STUDIES)

Sirisha Bandi[1,2],Venkata Nagendra Kumar Putta[2]*, , Phani Raja Kanuparthy[2],Girija Venkateswara Koneru[2],Reddy Prasad Puthalapattu[3].
1. B V Raju Institute of Technology, Narsapur,502313, Telangana, India
2. Dept. of Chemistry, GITAM deemed to be University, Rudraram, Hyderabad-502329
3. Institute of Aeronautical Engineering Hyderabad
*Corresponding Author,Email:
pvenkatanagendrakumar@gmail.comMobile: 9885357559

ABSTRACT:

By using polyol synthesis Yb^{3+}/Ho^{3+} co-doped $CePO_4$nanophosphors were prepared which appear both up-conversion (UC) and down-conversion (DC) with excellent luminescence properties. DC peaks were observed at ~460, ~550, ~650, and ~750 nm, at 300 nm excitation. A very weak P-O Charge Transfer(CT) band of Ho^{3+}ionsis observed. We discovered that $CePO_4$: Yb^{3+}/Ho^{3+}, anup-conversion (UC) nano phosphor also observed. At strong 980 nm laser illumination, the up-conversion emission spectra show a visible expectant peak of the Ho^{3+} ion at ~550 and ~650 nm. This process yields high-quality nanocrystal materials with sizes between the tens of nm range. Considering the results of the study at 300nm excitation, $CePO_4$: Yb^{3+}/Ho^{3+} produced a high quantum yield value. These findings are useful for making highly efficient phosphors, and it demonstrates the many applications of the nanophosphor materials covered by this approach.

KEYWORDS: polyolmethod, ytterbium ion, holmium ion, cerium ion, photoluminescence.

INTRODUCTION:When activated by a near-infrared (NIR) laser, the majority of lanthanide ion-doped materials generate visible radiation. Due to their simple synthesis, rare-earth (RE) based materials are receiving more and more attention. Different RE-doped nanomaterials have been developed and employed in a variety of applications, including solar cells, temperature sensors, spectrum converters, and biological areas. A poor protocol has been in place up until now for the mass fabrication of up &down-conversion nanomaterials. Fascinatingly, rare-earth (RE) orthophosphates are frequently referred to as important hosts for the adsorption of nuclear waste due to their strong thermal (up to 2200^{0}C) and chemical stability, required optical characteristics, and poor solubility. In our recent study, we have reported polyol methods for the production of the nanomaterial $CePO_4$, a $Yb^{3+/}Ho^{3+}$ dual-mode converter. In accumulation, $CePO_4$ nanoparticles are utilized as a host for (DC)/(UC) luminescence because of this method's ability to modify the size and shape, which can improve the luminous property upon continuous wave (CW) laser stimulation. This will be caused by the acceptable transition, which involves the charge transfer (CT) process of O^{2-} toward Ce^{3+}, which has an intense absorption at 300 nm and absorbs light from 240 to 280 nm. Depending on UV light, We can observe the emission spectrum exhibiting sharpened peaks of the Ho^{3+} ion at ~460, ~550, ~650, and ~750 nm, as well as the same peak when excitation is at 300 nm, demonstrating the down-conversion. In this case, Yb^{3+} functions as a sensitizer[12] to increase the strength of the Ho^{3+} ion emission in the spectrum. Ho^{3+} emits intensely when stimulated by near-IR light at about 980 nm. Appearancesof the room-temperature emission spectrum about $CePO_4$ up-conversion. The sample was stimulated using a 980 nm laser. In this study, we created $CePO_4$:Ho^{3+}/Yb^{3+}nano phosphor via a polyol-mediated process. Its stunning behavior has been investigated using excitations at 980 nm (due to Yb^{3+} absorption), 300 nm (due to indirect P-O) weak charge transfer band, (CTB), and 460 nm (because of Ho^{3+} absorption). We talk about up-conversion, down-conversion, and energy transfer efficiency. The sensing characteristics of such particles will increase their effectiveness in optics, displaying, cybersecurity, and microbial systems.when the synthesized nanomaterial's functional groups are activated.

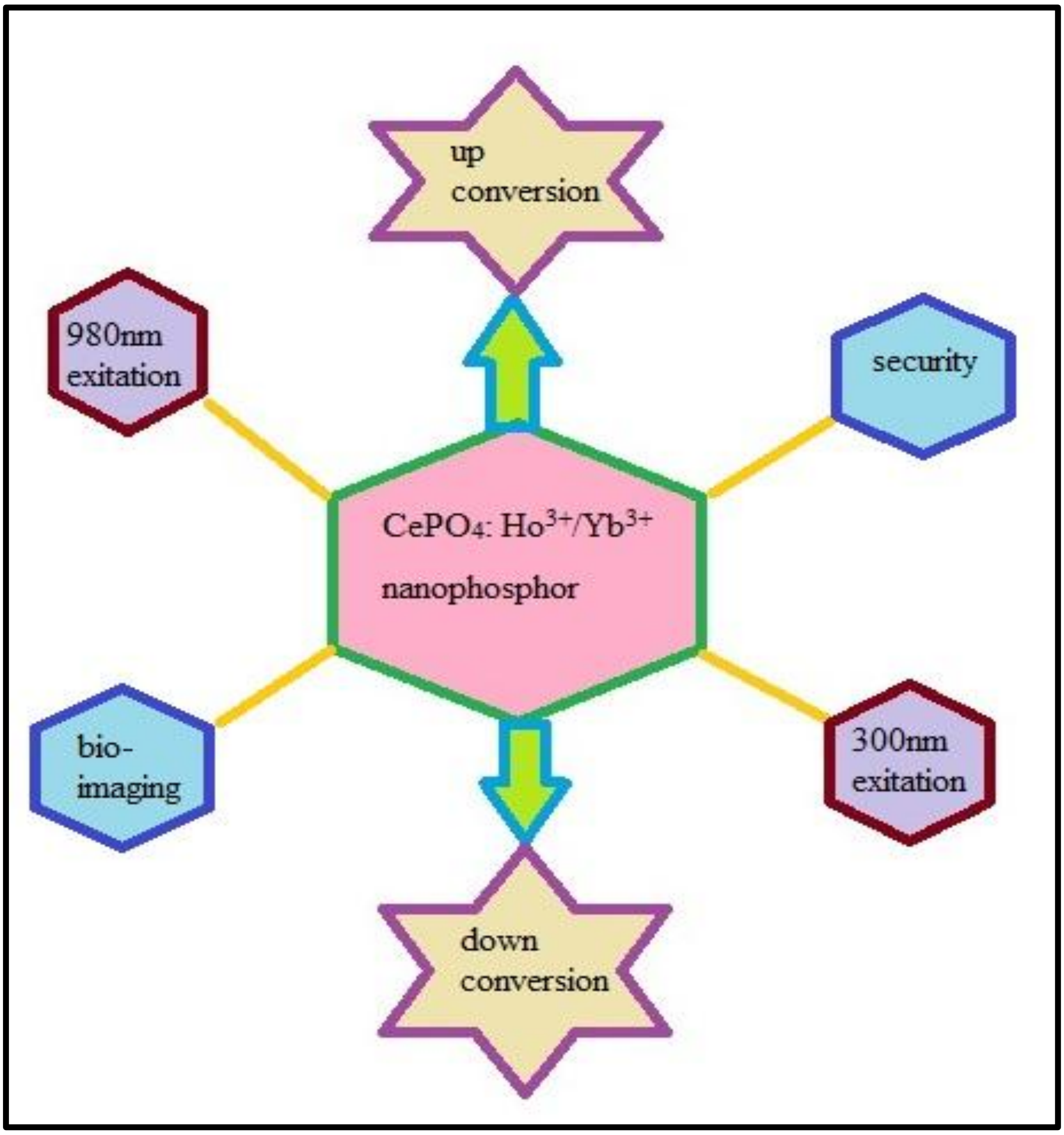

Figure-1. Schematic diagram representing the synthesis of $CePO_4$: Ho^{3+}/Yb^{3+}

Nanophosphor and its various applications

2. ***EXPERIMENTAL METHODS***

2.*1*. ***CHEMICAL COMPOUNDS & SYNTHESIS:***

CHEMICAL COMPOUNDS:Very pure Analytical grade reagents from Sigma-Aldrich were used as reactants.
Cerium (III) Acetate Hydrated [$Ce(Ac)_3.XH_2O$],Ammonium dihydrogen phosphate [$(NH_4)_2HPO_4$],Holmium (III) Acetate Hydrated [$(Ho(Ac)_3).XH_2O$],Ytterbium (III)

AcetateHydrated [Yb(Ac)$_3$.X H_2O], HCl,Ethylene glycol(EG), Sodium hydroxide,De-ionised water used as precursors.

***SYNTHESIS OF CEPO$_4$: Ho^{3+}/Yb^{3+} NANOPARTICLES*:**

To prepare the sample, the polyol technique is used. Figure-1 the following is a list of the samples that were created: $CePO_4$:Ho^{3+} and Yb^{3+} luminous nanoparticles are doped with 1% and 20% Ho^{3+} and Yb^{3+}, respectively. Polyol-mediated synthesis was used to create this item. In a typical synthesis, 5 ml of concentrated HCl was added, along with 730.76 mg of $(CH3CO_2)_3CeXH_2O$, 8.7 mg of $(CH3CO_2)_3HoXH_2O$, and 178.48 mg of $(CH3CO_2)_3YbXH_2O$. In a pure, clear solution, metal ions were dissolved. Deionized water of 10 ml was alternately added, followed by heating (80 °C), to eliminate any leftover HCl. The evaporation technique 4 was performed at least five times. Furthermore, 298.28 mg of $(NH_4)_2HPO_4$was dissolved in 10 ml of deionized water, and 2.64 g of NaOH was dissolved in 10 ml of deionized water to get a transparent solution. [5]. The $(NH_4)_2HPO_4$ solution was received drop by drop until it became transparent. In a 100 ml flask with a circular bottom Before adding the $(NH_4)_2HPO_4$ solution dropwise, 20 ml of ethylene glycol was incorporated into the mixture[10], the evaporated metal ion solution was shifted, and the combination was then refluxed for at least 10 minutes at 75 °C. A pale-yellow tint was seen upon adding $(NH_4)_2HPO_4$ solution to the round bottom flask, but after two hours of heating at 120 °C, the color turned from pale yellow to white.Eventually, white precipitation appeared. As a result, it was allowed to settle to ambient temperature. It was obtained following the dry powder's centrifugation at 5000 rpm for five minutes, two washes with 10 ccs of acetone, and IR-light drying took place. The prepared sample was calcinated at 900 °C for four hours. Similarly, fixed amounts of Yb^{3+} (10 at. percent) and Ho^{3+} (3, 5, and 7 at. percent). After producing doped $CePO_4$ nanoparticles, the samples underwent a 4-hour annealing process at 900 °C.

2.2:***CHARACTERIZATION*:**

Equipment Utilizing Synchrotrons angle disperssiveX-ray difraction, the sample's average crystal size was investigated (Source: India).Using a scanning electron microscope, microstructural analyses andmeasurements of the particle size and the surface morphology were obtained. (SEM: quanta) Analysis of the vibrational structure of the produced materials was done using 200FTIR spectroscopy,a monochromator (ihr3211, Horiba Jobinn Yvonne) outfitted with a photomultiplier tube that allowed researchers to observe UC emission. To excite the samples, 980 nm light from a diode laser was used. UC studiesdeal with photoluminescence excitation (PLE). Utilizing the excitation WL (wavelength) of an Nd: YAG Laser strong ultraviolet excitation at 280–300 nm, the DCemission ranges of $CePO_4$:Ho^{3+}/Yb^{3+} are studied.

3:***RESULTS AND DISCUSSION***

3.1.***XRD SAMPLE STUDY:***

Nanophosphor material $CePO_4$: 1 at. % Ho^{3+} and 20 at. % Yb^{3+} co-doped $CePO_4$ (also known as $CePO_4$:Ho^{3+}/Yb^{3+}) is seen in *Figure-2* in its XRD form. This material can be annealed at 900 °C. The nanophosphor material $CePO_4$: 1 % Ho^{3+} and 20 % Yb^{3+} co-doped $CePO_4$ (which is capable of 900 °C annealings and was referred to as $CePO_4$:Ho^{3+}/Yb^{3+}) can be seen in Figure-2 in its XRD form.Strong, sharp peaks that are continuous with the normal monoclinic phase can be seen in the diffraction patterns.Because there is no impurity peak, it is expected that the dopants are distributed evenly throughout the host lattice. The diffraction patterns that occurred and two of the highest intensity peaks in the XRD pattern are closely aligned with the tetragonal structure of pure $CePO_4$.Based on CN 9, Yb^{3+} and Ho^{3+} ions were substituted at Ce^{3+} positions of the $CePO_4$ lattice since their ionic radii are similar. A Pentagonal Interpenetrating Tetrahedral Polyhedron with the monoclinic structure of $CePO_4$ was created in the nanophosphor where nine O^{2-}ions surround the Ce^{3+} ion(PITP).

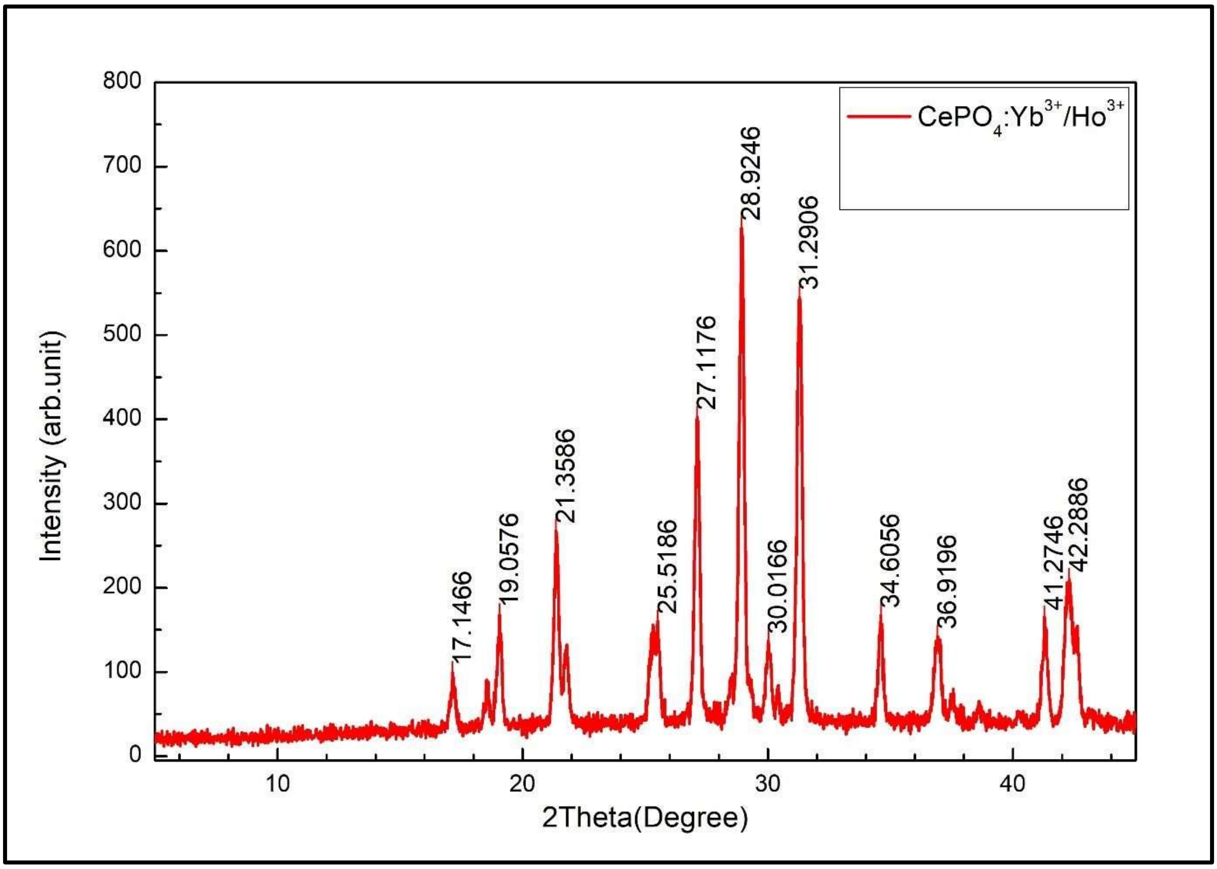

Figure-2: XRD pattern of $CePO_4$:Ho^{3+}/Yb^{3+}samples respectively

3.2.***SEM STUDY***:

Figure -3 shows a $CePO_4$:Ho^{3+}/Yb^{3+} SEM picture. At 900 °C, nanophosphor material was annealed. This displays the irregular forms of nanoparticles (a significant proportion of sponge-shaped particles and a small number of (cones, cuboids, and spherical Shapes,). 50 nanometres is the typical size obtained from spherical particles. *Figure-3* showed the specific basic compositional images of Ce, O, Yb, Ho, and P.

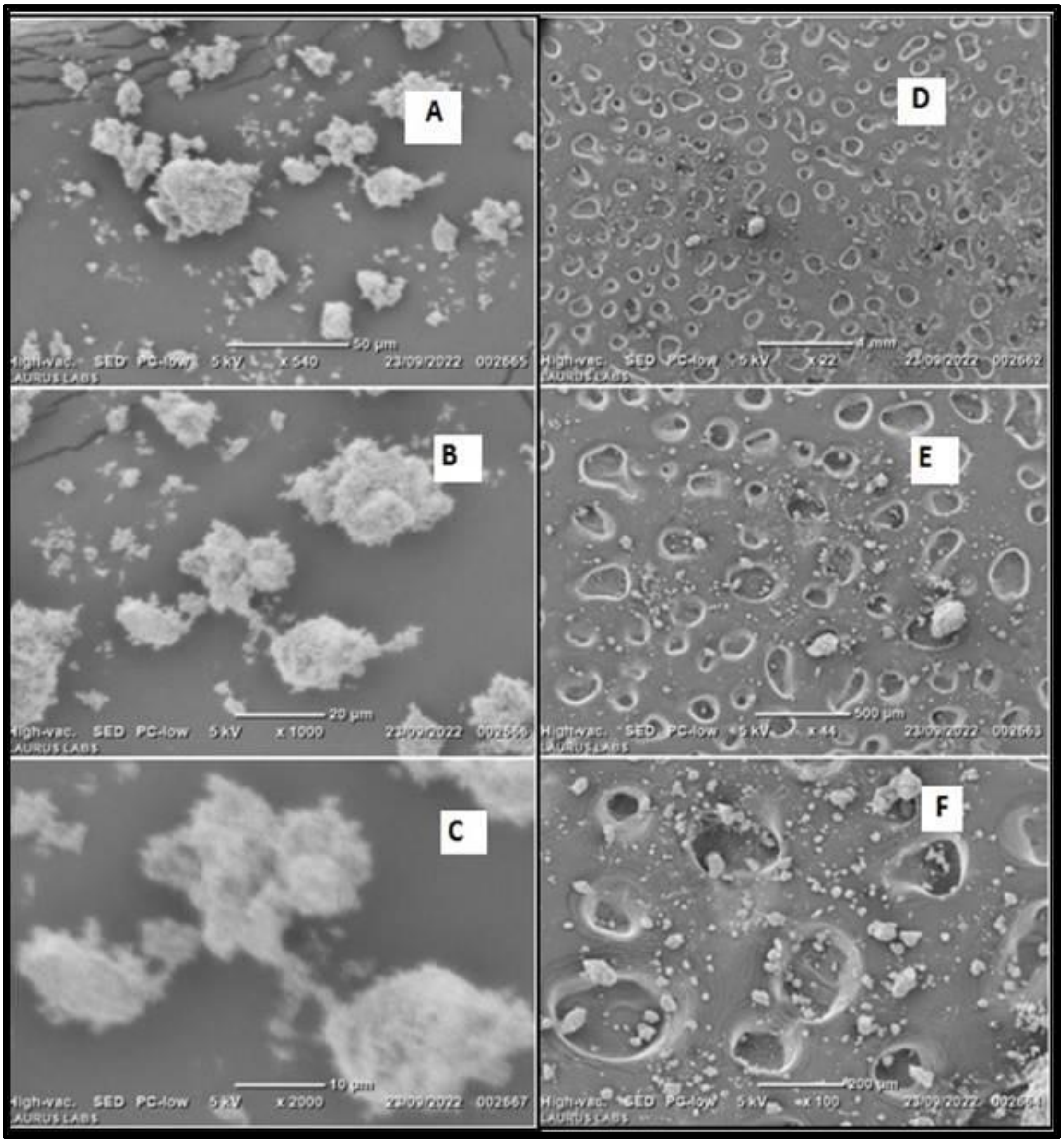

Figure-3: SEM images ofCePO$_4$:Ho^{3+}/Yb^{3+}

3.3 FTIR**:**Using FTIR Spectroscopy with 1 cm^{-1} resolution, the vibrational structure of the generated materials was examined (Bomemn *MB* 104 spectrophotometer). *Figure-4*shows what we have been discussing.

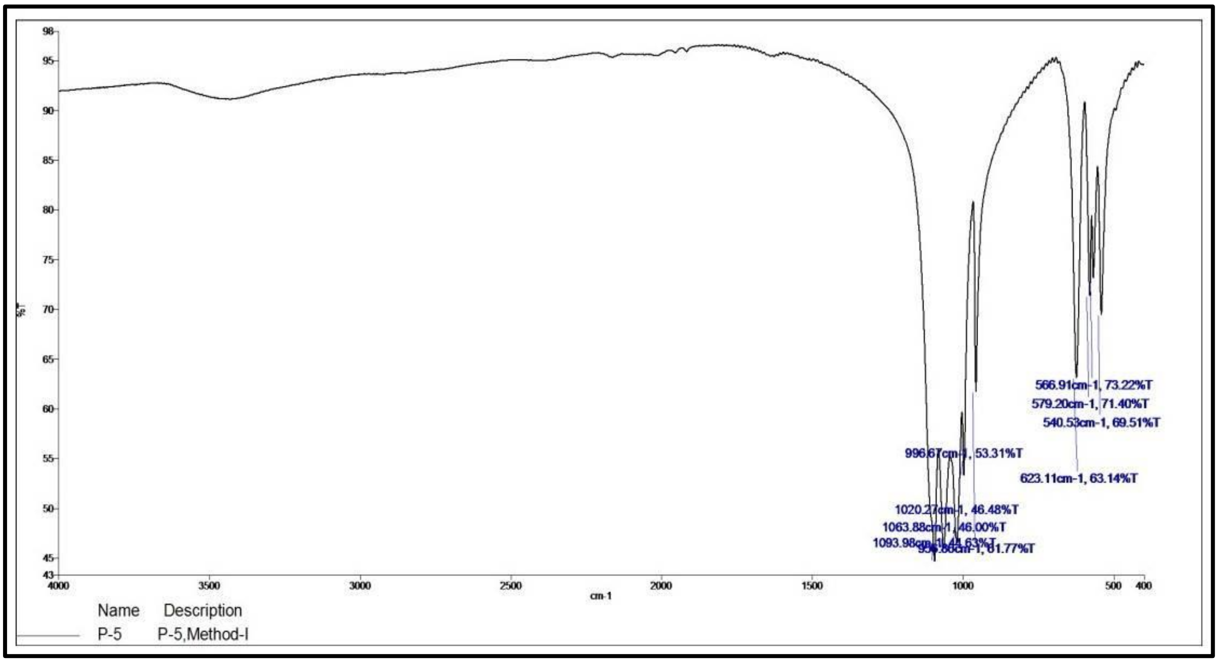

Figure-4: FTIR ofCePO$_4$:Ho^{3+}/Yb^{3+}

3.*4PHOTOLUMINESCENCE STUDY:*

PHOTOLUMINESCENCE OF CePO$_4$:Ho^{3+},Yb^{3+}:

UP-CONVERSION STUDY: Anti-Stokes luminescence is the source of up-conversion luminescence, an optical phenomenon that releases high-energy photons while absorbing low-energy photons (multiphoton).

Ho^{3+} can release either green or red emission[3] based on the relative concentrations of the host and co-dopant. Figures- 5 and 6 depict the (DC) & ultraviolet (UC) emission spectra of $CePO_4$: Ho^{3+}, Yb^{3+}. Interestingly,

We combined Ho^{3+} doped $CePO_4$ (Ho^{3+} = 1 at.%) and Yb^{3+} doped $CePO_4$ (20 at.%) to create $CePO_4$:0.01Ho^{3+}/0.2Yb^{3+} nanophosphor material. Further research is done on the optimizednanophosphor material for UC and DC luminescence tested. The up-conversion emission spectra for $CePO_4$:Ho^{3+}/Yb^{3+} (1% Ho^{3+} and 20% Yb^{3+}) at differing laser powers beyond 980 nanometresof excitation are shown in Figure-5. The electronic transitions of the Ho^{3+} ion at $^5F_4$, $^5S_2 \rightarrow ^5I_8$, $^5F_5 \rightarrow ^5I_8$, and 650 nm result in the g*r*eencolouremi*ss*ion bands by550 nm and *r*edcolor emissionbased on the relative concentrations of the host and co-dopant bands at 650 nm (R = red) in the UC spectra.With a higher absorption fraction than Ho^{3+} at 980 nm excitation[1,2], Yb^{3+} ions are acting as sensitizers. The percentage of Yb^{3+} that is absorbed in 980 nanometres of excitation is 11.6* 10-20 cm^2. Figure-5 shows how many photons make up one. Excitation spectra of $CePO_4$ reveal the P-O CTB, the peak at 460 nm,Ho^{3+}emission = 550 nm, as well as emission spectra at excitation = 300 and 460 nm that show the P-O and Ho^{3+}peaks.

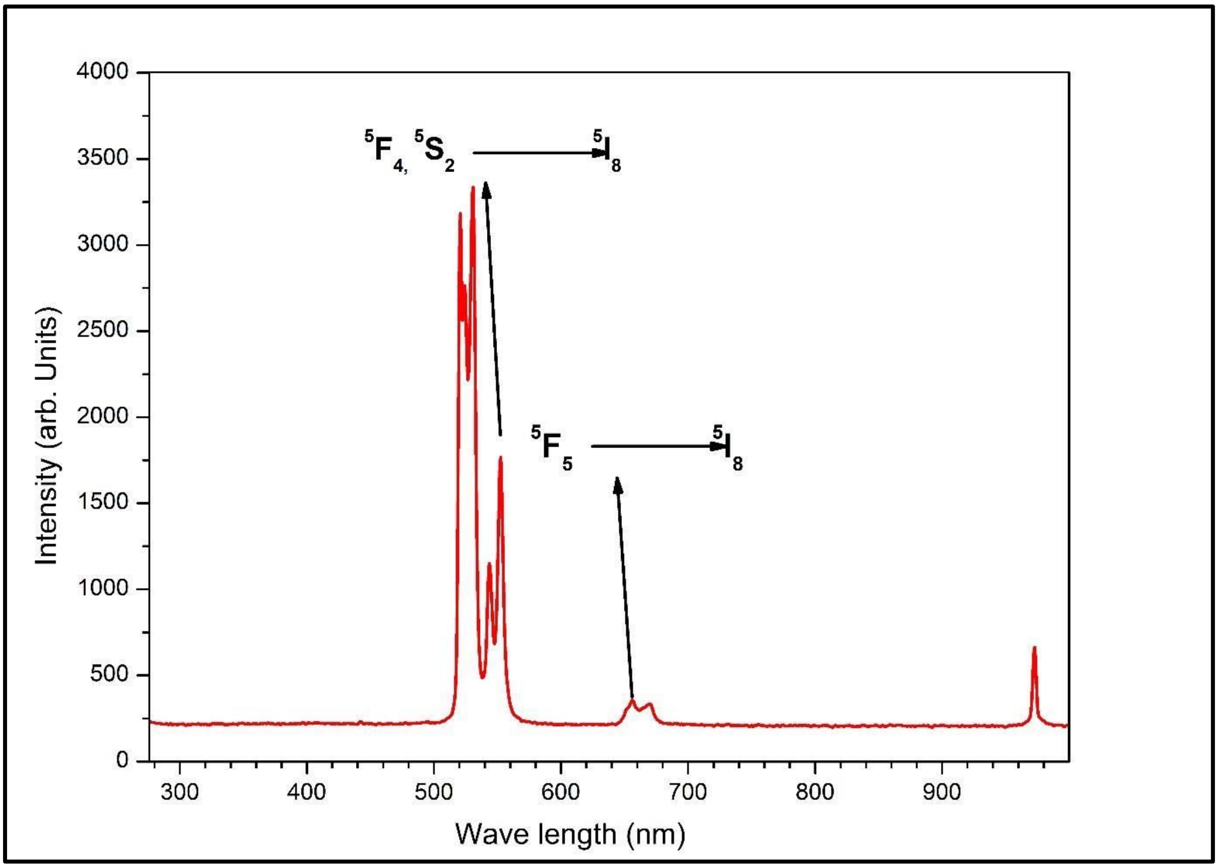

Figure-5 Emission spectra of $CePO_4$: Ho^{3+}/Yb^{3+}(1 %Ho) excited at 980 nm

Table 1. Wavelength Vs Intensity peaks for up-conversion nanophosphors

Wavelength(nm)	***Intensity(arb.Units)***
520.77	*3182.51*
524.31	*2763.19*
530.78	*3334.11*
543.72	*1150.43*
552.53	*1767.13*
655.90	*356.12*
669.25	*332.76*

DC STUDY:

DOWN-CONVERSION:

In this method which light (Exec) that has been absorbed is followed by the discharge of lower-energy radiative light (Eem). This is stated as the Stokes shift occurs. Figure 6 depicts the DC Emission Spectrum of $CePO_4$:Ho^{3+}/Yb^{3+} (1 at.% Ho) beyond UV Excitation at 300 nanometres. The Ho^{3+} ion's $^5F_4$and$^5S_2$ →$^5I_8$ and $^5F_5$→$^5I_8$ ET'S are observed, whereasthe *g*reen (550 nanometres), *r*ed (650 nanometres), and NIR (750 nanometres)emissi0n b*a*nds[3,4], respectively[1,2]. At ∼260, ∼290, ∼300, and ∼460 nm, four separate excitation wavelengths are used to monitor the emission spectra. For each excitation, the Ho^{3+} emission peaks are displayed. When Ho^{3+} is stimulated directly at ∼460 nm (^{5} I_8→$^5G_6$) as opposed to indirectly at 300 nm, its emission intensity is weaker. This arises from Ho^{3+} f-f transitions' low absorption cross-section[4]. When excitation occurs at 300 nm, the broad emission band ~460nm and PO_4^{3-}peaks as well as peaks of Ho^{3+} are observed.For each excitation, the Ho^{3+} emission peaks are displayed. When Ho^{3+} is directly excited at ~460 nm ($^5I_8 \rightarrow ^5G_6$) as opposed to indirectly excited at ~300 nm, its emission intensity is weaker. This is because the transitions involving Ho^{3+} have a small cross-section for absorption. Peaks of Ho^{3+} and the large emission band associated with PO_4^{3-} at 460 nm are observed for excitation at 300 nm.The permitted transition of the P-O CTB causes a considerable absorption cross-section at 300 nm. As a significant proportion of exciting photons from P-O are de-excited and the exciting energy is transferred from P-O to Ho^{3+}, the radiative rate of Ho^{3+} rises.This is the so-called ET from PO_4^{3-} to Ho^{3+} resonance. Figure-6 [24] displays the monitoring of $CePO_4$:Ho^{3+}/Yb^{3+} emission at 550 nm. A broad peak, having the highest point at 300 nm, is seen from 260 to 360 nm[8]. This relates to the permitted P-O CTB transition. *S*harp peaks with fewer*i*ntensities were found at ~460nm due to Ho^{3+} (~550-580nm). To demonstrate the Concentration-Dependent Luminescence (20 at. Percent), the $CePO_4$ host is doped with [15,16] or more different concentrations of Ho^{3+} at the prescribed concentration of Yb^{3+}. $CePO_4$:Ho^{3+},Yb^{3+} (x at.% = 1, y at.% = 20) shows emission peaks of Ho^{3+} when stimulated at 300 nm and 460 nm.*Every 1% increase in Ho^{3+} ion concentration results in a 1% decrease in light intensity(Figure-6).*The key element is the concentration quenching effect.[25,36]

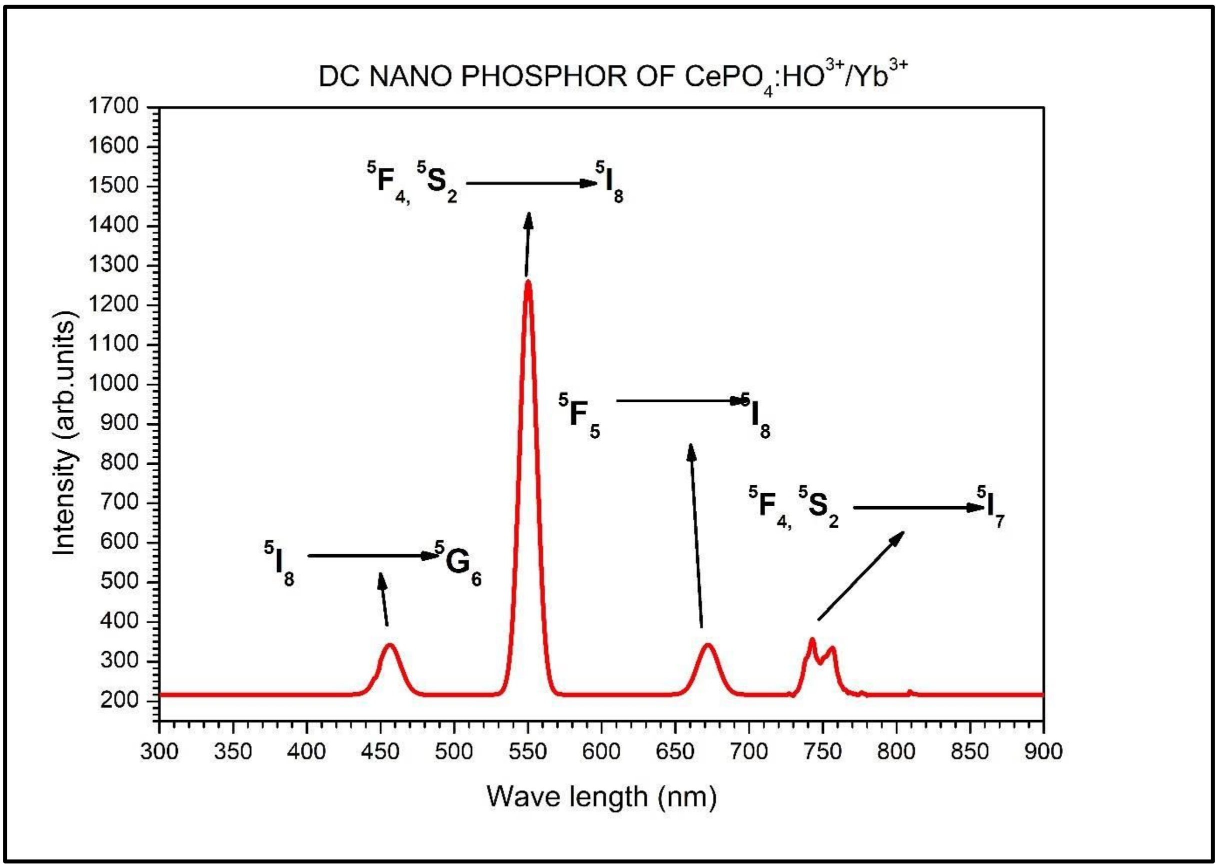

*Figure-6.E**x**citation **s**pectrum for $CePO_4$: Ho^{3+}/Yb^{3+}(1 % Ho) excitted by 300nm and ~460 nm.*

Table 2.Wavelength Vs Intensity peaks for down-conversion nanophosphors

Wavelength(nm)	***Intensity(arb.Units)***
454.60	338.68
560.77	1255.29
670.41	338.68
743.72	348.58
757.50	327.67

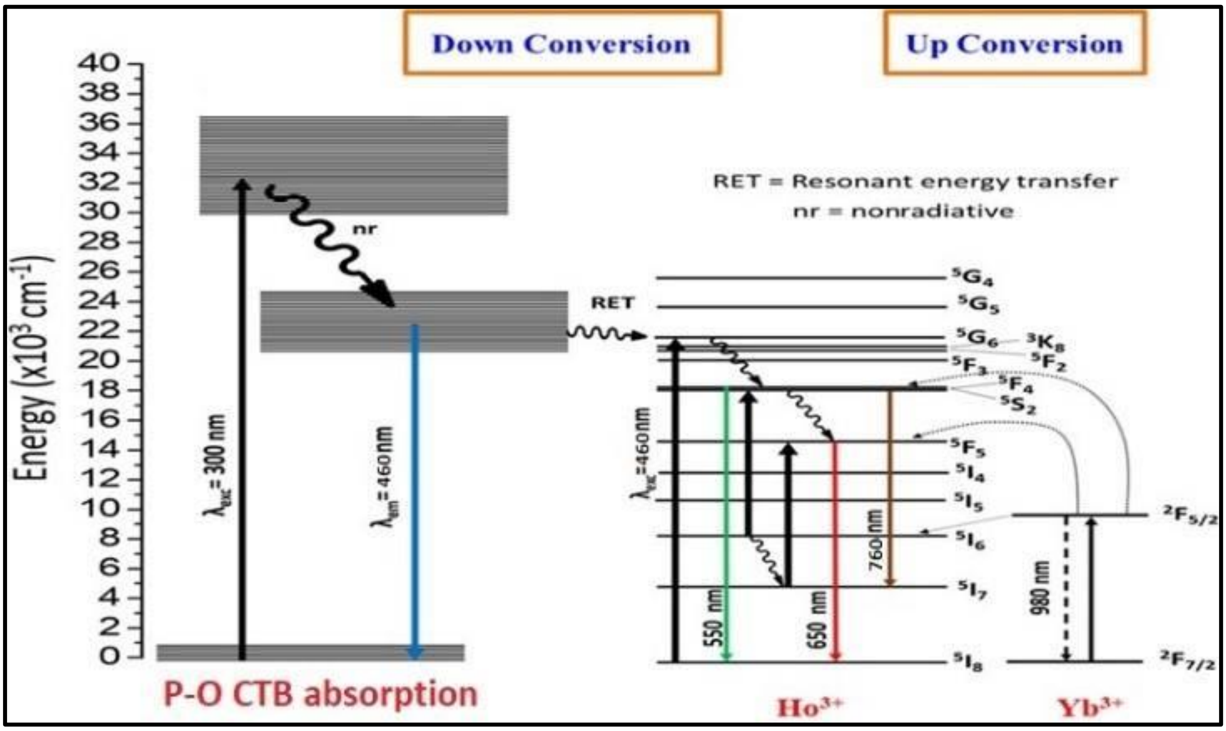

Figure-7.Energy level diagram of DC&UC of $CePO_4$:Ho^{3+}/Yb^{3+}nanophosphor[1].

4. ***CONCLUSIONS***:

Finally, $CePO_4$:0.01Ho^{3+}/0.2Yb^{3+} nanophosphor material was effectively synthesized using a polyol-mediated approach. To improve crystallinity, get rid of organic matter, and evaporate water,The sample was annealed at 900 °C for 4 hours.XRD pattern revealed the *m*0n0clinic structural phase with space group I42/amd. Strong up converting green and red color bands are produced by $CePO_4$:0.01Ho^{3+}/0.2Yb^{3+} at 550 nm ($^5F_4$, $^5S_2 \rightarrow {}^5I_8$) and 650 nm ($^5F_5 \rightarrow {}^5I_8$) of Ho^{3+} under 980 nm illumination. Excitation at 300 nm, a wide-ranging emission peak at ~460 nm, ~550 nm($^5F_4$, $^5S_2 \rightarrow {}^5I_8$), ~650 nm ($^5F_5 \rightarrow {}^5I_8$), ~750 nm ($^5F_4$, $^5S_2 \rightarrow {}^5I_7$), and Ho^{3+} characteristic peaks are found[2].Figure -7 shows that the broad emission band is mostly the result of the charge transfer band from the ligand to the metal due to lower conversion rates (P-O). The green and red bands are caused by two-photon absorption, according to the UC study.

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