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Green Synthesis and Spectroscopic Investigations of Dy³⁺Doped Iron Oxide Nanophosphors

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Abstract: In the present investigation Dy³⁺:Iron oxide nanophosphors were synthesized by green approach using the plant extract of *Capsicum frutescences* at room temperature. Iron oxide nanophosphors were generated by reaction of ferric chloride (FeCl₃) solution with plant extracts. The phytochemicals present in the plant extracts act as reducing and stabilizing agents. Synthesized nanoparticles were characterized using XRD and Photoluminescence studies. The CIE color co-ordinates of the prepared phosphor samples lie in the white and green region. Changes in correlated color temperature (CCT) were obtained for Dy³⁺:Iron oxide nanophosphor samples with different excitation wavelength. The observed luminescence spectra indicate that the Dy³⁺ doped Iron oxide nanophosphors are an ultimate candidate for white light generation. Novelty of this present study is that the plant extract is very cost effective and eco friendly and thus can be economic and valuable alternative for the large scale production of iron nanoparticles.

Keywords: Iron oxide nanoparticle; Plant extract; XRD; Photoluminescence; color co-ordinates

I. INTRODUCTION

The field of nanoscience and nanotechnology deals with development and understanding of materials with at least one of its dimensions in nanoscale in the range 1–100 nm. Properties of these nanomaterials have been found to be significantly different from that of the compositional atoms as well as corresponding bulk materials. Most importantly, properties of materials change as their size approaches the nanoscale and the percentage of atoms at the surface of a material becomes more significant. Nanostructures, whether synthetic or natural, show fascinating properties like quantum confinement in semiconductor particles, surface plasmon resonance in noble metal particles, superparamagnetism in magnetic materials, metallic or semiconducting properties of single wall carbon nanotubes depending upon their diameter, extremely high electron mobility of graphene, significant decrease in electrical resistance in presence of a magnetic field for giant magneto resistance etc [1-4]. These properties of nano particles make their synthesis equally important. In this project we are dealing with the synthesis Dy³⁺ doped Iron green nanophosphors by green reduction technique and colorimetric analysis of corresponding ionic salts.

Recently, rare earth doped metal oxide hosts find large number of applications including luminescent materials, catalysts, photonic applications, displays, optoelectronic applications, etc. Rare earth dysprosium ions attracted considerable attention because they act as a potential candidate to absorb UV light and emit light mainly in blue spectral region and yellow region which combine together to generate white light. These emissions originate due to the 5d–4f transition and the 5d state can easily be affected by the crystal field environment. Biosynthesis of metal nanoparticles from plant systems is an emerging as a new and recent development technique. The nanoparticles are of great interest due to their extremely small size and large surface to volume ratio, and they exhibited utterly novel characteristics compared to the large particles of bulk material. There is increasing in commercial demand for nanoparticles due to their wide applicability in various areas such as energy, electronics, catalysis, chemistry and medicine. Recently, an extensive research has been focussed on nano-structured magnetite because it posses unique magnetic and electric properties and its application in medical treatment. A number of approaches are available for the synthesis of iron oxide nanoparticles such as attrition, top-down method, bottom-up method, sonochemical process, hydrodynamic cavitation, microemulsion process, radiolysis, microwave, laser ablation method and recently via the biosynthesis route [7-9]. The synthesis of metal nanoparticles using inactivated plant tissue, plant extract, exudates and other parts of living plants is a modern alternative for their production. The stable iron oxide nanoparticle synthesized from plants towards green principle approach is a novel method to overcome the limitation of other conventional methods. The main advantage of this method is its ability to control the size and shape of nanoparticle and its properties. In this green synthesis route, the bio-molecules in plants can act as capping and reducing agents and thus increases the rate of reduction and stabilization of nanoparticles.

Hence in the present work, we have investigated the XRD and photoluminescence characteristics of Dy³⁺ doped Iron oxide nanophosphors synthesized by green method. To the best of our knowledge, there are no prior report exists in the literature

regarding the luminescence properties of Dy³⁺ doped Iron oxide nanophosphors. The CIE color coordinates and CCT values were determined for different excitation wavelengths. It is found that the present phosphors exhibit white luminescence.

II. EXPERIMENTAL

Ferric chloride hexahydrate (FeCl₃.6H₂O, AR) and Dysprosium nitrate hexahydrate, were purchased from Nice Chemicals, India without purification. Solutions prepared from double distilled water. About 20-25g of fresh leaves of Capsicum frutescences were thoroughly washed with distilled water and cut into small pieces then heated at 70°C in 250 ml glass beaker along with 100 ml of double distilled water for 15 minutes. After boiling, the colour of the aqueous solution changed from watery to brown colour and allowed to cool to room temperature. The aqueous extract of Capsicum frutescences was separated by filtration with Whatman No. 1 filter paper. The Fe₃O₄ nanoparticles were prepared by using a 0.5M stock solution of FeCl₃.6 H₂O mixed with 20 ml of extract was slowly added under vigorous stirring at 50-60°C for about 2 h. To prepare phosphor material, 3 wt% of Dysprosium nitrate is also added to the above solution. After few minutes depending on the concentration of metal ions and volume of the extract, the color of the solution changed from brown to black indicating the formation of iron oxides nanoparticles. The solid product was filtered and washed with distill water and then dried at room temperature. The synthesized sample was characterized using XRD and photoluminescence techniques.

III. BASICS OF COLORIMETRY

Red, green, and blue has been selected by the Commission Internationale d'Eclairage (CIE) in 1931 as primary colors. Other primaries as e.g. cyan, magenta and yellow are often used in color printers to obtain full color printing. White color can be achieved by mixing of three primaries, whereas additive mixing of two of three primaries results in non-monochromatic colors perceived by a human eye. In terms of color, we have additive processes (emittance) and subtractive processes (reflectance). For the emittance the primaries RED, GREEN and BLUE are setup for the colour matching system. This is the way by which colour is produced in the colour display. YELLOW, CYAN and MAGENTA is termed as the colour primaries for the subtractive colour mixtures, because these are the minimal number of pigments required to produce all other colours. The CIE has defined a set of three colour-matching functions, called $\bar{x}(\lambda)$, $\bar{y}(\lambda)$ and $\bar{z}(\lambda)$, which is the amount of primaries required to reproduce all of the monochromatic light. They are merely the auxiliary functions, which give how these primaries should be mixed together to generate the metamer (matching visual appearances of two colour stimuli, two light sources, made up of different mixtures of various wavelengths, may appear to be the same colour; this effect is called metamerism.) of the monochromatic colours. These are the spectral sensitivity curves of three linear light detectors that yield the CIEXYZ 'tristimulus values' X, Y, and Z. The tabulated numerical values of these functions are known collectively as the CIE standard observer. The tristimulus values of a colour are the amounts of the three primary colours in a three-component additive colour model needed to match that test colour. The tristimulus values are most often given in the CIE 1931 colour space. Two light sources have the same apparent colour to an observer when they have the same tristimulus values, no matter what spectral distributions of light were used to produce them. The CIE standard colour primaries model the response of the three photoreceptors in the human eye and are referred to as 'standard CIE observer'. The standard observer is characterized by three colour matching functions. The colour matching functions are the numerical description of the chromatic response of the observer. The finalized response curves for the standard observer are known as the Tristimulus Response Curves. These are defined in terms of the colour matching functions \bar{x} , \bar{y} and \bar{z} or the tristimulus response functions. From this figure it is clear that \bar{x} , the red tristimulus value has a certain amount of blue in it in order to duplicate the response of the red preceptor in the retina of the eye. The energy of any spectral curve is defined as a summation of intensities times wavelengths. By multiplying the spectral curve energy by the overlap of each tristimulus response curve we get the 'tristimulus values'. The tristimulus values for a colour with a spectral power distribution $I(\lambda)$ can be calculated using the colour matching function $\bar{x}(\lambda)$, $\bar{y}(\lambda)$ and $\bar{z}(\lambda)$.

Using these three color matching functions, we calculate so called tristimulus X, Y, and Z values. Tristimulus values are obtained from the following integrals:

$$X = \int_0^{\infty} I(\lambda) \bar{x}(\lambda) d\lambda$$

$$Y = \int_0^{\infty} I(\lambda) \bar{y}(\lambda) d\lambda$$

$$Z = \int_0^{\infty} I(\lambda) \bar{z}(\lambda) d\lambda$$

where integration is performed over the entire visible spectrum of the emission and $I(\lambda)$ is emission spectrum of the sample. Then the evaluation of so-called emission chromaticity is accomplished by defining three chromaticity coordinates:

$$x = \frac{X}{X+Y+Z}, y = \frac{Y}{X+Y+Z}, z = \frac{Z}{X+Y+Z}$$

$$x + y + z = 1$$

Since chromaticity parameters are defined as follows, it is sufficient to give only two of the three coordinates—commonly x and y . We can find any colour or hue, in terms of its x and y coordinates. These diagrams are based on the 1931 2-degree CIE xyz colour matching functions that remain international standards in both colourimetry and photometry. CIE defined a standard set of real primaries of wavelengths red = 700, green = 546 and blue = 435nm. They have defined the chromaticity coordinates for this in the CIE space as R (0.73467, 0.26533, 0.00), G (0.27376, 0.71741, 0.00883) and B (0.16658, 0.00886, 0.82456) respectively [10,11]. The chromaticity coordinates can be calculated from the luminescence spectrum according to the chromaticity definition and using CIE data. It is nearly impossible to use each and every wavelength present.

For these vertical lines that are spaced according to the peak height of each function is drawn. Thus we have a set of lines whose spacing varies inversely to peak height, i.e. the higher intensity, the closer the spacing, $x = 550-650$ nm, $y = 510-600$ nm and $z = 420-480$ nm. This could be achieved by using tristimulus values times the height of the experimental curve, times the energy distribution of the standard source.

By multiplying the line heights of a spectrum by these values and then summing up we obtain the values of X , Y and Z . The light colour of a luminescent lamp depends on its spectral power distribution in the visible range.

However, it is difficult to compare different lamps on the basis of their spectral distribution. It is much easier to use their correlated colour temperatures (CCTs) and colour rendering indexes. The correlated colour temperature (CCT) of a light source is defined as the light colour that corresponds to the temperature of a standard radiator (black body radiator). It is expressed in kelvin (K). The colour temperature of a lamp gives us an idea of its light colour. The light colours or colour temperatures of fluorescent lamps are determined by the composition of the phosphor coating on the inside of the tubes.

IV. RESULTS AND DISCUSSION

A. X-ray Diffraction Analysis]

XRD is an effective characterization to confirm the crystal structure of the synthesized Dy³⁺ doped iron nanophosphors. Fig. 1 shows the XRD patterns of the Dy³⁺ doped iron nanophosphors. Peaks at $2\theta = 29.73^\circ, 42.55^\circ, 51.8^\circ, 67.67^\circ$ and 74.44° are attributed to magnetite Fe₃O₄ (0 2 2), (4 0 0), (0 2 5), (2 1 0) and (2 3 0) planes, respectively. Clearly, all the peaks in the patterns are consistent with the values of the standard JCPDS values (File no. 89-6466, a=2.7992, b= 9.4097, c= 9.4832) can be indexed to pure Fe₃O₄ with Orthorhombic structure. No peaks due to impurities were detected. Crystal size of the synthesized nanoparticles was calculated from the Debye-Scherrer equation $D = K\lambda / \beta \cos\theta$. Where D is the crystallite size of iron oxide nanoparticles, λ is the wavelength of the X-ray source (0.1541 nm), β is the full width at half maximum of the diffraction peak, K is the Scherrer constant with a value of 0.9, and θ is the half diffraction angle - Bragg angle. The average crystals size of the Dy³⁺ doped iron nanoparticles was found to be 26 nm. XRD pattern reveals that the iron oxide nanoparticles prepared by bio-route method are crystalline.

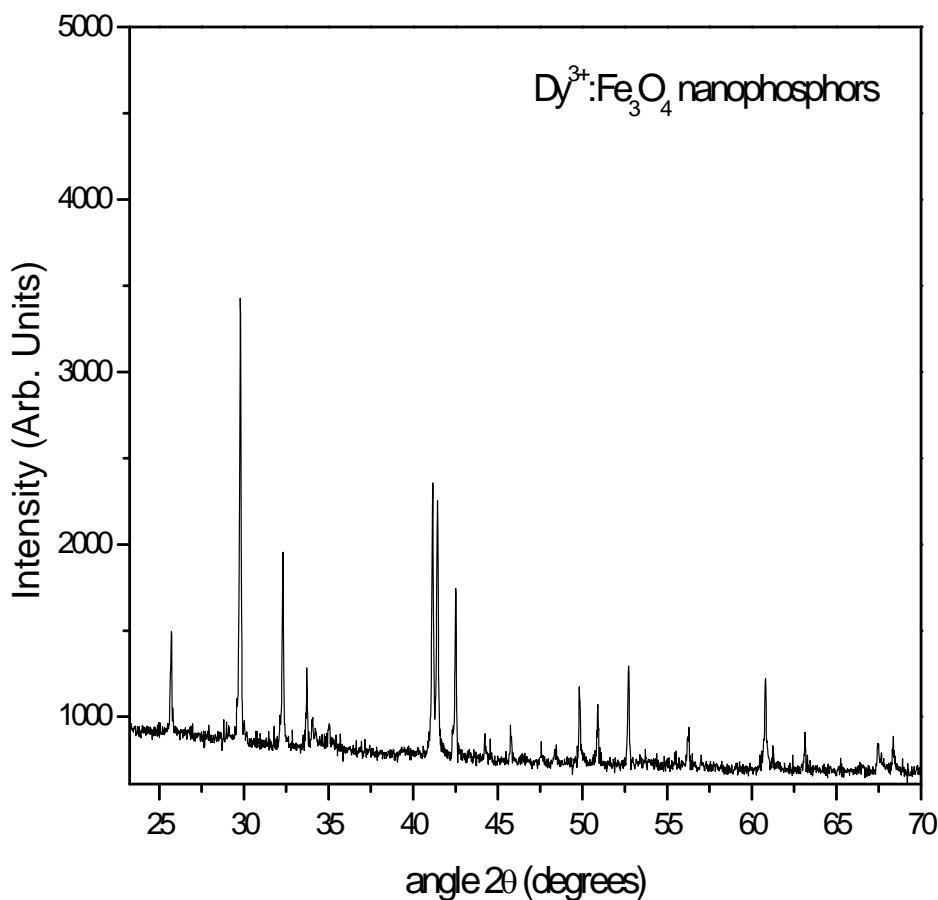


Fig. 1: XRD pattern of Dy³⁺ doped Fe₃O₄ nanophosphors

B. Excitation And Luminescence Spectra

The excitation spectra of Dy³⁺ doped iron nanophosphor under an emission wavelength of 574 nm are shown in Fig.2. The spectrum shows six excitation bands centered at 348, 394, 421, 447 and 521 nm corresponding to the transitions ⁶H_{15/2}→⁶P_{7/2}, ⁴I_{13/2}, ⁴G_{11/2}, ⁴I_{15/2} and ⁴F_{9/2} respectively. The light peaks at 348, 421, 447 and 521 nm was used as the excitation wavelengths for the efficient

emission from Dy^{3+} doped Fe_3O_4 nanophosphors. In order to study the effect of excitation wavelengths on the photoluminescence intensity of Dy^{3+} doped Fe_3O_4 nanophosphors. The PL spectra were recorded with different excitation wavelengths (at 349, 421, 466 and 523 nm) and are shown in Fig. 10(a), (b), (c) and (d) respectively. It is observed that under 349 nm excitation wavelengths we achieved maximum emission intensity. The emission spectra show two luminescence peaks at 489 and 571 nm corresponding to the transitions ${}^4F_{9/2} \rightarrow {}^6H_{15/2}$ and ${}^4F_{9/2} \rightarrow {}^6H_{13/2}$ respectively under 349 and 421nm excitation. But, in the case of the 466nm excitation, in addition to the characteristic blue and yellow emissions we observed a weak red emission peak at 634 nm corresponding to the transition ${}^4F_{9/2} \rightarrow {}^6H_{11/2}$. The blue emission at 489nm corresponding to the transition ${}^4F_{9/2} \rightarrow {}^6H_{15/2}$ and belongs to the magnetic dipole (MD) transition ($\Delta J=0, \pm 1$ but $0 \rightarrow 0$ is forbidden) and is less sensitive to the host, whereas the yellow emission corresponding to the transition, ${}^4F_{9/2} \rightarrow {}^6H_{13/2}$ and belongs to the electric dipole (ED) transition ($\Delta J = \pm 2$) and is more hypersensitive to the host matrix [12,13] . The asymmetry ratio of Dy^{3+} can be found by calculating the ratio of yellow to blue emission (ED to MD), which varies in different host lattices.

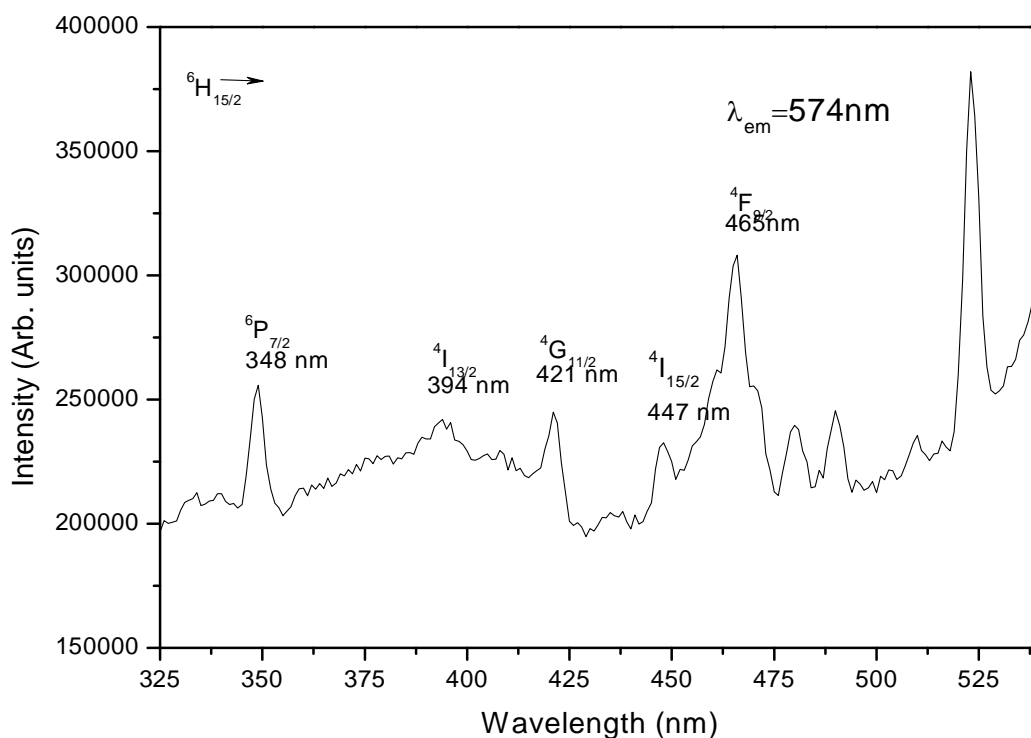


Fig.2: Excitation spectra of Dy^{3+} doped Fe_3O_4 nanophosphors with $\lambda_{em} = 574$ nm

C. Cie co-Ordinates and Correlated Color Temperature

The Commission de l'Eclairage (CIE) chromaticity co-ordinates (x, y) and correlated color temperature (CCT) of Dy^{3+} -doped Fe_3O_4 nanophosphors sample at different excitation wavelengths, namely 349, 421 and 466 nm are listed in Table 1. The chromaticity co-ordinates of 3 wt% Dy^{3+} doped Fe_3O_4 nanophosphor material at an excitation wavelengths of 349, 421, 466 nm and 523 nm were found to be (0.287,0.296); (0.281,0.306); (0.427,0.495) and (0.441,0.554) respectively. All the CIE co-ordinates lie in the blue and yellowish green light region of the chromaticity diagram (Fig.4), which can find application in the fabrication of color light-emitting diodes.

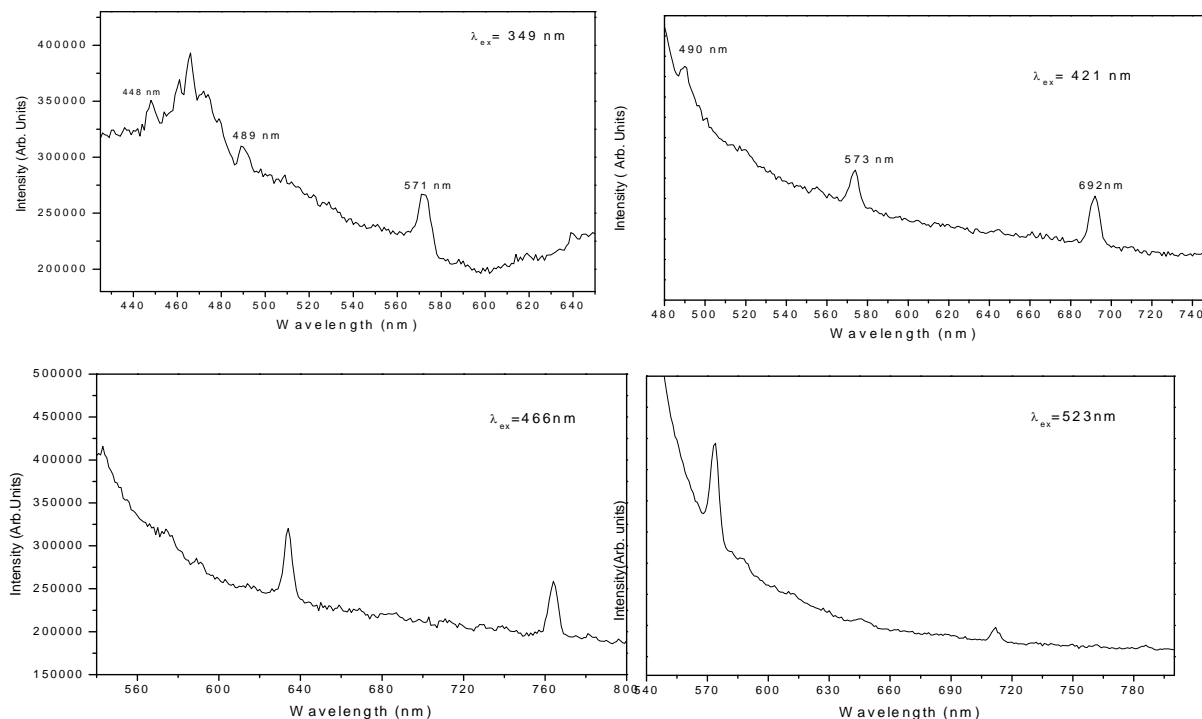


Fig.3. Emission spectra of Dy³⁺-doped Fe₃O₄ phosphors under an excitation wavelength of (a) 349 nm, (b) 421 nm. and (c) 466 nm and (d) 523nm

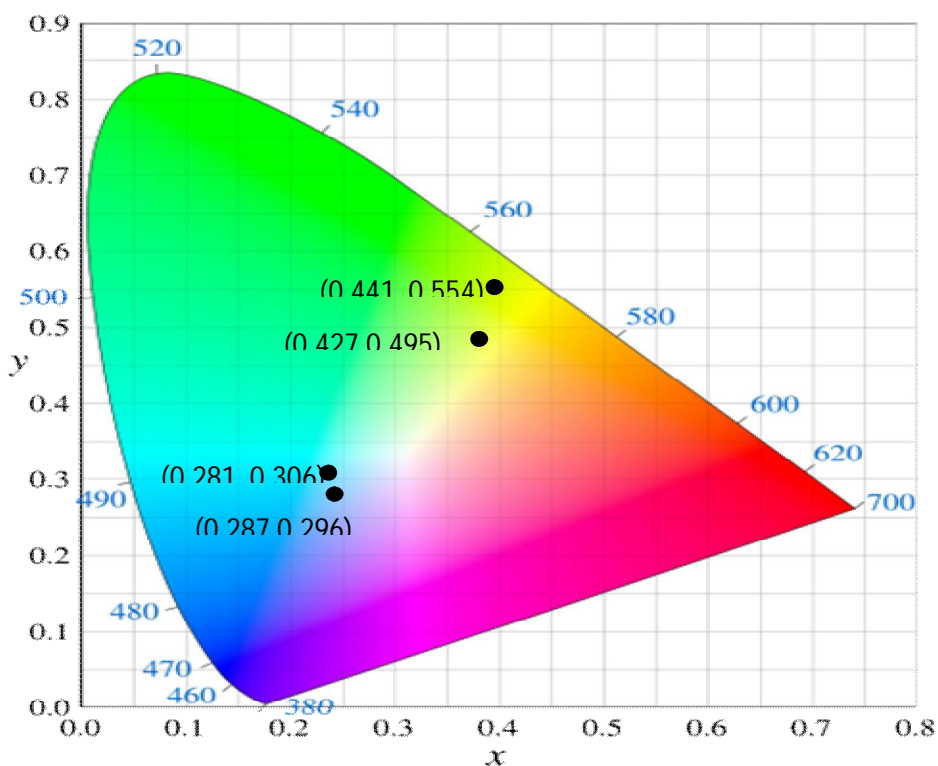


Fig.4: CIE coordinates of Dy³⁺-doped Fe₃O₄ nanophosphors

CCT values of the prepared phosphor samples were calculated using the chromaticity co-ordinates and McCamy's approximate formula, and is given by [14,15]:

$$\text{where } CCT = n = \frac{x-x_e}{y-y_e} \cdot 3525 n^2 - 6823.3 n + 5520.33$$

and ($x_e = 0.3320$, $y_e = 0.1858$) is the epicentre of convergence of reference luminescent reference material. The CCT values calculated for the prepared phosphor samples at different excitation wavelengths are presented in Table 1. These findings suggest that the CCT values of Dy^{3+} doped Fe_3O_4 phosphor material can be controlled by changing the excitation wavelength. The CCT values of Dy^{3+} doped Fe_3O_4 phosphor material were found to be higher than fluorescent tube (3935 K) and commercial white light-emitting diodes (LEDs) (6400 K).

Table 1: CIE color coordinates for different excitation wavelengths

Excitation wavelengths	CIE co-ordintaes	CCT(Kelvin)
349 nm	(0.287,0.296)	8925
421 nm	(0.281,0.306)	9084
466 nm	(0.427,0.495)	3744
523 nm	(0.441,0.554)	3798

V. CONCLUSIONS

Dy^{3+} doped Fe_3O_4 nanophosphors were synthesized via green reduction technique. The XRD profile confirmed orthorhombic structure of Fe_3O_4 of the prepared phosphor samples. The prepared phosphor samples gave strong blue and yellow emissions corresponding to ${}^4F_{9/2} \rightarrow {}^6H_{15/2}$ and ${}^4F_{9/2} \rightarrow {}^6H^{3/2}$ transitions respectively, whereas less than 366 nm excitation a weak red emission corresponding to the ${}^4F_{9/2} \rightarrow {}^6H_{11/2}$ transition was also observed. The Y/B ratio depends on the Dy^{3+} concentration as well as on the excitation wavelength. The CIE color co-ordinates of the prepared phosphor samples lie in the blue and yellowish green region. Changes in CCT were obtained for Dy^{3+} doped Fe_3O_4 nanophosphor samples with different excitation wavelengths. The observed luminescence spectra indicate that the Dy^{3+} doped Iron oxide nanophosphors are an ultimate candidate for white light generation.

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