Green Synthesis of Ce$^{3+}$ Doped ZnAl$_2$O$_4$ Phosphor Using Aloe-Vera Extract and Its Characterization

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Abstract: Cerium ion activated ZnAl$_2$O$_4$ phosphors were first time prepared by efficient and simple biogenic synthesis approach using aloe vera extract. The prepared samples were characterized by x-ray diffraction (XRD), ultraviolet visible spectroscopy (UV), and photoluminescence technique (PL). From XRD technique, the crystal structure of the prepared Ce$^{3+}$ doped ZnAl$_2$O$_4$ phosphors was calculated and it was a cubic structure. The optical band gap energies of ZnAl$_2$O$_4$ host and Ce$^{3+}$ doped ZnAl$_2$O$_4$ were calculated using the UV spectroscopy technique. The PL spectra showed the maximum intensity for Ce$^{3+}$ doped ZnAl$_2$O$_4$ at 530 nm and 598 nm under 398 nm excitation wavelength. The CIE color co-ordinates of the Ce$^{3+}$ doped ZnAl$_2$O$_4$ are calculated using radiant imaging color calculator program refer to the 1931 CIE Standard Source C (illuminant Cs (0.3101, 0.3162)).

1. Introduction:
Luminescence is new promising and emergent research field due to its different technological applications [1-6]. Specially the rare earth ions activated luminescent materials are widely studied and applied in different lighting field due to their characteristic emission in visible and near visible regions. These emissions in visible and near visible region are because of the different characteristic transitions created in rare earth ions [7-9]. The emission property of the luminescent materials depends upon the positions captured by the rare earth ion in the host, method of the preparation and nature of the surrounding present around the rare earth ion [10-13]. The cerium ion has importance due to its emission in blue and near blue region. Ce$^{3+}$ doped phosphors are synthesized by different methods including sol-gel synthesis [14], co-precipitation technique [15], hydrothermal technique [16], and combustion technique [17]. These chemical methods have many disadvantages such as energy consumption, assembly required for setup, purification and formation of hazardous chemicals during reaction. Recently researchers employed the formation of the compound by using the plant extract and bacteria like Citrus limon juice [18], Pseudomonas aeruginosa [19], Carica papaya leaves [20], Aloe barbadensis leaves [21], Calotropis giganteanleaf [22] and Punica granatum peels [23].

The spinal ZnAl$_2$O$_4$ possess the chemical formula AB$_2$O$_4$, where A is a metal (Zn) cation that occupies a tetrahedral site and B represents Al that occupies the octahedral sites in cubic crystal. This spinel crystal structure (AB$_2$O$_4$) has space group Fd$ar{3}$m and consists of a cubic unit cell. ZnAl$_2$O$_4$ spinel has unique optical as well as chemical and thermal stability. Ce$^{3+}$ doped ZnAl$_2$O$_4$ have much attracted...
interest due to its applications in luminescence, ceramics, electronic, optical, catalyst, catalyst supports, aerospace, paints, dielectrics and sensing applications [23].

Aloe vera is a permanent juicy plant belonging to the Liliaceal family and recently, its extract gelling solution has been used in the preparation different materials [24]. Aloe vera plant extracted gelling solution acts as a reducing agent during reaction and yields nano structured materials applicable in different applications.

In this paper, we are going to present the synthesis of the Ce\textsuperscript{3+} doped ZnAl\textsubscript{2}O\textsubscript{4} nano phosphor and the characterization of it using x-ray diffraction technique, UV-visible technique and spectrophotometer technique.

2. Method of Preparation:

2.1. Extract Preparation:

We have prepared the Ce\textsuperscript{3+} doped ZnAl\textsubscript{2}O\textsubscript{4} using the green synthesis method. The biological extract used is aloe vera extract. In this method fresh Aloe-vera leaves are collected, washed by distilled water and dried at room temperature. The dried leaves are cut and the gel is collected. The distilled water of an amount 15 ml is mixed with 15 ml of aloe vera gel. This solution is stirred for 30 minutes (500 rpm) at room temperature and finally homogeneous solution is obtained. The extract is obtained by filtering of the homogeneous solution and further it is used for the preparation of samples.

2.2. Phosphor Preparation:

The precursors used for the preparation are Zn(NO\textsubscript{3})\textsubscript{2} 6H\textsubscript{2}O, Al(NO\textsubscript{3})\textsubscript{3} 9H\textsubscript{2}O and Ce(NO\textsubscript{3})\textsubscript{3} 6H\textsubscript{2}O. The weight concentration of Ce(NO\textsubscript{3})\textsubscript{3} 6H\textsubscript{2}O is taken as a 0.1 m\% and 0.5 m\%. All these precursors are weighted and added in the aloe vera extract and stirred for 30 minutes. Then this homogeneous solution with alumina crucible is placed in to a clean muffle furnace at 500 °C. The solution is boiled and black material is obtained. It is grinded and again annealed at 800 °C for 3 hours, cooled to room temperature naturally. Again remaining white sample is grinded and kept in a glass bottles with proper labeling. These samples are used for further characterization part.

3. Characterization of cerium doped ZnAl\textsubscript{2}O\textsubscript{4}:

The prepared Ce\textsuperscript{3+} doped ZnAl\textsubscript{2}O\textsubscript{4} samples are characterized by the x-ray diffraction technique, UV-visible technique and spectrophotometer technique.

3.1. Powder X –Ray Diffraction Analysis:

Figure 1 represents the powder diffraction pattern of the 5 m\% Ce3+ doped ZnAl2O4. The XRD pattern of the prepared sample of Ce3+ doped ZnAl2O4 is well match with standard JCPDS file no. 082 -1538 which having cubic crystal structure. The lattice parameters are a = b = c = 8.084 Å, α = β = γ = 90° and space group is Fd3m (227).

The particle size from the XRD data is calculated by Debye- Scherrer’s formula as given below and it is observed to be in nanometer range.

\[
d = \frac{0.9 \lambda}{\beta \cos \theta}
\]

Where, \(\lambda\) is the wavelength of x-rays, \(\beta\) is the FWHM of the highest intensity peak and \(d\) is the particle size.

The calculated particle size for 0.5 m\% Ce3+ doped ZnAl\textsubscript{12}O\textsubscript{19} is 23.83 nm.
3.2. UV Visible Spectroscopic Measurements:

Figure 2. UV absorbance spectra of pure ZnAl₂O₄ and Ce³⁺ doped ZnAl₂O₄

Figure 2 shows the UV absorbance spectra of ZnAl₂O₄ and Ce³⁺ doped ZnAl₂O₄ samples. Due to doping of cerium in the ZnAl₂O₄, the change in the absorption edge is observed. The change in the concentration Ce³⁺ doping results into red shift of the absorption edge. The absorption edges as well as band gap energies of the pure ZnAl₂O₄ and Ce³⁺ and activated ZnAl₂O₄ are calculated by using the
Tauc plot as shown in the figure 3. The Tauc plot is plotted as \((ahv)^2\) vs. \(hv\) (energy) and the tangents are drawn to the curves to calculate optical band gap energies. The calculated optical band gap energies are 3.77 eV, 3.30 eV and 3.14 eV for pure ZnAl2O4, 0.1 m% Ce3+ doped ZnAl2O4 and 0.5 m% Ce doped ZnAl2O4 respectively. The calculated band gaps are consistent with the theoretical predictions [25].

![Figure 3. Optical energy band gap using Tauc plot of pure ZnAl₂O₄ and Ce³⁺ doped ZnAl₂O₄](image)

3.3. Photoluminescence measurements:

![Figure 4. PL excitation spectrum of Ce³⁺ doped ZnAl₂O₄ monitored at 598 nm emission.](image)
Figure 4 denotes the excitation spectrum of the 0.5 m% Ce\textsuperscript{3+} doped ZnAl\textsubscript{2}O\textsubscript{4} under the 598 nm emission wavelength. The maximum excitation is occurred at 398 nm wavelength. Figure 5 shows the emission spectra of the Ce\textsuperscript{3+} doped ZnAl\textsubscript{2}O\textsubscript{4} under the excitation of 398 nm wavelength. The emission spectrum of Ce\textsuperscript{3+} doped ZnAl\textsubscript{2}O\textsubscript{4} phosphor excited at 398 nm consist two maxima at 530 nm and 598 nm as shown in figure 5. These emissions corresponds to the allowed transitions from the lowest excited sublevel of the 5d state to the 2F\textsubscript{7/2} and 2F\textsubscript{5/2} multiplets of ground state of the 4f configuration of Ce\textsuperscript{3+}. The slight emission is occurred at 480 nm due to the charge transfer from metal ion Zn\textsuperscript{2+} to Ce\textsuperscript{3+}. Normally Ce\textsuperscript{3+} shows the broad emission in blue or near blue region. But here, it shows the two emission pecks due the defects produced in the crystal structure of the host sample by the addition of Ce\textsuperscript{3+} ion in the host ZnAl\textsubscript{2}O\textsubscript{4}. Stokes shift 1580 cm\textsuperscript{-1} between two levels is observed consistent with reported by the scientists [26, 27]. The emission of Ce\textsuperscript{3+} doped ZnAl\textsubscript{2}O\textsubscript{4} is observed in visible region therefore it is applicable in display devices.

3.4. **Color Co-ordinates:**

![Color Co-ordinates CIE diagram](image)

Figure 6. Color co-ordinates CIE diagram
The color calculator program radiant imaging refers to the 1931 CIE Standard Source C (illuminant Cs (0.3101, 0.3162)) is used for the calculation of the color co-ordinates [28]. The color co-ordinates of the Ce$^{3+}$ doped ZnAl$_2$O$_4$ for 5 m% concentration are X= 0.2432, Y=0.7620 for 530 nm and X= 0.5940, Y=0.4200 for 598 nm emissions as shown in figure 6. It is seen that color properties of the phosphor powder prepared by green synthesis are approaching the requirements of lighting field.

4. Conclusions:
The cerium ion doped ZnAl$_2$O$_4$ phosphor prepared by the green synthesis. The XRD measurement shows that the prepared phosphor has cubic structure. The band gap energies are calculated using the UV spectroscopy and these values are 3.77 eV, 3.30 eV and 3.14 eV for pure ZnAl$_2$O$_4$, 0.1 m% Ce$^{3+}$ doped ZnAl$_2$O$_4$ and 0.5 m% Ce doped ZnAl2O4 respectively. PL measurement shows the maximum intensity at 530 nm and 598 nm and therefore these phosphors are applicable for lighting purpose.

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