Publications
Synthesis and Spectral Investigations of Co(II) Ions Doped NaCaAlPO₄F₃ Phosphor

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ABSTRACT

Co(II) ions doped NaCaAlPO₄F₃ phosphor have been synthesized using solid state reaction. The prepared sample was characterized by powder XRD, Optical absorption, Photoluminescence, Electron Paramagnetic Resonance and Fourier Transform Infrared Spectroscopy techniques. From powder XRD data the average crystallite size was calculated as 55nm. Optical absorption spectrum showed characteristic bands in visible and IR regions related to d-d electronic transitions of Co(II) ions. The room temperature EPR spectrum exhibited broad resonance signal at g value ≈ 2.00 which is characteristic of Co(II) ions in octahedral site symmetry. PL spectrum exhibited UV and blue-green emission under 285 nm excitation. FT-IR spectrum marked the characteristic vibration bands of the prepared phosphor material.

Keywords: phosphor, cell parameters, optical absorption, CIE coordinates, photoluminescence, site symmetry.

1.0 INTRODUCTION

Recently the ever increasing energy saving demands drive the lighting technology to develop advanced optoelectronic devices, white emission sources and light emitting diodes [1]. Phosphate compounds have been employed as host materials of lamp phosphors for many years due to their relatively low material cost, easy synthesis and reasonable stability in lamp applications [2]. In inorganic phosphor materials, NaCaAlPO₄F₃ is a halophosphate based phosphor and its crystal structure resemble with alumina fluorophosphate of sodium and calcium reported as a new mineral in 1983 and named as Viitaniemiiite, NaCaAlPO₄(F,OH)₃. This mineral belongs to monoclinic structure with the space group P2₁/m. Typically, phosphors are synthesized at high temperatures by doping transition or rare earth elements, called activators into various inorganic hosts. The doped activators provide the desired colors from d-d, d-f or f-f transitions. The presence of Co(II) ions in various hosts activates luminescence emission in the UV and visible regions [3]. The present study aim to investigate Co(II) ions doped NaCaAlPO₄F₃ phosphor by solid state reaction method.

2.0 SYNTHESIS AND CHARACTERIZATION

Sodium carbonate (Na₂CO₃) Calcium carbonate (CaCO₃), Diammonium hydrogen orthophosphate ((NH₄)₂HPO₄) were purchased from Sigma-Aldrich Corp., Aluminum tri fluoride (AlF₃.3H₂O) and cobalt chloride (CoCl₂) were purchased from Merck Chemicals, India. Co(II) ions doped NaCaAlPO₄F₃ phosphors prepared by solid state reaction method using flux. The starting chemicals Na₂CO₃, AlF₃.3H₂O, CaCO₃ (NH₄)₂HPO₄ were weighed in a requisite stoichiometric proportion and ground into fine powder for 30 min. using an agate mortar and pestle. After that CoCl₂ was added to the above mixture and ground in an agate mortar for another one hour. The obtained chemical mixture was taken in a crucible for sintering at 650 °C for 8 h, 700 °C for 4 h, 750 °C for 2 h in a high temperature furnace with several intermediate grindings for 30 min. and with excess of 20 mol% AlF₃.3H₂O was also used as a flux finally to obtain Co(II) ions doped NaCaAlPO₄F₃ phosphor.

X-ray diffraction (XRD) pattern of the prepared sample is recorded on PANalytical Xpert Pro diffractometer with Cu Kα radiation. SEM and EDS images are taken on JEOL JSN 6610 LV. Optical absorption spectrum is recorded at room temperature on JASCO V670 spectrophotometer in the wavelength region of (200-1300 nm). PL spectrum is recorded at room temperature on Horiba Jobin-Yvon Fluorolog-3 Spectrofluorometer with Xe continuous (450W) and pulsed (35W) lamps as excitation sources. EPR spectrum is recorded at room temperature on JES-FA series X-band EPR Spectrometer having 100 KHZ field modulations. Bruker FT-IR Spectrophotometer is used for recording the FT-IR spectrum of the prepared sample in the region 4000 - 500 cm⁻¹.
3.0 RESULTS AND DISCUSSION

3.1 Powder XRD Study

The Powder XRD pattern of Co(II) ions doped NaCaAlPO₄F₃ phosphor is shown in Fig. 1. The powder XRD data is indexed to monoclinic crystal system and the corresponding lattice cell parameters are evaluated: a = 0.689 nm, b = 0.718 nm, c = 0.552 nm and β = 109.5°. The peak positions observed in Fig. 1 are well matched with those of the standard pattern of Viittaniitie with a monoclinic crystal structure (JCPDS file no 35-0598). The average crystallite size of the sample is calculated using Scherrer’s formula, \( d = (K \lambda / \beta \cos \theta) \), where K is a constant, \( \lambda \) is the wavelength of X-ray radiation (1.5405 Å) used, \( \beta \) is the full width at half maximum (FWHM) intensity of the diffraction line and \( \theta \) is the diffraction angle. Based on the value of FWHM, the average crystallite size was evaluated as 55 nm which indicated that the prepared Co(II) ions doped NaCaAlPO₄F₃ phosphor material contains nano crystallites. The evaluated value is close to the undoped phosphor [4].

![Fig. 1. Powder X-ray diffraction pattern of Co(II) ions doped NaCaAlPO₄F₃ phosphor](image)

3.2 SEM with EDS Analysis

Fig. 2 shows the representative SEM image of the Co(II) ions doped NaCaAlPO₄F₃ phosphor. The images taken at different magnifications shows the particles are in the range of sub-micrometer to a few micrometers. The final product mainly consisted of solid microcrystalline structures which are well dispersed and having irregular shaped agglomerated particles among the crystalline grains. In addition, the samples showed some aggregations with non-uniform in size which is due to high temperature involved in the synthesis of phosphor materials.

![Fig. 2. SEM images of Co(II) ions doped NaCaAlPO₄F₃ phosphor](image)

The selected area of the prepared sample was also performed by EDS measurement for characterizing the compositions of the phosphor and the corresponding spectrum was given Fig. 3. EDS data also showed the presence of doped cobalt species in the prepared sample.

![Fig. 3. EDS spectrum of Co(II) ions doped NaCaAlPO₄F₃ phosphor](image)

The bands in visible part of the absorption spectrum 424, 447, 545, 605 nm are attributed to electronic transitions \( ^4T_{2g}(F) \) to \( ^2A_{2g}(G), \quad ^2T_{1g}(P), \quad ^4A_{2g}(F), \quad ^2T_{2g}(G) \) respectively. The band in IR region 1190 nm is assigned to the spin allowed transition \( ^4T_{2g}(F) \) to \( ^4T_{2g}(F) \). These are the characteristic bands of d-d transitions of Co(II) ions in octahedral site symmetry. In the present study, from the band positions the ratio of \( v_2 \) to \( v_1 \) is found to be nearly 2.14 [5] and this value indicates the characteristic nature of Co(II) ions in octahedral symmetry.

![Fig. 4. Optical absorption spectrum of Co(II) ions doped NaCaAlPO₄F₃ phosphor](image)

The energy matrix for (d⁵) configuration was solved for different sets of crystal field (Dq) and inter-electronic repulsion (B and C) parameters as \( Dq = 980, \quad B = 980 \) and \( C = 3695 \) cm⁻¹, these parameters gave a good fit with the observed band positions. The observed and calculated band head data of Co(II) ions doped NaCaAlPO₄F₃ phosphor is given in Table 1.

<table>
<thead>
<tr>
<th>Transition from (^4T_{2g}(F))</th>
<th>Band position</th>
<th>Wavenumber (cm⁻¹)</th>
<th>Calculated Wave number (cm⁻¹)</th>
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<tbody>
<tr>
<td>(^2A_{2g}(G))</td>
<td>424</td>
<td>23578</td>
<td>23566</td>
</tr>
<tr>
<td>(^4T_{1g}(P))</td>
<td>447</td>
<td>22265</td>
<td>22022</td>
</tr>
<tr>
<td>(^4A_{2g}(F))</td>
<td>545</td>
<td>18343</td>
<td>18361</td>
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<tr>
<td>(^2T_{2g}(G))</td>
<td>605</td>
<td>16524</td>
<td>16583</td>
</tr>
<tr>
<td>(^4T_{2g}(F))</td>
<td>1190</td>
<td>8401</td>
<td>8561</td>
</tr>
</tbody>
</table>
3.4 EPR Study

The EPR spectra of Co(II) ions doped NaCaAlPO₄F₃ phosphor is shown in Fig. 5. The spectrum exhibited broad resonance signal at $g \approx 2.00$ which is an indication of low spin Co(II) ions in octahedral symmetry. It is consistent with the $d^7$ configuration in the low-spin state, leading to a $S = 1/2$ system, in which the single unpaired d electron is localized on the $dz^2$ orbital [6].

3.5 Photoluminescence Study

The PL spectrum of Co(II) ions doped NaCaAlPO₄F₃ phosphor recorded at room temperature is shown in Fig. 6. PL spectrum of the sample consists of three luminescent peaks: a strong and dominated UV emission centered at 386 nm, weak blue emission centered at 467 nm and broad blue-green emission peak at 498 nm with an excitation wavelength of 285 nm. Co(II) ions doped NaCaAlPO₄F₃ phosphor exhibited a strong UV and blue-green emission. The emission colour of any light source can be represented in CIE colour space by $(x, y)$ coordinates [7]. The CIE chromaticity coordinates of Co(II) ions doped NaCaAlPO₄F₃ phosphor is shown in Fig. 7 and the CIE coordinates are located in the blue region at $(x = 0.125, y = 0.129)$.

![Photoluminescence spectrum of Co(II) ions doped NaCaAlPO₄F₃ phosphor](image6.png)

Fig. 6. Photoluminescence spectrum of Co(II) ions doped NaCaAlPO₄F₃ phosphor

![CIE chromaticity diagram of Co(II) ions doped NaCaAlPO₄F₃ phosphor](image7.png)

Fig. 7. CIE chromaticity diagram of Co(II) ions doped NaCaAlPO₄F₃ phosphor

3.6 FT-IR Study

FT-IR spectrum of Co(II) ions doped NaCaAlPO₄F₃ phosphor is shown in the Fig. 8. The band observed at 1651 cm$^{-1}$ is attributed to H-O-H bending mode [8]. The bands observed at 564 cm$^{-1}$ are attributed to triply degenerate ($v_1$) modes and the band observed at 1054 cm$^{-1}$ is attributed to triply degenerate ($v_3$) mode. The vibrational band observed at 846 cm$^{-1}$ is assigned to non-degenerate ($v_i$) mode. The stretching vibrations of Co-O are observed around 646 cm$^{-1}$ [9]. The stretching vibrations of F-P-F are observed at 720 cm$^{-1}$ which indicates the formation of F-P-F bonds and their existence as fluorophosphates units [10]. The detailed assignments of various vibrational bands were given in Table 2.

![FT-IR spectrum of Co(II) ions doped NaCaAlPO₄F₃ phosphor](image8.png)

Fig. 8. FT-IR spectrum of Co(II) ions doped NaCaAlPO₄F₃ phosphor

<table>
<thead>
<tr>
<th>Vibrational frequency (cm$^{-1}$)</th>
<th>Band assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>3859, 3735, 3665,</td>
<td>Symmetric and Asymmetric modes</td>
</tr>
<tr>
<td>3612, 3394</td>
<td>$(v_1, v_3)$ of vibrations of hydroxyl ions</td>
</tr>
<tr>
<td>2971, 2901, 2379, 2308, 1758,</td>
<td>P-O-H modes of vibrations</td>
</tr>
<tr>
<td>1703, 1519</td>
<td></td>
</tr>
<tr>
<td>1651</td>
<td>Bending mode ($v_2$) of H-O-H</td>
</tr>
<tr>
<td>1054</td>
<td>Triply degenerate ($v_1$) PO$_4^{3-}$ ion</td>
</tr>
<tr>
<td>846</td>
<td>Non- degenerate ($v_1$) PO$_4^{3-}$ ion</td>
</tr>
<tr>
<td>720</td>
<td>Stretching vibrations of F-P-F</td>
</tr>
<tr>
<td>564</td>
<td>Triply degenerate ($v_3$) PO$_4^{3-}$ ion</td>
</tr>
</tbody>
</table>

4.0 CONCLUSION

From the powder XRD study, it was observed that the prepared phosphor belongs to monoclinic crystal system and the corresponding lattice cell parameters are evaluated. The average crystallite size is calculated from Scherrer’s formula found to be 55nm. Optical and Room temperature EPR studies confirmed the presence of Co(II) at octahedral site symmetry. PL spectrum exhibited UV and blue-green emission at excitation 285 nm and their corresponding CIE coordinates are in the blue region at $(x = 0.125, y = 0.129)$ which indicates that prepared phosphor may be suitable for UV LEDs and lamps. FT-IR spectrum exhibited various vibrational bands characteristic of Phosphate, F-P-F, P-O-P and hydroxyl groups.
ACKNOWLEDGEMENT

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References:

Structural and optical investigations of VO(II) ions doped NaCaAlPO$_4$F$_3$ phosphor

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Structural and optical investigations of VO(II) ions doped NaCaAlPO$_4$F$_3$ phosphor

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Abstract VO(II) ions doped NaCaAlPO$_4$F$_3$ phosphor have been synthesized by solid state reaction. The prepared sample was characterized by powder X-ray diffraction (P-XRD), Optical absorption, Photoluminescence (PL), Electron Paramagnetic Resonance (EPR) and Fourier Transform Infrared Spectroscopy (FT-IR) techniques. From powder XRD data the average crystallite size and structural parameters are evaluated. The morphology of prepared sample was examined by Scanning Electron Microscope (SEM) images at different magnifications. Optical absorption spectrum showed characteristic bands corresponding to d–d transitions of VO(II) ions. EPR spectrum of prepared sample exhibited resonance signal characteristic of VO(II) ions in octahedral symmetry with tetragonal compression having C$_{4v}$ symmetry. The spin-Hamiltonian parameters (g and A), dipolar hyperfine coupling parameter (P) and Fermi contact interaction parameter (j) have been evaluated. From the optical and EPR data, various molecular coefficients are evaluated, and the nature of bonding with ligands is covalent. PL spectrum exhibited visible emission at green, yellow and red regions under 420 nm photon excitation. The calculated Commission Internationale de l’Eclairage (CIE) coordinates are in yellowish green region at (0.382, 0.509). The prepared material is suitable for display devices. FT-IR spectrum marked the characteristic vibration bands of prepared phosphor material.

1 Introduction

The generalization of light emitting sources based on LED technology has considerably stimulated the research of inorganic phosphors due to their most plausible convention in next-generation displays and new solid state lighting devices [1]. High efficiency lighting devices are highly desired under the driving forces of energy saving and low power consumption [2, 3]. The pursuit for phosphors in lighting is one of the most important challenge to be met by advanced science and technology, and to introduce a novel host materials able to absorb with high efficiency in the blue region and emit with high quantum yield in the high spectral range for lighting applications [4, 5]. At present, researchers have paid substantial attention to study design and synthesis of a wide family of compounds, aluminate halophosphate phosphors having structural diversity, chemical stability and high absorption yields in the blue spectral range for various practical applications [6, 7]. Recently Shinde and his co-workers reported various halophosphates for lighting applications [8–10]. As a significant host of luminescent material, NaCaAlPO$_4$F$_3$ is a haloaluminium-orthophosphate based phosphor and its crystal structure resembles with alumina fluorophosphate of sodium and calcium reported as a new mineral in 1983 and named as viitaniemiite, NaCaAlPO$_4$ (-F,OH)$_3$. This mineral belongs to monoclinic structure with the space group P2$_1$/m. The crystal structure of viitaniemiite consists of a Al, Ca, P and Na atoms accommodated in octahedral, distorted octahedral, tetrahedral and dodecahedral sites surrounded by oxygen and fluorine atoms, respectively [11, 12].

During the past decades great interest in complexes of transition metals has been sparked for the development of display devices. In inorganic phosphor materials transition metal impurity plays an important role in the electronic
Vanadium is an excellent transition metal ion which acts as a self-activated luminescence centre and also coloring agent exhibiting various colours from blue to pink [13]. It can exist in three possible oxidation forms, namely, trivalent, tetravalent, and pentavalent states, and their spin–orbit coupling could be changed sensitively in different coordinations. Vanadyl ions have significant utility in basic and applied research due to their diversified applications in the field of luminescence, sensors and as laser material [14]. The study of vanadyl ions embedded in various host matrices have been carried out recently and it exhibits luminescence emission in visible region [15, 16]. The prospective use of vanadyl as a dopant in phosphor application is vital due to their long-wavelength excitation and emission properties.

Recently authors reported the synthesis and characterization of undoped, Fe(III), Mn(II), Cu(II) and Cr(III) ions doped NaCaAlPO4F3 phosphor and the ions are ascertained to be in octahedral sites by demonstrating better luminescent properties [17–20]. In the case of trivalent ions doped phosphors the crystallite size is above 50 nm where as undoped and divalent ions doped size is below 50 nm. As a part of our ongoing studies in transition metal ions doped phosphor, here we investigate on the structural and optical properties of VO(II) ions doped NaCaAlPO4F3 phosphor by solid state reaction method. In order to obtain structural properties like the crystal structure and morphology, the prepared phosphor material was characterized by powder X-ray diffraction, SEM with EDS and spectroscopic techniques. EPR and optical absorption studies were carried out to collect the information about the coordination/local site symmetry and bonding nature of doped VO(II) ions respectively in the host lattice. Photoluminescence properties and the colour perception with respect to VO(II) ions were also discussed.

2 Experimental section

2.1 Chemicals and synthesis procedure

Sodium carbonate (Na2CO3), Calcium carbonate (CaCO3), Diammonium hydrogen orthophosphate ((NH4)2HPO4) were purchased from Sigma-Aldrich Corp., Aluminum tri fluoride (AlF3·3H2O) and Vanadium Pentoxide (V2O5) were purchased from Merck Chemicals. All of the chemical reagents used in this experiment were analytical grade and used without further purification.

VO(II) ions doped NaCaAlPO4F3 phosphor is prepared by solid state reaction method. The starting chemicals Na2CO3, AlF3·3H2O, CaCO3, (NH4)2HPO4 were weighed in a requisite stoichiometric proportion and ground into fine powder for 30 min using an agate mortar and pestle. After that V2O5 was added to the above mixture and grounded in an agate mortar for another 1 h. The obtained chemical mixture was taken in a crucible for sintering at 650 °C for 8 h, 700 °C for 4 h, 750 °C for 2 h in a high temperature furnace with several intermediate grindings for 30 min and with excess of 20 mol% AlF3·3H2O was also used as a flux finally to obtain VO(II) ions doped NaCaAlPO4F3 phosphor.

3 Characterizations

X-ray diffraction (XRD) pattern of the prepared sample is recorded on PANalytical Xpert Pro diffractometer with Cu Kα radiation. Scanning Electron Microscope (SEM) and Energy Dispersive Spectrum (EDS) images are taken on JEOL JSM 6610 LV. Optical absorption spectrum is recorded at room temperature on JASCO V670 spectrophotometer in the wavelength region of (200–1,300) nm. Photoluminescence spectrum is recorded at room temperature on Horiba Jobin–Yvon Fluorolog-3 Spectrofluorimeter with Xe continuous (450 W) and pulsed (35 W) lamps as excitation sources. EPR spectrum is recorded at room temperature on JES-FA series X-band EPR Spectrometer having 100 KHZ field modulations. Bruker FT-IR Spectrophotometer is used for recording the FT-IR spectrum of the prepared sample in the region 500–4,000 cm⁻¹.

4 Results and discussion

4.1 Powder X-ray diffraction study

The Powder XRD profile of VO(II) ions doped NaCaAlPO4F3 phosphor is shown in Fig. 1. The pattern exhibits well sharp and intense peaks which is a signature of crystalline phase of prepared phosphor. The powder X-ray diffraction data is
indexed to monoclinic crystal system and the corresponding lattice cell parameters are evaluated: \( a = 0.6858 \text{ nm}, b = 0.7218 \text{ nm}, c = 0.5554 \text{ nm}, \beta = 108.98^\circ \). These values are inconsistent with previously reported unit-cell parameters [17]. The peak positions observed in Fig. 1 are well matched with those of the standard pattern of Viitaniemiite with a monoclinic crystal structure (JCPDS file no 35-0598).

Applying the well-known, Scherrer’s formula, average crystallite size of the sample is calculated

\[
d = \left( \frac{K \lambda}{\beta \cos \theta} \right)
\]

where \( K \) is a constant (shape factor and its value is about 0.9), \( \lambda \) is the wavelength of X-ray radiation (1.5405 Å) used, \( \beta \) is full width at half maximum (FWHM) intensity of the diffraction line and \( \theta \) is the diffraction angle. Based on the value of FWHM, the average crystallite size was evaluated as 46 nm which indicated that the prepared VO(II) ions doped NaCaAlPO₄F₃ phosphor material contains nano crystallites. The micro-strain (\( \epsilon \)) and dislocation density (\( \delta \)) values are also calculated from

\[
\epsilon = \frac{\beta}{4 \tan \theta}
\]

and

\[
\delta = 15 \epsilon \text{ad} \]

The values of micro-strain and dislocation density are \( 0.198 \times 10^{-3} \) and \( 0.094 \times 10^{15} \) lines m⁻¹ respectively.

4.2 SEM and EDS analysis

The particle sizes and morphology of phosphor powders were investigated by photomicrographs that measured via SEM and are depicted in Fig. 2. The images of particles were shown at about 2 and 1 µm magnification. The size distribution is fairly narrow and well dispersed with non-uniform allocation, as illustrated by micrographs. Slightly agglomeration phenomena were also observed, which were due to calcination at high temperatures for the samples. Correspondingly, image at 1 µm magnification showed the product was dense without cracking which indicates the better crystallization effect. The characteristics of sample were suitable for coating requirements of luminescence powder materials.

Figure 3 shows the representative EDS spectrum of VO(II) ions doped phosphor. The peaks at 1.04, 0.34, 3.36, 1.5, 0.7, 0.52 and 2.01 keV indicate the K series X-ray emissions of Na, Ca, Al, F, O and P species respectively present in the prepared sample. The peak at 4.94 keV contributes the Kα X-ray emissions from vanadyl atoms, which gives evidence of the incorporation of VO(II) ions in the prepared phosphor material. Wt% and at.% of constituent atoms are also given in inset.

4.3 Optical absorption study

The single d-electron of the VO(II) ions occupies the \( t_{2g} \) orbital in octahedral crystal field and gives rise to \( ^2T_{2g} \) ground state. When excited, the electron occupies upper \( e_g \) orbital and gives rise to \( ^2E_g \) term. In an ideal octahedral symmetry, only one band arising from the transition \( ^2T_{2g} \rightarrow ^2E_g \) is expected. However, VO(II) ions never exhibits an ideal octahedral symmetry but lowers to the tetragonal one (\( C_{4v} \)). In a \( C_{4v} \) symmetry environment, the ground state is an orbital singlet and the d electron is in the non-bonding \( (2B_{2g}) \) type dx²y orbital. \( ^2T_{2g} \) splits into \( ^2B_2 \) and \( ^2E \), whereas \( ^2E_g \) splits into \( ^2B_1 \) and \( ^2A_1 \). Accordingly three bands are expected due to the transitions from the ground state \( (^2B_2) \) to the excited states \( (^2E, ^2B_1 \text{ and } ^2A_1) \). The general ordering of these energy levels is as follows: \( ^2B_2 < ^2E < ^2B_1 < ^2A_1 \) [22].
The optical absorption spectrum of VO(II) ions doped phosphor is depicted in Fig. 4. Three absorption bands in the UV–Vis region centered at 838 nm (11,929 cm⁻¹), 650 nm (14,405 cm⁻¹) and 430 nm (23,249 cm⁻¹) are identified for the prepared phosphor. The d-energy level ordering of vanadyl complex was given by Ballhausen and Gray [23] in terms of molecular orbitals. On the basis of molecular orbital theory, the observed bands are attributed to d–d transitions and are assigned to [24],

$$2B_{2g} \rightarrow 2E_g (d_{xy} \rightarrow d_{xz}, d_{yz})$$

$$2B_{2g} \rightarrow 2B_{1g} (d_{xy} \rightarrow d_{x^2-y^2})$$

$$2B_{2g} \rightarrow 2A_{1g} (d_{xy} \rightarrow d_{z^2})$$

The cubic field parameter Dq and tetragonal field parameters Ds and Dt are evaluated from the following expressions:

$$2B_{2g} \rightarrow 2E_g = -3D_s + 5D_t$$

$$2B_{2g} \rightarrow 2B_{1g} = 10D_q$$

$$2B_{2g} \rightarrow 2A_{1g} = 10D_q - 4D_s - 5D_t$$

These parameters are evaluated as Dq = 1440, Ds = −2993 and Dt = 598 cm⁻¹. These parameters are well comparable with the values reported for VO(II) ions [25, 26] under tetragonal distortion. These evaluated values suggest that the vanadyl ion is in octahedral site with tetragonal compression.

4.4 EPR study

EPR spectroscopy is a powerful tool that provides information about the elemental composition, nuclearity and electronic structure of a paramagnetic state. VO(II) ions are paramagnetic species of 3d¹ configuration, having electron spin (S = 1/2) with the ⁵¹V nucleus (I = 7/2). The g values for vanadium complexes are smaller than that for free electrons (gₑ = 2.0023).

An octahedral site with a tetragonal compression would give \( g_{||} < g_{⊥} < g_e \) and \( A_{||} > A_{⊥} \) [27, 28]. Here g is the g-factor (Lande g-factor) and A is hyperfine coupling constant. The present values of the spin-Hamiltonian parameters given in Table 1 are agree with the above order. From this observation, it is suggested that the paramagnetic V(IV) ion in a lattice exists as the vanadyl ion, VO(II), in an octahedral environment of oxygen with tetragonal distortion (C₄ᵥ) [29]. The powder spectrum of vanadium ions doped phosphor was recorded at room temperature and is given in Fig. 5.

The \( \Delta_{||}/\Delta_{⊥} = (g_e - g_{||})/(g_e - g_{⊥}) \) ratio measures the tetragonality of VO(II) ions site in the prepared phosphor and is given in Table 1. Referring to Table 1 it can be seen that \( \Delta_{||}/\Delta_{⊥} \) ratio is greater than unity and it confirms that the VO(II) ions are tetragonally distorted [27, 30]. From Table 1, the principal g and A values have nearly axial symmetry. In an octahedral crystal field, the d¹ electron occupies lowest lying orbital \( ^2T_{2g} \), the next excited state being \( ^2E_{2g} \). These two absorption bands 14,405, 11,925 cm⁻¹ as given in Fig. 4 are typical for VO(II) ions and can be assigned to \( \Delta_{||} = ^2B_{2g} \rightarrow ^2E_{2g} (d_{xy} \leftrightarrow d_{xz}, d_{yz}) \) and \( \Delta_{⊥} = ^2B_{2g} \rightarrow ^2B_{1g} (d_{xy} \leftrightarrow d_{x^2-y^2}) \) transitions, respectively. The molecular orbital coefficients are determined by using optical and EPR results through the following expressions [31, 32]:

Fig. 3 EDS spectrum of VO(II) ions doped NaCaAlPO₄F₃ phosphor

Fig. 4 Optical absorption spectrum of VO(II) ions doped NaCaAlPO₄F₃ phosphor
Table 1  Principal $g$, hyperfine (A) and molecular orbital coefficients for VO(II) ions doped NaCaAlPO$_4$F$_3$ phosphor

<table>
<thead>
<tr>
<th>$g_\parallel$</th>
<th>$g_\perp$</th>
<th>$A_\parallel$ ($10^{-4}$ cm$^{-1}$)</th>
<th>$A_\perp$ ($10^{-4}$ cm$^{-1}$)</th>
<th>$\beta_1$</th>
<th>$\beta_2$</th>
<th>$\gamma^2$</th>
<th>$1-\beta_1^2$</th>
<th>$1-\gamma^2$</th>
<th>$\kappa$</th>
<th>$P$</th>
<th>$\Delta_\parallel/\Delta_\perp$ ($10^{-4}$ cm$^{-1}$)</th>
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</thead>
<tbody>
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<td>1.946</td>
<td>1.988</td>
<td>177</td>
<td>57</td>
<td>0.57</td>
<td>1.03</td>
<td>0.117</td>
<td>0.43</td>
<td>0.883</td>
<td>0.722</td>
<td>139</td>
<td>3.93</td>
</tr>
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</table>

Fig. 5  EPR spectrum of VO(II) ions doped NaCaAlPO$_4$F$_3$ phosphor

$g_\parallel = g_e \left(1 - \frac{4\lambda A_\parallel^2}{\Delta_\parallel}\right)$  \hspace{1cm} (1)

$g_\perp = g_e \left(1 - \frac{4\lambda A_\perp^2}{\Delta_\perp}\right)$  \hspace{1cm} (2)

In the equations, the values of $g_\parallel$ and $g_\perp$ are related to bonding parameters and $g_e$ (2.0023) is free electron $g$ value; $(\lambda = 170$ cm$^{-1}$) is the spin–orbit coupling constant of the VO(II) ion [33];

$\beta_1$, $\beta_2$ and $\gamma^2$ are the coefficients of molecular orbital coefficients of $d^1$ electrons. $\beta_1$ and $\gamma^2$ are the measure of degree of $\sigma$ and $\pi$ bonding with the equatorial ligands, respectively. $\beta_2^2$ is the covalency ratio of V=O bonds. The bonding coefficients $\beta_1$, $\beta_2$ and $\gamma^2$ characterize in-plane $\sigma$ bonding, in-plane $\pi$ bonding and out-of plane $\pi$ bonding, respectively. The parallel and perpendicular components of hyperfine interaction $A_\parallel$ and $A_\perp$ are related to the molecular orbital coefficients by the following expressions [34, 35],

$A_\parallel = P \left[-\kappa - \frac{4}{7} \beta_2 + \frac{3(g_\parallel - g_e)}{7} \right]$  \hspace{1cm} (3)

$A_\perp = P \left[-\kappa + \frac{2}{7} \beta_2 + \frac{11(g_\perp - g_e)}{14} \right]$  \hspace{1cm} (4)

The degree of distortion can be estimated from the Fermi contact terms $\kappa$ and the $P$ parameter, which are related to radial distribution of wave function of the ions as given by the expression $P = g_e g_N \beta_0 \beta_N (r^{-3})$. Where $P$ is dipolar term and it accounts for direct dipole interaction of electron and nuclear moments, $g_n$ is the nuclear $g$ factor, $\beta_0$ and $\beta_N$ are the Bohr and nuclear magnetons and $r$ is the effective radius of 3d shell [36]. The Fermi contact term is directly related to the isotropic hyperfine coupling and represents the amount of unpaired electron density at the nucleus. Neglecting the second order effects and taking negative values for $A_\parallel$ and $A_\perp$, $P$ values were calculated from Eq. (5) and the results are given in Table 1 [37].

$P = \frac{7(A_\parallel - A_\perp)}{6 + (\frac{\lambda}{A_\perp})}$  \hspace{1cm} (5)

The isotropic and anisotropic ($g$ and $A$) parameters are calculated from Eqs. (6) and (7):

$g_{iso} = \frac{2g_\perp + g_\parallel}{3}$  \hspace{1cm} (6)

$A_{iso} = \frac{2A_\perp + A_\parallel}{3}$  \hspace{1cm} (7)

using these equations with Eqs. (5) and (6) one gets

$\kappa = \frac{-A_{iso}}{P} - (g_e - g_{iso})$  \hspace{1cm} (8)

and the Fermi contact parameter is calculated. The parameter $\kappa$ indicates extreme sensitivity to the deformations of the electron orbitals of the central vanadium ion. The value of $P$ ranges from 100 to 160 ($\times 10^{-4}$) cm$^{-1}$ [38]. The $P$ value decreases as covalency increases. The $P$ and $\kappa$ values obtained in this study are consistent with the vanadyl complexes having tetragonal symmetry [39, 40]. The standard value of $P$ for a free VO(II) ions is 160 $\times 10^{-4}$ cm$^{-1}$ [41]. The calculated value of $P$ in the system is considerably reduced from the free-ion value indicating that the complex is fairly covalent.

Using the $P$ and $\kappa$ in Eqs. (3) and (4), $\beta_2^2$ the covalency ratio of V=O bonds, is calculated, and the use of this value with Eqs. (1) and (2) gives $\beta_1$ and $\gamma^2$. All parameters obtained in this lattice are given in Table 1. The deviation of $\beta_2^2$ from unity usually represents the degree of the admixture of the ligand orbitals and increase in the degree of the covalency. $\beta_2^2$, found in this work, clearly indicates that the bonding is ionic and represents poor $\pi$ bonding of the ligands. It is seen from Table 1 that $\kappa$ is lower than in most of the other cases, which indicates mixing of the 4 s orbital into the $d_{xy}$ orbital [42].

If $\beta_1^2 = 1$, the bond would be completely ionic. If $\beta_1^2 = 0.5$, the bond would be completely covalent. The
parameters $1 - \beta_1^2$ and $1 - \gamma^2$ are considered to be measures of covalency. The first parameter gives an indication of the influence of $\sigma$ bonding between vanadium atom and equatorial ligands, while the second parameter indicates the influence of $\pi$ bonding between the vanadium ion and the vanadyl oxygen, the results are given in Table 1. In the present case, the high value of $1 - \beta_1^2$ indicates the strong covalent inplane $\sigma$ bonding whereas $1 - \gamma^2$ corresponds to moderately covalent out-of-plane $\pi$ bonding. So, from the optical and EPR studies it is confirmed that the paramagnetic V(IV) ion exists as the vanadyl ion (VO(II)) in an octahedral coordination with tetragonal compression.

4.5 Photoluminescence study

The optical properties of the phosphor samples have been investigated by PL spectrum at room temperature. The PL spectrum of VO(II) ions doped NaCaAlPO$_4$F$_3$ phosphor recorded at room temperature is shown in Fig. 6. PL spectrum of VO(II) ions doped NaCaAlPO$_4$F$_3$ phosphor sample exhibits three luminescence peaks at an excitation wavelength of 420 nm. An intense peak is observed in the green region centered at 499 nm and two small peaks in yellow & red regions centered at 546 and 657 nm, respectively. The appearance of PL emission bands in visible region is characteristic of deep level emission associated with defects such as oxygen or fluorine vacancies during preparation of VO(II) ions doped phosphor [43]. Similar suitable emission was also observed in various VO(II) ions doped host materials [15, 44]. The emission bands are assigned to the allowed d–d transitions $^2E_g \rightarrow ^2B_{2g}$, $^2B_{1g} \rightarrow ^2B_{2g}$ and $^2A_{1g} \rightarrow ^2B_{2g}$.

4.6 Evaluation of colour coordinates

A better understanding of the trueness of color is important in the applications of lighting and display devices. In general, color is represented by chromaticity coordinates in CIE chromaticity diagram which illustrates the visual perception of the color for sample. CIE system offers high precision in color measurements and all existing colors can be represented in CIE chromaticity diagram [45, 46]. Thus, CIE coordinate calculation from the luminescence spectrum gives the theoretical possibility of color of light emission from the luminescent material. In our present work, the chromaticity coordinates are calculated from PL spectra. The values of $x$ and $y$ coordinates of the present phosphate system were calculated to be (0.382, 0.509) respectively.

![Fig. 6 Photoluminescence spectrum of VO(II) ions doped NaCaAlPO$_4$F$_3$ phosphor](image1)

![Fig. 7 CIE chromaticity diagram of VO(II) ions doped NaCaAlPO$_4$F$_3$ phosphor](image2)

![Fig. 8 FT-IR spectrum of VO(II) ions doped NaCaAlPO$_4$F$_3$ phosphor](image3)
Vibrational frequency (cm\(^{-1}\)) | Band assignment
---|---
3,952, 3,897, 3,830, 3,756, 3,609, 3,475 | Symmetric and asymmetric modes 
3,348, 3,120 | \(v_1 + v_3\) of vibrations of hydroxyl ions
2,308, 1,845, 1,744, 1,523, 1,630 | P–O–H modes of vibrations 
1,697 | Bending mode \((v_2)\) of H–O–H 
1,053 | Triply degenerate \((v_3)\) PO\(_4^{3-}\) ion 
859 | Stretching vibrations of V–O 
792 | Stretching vibrations of F–P–F 
631,664 | Triply degenerate \((v_4)\) PO\(_4^{3-}\) ion

This is pictorially represented in Fig. 7, where the point is denoted by ‘black dot’. As evident from Fig. 7, the CIE index for the phosphor system is visualized as ‘yellowish-green’. Thus, it can be inferred that the prepared phosphor may be a potential yellowish-green phosphor material.

4.7 FT-IR study

FT-IR spectrum of VO(II) ions doped NaCaAlPO\(_4\)F\(_3\) phosphor is shown in Fig. 8. The spectrum exhibited characteristic bands of symmetric, asymmetric stretching and bending vibrations of water, hydroxyl groups, triply degenerate modes of phosphate ion (PO\(_4^{3-}\)), P–O–H modes of vibrations. H\(_2\)O has C\(_2v\) symmetry and accordingly it has three fundamental modes of vibrations, the symmetric O–H stretch \((v_1)\), asymmetric O–H stretch \((v_3)\) and H–O–H bending mode \((v_2)\) [47]. The bands observed at 1,697 cm\(^{-1}\) is attributed to H–O–H bending mode. The vibrational modes of hydroxyl ions are observed in the region of 4,000–3,000 cm\(^{-1}\).

The bands observed in the region 1,400–500 cm\(^{-1}\) are characteristic vibrations of PO\(_4^{3-}\). The phosphate ion in free state exists in T\(_4\) symmetry and exhibits four fundamental modes of vibrations [48]. In these, \(v_1\) is non-degenerate, \(v_2\) is doubly degenerate, \(v_3\) and \(v_4\) vibrations are triply degenerate and infrared active. In present phosphor the phosphate group exhibit strong characteristic vibrational bands centered at around 1,053 and 631,664 cm\(^{-1}\) which have been assigned to triply degenerate \((v_3\) and \(v_4)\) modes respectively. The stretching vibrations of V–O are observed around 859 cm\(^{-1}\) [49]. The stretching vibrations of F–P–F are observed at 792 cm\(^{-1}\) which indicates the formation of F–P–F bonds and their existence as fluorophosphate units [50]. Vibrational modes of P–O–H occur generally in the region of 3,000–1,500 cm\(^{-1}\) [51]. The detailed assignments of various vibrational bands were given in Table 2.

5 Conclusion

VO(II) ions doped NaCaAlPO\(_4\)F\(_3\) phosphor was successfully synthesized by solid state reaction method using flux. From the powder X-ray diffraction studies, it was observed that the prepared phosphor belongs to monoclinic crystal system. The average crystallite size is about 46 nm and the corresponding lattice cell parameters are evaluated. The sharp and high intense X-ray diffraction peaks reveal that the prepared phosphor material is well crystalline material which can result in the high luminescence intensities. The optical absorption spectrum and calculated spin-Hamiltonian parameters indicate that the VO(II) ions are in octahedral coordination with a tetragonal compression and have a C\(_{4v}\) symmetry. The degree of covalency in in-plane \(\sigma\)-bonding and out-plane \(\pi\)-bonding suggest that the VO(II) ions establish a covalent bonding with its ligands. PL spectrum exhibited green, yellow and red emission peaks at excitation 420 nm and their corresponding CIE coordinates are in the yellowish green region at \((0.382, 0.509)\) which emphasize that prepared phosphor may be suitable for displays. FT-IR spectrum exhibited various vibrational bands characteristic of Phosphate, F–P–F, P–O–P and hydroxyl groups.

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