Chapter 7

Spectroscopic Studies of Co(II) Ions Doped Viitaniemiite Nanophosphor
7.1 Introduction

Nowadays a great attention is paid to the research and development in the field of lighting technology in relation to the global problem of saving energy [1,2]. One of the rapidly developing technologies is efficient LEDs in light sources for general lighting [3,4]. Among the several inorganic phosphors, Alkali and Alkaline-earth phosphate materials are extensively studied for lighting applications due to their structural diversity [5,6] and high luminescence efficiency [7,8]. They are suitable hosts for doping of 3d and 4f elements. The doped activators provide the desired colors from d-d, d-f or f-f transitions. The 3d electrons in transition metals have much stronger phonon-electron coupling and they have only one meta-stable excite state with a lifetime long enough to show luminescence making them suitable for LASER and lighting applications [9].

Co(II) ions (3d$^7$ electron configuration) are of special interest because of its optically active nature. It strongly influences the optical and magnetic properties due to its abundant electron states [10,11]. $^{59}$Co is the only stable cobalt isotope and the only isotope to exist naturally on Earth. Cobalt compounds have been used for centuries to impart a rich blue color to glass, glazes and ceramics. Common oxidation states of cobalt include +2 and +3, although compounds with oxidation states ranging from −3 to +4 are also known. A common oxidation state for simple compounds is +2 (Co(II)). Cobalt has a well-known catalytic activity in many chemical reactions. Therefore it is commonly used for photocatalysis and electromagnetic applications. Cobalt oxide (CoO and Co$_3$O$_4$) materials possess remarkable optical, electrical and magnetic properties. Co(II) ions doped materials exhibit various emission colors due to d-d electronic transitions and can be used as a solid state lasers and passive Q-switches. In particular, the presence of Co(II) ions in various hosts activates luminescence emission in the UV and visible region [12-15].
The present chapter discusses the effect of Co(II) ions doped on Viitaniemiite phosphor to determine the dynamic behaviour, site symmetry and the luminescence of the transition metal ion in the host lattice by means of photoluminescence studies coupled with X-ray diffraction, SEM, optical absorption, EPR and FT-IR measurements.

**Synthesis of Co(II) Ions Doped NaCaAlPO$_4$F$_3$ Phosphor**

Co(II) ions doped NaCaAlPO$_4$F$_3$ phosphor was prepared by solid state reaction method. The starting chemicals Na$_2$CO$_3$, AlF$_3$.3H$_2$O, CaCO$_3$, (NH$_4$)$_2$HPO$_4$, were weighed in a requisite stoichiometric proportion and ground into fine powder for 30 minutes using an agate mortar and pestle. After that CoO was added to the above mixture and grounded in an agate mortar for another one hour. The obtained chemical mixture was taken in a crucible for sintering at 650 °C for 8 hours, 700 °C for 4 hours, 750 °C for 2 hours in a high temperature furnace with several intermediate grindings for 30 minutes each and with excess of 20 mol% AlF$_3$.3H$_2$O was also used as a flux finally to obtain Co(II) ions doped NaCaAlPO$_4$F$_3$ phosphor.
7.2 Theory

Co(II) ions has an electronic configuration [Ar] 3d⁷, which gives rise to free ion terms ⁴F, ⁴P, ²G and several other doublet terms. In weak O₉h crystal field, ⁴F and ²G splits into ⁴T₁g(F) + ⁴T₂g(F) + ⁴A₂g(F) and ²A₁g(G) + ²T₁g(G) + ²T₂g(G) + ²E₂g(G) respectively, whereas ⁴P transforms as ⁴T₁g(P). For weak O₉h crystal field, ⁴T₁g(F) occupy the ground state. In strong crystal field (D_q > 1500 cm⁻¹) of O₉h symmetry, ²E₂g(G) occupy the ground state. In the present study, ⁴T₁g(F) occupies the ground state, however their intermediate crystal field strength D_q is around 900 cm⁻¹.

Optical absorption spectroscopy detects the d-d transitions of Co²⁺ in near infrared and visible region and the O → Co(II) charge transfer transitions in UV region. Two representative cases for Co²⁺ are observed high-spin octahedral and tetrahedral. The ligand field energy level diagram is given in Fig. 7.1. Δ₁ and Δ₀ represent the tetrahedral and octahedral ligand field splitting parameter 10D_q respectively. Octahedral complexes exhibit three transitions from their ground state ⁴T₁g(F) (t⁵₂ge₂g): ν₁ = ⁴T₁g(F) → ⁴T₂g(F); ν₂ = ⁴T₁g(F) → ⁴A₂g(F); ν₃ = ⁴T₁g(F) → ⁴E₂g(F) and ν₁ - ν₂ equals 10D_q, the ligand field splitting parameter. All d-d transitions in octahedral complexes are symmetry forbidden. Complexes with a symmetry centre can gain intensity through vibronic coupling; i.e. coupling between the electronic states and normal modes of vibration of appropriate symmetry. Similarly, spin forbidden transitions may become partially allowed by spin-orbit coupling, connecting states with ΔS = ±1. Fig. 7.2 shows the correlation between weak and strong crystal field terms.
Fig. 7.1 Energy level diagram for tetrahedral and octahedral Co$^{2+}$

Fig. 7.2 Correlation between weak and strong field terms for d$^7$ configuration
7.3 Results and Discussion

7.3.1 Powder XRD Study

The Powder XRD pattern of Co(II) ions doped NaCaAlPO₄F₃ phosphor was shown in Fig. 7.3. The powder X-ray diffraction data is indexed to monoclinic crystal system and the corresponding lattice cell parameters are evaluated: a = 0.6895, b = 0.7181, c = 0.5525 nm and β = 109.5°. The peak positions observed in Fig. 7.3 are well matched with those of the standard pattern of Viitaniemiite with a monoclinic crystal structure (JCPDS file no: 35-0598).

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

The average crystallite size of the sample is calculated using Scherrer’s formula, \( d = \frac{K\lambda}{\beta\cos\theta} \), where K is a constant (shape factor and its value is about 0.9), \( \lambda \) is the wavelength of X-ray radiation (1.5406 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 NaCaAlPO$_4$F$_3$ phosphor material contains nano crystallites. The micro-strain ($\varepsilon$) and dislocation density ($\delta$) values are also calculated from $\varepsilon = \beta/4 \tan \theta$ and $\delta = 15\varepsilon/\alpha d$ [21]. The values of micro-strain and dislocation density are $0.186 \times 10^{-3}$ and $0.089 \times 10^{15}$ lines/m respectively. The evaluated value is close to the undoped phosphor [16].

7.3.2 SEM with EDS Analysis

Fig. 7.4 shows the representative the SEM image of the Co(II) ions doped NaCaAlPO$_4$F$_3$ phosphor. The images are taken at different magnifications and 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. The grain sizes from the SEM images do not match with the crystallite size evaluated from powder XRD studies. This can be explained by the fact that the grains seen in the SEM images are the domains formed by aggregation of the nanosize crystallites.

Fig. 7.4 SEM images of Co(II) ions doped NaCaAlPO$_4$F$_3$ phosphor
The selected area of the prepared sample was also performed for EDS measurement for characterizing the compositions of the phosphor and the corresponding spectrum was given Fig. 7.5. The approximately atomic ratio consistent to the formula confirms the formation of sample by the synthesis method. EDS data also showed the presence of doped cobalt species in the prepared sample.

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight%</th>
<th>Atomic%</th>
</tr>
</thead>
<tbody>
<tr>
<td>F K</td>
<td>4.24</td>
<td>4.96</td>
</tr>
<tr>
<td>Co K</td>
<td>4.46</td>
<td>4.04</td>
</tr>
<tr>
<td>Na K</td>
<td>5.43</td>
<td>5.25</td>
</tr>
<tr>
<td>Al K</td>
<td>18.65</td>
<td>15.33</td>
</tr>
<tr>
<td>P K</td>
<td>9.04</td>
<td>6.77</td>
</tr>
<tr>
<td>Ca K</td>
<td>18.58</td>
<td>12.52</td>
</tr>
<tr>
<td>O</td>
<td>39.61</td>
<td>51.13</td>
</tr>
<tr>
<td>Totals</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>

Fig. 7.5 EDS spectrum of Co(II) ions doped NaCaAlPO$_4$F$_3$ phosphor

7.3.3 Optical Absorption Study

The electron configuration of Co(II) ions is 3d$^7$ in high spin state gives rise to the free ion terms $^4$F, $^4$P, $^2$G and several other doublet terms. In a weak octahedral (O$_h$) crystal field, the terms $^4$F and $^2$G splits into $^4$T$_{1g}$(F) + $^4$T$_{2g}$(F) + $^4$A$_{2g}$(F) and $^2$A$_{1g}$(G) + $^2$T$_{1g}$(G) + $^2$T$_{2g}$(G) + $^2$E$_g$(G) respectively while $^4$P splits into $^4$T$_{1g}$(P). In the weak and intermediate crystal fields ($D_q < 1500$) the term $^4$T$_{1g}$(F) will occupy the ground state in octahedral crystal [17]. In the present investigation of the intermediate crystal field strength $D_q = 980$ cm$^{-1}$, $^4$T$_{1g}$(F) is the ground state. Optical UV-Vis absorption spectrum of Co(II) ions doped NaCaAlPO$_4$F$_3$ phosphor was shown in Fig. 7.6.
The evidence for Co(II) ions substitution in the host lattice can be inferred from optical UV–Vis absorption spectra. In the spectrum five absorption bands are observed in the visible and IR regions. The bands in visible part of the absorption spectrum 424 (23578 cm⁻¹), 447 (22365 cm⁻¹), 545 (18343 cm⁻¹), 605 (16524 cm⁻¹) nm are attributed to electronic transitions $^4T_{1g}(F)$ to $^2A_{1g}(G)$, $^4T_{1g}(P)$, $^4A_{2g}(F)$, $^2T_{2g}(G)$ respectively. The band in IR region 1190 (8401 cm⁻¹) nm is assigned to the spin allowed transition $^4T_{1g}(F)$ to $^4T_{2g}(F)$. These are the characteristic bands of d-d transitions of Co(II) ions in octahedral site symmetry. Theoretically the ratios of the energies of the transitions $^4T_{1g}(F)$ to $^4A_{2g}(F)$: $v_2$ and $^4T_{1g}(F)$ to $^4T_{2g}(F)$: $v_1$ are almost invariable from 1.9 to 2.2 [18]. In the present study, from the band positions the ratio of $v_2$ to $v_1$ is found to be nearly 2.14 [19] and this value indicates the characteristic nature of Co(II) ions in octahedral symmetry. The energy matrix for (d⁷) configuration was solved for
different sets of crystal field (Dq) and inter-electronic repulsion (B and C) parameters as Dq = 980, 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 NaCaAlPO\(_4\)F\(_3\) phosphor is given in Table 7.1.

**Table 7.1 Optical absorption band head data of Co(II) ions doped NaCaAlPO\(_4\)F\(_3\) phosphor**

<table>
<thead>
<tr>
<th>Transition from  (^4)T(_{1g}) (F)</th>
<th>Band position</th>
<th>Calculated Wave number (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Wavelength (nm)</td>
<td>Wavenumber (cm(^{-1}))</td>
</tr>
<tr>
<td>2(^A_1g)(G)</td>
<td>424</td>
<td>23578</td>
</tr>
<tr>
<td>4(^T_1g)(P)</td>
<td>447</td>
<td>22365</td>
</tr>
<tr>
<td>4(^A_2g)(F)</td>
<td>545</td>
<td>18343</td>
</tr>
<tr>
<td>2(^T_2g)(G)</td>
<td>605</td>
<td>16524</td>
</tr>
<tr>
<td>4(^T_2g)(F)</td>
<td>1190</td>
<td>8401</td>
</tr>
</tbody>
</table>

7.3.4 EPR Study

EPR spectrum of Co(II) ions is observed only at low temperatures because the spin lattice relaxation time is extremely short for Co(II) ions. At higher temperature, the spectra become broader probably due to short relaxation time characteristic of the Co(II) ions [20-22]. The \(^4\)F state of d\(^7\) ions in octahedral field splits to \(^4\)T\(_{1g}\) triplet ground state. The splitting of spectroscopic states of Co(II) in coordination complexes is due to the combined effects of the symmetry of the crystal field and spin-orbit coupling. Spin-orbital interaction splits the triplet states so that the lowest state is Kramer’s doublet with isotropic g = 4.3 [23]. The next excited states are only a few hundred wavenumbers higher in energy. Distortions, which lower the symmetry, mix these states. Therefore, the g values become anisotropic and are sensitive to variations in the crystal field [24,25]. In the present investigations of Co(II) ions doped NaCaAlPO\(_4\)F\(_3\)
phosphor, the characteristic EPR spectrum is recorded at room temperature and is shown in the Fig. 7.7. 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 $d_{z^2}$ orbital [26, 27].

![EPR spectrum](image)

**Fig. 7.7 EPR spectrum of Co(II) ions doped NaCaAlPO$_4$F$_3$ phosphor**

### 7.3.5 Photoluminescence Study

The optical properties of the as-synthesized samples have been investigated by PL spectrum at room temperature. PL is a key optical property that offers useful information on exciton and defect states. The PL spectrum of Co(II) ions doped NaCaAlPO$_4$F$_3$ phosphor recorded at room temperature is shown in Fig. 7.8. 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. The excitation mechanism at 285 nm attributed to ligand to metal charge transfer (CT) transition between O$^{2-}$ and Co$^{2+}$ [28].
Co(II) ions doped NaCaAlPO₄F₃ phosphor exhibited a strong UV and blue-green emission. The intense UV emission is due to free exciton recombination and the visible blue-green emission is due to the defect related emission [29,30]. The visible emission comes mainly from radiative recombination of trapped ions occupying the oxygen or fluorine vacancies. By doping cobalt in the phosphor, it exhibits a blue shift in UV emission and red shift in the visible emission with respect to the host lattice related emission [16]. The shifting in emission bands may be due to mismatch among the crystal structures of host ions and activators. Similar PL emission peaks are observed in various Co doped phosphor hosts [31,32]. In this study, a sharp and dominated UV emission at 386 nm indicates that the prepared phosphor have better crystal quality with good optical properties [33].
7.3.6 Evaluation of Colour Coordinates

Most lighting specifications refer to colour in terms of the 1931 CIE chromatic colour coordinates which recognize that the human visual system uses three primary colours: red, green and blue [34, 35]. In general, the colour of any light source can be represented on the \((x, y)\) coordinate in the colour space. The chromatic coordinates \((x, y)\) was calculated using the CIE coordinate calculator. The emission colour of the prepared \(\text{NaCaAlPO}_4\text{F}_3\) phosphor was analysed and confirmed with the help of CIE chromaticity coordinates. The CIE chromaticity coordinates for prepared phosphor is calculated from emission spectrum. The CIE chromaticity coordinates of Co(II) ions doped \(\text{NaCaAlPO}_4\text{F}_3\) phosphor is shown in the Fig. 7.9 and the CIE coordinates are located in the blue region at \((x = 0.125, y = 0.129)\).

![CIE chromaticity diagram of Co(II) ions doped NaCaAlPO₄F₃ phosphor](image)

Fig. 7.9 CIE chromaticity diagram of Co(II) ions doped NaCaAlPO₄F₃ phosphor
7.3.6 FT-IR Study

FT-IR spectrum of Co(II) ions doped NaCaAlPO$_4$F$_3$ phosphor is shown in the Fig. 7.10. 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 and F-P-F modes of vibrations.

![FT-IR spectrum of Co(II) ions doped NaCaAlPO$_4$F$_3$ phosphor](image)

**Fig. 7.10 FT-IR spectrum of Co(II) ions doped NaCaAlPO$_4$F$_3$ phosphor**

The band observed at 1651 cm$^{-1}$ is attributed to H-O-H bending mode [36]. The vibrational modes of hydroxyl ions are observed in the region of 3000-4000 cm$^{-1}$. These are associated to the OH content absorbed at the powder surface when the sample was in contact with the environment during the preparation process of measurement [37, 38]. Usually the IR absorption bands of PO$_4^{3-}$ ions are observed in two regions 1120-940 cm$^{-1}$ and 600-550 cm$^{-1}$ [39].
The bands observed at 564 cm\(^{-1}\) are attributed to triply degenerate (\(\nu_4\)) modes and the band observed at 1054 cm\(^{-1}\) is attributed to triply degenerate (\(\nu_3\)) mode. The vibrational band observed at 846 cm\(^{-1}\) is assigned to non-degenerate (\(\nu_1\)) mode. The stretching vibrations of Co-O are observed around 646 cm\(^{-1}\) [40,41]. 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 [42]. Vibrational modes of P-O-H occur generally in the region of 3000-1500 cm\(^{-1}\) [43]. The detailed assignments of various vibrational bands were given in Table 7.2.

**Table 7.2 Assignments of vibrational bands in FT-IR spectrum of Co(II) ions doped NaCaAlPO\(_4\)F\(_3\) phosphor**

<table>
<thead>
<tr>
<th>Vibrational frequency (cm(^{-1}))</th>
<th>Band assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>3859, 3735, 3665, 3612, 3394</td>
<td>symmetric and asymmetric modes ((\nu_1+\nu_3)) of vibrations of hydroxyl ions</td>
</tr>
<tr>
<td>2971, 2901, 2379, 2308, 1758, 1703, 1519</td>
<td>P-O-H modes of vibrations</td>
</tr>
<tr>
<td>1651</td>
<td>bending mode ((\nu_2)) of H-O-H</td>
</tr>
<tr>
<td>1054</td>
<td>triply degenerate ((\nu_3)) PO(_4^{3-}) ion</td>
</tr>
<tr>
<td>846</td>
<td>non - degenerate ((\nu_1)) PO(_4^{3-}) ion</td>
</tr>
<tr>
<td>720</td>
<td>stretching vibrations of F-P-F</td>
</tr>
<tr>
<td>646</td>
<td>stretching vibrations of Co-O</td>
</tr>
<tr>
<td>564</td>
<td>triply degenerate ((\nu_4)) PO(_4^{3-}) ion</td>
</tr>
</tbody>
</table>
7.4 Conclusion

Inorganic Co(II) ions doped NaCaAlPO₄F₃ phosphor was synthesized successfully by solid-state reaction method. From the above results and discussions following conclusion are drawn.

- From the powder X-ray diffraction studies, it was observed that the prepared phosphor belongs to monoclinic crystal system and the corresponding lattice cell parameters \( a = 0.689 \), \( b = 0.718 \), \( c = 0.552 \) nm and \( \beta = 109.5^0 \).
- The average crystallite size is calculated from Scherrer’s formula found to be 55 nm.
- Room temperature EPR spectrum showed broad resonance signal with effective g value \( \approx 2.00 \) which confirms the low spin Co(II) ions are in octahedral site symmetry.
- Optical absorption spectrum exhibited bands in visible and IR regions which are the characteristic of Co(II) ions in octahedral 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.
- FTIR spectrum exhibited various vibrational bands characteristic of Phosphate, F-P-F, P-O-P and hydroxyl groups.
7.5 References


