

Transition Metal Ions Doped Novel Phosphor for Solid State White Lighting

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Abstract: *Transition metal ions doped NaCaAlPO₄F₃ phosphors have been synthesized using a solid state reaction method. The prepared samples are characterized by powder XRD, SEM, optical absorption, EPR, PL and FT-IR techniques. The XRD studies confirm the crystal structure of prepared phosphor samples as monoclinic system. SEM images show nanoclusters. Optical absorption and EPR spectra of TM ions doped phosphor exhibited the characteristic absorption bands and resonance signals of TM ions. The site symmetry of Cr(III), Mn(II) and Fe(III) ions in host lattice is ascribed to octahedral and distorted octahedral site symmetries respectively whereas in the case of Cu(II) ions doped phosphor, the site symmetry is tetragonally distorted octahedral. The PL spectra of all the dopants exhibit various emission bands which correspond to different regions like UV, blue, green, orange, yellow and red regions by exciting phosphors in UV or blue regions and the corresponding CIE coordinates are in blue, blue-green, red and near white regions. FT-IR spectra of all the TM ions doped phosphors exhibited the fundamental vibrations of PO₄, P-O-H, F-P-F and water molecules.*

Keywords: NaCaAlPO₄F₃ phosphor, Solid State Reaction, Monoclinic, EPR, PL.

1. Introduction

Recently nanophosphors have received considerable attention due to their unique luminescence characteristics apart from their bulk phosphor materials. Phosphors based on phosphate host matrix have good thermal and charge stability. Novel inorganic phosphor luminescent materials are widely used in various optoelectronic devices. W-LEDs offer benefits such as high luminous efficiency, low energy consumption, long lifetime and so on. Designing and investigating of new phosphors activated with rare earth or transition metal ions have boosted the development of phosphor industry [1]. Mainly orthophosphates with tetrahedral rigid three-dimensional matrix are of high interest due of the large band gap and high absorption of PO₄³⁻ in UV region. Among halo based phosphors, halophosphate phosphors have attracted tremendous attention due to their intense luminescence intensities, high emission efficiencies and wide application fields in displays and UV devices [2,3]. Inorganic phosphor NaCaAlPO₄F₃ is a halophosphate based phosphor and its crystal structure resemble with a rare mineral phosphate compound viitaniemiite, NaCaAlPO₄(F,OH)₃. This mineral belongs to monoclinic structure with the space group P21/m. The crystal structure consists of a 6-coordinated Al atom, a 6-coordinated Ca atom, a 4-coordinated P atom and 8-coordinated Na atom. Doping with specific ions is a normal way of obtaining new optical properties or improving properties of an undoped phosphor. The ions of 3d-transition metals [4] in strongly correlated compounds completely or partially determine their magnetic, optical and other spectroscopic properties. The 3d electronic states originated from transition metal ions (TM) doped in the nanophosphor particles show advanced properties which can extend nanophosphors use in optical, electrical, medical and biological technologies. The TM doped halophosphor materials find potential applications in LEDs, displays and lamps.

2. Experimental Procedure

Sodium carbonate (Na₂CO₃), Calcium carbonate (CaCO₃), Diammonium hydrogen orthophosphate ((NH₄)₂HPO₄) were purchased from Sigma-Aldrich Corp., Aluminium tri fluoride (AlF₃·3H₂O) and Transition metal oxides were purchased from Merck chemicals. All of the chemical reagents used in this experiment were of analytical grade and are used without further purification. Inorganic phosphor NaCaAlPO₄F₃ was synthesized by employing conventional solid-state reaction method. The starting chemicals Na₂CO₃ (0.5299 gm), AlF₃·3H₂O (1.6562 gm), CaCO₃ (1.00 gm), (NH₄)₂HPO₄ (1.3206 gm) were weighed in a requisite stoichiometric proportion and ground into fine powder for one hour using an agate mortar and pestle. 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% AlF₃·3H₂O was also used as a flux. Finally the NaCaAlPO₄F₃ phosphor was formed. During the preparation time 1 mol% of transition metal oxide are added with the host lattice. To facilitate the reaction and to improve the crystallinity of luminescent materials, flux agents were often added to provide a more interactive medium for solid-state reaction. To reduce the reaction temperature and control the particle growth, fluxes such as metal fluoride (AlF₃ or MgF₂) were also used. Here the flux AlF₃·3H₂O was used to improve the phase purity and control the particle size of phosphor.

Powder X-ray diffraction pattern of the prepared samples are recorded on PANalytical Xpert pro diffractometer with CuK α radiation. Scanning Electron Microscope and Energy Dispersive spectra (EDS) images were taken from ZEISS EVO18. Optical absorption spectra are recorded at room temperature on JASCO V-670 Spectrophotometer in the wavelength region of 200-1200 nm. EPR spectra are

UGC Sponsored National Conference on

Advanced Technology Oriented Materials (ATOM-2014), 8-9th Dec-2014

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recorded at room temperature on JES-FA series X-band EPR Spectrometer having 100 KHZ field modulations. Photoluminescence spectra was recorded on Horiba Jobin-Yvon Fluorolog-3 Spectrofluorimeter with Xe continuous (450W) and pulsed (35W) lamps as excitation sources. FT-IR spectra of the prepared sample was obtained from Bruker's FT-IR Spectrophotometer in the region of 4000-500 cm^{-1} .

3. Results

3.1 NaCaAlPO₄F₃ (SCAPF) Nanophosphor

From the powder X-ray diffraction data, the crystal system corresponds to monoclinic and lattice cell parameters are evaluated as $a = 0.683$, $b = 0.721$, $c = 0.549$ nm and $\beta = 109.97^\circ$. The parameters are in accordance with the lattice parameters of natural mineral Viitaniemiite $a = 0.680$, $b = 0.721$, $c = 0.552$ nm and $\beta = 109^\circ$. The average crystallite size of SCAPF phosphor is calculated using Scherrer's formula as 53 nm. The slight decrease in lattice cell parameters leads to shift of peaks towards higher side of 2θ values may be due the prepared sample is in nano size. The SEM images shows irregular shaped particles with agglomeration. EDS analysis confirms the presence of constituent elements of prepared phosphor material. PL spectrum of SCAPF phosphor exhibited emission peaks in UV and blue regions. The CIE coordinates of prepared phosphor are in blue region at ($x = 0.139$, $y = 0.125$) which suggested that the materials may be used as UV-LEDs and UV backlights. The dominated UV emission of SCAPF phosphor indicates that the prepared material has better crystal quality with good optical properties. The vibrational modes of phosphate ions in ν_3 & ν_4 , P-O-H, F-P-F and water molecules are confirmed from FT-IR studies [5].

3.2 Cr(III) ions doped SCAPF Nanophosphor

Powder XRD investigations confirmed that the prepared phosphor belongs to monoclinic crystal system. Average crystallite size is calculated using Scherrer's formula is about 86 nm. The SEM images shows irregular shaped particles with agglomeration. EDS analysis confirms presence of constituent inorganic species in the prepared phosphor material. From optical absorption spectrum characteristic absorption bands are observed. EPR spectrum exhibits resonance signal at $g = 1.972$ which is attributable to Cr(III) ions. From the optical absorption and EPR studies, Cr(III) is ascertained to octahedral site symmetry with the host lattice. The evaluated bonding parameter α indicates ionic nature of Cr(III) ions in the lattice. The PL spectrum exhibited emission bands at 470, 518 and 693 nm under photon excitation ($\lambda_{\text{exc}} = 420$ nm). The deep level red emission is characteristic of Cr(III) ions and the appropriate CIE chromaticity coordinates ($x = 0.297$, $y = 0.356$) near to white region suggests that the prepared material may be used in lamps and displays devices. The characteristic vibrational modes of phosphate ions, P-O-H and F-P-F molecules are evident from FT-IR studies [6].

3.3 Mn(II) ions doped SCAPF Nanophosphor

The observed X-ray diffraction indicates that the prepared phosphor belongs to monoclinic crystal system and the

corresponding lattice cell parameters are evaluated as $a = 0.694$, $b = 0.715$, $c = 0.511$ nm and $\beta = 109.18^\circ$. The average grain size was calculated as 46 nm and it indicates the formation Mn(II) ions doped SCAPF phosphor in the order of nanosize. SEM images at different magnifications showed the formation of irregular shaped grains. The observed bands in the optical absorption spectrum are assigned to d-d transitions of Mn(II) ions and are the characteristic of octahedral site symmetry. EPR spectrum at room temperature exhibits a weak hyperfine sextet with $g = 2.005$. The hyperfine splitting constant 'A' is evaluated and is found to be $78.88 \times 10^{-4} \text{ cm}^{-1}$. EPR and optical absorption spectral data revealed, the doped Mn(II) ions occupied octahedral site symmetry in the host lattice and there is a covalent bonding between Mn(II) ions and its ligands. The PL spectrum exhibited yellow to red emission with blue excitation. The characteristic orange-red emission confirms the presence of Mn(II) ions in octahedral symmetry. The appropriate CIE chromaticity coordinates ($x = 0.661$, $y = 0.338$) in red region suggests that the prepared material may be used in lamps and displays devices. FT-IR studies demonstrate the characteristic vibrational modes of phosphate and hydroxyl molecules in the prepared phosphor [7].

3.4 Fe(III) ions doped SCAPF Nanophosphor

The crystal system is indexed to monoclinic system and the lattice cell parameters are evaluated from the powder X-ray diffraction studies. The average crystallite size for Fe(III) ions doped phosphor were calculated as 69 nm, indicates the formation of nano sized phosphor. SEM micrographs shows irregular shaped nanoclusters. EDX analysis confirms the presence of constituent elements of the prepared phosphor material. The optical absorption spectrum exhibited four bands characteristic of Fe(III) ions in octahedral site symmetry. EPR spectrum exhibits resonance signals at $g = 2.00$ and 4.23 , due to distorted octahedral symmetry in the presence of oxygen ligands and represent the population of one of the Kramer's doublets. PL spectrum of Fe(III) ions doped phosphor exhibited the emission peaks in UV and blue regions, the emission was blue shifted compared to SCAPF phosphor due to the presence of Fe(III) ions in the lattice. The CIE coordinates of the Fe(III) ions doped phosphor are in blue region at ($x = 0.143$, $y = 0.049$) which suggested that the materials may be used as UV LEDs and UV back lights. The colour purity of the Fe(III) ions doped phosphor is high compared to SCAPF phosphor. The vibrational modes of inorganic elements in the prepared phosphor are identified from FT-IR studies [5].

3.5 Cu(II) ions doped SCAPF Nanophosphor

From the powder X-ray diffraction studies, the crystal system is indexed to monoclinic crystal system and the crystallite size was evaluated from Scherrer's formula and is found to be 50 nm which is in the order of nanosize. SEM images taken at different magnifications clearly showed prepared sample contains the irregular shaped nanoclusters with agglomeration. From optical absorption studies crystal field (Dq) and tetragonal field (D_s and D_t) parameters are evaluated. The same sign of tetragonal field parameters confirms the doped Cu(II) ions are in tetragonally elongated octahedral site symmetry. From the EPR spectrum it is

observed that $g_{\parallel} > g_{\perp} > 2.0023$ which indicates that Cu^{2+} ions are identified at octahedral coordination with tetragonal elongation. From optical and EPR studies, the doped Cu(II) ions are occupied at distorted octahedral site symmetry with tetragonal elongation in the host lattice. The evaluated bonding parameters suggests that there exists a covalent bonding between Cu(II) ions and its ligands. PL spectrum showed UV, blue and green emission bands and the emission colour of the phosphor identified at blue-green region with the coordinates ($x = 0.159$, $y = 0.204$) which indicates that the prepared phosphor may well suited for UV lamps. Cu(II) ions doped SCAPF phosphor exhibits the host lattice UV emission and characteristic emission of Cu(II) ions in blue-green region. The characteristic vibrational modes of P-O-H, phosphate molecules are evident from FT-IR studies [8].

4. Discussion

The investigations on SCAPF phosphor and transition metal ions (Cr(III) , Mn(II) , Fe(III) and Cu(II) ions) doped SCAPF phosphors prepared by solid state reaction. The prepared samples were characterized by various experimental techniques like powder XRD, SEM, optical absorption, EPR, PL and FT-IR studies.

The powder X-ray diffraction results confirm the crystal structure of prepared phosphor samples has monoclinic system. The observed diffraction patterns are in good agreement with the standard pattern of Viitaniemiite with diffraction data of JCPDS file No: 35-0598. The lattice cell parameters and crystallite size are evaluated from XRD data. The slight variations are observed in lattice cell parameters which may be due to the presence of TM ions in the host lattice. The average crystallite sizes of the prepared phosphor powders are in the range 40-90 nm, which are in the order of nanoscale. The lattice cell parameters and crystallite size of all samples are given in Table 1. From this it is clear that for trivalent ions doped SCAPF phosphor the crystallite size is more compared to divalent ions doped SCAPF phosphor.

Table 1 The lattice cell parameters and crystallite size of SCAPF phosphor and TM ions doped SCAPF phosphor

Phosphor Sample	Crystallite Size (nm)	Lattice Cell Parameters			
		a (nm)	b (nm)	c (nm)	β ($^{\circ}$)
SCAPF	53	0.683	0.721	0.549	109.97
Cr doped	86	0.689	0.719	0.552	109.00
Mn doped	46	0.694	0.715	0.511	109.18
Fe doped	69	0.689	0.721	0.552	109.50
Cu doped	50	0.685	0.716	0.554	108.80

SEM images shows nanoclusters and particles with irregular morphologies and agglomeration was observed due to high temperature involved in the synthesis of phosphor material. EDS spectrum confirms the presence of Na, Ca, Al, F, P, O and TM ions in the prepared phosphor materials.

Optical absorption studies and EPR spectra of TM ions doped SCAPF phosphor exhibited the characteristic absorption bands and resonance signals of TM ions. They are attributed to the octahedral site symmetry of doped TM ions. From the absorption bands, crystal field (Dq), Racah parameters (B , C) and tetragonal field parameters (in the case of Cu(II) ion doped) are evaluated by using their respective cubic field energy matrices. For Cr(III) ions the site symmetry is octahedral and bonding between the metal ions with ligands is ionic nature. The site symmetry of Mn(II) and Fe(III) ions in SCAPF host lattice is ascribed to octahedral and distorted octahedral site symmetry whereas in case of Cu(II) ions doped SCAPF phosphor, the site symmetry is tetragonally distorted octahedral. By correlating optical and EPR spectral data, the evaluated bonding parameters suggested that there exists a moderate covalent bonding nature between doped Mn(II) and Cu(II) ions and its ligands. The crystal field, tetragonal field and Racah parameters for TM ions doped SCAPF phosphor are given in Table 2.

Table 2 Variation in crystal field, tetragonal field and Racah parameters for TM ions doped SCAPF phosphor

Phosphor Sample	Crystal field, tetragonal field and Racah parameters (cm^{-1})		
Cr doped	$Dq = 1715$	$B = 610$	$C = 3340$
Mn doped	$Dq = 630$	$B = 630$	$C = 3165$
Fe doped	$Dq = 740$	$B = 680$	$C = 2800$
Cu doped	$Dq = 1215$	$Ds = 1547$	$Dt = 439$

The PL spectra of all the dopants exhibit various emission bands which correspond to different regions like UV, blue, green, orange, yellow and red regions. The excitation wavelengths of all the dopants are in UV or blue region.

PL spectrum of SCAPF phosphor exhibited emission peaks at 407, 413 and 469 nm under photon excitation 370 nm. Cr(III) ions doped SCAPF phosphor exhibited emission peaks at 470, 518 and 693 nm under photon excitation 420 nm, characteristic of undoped phosphor emission and Cr(III) ions. Mn(II) ions doped SCAPF phosphor exhibited emission peaks at 562, 633, 677 and 764 nm under photon excitation 465 nm, characteristic of Mn(II) ions. Fe(III) ions in the SCAPF phosphor exhibited emission peaks at 373, 450 nm under photon excitation 272 nm, the peaks are blue shifted with respective SCAPF emission due to the presence of

Fe(III) ions. Cu(II) ions in the SCAPF phosphor exhibited emission peaks at 378, 435, 550 nm under photon excitation 335 nm, characteristic of undoped phosphor emission and Cu(II) ions. From PL data of all phosphors the chromaticity coordinates are calculated and plotted in chromaticity diagram as shown in Figure 1. The chromaticity coordinates of SCAPF phosphor and TM ions doped SCAPF phosphor is given in Table 3. From PL studies it was clear that the prepared phosphors are well suited for light emitting materials in lamps and displays.

FT-IR spectra of all the TM ions doped SCAPF exhibited the fundamental vibrations of PO_4 , P-O-H, F-P-F and water molecules. Slight shifting of band positions is observed due to change in ionic radii of TM ion dopants.

Table 3 Chromaticity coordinates of SCAPF phosphor and TM ions doped SCAPF phosphor

Phosphor Sample	CIE Coordinates		Colour
	x	y	
SCAPF	0.139	0.120	Blue
Cr doped	0.297	0.356	Near white
Mn doped	0.661	0.338	Red
Fe doped	0.143	0.049	Blue
Cu doped	0.159	0.204	Blue-green

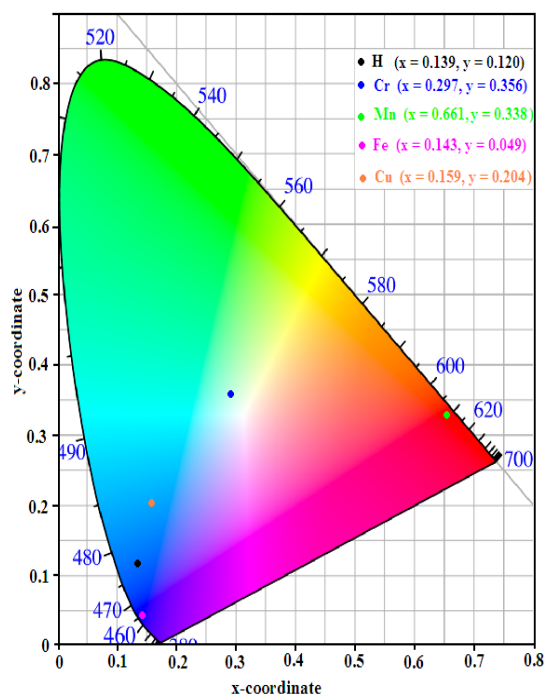


Figure 1 Chromaticity diagram of undoped (H) and TM ions doped SCAPF phosphor

Conclusion

Undoped and 3d transition metal ions (Cr(III), Mn(II), Fe(III) and Cu(II) ions) doped $\text{NaCaAlPO}_4\text{F}_3$ phosphor prepared by solid state reaction. The prepared phosphor samples are characterized to evaluate the site symmetry,

photoluminescence and bonding nature of doped metal ions in the host lattice. All the prepared phosphor materials are in monoclinic crystal system and calculated average crystallite size is observed in the order of nanoscale. Optical, EPR studies confirm that the site symmetry of Cr(III), Mn(II) ions in octahedral site symmetry, where as in the case of Fe(III) and Cu(II) ions the site symmetry is in distorted octahedral site. SEM images showed that the prepared samples contain nanoclusters with agglomeration and EDS data confirms the presence of constituent atoms. Photoluminescence studies identified that the prepared phosphor samples exhibit various colours as light emitting materials. From optical and EPR spectral studies the bonding between the doped ions and its ligand is covalent, in case of Cr(III) ions it is ionic. FT-IR spectra clearly depict the formation of characteristic vibrational bands of inorganic elements in the prepared phosphor.

Acknowledgements

R.V.S.S.N. would like to thank the UGC-DRS and DST-FIST, New Delhi for sanctioning to the Department of Physics, Acharya Nagarjuna University to carry out the present research work.

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