Research Article

EPR and Optical Studies of Cr (III) Ions Doped NaCaAlPO$_4$F$_3$ Nano Phosphor

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Abstract

Cr(III) ions dopedNaCaAlPO$_4$F$_3$phosphorwas synthesized by using solid state reaction method using flux. The prepared sample was characterized by various spectroscopic techniques such as powder XRD, SEM with EDS, Optical absorption, Electron Paramagnetic Resonance (EPR), Photoluminescence and FT-InfraRed. From powder XRD studies, the average crystallite size was calculated about 86 nm. SEM images showed the irregular shaped particles present in the sample. Optical absorption spectrum gave the absorption bands in UV-VIS region which are the characteristic of Cr(III) ions in octahedral symmetry. The room temperature EPR spectrum exhibited a broad signal centered at g~1.972.Photoluminescence spectrum showed the emission peaks in visible region, from blue to red with an excitation wavelength of 420nm.The CIE chromaticity coordinates were calculated as (x = 0.297, y = 0.356).

Keywords: Inorganic Phosphor material, X-ray diffraction, Photoluminescence, Optical properties, Local site symmetry.

1. Introduction

Inorganic luminescence materials have drawn great attention, as they are widely applied in light emitting display, lasers, optoelectronics and as fluorescent markers in biomedicine(Zhu *et al*, 2012),(Wang *et al,* 2011), (Shen *et al*, 2010).Now-a-days, the synthesized luminescent particles in nanoscale are essential for ongoing device improvements and miniaturization. The nanoparticles are needed for a better display resolution, smaller pixel sizes and so on(Ashwini Kumar *et al*,2013).The phosphate-based luminescent materials in nano-dimensions are extensively studied owing to their potential application in solid-state lighting, whichcould besupplantingthe conventional incandescent and fluorescent lampsin the coming future (Dillip *et al*,2012).

Recentlyhalo phosphate phosphors have received great importance due to their intense luminescence intensities, highemission efficiencies and wide application fields in displays and devices(Shinde *et al*, 2012), (Puppalwar *et.al*,2012).Inorganic phosphor NaCaAlPO$_4$F$_3$ is halophospate based phosphor and its crystal structure resemble with a rare mineral phosphate compound Viitaniemiite,NaCaAlPO$_4$(F,OH)$_3$. This mineral presents a monoclinic structure with a unit cell belonging to P2$_1$/m space group. The crystal structure consists of a six-coordinated Al atom,a six-coordinated Ca atom, a four-coordinated P atom and aneight-coordinated Na atom (Ramik*et al*,1983), (Pajunen *et al*,1984).

Among various optically active systems, materials doped with chromium ions in inorganic hosts are widespread because ofdeep colors and bright photoluminescence(Tanner, 2004).Trivalent chromium is the most stable state of chromium and it effectively interacts with lattice and has high luminescent quantum efficiency as dopant (Jastrabik *et al*, 2003).Usually, aluminates based phosphor materials generate more defect related traps when they are activated with transition metal ions. It shows very interesting optical properties, originated from the coupling between electronic transitions and vibrational modes around the impurity ion(Wang *et al*, 2009). In general, these systems are attractive because the transitions occur in the visible and infrared regions, if the ions are in octahedral sites (Pedro *et al*,2013), or only in infrared region, if ions are in tetrahedral sites (Yamaga *et al*, 2004). Cr(III) ions tend to form octahedral complexes and the colors of these complexes can be determined by the ligands attached to the Cr center. This unique feature has attained a technological importance in the development of tunable solid state lasers and new luminescent materials (Kuck,2001), (Wenger *et al,* 2001), (Ohtake *et al*, 2000).

The EPR and optical properties of Cr(III)ions doped hosts has been reported by various researchers recently (Kundu *et al*,2013),(Sugiyama *et al*,2013),(Singh et al, 2012), (Premkuma r*et al,*2012).Godlewska *et al.*,reported the optical and EPR studies of undoped and Cr(III) ions doped NaCe(PO$_3$)$_4$metaphosphates. The Cr(III) ions appear in the distorted octahedral environment of the weak crystal field and exhibit a broad emission band in the visible region. The Cr(III) ions reveal negligible ferromagnetic interactions(Godlewska *et al*, 2014). Molla *et al.* investigated the microstructure, mechanical, thermal, EPR, and optical properties of MgAl$_2$O$_4$:Cr^{3+} spinel glass-ceramic nano-composites (Molla etal, 2014).

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Recently, we have reported the synthesis and characterization of undoped and Fe(III)ions doped $NaCaAlPO_4F_3$ phosphor (Pushpa Manjari et al, 2014).Fe(III) ions entered in to the host lattice as distorted octahedral site symmetry and exhibits luminescence in UV and blue regions. The present chapter discusses the effect of chromium on $NaCaAlPO_4F_3$(SCAPF) phosphor to determine the dynamic behavior, site symmetry and the luminescence of the transition metal ion in the host lattice bymeans of optical absorption, EPR and PL studies coupled with X-ray diffraction, Scanning Electron Microscopy and FT-IR measurements.

2. Experimental Procedure

2.1Synthesis of Cr(III) ions doped NaCaAlPO₄F₃ (SCAPF) phosphor

Cr(III) ions doped SCAPF phosphor was prepared by solid state reaction method. The starting chemicals Na_2CO_3 (0.5299 gm),$AlF_3.3H_2O$ (1.6562 gm), $CaCO_3$ (0.9008 gm), $(NH_4)_2HPO_4$(1.3206 gm)were weighed in a requisite stoichiometric proportion and ground into fine powder for 30 minutes using an agate mortar and pestle. After that Cr_2O_3 (0.049 gm) 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 andwith excess of 20 mol% $AlF_3.3H_2O$ was also used as a flux finally to obtain Cr(III) ions doped SCAPF phosphor.

2.2 Characterizations

Powder X-ray diffraction pattern of the prepared sample is recorded on PANalytical Xpertpro diffractometer with CuKα radiation. Scanning Electron Microscope and Energy Dispersive Spectrum (EDS) images were taken from ZEISS EVO18. Optical absorption spectrum is recorded at room temperature on JASCO V-670 Spectrophotometer in the wavelength region of 400-800 nm. EPR spectrum is recorded at room temperature on JES-FA series X-band EPR Spectrometer having 100 KHZ field modulations. To record the photoluminescence (PL) spectrum Horiba Jobin-Yvon Fluorolog3 Spectrofluorimeter with Xe continuous (450W) and pulsed (35W) lamps as excitation sources was used. FT-IR spectrum of the prepared sample was obtained from Bruker's FT-IR Spectrophotometer in the region of 4000-500cm⁻¹.

3. Results and Discussion

3.1 Powder X-ray diffraction, SEMand EDS analysis

Fig. 1shows the XRD pattern of the as-synthesized Cr(III) ions doped SCAPF phosphor sample. The XRD patterns of these optimized phosphor samples are in good agreement with the reference pattern of Viitaniemiite with standard diffraction data of JCPDS file No.35-0598.The pattern shows narrow reflections indicating that the samples are crystalline in nature. The diffraction data is indexed to a monoclinic crystal system and the corresponding lattice cell parameters are evaluated

a =0.689, b =0.719, c =0.552 nm and β = 109°.

The average crystallite size of the prepared sample is calculated by using Scherrer's formula,

t= (k λ / β Cos θ)

Where k is a constant (about 0.9), λ is the wavelength of X-ray radiation (1.5405Å), β is the full width at half maximum (FWHM) intensity of the diffraction line and θ is the diffraction angle. Based on the FWHM, the average crystallite size is estimated to be around 86 nm which is the order of nano size.
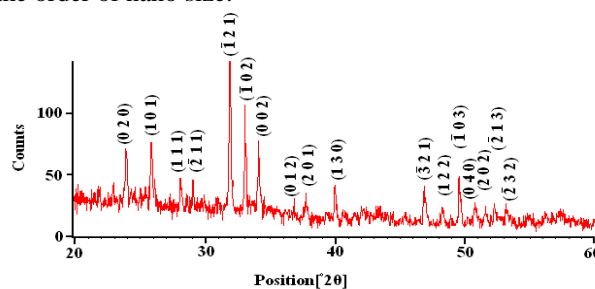

Fig. 1 XRD pattern of Cr(III)ions doped SCAPF phosphor

Fig.2 showed the SEM images of Cr(III) ions doped SCAPF phosphor. The obtained SEM image showsthe solid nano crystalline particles with some conglomeration among the crystalline grains and it possess an irregular morphology which is due to high temperature involved in the synthesis of phosphor material. The grains seen in the SEM images are the domains formed by aggregation of the nano-size crystallites.

To determine the composition of the prepared products, an EDS spectrum is presented in Fig.3. The selected area of the prepared sample was also performed for EDS measurement for characterizing the compositions of the phosphor. The spectrum reveals the elemental composition as per the stoichiometric ratio of the phosphor and confirms the formation of the sample by the synthesis method. It is found that EDS data demonstrates the prepared phosphor is composed of Na, Ca, Al, P, O, F and Cr species.

3.2 Optical absorption Studies

Fig.4 shows the optical absorption spectrum of Cr(III) ions doped SCAPF phosphor. The optical absorption spectrum consists of three bands at 685 (14595 cm⁻¹), 583 (17148 cm⁻¹) and 427 nm(23412 cm⁻¹). The bands consistent with Cr(III) ions are in an octahedral environment, assigned on the basis of Tanabe-Sugano diagrams. The visible absorption bands observed in the spectrum are due to octahedrally coordinated Cr(III) ions (Bates, 1962), (Stroud, 1971).The bands observed at 427 and583 nm arise from the spin-allowed d-d transitions of octahedral Cr(III) ions, which are assigned to $^4A_{2g}(F) \rightarrow {}^4T_{1g}(F)$ and $^4A_{2g}(F) \rightarrow {}^4T_{2g}(F)$. The band observed at 684 nm is assigned to spin forbidden transition $^4A_{2g}(F) \rightarrow {}^2E_g(G)$. The band energy associated with the transition $^4A_{2g}(F) \rightarrow$

$^4T_{2g}$(F) gives crystal field splitting parameter (10Dq). The Racah inter-electronic repulsion parameter (B) is evaluated from the observed energy bands by using the following expression (Peruma Reddi, 1969):
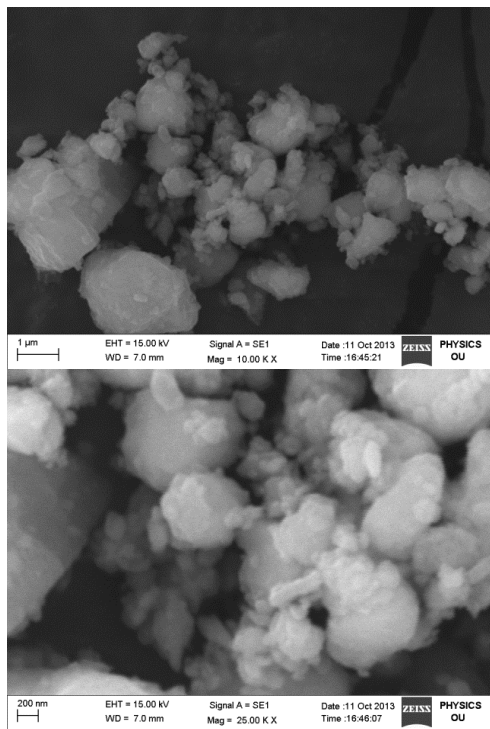
$$B = (2v_1^2 + v_2^2 - 3\ v_1\ v_2)/\ (15v_2 - 27v_1)$$

Fig. 2 SEM images of Cr(III) ions doped SCAPF phosphor

Where v_1 and v_2 are the energies corresponding to the $^4A_{2g}$(F) $\rightarrow$ $^4T_{2g}$ (F) and $^4A_{2g}$(F) $\rightarrow$ $^4T_{1g}$(F) respectively. The evaluated value of B is 610cm^{-1}. The value of B is a measure of inter-electronic repulsion in the d-shell and is useful in discussing the ionic/covalent properties of Cr(III)ligand bonding. The value of C is evaluated using the relationgiven by (Rasheed *et al*,1991).

$$C/B = 1/3.05\ [E\ (^2E)/B\ -7.9\ +\ 1.8\ (B\ /\ Dq)]$$

The evaluated value of C is 3340 cm^{-1}. Crystal field and Racah parameters are evaluated by using the experimental values are:
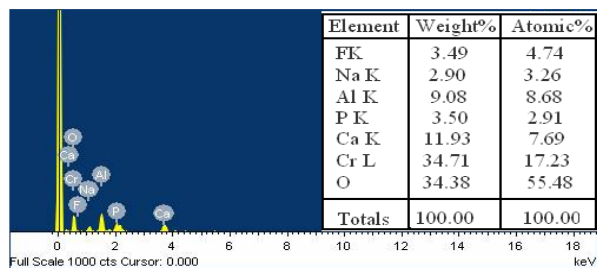**Dq =1715, B = 610 and C = 3340 cm^{-1}**

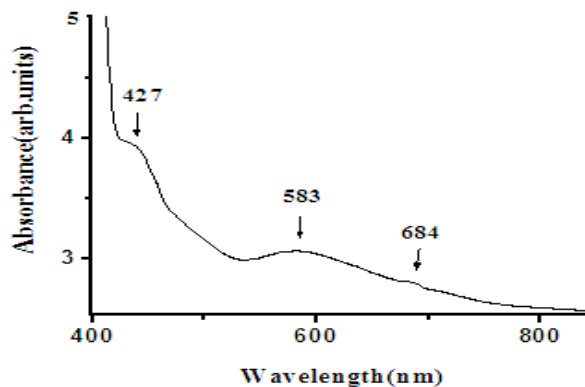**Fig. 3** EDS spectrum of Cr(III) ions doped SCAPF phosphor

Fig. 4 Optical absorption spectrum of Cr(III) ions doped SCAPF phosphor

Table 1 Observed and calculated band positions of Cr(III) ions doped SCAPF phosphor

Transition From $^4A_{2g}$(F)	Observed band position		Calculated Wavenumber (cm^{-1})
	Wavelength (nm)	Wavenumber (cm^{-1})	
$^4T_{1g}$(F)	427	23412	23416
$^4T_{2g}$(F)	583	17148	17150
^2E_g (G)	684	14616	14618

3.3 EPR studies

Cr(III) ions has large octahedral site preference energy (OSPE)(Ford*et al*, 1960)and it has three unpaired electrons, with electronic spin S = 3/2 and nuclear spin I = 3/2 or 0 for ^{53}Cr (natural abundance 9.54%) and for ^{52}Cr (natural abundance 90.46%), respectively.Within an octahedral crystal field, the ^{4}F ground state splits into an orbital singlet $^4A_{2g}$ and two orbital triplets $4T_{1g}$ and $^4T_{2g}$(Fuxi, 1992). In a distorted octahedral site, the electronic levels can be described by a spin Hamiltonian of the form (Carrington, 1967),

$$H = \beta BgS + D[S_z^2 - S(S + 1)/3] + E(S_x^2 - S_y^2)]$$

Where the terms involving D and E are the axial and orthorhombic crystal-field components respectively, S is the spin operator and g is the gyro magnetic tensor. In the absence of an external magnetic field H, the four fold spin degeneracy of the $^4A_{2g}$ state is removed by a subsequent low symmetric field resulting in a zero-field splitting of the Kramer's doublets |$\pm$3/2> and |$\pm$1/2>separated by an energy $\Delta_{zfs}=2(D^2+3E^2)^{1/2}$. In the presence of a magnetic field, the degenerate doublets split further. On applying rf field a transition with $\Delta_{ms}=\pm1$ may be observed in the EPR spectrum. However, the number of resonance peaks depends on the magnitude of the zero-field splitting for a given rf photon energy (Knutson, 1989). Investigations on the EPR spectrum of Cr(III) ions ascribe the observed signals to transitions between the perturbed Kramer's states suggesting octahedral site with a large zero field splitting compared with the rf photon energy (Griscom,1980), (Legein*et al*, 1995). EPR spectrum of

Cr(III) ions doped SCAPF phosphor is shown in Fig.5. It has two principal features. The first is a broad asymmetric band at low magnetic field with an effective g value of ~5. The second is a broad and asymmetric line at high magnetic field with an effective g value of ~1.9.According to the theory of Landry, the low field portion of the spectrum is attributed to the isolated Cr(III) ions and the high field portion mainly belongs to the exchange coupled Cr(III)-Cr(III) pairs (Landry *et al*,1967), (Orgel,1966)

EPR spectra of Cr(III) ions in phosphates glasses (Ravikumar *et al*, 2003), fluorophosphates glasses(Murali*et al*,1999),were reported. In all these host materials, two resonances were observed at g ~5.0 and g ~2.0(Gan *et al*, 1982). In the present investigation, a broad resonance signal is observed with effective g value at 1.972. The g value is in good agreement with Cr(III) ions doped phosphate hosts (Chandrasekhar *et al*, 2002), (Premkumar *et al*,2012).Cr(III) ions tend to occupy approximately octahedral sites. By correlating optical and EPR data, the chemical bonding parameter α is evaluated using the formula (Orton,1968).

$$g_o = g_e - 8\alpha\lambda/\Delta$$

where g_e is free electron g factor (2.0023), λ is the spin–orbit coupling constant ($91 cm^{-1}$), Δ is the energy gap between the excited and ground levels. From experimental values g_o=1.972 and Δ=17148cm^{-1}, then the value of α is evaluated as 0.713.The value of α ($0 \le \alpha \le 1$) is the Cr(III) ions and its ligands. The evaluated value of α=0.713 suggests the ionic contribution of Cr(III) ions in the host lattice.

3.4 Photoluminescence Studies

To study the influence of Cr doping on emission and defects formations photoluminescence spectrum of Cr(III) ions doped SCAPF phosphor was recorded. Fig. 6 shows the emission spectrum of Cr(III) ions doped SCAPF phosphor with an excitation of 420 nm. The emission spectrum shows three sharp emission peaks in the visible region at 470, 518 and 693nm.
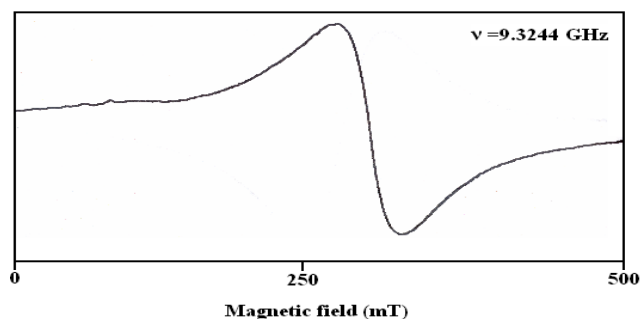

Fig.5EPR spectrum of Cr(III)ions doped SCAPF phosphor

The blue emission peak at 470 nm is a host lattice emission due to intrinsic impurities in host lattice, which was observed even in undoped SCAPF phosphor(Pushpa Manjari *et al*, 2014). The green emission band near 518 nm is assigned to the transition$^4T_{2g}(F) \to {}^4A_{2g}(F)$. The red emission band at 693 nm (R line) is a deep level emission

band characteristic of Cr(III) ions which is caused by the spin-forbidden $^2E_g \to {}^4A_{2g}$ transition (Singh *et al*, 2009) and also the emission band results from coupling of phonon with emission photon of Cr(III) ions(Rack et al, 2001),(Henderson, 1896).Similar emission was also observed in various chromium doped hosts (Amaranatha Reddy *et al*, 2012).The emission of Cr(III) ions in SCAPF phosphor might be used in the field of display and lighting.

3.5 Chromatic properties

The CIE chromaticity coordinates of Cr(III) ions doped SCAPF phosphor are calculated from their corresponding emission spectrum under excitation of 420 nm. The colour of the prepared phosphor is graphically represented in a two dimensional CIE x−y plot and is depicted in the Fig.7. The CIE coordinates are observed at (x = 0.297, y = 0.356) indicated with a solid sign (**.**). This indicates that the emission color of prepared phosphor is near to that of white region.

3.6 FT-IR studies

Fig. 8 shows the FT-IR spectrum (4000-500cm^{-1}) of Cr(III) ions doped SCAPF phosphor. The spectrum exhibited the 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.
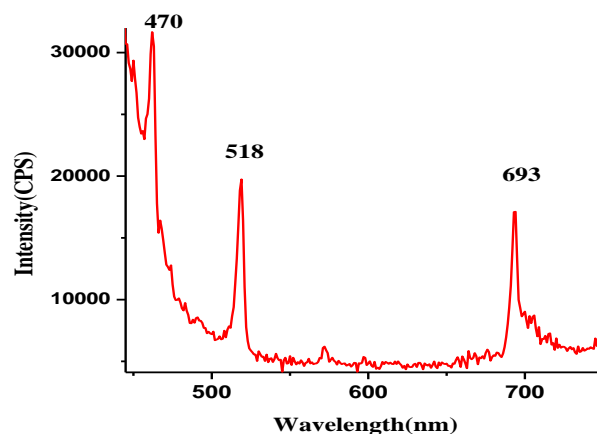

Fig. 6 Photoluminescence spectrum of Cr(III) ions doped SCAPF phosphor

The bands observed in region 3300-4000 cm^{-1} are due to symmetric and asymmetric (v_1+v_3) vibrations of hydroxyl ions situated at different sites in the lattice. The bands observed at around 1695 cm^{-1} is attributed to H-O-H bending mode (v_2)(Hunt, 1970). 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 (Nyquist *et al*, 1997) (Vivekanandan *et al*, 1997).Usually the IR absorption band of PO_4^{3-} ions has two regions of 1120-940 cm^{-1} and 600-580 cm^{-1}.These two regions are characteristic of triply degenerate modes (v_3&v_4) of PO_4^{3-} ions (Herzberg,

1962).P-O-H modes of vibrations occur generally in the region 3000-1500 cm^{-1} (Hunt *et al*, 1972).The stretching vibrations of F-P-F are observed at 844 cm^{-1} which indicates the formation of F-P-F bonds and their existence as fluorophosphates units (Nakamoto, 1986).The observed IR band positions of Cr(III) ions doped SCAPF phosphor and their assignments are given in Table 2.
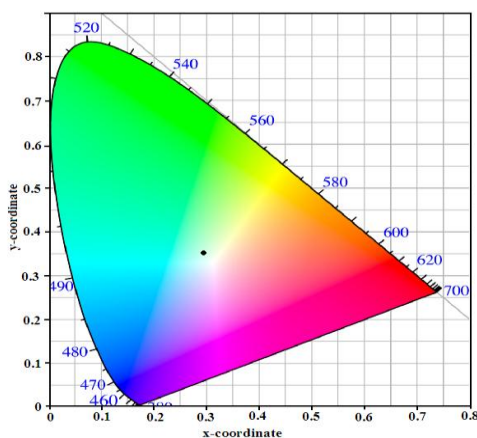

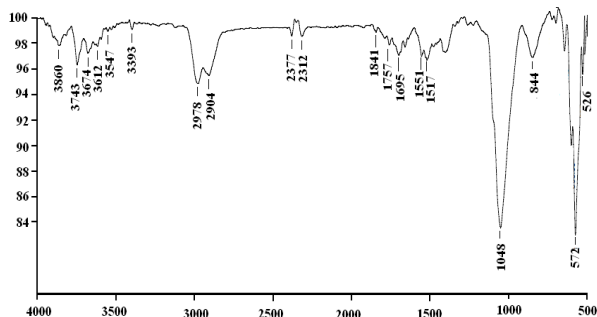**Fig. 7**CIE plot of Cr(III) ions doped SCAPF phosphor

Fig.8 FT-IR spectrum of Cr(III)ions doped SCAPF phosphor

Table 2 Assignment of peak positions in FT-IR spectrum of Cr(III) ions doped SCAPF phosphor

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Vibrational frequency (cm^{-1})	Band assignment
3860, 3743, 3674, 3612, 3393	symmetric and asymmetric modes (ν_{1+} ν_3) of vibrations of hydroxyl ions
2978, 2904, 2377, 2312,1841,1757, 1517	P-O-H modes of vibrations
1695	Bending mode (ν_2) of H-O-H
1048	ν_3 PO$_4^{3-}$ ion
844	F-P-F
572	ν_4PO$_4^{3-}$ ion

4. Conclusion

Cr(III) ions doped SCAPF phosphor was successfully synthesized by solid state reaction using flux. From the results and discussion the following conclusion are drawn:

From the X-ray diffraction studies, it was observed that the prepared phosphor belongs to monoclinic crystal system and the corresponding lattice cell parameters are evaluated. The average crystallite size calculated from Debye-Scherrer's formula is about 86 nm which confirms the prepared sample is in the order of nanosize.

The SEM images shows irregular shaped particles with agglomeration. EDS analysis confirms the presence of constituent elements of the prepared phosphor material. The absorption bands observed in the spectrum are due to octahedrally coordinated Cr(III) ions. EPR spectrum exhibits resonance signal at g = 1.972 which is attributable to Cr(III) and this indicates octahedral site symmetry for the Cr(III) ions in the lattice. From the optical absorption and EPR studies, Cr(III) is ascertained to octahedral site symmetry. By correlating optical and EPR data, the chemical bonding parameter α has evaluated which indicates ionic nature of Cr(III) ions in the lattice.

The PL spectrum exhibited emission bands at 470, 518 nm and 693nm under photon excitation (λ_{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 and F-P-F molecules are evident from FT-IR studies

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