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Novel Nanophosphor materials for LED Applications.

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Abstract

Recently, solid-state lighting using white light-emitting diodes (LEDs) have attracted worldwide attention because of their important benefits including energy saving, safety, reliability, maintenance and environmentally friendly characteristics. White-light LED devices convert electrical energy to light much more effectively than conventional lighting sources. The phosphate based luminescent materials in nano-dimensions are extensively studied owing to their potential applications like lighting devices which could be supplanting the conventional incandescent and fluorescent lamps in future lighting. In order to produce high efficiency-low cost LED devices, in our laboratory transition metal ions (Mn^{2+}, Cu^{2+}) doped different phosphor materials ($NaCaAlPO_4F_3$, $Li_2CaAl_4(PO_4)_4F_4$, Ca–Li hydroxyapatite) using solid-state reaction and mechanochemical synthesis are prepared. The prepared samples were characterized by powder X-ray diffraction (XRD), Scanning Electron Microscope (SEM), Transmission Electron Microscope (TEM) and Photoluminescence (PL) techniques. PL spectra of the prepared samples at room temperature show blue, orange, yellow, red to white emission in visible regions. The evaluated CIE and CCT coordinates shows that the prepared phosphor materials are useful for W-LEDs, electroluminescence panels and plasma display devices.

Keywords: Hydroxyapatite, Luminescent materials, Nanophosphor, Photoluminescence and CCT coordinates.

1. Introduction

Inorganic materials having high luminous efficiency, energy saving and environmental protection are long-lasting pursuits of researchers. Novel phosphor luminescent materials have drawn great attention, as they are widely used in various optoelectronic devices such as field emission displays, plasma display panels, light emitting diodes (LED) and as fluorescent markers in biomedicine [1]. Now-a-days, the synthesized luminescent materials in nanoscale are essential for ongoing device improvements and miniaturization. Such materials find applications in displays like television i.e., cathode ray tubes (CRT), plasma display panels (PDPs), electroluminescence (EL) based displays, White LEDs (W-LEDs) and field emission displays (FEDs) [2]. (W-LEDs) are an important class of solid-state lightening (SSL) devices. The LED-based lighting can provide significant power saving, higher luminous efficiency and longer lifetime [3].

White LEDs are in general well thought-out to be the new generation light sources. For all intents and purposes, W-LEDs are two methods in study to produce white light from LEDs. The first one is to convert the emission from blue or ultraviolet (UV) LED by adding longer wavelength light using phosphors and the second one is different colors of light mixing and emitted by several LED chips. Phosphate phosphor compounds doped with transition metal (TM) ions continue to draw attention in view of their variety of applications. It is distinguished that impurity elements play a major role because they can manipulate the properties of host materials. A large number of investigations are dedicated to optical properties of transition metals in solids for laser applications. In the present work transition metal ions (Mn^{2+}, Cu^{2+}) doped different phosphor materials ($NaCaAlPO_4F_3$, $Li_2CaAl_4(PO_4)_4F_4$, Ca–Li hydroxyapatite (CLHA)) using solid-state reaction and mechanochemical synthesis were prepared.

2. Experimental

2.1 Synthesis

Transition metal ions (Mn^{2+}, Cu^{2+}) doped different phosphor materials ($NaCaAlPO_4F_3$, $Li_2CaAl_4(PO_4)_4F_4$, CLHA) were synthesized by previously reported methods [4-6].

2.2 Characterization

Powder X-ray diffraction patterns of the prepared samples are recorded on PANalytical Xpert Pro diffractometer with CuKα radiation. Scanning electron microscope (SEM) and energy dispersive spectrum (EDS) images are taken on ZEISS EVO 18. Transmission electron microscope (TEM) images are recorded on HITACHI H-7600 and CCD CAMERA system AMTV-600 by dispersing the samples in ethanol. Photoluminescence (PL) spectrum is taken at room temperature on Horiba Jobin-Yvon Fluorolog-3 spectrofluorimeter with Xe continuous (450 W) and pulsed (35W) lamps as excitation sources.

3. Results and discussion

3.1 Powder X-ray diffraction studies

Powder X-ray diffraction profiles of Mn^{2+} and Cu^{2+} doped $NaCaAlPO_4F_3$, $Li_2CaAl_4(PO_4)_4F_4$, CLHA nanophosphors were shown in Fig. 1. The peak positions observed in Fig. 1 are well matched with standard diffraction data of JCPDS file no. 35-0598, 41-1450 and 09-0432 respectively.

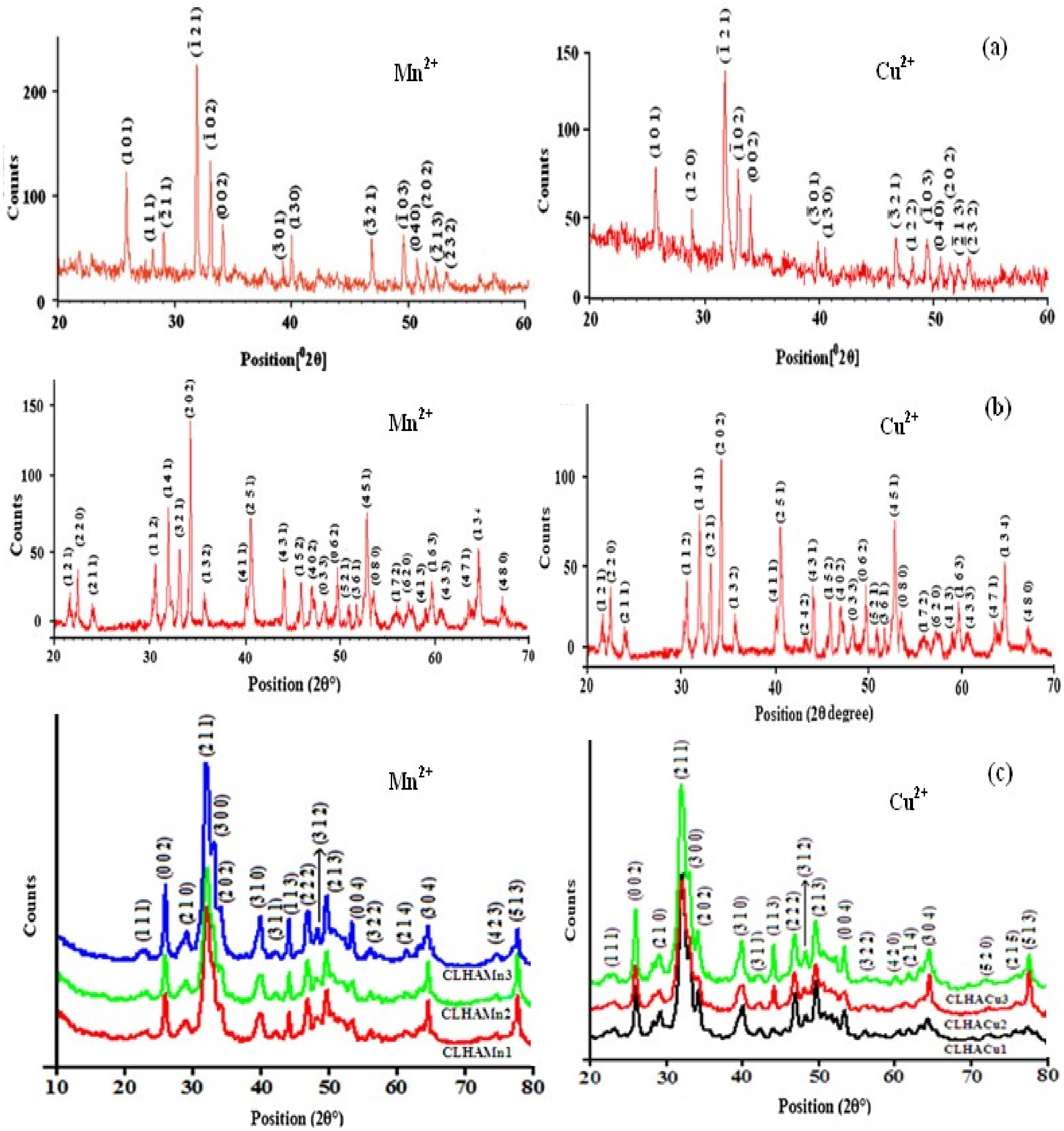

Fig. 1 Powder XRD pattern of Mn^{2+} and Cu^{2+} doped (a) $NaCaAlPO_4F_3$, (b) $Li_2CaAl_4(PO_4)_4F_4$, (c) CLHA nanophosphors.

The pattern shows narrow reflections indicating that the samples are crystalline in nature. The diffraction data of prepared samples are indexed to monoclinic, orthorhombic, hexagonal crystal systems and the corresponding lattice cell parameters, average crystallite size are evaluated, which are given in Table 1.

Table1: The crystallite size, lattice parameters and crystal system of Mn^{2+} and Cu^{2+} doped $NaCaAlPO_4F_3$, $Li_2CaAl_4(PO_4)_4F_4$, CLHA nanophosphors

S.No.	Sample	Crystallite size (nm)	Lattice cell parameters (nm)			Crystal System
			a	b	c	
1	$NaCaAlPO_4F_3$: Mn^{2+}	46	0.694	0.715	0.511	Monoclinic
2	$Li_2CaAl_4(PO_4)_4F_4$: Mn^{2+}	48	1.147	1.592	0.724	Orthorhombic
3	CLHAMn1	10	0.938	--	0.686	Hexagonal
	CLHAMn2	11	0.938	--	0.686	
	CLHAMn3	12	0.938	--	0.686	
4	$NaCaAlPO_4F_3$: Cu^{2+}	50	0.685	0.716	0.554	Monoclinic
5	$Li_2CaAl_4(PO_4)_4F_4$: Cu^{2+}	52	1.145	1.589	0.726	Orthorhombic
6	CLHACu1	6.32	0.942	--	0.687	Hexagonal
	CLHACu2	7.91	0.943	--	0.686	
	CLHACu3	9.19	0.943	--	0.685	

3.2 Morphological studies

The morphology of Mn^{2+} and Cu^{2+} doped $NaCaAlPO_4F_3$, $Li_2CaAl_4(PO_4)_4F_4$, CLHA nanophosphors with EDS pattern were observed from SEM and EDS images and are given in Fig. 2 and Fig. 3. The images are taken at different magnifications and shows that each of them composed of irregular shaped agglomerations with non-uniform distribution. The grain sizes from 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 nano-size crystallites [7]. EDS pattern confirms the presence of constituent elements in the prepared samples.

It is necessary to obtain the particle size and the information about the nanostructures by direct measurement, such as TEM, which can reveal the size and morphology of particles. It can be seen that the formation of prepared phosphor material in the nanometer range with tiny nanoparticles is clearly observed and well-separated individual non-uniform rods and aggregates of various sized particle-like structures are noted in the TEM images. Fig. 4 shows the TEM images of Mn^{2+} and Cu^{2+} doped $NaCaAlPO_4F_3$, $Li_2CaAl_4(PO_4)_4F_4$, CLHA nanophosphors respectively.

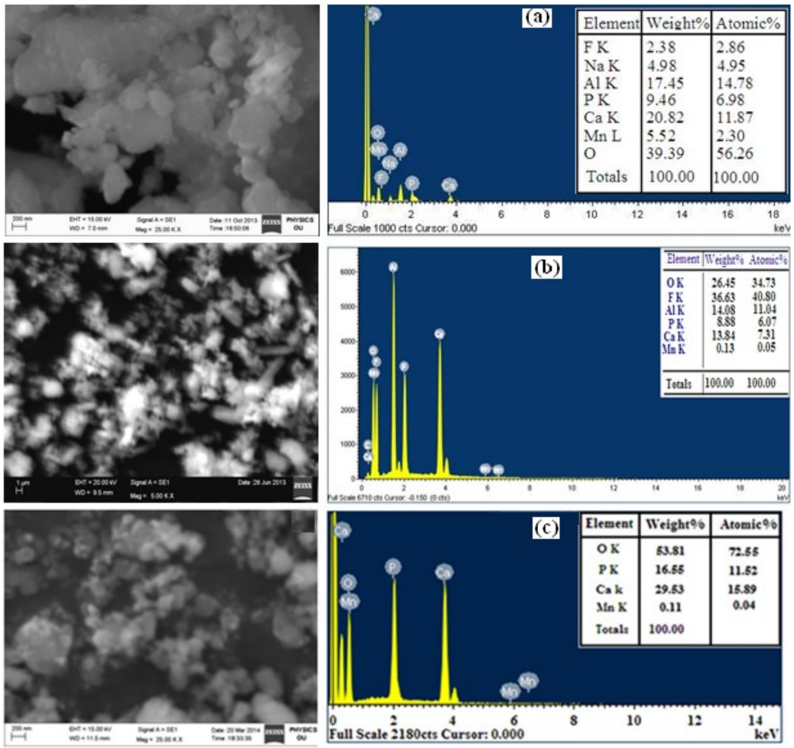

Fig. 2 SEM and EDS pattern of Mn^{2+} doped (a) $NaCaAlPO_4F_3$, (b) $Li_2CaAl_4(PO_4)_4F_4$, (c) CLHA nanophosphors.

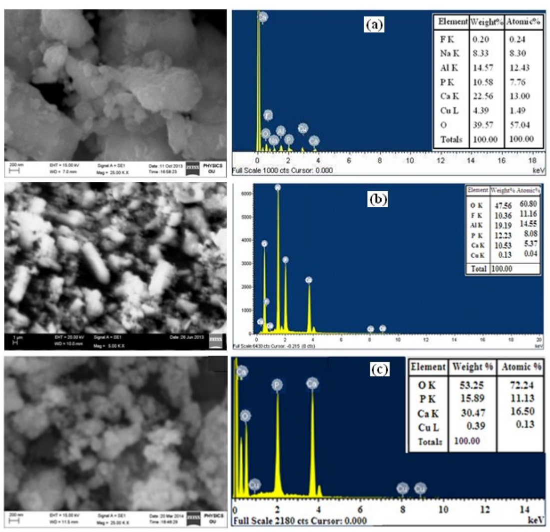

Fig. 3 SEM and EDS pattern of Cu^{2+} doped (a) $NaCaAlPO_4F_3$, (b) $Li_2CaAl_4(PO_4)_4F_4$, (c) CLHA nanophosphors

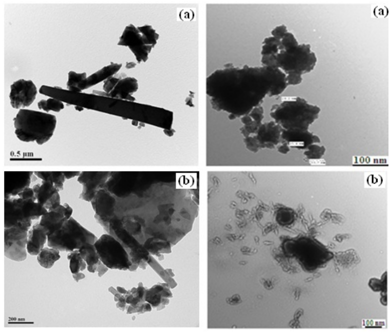

Fig. 4 TEM images of (a) Mn^{2+} and (b) Cu^{2+} doped $Li_2CaAl_4(PO_4)_4F_4$, CLHA nanophosphors.

3.3 Photoluminescence studies

Photoluminescence (PL) phenomenon is directly related to electronic structure and transitions. Differences in the electronic behavior between bulk and low-dimensional semiconductors arise due to difference in the electronic density of states. PL emission spectra and the corresponding CIE diagram of Mn^{2+} and Cu^{2+} doped $NaCaAlPO_4F_3$, $Li_2CaAl_4(PO_4)_4F_4$, CLHA nanophosphors were shown in Fig. 5 and Fig. 6. The PL spectra of transition metal ions doped different nanophosphors exhibit various emission bands which correspond to different regions like UV, blue, green orange and red regions. The excitation wavelengths for all the prepared samples are in UV region and are given in Table 2.

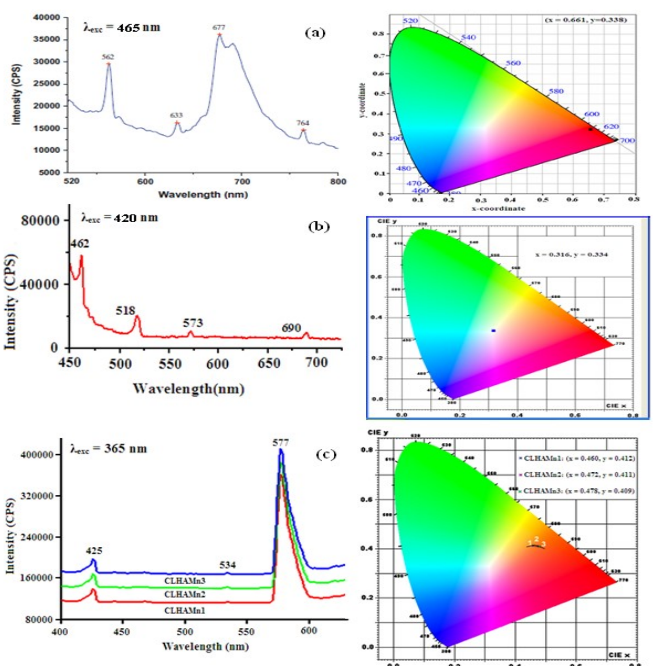

Fig. 5 PL and CIE spectra of Mn^{2+} doped (a) $NaCaAlPO_4F_3$, (b) $Li_2CaAl_4(PO_4)_4F_4$, (c) CLHA nanophosphors.

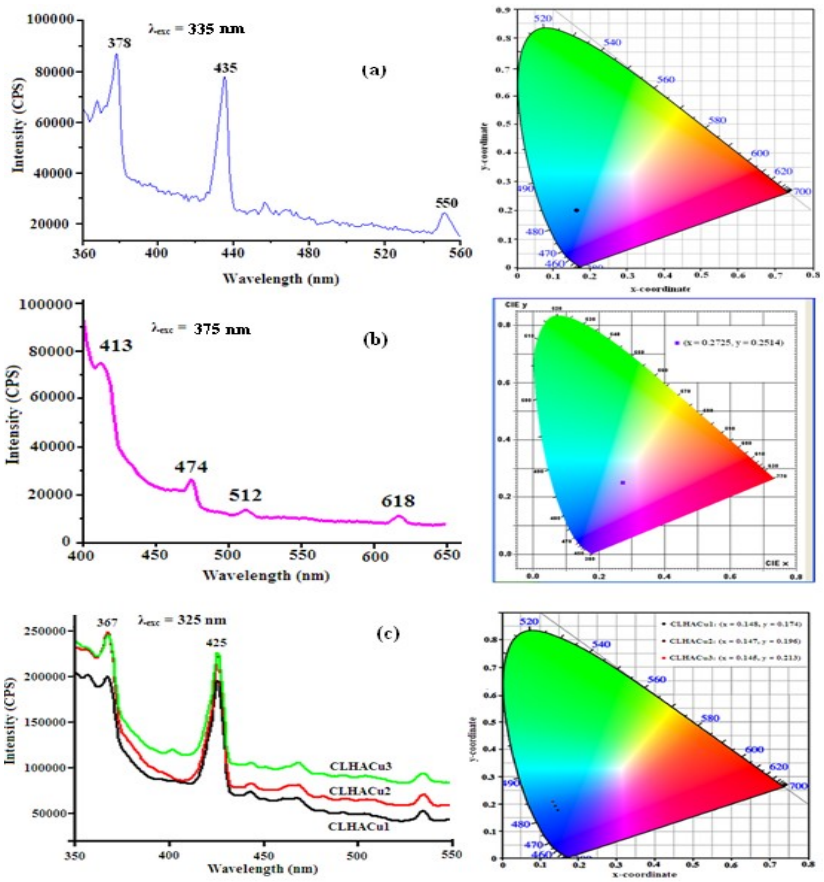

Fig. 6 PL and CIE spectra of Cu^{2+} doped (a) $NaCaAlPO_4F_3$, (b) $Li_2CaAl_4(PO_4)_4F_4$, (c) CLHA nanophosphors.

Table 2: Emission peaks and excitation wavelengths of Mn^{2+} and Cu^{2+} doped $NaCaAlPO_4F_3$, $Li_2CaAl_4(PO_4)_4F_4$, CLHA nanophosphors

Sample	Emission peaks (nm)	Excitation wavelength (nm)
$NaCaAlPO_4F_3$: Mn^{2+}	562, 633, 677, 764	465
$Li_2CaAl_4(PO_4)_4F_4$: Mn^{2+}	462, 518, 573, 690	420
CLHA: Mn^{2+}	425, 534, 577	365
$NaCaAlPO_4F_3$: Cu^{2+}	378, 435, 550	335
$Li_2CaAl_4(PO_4)_4F_4$: Cu^{2+}	413, 474, 512, 618	375
CLHA: Cu^{2+}	367, 425	325

In general, CIE chromaticity diagram represents the color of any light source [8, 9]. To characterize the color emission, the CIE parameters such as the colour coordinates (x, y) and the color correlated temperature (CCT) were calculated from the PL emission spectral data. The CCT value has been calculated using McCamy formula [10] to check the quality of light.CCT = $-437n^3 + 3601n^2 - 6861n + 5514.31$ where n = (x -xe)/(y - ye) and the chromaticity epicenter is at $x_e = 0.3320$ and $y_e = 0.1858$, and (x, y) are the calculated coordinates of prepared phosphor. The color coordinates and CCT values of prepared nanophosphors are given in Table 3. These materials may be used for various applications in LED and other display devices.

Table 3 : CIE and CCT coordinates of Mn^{2+} and Cu^{2+} doped $NaCaAlPO_4F_3$, $Li_2CaAl_4(PO_4)_4F_4$, CLHA nanophosphors

Sample	CIE Coordinates		Color	CCT
	x	y		
SCAPF: Mn^{2+}	0.661	0.338	Red	3103
$Li_2CaAl_4(PO_4)_4F_4$: Mn^{2+}	0.316	0.334	White	6299
CLHAMn1 CLHAMn2 CLHAMn3	0.460 0.472 0.478	0.412 0.411 0.409	Yellow Orange Orange-red	2704 2534 2443
$Li_2CaAl_4(PO_4)_4F_4$: Cu^{2+}	0.272	0.251	Violet	16560

Conclusions

From the synthesis and characterization of transition metal ions (Mn^{2+}, Cu^{2+}) doped different phosphor materials ($NaCaAlPO_4F_3$, $Li_2CaAl_4(PO_4)_4F_4$, CLHA), the following conclusions were drawn:

From the powder XRD studies, the crystal system is indexed to monoclinic, orthorhombic and hexagonal crystal system for the respective phosphor materials and the crystallite sizes were evaluated from Scherrer's formula and is found to be in the order of nanoscale. The morphology of prepared samples exhibit stones/sphere like structures indicates that each of them is composed of agglomerates with irregular shape and dimension distributions. EDS spectra confirms the presence of constituent elements and transition metal ions in the prepared phosphor materials. TEM measurements also confirmed the nanocrystalline nature of prepared samples. The PL spectra of prepared nanophosphors exhibit various emission bands which correspond to different regions like UV, blue, green, red, orange and white regions.The evaluated CIE and CCT coordinates shows that the prepared phosphor materials are useful for W-LEDs, electroluminescence panels and plasma display devices.

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