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Doping-Concentration Dependence of the Luminescence of Mn^{2+} Activated Calcium Aluminate Nanoparticles

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Abstract

Mn^{2+} doped $CaAl_2O_4$ nanoparticles were prepared by the solid state reaction method –the slurry in water approach. The crystal structures determined by XRD were monoclinic. Photoluminescence emission investigation at 465 nm excitation showed blue-green emission with emission color been doping-concentration dependent. Photoluminescence emission intensity decreased at twice doping ratio but increased at triple doping concentration. Crystal size of the nanoparticles decreased with temperature from 40.17 nm to 20.06 nm.

Keywords: Photoluminescence**,** phosphorescence**,** rare earth, transition metals.

Introduction

The phenomenon of persistent luminescence had been known to mankind for over a thousand years[1,2]. Since then**,** efforts are been made by scientists into finding more and better ways of harnessing this nanomaterials which have a wide range of technological applications. According to[3] the demand for economically viable phosphors for newly emerging display devices is on the increase with present technological advancements.

Rare earth and non-rare earth activated inorganic phosphors have great potential applications such as luminous paints, radiation dosimetry, x-ray imaging, color display, light emitting diodes, solar energy conservation, photonics, optoelectronics and biomedical engineering[4-8]. The phosphors find major applications in fluorescence lamps and display devices such as Electroluminescent Panels (ELP), Field Emission Displays (FED), Plasma Display Panels (PDP), and so on[3,4,9,10]. These interesting areas of application of phosphors have spurred researchers into finding new methods of synthesis and new ways of manipulating the phosphors through variables to arrive at unique characteristics for deeper applications.

Alkaline earth aluminates materials, doped rare earth and transition metal ions can be synthesized by many methods[11] such as solid state reaction, sol-gel, hydrothermal, co-precipitation, pechini and combustion method[9,12]. Solid state reaction is the most popular method used in the preparation of commercial luminescence phosphors as it is easily reproducible and amenable to large scale production[13].

Persistent phosphor rare-earth-doped aluminates and silicates such as $CaAl_2O_4$: Eu^{2+}, Nd^{3+}, $CaAl_2O_4$: Eu^{2+}, Dy^{3+}, $CaAl_2O_4$: Tb^{3+}, Ce^{3+}, $CaAl_2O_4$: Eu^{2+}, Nd^{3+}, Dy^{3+}, $CaAl_{12}O_{19}$: Eu^{2+}, $SrAl_2O_4$: Eu^{2+}, Dy^{3+}, $CaAl_2O_4$: Eu^{2+}, and silicates $R_3MgSi_2O_8$: Eu^{2+}, Dy^{3+} (R = Ca, Sr, Ba) have been prepared because of their phosphorescence and improved chemical stability[9,14-18].

The stabilization of Mn^{2+} in host compounds has also been extensively studied. Mn can be stabilized in host lattice in divalent, trivalent, and tetravalent oxidation states[3]. Mn^{2+} luminescence can be useful in obtaining a low cost blue, green or red emitting phosphor. A great number of publications have emerged in recent years relating to the synthesis and luminescence investigation of Mn^{2+} doped aluminates. For example, Mn^{2+} emission has been investigated in $CaAl_2O_4$: Mn^{2+} [4,17], $CaAl_{12}O_{19}$: Mn^{2+} [3], $LiBaF_3$:Mn^{2+}, $SrAl_20_4$:Mn^{2+} [18], $RbCaF_3$: Mn^{2+} [19], ZnS:Mn^{2+} [2,20]. We can infer that several studies are been made on the luminescence of Mn^{2+} in many host lattices. Although little or no investigation is made on the effect of doping concentration levels on the luminescence of Mn^{2+} doped monocalcium aluminate nanocrystals. It is therefore a part of our interest to study the effect of dopant concentration levels on the luminescence of $CaAl_2O_4$: Mn^{2+}.

Materials and Methods

Analytical grade 18.60g $CaCO_3$, 20.40g Al_2O_3, 0.78g CaF_3 and 0.4mol% Mn in $MnCO_3$ were slurred in a solution of urea for 20 minutes and left to dry in air. The mixture was crushed into powder in a mortar, poured into crucibles and fired in air using a muffle furnace at 1300^0C and 1000^0C for one hour. The ash was then grounded and washed with 4.0g NH_4Cl in 0.25L of water to remove impurities and left to dry in air. The as-synthesized phosphor was then poured in sample bottles for characterization. Three samples were prepared at different dopant concentrations, namely: sample E1 ($CaAl_2O_4$:Mn^{2+}-0.4mol% annealed at 1300^0C), sample E2 ($CaAl_2O_4$:Mn^{2+}-0.8mol% calcined at 1300^0C), and sample E3 ($CaAl_2O_4$:Mn^{2+}-1.2mol% fired at 1000^0C). The as-prepared nanoparticles were characterized for structural identification using X-ray diffractometer PW3050/60

by PANanalytical. Photoluminescence measurements were carried out using photoluminescence spectrometer (PLS) Perking-Elmer LS-55.

Results and Discussion

Structural Study: X- ray diffraction pattern of the $CaAl_2O_4:Mn^{2+}$ nanocrystals are as shown in Figure-1 to Figure-3. The diffraction peaks match with all the planes which can be indexed to the pure monoclinic structure with average crystal sizes of 40.17 nm for E1 and E2, and 20.06 nm for E3. Similar peaks have also been reported in[3] according to the JCPDS file no. 88-2477 in[21]. The particle size was observed to be temperature dependent, with a low crystal size obtained at 1000^0C.

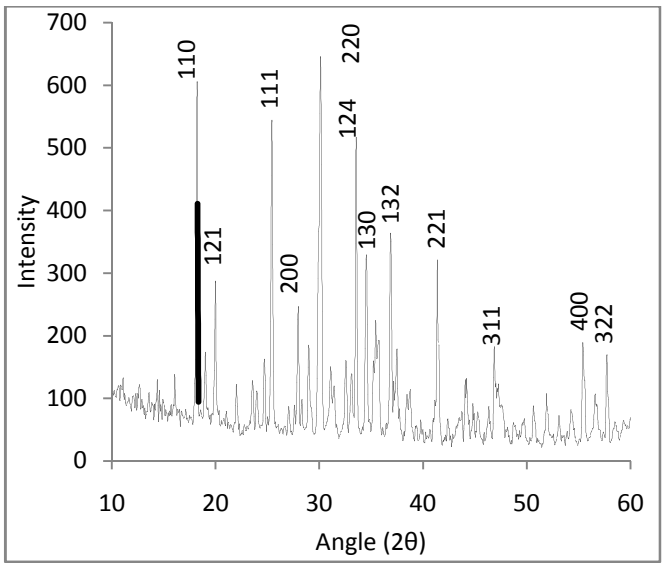

Figure-1
XRD pattern of $CaAl_2O_4:Mn^{2+}$-0.4mol%

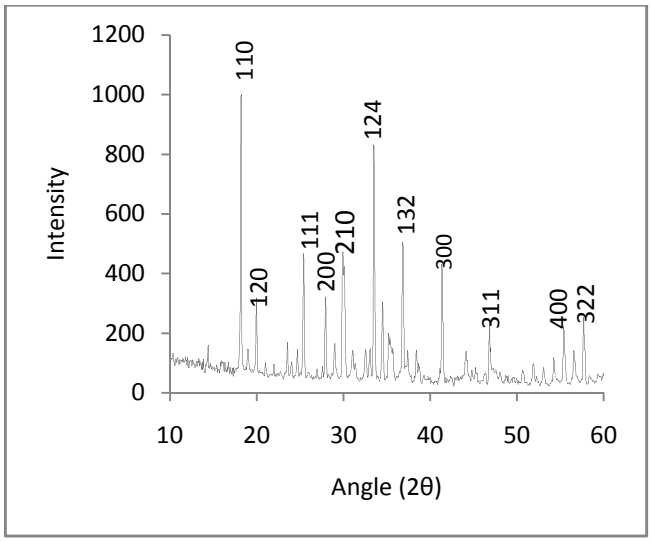

Figure-2
XRD pattern of $CaAl_2O_4:Mn^{2+}$-0.8mol%

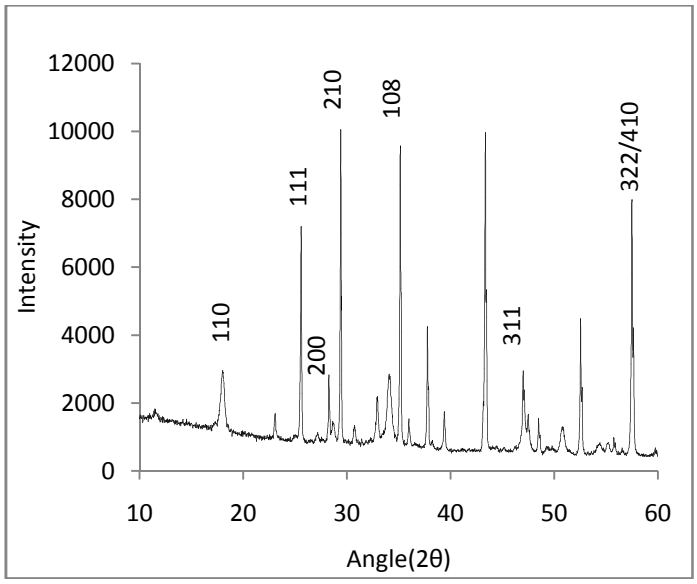

Figure-3
XRD pattern of $CaAl_2O_4:Mn^{2+}$-1.2mol%

Photoluminescence Study: The introduction and stabilization of Mn ions in the nanomaterials was confirmed by the luminescence investigations. The photoluminescence emission spectra of the samples with 465nm (2.67eV) excitation are shown in Figure-4. The emission spectra reveal peaks at 474 nm for E1, 479 nm for E3, and 510 nm, 557 nm for E2. The emission wavelengths fall within the blue-green (450-570) nm range of the electromagnetic spectrum. It was observed that the emission color of the nanocrystals is dependent on doping concentration. Recombination of the impurity sites led to green emission with low intensity for E2 while isolated luminescence centers gave blue emission with high intensity for E1 and E3. Similar blue-green emission was also recorded from $CaAl_2O_4:Mn^{2+}$ prepared by the solid state reaction technique[3,17].

The photoluminescence emission intensities of $CaAl_2O_4:Mn^{2+}$ nanostructure were observed to vary with dopant concentrations of 0.4mol% Mn^{2+}, 0.8mol% Mn^{2+} and 1.2mol% Mn^{2+}. It was observed that the photoluminescence emission intensity 2.21×10^7 at doping level of 0.4mol% Mn^{2+} decreased to 4.30×10^6 at doping level of 0.8mol% Mn^{2+} and sharply increased to 2.21×10^7 at doping concentration of 1.2mol% Mn^{2+}. A similar kind of behavior was also reported in[22] while studying ZnS:Al, Cu at different Al,Cu-doping concentration levels. The emission wavelengths of 474 and 479 nm can be traced to transitions between $^4E_g(G) + {}^4A_{1g}(G)$ and $^4T_{2g}(G)$ of Mn^{2+}; while 510 and 557 nm can be attributed to $^4T_{2g}(G)$ and $^4T_{1g}(G)$ transitions of Mn^{2+}.

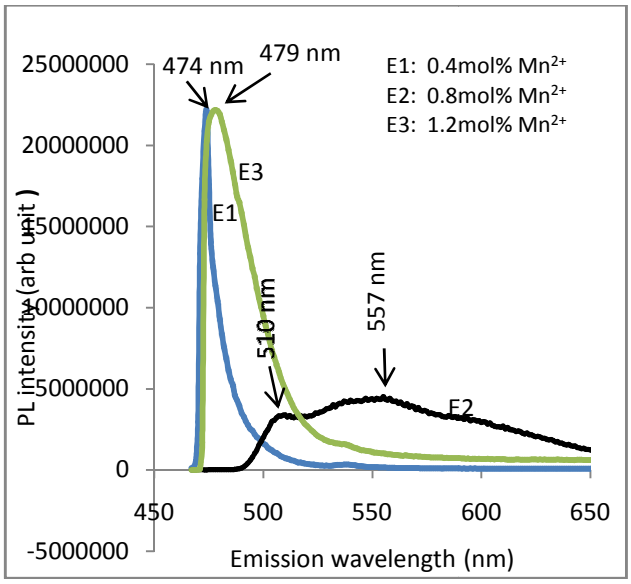

Figure-4
Photoluminescence emission spectra of $CaAl_2O_4$: Mn^{2+} at 465 nm excitation

Conclusion

It has been established that Mn was stabilized as Mn^{2+} in the $CaAl_2O_4$ nanocrystal lattice. The $CaAl_2O_4$:Mn^{2+} fluorescence material is monoclinic in crystal structure with light emitting in the blue-green region of the electromagnetic spectrum. The emission color is observed to be doping-concentration dependent. Photoluminescence emission intensity was found to decrease with double dopant concentration but increase with triple dopant concentration. The crystal size of the nanocrystals decreased with temperature from 40.17 nm at 1300^0C to 20.06 nm at 1000^0C.

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