Chapter 5

Influence of Pb$^{2+}$ doping on photoluminescence properties CaSiO$_3$: Mn$^{2+}$ nanophosphor
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Table of Contents

5.1 Introduction 144
5.2 Synthesis of CaSiO$_3$:Pb$^{2+}$, Mn$^{2+}$ phosphor 145
5.3 Results and discussion 147
  5.3.1 Powder X-ray diffraction 147
  5.3.2 Scanning electron microscopy 150
  5.3.3 Transmission electron microscopy 151
  5.3.4 Fourier transform infrared spectroscopy 152
  5.3.5 UV-Visible absorption 153
  5.3.6 Photoluminescence studies 154
  5.3.6.1 Racah parameter calculation for Mn$^{2+}$ 157
5.4 Conclusions 160
5.1. Introduction

The research on low cost luminescence material which has more stable is a challenging task. A large number of phosphors which can excited by X-rays, ultra–violet radiation of shorter wavelengths cannot be excited by ultra–violet radiation of longer wavelengths, because they do not absorb this radiation. To make excitation of longer wavelength region by the incorporation of suitable sensitizer [205]. Transition metal ions have been largely used as luminescent materials, in recent years silicate based phosphors have been paid considerable attention because they are resistant to acid, alkali and oxygen. Rare earth doped silicate phosphor materials had been discussed in larger extent but transition metal ion doped silicate phosphors are reported very few, hence we chosen lead (Pb) and manganese (Mn) as dopants in calcium silicate. Manganese ions are good candidates as activators in phosphors because they can have higher luminescence intensity, emit broadband visible light and higher quenching concentration. A lack in response of CaSiO$_3$:Mn$^{2+}$ is indicated by qualitative absorption experiments upto 254 nm excitation and is due to the absence of absorption for this radiation. The introduction of lead as an auxiliary impurity makes possible the excitation of CaSiO$_3$: Mn$^{2+}$ by radiation, here lead acts as a sensitizer for the manganese by introducing an absorption band in the vicinity of 254 nm [206]. The divalent
manganese ion (Mn$^{2+}$) acting as an activator and the energy states of incorporated atoms are depended on surroundings.

Mn$^{2+}$, Pb$^{2+}$ doped CaSiO$_3$ nano powders had been synthesised by low temperature solution combustion method. This method became an unique to obtain a fine particles with high surface area which involves rapid heating of an aqueous redox mixture containing stoichiometric amounts of corresponding metal nitrates and diformal hydrazine [DFH] as a fuel [207, 208]. Therefore we are interested to synthesis, Mn$^{2+}$, Pb$^{2+}$ doped CaSiO$_3$ nanophosphor by solution combustion method. The obtained nano phosphor powders are characterised by powder X-ray diffraction [PXRD], SEM, TEM, FTIR, Optical absorption and PL studies.

**5.2 Synthesis of CaSiO$_3$:Pb$^{2+}$, Mn$^{2+}$ phosphor**

The calculation of the stoichiometry of the redox mixture used for combustion process was done using the total oxidizing reducing valencies of the ingredients as the stoichiometric balance that requires numerical co-efficients is provided by this so that the energy released by the combustion is maximum and equivalence ratio is unity. The starting materials used for preparation of CaSiO$_3$:Pb$^{2+}$Mn$^{2+}$ phosphor powders were analar grade of calcium nitrate (Ca(NO$_3$)$_2$ 4H$_2$O), fumed silica (SiO$_2$, surface area 200 m$^2$/gm), lead nitrate (Pb(NO$_3$)$_2$) and manganese nitrate (Mn(NO$_3$)$_2$).
The fuel Diformyl hydrazine (C$_2$H$_4$N$_2$O$_2$, DFH) was used for combustion synthesis. Calcium nitrate, lead nitrate, manganese nitrate and DFH was dissolved in a minimum quantity of water in a cylindrical Petri dish of 300 ml capacity, to this fumed silica is added and dispersed well using magnetic stirrer about 10-150 minutes. The heterogeneous mixture was rapidly heated in a muffle furnace maintained at 500 °C. DFH is a good fuel like other N-N bonded hydrazine derivatives. These gaseous products
are formed by the decomposition of metal nitrates are hypergolic at 400 - 500° C. The redox mixture when heated at 500°C boils froths and finally dehydrates forming a gel, which ignites to yield voluminous CaSiO₃:Pb²⁺, Mn²⁺ powder. The entire combustion process was complete in short interval of time say about 5-10 minutes. In Fig 5.1 shows the detailed flow chart of the combustion process.

5.3. Results and discussion

5.3.1 Powder X-ray Diffraction

Fig 5.2 shows the PXRD patterns of CaSiO₃:Pb²⁺, CaSiO₃:Mn²⁺ and CaSiO₃:Pb²⁺ Mn²⁺ doped and codoped samples calcined at 950° C for 3h respectively. All diffraction peaks are in good agreement with typical phase of β-CaSiO₃ (JCPDS file No.72–2284) and space group p-1(2)/a [209]. No additional peaks corresponding to any secondary or impurity phase were observed. Thus, it is clear that the formed CaSiO₃:Pb²⁺, CaSiO₃:Mn²⁺ and CaSiO₃:Pb²⁺ Mn²⁺ are in singular phase.
Fig 5.2. PXRD patterns of (a) Ca_{0.95}Pb_{0.05}SiO_{3} (b) Ca_{0.95}Mn_{0.05}SiO_{3} (c) Ca_{0.90}Pb_{0.05}Mn_{0.05}SiO_{3}

It is found that as dopants (Pb^{2+}, Mn^{2+}) concentration are in smaller quantities compared to host therefore no significant changes in the PXRD profiles.

The average crystallite size of an doped samples (950° C for 3h) calculated from full width at Half maximum (FWHM) of the diffraction peaks by Scherrer’s formula [Ref. Eqn 2.3, chapter-2]. The strongest diffraction peak (202) (320) (521) are chosen for the calculation of an average crystallite size of the phosphor and it is found to be in the range of 20-38 nm. The grain size were also calculated from powder X-ray diffraction line broadening (B) using the analysis described by Williamson and Hall (W-H) method [Ref. Eqn 2.4, chapter-2]. The equation represents
a straight line between $4\sin\theta$ along x-axis and $\beta \cos\theta$ along y-axis. The slope of the line gives the strain ($\varepsilon$) intercept ($\lambda \, D$) on the y-axis gives the grain size ($D$), hence the $D$ values are tabulated in Table 5.1.

![Williamson-Hall plots](image)

**Fig 5.3.** Williamson-Hall plots of (a) Ca$_{0.95}$Pb$_{0.05}$SiO$_3$ (b) Ca$_{0.95}$Mn$_{0.05}$SiO$_3$ (c) Ca$_{0.90}$Pb$_{0.05}$Mn$_{0.05}$SiO$_3$

The crystallite size values calculated by D-S formula and W-H method are not similar because in Scherrer’s formula strain component is assumed to be zero.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Crystallite size (nm)</th>
<th>Band gap (eV)</th>
<th>Strain x10$^{-3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcined 950° C (3h)</td>
<td>Scherer's method (d)</td>
<td>W-H method (D)</td>
<td></td>
</tr>
<tr>
<td>Ca$<em>{0.95}$Pb$</em>{0.05}$SiO$_3$</td>
<td>24</td>
<td>28</td>
<td>5.54</td>
</tr>
<tr>
<td>Ca$<em>{0.95}$Mn$</em>{0.05}$SiO$_3$</td>
<td>26</td>
<td>25</td>
<td>5.86</td>
</tr>
<tr>
<td>Ca$<em>{0.90}$Pb$</em>{0.05}$Mn$_{0.05}$SiO$_3$</td>
<td>35</td>
<td>34</td>
<td>5.1</td>
</tr>
</tbody>
</table>
Table 5.1. Estimated values of Crystallite size (D) by W-H plots, Scherer’s formula, strains and band gap of undoped and different concentration of Pb, Mn doped CaSiO$_3$.

The calculated values of D from W-H plots and Scherer’s formula and the corresponding strains of undoped and different concentration of Pb, Mn doped CaSiO$_3$ are presented in Table 5.1.

**5.3.2 Scanning electron microscopy (SEM).**

![SEM micrographs](image)

**Fig. 5.4.** SEM micrographs of (a) Ca$_{0.95}$Pb$_{0.05}$SiO$_3$ (b) Ca$_{0.95}$Mn$_{0.05}$SiO$_3$ (c and d) Ca$_{0.95}$Pb$_{0.05}$Mn$_{0.05}$SiO$_3$

**Fig. 5.3.** shows SEM micrographs of CaSiO$_3$: Pb$^{2+}$, CaSiO$_3$: Mn$^{2+}$ and CaSiO$_3$: Pb$^{2+}$ Mn$^{2+}$. It reveals voluminous mesoporous structure contains
several voids and pores with an irregular shapes of crystallites. When dopant concentration increases, the porous nature of the phosphor powder also increases.

5.3.3 Transmission electron microscopy (TEM)

TEM images of CaSiO$_3$:Pb$^{2+}$ Mn$^{2+}$ sample calcinated at 950$^\circ$ C, 3h as shown in Fig 5.4. The observation that the crystallites are irregular in shape and size, the mean diameters of the particles are 200 nm [210]. The mean crystallite size were calculated using Scherrer’s formula and W-H method are nearly equal to the observation done in TEM micrographs.

Fig.5.5. TEM Image of Ca$_{0.90}$Pb$_{0.05}$Mn$_{0.05}$SiO$_3$
5.3.4 Fourier transform infrared spectroscopy

The FTIR spectra of CaSiO$_3$ Pb$^{2+}$, CaSiO$_3$ Mn$^{2+}$, CaSiO$_3$: Pb$^{2+}$ Mn$^{2+}$ nano powders were recorded in order to interpret the structure of the obtained samples in fig.5.5. The IR-spectroscopic data analysis confirms the peaks at 464, 567, 645, 964 cm$^{-1}$ are due to β-CaSiO$_3$ [211, 212]. The existence of Ca-o in the structure gives rise to the peak at 1460 cm$^{-1}$.

![FTIR Spectra](image)

**Fig.5.6.** FTIR Spectra of (a) Ca$_{0.95}$Pb$_{0.05}$SiO$_3$ (b) Ca$_{0.95}$Mn$_{0.05}$SiO$_3$

(c) Ca$_{0.90}$Pb$_{0.05}$Mn$_{0.05}$SiO$_3$

The presence of CH$_3$, CH$_2$ group is indicated by the absorption peak at 2400 cm$^{-1}$ and the absorption band at 3430 cm$^{-1}$ is due to stretching of OH groups of water molecules coordinated at metals [213].
5.3.5 UV-Visible absorption and energy gap

The UV-Vis absorption spectra of an undoped and Pb$^{2+}$, Mn$^{2+}$ doped CaSiO$_3$ was recorded by using UV-Vis absorption spectroscopy in Fig 5.7. An intense absorption band at 240-270 nm which corresponding to oxygen to silicon (O-Si) ligand - to- metal charge-transfer (LMCT) in the SiO$_3^{2-}$ group [214]. The optical energy gap $E_g$ of CaSiO$_3$, CaSiO$_3$ Pb$^{2+}$, Mn$^{2+}$ and CaSiO$_3$ Pb$^{2+}$ Mn$^2$ doped samples were calculated using [Ref.Eqn 2.5, chapter 2] Tauc relation [215] and shown in Fig.5.8.

![Absorption Spectra](image)

Fig.5.7. UV-Vis absorption spectra of (a) Ca$_{0.95}$Pb$_{0.05}$SiO$_3$ (b) Ca$_{0.95}$Mn$_{0.05}$SiO$_3$ (c) Ca$_{0.90}$Pb$_{0.05}$Mn$_{0.05}$SiO$_3$

The observations from the present data reflects that the plots of $(\alpha E)^n$ against $h\nu$ give linear relations which are the correct fitted for the W-H equation with $n=2$ for the samples. Inter band transitions occurs due to
allow direct transition is in the samples. The optical band gap energy for the samples is found to be in the range of 5.24 - 5.88 eV. Pb\(^{2+}\), Mn\(^{2+}\) doped samples are 5.24, 5.54 eV and Pb\(^{2+}\) Mn\(^{2+}\) doped sample is 5.88 eV these are well matched with the reported literature.

![Graph showing optical band gap](image)

**Fig.5.8.** Optical band gap of (a) Ca\(_{0.95}\)Pb\(_{0.05}\)SiO\(_3\) (b) Ca\(_{0.95}\)Mn\(_{0.05}\)SiO\(_3\)

(c) Ca\(_{0.95}\)Pb\(_{0.05}\)Mn\(_{0.05}\)SiO\(_3\)

### 5.3.6 Photoluminescence Studies

In order study the effect of Pb\(^{2+}\) on the luminescence behaviour of Mn\(^{2+}\) doped CaSiO\(_3\), the photo excited luminescence properties of single Pb\(^{2+}\) doped, Mn\(^{2+}\) doped as well as the Pb\(^{2+}\) Mn\(^{2+}\) co-doped phosphor were studied. Fig 5.9(a) and (b) depicts the excitation and emission spectra of CaSiO\(_3\); Pb\(^{2+}\), under 256 nm excitation, the emission spectrum displays a
strong band at 376 nm and shoulder peaks with very less intensity at 472 nm and 532 nm [216].

When Pb$^{2+}$ is doped into CaSiO$_3$, the Pb$^{2+}$ ions substitute for Ca$^{2+}$ ions, since the ionic radius of Ca$^{2+}$ ion is 1 Å and Pb$^{2+}$ ion is 1.19 Å. When Pb$^{2+}$ ion is placed in lattice, the Pb$^{2+}$ ions at seven co-ordinated sites gives the emission band at shorter wavelength, while another band may be responsible for Pb$^{2+}$ ions at the six co-ordinated sites. Usually Pb$^{2+}$ ions in the β-CaSiO$_3$ effectively dispersed in the matrix, hence the interaction between the neighbouring Pb$^{2+}$ ions must be relatively less in strength [217-219]. Therefore the observed emission of Pb$^{2+}$ (376 nm) in present study can be attributed to the interaction between Pb$^{2+}$ ion and the host lattice (CaSiO$_3$). Similar kind of results were also reported by K. Macchide et.al [220] in their study on luminescence property of Pb$^{2+}$ doped CaSiO$_3$.

Fig.5.9. PL Spectra of Ca$_{0.95}$Pb$_{0.05}$SiO$_3$ (a) excitation (b) emission
Fig. 5.10(a) and (b) depicts the luminescence behavior of Mn$^{2+}$ ions in CaSiO$_3$. The excitation spectra Fig.5.10(a) recorded by monitoring emission at 600 nm shows peaks at 364 nm and 480 nm corresponding to the transitions from $^6A_1 \rightarrow ^4T_2$ and $^6A_1 \rightarrow ^4E$ respectively.

The luminescence properties of the nanopowder are strongly dependent on the crystal structure of the host material. In the present study the luminescence emission is driven by the transition of 3d$^5$ of Mn$^{2+}$ ions corresponding to $^4T_1 \rightarrow ^6A_1$ relaxation [220-222]. The luminescence behaviors of the Mn$^{2+}$ activator have been extensively studied by many researchers [223-225]. The color emission of the Mn$^{2+}$ ions strongly depends on the relevant crystal field environment. Due weak crystal field formation the tetrahedrally coordinated Mn$^{2+}$ ion gives a green emission. In contrast, yellow to red emission is associated with octahedrally coordinated Mn$^{2+}$ and a comparatively strong crystal field [226]. Therefore the observed emission (~590 nm) in the current PL spectrum is attributed to octahedrally coordinated Mn$^{2+}$ ions and is assigned to $^4T_1 \rightarrow ^6A_1$ transition.
Fig. 5.10. PL Spectra of Ca$_{0.95}$Mn$_{0.05}$SiO$_3$ (a) excitation (b) emission

5. 3. 6. 1 Solving for Racah parameters.

The total repulsion between the electrons is expressed in terms of Racah parameters $A$, $B$ and $C$. If an atom has more than one electron there will be some electrostatic repulsion between them, it varies from atom to atom. The values of $A$, $B$ and $C$ describes the effects of electron – electron repulsion within the crystal lattices. Here, $A$ is ignored because it is roughly the same for any metal center and $C$ is approximately 3.7 to 4.1 times of $B$. The most important parameter $B$ signifies the approximation of the bond strength between the ligand and metal. This parameter $B$ can be calculated by measuring $\Delta E$, the energy difference between the $^4T_1$ and the $^4T_2$ energy states from the absorption spectrum in Fig. 5.7(a). From the experimentally derived optical absorption spectrum spectra the $\Delta E$ (6052 cm$^{-1}$) that corresponds to energy difference between $\gamma_1$- 403 nm (24813 cm$^{-1}$) and $\gamma_2$ = 533 nm
(18761 cm\(^{-1}\)) was calculated. Using the equation 4.1, 4.2 and 4.3 (Ref. Chapter 4), the Dq, Racah parameters B and C have been experimentally determined to be 1876 cm\(^{-1}\), 571 cm\(^{-1}\) and 3241 cm\(^{-1}\) respectively for CaSiO\(_3\):Mn\(^{2+}\). The strength of tetrahedral field (Dq/B) is calculated to be 3.28 [227]. The crystal field is weak then the values of Dq/B are lies between 2.5 to 3.5. This value indicates that manganese ion is in tetrahedral field. Comparison of free ions Racah parameter in free ion and in crystal gives the strength of Nephelauxetic ratio. The B value for free ion is 900 cm\(^{-1}\) [228]. Whereas for CaSiO\(_3\):Mn\(^{2+}\) it is 571 cm\(^{-1}\). This shows that there is 37% reduction in the Racah parameter indicating the moderate Nephelauxetic effect.

Aiming to investigate the effect of co-doping Pb\(^{2+}\) with the CaSiO\(_3\):Mn\(^{2+}\), we have synthesized a sample with the chemical composition Ca\(_{0.9}\)Pb\(_{0.05}\)Mn\(_{0.05}\)SiO\(_3\). Fig 5.11(b) shows the emission spectra of Pb\(^{2+}\) doped CaSiO\(_3\):Mn. Under 254 nm excitation it shows two dominant emission peaks corresponding to the characteristic
Fig 5.11. PL Spectra of Ca$_{0.90}$Pb$_{0.05}$Mn$_{0.05}$SiO$_3$

(a) Excited Spectra at 254 nm (b) Emission spectra.

emission of Pb$^{2+}$ at 350 nm, and it originates from $^3P_1 \rightarrow ^1S_0$ optical transition along with characteristic emission of Mn$^{2+}$ at 630 nm ($4T_1 \rightarrow ^6A_1$ transition). Mn$^{2+}$ cannot absorb energy competently but it can be excited by the dipole allowed transition of Pb$^{2+}$ and the excitation transition is parity forbidden but spin allowed [229]. CaSiO$_3$ co-doped
Pb$^{2+}$ Mn$^{2+}$ shows the same absorption behavior as CaSiO$_3$: Pb$^{2+}$. Further it is fascinating to note that there is red shift in the emission spectrum of Pb$^{2+}$ co-doped sample. In contrast to the emission band at 590 nm in CaSiO$_3$:Mn$_{0.05}$ sample, emission band is shifted to higher wavelength region when Pb$^{2+}$ is doped into the system [230]. This shift is attributed to crystal field effects that come into picture in presence of Pb$^{2+}$. When Pb$^{2+}$ is substituted for Ca$^{2+}$ stronger crystal field can be expected and the red shift of Mn$^{2+}$ emission can occur [231]. In Fig.5.11b the emission peaks at 655 nm which confirms that the Mn$^{2+}$ ions possess octahedral coordination.

5.4 Conclusion

CaSiO$_3$:Pb$^{2+}$, CaSiO$_3$:Mn$^{2+}$ and CaSiO$_3$:Pb$^{2+}$ Mn$^{2+}$ doped and codoped samples have been prepared and emission spectrum of 5 mol% Pb$^{2+}$ and 5 mol% Mn$^{2+}$ doped CaSiO$_3$ are investigated. Pb$^{2+}$ gives violet-blue sharp emission peak at 376 nm under 256 nm excitation. The interaction between Pb$^{2+}$ ion and host lattice gives rise to emission from Pb$^{2+}$, it seems that ionic radius of Ca$^{2+}$ ion is 1Å and Pb$^{2+}$ ion is 1.19 Å. The observed emission peaks in the CaSiO$_3$:Mn$^{2+}$ at 592 nm can be attributed to the transitions from $^4T_1 \rightarrow ^6A_1$. Dq/B value indicates that manganese ion is in tetrahedral field. CaSiO$_3$: Pb$^{2+}$Mn$^{2+}$ excited at 254 nm and we observed two prominent emission peaks at 35 nm and 655 nm. CaSiO$_3$ activated with manganese and lead gives an orange-red emission.
There will be energy transfer between Pb$^{2+}$ to Mn$^{2+}$ because the coordination of the CaSiO$_3$:Pb$^{2+}$Mn$^{2+}$ changes from tetrahedral to octahedral. Hence it gives red-orange emission at 655 nm.