Manganese doped nanocrystalline willemite powder phosphors \( \text{Zn}_2\text{MnSiO}_4 \) (\( 0.1 \leq x \leq 0.5 \)) have been synthesized by a low-temperature initiated, self-propagating, gas producing solution combustion process. The phosphors have been characterized by using x-ray diffraction (XRD), energy dispersive spectroscopy, scanning electron microscopy, Fourier transform infrared spectroscopy (FTIR), electron paramagnetic resonance (EPR), and photo luminescence (PL) spectroscopic techniques. The lattice parameters calculated from XRD confirm that \( \text{Zn}_2\text{MnSiO}_4 \) has a rhombohedral space group \( R3H \). The XRD patterns confirm that \( \text{Zn}_2\text{MnSiO}_4 \) phosphor samples undergo a phase transformation from \( \beta \)-willemite to \( \alpha \)-willemite phase at 950 °C. The EPR spectra of \( \text{Mn}^{2+} \) ions exhibit resonance signals at \( g \approx 3.24 \) and \( g \approx 2.02 \), with a sextet hyperfine structure centered around \( g \approx 2.02 \). The EPR signals of \( \text{Mn}^{2+} \) give a clear indication of the presence of two different \( \text{Mn}^{2+} \) sites. The magnitude of the hyperfine splitting (A) indicates that the \( \text{Mn}^{2+} \) is in an ionic environment. The number of spins participating in resonance (N), the paramagnetic susceptibility (\( \chi \)), and the zero-field splitting parameter (\( D \)) have been evaluated as function of \( x \). It is interesting to observe that the variation of \( N \) with temperature obeys Boltzmann. The paramagnetic susceptibility is calculated from the EPR data at various temperatures and the Curie constant and Curie paramagnetic temperature was evaluated from the \( 1/N \) versus \( T \) graph. The luminescence of \( \text{Mn}^{2+} \) ion in \( \text{Zn}_2\text{SiO}_4 \) shows a strong green emission peak around 520 nm from the synthesized phosphor particles under UV excitation (251 nm). The luminescence is assigned to a transition from the upper \( 4T_1 \rightarrow 6A_1 \) ground state. The mechanism involved in the generation of a green emission has been explained in detail. The effect of Mn content on luminescence has also been studied.

I. INTRODUCTION

Willemite (\( \alpha \)-\( \text{Zn}_2\text{SiO}_4 \)), with phenacite structure occurs naturally and belongs to the group of orthosilicates.\(^4\) Willemite possesses a wide range of applications such as phosphor host,\(^2,3\) electrical insulators,\(^4\) glazes and pigments,\(^5,6\) and is also an important component in glass ceramics.\(^7\) Mn-activated willemite (\( \text{Zn}_2\text{SiO}_4 \cdot \text{Mn} \)) is an efficient green phosphor, and it has attracted many researchers for its potential applications to various types of display panels such as plasma display panel (PDP), vacuum fluorescent display (VFD), and field emission display (FED).\(^8\)\(^\text{–}11\) For enhancing the brightness and resolution of these displays, it is important to synthesize phosphors with high quantum efficiency, controlled morphology and small particle sizes, either amorphous or crystalline is of interest. It is also used as a luminescent material for lamp and cathode ray tubes (CRTs) because of its luminescent efficiency and chemical stability.\(^12\) It has also been tested in thin film electroluminescent (EL) devices\(^13\) and medical imaging radiation detectors.\(^14\)

In spite of wide range of applications only limited literature is available on the synthesis and characterization of these materials. Owing to the less attention given in the past and considering its practical importance, the authors decided to extend the studies on the synthesis, characterization, and microstructure of the willemite phosphors. The conventional methods of mechanical mixing of component oxides or precursors and their subsequent reaction at elevated temperatures\(^12,15\) for the preparation of inorganic materials are currently giving way to the newer processing methods with solutions and sols as starting materials. Such starting materials when carefully used, satisfy all the requirements of homogeneity, chemical purity of phases and low processing...
temperatures besides fine particle size with uniform size distribution and large surface area of the synthesized phases.\textsuperscript{16,17} The other methods like r.f. magnetron sputtering,\textsuperscript{12} sol-gel process,\textsuperscript{18,19} single polymer precursor route,\textsuperscript{20} charge liquid cluster beam technique\textsuperscript{21} have also been reported in the literature.

The present work aims to synthesize nanosized crystalline \( \mathrm{Zn}_{x-1-1} \mathrm{Mn}_x \mathrm{SiO}_4 \) \((0.1 \leq x \leq 0.5)\) powder phosphors by a low temperature initiated, self-propagating, gas producing solution combustion process.\textsuperscript{22,23} The advantages of solution combustion method includes (a) well crystallized oxides can be obtained at shorter times, (b) it requires little or no further processing such as milling and firing, (c) there is substantial saving of energy as well as cost since the reaction is sustained by heat generated from the chemical reaction between metal nitrates and fuel. The synthesized powders have been characterized by using XRD, EDS, SEM, FTIR, EPR, and PL spectroscopic techniques and the results obtained are discussed in detail.

II. EXPERIMENT

A. Combustion synthesis of willemite phosphors

The starting materials \( \mathrm{Zn} (\mathrm{NO}_3)_2 \cdot 6\mathrm{H}_2\mathrm{O} \), silica fume (\( \mathrm{SiO}_2 \) surface area 200 m\(^2\)/g) were the source of Zn and Si used for combustion synthesis of willemite phosphor. Di-formyl hydrazine (\( \mathrm{C}_2\mathrm{H}_4\mathrm{N}_2\mathrm{O}_2 \), DFH) was used as a fuel for combustion synthesis which was prepared by the reaction of formic acid and hydrazine hydrate as described in the literature.\textsuperscript{24} \( \mathrm{Mn} (\mathrm{NO}_3)_2 \cdot 4\mathrm{H}_2\mathrm{O} \) is used as a source of Mn. All the chemicals used were of Analar grade quality.

B. Calculation of stoichiometry

The stoichiometry of the redox mixture used for the combustion has been calculated using the total oxidizing and reducing valencies of the compounds which serve as numerical coefficients for the stoichiometric balance so that the equivalent ratio (\( \phi_r \)) is unity and the energy released by the combustion is maximum.\textsuperscript{25} According to this concept, the valence of C\( = +4, \mathrm{H} = +1, \) divalent metal ions\( = +2, \) trivalent metal ions\( = +3, \) and O\( = -2. \) The valence of nitrogen is considered to be zero. Based on these considerations, the zinc nitrate has an oxidizing valence of \(-10\) and DFH (\( \mathrm{C}_2\mathrm{H}_4\mathrm{N}_2\mathrm{O}_2 \)) a reducing valence of \(+8\). The detailed calculation of stoichiometry has been reported elsewhere.\textsuperscript{25}

In the actual synthesis appropriate stoichiometry of \( \mathrm{Zn} (\mathrm{NO}_3)_2 \cdot 6\mathrm{H}_2\mathrm{O} \) and DFH were dissolved in a minimum quantity of water in a cylindrical petridish (100 mm diameter and 50 mm height) capacity. To this solution fumed silica was added and dispersed well. The heterogeneous redox mixture was rapidly heated by introducing into a muffle furnace maintained at \( 500 \pm 10^\circ\mathrm{C} \). The redox mixtures containing the metal nitrates, silica fume and DFH when rapidly heated around \( 500^\circ\mathrm{C} \), dehydrates forming a honeylike gel, which ignites to yield voluminous foamy willemite powder.

Theoretical equations assuming the complete combustion of the redox mixture used for the synthesis of willemite may be written as

\[
\begin{align*}
4\mathrm{Zn} (\mathrm{NO}_3)_2 (aq) + 2\mathrm{SiO}_2(s) + 5\mathrm{C}_2\mathrm{H}_4\mathrm{N}_2\mathrm{O}_2 (aq) & \quad (\text{DFH}) \\
& \rightarrow 2\mathrm{Zn}_2\mathrm{SiO}_4(s) + 9\mathrm{N}_2(g) + 10\mathrm{H}_2\mathrm{O}(g) + 10\mathrm{CO}_2(g). 
\end{align*}
\]

It is interesting to note that the combustion reaction was violent when fused \( \mathrm{SiO}_2 \) (particle size\( \approx 10 \mu\mathrm{m} \)) was used instead of fumed silica (particle size\( \approx 1 \mu\mathrm{m} \)) as source of silicon. The violent combustion reaction may be due to the noninvolvement of fused \( \mathrm{SiO}_2 \) with other constituents during combustion because of its large particle size as compared to fumed \( \mathrm{SiO}_2 \). The dispersed phase (fumed \( \mathrm{SiO}_2 \)) controls the violent reaction as the combustible gases get trapped in the pores of the foam. In the synthesis of Mn-doped samples, \( \mathrm{Mn} (\mathrm{NO}_3)_2 \cdot 4\mathrm{H}_2\mathrm{O} \) was added along with \( \mathrm{Zn} (\mathrm{NO}_3)_2 \cdot 4\mathrm{H}_2\mathrm{O} \).

C. Characterization of phosphors

An x-ray powder diffractometer (Philips PW 1050/70) using Cu \( K_a \) radiation with a Ni filter was used to estimate the crystallinity of the phases. The surface morphology, distribution of the grains and EDS (energy dispersive spectroscopy) of the samples were examined on a JEOL (JSM-840A) SEM. The FTIR spectral studies have been performed on a Perkin-Elmer spectrophotometer (spectrum 1000) with KBr pellets.

The EPR spectra were recorded at room temperature as well as at different temperatures using a JEOL-FE-1X ESR spectrometer operating in the X-band frequency (\( \approx 9.2 \) GHz) with a field modulation frequency of 100 kHz. The magnetic field was scanned from 0 to 500 mT and the microwave power used was 5 mW. A powdered specimen of 100 mg was taken in a quartz tube for EPR measurements. The EPR spectrum of \( \mathrm{Zn}_{1.50} \mathrm{Mn}_{0.50} \mathrm{SiO}_4 \) powder phosphor sample was recorded at different temperatures using a variable temperature controller (JES UCT 2AX). A temperature stability of \( \pm 1 \) K was easily obtained by waiting approximately half an hour at the set temperature before recording a spectrum at each temperature. Photoluminescent excitation and emission spectra were recorded with a Shimadzu spectrofluorophotometer (model RF 510) equipped with a 150 W xenon lamp as an
excitation source. The emission spectra were studied using an excitation wavelength of 251 nm.

III. RESULTS AND DISCUSSION

The powder x-ray diffraction patterns of undoped and doped willemite phosphors obtained by solution combustion process are shown in Figs. 1 and 2, respectively. The as-formed willemite powder is weakly crystalline with broad peaks corresponding to Zn$_2$SiO$_4$ along with ZnO (JCPDS No. 37-7485 and 37-1485) phases. On calcination (950 °C), the powders fully crystallize at the expense of ZnO to give a single phase Zn$_2$SiO$_4$ (Fig. 1). Similarly, the Mn doped willemite powders sintered at 950 °C show full crystallinity with small ZnO peak at low Mn doped, but it disappears in high doped powders as shown in Fig. 2. Most intense peaks at $d$ = 2.624, 2.823, and 3.465 Å do not vary significantly with Mn doping. This suggests crystallinity is therefore independent of Mn content. Table 1 lists the composition and lattice parameters of Zn$_{2-x}$Mn$_x$SiO$_4$ (0.1 $\leq x \leq$ 0.5) phosphors evaluated from the XRD patterns by using Rietveld analysis program Fullprof,$^{26}$ assuming the $R\bar{3}H$ space group. The analysis confirm that these powders have a rhombohedral space group ($R\bar{3}H$) and are in good agreement with those reported in literature.$^{27,28}$ The nominal compositions of the samples were also confirmed by EDS method.

The SEM micro graphs of Zn$_{2-x}$Mn$_x$SiO$_4$ ($x$ = 0.1 and 0.5) sintered (950 °C) (3 H) samples are shown in Fig. 3. The SEM morphology shows small and round shaped grains which are little bit agglomerated. On calcination the agglomeration size increases. The mean size measured from the scanning electron micrographs is about 0.2–1.2 μm. Also it is well known that the particles prepared using other techniques such as solid state, coprecipitate and hydrothermal are irregular in shape and large.$^{29-31}$ The use of spherical shape particles should increase screen brightness and improve the resolution due to lower scattering of the evolved light and higher packing densities than irregular shaped particles.$^{11}$ Using Scherrer’s formula,$^{32}$ the crystallite size of the samples was calculated from the XRD patterns also. The results show that the particles synthesized in the present investigations are $\approx$29 to 37 nm.

Figure 4 shows the FTIR spectra of the undoped willemite, as formed and calcined sample (950 °C). It is interesting to observe that as-formed samples exhibit $\beta$-willemite phase whereas calcined sample shows $\alpha$-willemite phase. This also supports our XRD studies (Fig. 1). Figure 5 shows the FTIR spectra of all the doped samples calcined at 950 °C which are in $\alpha$-willemite phase. It is observed that the main absorption peaks of this phosphor fall in the frequency region 350–1200 cm$^{-1}$. The IR bands and corresponding vibrational modes for willemite are 870 cm$^{-1}$ ($\nu_1$ SiO$_4$); 978, 934, and 900 cm$^{-1}$ ($\nu_3$ SiO$_4$); 460, 396, and 380 cm$^{-1}$ ($\nu_1$ SiO$_4$); 578 cm$^{-1}$ ($\nu_1$ ZnO$_4$); and 616 cm$^{-1}$ ($\nu_3$ ZnO$_4$), where $\nu_1$ corresponds to totally symmetric stretching, $\nu_3$ is asymmetric stretching and $\nu_4$ asymmetric deformation.$^{23,33,34}$ The absorption at 470 cm$^{-1}$ corresponds to ZnO stretching$^{35}$ and it is observed that the intensity of this absorption increases with increase of Mn content.

A. Electron paramagnetic resonance studies

The EPR spectroscopy has been used as a tool to elucidate the structural evolution of the materials. We used divalent Mn as a probe; Mn$^{2+}$ is a sensitive indicator of structural changes owing to its unshielded $d^5$ ions. Host-activator compositions are of considerable interest for elucidating the structure and bonding in vitreous (isotropic) and crystalline (anisotropic) systems. In undoped samples we have not ob-

FIG. 1. Powder XRD patterns of solution combustion derived undoped willemite (a) as-formed, (b) 500 °C (3 H), (c) 950 °C (3 H).

FIG. 2. Powder XRD patterns of solution combustion derived Zn$_{2-x}$Mn$_x$SiO$_4$ (0.1 $\leq x \leq$ 0.5) calcined at 950 °C (3 H) as a function of $x$. 
served EPR signal indicating that the starting materials used in the present work are free from paramagnetic impurities.

Figure 6 shows the EPR spectra of Mn$^{2+}$ doped Zn$_{2-}$.Mn$_{x}$SiO$_4$ (0.1$\leq x \leq$ 0.5) phosphors as a function of $x$. The EPR spectra of all the investigated samples exhibit a six-line hyperfine structure centered at $g \approx 2.02$ with a total peak width of $\approx 490$ G as shown in Fig. 6. The six-line hyperfine structure (hfs) arising at $g \approx 2.02$ is due to the interaction of electron spin of manganese ions with its own nuclear spin $I = 5/2$. In addition to this, a broad shoulder around $g \approx 3.24$ has also been observed. The observation of EPR signals of Mn$^{2+}$ give a clear indication of two kinds of Mn$^{2+}$ sites. Therefore the EPR spectrum of Mn$^{2+}$ ions is due to isolated Mn$^{2+}$ ions giving the six-line hyperfine structure plus a very broad line due to dipolar interaction between Mn$^{2+}$–Mn$^{2+}$ neighbors. An EPR study of Mn doped willemite by Perkins and Sienko$^{36}$ also indicated that both sites are accessible to Mn$^{2+}$.

Bulk Zn$_2$SiO$_4$ : Mn (at 950°C) crystallizes in phenacite structure and belongs to rhombohedral space group as both Zn$^{2+}$ and Si$^{4+}$ ions coordinated tetrahedrally to four oxygen atoms. There are two nonequivalent crystallographic Zn sites present in willemite both having nearest neighboring oxygen in a slightly distorted tetrahedral ($T_d$) configuration. Both sites are accessible to Mn$^{2+}$, since ionic radii of the two ions are very similar (0.74 Å for Zn$^{2+}$ and 0.80 Å for Mn$^{2+}$) and also due to the identical valency. Therefore the Mn ions doped Zn$_2$SiO$_4$ also have four-coordination (weak crystal field) because they replace some of the Zn$^{2+}$ ions in the lattice.$^2$

From EPR spectra, the spin-Hamiltonian parameters $g$ and $A$ have been evaluated. Table 2 gives some typical values of the hyperfine splitting ($A$) values for the Zn$_{2-}$.Mn$_{x}$SiO$_4$ (0.1$\leq x \leq$ 0.5) phosphors as a function of $x$ at room temperature. It is apparent from different average values of $A$ measured from peak to peak ($A_{pp}$) and trough to trough ($A_{tt}$) that the individual lines are strain broadened, leading to an asymmetry in the absorption spectrum.$^{37}$ The

<table>
<thead>
<tr>
<th>Sample</th>
<th>Crystal structure</th>
<th>Lattice parameters (Å)</th>
<th>Cell volume (Å$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$a$</td>
<td>$c$</td>
</tr>
<tr>
<td>Zn$<em>{1.90}$Mn$</em>{0.1}$SiO$_4$</td>
<td>$R\bar{3}H$</td>
<td>13.947(7)</td>
<td>9.313(3)</td>
</tr>
<tr>
<td>Zn$<em>{1.85}$Mn$</em>{0.15}$SiO$_4$</td>
<td>$R\bar{3}H$</td>
<td>13.953(6)</td>
<td>9.317(2)</td>
</tr>
<tr>
<td>Zn$<em>{1.80}$Mn$</em>{0.2}$SiO$_4$</td>
<td>$R\bar{3}H$</td>
<td>13.951(5)</td>
<td>9.316(2)</td>
</tr>
<tr>
<td>Zn$<em>{1.75}$Mn$</em>{0.25}$SiO$_4$</td>
<td>$R\bar{3}H$</td>
<td>13.948(6)</td>
<td>9.314(2)</td>
</tr>
<tr>
<td>Zn$<em>{1.70}$Mn$</em>{0.3}$SiO$_4$</td>
<td>$R\bar{3}H$</td>
<td>13.944(5)</td>
<td>9.312(2)</td>
</tr>
<tr>
<td>Zn$<em>{1.50}$Mn$</em>{0.5}$SiO$_4$</td>
<td>$R\bar{3}H$</td>
<td>13.946(5)</td>
<td>9.315(2)</td>
</tr>
</tbody>
</table>

FIG. 3. The SEM morphology of solution combustion derived Zn$_{2-}$.Mn$_{x}$SiO$_4$ samples calcined at 950°C (3 H) (a) $x = 0.1$, (b) $x = 0.5$.

FIG. 4. FTIR spectra of the solution combustion derived undoped willemite powders (a) as-formed and (b) calcined at (950°C) (3 H).
first derivative spectrum as a consequence, shows larger values of $A$, when measured trough to trough, rather than peak to peak. An overall average was calculated from

$$A_{\text{avg}} = \frac{(\Delta_{\text{Opp}} + \Delta_{\text{Ott}})/5 + (\Delta_{\text{Mpp}} + \Delta_{\text{Mtt}})/3 + (\Delta_{\text{Ipp}} + \Delta_{\text{Itt}})}/6,$$

where $\Delta_{\text{Opp}}$ and $\Delta_{\text{Ott}}$ represent the differences between the first and sixth peak positions, measured peak to peak and trough to trough respectively. $\Delta_{\text{Mpp}}$ and $\Delta_{\text{Mtt}}$ represents difference in positions between second and fifth peaks and $\Delta_{\text{Ipp}}$ and $\Delta_{\text{Itt}}$ between second and third peaks. It is interesting to note that, in all of the samples, $\Delta_{\text{Opp}}/5 \approx \Delta_{\text{Mpp}}/3 \approx \Delta_{\text{Ipp}}$ and $\Delta_{\text{Ott}}/5 \approx \Delta_{\text{Mtt}}/3 \approx \Delta_{\text{Itt}}$. This indicates that the $g$ value in each case is well behaved.\(^{37}\)

FIG. 6. The X-band EPR spectra of Zn$_{2-x}$Mn$_x$SiO$_4$ (0.1 $\leq x \leq$ 0.5) phosphor samples as a function of $x$ at room temperature.

The strength of the hyperfine splitting ($A$) depends on the matrix into which the ion is dissolved and is mainly determined by the electronegativity of the neighbors. This means a qualitative measure of the covalency of the bonding in the matrix which can be determined from the value of $A$; the smaller the splitting, the more covalent the bonding of the anion. The $g$ value for the hyperfine splitting is indicative of the nature of bonding in the matrix. If the $g$ value shows a negative shift with respect to 2.0023, then the bonding is ionic and conversely, if the shift is positive, then the bonding is more covalent in nature. In the present work, from the measured negative shift in the $g$ value, with respect to 2.0023 as well as from $A$ values, it is apparent that the Mn$^{2+}$ ion is in an ionic environment. It is also observed that the linewidth, and $g$ and $A$ values are found to be independent of temperature.

### B. Calculation of number of spins ($N$) participating in resonance

The number of spins participating in resonance can be calculated by comparing the area under the absorption curve with that of a standard (CuSO$_4$$\cdot$5H$_2$O in this study) of known concentration. Weil et al.\(^{38}\) gave the following expression which includes the experimental parameters of both sample and standard:

<table>
<thead>
<tr>
<th>Sample (Zn$_{2-x}$Mn$_x$SiO$_4$)</th>
<th>$A_{\text{avg}} \times 10^{-4}$ cm$^{-1}$</th>
<th>$N \times 10^{20}$ (arbitrary units)</th>
<th>$\chi \times 10^{-4}$ (m$^3$ Kg$^{-1}$)</th>
<th>$D$ (Gauss)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$x = 0.10$</td>
<td>75.1</td>
<td>7.44</td>
<td>1.87</td>
<td>227</td>
</tr>
<tr>
<td>$x = 0.15$</td>
<td>74.8</td>
<td>11.75</td>
<td>2.95</td>
<td>232</td>
</tr>
<tr>
<td>$x = 0.20$</td>
<td>75.5</td>
<td>17.36</td>
<td>4.36</td>
<td>234</td>
</tr>
<tr>
<td>$x = 0.25$</td>
<td>78.3</td>
<td>19.67</td>
<td>4.94</td>
<td>247</td>
</tr>
<tr>
<td>$x = 0.30$</td>
<td>74.1</td>
<td>20.24</td>
<td>5.08</td>
<td>258</td>
</tr>
<tr>
<td>$x = 0.50$</td>
<td>75.2</td>
<td>45.83</td>
<td>11.5</td>
<td>268</td>
</tr>
</tbody>
</table>
The EPR data can be used to calculate the paramagnetic susceptibility of the sample using the formula, 39

\[ \chi = \frac{Ng^2\beta^2J(J+1)}{3k_B(T+\Delta)} \]

where \( N \) is the number of spins per m\(^3\) and the other symbols have their usual meaning. When Weiss constant \( \Delta \) vanishes, Eq. (4) follows Curie’s law. \( N \) can be calculated from Eq. (3) and \( g = 2.02 \) is taken from EPR data. The paramagnetic susceptibility have also been evaluated with respect to \( x \) and is presented in Table 2. The temperature dependence of reciprocal of the paramagnetic susceptibility \((1/\chi)\) of Mn\(^{2+}\) ions in Zn\(_{1.5}\)Mn\(_{0.5}\)SiO\(_4\) phosphor sample is presented in Fig. 8. The data is fit to a straight line in accordance with Curie-Weiss-type behavior \([\chi = C/(T - \theta_p)]\). It is interesting to note that with increasing temperature, the susceptibility of the sample decreases obeying the Curie-Weiss law. Further from the slope of the line the Curie constant and the paramagnetic Curie temperature have also been evaluated with respect to \( x \). The paramagnetic Curie temperature is negative for the investigated sample implying that the manganese ions are antiferromagnetically coupled by negative super exchange interactions at very low temperatures.

D. Calculation of zero-field splitting parameter \((D)\) from EPR spectra from the allowed hyperfine lines

The intensity of hyperfine lines can be used to calculate the zero-field splitting parameter \((D)\) from the ratio of allowed hyperfine lines (corresponding to the selection rule \( \Delta m = 0 \)) using the formula\(^{31} \)

\[
I_m \propto 2 \frac{A^2(35-4m^2)}{2(\gamma \beta H)^2} - \frac{5.334D^2}{(\gamma \beta H)^2} - \frac{35.14D^2(35-4m^2)}{(\gamma \beta H)^2} + \frac{208D^4(35-4m^2)^2}{(\gamma \beta H)^4},
\]
where $m$ is the nuclear spin magnetic quantum number, $I_m$ is the intensity of the $m$th allowed hyperfine (HF) line, $A$ is the HF splitting constant, $D$ is the zero-field splitting parameter, and the rest of the symbols have their usual meaning. The $D$ values evaluated in the present work is listed in Table 2. It is observed that $D$ increases with $x$.

IV. PHOTOLUMINESCENCE STUDIES

The photoluminescence (PL) of Zn$_{2-x}$Mn$_x$SiO$_4$ (0.1$\leq x \leq$0.5) phosphors have been characterized by the transitions of $3d^5$ of Mn$^{2+}$ electrons in the manganese ion acting as an activating center. In a cubic crystalline field of low to moderate strength, the five $d$ electrons of Mn$^{2+}$ ion are distributed in the $t_{2g}$ and $e_g$ orbitals, with three in the former and two in the latter. Thus the ground state configuration is $(t_{2g})^3(e_g)^2$. This configuration gives rise to the electronic states, $^6A_{1g}$, $^4A_{1g}$, $^4E$, $^4T_{1g}$, $^4T_{2g}$, and to a number of doublet states of which $^2A_{1g}$ lies lowest according to Hund’s rule. Since, all the excited states of Mn$^{2+}$ ion belonging to $d^5$ configuration will be either quartets or doublets, the luminescence spectra of Mn$^{2+}$ ions will have only spin forbidden transitions.

FIGURE 9 shows an excitation spectrum of Zn$_{2-x}$Mn$_x$SiO$_4$ (0.1$\leq x \leq$0.5) phosphor with a strong excitation peak at 251 nm, obtained by monitoring the strong green emission wavelength at 520 nm. The broad strong excitation peak at 251 nm could be attributed to a charge transfer transition from the divalent manganese ground state $^6A_{1g}(S)$ of (Mn$^{2+}$) to the conduction band (CB). The corresponding emission spectra of Zn$_2$SiO$_4$:Mn (0.1$\leq x \leq$0.5) phosphor is shown in FIGURE 10. In the present work we observed interesting new results. In addition to strong green emission (520 nm), we also observed weak blue (430–460 nm) and violet (390 nm) emissions from the same material for a single excitation wavelength of 251 nm. To the best of our knowledge we have not come across such an emission spectra consisting of three wavelengths simultaneously in this series of Zn$_2$SiO$_4$:Mn phosphors.
phors reported so far. Most of the available reports indicate only green emission. In order to probe for the origin of additional colors in the emission spectra we have performed PL studies in undoped samples also.

Surprisingly the PL spectra of undoped samples also showed very weak two emission peaks at about 395 nm (UV band) and 465 nm (blue band) from emission spectra when excited at 260 nm. The excitation and emission spectra of undoped sample is shown in Fig. 11 and the absence of green emission is due to the absence of Mn$^{2+}$. Further our EPR experiment in undoped sample also shows the absence of EPR signal, indicating that it is free from paramagnetic impurities. Therefore, we attribute these additional bands in our samples at about 390 and 460 nm to be originating from ZnO. The UV emission at 390 nm has been well studied and was ascribed to excitonic recombination of ZnO. It is well known\textsuperscript{42} that the valence band (VB) and CB in semiconductors retain their meaning even in the amorphous state, and the density of bands is almost unaltered by amorphisation since the gross feature of electronic states is determined by the short range order. The photophysics of emission band at $\sim$390 nm can be predicted by the following scheme: First, the excitation photon may lose energy of $\sim$2 eV due to vibrational absorption in the silica network before exciting the electron from VB to CB of ZnO. A similar energy loss process is reported in porous silica.\textsuperscript{33} Second, the excited electrons move towards the band edge and recombine directly with the photogenerated holes to give the 390 nm emission. For different syntheses approaches, the near band edge emission peaked at $\sim$380 nm was also reported.\textsuperscript{44–47}

Blue light luminescence located at 430–460 nm has been reported by Fu \textit{et al.}\textsuperscript{48} in their ZnO films deposited on a Si substrate. Similarly, a very weak 470 nm blue emission peak was reported by Li \textit{et al.}\textsuperscript{49} in their ZnO/Zn phosphor films. Only a few results\textsuperscript{48–52} on this emission have been reported and its mechanism is still being debated. Zhang \textit{et al.}\textsuperscript{52} reported monochromatic blue luminescence from sputtered ZnO films and ascribed it to shallow donor level of oxygen vacancy and interstitial zinc. Other possible origins such as zinc vacancy\textsuperscript{48} and interstitial oxygen\textsuperscript{50} have also been proposed to explain this blue emission. Zhang \textit{et al.} reported that a 446 nm blue emission was observed in their

![Excitation and emission spectra of undoped solution combustion derived willemite sample calcined at 950 °C (3 H).](excitation_spectrum.png)  

**FIG. 11.** The excitation and emission spectra of undoped solution combustion derived willemite sample calcined at 950 °C (3 H).
could be well distributed as the substitutes of Zn\(^{2+}\) in the zinc silicate host matrix and hence the encouraging green emission. The valence matching between Mn and Zn could be well distributed as the substitutes of Zn\(^{2+}\) in the zinc silicate host matrix and hence the encouraging green emission. The fact that it may be originating from the zinc vacancy.

**V. CONCLUSIONS**

Zn\(_{2-x}\)Mn\(_x\)SiO\(_4\) \(0.1 \leq x \leq 0.5\) nanocrystalline powder phosphors have been synthesized by a low-temperature initiated, self-propagating, gas production combustion process. The lattice parameters calculated from XRD confirm that Zn\(_{2-x}\)Mn\(_x\)SiO\(_4\) has a rhombohedral space group \((R\bar{3}H)\). The XRD patterns confirm that Zn\(_{2-x}\)Mn\(_x\)SiO\(_4\) phosphor samples undergo a phase transformation from \(\beta\)-willemite to \(\alpha\)-willemite phase at 950 °C. The EPR spectra of Mn\(^{2+}\) ions exhibit resonance signals at \(g \approx 3.24\) and \(g \approx 2.02\), with a sextet hyperfine structure centered around \(g \approx 2.02\). The observation of EPR signals of Mn\(^{2+}\) gives clear indication of two kinds of Mn\(^{2+}\) sites. The magnitude of hyperfine splitting (A) for Mn\(^{2+}\) ion indicates that the Mn\(^{2+}\) ion is in an ionic environment. It is observed that \(N\), \(\chi\), and \(D\) increases with increase of \(x\). The variation of \(N\) with temperature obeys usual Boltzmann law. The activation energy was calculated and found to be 0.0112 eV. It is interesting to observe that the temperature dependence of reciprocal of susceptibility obeys Curie-Weiss law. The Mn ions in doped Zn\(_2\)SiO\(_4\) also have four-coordination because they replace some of the Zn\(^{2+}\) ions in the lattice. The luminescence of Mn\(^{2+}\) ion in Zn\(_2\)SiO\(_4\) shows a strong green emission peak around 520 nm from the synthesized phosphor particles under UV excitation (251 nm). The luminescence is assigned to a transition from the upper \(^4T_1 \rightarrow ^6A_1\) ground state. In addition to this, blue and violet emissions are also observed for single excitation wavelength (251 nm). The origin for green emission is from Mn\(^{2+}\) center, whereas blue and violet emissions may be originating from the zinc vacancy.

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