Chapter – VI

EPR, luminescence and IR spectral investigations of Mn$^{2+}$ activated ZnGa$_2$O$_4$ phosphor

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1. Introduction

In recent years, luminescent properties of inorganic phosphors have been extensively investigated for commercial flat panel display (FPD) devices [1]. The long lasting inorganic phosphors have been of great interest for several years because of their ability to emit light in the dark after irradiation with artificial light or sunlight. Long-lasting phosphors, generally, consist of many cation and/or anion vacancies, which can serve as carrier traps by capturing electrons or holes when irradiated with ultraviolet light.

ZnGa₂O₄ phosphor is one of the long lasting phosphors. It has been recognised as one of the promising phosphors for field emission displays, good luminescent characteristics at low voltages and exhibits excellent chemical stability [2-7]. It also exhibits various self-activated emission colours from 360 to 430 nm depending on the post annealing ambient or the zinc to gallium ratio [8].

Manganese activated zinc gallate phosphor exhibits an intense green emission [9] and it has been widely used in cathode ray tubes, image intensifiers, television screens, etc. [10]. Uheda et al. [11] and Matsui et al. [12] have extensively studied the synthesis, long period phosphorescence and mechanoluminescence of ZnGa₂O₄: Mn²⁺ phosphor. Jung et al. [13] prepared ZnGa₂O₄: Mn²⁺ phosphor by chemical synthesis method and reported EPR spectrum having hyperfine (hf) structure. Kim et al. [14] investigated the correlation between the crystalline environment and the optical property of Mn²⁺ ions in ZnGa₂O₄: Mn²⁺ phosphor.

In this Chapter, the author presents the results of the investigations on EPR spectra of ZnGa₂O₄: Mn²⁺ phosphor at room and at different temperatures.
The luminescence and the IR spectra of ZnGa$_2$O$_4$: Mn$^{2+}$ phosphor are also studied at room temperature and the results are discussed.

2. Experimental

The phosphors studied in the present work were kindly provided by Prof. Ha-Kyun Jung (Korean Institute of Chemical Technology, Republic of Korea).

Approximately, 100 mg of the finely powdered samples of phosphor were used for EPR measurements. The EPR spectra were recorded at room temperature on a JEOL FE1X ESR spectrometer operating in the X-band frequency with a field modulation of 100 kHz. The magnetic field was scanned from 280 mT to 380 mT and was swept at a rate of 6.25 mT-min$^{-1}$. The EPR spectrum of the CuSO$_4$.5H$_2$O powdered substance was recorded as a reference to calculate the number of spins. EPR spectra were also recorded at different temperatures (123 – 433 K) using a JES-VT-3A2 variable temperature controller.

The luminescence emission and excitation spectra of ZnGa$_2$O$_4$: Mn$^{2+}$ (0.08 mol %) were recorded at room temperature using Shimadzu spectrofluorophotometer (Model RF 510) and a 150 W Xenon lamp. The wavelength accuracy of emission and excitation was ±1 nm. The FT-IR spectrum of ZnGa$_2$O$_4$: Mn$^{2+}$ (0.06 mol %) was recorded on a Perkin-Elmer FT-IR Spectrometer using KBr pellet technique.
3. Theory

3.1 EPR studies

A neutral manganese atom has 25 electrons out of which 18 reside in the closed shells and the remaining 7 electrons have the electronic configuration of 3d^5 4s^2. The electronic configuration of Mn^{2+} ion is [Ar]3d^5, where [Ar] stands for closed Argon shell. In d^5 configuration, the five electrons will occupy the d-orbitals and give rise to a spin, S = 5/2. Since the nuclear spin (I) of Mn^{2+} ion is 5/2, the five unpaired electrons will interact with its nucleus and give rise to (2I + 1) EPR hyperfine lines i.e. six lines.

The hyperfine structure of Mn^{2+} ion with S = 5/2 and I = 5/2 can be explained by using the spin-Hamiltonian [15]

\[ \mathcal{H} = \beta B g S + D [S_z^2 - 1/3 S(S + 1)] + S.A.I \]  

where the symbols have their usual meaning. If the magnetic field 'B' is at a finite angle to the axis of zero-field splitting term D then the spin-Hamiltonian can be written as [15]

\[ \mathcal{H} = \beta B g S + 1/2 D [S_z^2 - 1/3 S(S+1)] (3\cos^2 \theta - 1) + D (S_z S_+ + S_+ S_z) \sin \theta \cos \theta + D (S_+^2 + S_-^2) \sin^2 \theta + S.A.I \]  

Here one takes the z-axis as the direction of the magnetic field. The main levels will be produced by \( \beta B g S \) and the rest of the terms in the spin-Hamiltonian are considered as perturbation on these levels.

The hyperfine spectrum for polycrystalline sample results from a transition \( | -1/2, M_I \rangle \) level to \( | +1/2, M_I \rangle \) level, where +1/2 and -1/2 represent
the electronic spin magnetic quantum numbers and 'M_i' is the nuclear magnetic quantum number. Because of the perturbations, each of |1/2, M_i⟩ and |-1/2, M_i⟩ states will be mixed with the other states. This admixture affects the probability of the |-1/2, M_i⟩ → |1/2, M_i⟩ transition for ΔM_i = 0. If the perturbed levels of |-1/2, M_i⟩ and |1/2, M_i⟩ are represented by |-1/2, M_i⟩\_p and |1/2, M_i⟩\_p and the raising (S\_+) and the lowering (S\_-) operators are introduced, then the intensity of the transition |-1/2, M_i⟩\_p → |1/2, M_i⟩\_p is proportional to

\[ \left| \langle \langle +1/2, M_i \mid S_+ + S_- \mid -1/2, M_i \rangle \rangle \right|^2 \]

The schematic representation of energy levels of Mn\(^{2+}\) ions with the allowed hyperfine lines is shown in Fig. 1.

3.2 Luminescence studies

In a cubic crystalline field of low to moderate strength, the five d-electrons are distributed in the t\(_{2g}\) and e\(_g\) orbitals; three in the former and two in the latter. The d\(^5\) configuration will have free ion terms \(^6\)S, \(^4\)G, \(^4\)D, \(^4\)P and a number of doublet states (see Table 4 of Chapter I). In an octahedral crystal field, these states transform as \(^6\)A\(_{1g}\)(S), \(^4\)A\(_{1g}\)(G), \(^4\)E\(_g\)(G), \(^4\)T\(_{1g}\)(G), \(^4\)T\(_{2g}\)(G), \(^4\)A\(_{2g}\)(F), \(^4\)T\(_{2g}\)(F), \(^4\)T\(_{1g}\)(F), \(^4\)T\(_{2g}\)(D), \(^4\)E\(_d\)(D) and \(^4\)T\(_{1g}\)(P) (see Table 7 of Chapter I). Among these states \(^6\)A\(_{1g}\)(S) will be the ground state.

4. Results and analysis

4.1 EPR studies

The EPR spectra of Zn\(_{1-x}\)Mn\(_x\)Ga\(_2\)O\(_4\) (x = 0.01 to 0.08 mol %) powder phosphor, recorded at room temperature, are shown in Fig. 2. The EPR spectra
Fig. 1. The schematic representation of energy levels of Mn$^{2+}$ ions with the allowed hyperfine lines.
Fig. 2. The EPR spectra of $\text{Zn}_x\text{Mn}_{1-x}\text{Ga}_2\text{O}_4$ ($x = 0.01$ to $0.08$ mol%) powder phosphor recorded at room temperature.
of all the samples show a well-resolved hyperfine structure at $g_{\text{eff}} = 2.00$. The typical six-line hyperfine structure is due to Mn$^{2+}$ ion from the fine structure transition \( |+1/2 \rangle \leftrightarrow |-1/2 \rangle \). The hyperfine structure originates from the interaction between the Mn$^{2+}$ electron cloud and the $^{55}$Mn nucleus (99.98 % natural abundance) of spin, $I = 5/2$. The hyperfine lines have been analysed using the following expression [16].

$$B_{M_1} = B_0 - A M_1 = \{(A/8 B_0) (35 - 4 M_1^2)\}$$

where $B_{M_1}$ is the magnetic field corresponding to $M_1$ hyperfine line, $B_0$ is the resonance magnetic field, $B_0 = \hbar v/g_0\beta$. $g_0$ is the isotropic g factor and $A$ is the isotropic hyperfine interaction parameter. The nuclear magnetic quantum number, $M_1 = -5/2, -3/2, -1/2, 1/2, 3/2, 5/2$. In the present study, the hyperfine splitting constant, $A$ is found to be $8 \pm 0.2$ mT at room temperature.

From the EPR spectra, it is observed that beyond 0.03 mol % of Mn$^{2+}$ content, the EPR signal intensity decreased and the line width slightly increased from 1.8 mT to 2.5 mT.

The number of spins participating in the resonance can be calculated with the help of the reference sample [CuSO$_4$·5H$_2$O] using the formula given by Weil et al. [17]

$$N = \frac{A_x (\text{Scan}_x)^2 G_{\text{std}} (B_{m})_{\text{std}} (B_{0})_{\text{std}}^2 [S (S+1)]_{\text{std}} (P_{\text{std}})^{1/2}}{A_{\text{std}} (\text{Scan}_{\text{std}})^2 G_x (B_{m})_x (g_s)^2 [S (S+1)]_x (P_x)^{1/2}}$$

where the symbols have their usual meaning (see Chapter III).

Fig. 3 shows the plot of number of spins participating in the resonance for ZnGa$_2$O$_4$: Mn$^{2+}$ with various concentrations of manganese content.
Fig. 3. A plot of number of spins participating in resonance for ZnGa$_2$O$_4$: Mn$^{2+}$ phosphor with various concentrations of manganese.
Fig. 4 shows the EPR spectra of ZnGa$_2$O$_4$: Mn$^{2+}$ (0.03 mol %) phosphor recorded at different temperatures. The number of spins (N) participating in the resonance at $g_{\text{eff}} = 2.00$ is calculated at different temperatures ($T$) using equation 4. Fig. 5 shows a plot of Log N as a function of $1/T$.

4.2 Calculation of paramagnetic susceptibility from EPR data

EPR data can be used to calculate the paramagnetic susceptibility of the sample using the formula [18]

$$\chi = \frac{N g^2 \beta^2 J(J+1)}{3 k_B T} \quad \text{(5)}$$

where the symbols have their usual meaning (see Chapter III). The values of N and g are taken from the EPR data.

The paramagnetic susceptibility was calculated at various temperatures. Fig. 6 shows a plot of the reciprocal of susceptibility ($1/\chi$) as a function of absolute temperature ($T$).

4.3 Luminescence studies

The emission spectrum of ZnGa$_2$O$_4$: Mn$^{2+}$ (0.08 mol %) phosphor recorded at room temperature, under excitation at 248 nm is shown in Fig. 7(a). The spectrum exhibits two bands centered at 502 nm and 468 nm. The green emission band observed at 502 nm is attributed to the $^4T_1 \rightarrow ^6A_1$ transition of Mn$^{2+}$ ions. The blue emission band observed at 468 nm is attributed to the transitions involving radiative recombination of a delocalised charge carrier (electron) with a trapped charge carrier (hole) [19-21].
Fig. 4. The EPR spectra of ZnGa$_2$O$_4$: Mn$^{2+}$ (0.03 mol %) phosphor recorded at different temperatures.
Fig. 5. A plot of log N as a function of 1/T of ZnGa$_2$O$_4$: Mn$^{2+}$ (0.03 mol %) phosphor.
Fig. 6. A plot of the reciprocal of susceptibility ($1/\chi$) as a function of absolute temperature (T) of ZnGa$_2$O$_4$: Mn$^{2+}$ (0.03 mol %) phosphor.
Fig. 7. (a) Emission spectrum of ZnGa$_2$O$_4$: Mn$^{2+}$ (0.08 mol %) monitored at 248 nm.
(b) Excitation spectrum of ZnGa$_2$O$_4$: Mn$^{2+}$ (0.08 mol %) monitored at 502 nm.
The excitation spectrum of the sample recorded at room temperature, monitored at 502 nm is shown in Fig. 7(b). The spectrum exhibits a strong band centered at 228 nm and a weak band centered at 280 nm.

4.4 IR spectral studies

The FT-IR spectrum of Zn$_{1-x}$Mn$_x$Ga$_2$O$_4$ (x = 0.06 mol %) is shown in Fig. 8. It exhibits two strong absorption bands around 600 cm$^{-1}$ and 450 cm$^{-1}$, each being split into two. The high frequency band is attributed to the stretching vibrations of M-O groups at tetrahedral sites and the low frequency band to the stretching vibrations of M-O groups at octahedral sites [22]. The weak band at 1020 cm$^{-1}$ is due to electronic transition, which is named as threshold frequency. It represents the activation energy for electron conduction.

5. Discussion

5.1 EPR studies

The magnitude of the hyperfine splitting constant $A$ provides a qualitative measure of the ionicity of bonding between Mn$^{2+}$ ion and its immediate ligands. The relation between $A$ and the local bonding of Mn$^{2+}$ and the nearest neighbour ligands has been derived phenomenologically on a quantitative basis by plotting $A$ versus Pauling covalency parameter [23,24]. From this curve, for $A = 8$ mT, an ionicity of 84 % is obtained. Hence, it is concluded that the bonding between Mn$^{2+}$ ions and its ligands in the sample is moderately ionic. This suggests that the concentration of the isolated Mn$^{2+}$ ions decreased with the increase of Mn content. This decrease in the concentration of the isolated Mn$^{2+}$ ions may be due to the formation of Mn clusters such as Mn$^{2+}$ ion pairs, triples, etc. [25,26].
Fig. 8. The FT-IR spectrum of Zn$_{1-x}$Mn$_x$Ga$_2$O$_4$ (x = 0.06 mol %) phosphor.
However, the author did not observe any new EPR signals corresponding to the ion pairs.

It is known that the formation of Mn clusters increases with the increase of total content of Mn in the sample, agreeing well with the interpretation of the statistical distribution probability [27]. In the present work, the highest concentration of the Mn$^{2+}$ ions in the samples is 0.08 mol %. According to Kreitman and Barnett [27], for 0.08 mol % of Mn content, the probability functions of singles (isolated Mn$^{2+}$ ions) and Mn-pairs are about 0.22 and 0.055 respectively. Hence, the EPR signal intensity of Mn pairs would be much lower than that of the isolated Mn$^{2+}$ ions. This may be the reason why new EPR signals corresponding to Mn$^{3+}$ ion pairs were not observed in the present study. However Yeom et al. [26] observed new EPR signals of Mn$^{3+}$ clusters in their samples (ZnS: Mn) when the total Mn content was greater than 1 mol %.

From Fig.3, it is observed that the number of spins participating in the resonance for ZnGa$_2$O$_4$: Mn$^{2+}$ is maximum for a concentration of 0.03 mol %. Hence it can be concluded that the optimum doping concentration of Mn$^{2+}$ in the zinc gallate phosphor is 0.03 mol %.

It is observed that the number of spins decreases with the increase of temperature (see Fig. 5). This is in good agreement with the assumption that the population of the energy levels is controlled by the Boltzmann law. From Fig. 5, the activation energy ($E_a$) has been calculated and is found to be 0.02 eV. This value is found to be in good agreement with those reported for other transition metal ions [28].

The plot of $1/\chi$ as a function of T (see Fig. 6) is a straight line in accordance with the Curie's law. From the plot, the Curie constant
(0.013 emu/mol) and Curie temperature (99 K) have been evaluated and these values are found to be in good agreement with those reported in the literature for Mn$^{2+}$ ions [29].

5.2 Luminescence studies

Generally, long-lasting phosphorescence materials consist of many cation and/or anion vacancies. On UV excitation, these vacancies serve as carrier traps by capturing electrons or holes [12, 20]. Hence, when ZnGa$_2$O$_4$: Mn$^{2+}$ is excited by UV light, the transfer of energy from host to Mn$^{2+}$ ions may take place by two mechanisms. In the first mechanism, the energy is transferred from host to Mn$^{2+}$ ions due to recombination of electron and hole or due to recombination of electron and hole trapped Mn$^{2+}$ ions. In the second mechanism, the energy is transferred from host to Mn$^{2+}$ ions due to recombination of donor and acceptor ions [20].

Jung et al. [13] studied the emission spectra of ZnGa$_2$O$_4$: Mn$^{2+}$ phosphors with various Mn concentrations. They reported that the emission intensity increases with increase of Mn concentration, reaches a maximum value and then decreases. This decrease in intensity was attributed to the concentration quenching.

In the present sample, it is observed that the intensity of the emission band observed at 502 nm is higher than that of the emission band observed at 468 nm. This suggests that the Mn$^{2+}$ luminescence occurs more efficiently than the trap-state luminescence, as reported by other workers [20, 30-32].
In the excitation spectrum, the band centered at 228 nm is attributed to the host-lattice absorption band. The weak and broad band centered at 280 nm is attributed to charge-transfer absorption band or $d^3 \rightarrow d's$ transition band [11].

5.3 IR spectral studies

ZnGa$_2$O$_4$ is known to have partial inverse spinel structure [12] with Mn$^{2+}$ ions (ionic radius = 0.080 nm) substituted at the Zn$^{2+}$ (ionic radius = 0.074 nm) sites. Due to the difference in masses and M–O bonding forces, Mn$^{2+}$ and Zn$^{2+}$ do not exhibit vibrational equivalence. Hence the vibrational spectrum exhibits additional bands. The higher frequency bands $v_1$ and $v_1'$ at 727 cm$^{-1}$ and 579 cm$^{-1}$ are assigned to the stretching vibrations of Mn–O and Zn–O groups at tetrahedral sites respectively. Similarly, the lower frequency bands $v_2$ and $v_2'$ at 466 cm$^{-1}$ and 446 cm$^{-1}$ are assigned to the stretching vibrations of Mn–O and Zn–O groups at octahedral sites respectively. However, there is one more band expected around 325 cm$^{-1}$ due to lattice vibrations, which is not shown due to lack of this range in the FT-IR instrument used [33].

6. Conclusions

(a) The EPR spectra of Mn$^{2+}$ doped zinc gallate phosphor exhibits a well-resolved hyperfine structure at $g_{\text{eff}} = 2.00$. From the magnitude of the hyperfine splitting constant, the bonding between Mn$^{2+}$ ions and ligands is found to be moderately ionic in zinc gallate phosphor.

(b) The temperature dependence of the intensities of the spectra reveals that the population of the energy levels is controlled by usual Boltzmann law.

(c) From the EPR data, the susceptibilities have been calculated for Mn$^{2+}$ ions at room temperature and at various temperatures. The susceptibility was
found to be increasing with decreasing temperature in accordance with the Curie's law.

(d) The green and blue bands observed in the emission spectrum are attributed to the $^4T_1 \rightarrow ^6A_1$ transition of Mn$^{2+}$ ions and the trap-state transition respectively. The bands observed at 228 nm and 280 nm in the excitation spectrum are attributed to the host-lattice absorption and the charge transfer absorption or $d^5 \rightarrow d^4$ transition respectively.

(e) The observed bands in the FT-IR spectrum have been assigned to the stretching vibrations of Mn–O and Zn–O groups in the presence of Ga$^{3+}$ ions in the spinel lattice.
References


SID Sym., 29 (1998) 1048

J. Lumin., 72 (1997) 997

[6] K. Akagi, H. Kukimoto and T. Nakayama, 
J. Lumin., 17 (1978) 237

J. Lumin., 16 (1978) 323

[8] J.S. Kim, H.L. Park, C.M. Chon, H.S. Moon and T.W. Kim, 

S.I. Mho, S.D. Han, 


[12] H. Matsui, C. -Nansu, M. Akiyama and T. Watanabe, 


[15] A. Abragam and B. Bleaney, 

[16] J.M. Nedelac, M. Bouazaui and S. Turrel, 

[17] J.A. Weil, J.R. Bolton and J.E. Wertz, 

[18] P.B. Ayscough, 

[19] S. Oda and H. Kukimoto, 
*J. Lumin.*, 18/19 (1979) 829


[21] M. Tanaka, 
*J. Lumin.*, 100 (2002) 163

[22] J. Preudhomme and P. Tarte, 

[23] O. Matumura, 

[24] E. Simanek and K.A. Muller, 

[25] R.V. Anavekar, N. Devaraj, K.P. Ramesh and J. Ramakrishna, 


[27] M.M. Kreitman and D.L. Barnett, 
*J. Chem. Phys.*, 43(2) (1965) 364

[28] S. Waplak and L.A. Shuvalov, 
[29] I. Ardelean, Gh. Illonea and M. Peteanu, 

[30] K. Sooklal, B.S. Cullum, S.M. Angel and C.J. Murphy, 
*J. Phys. Chem.*, 100 (1996) 4551

[31] D. Denzier, M. Olschewski and K. Sattler, 

[32] A.A. Bol and A. Meijerink, 

[33] S. R. Gavankar and V.S. Darshane, 

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