Electron paramagnetic resonance and luminescent properties of Mn$^{2+}$:MgGa$_2$O$_4$ phosphor

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Electron-paramagnetic-resonance (EPR) and photoluminescence (PL) studies on magnesium gallate (MgGa$_2$O$_4$) phosphor activated with divalent manganese have been carried out. The EPR spectrum exhibits a six-line hyperfine structure centered at $g=1.995$, which is a characteristic of a Mn$^{2+}$ ion with a nuclear spin $I=5/2$. The spin-Hamiltonian parameters have been evaluated. The concentration and temperature (123–433 K) dependences of EPR signals have been studied. The number of spins participating in resonance ($N$) with temperature obeys the Boltzman law and it is interesting to note that it obeys the Curie-Weiss behavior. The Curie constant has been evaluated from the $1/\chi$ versus $T$ graph. A bright green photoluminescence according to the transition $^4T_1 \rightarrow ^2A_1$ whose emission peak is located at 502 nm is observed from the phosphor under UV excitation when excited by 267-nm light. Such a stable luminescence performance is promising for use in the field of flat panel light-emitting devices. The mechanism involved in the generation of green emission has been explained in detail. © 2005 American Institute of Physics.

I. INTRODUCTION

In recent years, a great deal of interest has been focused on the fabrication and luminescence properties of a wide variety of oxide-based phosphors in order to obtain efficient luminescent materials for commercial flat panel displays. Among this, field-emission displays (FEDs) have emerged as one of the most promising flat panel display technology with great potential for many low power consumption applications. It is highly desirable to develop low voltage, high efficiency, chromaticity, brightness, and longevity phosphors. For a material to exhibit these characteristics, it is necessary to incorporate the various rare-earth or transition-metal ion luminescent activators in host materials with proper oxidation state and crystal-field symmetry.

It has been reported that sulfide phosphors are unstable due to chemical degradation of the phosphors under electron-beam exposure. Therefore, non-sulfide phosphors are more desirable for commercial applications. In the present study we have chosen MgGa$_2$O$_4$ as a host activated with Mn$^{2+}$. The reason for selecting this system is that MgGa$_2$O$_4$ phosphors when activated with a Mn$^{2+}$ ion exhibit green emission and will act as mechanoluminiscence materials. These materials have various applications such as optical stress sensors, stress imaging devices, and friction sensors. Mn$^{2+}$-activated MgGa$_2$O$_4$ phosphors (MGO:Mn) exhibit long lasting phosphorescence which have applications in optical storage media and flat display devices.

The MgGa$_2$O$_4$ has a relatively simple structure with high symmetry. It is partly inverted spinel belonging to the space group $Fd3m$ with lattice parameter $a_0=8.286\pm0.003$ Å. These eight tetrahedral sites and sixteen octahedral sites are both occupied by Mg$^{2+}$ and Ga$^{3+}$ ions. Mg$^{2+}$ occupation in the octahedral site is very temperature dependent varying from 0.9 at 900 °C to 0.84 at 1400 °C. Since the greater part of the Mg$^{2+}$ ion occupies octahedral sites, the remaining Mg$^{2+}$ and Ga$^{3+}$ ions occupy the tetrahedral site. In spite of this the most important requirement for reaction in the insulate oxide is that the doping ion has the same valence as the substituted ion; therefore it is most suitable to replace the Mg$^{2+}$ ion by Mn$^{2+}$ in this compound. Recently many studies have been reported on phosphors activated with Mn$^{2+}$ ions. Different studies have also been performed on MgGa$_2$O$_4$.

This paper reports on the Electron paramagnetic Resonance (EPR), photo excitation and emission spectra of the manganese ions in MgGa$_2$O$_4$ phosphor. EPR is sensitive to...
the crystal-field environment and can provide quantitative information regarding the concentration of Mn$^{2+}$ ions. We are interested to know the effect of temperature and concentration of this ion on the spin-Hamiltonian parameters, also to know the site symmetry around the Mn$^{2+}$ ion in these phosphors and the bonding nature of the ion.

II. EXPERIMENT

The starting chemicals used in the preparation were Analar grade MgCO$_3$, Ga$_2$O$_3$, and MnCO$_3$. The chemicals were mixed thoroughly in ethanol, dried at 90 °C for 12 h and then subjected to firing. The phosphors have been prepared by the solid phase reaction method. The process of preparing is schematically illustrated in Fig. 1. The process consists of two firing stages because Ga$_2$O$_3$ sublimes violently in a reducing atmosphere at temperatures greater than 1200 °C. The MGO:Mn were first fired at 1300 °C for 8 h in air and then heat treated at 1100 °C for 2 h in N$_2$/H$_2$. The phase purity of the samples was measured by x-ray diffraction (XRD).

The EPR spectra of the phosphor samples were recorded on a JEOL FE1X electron spin resonance (ESR) spectrometer operating at X-band microwave frequency equipped with TE$_{011}$ cylindrical cavity with 100-kHz field modulation. The temperature variation EPR studies were performed from 123 to 433 K using JES UCT 2AX variable temperature controller. The EPR spectrum of CuSO$_4$·5H$_2$O powdered sample was also recorded as a standard to calculate the number of spins participating in resonance.

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 267 nm.

III. RESULTS AND DISCUSSION

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. No EPR signal was detected in the spectra of undoped MgGa$_2$O$_4$ indicating that the starting materials used in the preparation were free from paramagnetic impurities. When various quantities of Mn$^{2+}$ ions were added to the phosphor, the EPR spectra of all the investigated samples exhibit a single resonance signal at $g=1.995$. The resonance signal $g=2.0$ shows a six-line hyperfine structure superimposed on a rather broad background signal. The +2 charge state of Mn$^{2+}$ has a half filled $d$ shell ($3d^5$) with angular momentum $L=0$ and spin $S=5/2$. The characteristic hyperfine structure (hfs) is due to the interaction of electron spin with its nuclear spin $I=5/2$.

The EPR spectra of Mn$^{2+}$ ions in this phosphor show remarkable concentration dependence. From Fig. 2 it is observed that the intensity of the hyperfine structural lines increases linearly with increasing concentration of Mn$^{2+}$. Up to a 1-mol % Mn$^{2+}$ concentration the spectrum shows a sextet hfs. The six resolved hyperfine lines spread over a region of approximately 500 G in width. The ability to observe the...
The manganese hyperfine structure has two tangible benefits. (1) It generally allows an unambiguous assignment of position of the complex resonance lines to manganese and (2) the magnitude of the hyperfine constant provides a measure of covalent bonding between Mn$^{2+}$ ions and its surrounding ligands. When the concentration of the Mn$^{2+}$ ions is increased the hyperfine structure disappears as shown in Fig. 2, due to increased dipolar interactions between the manganese ions.

The Mn$^{2+}$ ion belongs to the $d^5$ configuration and it has a $^6S$ ground state. When Mn$^{2+}$ impurity complexes are situated in a crystal field with a large axial component, the free ion $^6S$ state splits into three Kramers doublets $l\pm5/2$, $l\pm3/2$, and $l\pm1/2$, with their separations usually greater than the microwave energy. Application of the Zeeman field lifts the spin degeneracy of the Kramers doublets. The resonance observed at $g \approx 2$ is due to a Mn$^{2+}$ ion in an environment close to octahedral symmetry and is known to arise from the transition between the energy levels of the lower Kramers doublets.

The sextet observed at $g = 2$ has been analyzed using the following expressions for resonance fields:

$$B_m = B_0 - A_0 m - [\langle A_0^2/8B_0 \rangle (35 - 4m^2)],$$

where $B_m$ is the magnetic field corresponding to $m \rightarrow m$ hyperfine line, $B_0$ is the resonance magnetic field, $B_0 = \hbar \nu / g_0 \beta$, $m = -5/2, -3/2, \ldots, +5/2$, $g_0$ is the isotropic $g$ factor, and $A_0$ is the isotropic hyperfine interaction parameter. The hyperfine splitting constant $A_0$ is found to be $A_0 = 78$ G at 297 K (RT). The magnitude of the hyperfine splitting constant provides a qualitative measure of the ionicity of bonding between Mn$^{2+}$ ions and its ligands. Based on a $+$ve correlation determined between $A_0$ and the ionicity of the manganese-ligand bond, it is found that the bonding between the Mn$^{2+}$ and its ligand is moderately ionic.

The resolved hyperfine spectrum at $g = 1.995$ is strongly indicative of the Mn$^{1+}$ ions being sufficiently distant from each other.

The EPR spectrum of MgGa$_2$O$_4$ phosphor activated with 0.5% of Mn$^{2+}$ is recorded at different temperatures (123–433 K) and the spectra are shown in Fig. 3. The peak to peak width of the $g = 2$ resonance lines is found to be independent of the temperature between 123–433 K whereas the intensity of the resonance line decreases with increasing the temperature. From the temperature dependence of EPR spectra, it is clear that lowering the temperature does not change the values of $g$ and $A_0$.

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

The number of spins participating in resonance can be calculated using the area under the absorption curve of the signal with the help of a reference (CuSO$_4\cdot$5H$_2$O) by using the formula:

$$N = \frac{A_s (\text{scan})^2 G_s (B_m)^2 (S+1) [P_x]^2}{A_{\text{std}} (\text{scan std})^2 G_s (B_{\text{std}})^2 (S+1) [P_{\text{std}}]^{1/2}} [\text{std}],$$

where $A$ is the area under absorption curve which can be obtained by double integrating the first derivative absorption curve, “scan” is the magnetic field corresponding to unit length, $G$ is gain, $B_m$ is modulation field width, $g$ is $g$ factor, $S$ is the spin of the system in ground state, and $P$ is the power of the microwave. The subscript “$x$” and “std” represent the corresponding quantities for the Mn$^{2+}$ ion in the sample and the reference CuSO$_4\cdot$5H$_2$O.

Figure 4 shows the dependence of logarithmic intensity ($N$) on inverse temperature ($1/T$) for the resonance signal at $g \approx 2$ for 0.5 mol % of Mn$^{2+}$ ions in MgGa$_2$O$_4$ phosphor.

![FIG. 3. The temperature variation EPR spectra for MgGa$_2$O$_4$ activated with 5% Mn$^{2+}$ ions.](image)

![FIG. 4. A plot of log N vs 1/T for MgGa$_2$O$_4$ activated with 5% Mn$^{2+}$ phosphor.](image)
between log \( N \) and \( 1/T \), a phenomenon that can be expected from the Boltzman law. From the slope of this graph, the activation energy has been calculated and is found to be \( 14 \times 10^{-3} \) eV.

B. Calculation of paramagnetic susceptibility (\( \chi \)) from EPR data

The magnetic susceptibility (\( \chi \)) of the paramagnetic ion Mn\(^{2+} \) has been calculated at different temperatures using the expression

\[
\chi = \frac{N g^2 \beta J (J + 1)}{3 k_B T},
\]

where \( N \) is the number of spins per kilogram, which can be calculated from Eq. (2) and \( J = 5/2 \). The rest of the symbols have their usual meaning. We chose to determine the spin susceptibility from EPR, because this technique has several advantages over a static measurement, where a diamagnetic contribution must be subtracted off.

Figure 5 shows the variation of inverse susceptibility with temperature. It is interesting to observe that the variation of susceptibility with temperature obeys the Curie-Weiss law. From the slope of the graph, the Curie constant is calculated and it is found to be \( 2.41 \times 10^{-9} \) m\(^3\) mol\(^{-1}\) which is of the same order as reported earlier for amorphous materials.\(^{21,22}\)

IV. PHOTOLUMINESCENCE STUDIES

Mn\(^{2+}\)-doped luminescent materials have been known to show wide ranging emissions from 500 to 700 nm depending on the crystal field of the host material. The photoluminescence of this material has been characterized by the transitions of 3\( d^5 \) 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 \( ^6A_1^e, ^4A_1^e, ^4E_g, ^4T_{1g}, \) and \( ^4T_{2g} \), and to a number of doublet states of which \( ^4A_1^e \) lies lowest according to Hund’s rule. Since, all the excited states of the 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 6(a) displays the emission spectra of magnesium gallate sample doped with Mn\(^{2+} \) ion at room temperature. The emission spectrum obtained under an excitation at 267 nm consists of a broad peak at 502 nm. In particular the transition from the lowest excited state to the ground state, i.e., \( ^4T_{1g} \rightarrow ^6A_1^e \) transition, is directly responsible for the green light emission.\(^{23,24}\) Figure 6(b) shows the excitation spectra of Mn\(^{2+}\)-doped MgGa\(_2\)O\(_4\) at room temperature. In the present study we observed only three bands for Mn\(^{2+} \) ion in MgGa\(_2\)O\(_4\) at 249, 267, and 377 nm. The first intense band, i.e., at 249 nm, is due to host-lattice absorptions and the second intense band at 267 nm is due to charge-transfer absorption. The weak broad band at 377 nm is due to \( d-d \) transition. The same band position for manganese-doped magnesium gallate phosphor is observed by Uheda et al.\(^{25} \) and Matsui et al.\(^{26} \) The photoluminescence (PL) studies of manganese ions in other phosphors have also been reported by others.\(^{26–30}\)

The excitation light wavelength has been selected in such a way that the photon energy covers all the regimes of the possible absorption mechanisms. As far as the UV excitation is dealt with in the range from \( \sim 200 \) to \( \sim 207 \) nm for phosphors, the energy transfer from host lattice to activator is associated with charge-transfer transitions including intergap transition and ionization of activators.\(^{31}\) This kind of transi-
tion is also associated with trap-associated recombination processes. But such a process can not retard the PL process since relatively shallow traps of which the depth is about a few tenths of eV are operating. That is why the results at 267 nm are completely consistent with the case of Mn’s direct excitation.

The mechanism involved in the generation of green emission from MgGa2O4:Mn2+ phosphor has been shown schematically in Fig. 7. The electron from the ground state of Mn2+ (6A1) is excited to the conduction band of the MgGa2O4 by photons. This process may be explained as

\[ \text{Mn}^{2+} + h\nu \rightarrow \text{Mn}^{3+} + e^- \]  

where \( h\nu \) is the energy needed in causing the photoexcitation of Mn2+ in MgGa2O4. The free electrons in the conduction band can relax to the \( ^4T_1 \) excited state by a nonradiative process and then followed by radiative transition from the excited state \( ^4T_1 \) to the \( ^6A_1 \) ground state emitting a strong green light.

Due to the strong dependence of the energy of the \( ^4T_1 \) state on the metal-ligand distance, a broad green emission was obtained and prolonged luminescence occurred due to the fact that the energy levels of Mn2+ are located inbetween the conduction and valence bands of the host matrix; also several carrier trap levels are newly formed by the vacancies of Mg2+ sites in the matrix above the valence band. Thus it is elucidated that the role of vacancies and carriers has been quite significant in the phosphorescent green emission performance of this MgGa2O4 and this observation enables us to suggest this as a promising green luminescent display optical system.

V. CONCLUSIONS

The EPR spectra of a manganese-doped magnesium gallate phosphor exhibit a well-resolved sextet hyperfine structure centered at g=1.995. The g and A values are found to be independent of temperature. From the observed A value, it is found that the Mn2+ ions are in an ionic environment. The EPR spectra of manganese ion at different temperatures show a linear dependence between log N and 1/T obeying the Boltzman law. The activation energy is calculated and it is found to be \( 14 \times 10^{-3} \) eV. The paramagnetic susceptibilities are calculated using EPR data for Mn2+ ions at different temperatures and it is interesting to observe that it obeys the Curie-Weiss law. The linear dependence between 1/\( \chi \) and T is used to calculate the Curie constant and found to be in good agreement with the values reported in literature. The luminescence spectrum exhibits a strong green emission and is assigned to a transition from the upper \( ^4T_1 \rightarrow ^6A_1 \) ground state. There is a possibility that the excitation spectrum was ascribed to Mn2+ in octahedral symmetry which is in good agreement with the EPR studies.

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