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EPR and luminescence properties of $LiGa_5O_8$:Mn green emitting phosphor

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ABSTRACT

Green emitting $LiGa_5O_8$:Mn powder phosphor has been prepared in a short time by solution combustion method. Powder X-ray diffraction pattern indicated a dominant phase of $LiGa_5O_8$ with another secondary $LiGaO_2$ phase. Morphology aspects were studied by using field emission scanning electron microscopy. Upon UV light excitation (296 nm), the phosphor exhibits a strong green luminescence (510 nm), which corresponds to the $^4T_1 \rightarrow {}^6A_1$ transition of Mn^{2+} ions in an environment close to tetrahedral symmetry. EPR spectrum exhibits resonance signals characteristic of Mn^{2+} ions. It is observed that the spin-Hamiltonian parameters g and A do not vary with temperature. The magnitude of the hyperfine splitting constant (A) in the present study indicates that there exists a moderately covalent bonding between Mn^{2+} ions and the surrounding ligands. The zero-field splitting parameter (D), spin concentration (N) and paramagnetic susceptibility (χ) have also been evaluated.

1. Introduction

The study of spinel metal oxides has recently attracted a great deal of attention due to their unique properties and potential applications [1,2]. The intense interest in such materials is derived from their unique chemical and physical properties, which gives rise to their potential uses in the fields of nonlinear optics, luminescence, electronics, catalysis and optoelectronics [1–5]. The spinel $LiGa_5O_8$ has been used as a host for luminescent studies of many transition metal ions [6,7]. Besides this, $LiGa_5O_8$ has been widely studied to test its viability as a tunable laser system [8].

It has been reported that $LiGa_5O_8$ adopts the inverse spinel structure with space group O^6-$P4_332$, and contains four formula units in the cubic cell [9]. In such a structure, it is possible to incorporate a large variety of rare earth and transition metal ions as dopant. Significant efforts have been devoted by different research groups in the past and till recently, to the study of the optical properties of impurity-doped $LiGa_5O_8$. They reported several lithium gallium oxides such as $LiGa_5O_8$:Co [10], $LiGa_5O_8$:Ni [11], $LiGa_5O_8$:Cr [12], $LiGa_5O_8$:Mn [6], $LiGa_5O_8$:Fe [7], etc. However, for the Mn-doped $LiGa_5O_8$, the studies are much fewer. The spectroscopy of the Mn^{2+} ions incorporated as an impurity in various host materials has been well studied [13–16] in the visible (green and red) region. This paper reports the influence of manganese impurity on the luminescence and spectroscopic properties of the $LiGa_5O_8$ host.

The various techniques, which are used for the synthesis of oxide-based powders, include solid state reactions [17], microwave refluxing [18], sol–gel [19], hydrothermal [20], co-precipitation [21] and spray pyrolysis [22]. Among these, most of the preparation techniques involve a lengthy processing time, high temperature and require post-thermal treatments. In the case of sol–gel procedure, the method is expensive due to costly metal-organic precursors. Indeed, there is a great demand for economically viable techniques of synthesis. Recently, the authors have successfully employed an economically viable combustion process for the synthesis of several alkaline earth aluminate phosphors [23–26]. In continuation of this interest, $LiGa_5O_8$ phosphor has been prepared by a suitable combustion method. The structure, surface morphology of the powder and the photoluminescence properties were studied by X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), the excitation and emission spectroscopic techniques. In addition, electron paramagnetic resonance (EPR) studies were carried out on $LiGa_5O_8$:Mn^{2+} powder phosphor at room temperature and at 110 K.

2. Experimental

0.1 mol% of Mn^{2+}-doped $LiGa_5O_8$ ($LiGa_5O_8$:Mn) was prepared by using analar grade chemicals $LiNO_3$, $Ga(NO_3)_3 \cdot xH_2O$, urea and

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$MnCl_2 \cdot 4H_2O$. For the combustion, metal nitrates as oxidizers, urea as fuel and manganese as dopant were used. The oxidizer:fuel ratio was calculated on the basis of valencies of oxidizer (O) and fuel (F) of the reactants, keeping $O/F = 1$, as reported earlier [27].

Starting materials were crushed and ground in a China dish with minimum quantity of de-ionized water to form solution. The dish (with the solution) was introduced into a muffle furnace maintained at 500 ± 10 °C. The dehydrated solution undergoes decomposition with emission of large amount of gas. The mixture was allowed to froth and swell thus forming foam, which ruptured with a flame and glowed to incandescence. During incandescence, the foam further swelled to the capacity of the container. The entire combustion process was over in less than 5 min. The dish was immediately removed from the furnace. The voluminous product was crushed into a fine powder using pestle and mortar and was used for characterization.

A powder-phase analysis was done using XRD technique. The diffractogram was recorded (X'pert, Philips, Netherland) using Cu-K_α radiation ($\lambda = 0.15418$ nm) in between 10° and 70° range of 2θ. Morphology details were obtained using a scanning electron microscope (JSM-5610LV, JEOL, Japan). Photoluminescence measurements were carried out at room temperature on a Hitachi F-4500 fluorescence spectrophotometer. EPR measurements were carried out using a Bruker EMX 10/12 X-band ESR spectrometer.

3. Results and discussion

3.1. X-ray diffraction

The phase composition of the combustion product was determined by the XRD analysis. The XRD pattern of the as-prepared $LiGa_5O_8$:Mn^{2+} is shown in Fig. 1, which indicates the formation of $LiGa_5O_8$ as the major phase and $LiGaO_2$ as the secondary phase. The diffraction peak intensity of $LiGaO_2$ is weaker than that of $LiGa_5O_8$, as shown in the figure. All the reflections in Fig. 1 could be indexed to those of standard cubic $LiGa_5O_8$ (JCPDS File no. 76-0199) and orthorhombic $LiGaO_2$ (JCPDS File no. 72-1640) phases. The prepared materials are fully crystalline at furnace temperature 500 °C and therefore the post-crystallization heat-treatments are not required.

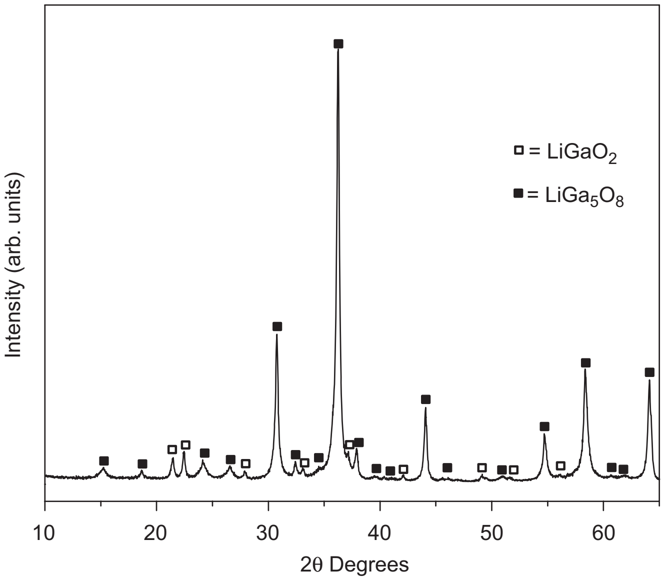

Fig. 1. Powder XRD patterns of $LiGa_5O_8$:Mn. Filled squares: $LiGa_5O_8$ (JCPDS File no. 76-0199); squares: $LiGaO_2$ (JCPDS File no. 72-1640).

3.2. Scanning electron microscopy

Fig. 2 shows the FESEM images of the $LiGa_5O_8$:Mn^{2+}. It can be observed that the particles are faceted and have varying sizes and shapes (Fig. 2A). It is also noticed that some regions contain pores while others do not (Fig. 2A and B). This may be due to the non-uniform distribution of temperature and mass flow in the combustion flame. Higher magnification SEM micrograph shows the presence of several small particles within the grains (Fig. 2C and D). Smaller particle size was produced from reactions that liberate the greatest amount of gas. The surface also has several pores, which are formed by the escaping gases during combustion reaction. This feature can be clearly observed in Fig. 2D, which is a magnified view of Fig. 2C (zone c).

3.3. Photoluminescence studies

The Mn^{2+} belongs to d^5 configuration and the ground state $^6A_{1g}$ (S) for octahedral and $^6A_1$ (S) for tetrahedral coordination. The successive energy levels are ^6S, ^4G, ^4P and ^4F for the free ion. In a crystal field, ^4G splits into $^4T_1$, $^4T_2$, and ^4E, $^4A_1$ levels, the first two being crystal field dependent. Since the transition energies are dependent on the magnitude of crystal field strength, normally the broad bands are observed for Mn^{2+} luminescence.

Fig. 3(a) and (b) shows the excitation and emission spectra of $LiGa_5O_8$:Mn^{2+} phosphor, respectively, at room temperature. The excitation spectrum exhibits an intense band with a maxima at 296 nm (33,783 cm^{-1}) and a weak shoulder at 238 nm (42,016 cm^{-1}). The former corresponds to charge transfer band of Mn^{2+} ion, and the latter originates from the absorption of the host lattice of $LiGa_5O_8$. This indicates that energy transfer occurs from the host $LiGa_5O_8$ lattice to the Mn^{2+}. Upon exciting the phosphor at 296 nm, the phosphor exhibits a green emission at 510 nm (19,607 cm^{-1}), which corresponds to $^4T_1 \rightarrow {}^6A_1$ transition of Mn^{2+} ions. When we excite the phosphor at 296 nm, the electrons from the $^6A_1$ ground state of Mn^{2+} ions are excited to the conduction band of $LiGa_5O_8$. The free electrons in the conduction band can relax to the $^4T_1$ excited state of Mn^{2+} by a non-radiative process and then followed by radiative transition from the excited state $^4T_1 \rightarrow {}^6A_1$ ground state emitting a strong green light at 510 nm.

Jaffe [28] measured the cathodoluminescence of Mn-doped $LiAl_5O_8$ and observed an emission in the green which was attributed to Mn^{2+} ions in tetrahedral coordination. There have also been a number of papers dealing with Mn^{2+} spinels and other oxide hosts [29–32] and luminescence varying from green to infrared has been reported. The interpretation of many of these emissions in terms of coordination of the activator is detectable but as a general rule Mn^{2+} in tetrahedral coordination emits at wavelengths less than 540 nm, where as red Mn^{2+} emissions are from centers with Mn^{2+} in octahedral or distorted tetrahedral coordination [33]. The emission in the present studied phosphor occurs at 510 nm, suggesting that the Mn^{2+} ions are in sites with a weak crystal field.

As in the case of $LiGa_5O_8$, Li is in octahedral coordination where as in $LiGaO_2$, Li is in tetrahedral coordination. $LiGa_5O_8$ is known to have inverse spinel structure and contains four formula units in the cubic cell [9]. One part of the Ga^{3+} ions occupy tetrahedral sites while the other part of the Ga^{3+} ions, together with the Li^+ ions, occupy octahedral sites. Mn^{2+} has the same luminescence transition, $^4T_1 \rightarrow {}^6A_1$, whether the ion occupies an octahedral or a tetrahedral site. Following Abritta et al. [34], it is mentioned that Mn^{2+} occupies in Ga sites of $LiGa_5O_8$. Further while analyzing the coordinate size of Ga ions in $LiGa_5O_8$ and $LiGaO_2$ it is clear that