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Electron paramagnetic resonance and low-field microwave absorption in the manganese–gallium oxide

H. Montiel [a,*], G. Alvarez [b,c,**], A. Conde-Gallardo [c], R. Zamorano [b]

[a] Centro de Ciencias Aplicadas y Desarrollo Tecnológico de la Universidad Nacional Autónoma de México, Cd. Universitaria, A.P. 70-186, México DF 04510, Mexico

[b] Escuela Superior de Física y Matemáticas del Instituto Politécnico Nacional, U.P. Adolfo López Mateos, Edificio 9, Av. Instituto Politécnico Nacional S/N, San Pedro Zacatenco, México DF 07738, Mexico

[c] Departamento de Física, CINVESTAV-IPN, A.P. 14-740, México DF 07360, Mexico

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ABSTRACT

Microwave absorption measurements in $MnGa_2O_4$ powders are carried out at X-band (8.8–9.8 GHz) in 92–296 K temperature range. For all temperatures, the electron paramagnetic resonance (EPR) spectra show a single broad line due to Mn^{2+} ions. Temperature dependence of the EPR parameters: the peak-to-peak linewidth (ΔH_{pp}), the integrated intensity (I_{EPR}) and the *g*-factor, suggests the presence of magnetic fluctuations that precede to antiferromagnetic ordering at low temperature. Additionally, the low-field microwave absorption (LFMA) is used to give further information on this material, giving also evidence of these magnetic fluctuations.

1. Introduction

The spinel-type oxides (AB_2O_4) have a structure described as a densely packed oxygen array with A and B cations in tetrahedral and octahedral sites, respectively, see Fig. 1. In these oxides, the 3D-transition metals can occupy either site (A or B) and they can have various oxidation states. In particular, the manganese has tendency of existing in two main oxidation states, Mn^{2+} or Mn^3, in spinel-type oxides; and knowing the ions distribution, one can have understanding on physical and chemical properties of these oxides. For manganese gallium oxide ($MnGa_2O_4$), the Mn ions are divalent and they are occupied the tetrahedral sites (A sites) while the Ga ions are trivalent and they are occupied the B sites (octahedral sites) [1]. It also is necessary to mention that spinel $MnGa_2O_4$ undergoes a magnetic transition around 33 K [2,3], where the Mn^{2+} ions are of primary importance for the magnetic properties of this material.

On the other hand, the electron paramagnetic resonance (EPR) is more powerful spectroscopic method available to determine the valence state of paramagnetic ions [4], local structural information and symmetry of paramagnetic ions incorporated in the structure [5–7]. This technique also allows the investigation of magnetic transitions in materials at different temperatures [8–10].

Additionally, the microwave absorption around zero magnetic field (low-field microwave absorption, LFMA) has been used to detect the magnetic and electric transitions in materials [8–15], and provide a high sensitive detection of the magnetic and electric orders. The origin of this signal is due to interaction of microwaves with the electric dipoles and/or magnetic moments, or also to magnetization processes which strongly depend of the magnetic order.

To our knowledge, however, studies on spinel $MnGa_2O_4$ with EPR and LFMA techniques are scarce. For this reason, in this work, we present a study of the changes in lineshape of the EPR spectra in $MnGa_2O_4$ powders; these changes are quantified by means of following parameters: the peak-to-peak linewidth (ΔH_{pp}), the integrated intensity (I_{EPR}) and the *g*-factor, as a temperature function from 296 K to 92 K. For the same temperature range, we use the LFMA technique to give a further knowledge on this material, showing their main characteristics highlighted.

2. Samples preparation and experimental details

Polycrystalline samples of $MnGa_2O_4$ are prepared from stoichiometric amounts of MnO (99.9% purity) and Ga_2O_3 (99.9%

* Corresponding author.
** Corresponding author at: Escuela Superior de Física y Matemáticas del Instituto Politécnico Nacional, U.P. Adolfo López Mateos, Edificio 9, Av. Instituto Politécnico Nacional S/N, San Pedro Zacatenco, México DF 07738, Mexico.
E-mail addresses: herlinda_m@yahoo.com (H. Montiel), memodin@yahoo.com (G. Alvarez).

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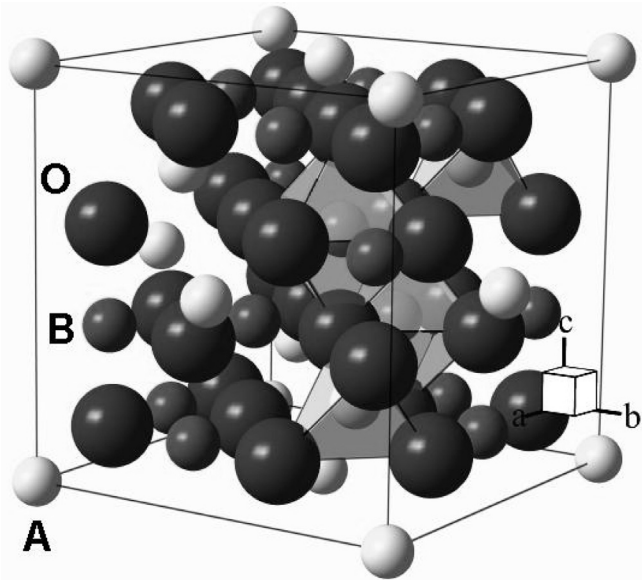

Fig. 1. Schematic representation of the unit cell structure for a spinel-type structure AB_2O_4, where A and B are tetrahedral and octahedral sites, respectively, in particular A=Mn and B=Ga for spinel $MnGa_2O_4$.

purity) by means of solid-state reaction method. Reagents are ground and mixed until obtaining a homogeneous mixture, and it is followed by a sintering at 1200 °C for 12 h under an air atmosphere. The X-ray diffraction (XRD) analysis is carried out with a Siemens D5000 diffractometer using the 1.5406 Å Cu Kα line to check phase purity; XRD measurements are made at 300 K.

The microwave absorption investigations employed a JEOL JES-RES3X spectrometer operating at X-band (8.8–9.8 GHz) with 100 kHz of modulation on the applied dc magnetic field (H_{dc}). All microwave absorption measurements are carried out in 92–296 K temperature range. For EPR spectra, the H_{dc} is varied from 0 to 7000 G; with amplitude of the modulation field (H_{mod}) of 0.3 G and an incident power of 1 mW. LFMA measurements are performed using a Jeol ES-ZCS2 zero-cross sweep unit that digitally compensates any remanence in the electromagnet, allowing the measurements to be carried out by cycling H_{dc} about their zero value, continuously from −1000 G to +1000 G. In this technique, the sample is cooled to the desired temperature, and then is maintained at that temperature with a maximum deviation of ±1 K during the whole LFMA measurement (~4 min of sweep). The complete scheme and details concerning the experimental setup for LFMA measurement can be found [16].

3. Results and discussion

Fig. 2 shows the XRD pattern in $MnGa_2O_4$ powders. All observed reflection lines are indexed as a single face-centered-cubic (fcc) structure corresponding to spinel phase. Additionally, in Fig. 3 (a), we show the scanning electron microscopy (SEM) image, revealing the morphology of the $MnGa_2O_4$ powders, where the product mainly consists of particles with an irregular shape. In order to confirm the chemical composition, the energy-dispersive X-ray spectroscopy (EDS) is employed, and it shows elemental signatures from Mn, Ga, and O, indicating a high quality in our samples; see Fig. 3(b).

In Fig. 4, we show the EPR spectra (dP/dH vs. magnetic field) for a few selected temperatures. It can be observed that resonance spectra exhibit a single broad line along the entire temperature range, due to the spin of Mn^{2+} ions, suggesting a strong dipolar interaction between manganese ions. This strong dipole–dipole

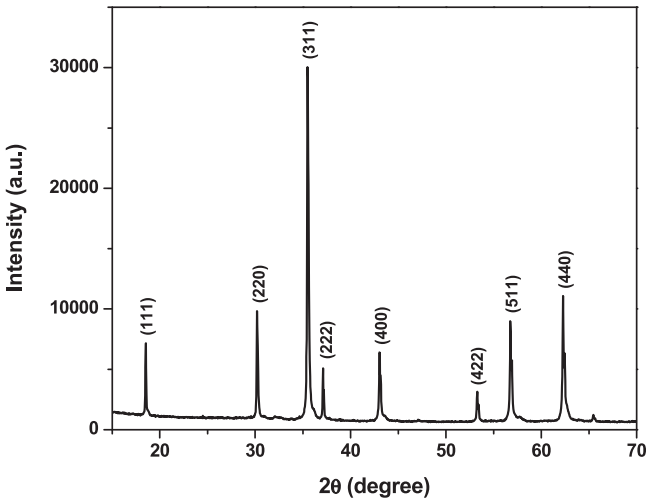

Fig. 2. XRD pattern of the polycrystalline sample of $MnGa_2O_4$.

interaction is due to that the Mn^{2+} ions are magnetically concentrated, perhaps closer of the grain boundaries. Additionally, to have a better precision of the lineshape parameters in EPR spectra, we fitted them into the two component Lorentzian equation accounting for the contributions from the clockwise and anticlockwise rotating components of the microwave magnetic field [17,18], as follows:

$$\frac{dP}{dH} \propto \frac{d}{dH}\left(\frac{\Delta H_{pp}}{(H_{dc}-H_{res})^2+\Delta H_{pp}^2}+\frac{\Delta H_{pp}}{(H_{dc}+H_{res})^2+\Delta H_{pp}^2}\right) \quad (1)$$

where H_{res} and ΔH_{pp} are the resonant field and the peak-to-peak linewidth, respectively, and good fits are obtained for all the EPR spectra. The temperature dependence of the EPR parameters obtained from these fits are plotted in Fig. 5.

Fig. 5(a) shows the temperature dependence of ΔH_{pp} for $MnGa_2O_4$ powders, where linewidth increases continuously as temperature decreases from 296 K to 92 K; in this temperature region the material have a paramagnetic behavior, being experimentally confirmed with the absence of a magnetic hysteresis at 100 K, see inset of Fig. 6. It is necessary to mention that a common feature of the EPR spectra around para–antiferromagnetic transitions is that the linewidth becomes broader with decreasing temperature, especially below the Néel temperature (T_N) [19]. Then, the increase in ΔH_{pp} can be due to the build-up of magnetic correlations preceding the transition to the long-range antiferromagnetic ordering at T_N, confirming the magnetic transition directly by means of thermal variation of the specific saturation magnetization, see Fig. 6, with T_N=14.3 K. Additionally, $MnGa_2O_4$ powders have a weak ferromagnetic behavior at low temperature, and it is confirmed with the presence of a magnetic hysteresis at 5 K, see the inset of Fig. 6.

The temperature dependence of I_{EPR}, which in the paramagnetic phase is directly proportional to static spin susceptibility [5–7], is shown in Fig. 5(b). Starting from 296 K, I_{EPR} increase with the temperature decrease, reaching a maximum at T_{max}=122 K. After T_{max}, when the temperature continues to decrease, I_{EPR} slowly diminishes until 92 K; this change can be associated with a decrease in the quantity of the paramagnetic centers, due to presence of the antiferromagnetic order at low temperature, see Fig. 6.

In Fig. 5(c), we show the temperature dependence of the g-factor, which is estimated from H_{res}, with $g=h\nu/\mu_B H_{res}$; where h is the Planck constant, ν is the frequency and μ_B is the Bohr magneton. For all the temperatures, the g-factor estimated is smaller than for a free electron (=2.0023), and it is explained through