AIP | Applied Physics Letters

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Citation: Applied Physics Letters **100**, 192404 (2012); doi: 10.1063/1.4712058
View online: http://dx.doi.org/10.1063/1.4712058
View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/100/19?ver=pdfcov
Published by the AIP Publishing

APPLIED PHYSICS LETTERS **100**, 192404 (2012)

Defect and adsorbate induced ferromagnetic spin-order in magnesium oxide nanocrystallites

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(Received 13 February 2012; accepted 10 April 2012; published online 8 May 2012)

We report the correlation between d_0 ferromagnetism, photoluminescence (PL), and adsorbed hydrogen (H^-) species in magnesium oxide (MgO) nanocrystallites. Our study suggests that the oxygen vacancies, namely singly ionized anionic vacancies (F^+) and dimers (F_2^{2+}) induce characteristic photoluminescence and the room-temperature ferromagnetic spin-order. Nanocrystallites with low population of oxygen vacancies have revealed diamagnetic behavior. Intriguingly, on adsorption of hydrogen (H^-) species in the MgO nanocrystallites, ferromagnetic behavior was either enhanced (in the case of highly oxygen deficient nanocrystallites) or begun to percolate (in the case of nanocrystallite with low population density of oxygen vacancies). © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4712058]

The traditional understanding about the carrier induced origin of magnetic coupling has been recently challenged by two experimental facts. First, the oxide diluted magnetic semiconductors have revealed magnetism on both sides of metal insulator transition and second, defect-rich undoped oxides exhibited the room temperature ferromagnetism (RTFM).[1,2] The origin of magnetic order in defect-rich undoped oxides is fundamentally and technologically fascinating as it does not results from partially filled *d* orbitals.[2] The phenomenon has been termed as d_0 magnetism. Venkatesan *et al.*[3] have experimentally shown RTFM spin-order in pristine HfO_2 thin films. The *ab initio* electronic structure suggested that the origin of FM in HfO_2 is due to cationic defects.[4] Nevertheless, the cationic vacancies induced RTFM order in HfO_2 was later questioned as the diamagnetic HfO_2 powder exhibited weak ferromagnetic order after annealing in vacuum at 750 °C for 2 h, which in turn suggested origin of FM to be related to oxygen vacancies.[5] Hong *et al.*[6] observed RTFM in TiO_2, HfO_2, and In_2O_3, and reported that the annealing of HfO_2 and TiO_2 films in oxygen ambient degraded/destroyed ferromagnetic ordering. They suggested that both oxygen vacancies and confinement effects were key factors in inducing RTFM order. Sundaresan *et al.*[7] recognized that the RTFM in CeO_2, Al_2O_3, ZnO, In_2O_3, and SnO_2 nanograins originated from oxygen vacancies at the surface of nanograins.

Similar to HfO_2, the *ab initio* electronic structure calculation for rock-salt type crystals attributed the origin of d_0 magnetic moments and the resulting FM to spin polarized holes residing on cation *p* orbitals either at vacancy or impurity sites.[8] Moreover, unlike HfO_2, the vacuum annealing of MgO films at 500 °C exhibited reduced magnetic moments.[9] It was assumed that vacuum annealing results in creation of oxygen vacancies, which subsequently reduces magnetic moments and, therefore, the observed RTFM spin-order was perceived as induced by magnesium vacancies. Recently, Maoz *et al.*[10,11] noticed that air annealing too reduced magnetic spin-order in MgO nano-sheets and suggested one electron trapped oxygen vacancies (F^+) to cause the observed ferromagnetic spin-order. Very recently, Wang *et al.*[12] exhibited invariable magnetic moments when annealing in air was performed below 1000 °C. Further, Balcells *et al.*[13] observed vacuum annealing of five months air exposed MgO thin films at 850 °C to reveal enhanced magnetic moments.

It is important to note that nanocrystalline MgO is highly hygroscopic and forms diamagnetic $Mg(OH)_2$ easily which, in turn, can reduce ferromagnetic spin-order. Moreover, hydrogen (H^-) adsorption at oxygen vacancies and Mg^{2+} lattice sites may improve magnetic moments. These two processes are competitive and, in turn, will depend on factors such as grain size, defect concentration, nature of defects, and synthesis temperature. Hence, correlating the origin of ferromagnetic spin-order solely to annealing may be injudicious. While it is evident that defects induce the d_0 magnetic moments in MgO nanocrystallites, their nature is still not well understood. In this study, we will show that the oxygen vacancies can induce RTFM spin-order in MgO nanocrystallites, and hydrogen (H^-) adsorption can drastically enhance the magnetic moments.

MgO nanocrystallites were synthesized through the sol-gel process. The magnesium nitrate hexahydrate [$Mg(NO_3)_2$ $6H_2O$] and oxalic acid [$(COOH)_2$ $2H_2O$] in 1:1 molar ratio were first dissolved separately in ethanol, and subsequently, mixed to yield a thick white gel (MgC_2O_4 $2H_2O$). The gel was digested for 12 h and dried afterward at 100 °C for 24 h, ground, sieved through 240 meshes, and calcined for 2 h each at 600 °C (in air or oxygen) and 1000 °C (in air) to yield MgO. The samples were divided in two parts (a) as synthesized-studied within few hours after synthesis and (b) stored in desiccator for one month and studied afterward. The structures of as synthesized MgO nanocrystallites were investigated by x-ray diffraction with CuK_α radiation. The magnetic characterization of MgO samples was performed using a superconducting quantum interference device

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(SQUID) magnetometer (Quantum Design Inc.). A spectrofluorophotometer (Jovin-Yvon model Spex Fluorolog II) equipped with xenon lamp of 450 W as excitation source, suitable color filters, and a double monochromator was employed for obtaining the photoluminescence (PL) spectra. In addition, a FTIR spectrometer (BRUKER Vertex-70) was used for the detection of Mg-H and H^- type substitution mass defect induced infrared modes.

X-ray diffraction patterns of MgO nanocrystallites exhibited formation of periclase phase (results not shown due to brevity). Based on Scherrer's method, their average crystallite sizes (t_{av}) were estimated as 6.0 nm (in oxygen at 600 °C for 2 h), 9.5 nm (in air at 600 °C for 2 h), and 73.5 nm (in air at 1000 °C for 2 h). The magnetization (M) versus magnetic field (H) characteristic for these nanocrystallites observed at room temperature is shown in Figs. 1(a) and 1(b). The nanocrystallites ($t_{av} \sim 9.5$ nm) synthesized at 600 °C in air ambient exhibit RTFM with the magnitude of saturation magnetization, coercive field, and remanent magnetization as being 0.013 emu/gm, 98 Oe, and 4.2×10^{-4} emu/gm, respectively. However, samples synthesized in oxygen atmosphere at 600 °C or at higher calcination temperature (~1000 °C) in air ambient reveal diamagnetic behavior. Complete bleaching of RTFM in the samples synthesized in oxygen ambient suggests oxygen vacancy induced origin of d_o magnetic moments. Moreover, above 900 °C oxygen vacancies become mobile, which, in turn, can get annihilated easily at 1000 °C, and subsequently destroy RTFM spin-order.[14] Very recently, Wang *et al.*[12] noticed extinction of magnetic moments in air annealed MgO nanocrystals above 1000 °C, which may be due to bleaching of oxygen vacancies. Our findings are consistent with the oxygen vacancies induced RTFM spin-order reported in oxides such as HfO_2, TiO_2, and ZnO, etc.[5,6]

Fig. 2 shows PL emission spectra of MgO nanocrystallites for the samples calcined for 2 h each at 600 °C (in air or oxygen) and 1000 °C (in air) recorded with excitation wavelengths of 350 nm. The emission at wavelength ~395 nm (3.14 eV) is due to $^2T_{1u} \rightarrow {}^2A_{1g}$ transition of F^+ (an oxygen vacancy retaining one electron) center relaxation and can be compared with the 390 nm (3.18 eV) emission peak reported earlier by Rosenblatt *et al.*[15] A broad emission band observed around ~430 nm (2.88 eV) is arising due to $^3B_{1u} \rightarrow {}^1A_g$ transitions of the F_2^{2+} center in D_{2h} symmetry.[16] Such centers consist of two oxygen vacancies in nearest neighbor positions along $\langle 110 \rangle$ with each having a trapped electron and have the ground and first excited states as ^1A_g and $^3B_{1u}$, respectively. The presence of oxygen during decomposition favors reduction in anionic vacancies. As a consequence, defect density is considerably reduced in oxygen ambient vis-à-vis air. The formation of oxygen vacancies can be understood as below.

The stoichiometry of magnesium oxide obtained by thermal decomposition process of magnesium oxalate dihydrate is known to vary due to release of excess CO_2 and less CO as given by the reaction[17]

$$MgC_2O_4.2H_2O \rightarrow MgO_{1-x} + (1+x)CO_2 + (1-x)CO + 2H_2O \quad (1)$$

with $x \geq 0$ depending upon the temperature and atmosphere used. The decomposition process of magnesium oxalate dihydrate in oxygen allows conversion of CO to CO_2. However, in air ambient (nitrogen ~78% and oxygen ~21%), CO may escape as CO_2 by consuming bulk/surface oxygen (O^{2-}) of MgO and forming F (an oxygen vacancy retaining two electrons) centers following the reaction:

$$CO + O^{2-} \rightarrow CO_2 + F \quad (2)$$

Thus, the presence of nitrogen in air ambient helps in enhancing the population density of F^- centers. However, at 1000 °C, the emission intensity in air synthesized samples is even less than the samples synthesized in oxygen ambient at

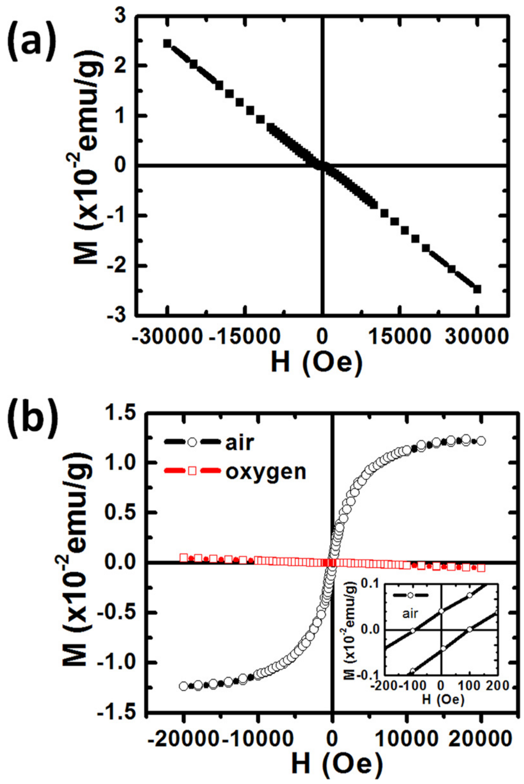

FIG. 1. Room temperature magnetization curve of MgO nanocrystallites synthesized at the calcination temperature of (a) 1000 °C in air and (b) 600 °C air and oxygen for 2 h each.

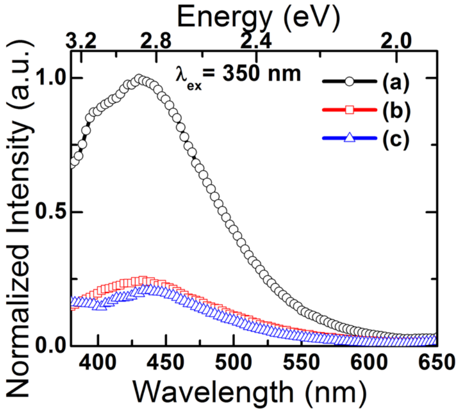

FIG. 2. The emission spectra of MgO nanocrystallites synthesized at the calcination temperature of (a) 600 °C in air, (b) 600 °C in oxygen, and (c) 1000 °C in air for 2 h each with excitation wavelength of 350 nm.

600 °C because above 900 °C oxygen vacancies become mobile and can get annihilated easily.[14] Our result does not exclude the possibility of other types of defects like cation vacancies contributing to long range FM order; however, PL results together with observed FM confirm that oxygen vacancies play a crucial role in percolation of RTFM spin-order. Moreover, recently, it has been realized that even prohibitive cation defects (~4.6% more than the thermodynamically allowed), suggested as percolation threshold for FM spin-order would not lead to FM.[10] The density functional theory (DFT) based calculations performed with local approximations of the exchange correlation potentials such as spin density approximation (LSDA) and the generalized gradient approximation (GGA) have themselves been criticized for their qualitative failures in description of hole centers in MgO.[18]

Fig. 3(a) shows M-H curves for MgO nanocrystallites stored in vacuum desiccator for one month and studied afterward. It is evident that saturation magnetization (M_s) of the sample synthesized in air at 600 °C is doubled and saturation field is reduced by a factor of four. Another interesting observation is that the samples synthesized in oxygen ambient exhibited RTFM spin-order after storage; the values of M_s, coercive field (H_c), and remanent magnetization (M_{rs}) being, 0.0045 emu/gm, 48 Oe, and 9×10^{-4} emu/gm, respectively. The sample synthesized in air ambient exhibits the M_{rs} value to be increased by the factor of six, while coercive field remains unchanged (98 Oe). Further, the sample synthesized in oxygen ambient reveals M_s value as one third, M_{rs} as twice, and the coercive field value just half of the as-synthesized sample in air ambient. This indicates easy percolation of ferromagnetic spin-order after storage of samples. We believe that vacuum storage may result in trapping of various H^- species at Mg^{2+} sites and substitution mass defect at F-type centers, which, in turn, can cause FM ordering due to an exchange interaction between the H^- captured by oxygen vacancy and Mg^{2+} ions. This means that the spins of the localized defects (oxygen vacancy) will align with the nearby Mg^{2+} ions, producing an effective magnetic field and percolating the long range ferromagnetic interactions. Khalid *et al.*[19] observed ferromagnetic spin-ordering due to hydrogenation in anionic vacancy rich ZnO. Moreover, hydrogenation induced bleaching of magnetic moments has been reported in oxides showing cationic vacancies induced FM spin-order.[13]

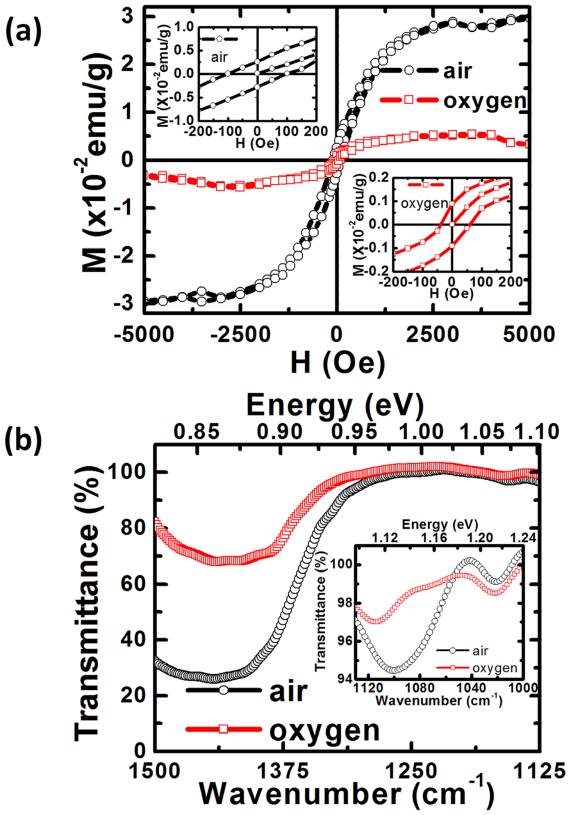

FIG. 3. Room temperature magnetization curve of MgO nanocrystallites (after storage in vacuum desiccator for one month) (a) and Mg-H and H^- type substitution mass defect induced infrared modes in the wavenumber range 1500–1125 and 1130–1000 cm^{-1} (b).

Fig. 3(b) shows Fourier transform infrared (FTIR) spectra of MgO nanocrystallites stored in vacuum desiccator for one month. The absorption peaks observed around 1442-1462, 1330, and 1155-1162 cm^{-1} are attributed to the vibration of the H^- species bonded to one, two, and three Mg^{2+} ions, respectively, which are similar to the bands observed at ~1418–1430, 1325, and 1125 cm^{-1} in MgO crystallites treated with H_2.[20–22] The source of hydrogen in MgO nanocrystallites is retained moisture which on heterolytic dissociation leads to surface hydride group and substitution mass defect H^- at oxygen vacancies (inset of Fig. 3(b)) as

$$\mathrm{Mg}^{2+}_{\mathrm{LC}} - \mathrm{F} + \mathrm{H}^{+} + \mathrm{H}^{-} \rightarrow \mathrm{Mg}^{2+}_{\mathrm{LC}}(\mathrm{H}^{-}) - \mathrm{F}(\mathrm{H}^{+}) \qquad (3)$$

The absorption bands noticed around 1020 and 1075 cm^{-1} are arising due to H^- defect. This finding is similar to the observations of absorption bands at 1024, 1032, and 1053 cm^{-1} in MgO crystals grown by arc-fusion method and reduced subsequently.[23] The shift (red or blue) of absorption bands is expected if H^- defect occupies slightly different or distorted octahedral symmetry. The band at higher wavenumber ~1100–1120 cm^{-1} is arising possibly due to $H^- - H^-$ pairs on adjacent $\langle 110 \rangle$ anion sites. Though it is obvious that H^- adsorption plays a vital role in percolation of FM spin-order, its mediating mechanism deserves further investigation.

In conclusion, our results revealed the existence of a close correlation between ferromagnetism, oxygen vacancies, namely singly ionized anionic vacancies (F^+) and dimers (F_2^{2+}), and adsorbed H^- species. MgO nanocrystallites with poor population of oxygen defects exhibited diamagnetism, and subsequently RTFM on H^- adsorption at Mg^{2+} sites, and substitution mass defect H^- at oxygen vacancies. The undoped MgO nanocrystallites with tunable magnetic and optical properties may be promising to find applications in multifunctional photonic nanodevices.

This work was supported by the office of basic energy sciences, Department of energy through the Grant No. DE-FG02-08ER 46484.

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