SYNTHESIS AND DISTRIBUTIONS OF Mn^{4+} IONS IN NONMAGNETIC SiO_2

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ABSTRACT

Mn-doped SiO_2 (with different Mn^{4+} ions concentration) were prepared by the solid-state method. The observations of phase and morphology display single-phase and identical morphology. The magnetization versus magnetic field of Mn-doped SiO_2 was measured using a superconducting quantum interference device magnetometer (SQUID) at 4 K. Electron paramagnetic resonance, EPR, study reveals Mn^{4+} spins in the nonmagnetic SiO_2 . The observed results indicate that isolated Mn^{4+} ions in the nonmagnetic SiO_2 matrix lead to ferromagnetic behavior.

Keywords: Mn^{4+} Spins, Hysteresis, Electron Paramagnetic Resonance, Ferromagnetic, SiO_2 .

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INTRODUCTION

Recently, diluted magnetic semiconductors (DMS) have fascinated researchers because of their potential applications in spin-based multi-functional electronic devices of field-effect transistors, field emission, optoelectronics, gas sensors, ultraviolet related absorbers, quantum computer and nonvolatile memories.¹⁻³

At more than room temperatures, the transition metal ions (TM) doped SiO_2 have no-magnetism, whereas $\text{Si}_{1-x}\text{Mn}_x\text{O}_2$ exhibits ferromagnetism at low temperatures.⁴ The doping at the Oxygen site by Carbon (C) or Nitrogen (N) also induces the ferromagnetism in the SiO_2 . However, both these C and N doping show quite different magnetic behavior. But the Nitrogen doping induces ferromagnetism, whereas Carbon substitution exhibits an anti-ferromagnetic behavior in SiO_2 matrix. The nitrogen-doped SiO_2 is a potential candidate for dielectric material for SiO_2 . The theoretical analysis indicates that nitrogen-doped SiO_2 behave as half-metal ferromagnetism at 300 K.⁴ The N-substitution induces an impurity band near the valence band of SiO_2 . Moreover, the impurity bandwidth increases with doping content. This bandgap narrowing is favorable for ferromagnetism. Experimentally ferromagnetism was obtained in N- SiO_2 films and Si- SiO_2 films.⁴⁻⁷

With varying physical conditions (Pressure (P), temperature (T)) of SiO_2 undergoes complex phase transformations. The framework of SiO_2 entailing of $[\text{SiO}_4]$ tetrahedra combined into a giant polymeric “open molecule” of oxygen sharing. This is due to the Si - O - Si angles adjustment between tetrahedra. SiO_2 is a simple compound, but many structural forms can vary from different properties.⁸ Le Page and Donnay was refined quartz structure.⁸ The trigonal symmetry, space group $P3_221$, with a lattice parameter of $a = 4.9134 \text{ \AA}$, and $c = 5.4052 \text{ \AA}$.¹⁰

In this paper, we investigated magnetic and electron paramagnetic measurements on Mn-doped SiO_2 (with different Mn^{4+} ions concentration) and found that the distributions of Mn^{4+} ions in nonmagnetic SiO_2 lead to ferromagnetic behavior at low temperature.

EXPERIMENTAL

Polycrystalline samples of nominal composition $\text{Si}_{1-x}\text{Mn}_x\text{O}_2$ (pure, 5 and 10 % Mn) were prepared using the solid-state method. The SiO_2 and MnO_2 high purity powders were mixed. These powders first fired at 600 °C for 12 h in air. The first heated powders were ground and finally calcinated at 1000 °C for 12 h. All the samples were prepared in identical conditions.

The pure, 5 and 10 % Mn-doped SiO_2 samples structure and phase purity were measured using room-temperature X-ray diffraction (XRD) with a Cu-K α radiation. The magnetization in zero fields cooled (ZFC) and field cooled (FC) conditions were measured in a SQUID magnetometer (Quantum Design). The hysteresis curves were measured for $-5 \text{ T} \leq H \leq +5 \text{ T}$. The background signal from the sample holder was corrected. Electron paramagnetic resonance (EPR) spectra of the samples were measured with the commercial Bruker ESP300 EPR spectrometer operating in the microwave X-band (9.45 GHz) equipped with the standard Bruker ER4102ST rectangular cavity with the TE102 microwave mode.

RESULTS AND DISCUSSION

Figure-1 represents the XRD patterns of the investigated pure, 5 and 10 % Mn-doped SiO_2 samples. The patterns show strong reflections located at $2\theta = 20.95^\circ, 26.73^\circ, 36.63^\circ, 50.23^\circ$ and 60.03° and indexed to the planes (100), (101), (110), (112) and (211). These patterns are compared and indexed according to the trigonal structure with a space group $P3_221$.^{9,10} The lattice parameter was found to be $a = 4.9134 \text{ \AA}$, and $c = 5.4052 \text{ \AA}$. It can be attributed to that the ionic radius of Mn^{4+} ions (54 pm) is the same as that of Si^{4+} (54 pm) as a result of which the lattice parameters are unchanged with increasing concentration of Mn. The XRD pattern reveals that the intensity of XRD peaks is decreased with increasing Mn content.

Fig.-1: The X-ray Diffraction Patterns of $\text{Si}_{1-x}\text{Mn}_x\text{O}_2$ ($x = 0, 0.05$ and 0.1) Samples. Bragg Reflections are indicated.

The prepared samples are homogenous in a single-phase confirmed by Scanning electron microscope (SEM) pictures as shown in Fig.-2.

The hysteresis (M–H) plot of both 5 and 10 % Mn-doped SiO_2 at 4 K is depicted in Fig.-3(a). The magnetization curves exhibit non-linear behavior for both 5 and 10 % Mn-doped SiO_2 . The saturation magnetization M_s was found to be 0.025 emu/g (5% Mn), and 0.036 emu/g (10 % Mn) doped SiO_2 samples. The magnified view of M– H curves near the center is shown in set of Fig.-3(a). The symmetrical elongated hysteresis loop appears in both 5 and 10 % Mn-doped SiO_2 samples, a small coercive field (H_c) around 48 Oe reveals ferromagnetism.

The temperature dependence of magnetization curves obtained an applied magnetic field of 1 kOe for the sample with $x = 0.10$ is depicted in Fig.-4. The ZFC M (T) curves show temperature-independent reveals

FM ordering persists for all measured samples. Fits of Curie Weiss law of the magnetic susceptibility down 100 K yield an effective Bohr magnetron number P_{eff} . The obtained P_{eff} value is $3.67 \mu_B$ is consistent with a spin only value ($3.87 \mu_B$) of Mn^{4+} ions and negative Curie temperature (-667 K) indicates interactions are strong anti-ferromagnetic for the samples with Mn content, $x = 0.1$.

Fig.-2: Scanning Electron Microscope Pictures of $Si_{1-x}Mn_xO_2$ Samples (a) $x = 0$, (b) 0.05, and (c) 0.1.

Fig.-3: The Isothermal $M(H)$ Curves for $Si_{1-x}Mn_xO_2$ ($x = 0, 0.05$ and 0.1) Samples measured at 4 K for $-20 \text{ kOe} \leq H \leq 20 \text{ kOe}$. Inset expanded View of Center Portion.

Fig.-4: The Variation of Susceptibility (χ) as a Function of Temperature for $Si_{1-x}Mn_xO_2$ ($x = 0.1$) Sample measured in a Field of 1 kOe. Right Axis shows $1/\chi$ and Red line shows Curie Weiss fitting.

Comparing the both hysteresis curve and EPR data concluded that the Mn–Mn strong interactions. To investigate the effects around the local Mn^{4+} sites in these samples, EPR studies were measured. The observed EPR spectra are shown in Fig.-5 for 5 and 10 % Mn-doped SiO_2 samples at room temperature. Similar reports of EPR spectra for Mn^{4+} ions in PbTiO_3 .¹¹ These measurements provide evidence for local structure changes at the Mn^{4+} substitution site.

Fig.-5: The EPR Spectra of 5 and 10% Mn doped SiO_2 Samples

CONCLUSION

Magnetization and EPR measurements in Mn-doped SiO_2 (Mn^{4+} ions concentration) were investigated. The phase and morphology display single-phase and identical morphology. The magnetization versus magnetic field of Mn-doped SiO_2 samples was measured at 4 K, which indicates small hysteresis behavior. EPR spectra show distinct Mn^{4+} spins in the nonmagnetic SiO_2 . The observed results indicate the ferromagnetic behavior of Mn-doped SiO_2 .

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