Research Article

Magnetic Characterizations of Sol-Gel-Produced Mn-Doped ZnO

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Nanoparticles of ZnO doped with 6 at.% Mn were produced by a sol-gel method. X-ray diffraction confirms the hexagonal structure as that of the parent compound ZnO, and high-resolution electron transmission microscopy reveals a single-crystallite lattice. Magnetic measurements using a superconducting quantum interference device indicate that about one half of the Mn2+ ions follow Curie’s law for paramagnetism. The remaining Mn2+ ions exhibit a weak ferromagnetic character, which might be induced through canted antiferromagnetic interactions.

1. Introduction

Wide-band gap semiconductor ZnO has a broad range of utilizations from ultraviolet protection to functional devices [1]. With a low-level substitution of Zn by certain magnetic cations, the generally categorized dilute magnetic semiconductors (DMSs) often exhibit ferromagnetism at ambient temperatures. After their discovery by Ohno et al. [2, 3], DMSs have attracted much attention in materials development towards spintronics application. Main emphases of the research so far appear to remain in the stage of processes evaluation in terms of magnetic behaviors of the products, while Toyoda et al. [4] have made self-interaction-correlated local-density approximation calculations on electronic structures for semiconductor spintronics. Beside the effort along this line, a sol-gel method was employed here to synthesize nanoparticles of (Zn0.94Mn0.06)O for comparison with other reported studies on Mn2+-doped zinc oxide including nanocrystals prepared by high-temperature hydrolysis [5] and films from plasma-assisted rf magnetron sputtering [6].

2. Experimental

All chemicals used were obtained from Sigma Aldrich unless otherwise specified. The relative amount of two precursors, Mn(NO3)2·4H2O and Zn(NO3)2·6H2O, correspond to a Mn/Zn atomic ratio of 0.06/0.94. They were thoroughly mixed in deionized water on a hot plate with a magnetic stirrer. At 5-minute intervals, benzoic acid, citric acid (Fisher Scientific), and ethylene glycol were subsequently added, each of the similar amount as that of zinc nitrate. The temperature was maintained at 30–40°C for complete dissolution. It was then raised and held at 70–80°C for 3 hours until all fluid was evaporated. Evaporation left behind a viscous gel, which was transferred to an oven for dehydration at 150°C over a period of 15 hours. The hard, porous product was crushed and ground to fine powders and placed in a crucible for heat-treatment at 550°C for two hours. Further regrinding yielded nanoparticles sample of (Zn0.94Mn0.06)O.

3. Results and Discussion

A high-resolution transmission electron micrograph (TEM) in Figure 1 shows single-crystallites having a 30-nm average size. The crystalline lattice is clearly revealed in Figure 2. X-ray diffraction (XRD) patterns in Figure 3 confirm the hexagonal wurtzite (ZnS) structure of spatial P6 3mc group for ZnO [1], which has little change due to Mn doping up to 6 at.%. This is not unexpected, considering the small difference between the ionic sizes of divalent Zn (0.74 Å) and Mn (0.80 Å) [5]. Presumably, Mn2+ enters the lattice substituting for Zn2+. However, one cannot be certain of
the actual distribution of Mn in lattice. The magnetic data analysis below could provide some information in this regard.

Magnetic behaviors are determined using a superconducting quantum interference device. Magnetization $M$, in units of emu/g with $g$ referring to 1 g of sample, varies with temperature $T$ in Figure 4 at a constant field $H$ of 100 Oe. $M$ increases with decreasing temperature from 300 K to 5 K, but it does not follow any simple fit to Curie’s law for paramagnetic magnetization $M_p$

$$\frac{M_p}{H} = \frac{N p^2 \mu_B^2}{3k_BT}, \quad (1)$$

where $N$, $p$, $\mu_B$, and $k_B$ are, respectively, the number of dipoles, effective moment for each dipole, Bohr magneton and Boltzmann constant. This is somewhat expected, since only uncoupled and non-interacting Mn$^{2+}$ ions should yield a pure paramagnetic (PM) behavior. Other Mn$^{2+}$ ions, if situated nearby to each other or in the form of clusters, could have ferromagnetic (FM) or antiferromagnetic (AFM) interactions among them. One way to observe these magnetic interactions is from the field dependence of magnetization at constant temperature. Consequently, magnetization data in Figure 5 were obtained at 300 K, but with varying fields up to 6,000 Oe. A curvature is obvious below approximately 3,000 Oe.

Delineation of the total magnetization into components relies on the individual characteristic of each magnetic behavior. For PM, (1) prescribes a linear relation between $M$ and $H$ at constant temperature. Ideal AFM would yield zero $M$ value. In contrast, for FM in single-domain nanoparticles, $M$ would increase initially with $H$ and reaches a saturation value at certain higher fields. Numerically, the delineation is successfully achieved as in Figure 4, with a paramagnetic magnetization $M_p = 5.3 \times 10^{-6}$ H emu/g and a ferromagnetic magnetization which saturates at $M_s = 0.0068$ emu/g near 3,000 Oe.

There are a total of $4.5 \times 10^{20}$ Mn$^{2+}$/g in (Zn$_{0.94}$Mn$_{0.06}$)O. By taking the often quoted effective moment $p = 5.9 \mu_B$ for the actual distribution of Mn in lattice. The magnetic data analysis below could provide some information in this regard.

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Zener’s double exchange mechanism [7]. Another source of $M_p$ which increases with increasing field to saturation near 3,000 Oe. following (1), and a ferromagnetic-type contribution (open circle), which increases with increasing field to saturation near 3,000 Oe.

Mn

Experimentally obtained magnetization (close circle) can be delineated into a paramagnetic contribution (open square) from 300 K to 77 K, signifying AFM. Meanwhile, a spin moment or a weak FM as observed here. Such a scenario is corroborated by electron spin resonance (ESR) experiments. In the present study, sol-gel-based (Zn$_{0.94}$Mn$_{0.06}$)O nanoparticles were synthesized using a sol-gel process and their magnetic properties were investigated. It was determined that the nanoparticles have roughly equal amount of Mn$^{2+}$ ions in either paramagnetic or magnetically interacting states. The latter is mainly antiferromagnetic in nature, but magnetic frustration causes part of them to exhibit a canted AFM, which results in a ferromagnetic-like behavior. These doped nanomaterials may be used in various applications, such as electronic, sensor, spintronic, coating, and solar and fuel cells.

4. Conclusions

In the present study, sol-gel-based (Zn$_{0.94}$Mn$_{0.06}$)O nanoparticles were synthesized using a sol-gel process and their magnetic properties were investigated. It was determined that the nanoparticles have roughly equal amount of Mn$^{2+}$ ions in either paramagnetic or magnetically interacting states. The latter is mainly antiferromagnetic in nature, but magnetic frustration causes part of them to exhibit a canted AFM, which results in a ferromagnetic-like behavior. These doped nanomaterials may be used in various applications, such as electronic, sensor, spintronic, coating, and solar and fuel cells.

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References


