Absence of room temperature ferromagnetism in bulk Mn-doped ZnO

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Structural and magnetic properties have been studied for polycrystalline \( \text{Zn}_{1-x}\text{Mn}_x\text{O} \) \((x = 0.02, 0.03, 0.05)\). Low-temperature \((\sim 500^\circ\text{C})\) synthesis leaves unreacted starting ZnO and manganese oxides. Contrary to a recent report, no bulk ferromagnetism was observed for single-phase materials synthesized in air at temperatures above 900°C. Single-phase samples show paramagnetic Curie-Weiss behavior.

In order to exploit spins as information carriers in functional spintronics it is necessary to develop new materials that would exhibit both room temperature ferromagnetism and semiconducting properties. Recent theoretical predictions of room temperature ferromagnetism in \( \text{Zn}_{1-x}\text{Mn}_x\text{O} \), where \( M = \text{Mn} \) \((p\text{-type})\) or \( \text{Fe}, \text{Co}, \text{Ni} \) motivated the study of this class of materials. In our recent paper, we have shown that the ferromagnetic contribution to the magnetization in polycrystalline \( \text{Zn}_{1-x}\text{Mn}_x\text{O} \) can originate from ferromagnetic impurities. A recent article in Nature Materials by Sharma et al. reported on observation of ferromagnetism above room temperature in bulk polycrystalline material and thin films of \( \text{Zn}_{0.98}\text{Mn}_{0.02}\text{O} \). Sharma et al. claim that such materials are obtained homogeneous and uniform from the low-temperature \((500-700^\circ\text{C})\) ceramic processing. Several papers alternatively reported the presence or absence \((9,10,11,12)\) of high temperature ferromagnetic ordering in \( \text{Zn}_{1-x}\text{Mn}_x\text{O} \), which is a result of different preparation methods. Here we show that single-phase \( \text{Zn}_{1-x}\text{Mn}_x\text{O} \) \((x \leq 0.05)\) can be synthesized in air only at higher temperatures \((> 900^\circ\text{C})\). Low-temperature synthesis leads to incompletely reacted mixture of diamagnetic ZnO and magnetic manganese oxides. Single-phase polycrystalline \( \text{Zn}_{1-x}\text{Mn}_x\text{O} \) is paramagnetic similar to other Mn-containing diluted magnetic semiconductors.

The \( \text{Zn}_{1-x}\text{Mn}_x\text{O} \) \((x \leq 0.05)\) samples in this study were prepared using a standard solid-state reaction, similar to that used by Sharma et al. Mixtures of ZnO and MnO\(_2\), (purity 99.999%, Johnson Matthey Materials, UK and Alfa Aesar, USA, respectively) were fired in air at 400°C for 12 hours, pressed into pellet and annealed at increasing temperatures \((T_{\text{ann}})\) up to 1350°C. For the high-temperature \((T_{\text{ann}} > 900^\circ\text{C})\) annealing, when Mn starts to substitute for Zn in the material, the samples were reground and re-pressed before each firing.

Magnetic ac susceptibility and dc magnetization were measured using a Physical Property Measurement System and a Magnetic Property Measurement System (both Quantum Design) at temperatures up to 400 K. X-ray diffraction (XRD) experiments have been performed using a Rigaku x-ray diffractometer. Energy dispersive x-ray spectroscopy (EDXS) analysis was performed by a Hitachi S-4700-II scanning electron microscope. Thermogravimetric analysis was done with a Cahn thermobalance.

In Fig. 1 we show a semi-logarithmic plot of XRD patterns for \( \text{Zn}_{0.97}\text{Mn}_{0.03}\text{O} \) annealed at various temperatures \(T_{\text{ann}}\). Essentially, the same results were obtained for \( \text{Zn}_{0.98}\text{Mn}_{0.02}\text{O} \). In all the XRD spectra, we observe the main peaks of the wurtzite structure of ZnO. Each strong peak is accompanied by a smaller peak due to incompletely filtered CuKβ radiation. Besides these peaks, secondary peaks of manganese oxides are observed after annealing at low temperatures. For \( T_{\text{ann}} < 500^\circ\text{C} \), peaks of MnO\(_2\) are observed. For \( T_{\text{ann}} > 500^\circ\text{C} \), the peaks of MnO\(_2\) are visible. The transformation of the secondary phase MnO\(_2\) to MnO\(_3\) in air is consistent with the structural transition of pure MnO\(_2\), observed with XRD and thermogravimetric measurements. At \( T_{\text{ann}} = 500^\circ\text{C} \), both manganese oxides are present for \( \text{Zn}_{1-x}\text{Mn}_x\text{O} \) samples annealed for 12 hours. The presence of manganese oxide peaks is an indication that the polycrystalline \( \text{Zn}_{1-x}\text{Mn}_x\text{O} \) is not single-phase after low-temperature annealing, contrary of the conclusion drawn by Sharma et al. When a standard ceramic synthesis

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FIG. 1: Semi-logarithmic plots of x-ray diffraction (XRD) patterns for \( \text{Zn}_{0.97}\text{Mn}_{0.03}\text{O} \) annealed at various temperatures (listed in the Figure). The spectra are shifted for clarity. CuKβ radiation peaks of ZnO are marked with β. Stars and crosses denote impurity peaks of MnO\(_2\) and MnO\(_3\), respectively. The silica standard peak is marked with ‘S’.
method is used, the Zn$_{1-x}$Mn$_x$O compound starts to form a single-phase compound at temperatures higher than 900°C.

The Mn substitution in Zn$_{1-x}$Mn$_x$O can also be easily verified by observing the change of the lattice parameters as a function of $T_{\text{ann}}$. The lattice parameters of the wurtzite structure are shown in Figs. 2(a–c), for several nominal Mn contents $x$. For comparison, the lattice parameters of similarly annealed pure ZnO are also shown. Fig. 2 demonstrates that the lattice parameters of Zn$_{1-x}$Mn$_x$O are fairly constant and almost identical with those of pure ZnO for $T_{\text{ann}} \leq 900°C$. For higher $T_{\text{ann}}$, the lattice constants gradually increase; this effect is evidence for substitution of Mn for Zn since Mn$^{2+}$ is larger than Zn$^{2+}$. At $T_{\text{ann}} > 900°C$, the compositions with $x = 0.02–0.05$ become single-phase. Subsequent annealing of the single-phase samples at 500°C does not significantly change the lattice parameters, indicating that the oxidation state of Mn incorporated to Zn$_{1-x}$Mn$_x$O does not change.

In Fig. 3 we show scanning electron micrographs of Zn$_{0.97}$Mn$_{0.03}$O pellets after annealing in air at various temperatures. We observe that the size of the grains increases with the increase of $T_{\text{ann}}$ from less than 1 µm for $T_{\text{ann}} = 500°C$ up to over 10 µm for $T_{\text{ann}} = 1300°C$.

EDXS spectra taken on selected areas show the presence of individual grains of pure manganese oxide for $T_{\text{ann}} = 500°C$ [marked with arrows in Fig. 4(a)] and pure ZnO. For higher $T_{\text{ann}}$, the material is more homogeneous and more substituted Mn can be detected in the grains. Fig. 4(d) presents the effective Mn content from the EDXS data. The EDXS data confirm that the Mn substitution gradually increases with increasing $T_{\text{ann}}$ and single-phase Zn$_{1-x}$Mn$_x$O ($x \leq 0.05$) forms at high temperatures (> 900°C).

In Fig. 4 we present temperature dependencies of magnetic susceptibility for the sample with nominal composition Zn$_{0.97}$Mn$_{0.03}$O annealed at various $T_{\text{ann}}$. The diamagnetic contribution of ZnO, equal to $-0.33 \times 10^{-6}$
em/g, was subtracted from the measured data. For $T_{\text{ann}} < 500^\circ\text{C}$, the susceptibility follows the temperature dependence expected for manganese oxides that were observed in the XRD spectra. The antiferromagnetic transition of MnO$_2$ can be seen at $T_N = 92$ K and in addition a very small contribution ($\sim 0.01\%$) of ferromagnetic Mn$_3$O$_4$ with $T_C = 43$ K is visible. The Mn$_3$O$_4$ present in trace amounts in the original MnO$_2$ (see: left inset to Fig. 4) shows how apparent vestiges of ferromagnetic impurities are in susceptibility data. Note that for correct identification of such phases it is critical to perform temperature dependent measurements. For $T_{\text{ann}} = 500^\circ\text{C}$, the antiferromagnetic transition of Mn$_2$O$_3$ is also present at $T_N = 76$ K. This behavior is expected for an incompletely reacted mixture of ZnO and manganese oxides. As a reference, we have also plotted the magnetic susceptibility for MnO$_2$ (dashed line in the left inset to Fig. 4) annealed at 500$^\circ\text{C}$, multiplied by 0.03. This curve matches well the magnetic susceptibility for Zn$_{0.97}$Mn$_{0.03}$O for $T_{\text{ann}}=500^\circ\text{C}$, except for lower temperatures, where a weak paramagnetic contribution is observed for Zn$_{0.97}$Mn$_{0.03}$O, probably due to a partial substitution of Mn for Zn in the grain boundaries region. For higher $T_{\text{ann}}$, when Mn is incorporated into the ZnO crystal lattice structure, the material becomes paramagnetic and the susceptibility increases one hundredfold. This reflects the random distribution of the low concentration of Mn$^{2+}$ ions on the lattice sites and is characteristic of diluted magnetic semiconductors. No ferromagnetism at room temperature was detected for any of the studied Zn$_{1-x}$Mn$_x$O samples. Generally, the magnetization shows a linear dependence on the applied magnetic field. Occasionally, a very small hysteretic contribution to the magnetization can be observed, but it is always traced to the contamination of the sample holder (see: right inset to Fig. 4).

In summary, we have synthesized polycrystalline Zn$_{1-x}$Mn$_x$O ($x \leq 0.05$). This compound can be formed at temperatures higher than 900$^\circ\text{C}$ using a ceramic route and shows paramagnetic properties analogous to other diluted magnetic semiconductors. Low-temperature annealing leaves an incompletely reacted mixture of ZnO and manganese oxides. No bulk ferromagnetism can be observed for any of the studied samples. At the moment, the origin of the room temperature ferromagnetic behavior observed by Sharma et al. is not clear. Nevertheless, we provide here conclusive evidence that the samples that exhibit ferromagnetism or antiferromagnetism are not single-phase Zn$_{1-x}$Mn$_x$O compounds.

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