Chemical synthesis and magnetic properties of dilute magnetic ZnTe:Cr crystals

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ZnTe and Cr doped ZnTe crystals have been synthesized using a solvothermal process. The characterizations by x-ray diffraction and transmission electron microscopy show that the synthesized ZnTe:Cr crystals have a cubic structure and Cr is incorporated into ZnTe. The magnetic properties of ZnTe:Cr are investigated. A hysteresis is observed in the magnetization versus magnetic field measurements below 10 K. The detailed analyses suggest that the hysteresis possibly originated from the magnetic short-range ordering of $\text{Zn}_{1-x}\text{Cr}_x\text{Te}$ compounds in the sample. © 2006 American Institute of Physics. [DOI: 10.1063/1.2337561]

ZnTe is an attractive material for various optoelectronic devices,^{1–4} such as green light-emitting diodes, electro-optic field detectors, and solar cells. In recent years, studies of transition metal doped dilute magnetic semiconductor (DMS) ZnTe start to attract a lot of attention as DMSs are promising candidates in spintronics studies and applications. It has been shown theoretically that the ferromagnetic state is more stable in Cr doped ZnTe than the spin glass state but is less stable in Mn, Fe, and Co doped ZnTe if the concentrations of these transition metals are larger than 5%.⁵ From the magnetic point of view the Cr^{2+} ion system represents an intermediate case between typical Brillouin-type paramagnetism (typical for Mn and Co DMSs) and Van Vleck-type paramagnetism (Fe-DMS).^{6,7} The most interesting feature of Cr doped DMS is the observed ferromagnetic p - d exchange interaction in excitonic magnetorefectance for ZnCrSe ,⁸ ZnCrS ⁹ and ZnCrTe .¹⁰ Recent work by Saito *et al.* on $\text{Zn}_{1-x}\text{Cr}_x\text{Te}$ thin films grown by molecular beam epitaxy showed that the ferromagnetic Curie temperature (T_C) was around 15 K with $x=0.035$ (Refs. 11 and 12) and even at room temperature with $x=0.20$.^{13,14} In addition, Pekarek *et al.* found that the transition temperature is slightly above 300 K for the ferromagnetic phase in a bulk $\text{Zn}_{1-x}\text{Cr}_x\text{Te}$ crystal grown by vertical Bridgman method.¹⁵ They ascribed the ferromagnetic signal to a pure CrTe minority phase. Their more recent work showed that single-crystalline $\text{Zn}_{1-x}\text{Cr}_x\text{Te}$ grown by vertical Bridgman method with $x=0.0033$ has a T_C above room temperature, which was believed to arise from precipitates of $\text{Zn}_x\text{Cr}_y\text{Te}_z$ within the II-VI DMS host.¹⁶ Nevertheless, rather few reports of the chemical preparation of ZnTe (Ref. 17) and transition metal doped ZnTe are available. In this work, we synthesized ZnTe and Cr doped ZnTe crystals by a simple solvothermal process. X-ray diffraction and transmission electron microscopy results show that the

synthesized ZnTe:Cr crystals have a cubic structure and Cr is incorporated into ZnTe. The magnetic properties of ZnTe:Cr are depicted by a hysteresis observed in the magnetization versus magnetic field measurements below 10 K.

ZnTe and Cr doped ZnTe crystals were synthesized using a solvothermal process. It was carried out by standard air-free techniques. A mixture of diethylzinc (1 mmol, 1 ml) and trioctylphosphine oxide (TOPO) (3 g) which was added as surfactant during the reaction process was heated in a three neck flask to 300 °C for 1 h. Then 6 ml tellurium-trioctylphosphine (TOP) solution (containing 1.2 mmol, 0.153 g tellurium powder) was quickly injected into this hot solution. The synthesis was carried out under N_2 flow. An aliquot at a given reaction time (1 h) was taken out from the reaction flask with a small syringe and transferred quickly into a vial with toluene. The products were washed with methanol. After centrifugal separation, we obtained ZnTe powders. Cr doped ZnTe crystals were obtained by the same procedure as described above, except adding 0.1 mmol CrCl_2 as the source of Cr to the mixture of diethylzinc and TOPO before heating. The following chemical reaction is assumed to take place during the reaction process:

The structures of the obtained materials were characterized by powder x-ray diffraction (XRD) and transmission electron microscopy (TEM). The Cr content was determined by an x-ray fluorescence (XRF) spectrometer JEOL JSX-3201Z. The magnetic properties were measured using a superconducting quantum interference device magnetometer (MPMS-5s).

A typical XRD spectrum for undoped ZnTe crystals is shown in Fig. 1(a). As can be seen, all of the diffraction peaks observed can be indexed in line with the reported data for the bulk cubic ZnTe lattice (Ref. 18, $a_0=6.1026$ Å). The expected diffraction peaks are indicated by the vertical bars on the top x axis and the bar lengths are proportional to

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FIG. 1. (Color online) XRD spectra of (a) undoped and (b) Cr doped ZnTe crystals. The upper vertical bars represent the position of the diffraction peaks for the bulk ZnTe cubic lattice structure and their lengths are proportional to intensity.

intensity. The XRD spectrum of a Cr doped ZnTe sample is shown in Fig. 1(b). It is evident that no significant difference in the spectrum can be detected in comparison with that of the undoped ZnTe sample. The Cr content of about 0.0521 mol % ($x \approx 0.00107$) in the doped sample is determined by the XRF result. At such a low Cr concentration, it is therefore expected that no significant change of the lattice parameter can be induced and the XRD spectra of the undoped and doped samples are identical.

Figure 2 shows the typical TEM images of undoped (a) and Cr doped (b) ZnTe samples. As it can be seen, the sizes of the synthesized crystals ranged from 100 to 200 nm. The crystal shape is irregular but most of the crystals are single crystalline. Energy dispersive spectrometry analysis indicates no other unexpected impurities in the crystals. It is known that the electron Bohr radius in ZnTe is ~ 5.2 nm,¹⁹ which implies that the quantum confinement effect is not observable in our samples.

The measured magnetization curves versus magnetic fields for Cr doped ZnTe sample at various temperatures are shown in Fig. 3. The diamagnetic signal due to the host ZnTe has been subtracted from these curves. A magnified view of the curve measured at 3 K in the low magnetic field range [Fig. 3(b)] clearly illustrates the existence of a hysteresis loop. This hysteresis loop can be observed up to 10 K. At 25 K or above, the hysteresis loop disappears.

The temperature-dependent magnetizations were measured in the zero-field-cooled (ZFC) and field-cooled (FC)

FIG. 2. TEM images of (a) undoped ZnTe and (b) Cr doped ZnTe crystals. The size of crystals ranges from 100 to 200 nm.

FIG. 3. (Color online) (a) Magnetization vs magnetic field curves for the Cr doped ZnTe sample measured at various temperatures. (b) A magnified view of the data at 3 K in low magnetic fields.

processes in a 200 Oe field in the temperature range from 300 to 5 K. Since the sample is purely paramagnetic at high temperatures, only low-temperature data are plotted in Fig. 4 for the sake of clarity. The divergence of the ZFC and FC curves below about 14 K indicates the existence of metastable states caused either by the blocking of the magnetic moment of the magnetic clusters²⁰ or the domain wall pinning.²¹ Since the FC curve monotonically increases with decreasing temperature and follows the Curie-Weiss law below the divergence temperature of 14 K (see inset of Fig. 4), the magnetic nature of the sample should be ascribed to a magnetic cluster system rather than a bulklike magnet.^{20,21} Due to the blocking of the magnetic clusters, hysteresis loops are expected to appear at temperatures below the divergence temperature, which is in good agreement with the data shown in Fig. 3.

Formation of the magnetic clusters might be due to some precipitates in Cr doped sample. The most likely magnetic precipitate in Cr doped sample is reported to be the NiAs-type CrTe compound, whose Curie temperature T_C is slightly above 300 K.²² For our sample, CrCl_2 precipitate is also possible as it is the source of Cr in the sample preparation process, and CrCl_2 is antiferromagnetic with a Néel temperature (T_N) of 16.05 K.^{23,24} If the NiAs-type CrTe compound par-

FIG. 4. Temperature dependence of magnetization under zero field cooling and 0.02 T field cooling for Cr doped ZnTe. Inset: $1/M$ as a function of temperature for FC magnetization data, the line is a guide to the eyes.

ticles or CrCl_2 precipitate particles were mixed into the sample, the particles size would be in the range of 100 to 200 nm, as shown in the TEM analysis. Magnetic particles of these sizes generally show a bulk behavior. Therefore, for the ferromagnetic NiAs-type CrTe compound, the $M(T)$ curve will weakly depend on temperature in the low-temperature range and exhibit a sharp drop at its Curie temperature around 300 K, whereas for the antiferromagnetic CrCl_2 , both ZFC and FC magnetizations will decrease with decreasing temperature below its Néel temperature of 16 K. However, the magnetization curves in Fig. 4 show completely different behaviors, which excludes the possibility that either NiAs-type CrTe compound and/or antiferromagnetic CrCl_2 particles are present in the sample.

The remaining possible mechanism responsible for the observed hysteresis and the divergence of low field magnetization curves at low temperatures is then related to short-range magnetic ordering in ZnTe:Cr sample. It has been shown by Saito *et al.*¹¹ that the paramagnetic Curie temperature is significantly higher than the ferromagnetic T_C in $\text{Zn}_x\text{Cr}_{1-x}\text{Te}$ thin film with $x=0.035$. This indicates that the magnetic short-range order remains even far above T_C . From Fig. 4, the T_C of our sample has not been found but a magnetic short-range order may already exist up to 14 K as indicated by the obvious hysteresis loops (Fig. 3) and the divergence of the ZFC and FC curves (Fig. 4). But where does the magnetic short-range order originate from? XRF result shows that the Cr concentration has a quite low value of $x=0.00107$. If the magnetic short-range ordering arises from precipitates of $\text{Zn}_x\text{Cr}_y\text{Te}_z$ due to concentration fluctuations, the Curie temperature T_C should be up to room temperature referring to the samples of Pekarek *et al.* with $x=0.0033$.¹⁶ It is therefore evident that the precipitates of Ni-As-type CrTe, or $\text{Zn}_x\text{Cr}_y\text{Te}_z$, or CrCl_2 , or other Cr ion based compounds are unlikely the origins for explaining the hysteresis loop observed in this sample. As a result, one would expect that a few small ferromagnetic $\text{Zn}_{1-x}\text{Cr}_x\text{Te}$ clusters might be formed inside the sample because of the low Cr concentration. These clusters distribute randomly in the ZnTe host and the coupling between them can be ignored for the small number and large separation. The magnetization directions of these clusters are stochastic when there is no external magnetic field, but upon application of a small magnetic field the magnetic moment of those clusters will try to align along the field direction, and moreover, the magnetic moment must overcome the magnetic anisotropy that exists in all magnetic materials to reach their equilibrium. These lead to the divergence between the ZFC and FC magnetization curves at low temperatures.^{20,25} In addition, at low temperature the blocked rotation of the magnetic moment by the anisotropy energy barriers will give rise to the hysteresis loops.^{20,25} It is therefore believed that the short-range magnetic ordering of $\text{Zn}_x\text{Cr}_{1-x}\text{Te}$ cluster is responsible for the observed hysteresis loops below 10 K.

In summary, we have synthesized ZnTe and Cr doped ZnTe crystals using a solvothermal process. XRD spectra of the Cr doped ZnTe show no difference from that of the undoped one for very low doping concentration. Magnetic measurements show that hysteresis is observable for Cr doped sample at and below 10 K. The observed hysteresis signal is believed to arise from the short-range magnetic ordering of $\text{Zn}_x\text{Cr}_{1-x}\text{Te}$ clusters.

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