## Bulk synthesis and high-temperature ferromagnetism of $(In_{1-x}Fe_x)_2O_{3-\sigma}$ with Cu co-doping

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The synthesis and magnetic properties of  $(In_{1-x}Fe_x)_2O_{3-\sigma}$  bulk ceramics with Cu co-doping are reported. Magnetic Fe ions are found to have high thermodynamic solubility (up to 20%) in the  $In_2O_3$  host compound. The lattice constant decreases almost linearly as Fe doping concentration increases indicating the incorporation of Fe ions into the host lattice. The samples with high Fe concentration annealed under Ar reduced atmosphere were found to be ferromagnetic, and the Curie temperature is around 750 K. The extensive structural and magnetic studies rule out the possibility that the observed magnetism is derived from magnetic impurity phases. © 2005 American Institute of Physics. [DOI: 10.1063/1.1854720]

The prediction of room-temperature ferromagnetism in Mn-doped ZnO and GaN (both *p*-type) by Dietl and coworkers, along with the discovery of ferromagnetism above room temperature in Co-doped TiO<sub>2</sub> anatase (suggested as *n*-type) by Koinuma *et al.*, triggered a worldwide search for new dilute magnetic semiconductor materials.<sup>1–11</sup> The doped magnetic ions, mostly 3*d* transition metals, exhibit very low solubility in host semiconductors. Hence, the origins of ferromagnetism in some of the compounds have been attributed to magnetic impurities.<sup>12</sup>

We searched for a host semiconductor with high solubility of magnetic ions using thin film combinatorial methodology,<sup>13</sup> and discovered a ferromagnetic semiconductor system of  $(In_{1-r}Fe_r)_2O_{3-\sigma}$  with Cu co-doping. The possibility of the high solubility of Fe in In<sub>2</sub>O<sub>3</sub> lattice was based on the fact that the most probable valence states of both In and Fe ions are the same, i.e., In<sup>3+</sup> and Fe<sup>3+</sup> (in contrast to many other similar semiconducting oxides, such as Zn<sup>2+</sup>O,  $Ti^{4+}O_2$ ,  $Sn^{4+}O_2$ ). The Curie temperature of  $(In_{1-r}Fe_r)_2O_{3-r}$ exceeds room temperature and its thermodynamic solubility of Fe ions in the host lattice is higher than 20%.<sup>14</sup> Such high thermodynamic solubility makes it amenable to fabricate bulk ceramic samples. In order to confirm the source of magnetism within the cation lattice rather than from an impurity phase, the bulk ceramic synthesis and characterization are carried out to carefully address the issues of structure, composition, and secondary-phase formation.

In<sub>2</sub>O<sub>3</sub>, host compound used in this study, is a transparent semiconductor with a direct band gap of 2.7 eV and cubic bixbyite crystal structure with a lattice constant of 10.12 Å and a bcc unit cell. In<sub>2</sub>O<sub>3</sub> can be an *n*-type semiconductor with high conductivity by introducing oxygen deficiencies ( $\sigma$ ) or by Sn doping. The ceramic synthesis was made by standard solid-state reaction method. High-purity In<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, and CuO precursors were mixed and then compressed at a pressure of 120 MPa to form cylindrical ceramic samples. They were then sintered at 1100 °C for 9 h. Valence variations of doped magnetic elements were induced by Cu co-doping in the range of 2% and/or annealing in reduced atmosphere (Ar), which create mixed valence cat-



FIG. 1. (Color online) Synchrotron XRD of Cu-doped  $(In_{1-x}Fe_x)_2O_{3-\sigma}$  bulk ceramic samples plotted in logarithmic scale. The intensity bars representing diffraction pattern for  $In_2O_3$ ,  $CuFe_2O_4$ , and  $Fe_3O_4$  are shown at bottom for comparison.

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FIG. 2. (a) Lattice constants as function of Fe contents for Cu-doped  $(In_{1-x}Fe_x)_2O_{3-\sigma}$  bulk ceramic samples with *x* changing from 0.01 to 0.2; lattice constants are calculated using nonlinear least-squares fitting; (b) large-scale TEM image near a grain boundary from a bulk with *x*=0.1; (c) high resolution TEM micrograph and the electron diffraction pattern taken along [001].

ions, i.e., Fe $^{2+},$  Fe $^{3+},$  necessary for the charge transport and ferromagnetism.  $^{15}$ 

To check for possible impurity phases, synchrotron source was used for XRD study to ensure high signal to noise ratio (sensitive to less than 1% impurity). The x-ray diffraction (XRD) patterns for synthesized bulk ceramic samples were measured using a wavelength of 0.7293 Å at XOR bending magnet beamline 2-BM-B of the Advanced Photon Source (APS), and selected curves are shown in Fig. 1. The standard XRD patterns for In<sub>2</sub>O<sub>3</sub> and possible impurity phases of  $Fe_3O_4$  and  $CuFe_2O_4$  are also exhibited at the bottom of the figure for comparison. The diffraction peaks of  $(In_{1-x}Fe_x)_2O_{3-\sigma}$  with Cu co-doping are consistent with the standard pattern of cubic In2O3. No significant impurity phase was detected to a level of 0.1% for most samples, except a small impurity phase of  $Fe_3O_4$  about 1% in x=0.1sample; see the later discussion for Fig. 4(c)]. More important, a clear linear decrease in d spacing (the  $Fe^{3+}$  ion is smaller than the In<sup>3+</sup> ion) was observed with increasing Fe doping as evidenced by a Vegard's law plot based on the nonlinear least-squares refinement [Fig. 2(a)], suggesting the incorporation of doped elements into a cubic lattices of  $In_2O_3$ . Beyond 20% Fe doping, we observed only a  $Fe_3O_4$ impurity phase, which has an inverted spinel structure with lattice constant of 8.4 Å and fcc unit cell, completely different from the crystal structure of  $In_2O_3$ .

Transmission electron microscopy (TEM) was carried out over a large-scale area across a grain boundary from a sample with Fe 10% [Fig. 2(b)]. The high-resolution TEM image and electron diffraction pattern of a selected area are shown in Fig. 2(c). The diffraction pattern is consistent with the cubic bixbyite structure of  $In_2O_3$ . The observed grain sizes range from 1 to 10  $\mu$ m. No impurity phase was ob-



FIG. 3. (Color online) M-H curves of Cu-doped  $(In_{1-x}Fe_x)_2O_{3-\sigma}$  bulk ceramic samples at 5 K; (a) for x=0.03, 0.05, and 0.07. The inset shows the sample with x=0.01. (b) Samples with x=0.1 and 0.2. The sample with x=0.2 was also measured at 300 K (indicated by black closed circles). The inset is a zoom-in of M-H curve for the sample with x=0.2 at 5 K. The coercivity  $(H_c)$  of the sample is 35 Oe.



FIG. 4. (Color online) (a) M-T curves for Cu-doped  $(In_{1-x}Fe_x)_2O_{3-\sigma}$  bulk ceramic samples with various Fe contents and CuFe<sub>2</sub>O<sub>4</sub>. M(T) is normalized by magnetization at room temperature,  $M_0$ . The M-T curve for the sample with x=0.2 was measured under 3 kOe field and others under 1 kOe. Brillouin–Weiss fitting for x=0.2 sample measured at 3 kOe is also shown for comparison; the inset shows M-T curve for the sample with x=0.2 measured at low temperatures (5–300 K) under 1 kOe field. (b) dM/dT vs T with the magnetic phase transition points defined by the minimum points in dM/dT curves, marked by arrows, and (c) 1/M vs T curves.

served within the grains or at grain boundaries.

The magnetic field dependence of magnetic moment was measured by superconducting quantum interference device magnetometer at 5 and 300 K (Fig. 3). There is a clear evolution of magnetic properties with increasing dopant concentration. The sample with Fe 1% [inset of Fig. 3(a)] shows a typical paramagnetic behavior due to nearly isolated Fe and Cu ions at the low dopant concentration. The high-field magnetic moment of  $\sim 6 \mu_B/Fe$  can be roughly accounted for if we combine the contributions of  $Fe^{3+}$  (5  $\mu_B/Fe$ ) and low spin Cu<sup>2+</sup> (1  $\mu_B$ /Cu) or high-spin Cu<sup>3+</sup> (2  $\mu_B$ /Cu) ions. The samples with increasing Fe content (up to 7%) show decreasing saturation magnetic moments per Fe ion which is likely due to antiferromagnetic Fe<sup>3+</sup>-O<sup>2-</sup>-Fe<sup>3+</sup> pairing as isolated  $Fe^{3+}_{2}O_{3}$  molecules dissolved in the  $In^{3+}_{2}O_{3}$  lattice [Fig. 3(a)]. When the doping concentration reaches x > 10%, ferromagnetic behavior becomes evident [Fig. 3(b)] with measured coercive fields of about 40-50 Oe at room temperature [inset of Fig. 3(b)]. From the M-H curves of the sample with Fe 20% measured at room temperature and 5 K, one can clearly see the significant paramagnetic contribution from magnetic ions, at least 30%, evidenced by the portion of nonsaturation magnetization at 5 K in addition to saturation magnetization at room temperature. Note that the M-Hcurve at room temperature appears to saturate easier because the relative paramagnetic contribution to the total magnetism is very small compared to that at low temperature and would not become evident until much higher fields. The hysteresis curve is characteristic of single domain particles of approximate spherical shape with a magnetocrystalline anisotropy field  $\sim 50$  Oe, which is typical of Fe<sup>3+</sup> in an octahedral oxygen site.<sup>15</sup> This anisotropy field can account for the coercive field, and the shape demagnetizing field of the clusters can explain the initial permeability, low remanence, and the  $\sim$ 3 kOe field required for saturation.

The selected magnetic moment versus temperature (M-T) curves were measured by a vibrating sample magnetometer for different compositions of Cu-doped  $(In_{1-x}Fe_x)_2O_{3-\sigma}$  and CuFe<sub>2</sub>O<sub>4</sub> [Fig. 4(a)]. Well-defined  $T_C$ 's can be observed better from the dM/dT curves as shown in Fig. 4(b) with  $T_C$ =715 K for CuFe<sub>2</sub>O<sub>4</sub>, 742 and 756 K for samples of Fe 10% and 20% doping, respectively. The  $T_C$ 's of Cu co-doped  $(In_{1-x}Fe_x)_2O_{3-\sigma}$  are clearly different from

oercivity ( $H_c$ ) of the sample is 35 Oe. Downloaded 10 Jan 2010 to 128.8.110.216. Redistribution subject to AIP license or copyright; see http://apl.aip.org/apl/copyright.jsp those of two most likely impurity phases,  $CuFe_2O_4$  (715 K) and  $Fe_3O_4$  (830 K). A small amount of  $Fe_3O_4$  phase is present in the CuFe<sub>2</sub>O<sub>4</sub> and the sample with x = 10% as evidenced in 1/M versus temperature curves [Fig. 4(c)], which is a powerful means of identifying small amounts of magnetic phases with different Curie temperatures. We found that CuFe<sub>2</sub>O<sub>4</sub> annealed under different reducing atmospheres have different ratios of magnetic contribution from  $CuFe_2O_4$ and  $Fe_3O_4$  phases with no significant change in their  $T_C$  values. The measured magnitude of magnetic moment due to a small amount of Fe<sub>3</sub>O<sub>4</sub> phase in the sample with x=10% is consistent with 1% impurity phase (based on 10% of total Fe dopants forming  $Fe_3O_4$ ) observed in XRD data for this particular sample. This observation further confirms that there is negligible Fe<sub>3</sub>O<sub>4</sub> phase in the sample of Cu-doped  $(In_{1-x}Fe_x)_2O_{3-\sigma}$  with x=20% and the main magnetism with  $T_C$  of about 750 K observed in both x=10% and x=20%samples are not from the impurity phase of either CuFe<sub>2</sub>O<sub>4</sub> or  $Fe_3O_4$ .

The overall temperature dependence of magnetization for  $(In_{1-x}Fe_x)_2O_{3-\sigma}$  sample with Fe 20% can be modeled by assuming that isolated ferromagnetic clusters comprise  $(Fe^{2+}Fe^{3+})O_{2.5}$  molecules with charge transfer superexchange between spins of average value S=2.25. The measured M-Tcurve can be fit closely by a Brillouin-Weiss function with a single ferromagnetic exchange field of 512 T, which produces an exchange stabilization energy of  $\sim 0.13$  eV. The corresponding exchange constant is estimated as  $J \approx 20$  K or 1.7 meV. In contrast, three antiferromagnetic exchange constants are needed to fit the M-T curve for the two magnetic sublattices of CuFe<sub>2</sub>O<sub>4</sub> ferrite.<sup>15</sup> CuFe<sub>2</sub>O<sub>4</sub> samples annealed in oxygen gain maximum magnetization (where all Fe takes  $Fe^{3+}$  valence state) while Cu-doped  $(In_{1-x}Fe_x)_2O_{3-\sigma}$  samples annealed in the same condition show no sign of ferromagnetism. If CuFe<sub>2</sub>O<sub>4</sub> impurity phase had been responsible for the observed magnetism in the samples, the ferromagnetism must be present in the samples annealed in oxygen. This observation rules out contribution by CuFe2O4 impurity phase. Since the saturated magnetic moment of Fe<sub>3</sub>O<sub>4</sub> is reported to be about 1.3  $\mu_B/\text{Fe}$ ,<sup>16</sup> if the observed magnetic moment of about 1.4  $\mu_B$ /Fe had been attributed to Fe<sub>3</sub>O<sub>4</sub>, one would have to assume that almost 100% of doped Fe ions ended up forming Fe<sub>3</sub>O<sub>4</sub>. This is impossible because significant XRD peaks of Fe3O4 would appear if such a large amount of Fe<sub>3</sub>O<sub>4</sub> were present. Also, if most of the doped Fe ions had formed  $Fe_3O_4$ , the significant lattice constant change, incorporation of Fe ions into In<sub>2</sub>O<sub>3</sub>, would not have been observed in Fig. 2(a). Furthermore,  $Fe_3O_4$  has a wellknown Verwey transition at around 120 K, where the magnetization exhibits a large (25%) step function change.<sup>17</sup> This evidence of Verwey transition was not found in our bulk ceramic samples in M-T measurements [Fe 20% doped sample shown in Fig. 4(a), inset], which would not have been missed if Fe<sub>3</sub>O<sub>4</sub> were responsible for the observed magnetization. These facts together systematically rule out the possibility that the observed magnetism in Cu-co-doped  $(In_{1-x}Fe_x)_2O_{3-\sigma}$  all comes from ferrimagnetic CuFe<sub>2</sub>O<sub>4</sub> or  $Fe_3O_4$ . Note also that the issue here is not whether there is a minute undetected amount of magnetic impurity present in the samples, but rather how such a phase could be the source of the observed bulk magnetism (up to 20% volume effect)

with a distinctive  $T_C \approx 750$  K that differs from other ironoxide compounds that could be present as an impurity phase. The electrical and magneto-transport properties of Cu-codoped  $(In_{1-x}Fe_x)_2O_{3-\sigma}$  has been studied in thin film, and its carriers are found to be *n*-type.<sup>13</sup>

The system described in this letter is a thermodynamically stable solid solution of a host lattice and a high concentration (up to 20%) of magnetic ions. This is in sharp contrast to most previously reported dilute magnetic semiconductors. The aspects of the thermodynamically stable solid solution and the large volume magnetization of this system are also important with regards to potential spintronics applications.

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