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Giant positive magnetoresistance in Fe doped In_2O_3 and InREO_3 (RE=Eu,Nd) composites

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Synthesis and characterization of Fe and rare earth (RE) (RE=Eu,Nd) codoped bulk In_2O_3 oxide are reported. Composites consisting of Fe-doped In_2O_3 and InREO_3 phases were formed, as determined by x-ray diffraction and transmission electron microscopy, with particle sizes of 50–120 nm. The composites exhibit superparamagnetic and semiconducting behavior. A giant positive magnetoresistance is observed at low temperatures, reaching 81% and 50% at 5 K in Eu–Fe and Nd–Fe codoped samples, respectively. © 2008 American Institute of Physics.

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In recent years, a great deal of effort has been placed into the investigation and development of materials that can utilize both the charge and the spin of electrons. These materials are called spintronic materials and are promising candidates for utilization in the emerging field of spin-electronic devices. Logic devices,¹ spin light emitting diodes,² or ferromagnetic field effect transistors³ are just few examples of devices based on spintronic materials. In order to make spintronic devices commercially viable, the principles and construction of these devices have to be based on already well established semiconductor technology and materials. Diluted magnetic semiconductors (DMSs) are good candidates for such purposes. It is crucial to design and develop other oxide DMS materials that would exhibit consistent and desirable electronic and magnetic properties. Following theoretical predictions on transition metal (TM) doping induced ferromagnetism in ZnO ,^{4,5} observations of ferromagnetism in this oxide^{6,7} were reported. High temperature ferromagnetism in both Cr and Mn doped In_2O_3 ,^{8–10} and also in Fe–Cu codoped thin films and bulks In_2O_3 ,^{11,12} have been reported. Recently, we have shown that room temperature ferromagnetism in this oxide can be realized with Fe–Mn and Fe–Cr codoping, while either Fe or Cr alone doped In_2O_3 is paramagnetic.^{13,14} Spin dependent positive or negative magnetoresistance (MR) effect, which is very useful for practical applications, has been observed in most of the abovementioned compounds.^{9,10,14} However, the MR values reported so far are lower than 50%.

Rare earth (RE) elements are widely used in magnetic materials. RE elements might enhance the magnetic or transport properties of functional oxides, such as DMS materials. In this paper, we report on the synthesis and characterization of RE–Fe codoped polycrystalline In_2O_3 , where RE

=Eu,Nd, and observation of giant magnetoresistance (GMR) effect.

All samples were prepared by a conventional solid state synthesis route. Factory prepared In_2O_3 , Nd_2O_3 , Eu_2O_3 , and Fe_2O_3 (high purity: 99.99%; Aldrich) were weighed and mixed in a mortar in corresponding molar ratios to obtain nominal $\text{In}_{1.98-x}\text{RE}_x\text{Fe}_{0.02}\text{O}_3$ ($0.02 \leq x \leq 0.05$) compositions. Prepared mixtures were then calcined at 850 °C for 12 h in an argon gas atmosphere with subsequent firing at 970 °C for 12 h in flowing argon gas. It has been reported that In_2O_3 and RE_2O_3 oxides can form solid solutions in the InREO_3 form.¹⁵ Thus, samples with the nominal $\text{In}_{0.99}\text{RE}_{0.99}\text{Fe}_{0.02}\text{O}_3$ chemical composition were also prepared. The detailed synthesis procedure is reported elsewhere.¹⁵

Phase purity and crystal structures of the prepared samples were investigated by means of x-ray diffraction (XRD) (Philips PW-1730) using $\text{Cu K}\alpha$ irradiation with an accelerating voltage of 40 kV and a current of 25 mA. Figure 1 shows XRD patterns for pulverized $\text{In}_{1.98-x}\text{RE}_x\text{Fe}_{0.02}\text{O}_3$ samples. All samples are of the cubic In_2O_3 crystal structure. The lattice parameter a for $\text{In}_{1.98-x}\text{RE}_x\text{Fe}_{0.02}\text{O}_3$ samples calculated from Rietveld refinements is 10.119 Å. As we can see, with increasing RE content, a secondary InREO_3 phase is formed. The top two XRD patterns in Fig. 1 are for $\text{In}_{0.99}\text{RE}_{0.99}\text{Fe}_{0.02}\text{O}_3$ samples prepared for identification purposes. The Eu-based phase has a pseudohexagonal unit cell¹⁵ with the lattice parameters $a=3.672$ Å and $c=12.318$ Å. These values are slightly lower than those reported by Schneider,¹⁵ probably due to the presence of Fe atoms in the unit cell. For Fe-doped InNdO_3 , the crystal structure is of orthorhombic perovskite type,¹⁶ with lattice parameters $a=5.631$ Å, $b=5.904$ Å, and $c=8.133$ Å. Although XRD patterns for the samples with 1% RE doping level do not show any impurity phases, we speculate that secondary InREO_3 can be formed, but is undetectable due to the limitations of the XRD method. Thus, we might assume that these samples

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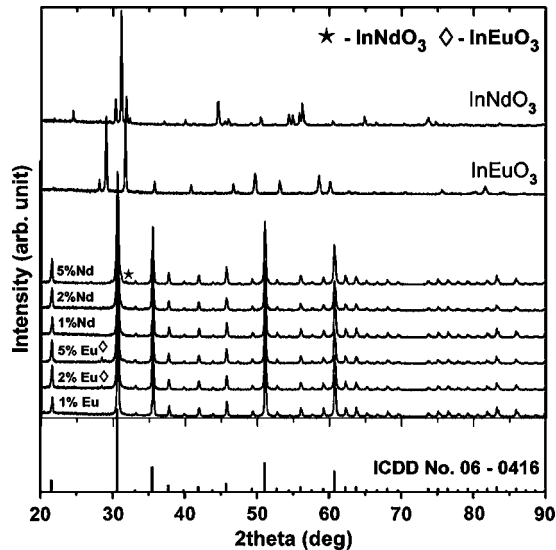


FIG. 1. X-ray powder diffraction patterns of pulverized $\text{In}_{1.98-x}\text{RE}_x\text{Fe}_{0.02}\text{O}_3$ pellets with reference peaks for In_2O_3 phase (bottom curve). The two top curves show XRD patterns for $\text{In}_{0.99}\text{Eu}_{0.99}\text{Fe}_{0.02}\text{O}_3$ and $\text{In}_{0.99}\text{Nd}_{0.99}\text{Fe}_{0.02}\text{O}_3$ samples.

are composite materials rather than single RE–Fe doped In_2O_3 phase. Results obtained by high resolution transmission electron microscopy (TEM) strongly support this fact.

Figures 2(a) and 2(b) show TEM images of the RE–Fe codoped In_2O_3 . As we can see from TEM energy dispersive spectroscopy (EDS) elemental analysis, there are two types of particles: Fe-rich particles [Fig. 2(a)] and RE-rich particles [Fig. 2(b)]. Fe-containing In_2O_3 particles are abundant and somewhat rectangular in shape [Fig. 2(a)]. The particle

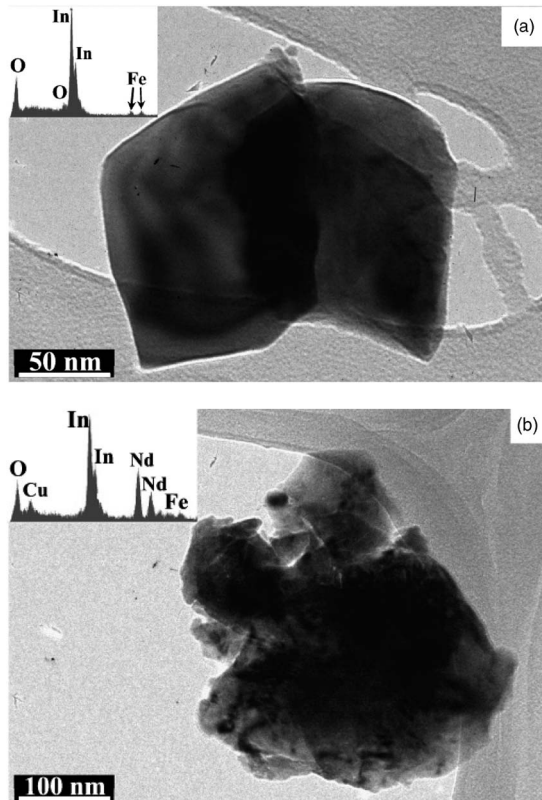


FIG. 2. TEM micrographs of (a) Fe-rich and (b) RE-rich particles in the samples. Insets represent elemental analysis acquired by TEM EDS.

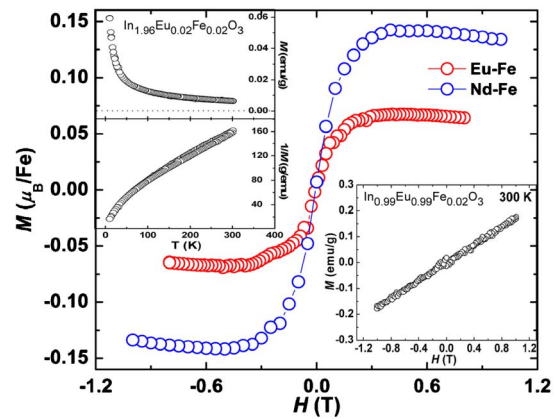


FIG. 3. (Color online) Magnetization (M) vs applied magnetic field (H) for $\text{In}_{1.98-x}\text{RE}_x\text{Fe}_{0.02}\text{O}_3$ at 300 K. Top inset: magnetization (M) vs temperature (T) for $\text{In}_{1.96}\text{Eu}_{0.02}\text{Fe}_{0.02}\text{O}_3$ sample. Bottom inset: magnetization (M) vs applied magnetic field (H) at 300 K for $\text{In}_{0.99}\text{Eu}_{0.99}\text{Fe}_{0.02}\text{O}_3$ sample.

size is about 50 nm. On the other hand, as discussed above, the amount of the InREO_3 secondary phase is very small, hence, it is difficult to identify or physically find such particles during TEM observations. The shape of RE-rich particles is irregular and their sizes are bigger (around 120 nm). These microstructural studies show that a composite material was indeed formed and two phases are actually prepared; $\text{In}_{2-x}\text{Fe}_y\text{O}_3$ and $\text{In}_y\text{RE}_y\text{Fe}_z\text{O}_3$.

The magnetization (M) versus applied magnetic field (H) curves at 300 K for the RE–Fe codoped In_2O_3 samples are shown in Fig. 3. The applied magnetic field was varied between 0 and 1 T and the data were obtained via a magnetic properties measurement system (XL, Quantum Design). The top inset in Fig. 3 shows magnetization (M) and inverse magnetization ($1/M$) versus temperature (T) plots for the $\text{In}_{1.96}\text{Eu}_{0.02}\text{Fe}_{0.02}\text{O}_3$ sample. The curve is typical for a paramagnetic material. (The background at room temperature originates from the sample, as the M - T measurement of the sample holder yielded no magnetic response.) The bottom inset in Fig. 3 shows M - H data for the $\text{In}_{0.99}\text{Eu}_{0.99}\text{Fe}_{0.02}\text{O}_3$ sample at the same temperature. (Note that the M - H curve for $\text{In}_{0.99}\text{Nd}_{0.99}\text{Fe}_{0.02}\text{O}_3$ has been measured. However, data is almost indistinguishable from Eu based sample and thus is not included in the plot.) It is clear that the secondary $\text{In}_y\text{RE}_y\text{Fe}_z\text{O}_3$ phase is antiferromagnetic at this temperature, which differs from magnetic data reported for InREO_3 .¹⁶ Thus, the magnetic properties of the samples are mainly determined by Fe-doped In_2O_3 primary phase. The observed saturation magnetization (M_s) for Eu–Fe and Nd–Fe were $M_s \approx 0.06\mu_B/\text{Fe}$ and $M_s \approx 0.14\mu_B/\text{Fe}$, respectively. The obtained M_s values are in good agreement with published data for bulk and thin film samples of Fe-doped In_2O_3 .^{11,12} On the other hand, the absence of a coercive field suggests that samples are superparamagnetic.

Transport properties were investigated using a four probe technique using physical properties measurement system (Quantum Design). The dependence of electrical resistivity (ρ) on temperature (T) was measured over a temperature range of 5–350 K. Pure $\text{In}_y\text{RE}_y\text{Fe}_z\text{O}_3$ compounds were found to be insulating. All the samples show semiconductor-like behavior, with a sharp increase in ρ at low temperatures.

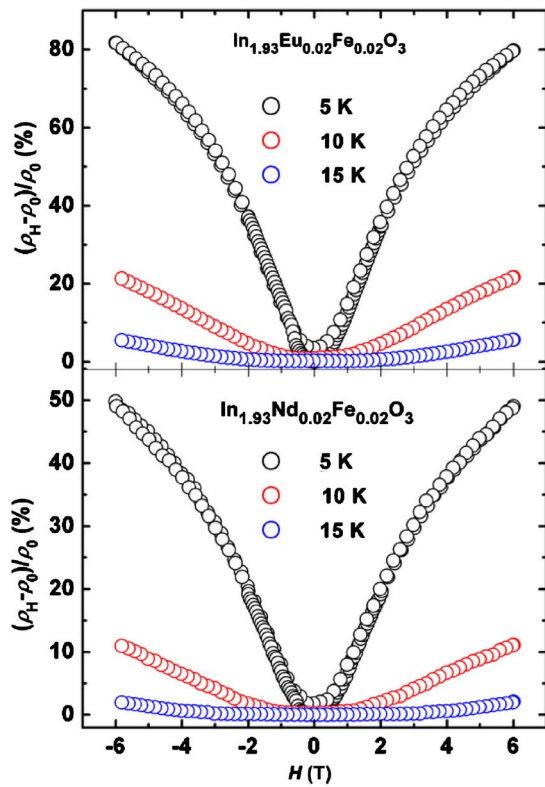


FIG. 4. (Color online) Magnetoresistance (MR) measured at various temperatures for $\text{In}_{1.96}\text{RE}_{0.02}\text{Fe}_{0.02}\text{O}_3$.

The MR effect in our samples was analyzed when electrical resistivity (ρ) was measured as a function of applied magnetic field ($-6 \text{ T} \leq H \leq 6 \text{ T}$) at a constant temperature (T). Figure 4 shows the MR effect measured at different temperatures for $\text{In}_{1.96}\text{RE}_{0.02}\text{Fe}_{0.02}\text{O}_3$ samples. The absolute values of MR were calculated using the relation $\text{MR} \% = [(\rho_H - \rho_0) / \rho_0] \times 100\%$. The maximum MR values were observed at 5 K and reached 81% and 50% for Eu–Fe and Nd–Fe codoped In_2O_3 samples, respectively. The obtained MR values are in excellent agreement with the data published by Zhang *et al.*,¹⁷ who reported observation of a GMR ($\text{MR} = 85\%$ at $T = 2 \text{ K}$) effect in Fe– In_2O_3 granular thin films. According to Zhang *et al.*,¹⁷ the observed GMR effect occurs due to the peculiar electrical transport mechanism in a magnetic disorder state and is directly related to the structural transition. However, we have not observed any irreversibility or magnetic disorder states in the M – T curves of our samples [Fig. 3 (top inset)]. This indicates that other mechanism should be responsible for the significant positive MR values at low temperatures. One of the possibilities would be a giant spin splitting of band states caused by the sp – d exchange interaction under applied H due to a Zeeman splitting effect in the vicinity of E_F .¹⁸ This results in enhanced electron scattering and, thus, leads to the sharp increase of ρ at low temperatures. This spin splitting model seems to be more appropriate to our system, as it provides quite a good explanation of data recently reported by Wang *et al.*,¹⁹ who

showed large positive MR $\sim 48\%$ at 10 K in Co–Mn codoped ZnO thin films. Deeper investigations of the magnetic properties of this composite system are essential to clarify this situation.

In summary, polycrystalline RE–Fe codoped In_2O_3 samples were prepared and characterized. TEM studies showed that prepared samples are a composite material consisting of $\text{In}_{2-x}\text{Fe}_x\text{O}_3$ and $\text{In}_y\text{RE}_z\text{Fe}_z\text{O}_3$ phases. The samples are superparamagnetic at 300 K, with $M_s \approx 0.06\mu_B/\text{Fe}$ and $M_s \approx 0.14\mu_B/\text{Fe}$ for Eu and Nd codoped samples, respectively. ρ – T characterization showed that samples are semiconducting. At room temperature ρ value increases with increasing RE content. Obtained MR ratios at 5 K for Eu–Fe and Nd–Fe codoped samples were 81% and 50%, respectively. Such high MR ratios seem to arise from a giant spin splitting of band states due to the sp – d exchange interaction at low temperatures.

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