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# Magnetic and transport properties of transition metal doped polycrystalline In2O3

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## Abstract

Synthesis and characterization of transition metal (TM)-doped $In_2O_3$ oxide is reported. Most of the samples were found to be paramagnetic, and only Ye and Cr co-doped sample showed as light trace of ferromagnetism at 300 K with saturation magnetization $M_s$ = 0.35 emug/g. Measured transport properties revealed significant differences in transport among the samples. The absolute value of electrical resistivity for the $In_{1.8}Fe_{0.1}Mn_{0.1}O_3$ sample at 300 K was rho= 9.4 x $10^3$ Omega middot cm, while $In_{1.8}Fe_{0.1}Cr_{0.1}O_3$ had rho = 62 Omega middot cm at the same temperature. Furthermore, magnetoresistance (MR) studies of $In_{1.8}Fe_{0.1}Cr_{0.1}O_3$ showed that the sign of MR changes from negative (200 K), with $MR_{(200\ K)}$ = -0.2%, to positive T < 50 K reaching maximum absolute value at 10 K, i.e., $MR_{(10K)}$ = 5.2 %.



## Keywords

Magnetic, transport, properties, transition, metal, doped, polycrystalline, In2O3


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# Magnetic and Transport Properties of Transition Metal Doped Polycrystalline $In_2O_3$

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**Synthesis and characterization of transition metal (TM)-doped $In_2O_3$ oxide is reported. Most of the samples were found to be paramagnetic, and only Fe and Cr co-doped sample showed as light trace of ferromagnetism at 300 K with saturation magnetization $M_s = 0.35$ emug/g. Measured transport properties revealed significant differences in transport among the samples. The absolute value of electrical resistivity for the $In_{1.8}Fe_{0.1}Mn_{0.1}O_3$ sample at 300 K was $\rho = 9.4 \times 10^3\ \Omega \cdot$ cm, while $In_{1.8}Fe_{0.1}Cr_{0.1}O_3$ had $\rho = 62\ \Omega \cdot$ cm at the same temperature. Furthermore, magnetoresistance (MR) studies of $In_{1.8}Fe_{0.1}Cr_{0.1}O_3$ showed that the sign of MR changes from negative (200 K), with $MR_{(200K)} = -0.2\%$, to positive $T < 50$ K reaching maximum absolute value at 10 K, i.e., $MR_{(10K)} = 5.2\%$.**

*Index Terms*—**Diluted semiconductors, magnetoresistance (MR) effect, spintronics.**

## I. Introduction

DURING recent years diluted magnetic semiconductors (DMS) have attracted great interest among researchers due to their potential to exhibit semiconducting and magnetic properties simultaneously [1]. Such coexistence of semiconducting and ferromagnetic properties is the top one feature for a material that is considered for "spintronic" applications [2]. DMS's are alloys with magnetic elements that are embedded into the semiconductor material. After reported ferromagnetism (FM) at relatively high temperatures in Mn-doped GaN [3] a lot of effort was put in finding new semiconductor materials that would be ferromagnetic at room temperature. Some theoretical works predicted that room-temperature (RT) ferromagnetism can be observed in transition metal doped ZnO [4] or $TiO_2$ [5]. Consequently these theoretical findings induced huge practical research in this field.

ZnO is one of the most widely researched semiconductors in the scope of spintronic application. Unfortunately, it is still unclear whether observed ferromagnetism [6] in transition metal (TM) doped ZnO is an intrinsic property of material or the phenomenon is caused by formation of magnetic impurities [7]. Poor reproducibility of ferromagnetism and contradictory reports from different authors in fact suggest that other TM doped oxide semiconductor materials, such as CuO or $In_2O_3$, must be investigated.

If one considers integrating electronic, magnetic and photonic properties in the new generation devices, the materials suitable for such devices should have high tunability of charge carriers, high carrier mobility, optical transparency, high abundance of the consisting elements and low impact on the environment. $In_2O_3$ is one of the most promising candidates for such tasks. $In_2O_3$ has a cubic bixbyite structure with the lattice parameter $a = 10.118$ Å [8]. Recently, Yoo *et al.* [9] and He *et al.* [10] have reported both bulk and thin film samples of a diluted magnetic semiconductor — Fe and Cu co-doped $In_2O_3$ oxide. The solubility of Fe ions in the host compound was found to be around 20%, which is very high. In addition to that Ni doped $In_2O_3$ thin films were also found to be ferromagnetic at room temperature [11], although the doping level of Ni ($\sim$6 wt%) was not as high as for samples reported in [10]. Furthermore, Cr doped indium-tin oxide (ITO) thin film samples were found to be ferromagnetic at room temperature along with negative magnetoresistance (MR) [12]. A strong fact supporting suitability of $In_2O_3$ for spintronic research is that magnetic ions, when introduced into the host lattice, are distributed uniformly in the whole material [11], which is in contrast to the TM doped ZnO samples [13], where TM ions are situated in the thin layer next to the surface of the film. On the other hand it is important to note that most of the samples, where RT ferromagnetism was observed are thin films and were prepared by techniques, such as PLD or magnetic sputtering, that use nonequilibrium conditions. Successful preparation of materials that would exhibit similar properties, but were prepared under equilibrium conditions, would identify intrinsic properties of these diluted magnetic semiconductors. In our article we report on transition metal doped $In_2O_3$ oxide prepared by conventional solid state synthesis technique.

## II. Experiment

$In_{1.8}TM_xO_3$ (TM = Fe, Cr, V, Mn) polycrystalline samples were prepared by a conventional solid state synthesis technique. Starting materials of $In_2O_3$, $Fe_2O_3$, $V_2O_5$, $Cr_2O_3$, and $MnCO_3$ (high purity: 99.99%; Aldrich) were weighed and mixed in a mortar in corresponding ratios to obtain nominal chemical compositions for the final products. Mixed powders were calcined in an argon atmosphere at 850°C for 12 hours. After that, the reacted material was ground in a mortar, pressed into rectangular shaped pellets and fired at 950°C for 12 hours in an argon atmosphere. Phase purity and structural parameters were analyzed by means of x-ray diffraction analysis technique using Cu $K_\alpha$ irradiation (Philips PW-1730) operating at 40 kV voltage and 25 mA current. Structure refinements were carried out employing Rietveld analysis using Rietica software [14]. Transport properties of the pellets were measured by standard four probe technique using Physical Properties Measurement System (PPMS, Quantum Design). Magnetic properties of our samples were investigated over a temperature range of 10 K to 340 K utilizing Magnetic Property Measurement System (MPMS XL,

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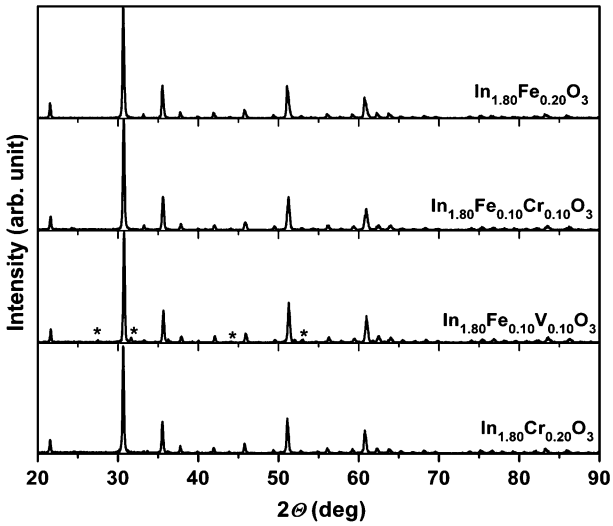


Fig. 1. X-ray diffraction patterns for $In_{1.8}TM_{0.2}O_3$ samples. $In_2VO_5$ impurity indicated by (*).

Quantum Design), applying 2000 Oe magnetic field for magnetization versus temperature data collection.

## III. Results and Discussion

Fig. 1 shows x-ray diffractograms for $In_{1.8}TM_xO_3$ (TM = Fe, Cr, V) samples. All peaks in the x-ray diffraction patterns correspond to that of cubic $In_2O_3$. Only $In_{1.8}Fe_{0.1}V_{0.1}O_3$ showed traces of secondary $In_2VO_5$ phase as marked by $*$. Calculated lattice parameter $a$ for various samples was close to that reported in [8], however we were unable to establish any sort of correlation of lattice parameter $a$ with ionic size or amount of the doped TM. For instance $a$ ($In_{1.8}Fe_{0.2}O_3$) = 10.119 Å and $a$ ($In_{1.8}Cr_{0.2}O_3$) = 10.107 Å, although $r_{(Fe^{3+})} = 0.49$ Å $< r_{(Cr^{3+})} = 0.62$ Å [15]. On the other hand, deviation from the standard value of lattice parameter $a$ and absence of impurity peaks in x-ray diffraction pattern suggest that TM ions were successfully introduced into the $In_2O_3$ host lattice.

Magnetic properties of $In_{1.8}TM_{0.2}O_3$ samples are represented in [Fig. 2(a) and (b)]. As we can see in Fig. 2(a), dependence of magnetization $(M)$ on temperature $(T)$ for all samples is typical to that of paramagnetic materials. However, it is clear that $In_{1.8}Fe_{0.1}Cr_{0.1}O_3$ sample has a very large background as compared to other samples measured. Therefore, magnetization $(M)$ versus applied magnetic field $(H)$ measurements were done at 300 K and 10 K temperatures and the resulting curves are shown in Fig. 2(b).

The observed data revealed that our Fe-Cr co-doped $In_2O_3$ has a very weak but ferromagnetic signal (this does not come from the sample holder, as it was measured separately and no $M$-$H$ loop was observed) at room temperature. Although in low temperature region (10 K), the antiferromagnetic coupling is dominating and $M$-$H$ curve of the sample changes to that of unsaturated type. The calculated saturation magnetization for $In_{1.8}Fe_{0.1}Cr_{0.1}O_3$ sample was $M_s = 0.35$ emu/g.

Fig. 3 represents logarithm of electrical resistivity $(\rho)$ as a function of temperature $(T)$ for $In_{1.8}TM_xO_3$ samples. When TM = Fe + V, sample is highly insulating as compared to that

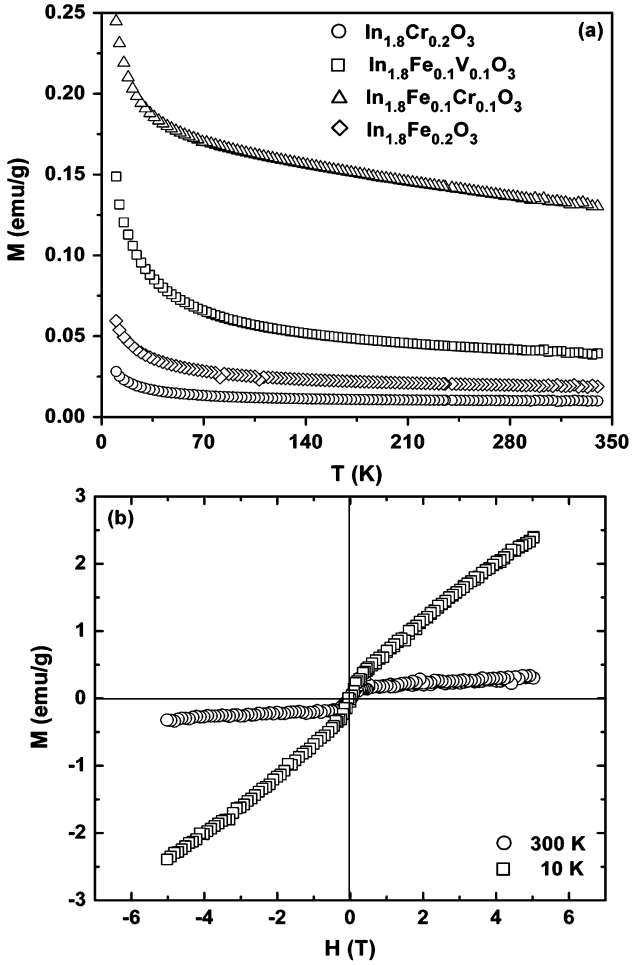


Fig. 2. (a) Magnetization $(M)$ as a function of temperature $(T)$ for $In_{1.8}TM_{0.2}O_3$ samples under 2000 Oe applied magnetic field. (b) Magnetization $(M)$ versus applied magnetic field $(H)$ for $In_{1.8}Fe_{0.1}Cr_{0.1}O_3$.

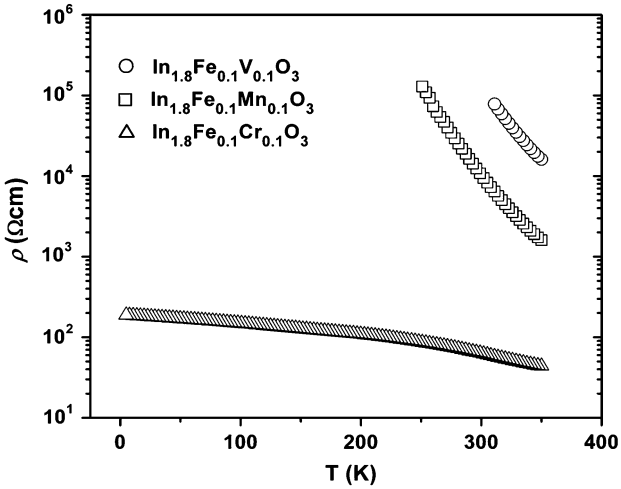


Fig. 3. Logarithm of resistivity $(\rho)$ for $In_{1.8}TM_{0.2}O_3$ samples as a function of temperature $(T)$.

when TM = Fe + Cr, which might be caused by the presence of $In_2VO_5$ impurity phase, although the amount of the impurity phase present (as determined from x-ray diffraction pattern) was not more than 2%. In the former case, electrical resistivity increases rapidly with decreasing temperature and goes already

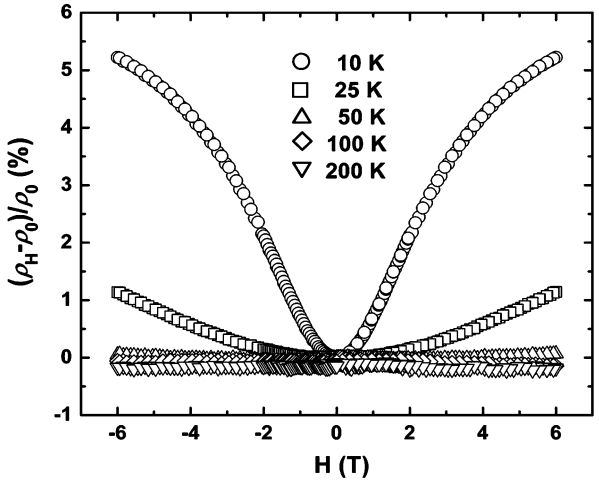


Fig. 4. Magnetoresistance (MR) at various temperatures for $In_{1.8}Fe_{0.1}Cr_{0.1}O_3$ sample.

out of bounds at 310 K. In the latter case, $\rho$ of Fe-Cr co-doped sample steadily increased throughout whole temperature range. The absolute value of $\rho$ for $In_{1.8}Fe_{0.1}Cr_{0.1}O_2$ sample at 300 K was $\rho = 62\,\Omega \cdot$ cm, which is well comparable with published data for TM doped $In_2O_3$ and ITO samples [11], [12].

Since $In_{1.8}Fe_{0.1}Cr_{0.1}O_3$ sample had low electrical resistivity in the whole temperature range, we were able to perform magnetoresistance (MR) measurements down to 10 K. MR effect was calculated applying following relationship: $(\rho_H - \rho_0)/\rho_0$, where $\rho_H$-resistivity under magnetic field and $\rho_0$ is resistivity, when $\mathrm{H} = 0$. The MR curves observed for this sample are shown in Fig. 4.

We have observed change in the sign of MR effect from negative (200 K) to positive ($\mathrm{T} < 50$ K). The maximal positive $\mathrm{MR} = 5.2\%$ effect was reached at 10 K. A similar extent of positive MR (10%) effect was observed in Mn doped ZnO [16]. The change in the sign of MR is believed to be a prove of spin polarization and thus suggests that new diluted magnetic semiconductor was prepared.

## IV. Conclusion

In summary, polycrystalline samples of TM (TM = Cr, Fe, Mn, V) doped $In_2O_3$ oxide were prepared by conventional solid state synthesis technique. $In_{1.8}Fe_{0.1}Cr_{0.1}O_3$ sample showed a trace of ferromagnetism at 300 K, with saturation magnetization $\mathrm{Ms} = 0.35$ emu/g, while other samples were paramagnetic. Transport properties measured revealed significant differences in the conductivity of the samples, with $In_{1.8}Fe_{0.1}Cr_{0.1}O_3$ having lowest $\rho$ values at 300 K, i.e., $\rho_{(300\ \mathrm{K})} = 62\,\Omega \cdot$ cm. A change in the sign of MR and large positive magnetoresistance effect ($\mathrm{MR} = 5.2\%$ at 10 K) was observed in $In_{1.8}Fe_{0.1}Cr_{0.1}O_3$ sample. Further structural and transport investigations such as Hall effect measurements are highly anticipated to clarify nature and density of the carriers in the system. Adjustment of TM doping level would be also important, in order to strengthen ferromagnetism at room temperature.

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