

Transition metal doped nanocrystalline ZnO – A novel room temperature ferromagnetic semiconductor

Sujeet Chaudhary^{1*}, Kanwal Preet Bhatti²,
Subhash C. Kashyap¹ and Dinesh K. Pandya¹

*E-mail:sujeetc@physics.iitd.ac.in

¹Thin Film Laboratory, Department of Physics

Indian Institute of Technology Delhi, New Delhi –110016 (India)

*²Department of Applied Physics, Guru Nanak Dev University, Amritsar,
Punjab (India)*

Introduction

SPINTRONICS, a new paradigm – **SPIN** based elec**TRONICS**

To realize working Spintronic-devices, key materials requirements are:

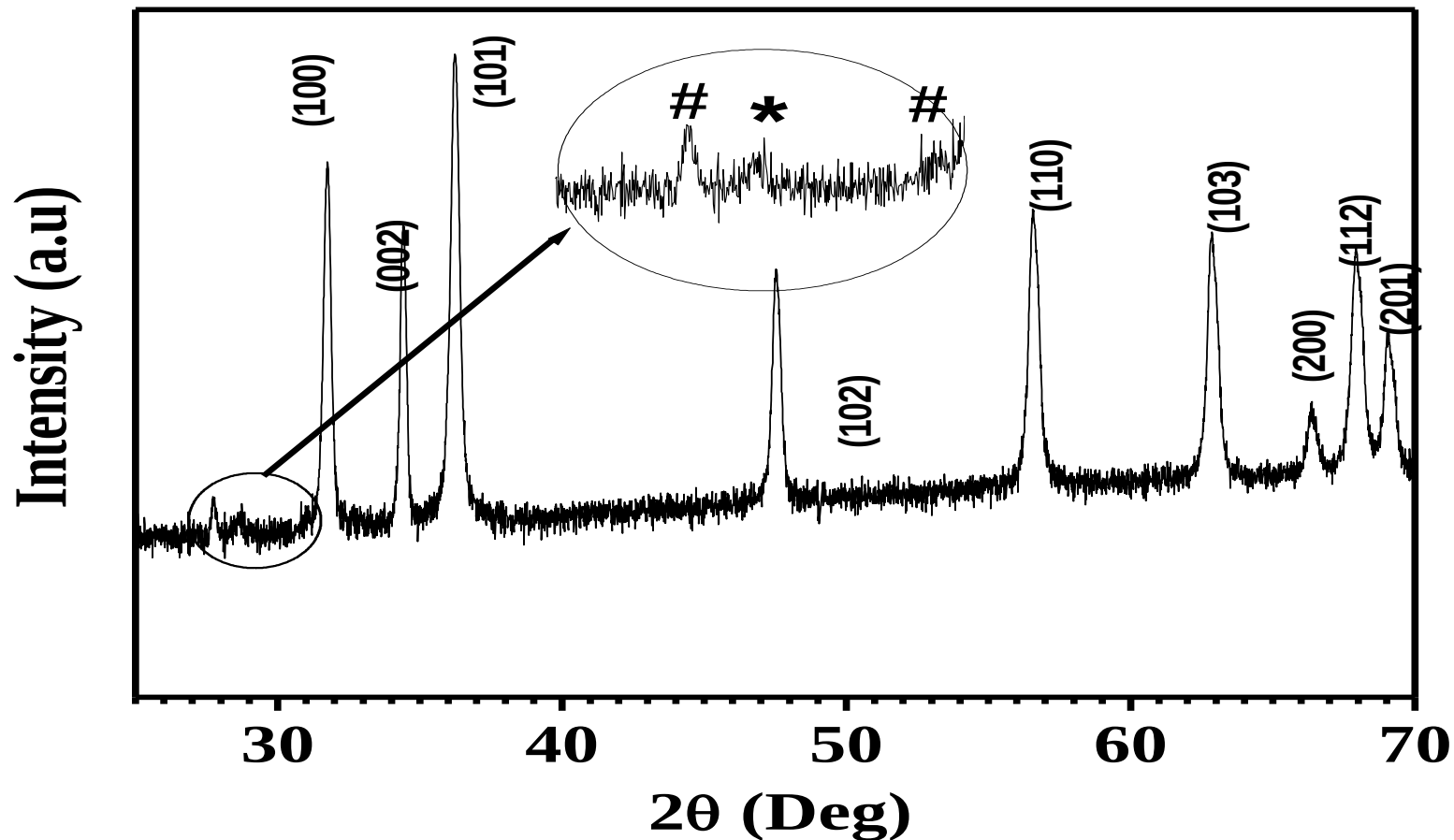
- Should exhibit **room temperature** ferromagnetic (RTFM) behavior
- RTFM should be **Stable** and **Intrinsic** in nature
- **Processing conditions** leading to **intrinsic** and **extrinsic** FM behavior should be distinctly identified

ZnO:Co system - One of the promising candidates for
Spintronic Devices

1. Polycrystalline ZnO:Mn System: Sample Preparation

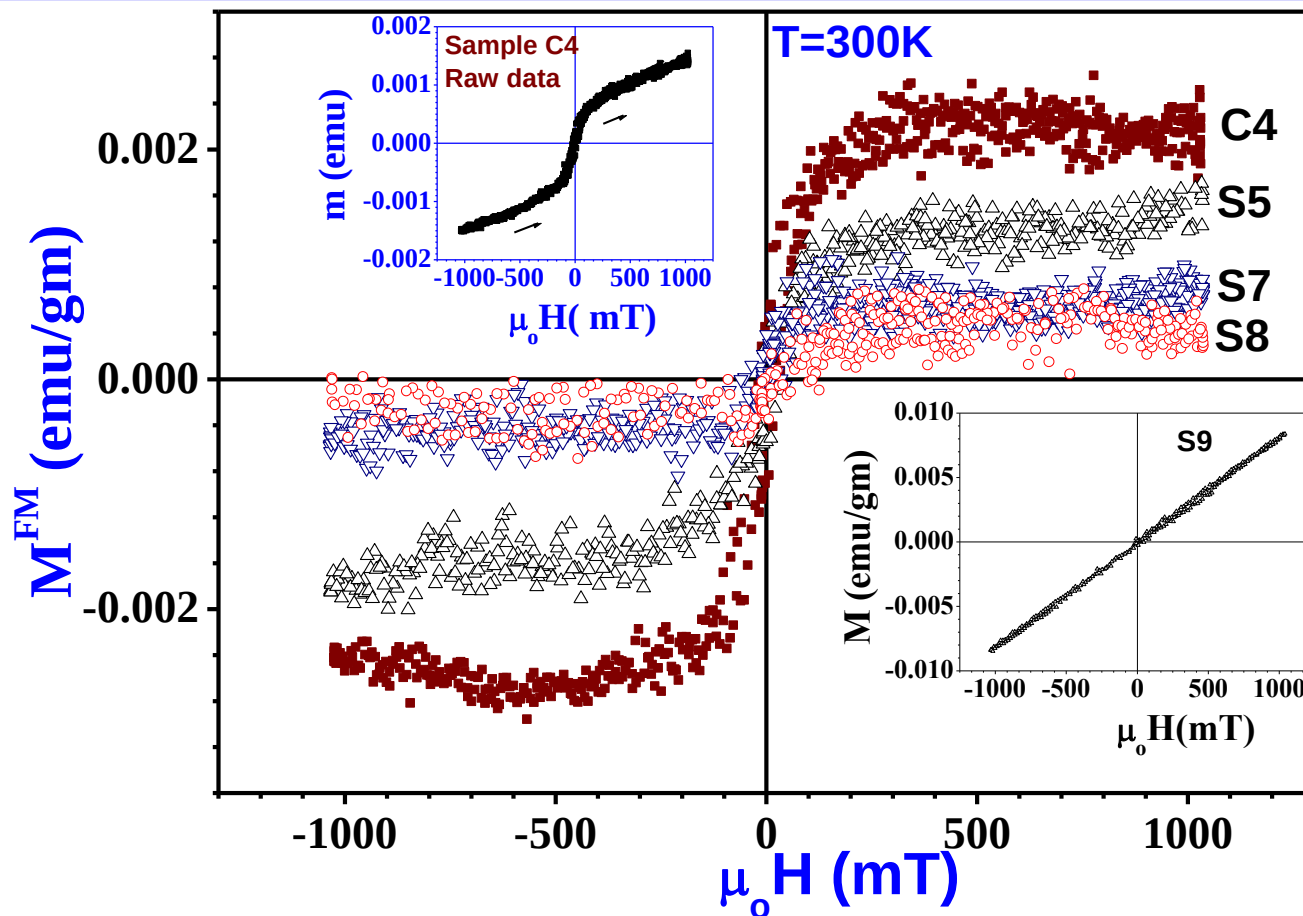
- Sequential Solid State Reaction method
- $(\text{ZnO})_x (\text{MnO}_2)_{1-x}$ with $0.01 \leq x \leq 0.97$: Calcined at 400°C for 8 h (C4), and successively sintered at 500°C (S5), 700°C, 800°C (S8) and 900°C (S9), each time for 12 h

High Resolution X-ray Diffractometry



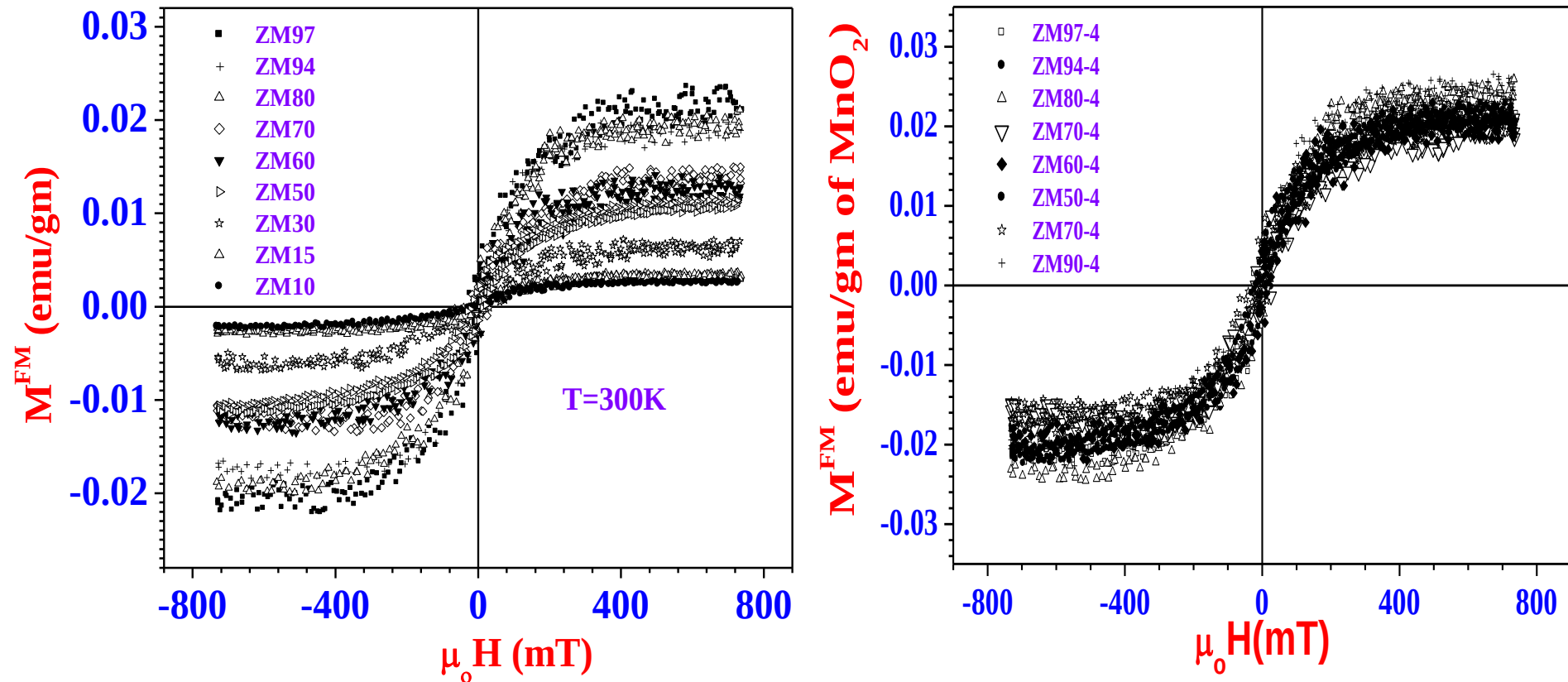
- Impurity peaks marked as '*' (for MnO_2) and '#' (for $\text{Zn}_2\text{Mn}_3\text{O}_8$) observed only during slow scan.
- Higher temperature sintered samples are phase pure.

M-H measurements of $(\text{ZnO})_{0.98}(\text{MnO}_2)_{0.02}$



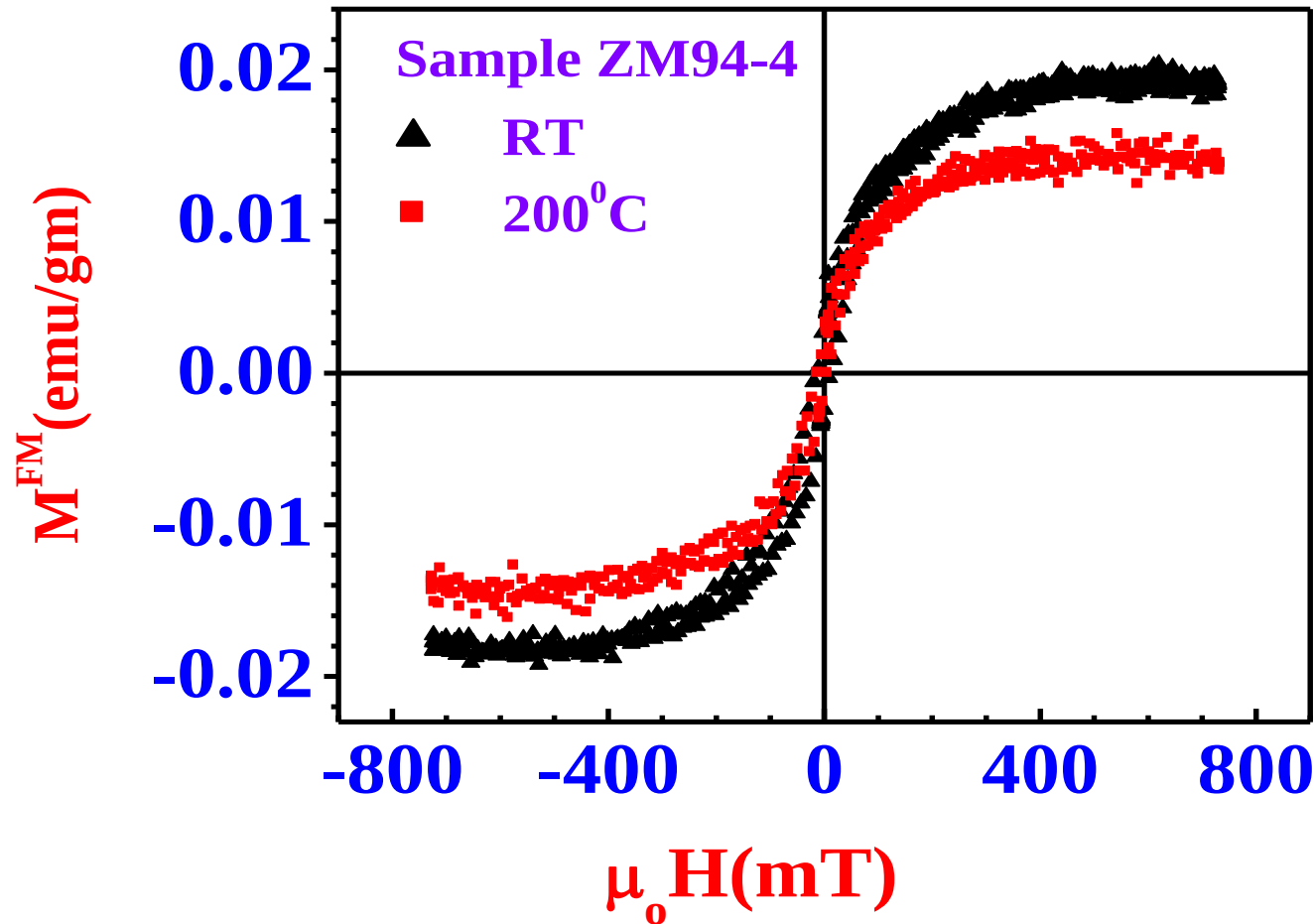
- RTFM observed in low temperature (400-800°C) sintered samples, along with some paramagnetic (PM) fraction.
- Higher temperature sintered samples are PM.

M-H behaviour of the FM fraction of ZMXX-4



- ZMXX-4 samples exhibit RTFM in the entire range $0.01 \leq \text{XX} \leq 0.97$
- M_s of FM phase increases with MnO_2 concentration.
- M (emu/gm of MnO_2) vs. H plots of the FM fraction in different samples scale on a single curve

High temperature (200°C) magnetization behavior of $(\text{ZnO})_{0.06}(\text{MnO})_{0.94}$ (clacined 400°C/8 h)

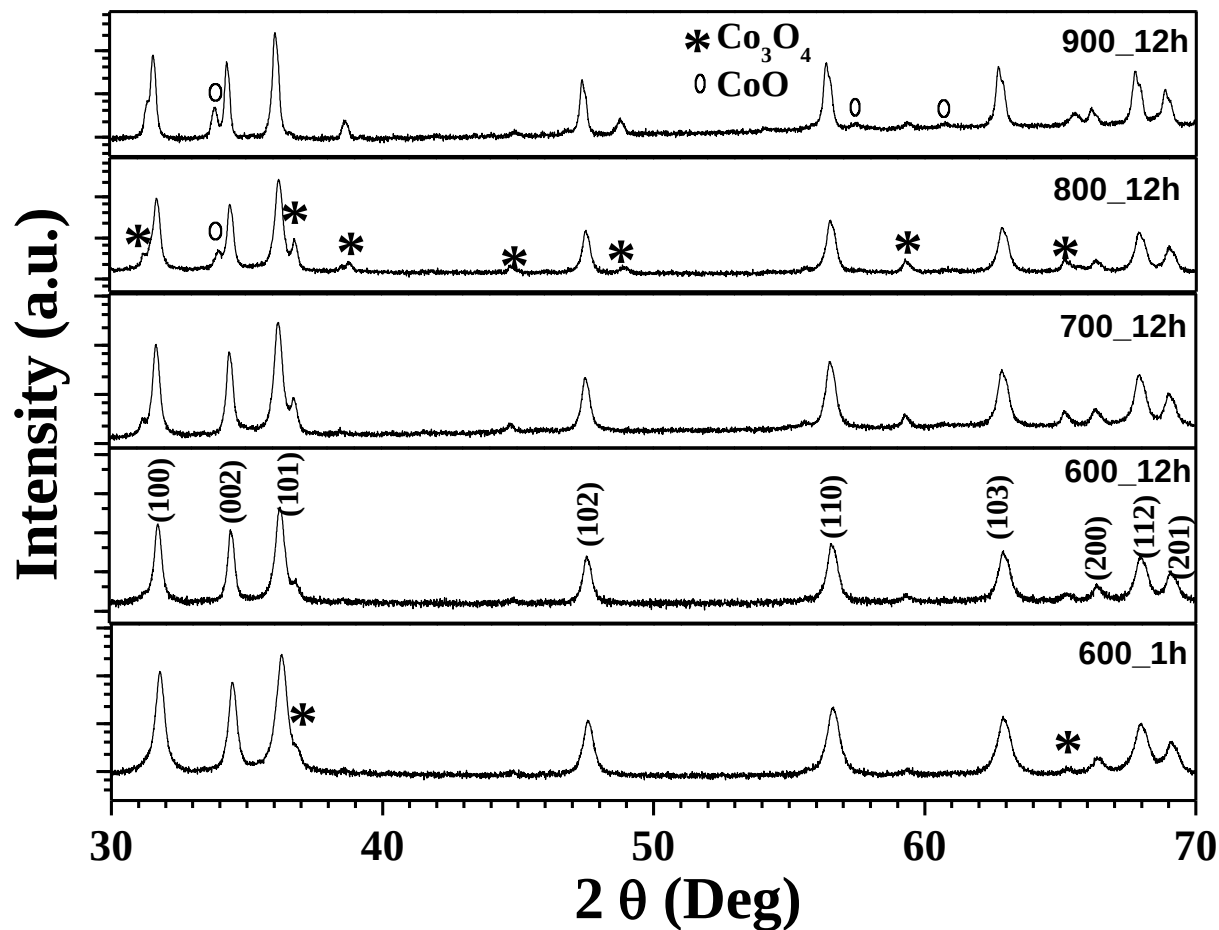


➤ Curie Temperature of the FM **impurity** phase >200°C

2. Nanocrystalline ZnO:Co System

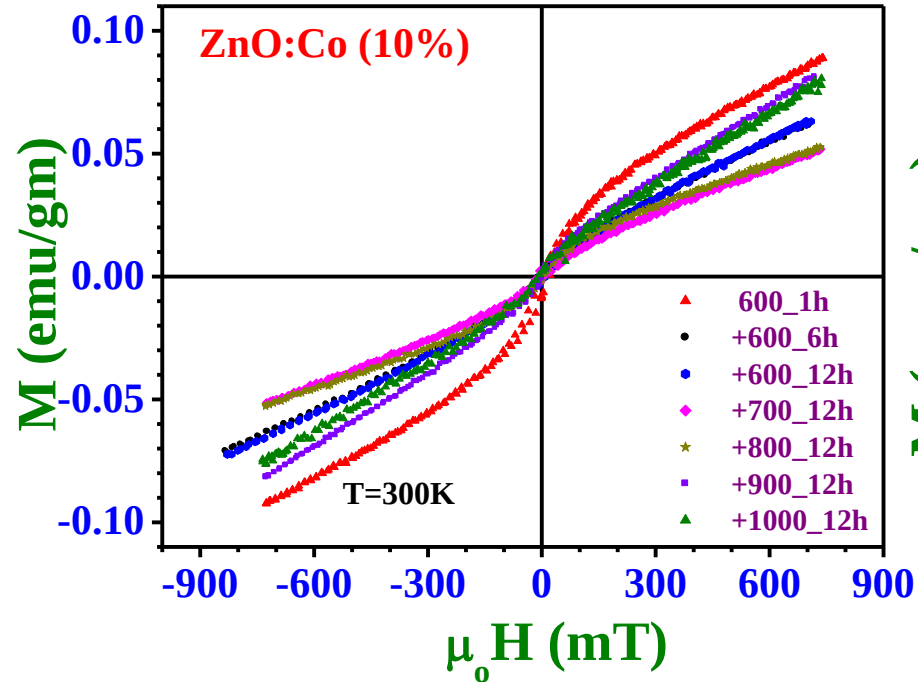
- **ZnO:Co (1-10 at%) samples prepared by chemical route.**
- **Precursors: Zinc acetate dihydrate, cobalt acetate tetrahydrate and poly vinyl pyrrolidane (PVP)**
- **Constituents were dissolved in DI water.**
- **Solution was heated at 90°C.**
- **Dried mass was calcined in air at 600°C for 1h and pelletize (labelled as C5C, C10C).**
- **The pellets were sintered at 800 and 900°C and labelled as 800/12h and 900/12h.**

Phase evolution vis. a vis. Sintering conditions

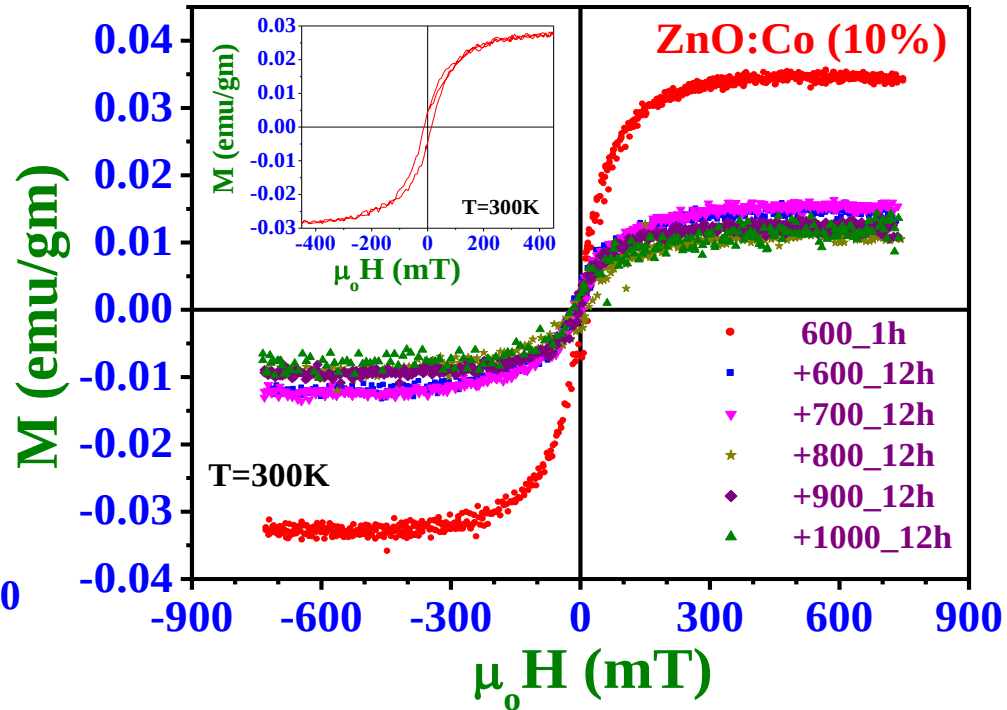


- Co_3O_4 is present even in as calcined sample
- No evidence of cobalt clustering
- CoO is present at higher temperatures

Raw data of ZnO:Co (10%)

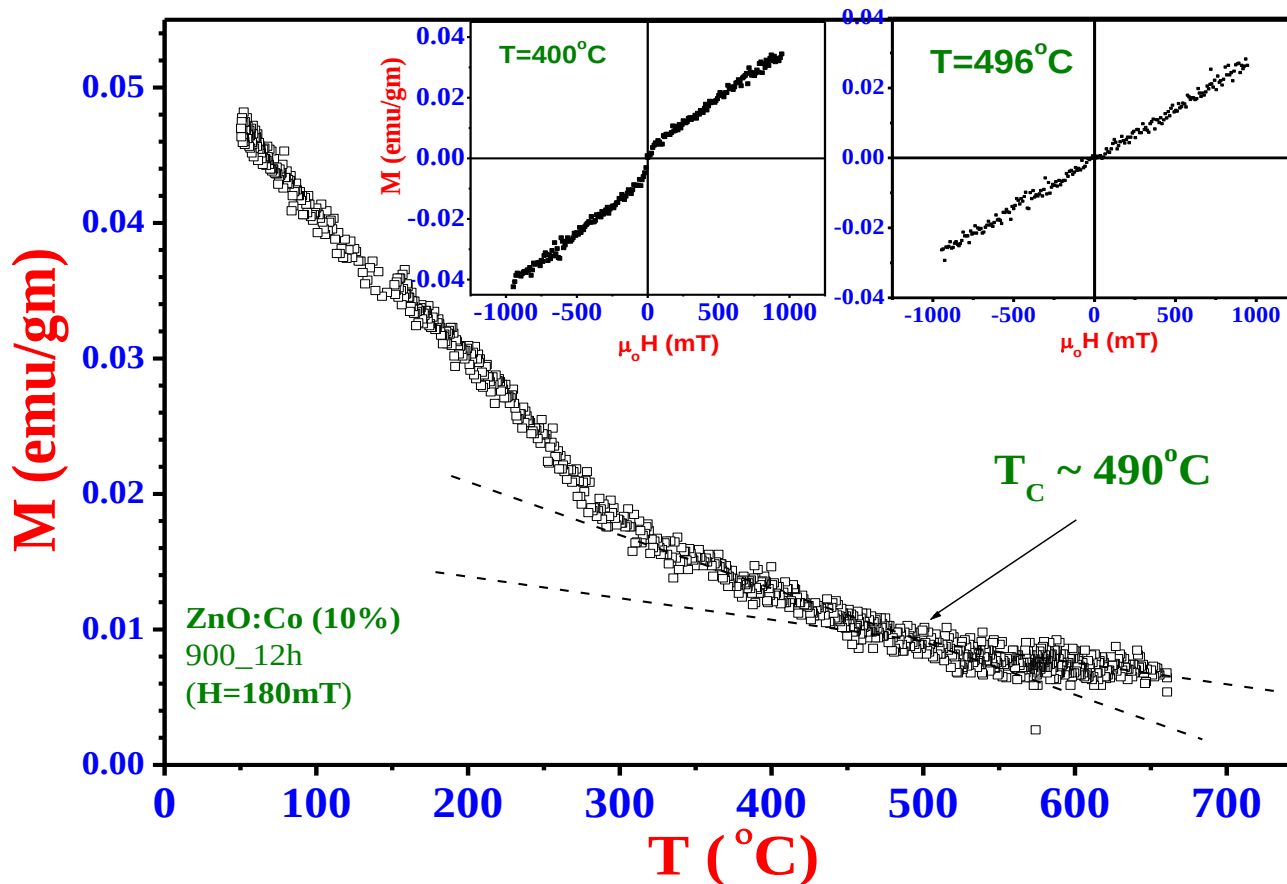


Magnetization behavior of FM phase in ZnO:Co (10%)



- Both FM and PM fractions are present; FM (PM)-fraction decrease(increases) with sintering temp. (T_s); PM fraction continue to increase for $T_s > 900^\circ\text{C}$, However, $M^{\text{sat}}(300\text{K})$ of FM-fraction remains unchanged for $T_s \geq 800-900^\circ\text{C}$
- Clear hysteresis is observed, $\Rightarrow$ No superparamagnetic behavior in these samples

High Temperature M-vs.-T plot



- Curie Temperature of ZnO:Co (10%) sample is $\sim 490^\circ\text{C}$
- Sample becomes paramagnetic at 496°C (inset)
- Observed T_C values $< 1130^\circ\text{C}$ (the T_C of cobalt) confirms that RTFM is not due to Co clusters

Effect of Vacuum annealing

Sample A

($\text{Zn}_{0.95}\text{Co}_{0.05}\text{O}$; 900°C/12h/air)



vacuum annealing

Sample B



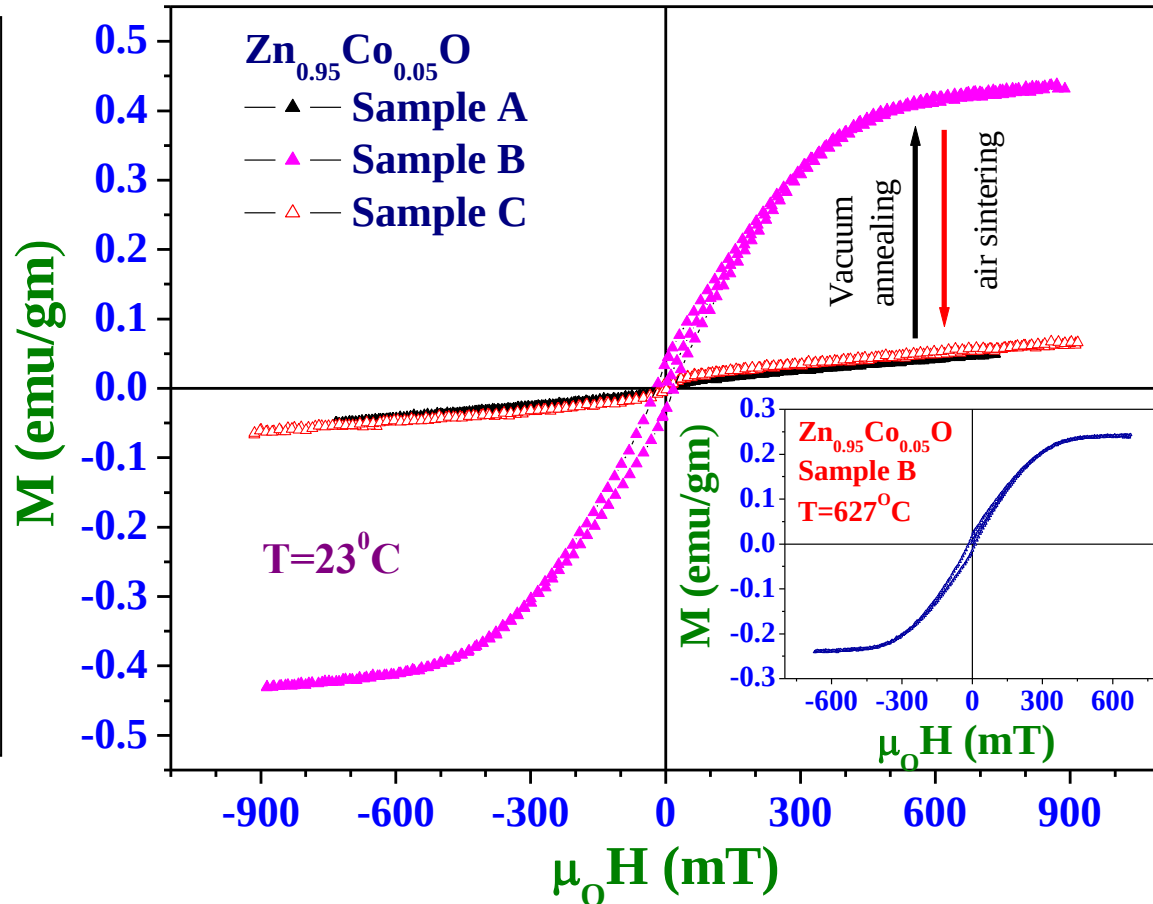
air annealed

Sample C



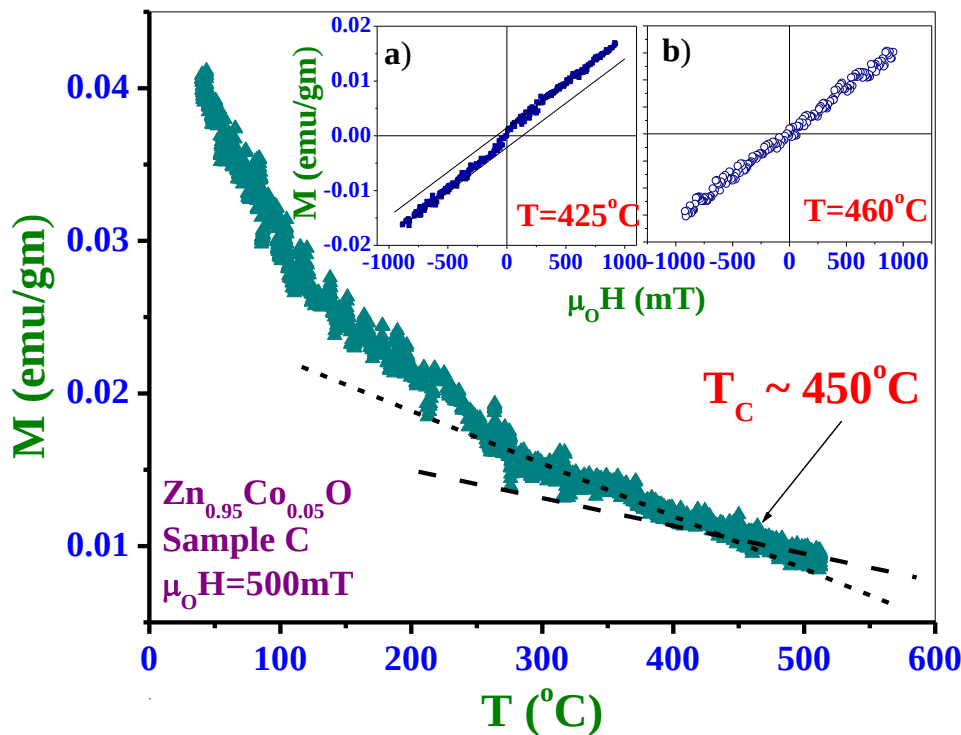
vacuum annealed

Sample D

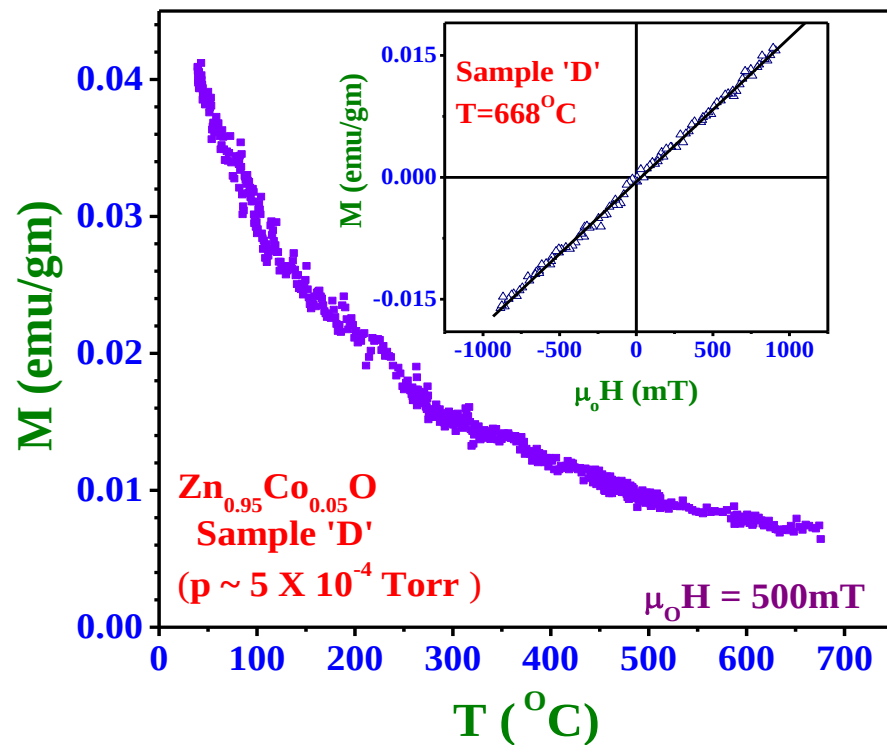


- Giant increase in magnetization with vacuum annealing
- Vacuum annealed samples remain ferrimagnetic at 627°C
- It is due to cobalt clustering

M-T behaviour on Subsequent Sinterings in (a) Air and then (b) Vacuum



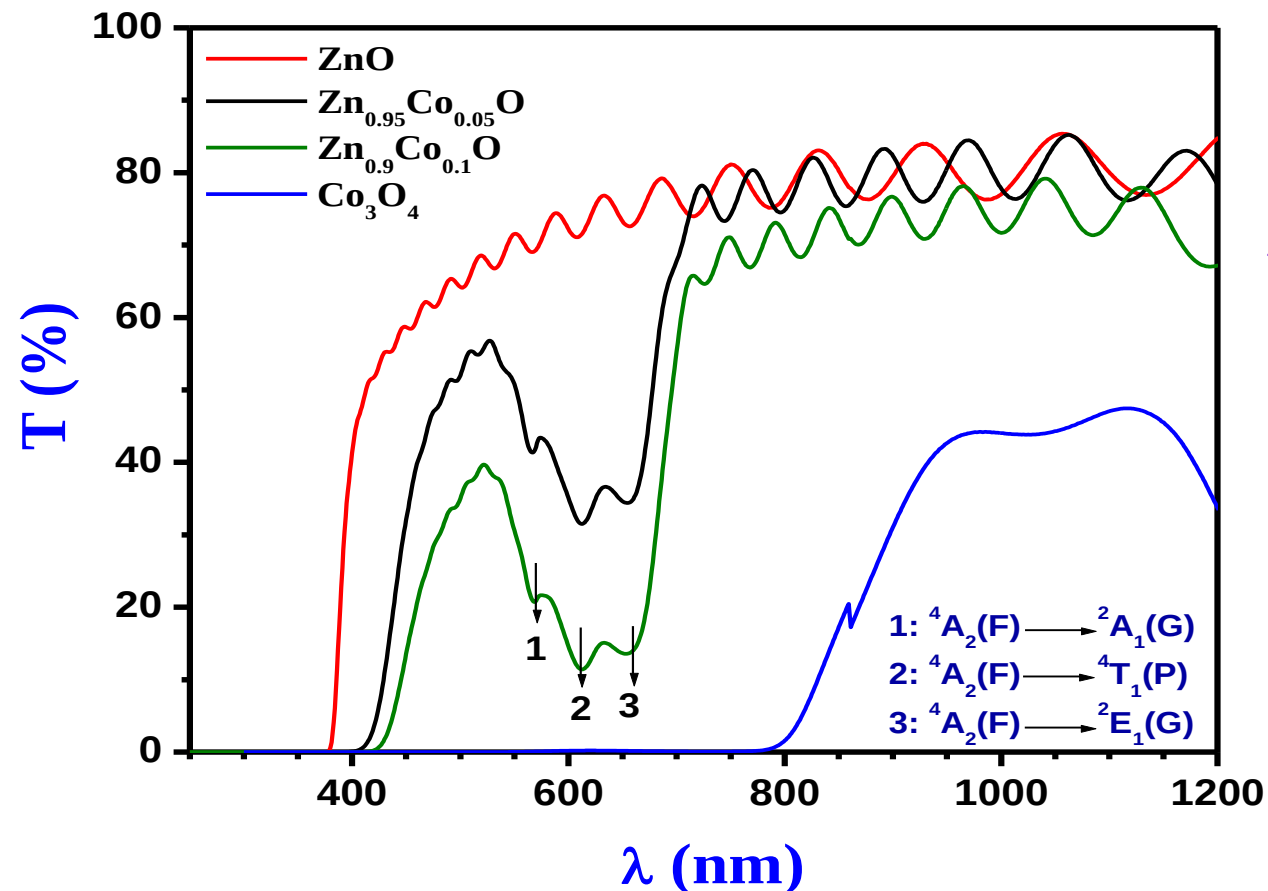
(a) Air Sint. $\rightarrow$ Vacuum Sint. $\rightarrow$ Air Sint.



(b) Air Sint. $\rightarrow$ Vacuum Sint. $\rightarrow$ Air Sint.
 $\rightarrow$ Vacuum Sintering

- Magnetization **unaffected** on subsequent annealing in air or vacuum
- T_c of $\text{Zn}_{0.95}\text{Co}_{0.05}\text{O}$ & $\text{Zn}_{0.90}\text{Co}_{0.10}\text{O}$ lie in $450\text{-}500^{\circ}\text{C}$

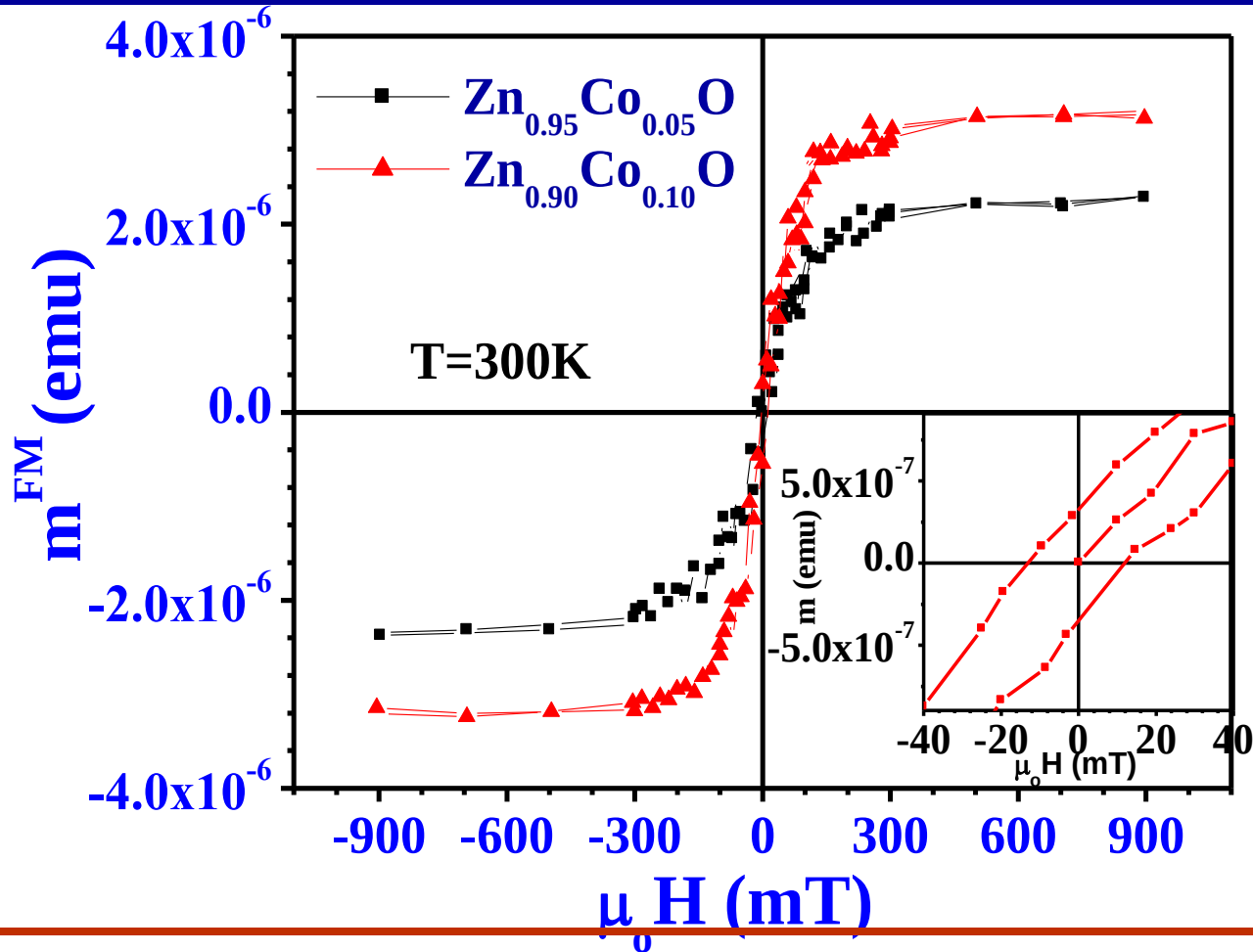
Optical Transmission spectrum of $\text{Zn}_{1-x}\text{Co}_x\text{O}$ thin Films



$\text{Zn}_x\text{Co}_{1-x}\text{O}$ thin films
with $0 \leq x \leq 0.1$,
deposited by **Spray**
Pyrolysis ($T_{\text{sub}} = 380^\circ\text{C}$)

- Cobalt is present in tetrahedral crystal field in +2 state
- Band gap shifts to lower energies with increase in Co content

Magnetization behavior of FM phase in $\text{Zn}_{1-x}\text{Co}_x\text{O}$ thin films



- The $m_{\text{sat}}(300\text{K})$ increases non-linearly with cobalt concentration
- Hysteretic M-H rules out the superparamagnetic contribution
- Observed FM not due to cobalt clusters as films are deposited in air

Conclusions

A. ZnO:Mn System

- Irrespective of the relative quantities of ZnO and MnO₂, all the samples prepared at low sintering temp. are **ferromagnetic at room temperature**, with $T_C > 200^\circ\text{C}$.
- The samples of (ZnO)_{1-x}(MnO₂)_x ($0.01 < x < 0.97$) calcined at 400°C have nearly same saturation magnetization (in units of emu/gm of MnO₂), which implies,
 - (a) **origin of FM is certainly not due ZnO phase,**
 - (b) **FM associated with the presence of impurity phases**
- The **phase pure** Zn_{1-x}Mn_xO samples formed at a higher sintering temperature of 900°C (or above) are completely paramagnetic.

Zn_{1-x}Mn_xO IS PARAMAGNETIC SYSTEM

B. ZnO:Co System

- RTFM is observed in air sintered nanocrystalline $\text{Zn}_{1-x}\text{Co}_x\text{O}$ powder and thin film samples
- PM contribution (partially due to cobalt oxides) always coexists with FM
- The RTFM can originate from both extrinsic as well as intrinsic effects
- Processing conditions resulting in stable $\text{Zn}_{1-x}\text{Co}_x\text{O}$ having intrinsic FM are distinctly identified
- The extrinsic RTFM in ZnO:Co is due to formation of cobalt clusters. By appropriate heat treatment these can be completely oxidised/removed
- RTFM in these semiconducting samples could be explained by bound magnetic polarons
- Curie temperature of $\text{Zn}_{1-x}\text{Co}_x\text{O}$ lies in the range of 450-495°C.

$\text{Zn}_{1-x}\text{Co}_x\text{O}$ IS AN INTRINSIC FERROMAGNET SYSTEM

References

1. [Effect of Indium incorporation in \$\text{Zn}_{1-x}\text{Co}_x\text{O}\$ Thin Films](#)
Sujeet Chaudhary, Kanwal Preet Bhatti, Dinesh K Pandya, Subhash C Kashyap and A K Nigam
J. Mag. Mag. Mat. (Accepted, Feb 2008).
2. [Cobalt substituted ZnO thin films – A potential candidate for Spintronics](#)
Kanwal Preet Bhatti, Vivek Kumar Malik, Sujee Chaudhary
J. Mat. Sci.: Mat. In Elect. (Online Since Dec 5, 2007).
3. [On the Intrinsic and Extrinsic Origin of Room Temperature Ferromagnetism in ZnO:Co \(5at %\)](#)
Kanwal Preet Bhatti, Sujee Chaudhary, D K Pandya , S C Kashyap
J. Appl. Phys. 101 (2007) pp 103919.
4. [Raman studies of ZnO:Co thin films](#)
Huijuan Zhou, Limei Chen, Vivek Malik, Christoph Knies, Detlev M. Hofmann, Kanwal Preet Bhatti, Sujeet Chaudhary, Peter J. Klar, Wolfram Heimbrod, Claus Klingshirn, and Heinz Kalt
Phys. Stat. Sol. (a) 204 (2007) pp 112–117.
5. [High temperature investigation of magnetization behavior in cobalt substituted ZnO](#)
Kanwal Preet Bhatti, Sujeet Chaudhary, D K Pandya , S C Kashyap
J. Appl. Phys. 101 (2007) pp 033902.
6. [Observation of room temperature ferromagnetism in nanocrystalline ZnO:Co system](#)
Kanwal Preet Bhatti, Shankhamala Kundu, Sujee Chaudhary, D K Pandya , S C Kashyap
J. Phys. D : Appl. Phys. 39 (2006) pp 4909-4914.
7. [Extrinsic nature of the room temperature ferromagnetism in \$\(\text{ZnO}\)_{1-x}\(\text{MnO}_2\)_x\$ for \$0.01 < x < 0.97\$](#)
Kanwal Preet Bhatti, Sujee Chaudhary, D K Pandya , S C Kashyap
Solid State Commun. 140 (2006) pp 23-27.
8. [On the room temperature ferromagnetism in \$\(\text{ZnO}\)_{0.98}\(\text{MnO}_2\)_{0.02}\$](#)
Kanwal Preet Bhatti, Sujee Chaudhary, D. K. Pandya, Subhash C. Kashyap
Solid State Commun. 136 (2005) pp 384-388.
9. [Ferromagnetic Ordering at room temperature in Co:ZnO Nanoparticles](#)
Sujeet Chaudhary, Kanwal Preet Bhatti, Shankhamala Kundu, Subhash C. Kashyap and D. K. Pandya
MRS Fall Meeting , Boston, MAS, USA, **Nov.27-Dec.1, 2006** in Zinc Oxide and Related Materials, edited by Jürgen Christen, Chennupati Jagadish, David C. Look, Takafumi Yao, Frank Bertram (**Mater. Res. Soc. Symp. Proc.** 957, Warrendale, PA, 2007), 0957-010-01