Synthesis and Characterization of Ferroic Nanocomposites of Spinel Ferrites and Perovskites

Jacob Faucheaux, Amin Yourdkhani, Shiva Adireddy, and Gabriel Caruntu*

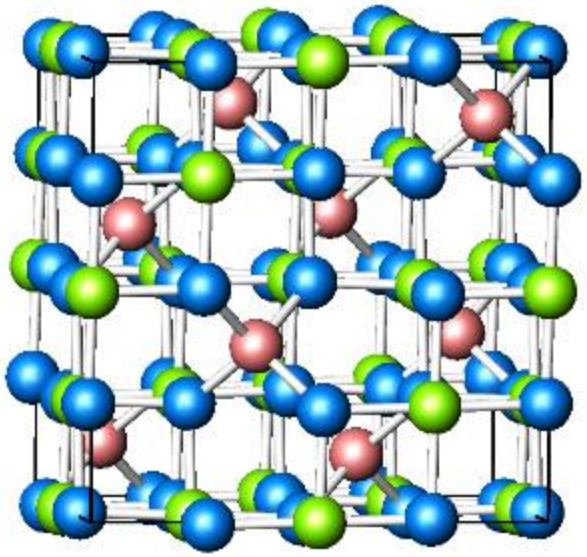
Abstract

In this research, 0-3 type ferroic nanocomposites have been fabricated using colloidal synthesis approaches. The zero dimensional (0D) magnetic phase ($CoFe_2O_4$) was synthesized by an elevated temperature hydrolysis reaction carried out in a three neck flask. The ferrites were incorporated into the matrix of the perovskite phases ($ATiO_3$, A= Ba and Pb) by two methods. Lead titanate was deposited onto the ferrites in an aqueous solution via the liquid phase deposition (LPD) method. Alternatively, the ferrites were incorporated into an amorphous titanium dioxide matrix via a sol-gel method which was used as a precursor for the hydrothermal synthesis of perovskite-spinel nanocomposites. The nanocomposites were characterized by XRD, VSM, TEM, FE-SEM, Raman, and PFM.

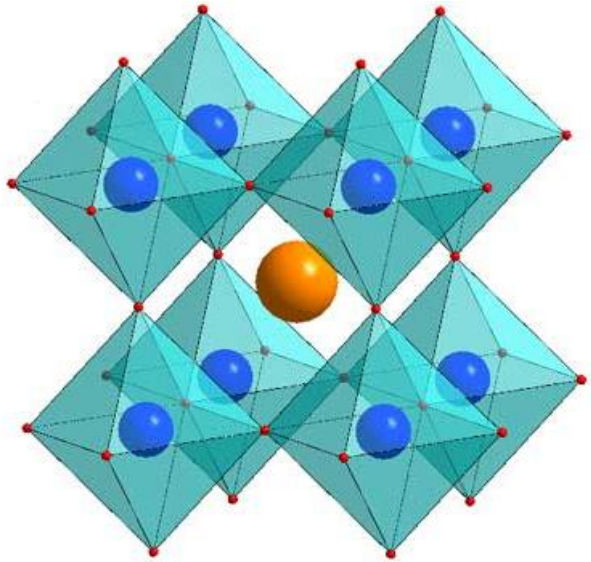
Introduction

- Perovskites ($ATiO_3$ A=Ba or Pb) are ferroelectric (they exhibit electric polarization) and Spinels ($CoFe_2O_4$) are ferro or ferrimagnetic (they exhibit spontaneous magnetic dipoles)

- Magnetoelectric composites consist of a ferroelectric phase coupled together with a ferromagnetic phase



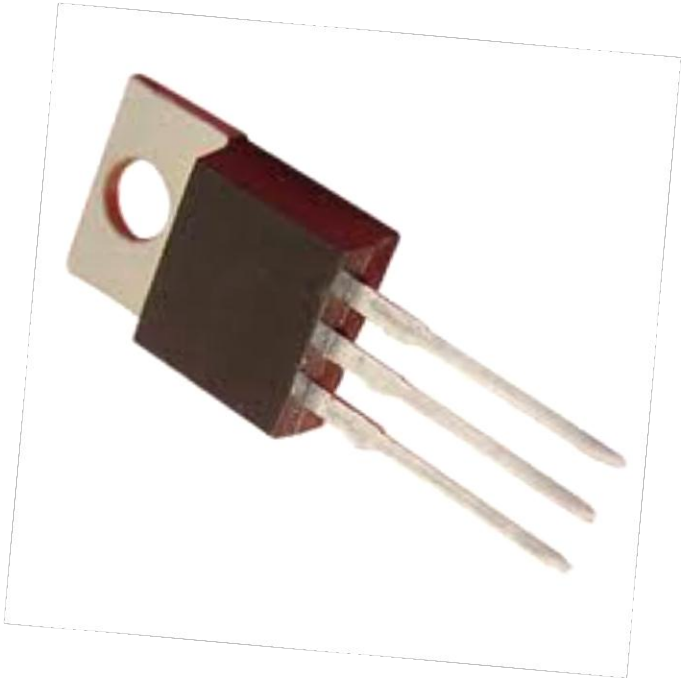
Spinel Crystal Structure

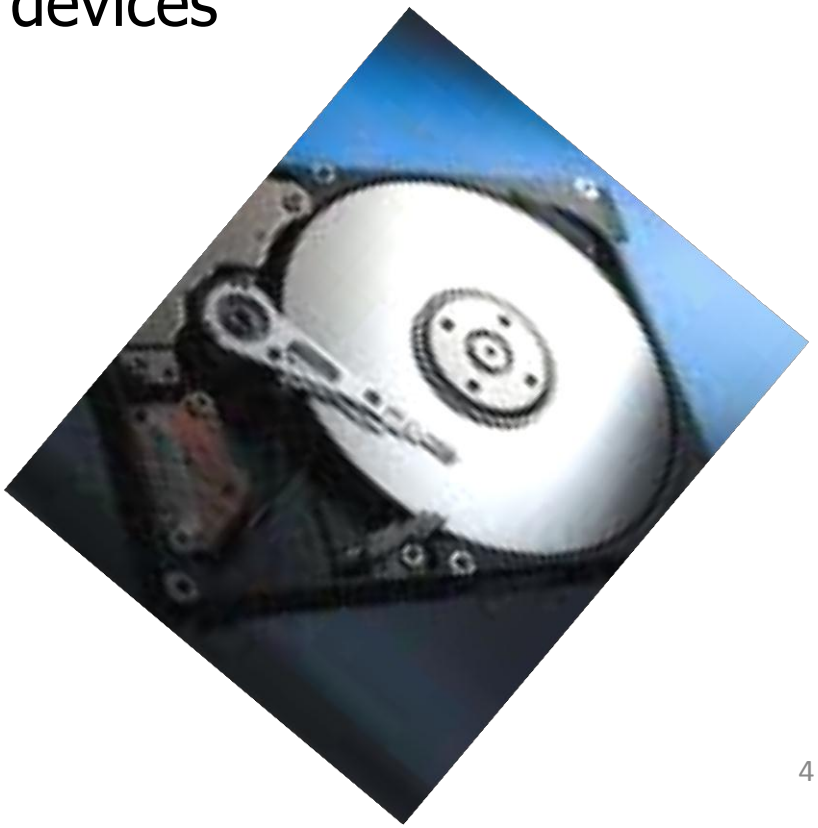


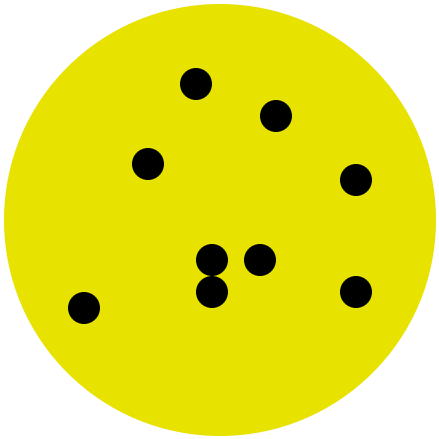
Perovskite Structure

- Applying a stimulus to either phase can transfer a physical strain to the coupled phase and induce a response

- These materials have a range of applications in electronics and computers specifically in sensors, transistors, and data storage devices



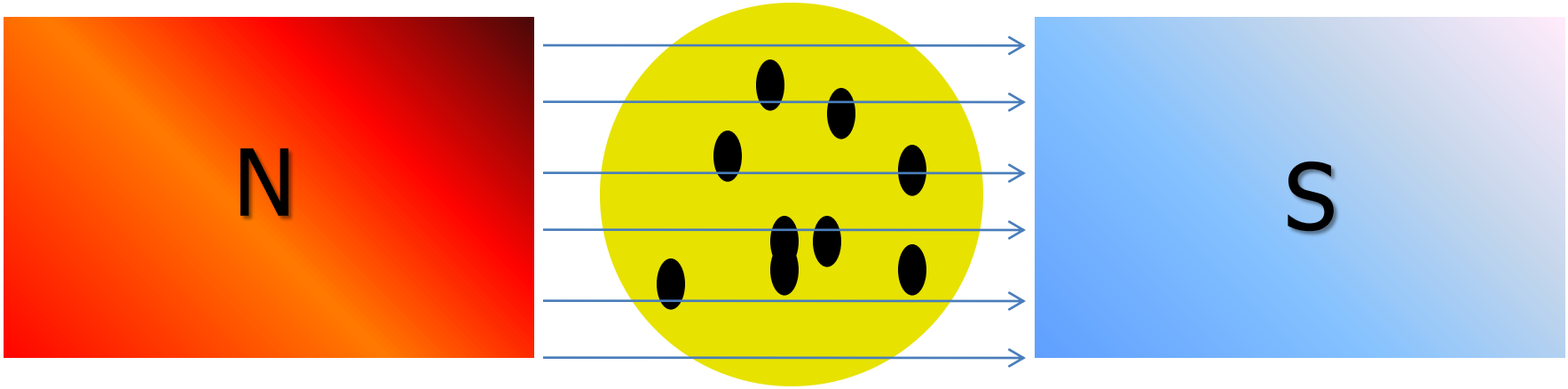




Cobalt Ferrite (Negative Magnetostriction Coefficient)

Lead Titanate (Electrostrictive Phase)

Polarization: $P(H=0)=P_0$



$$P(H)=P_0+\Delta P$$

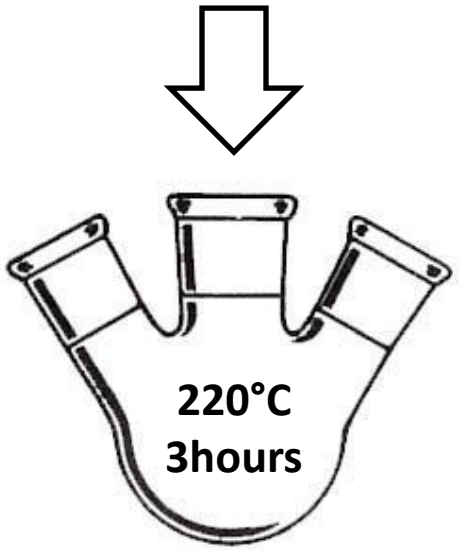
$$\alpha_{ME}=\frac{dP}{dH}=\left(\frac{dP}{dM}\right)\left(\frac{dM}{dH}\right)$$

Methods

Synthesis of Magnetic Nanoparticles

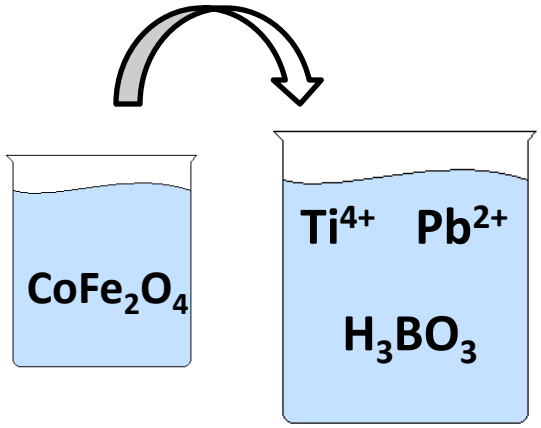
- The $CoFe_2O_4$ (CFO) nanoparticles are synthesized by a hydrolysis reaction
- The DEG and NMDA act as both the solvent and as capping agents
- The hydroxide groups on the capping agents make the particles dispersible in polar solvents

$CoCl_2 \cdot 6H_20$ +
$FeCl_3 \cdot 6H_20$ +
DEG + NMDA



$CoFe_2O_4$

Synthesis of Nanocomposites by LPD



1. 45°C, 3hrs
2. Annealed at 750°C 6hrs

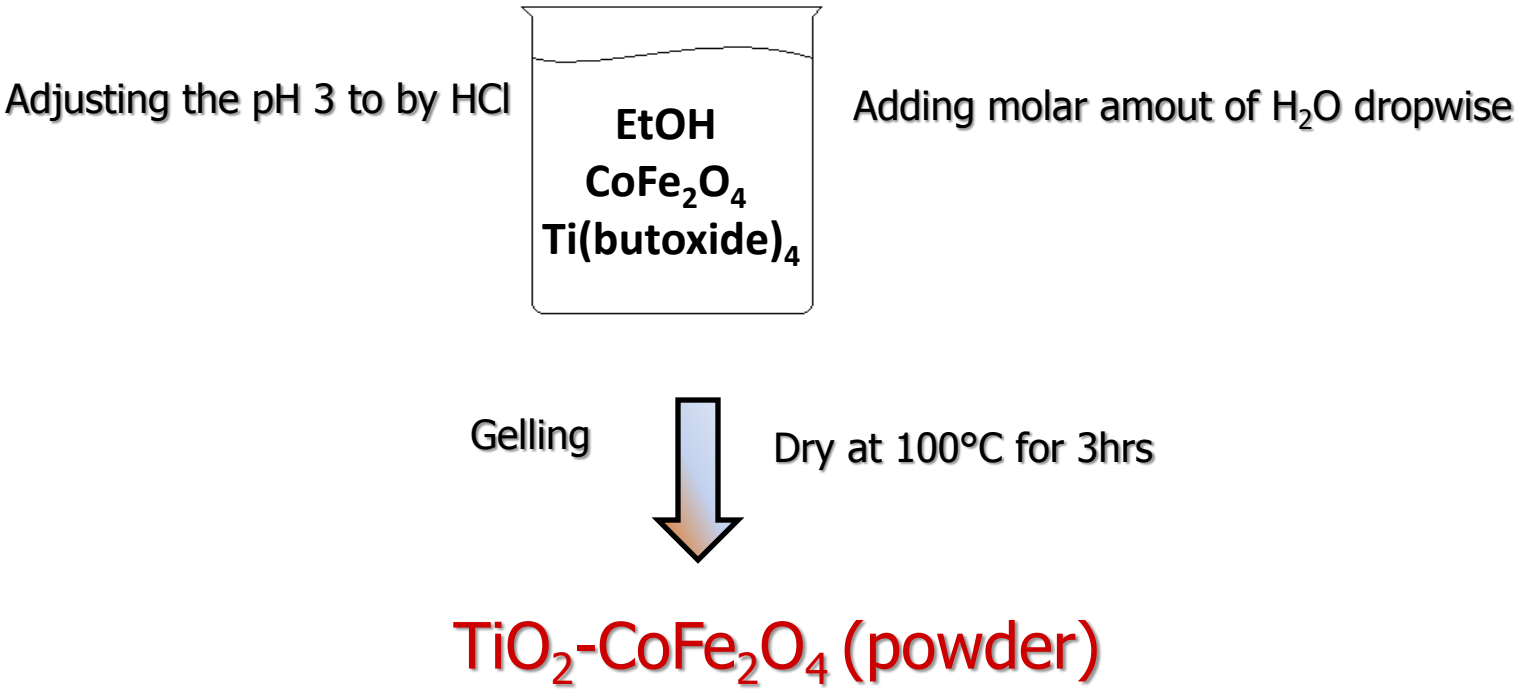
$PbTiO_3$-$CoFe_2O_4$

$$MF_n^{(n-2m)} + mH_20 \leftrightarrow MO_m + nF^- + 2mH^+ \quad (1)$$

$$H_3BO_3 + 4HF \leftrightarrow BF_4^- + H_3O^+ + 2H_2O \quad (2)$$

- LPD involves an equilibrium reaction
- Addition of Boric Acid shifts the equilibrium to the product side

Integration of CFO into TiO2 matrix



The CFO nanoparticles were integrated into amorphous TiO2 through a sol-gel method

Synthesis of PTO-CFO by Hydrothermal Method

The TiO2-CFO powder was then used as seeds for the formation of PTO-CFO nanocomposites under hydrothermal conditions

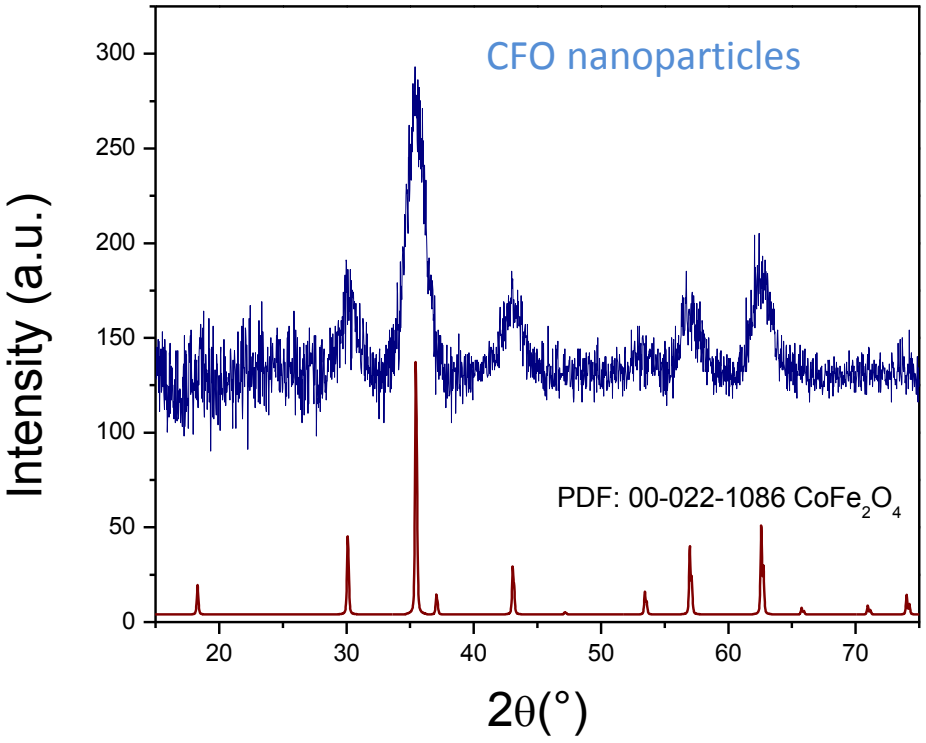
TiO_2-$CoFe_2O_4$ (powder)

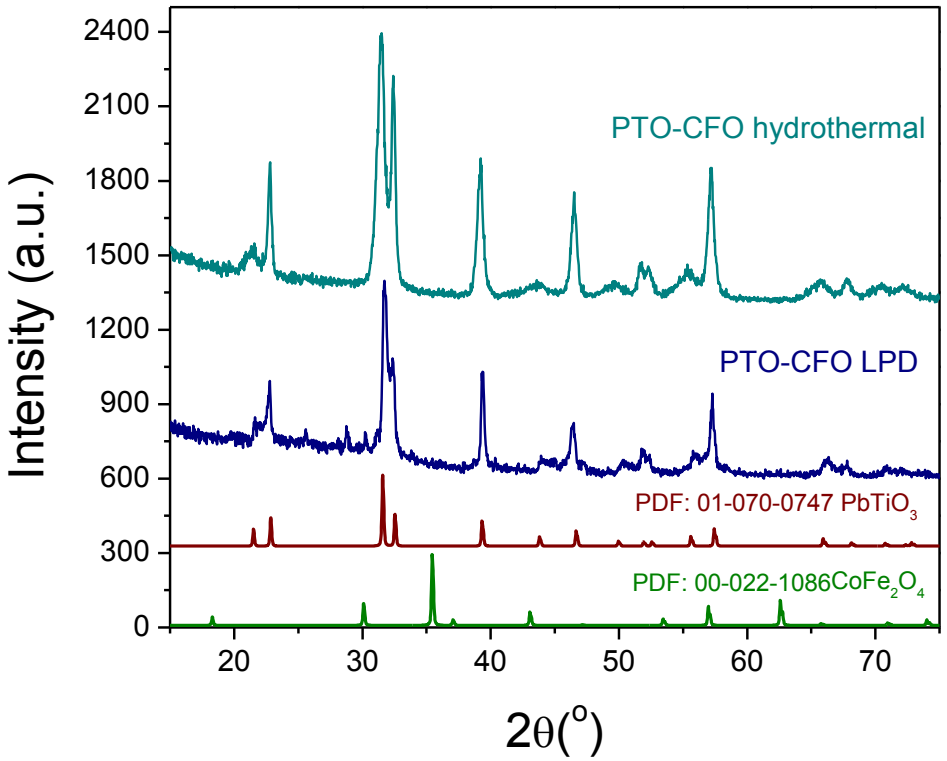
A^{2+} + KOH + 15 mL H_2O

180°C 12hrs (A = Ba or Pb)

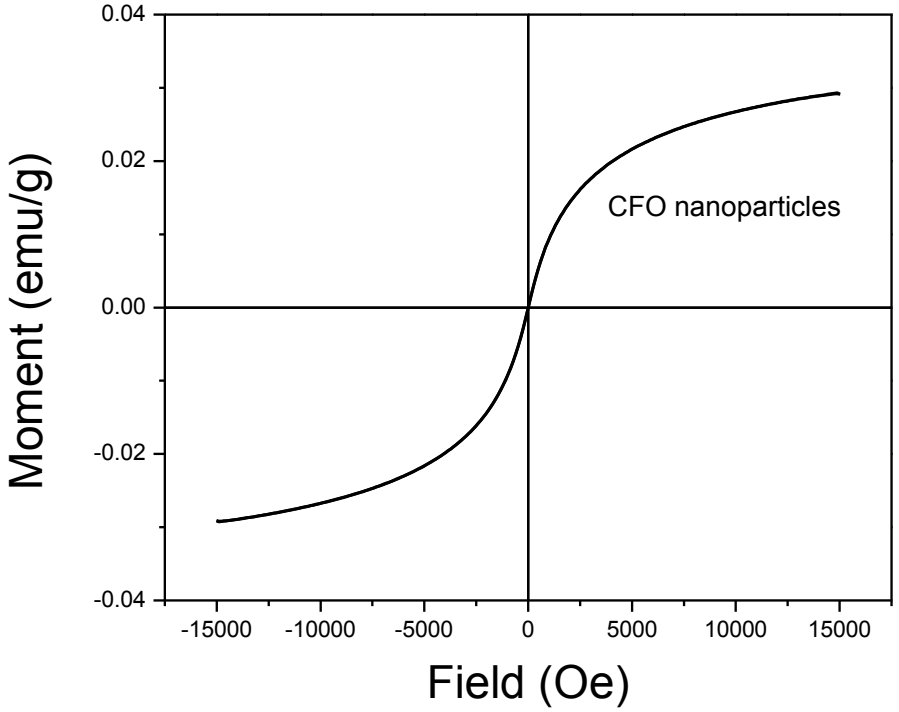
$ATiO_3$-$CoFe_2O_4$

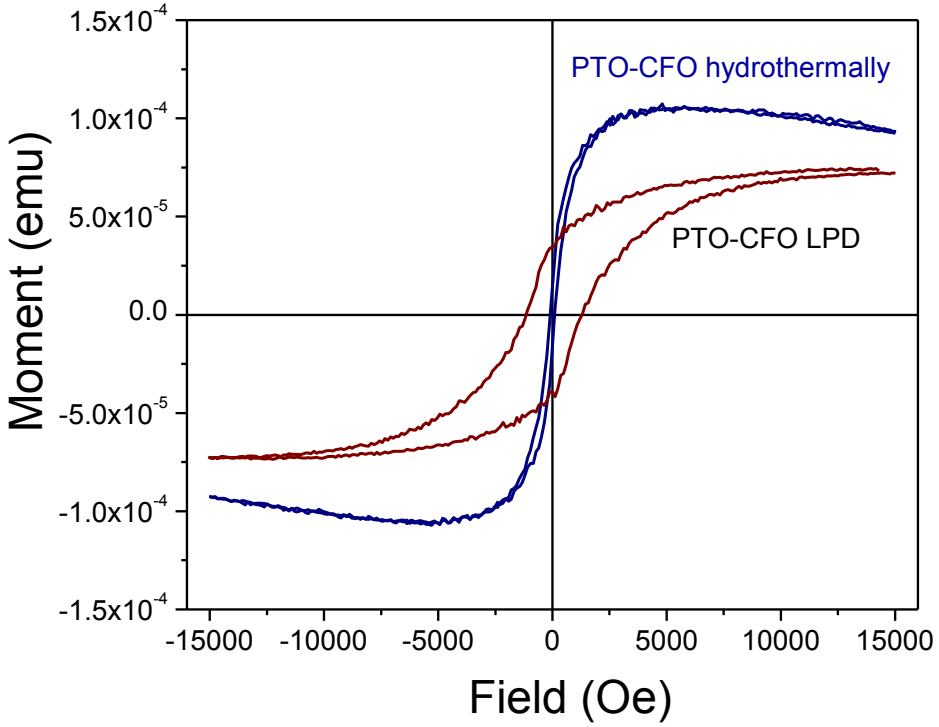
X-Ray Diffraction





Magnetic Properties

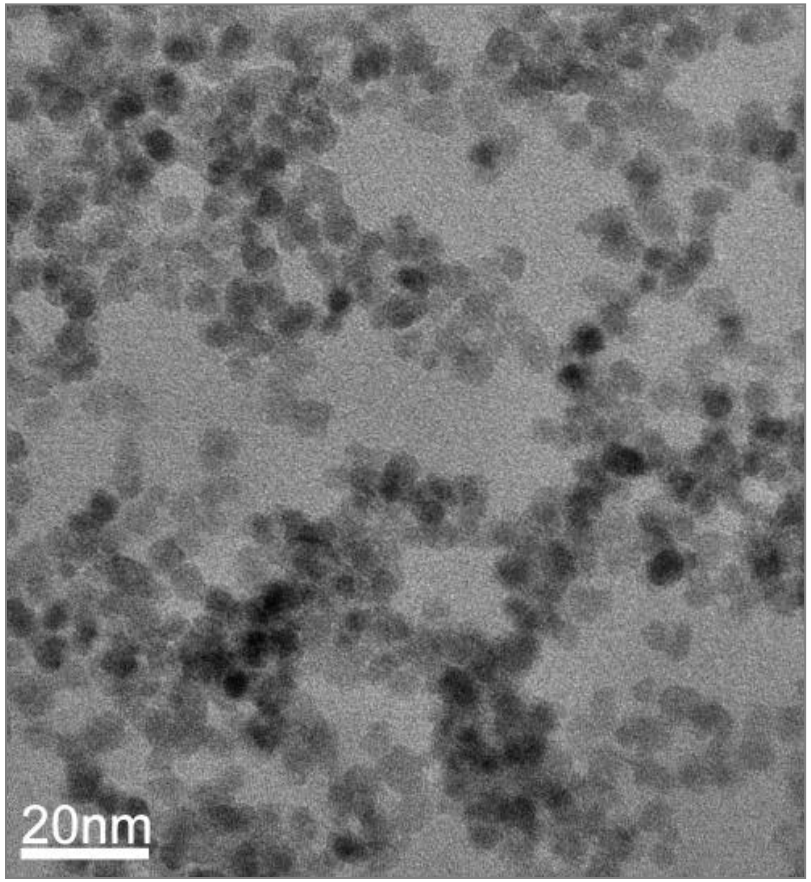


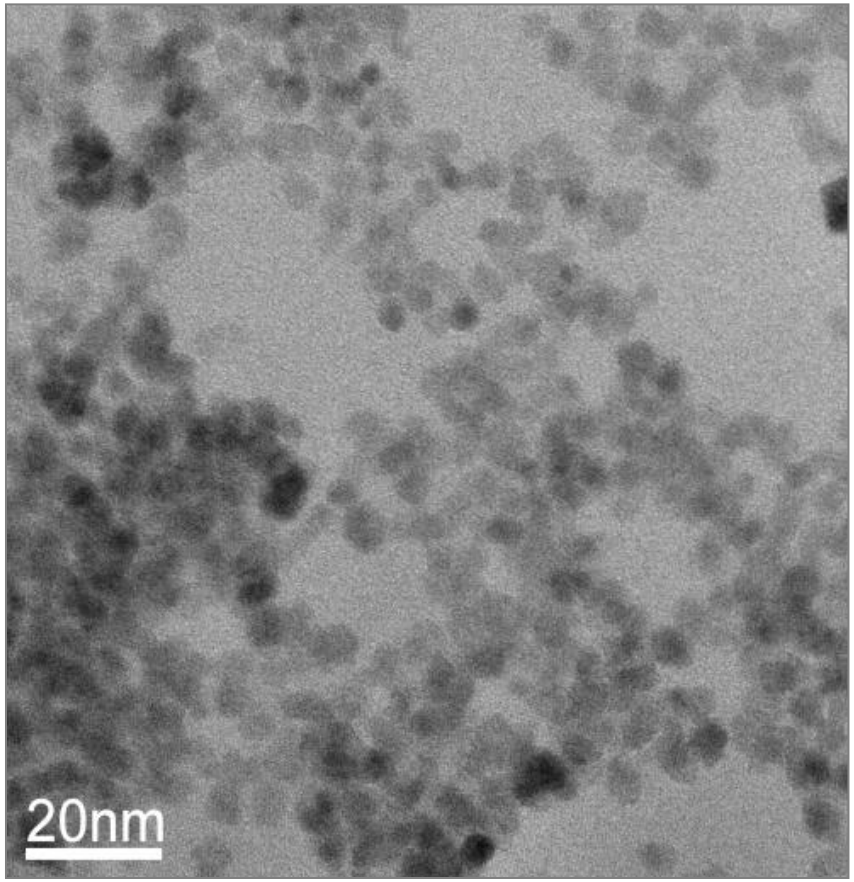


VSM measurements of the CFO nanoparticles.

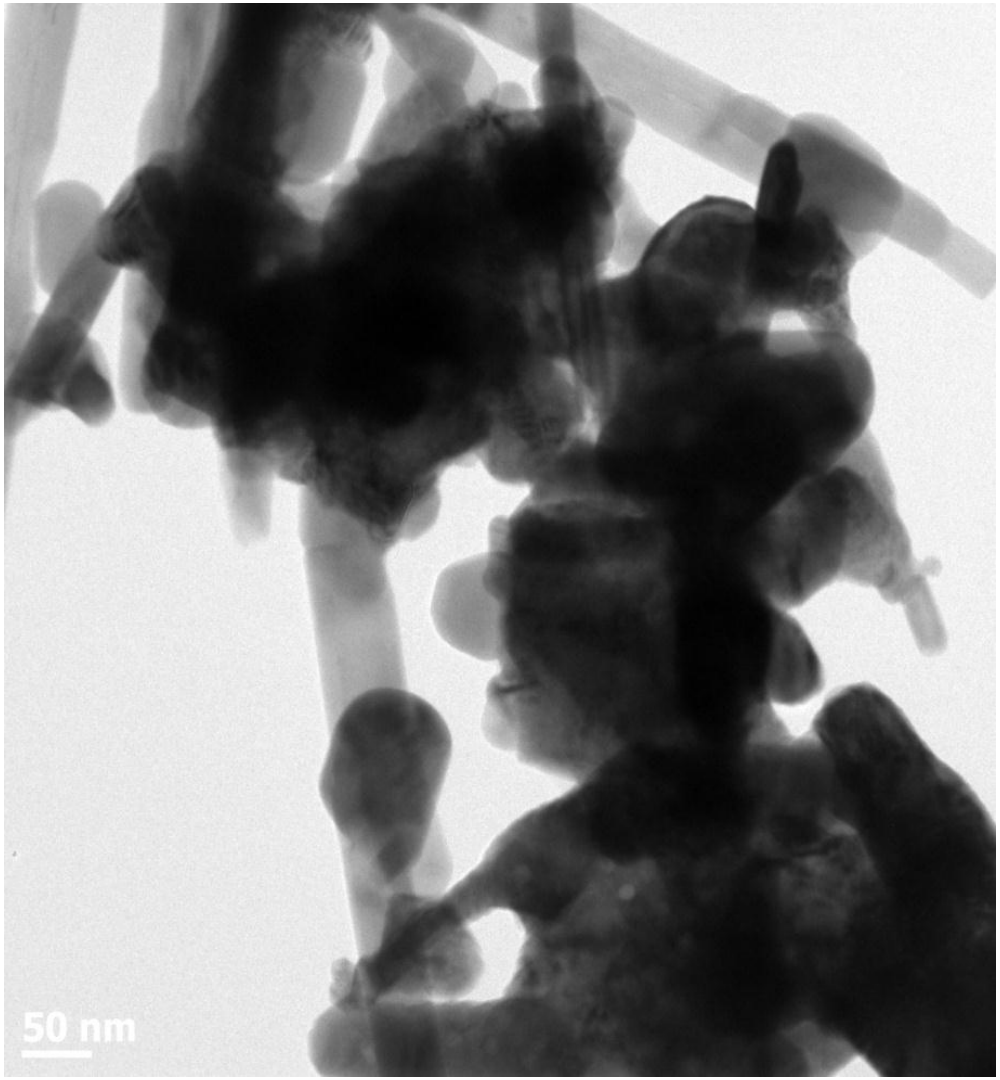
VSM measurements of PTO-CFO nanocomposites.

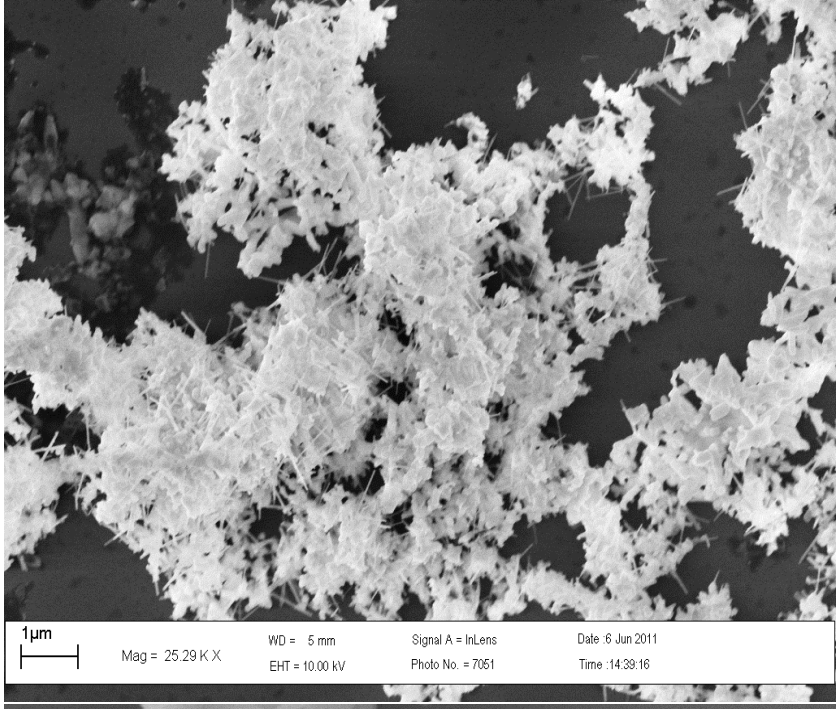
Morphology

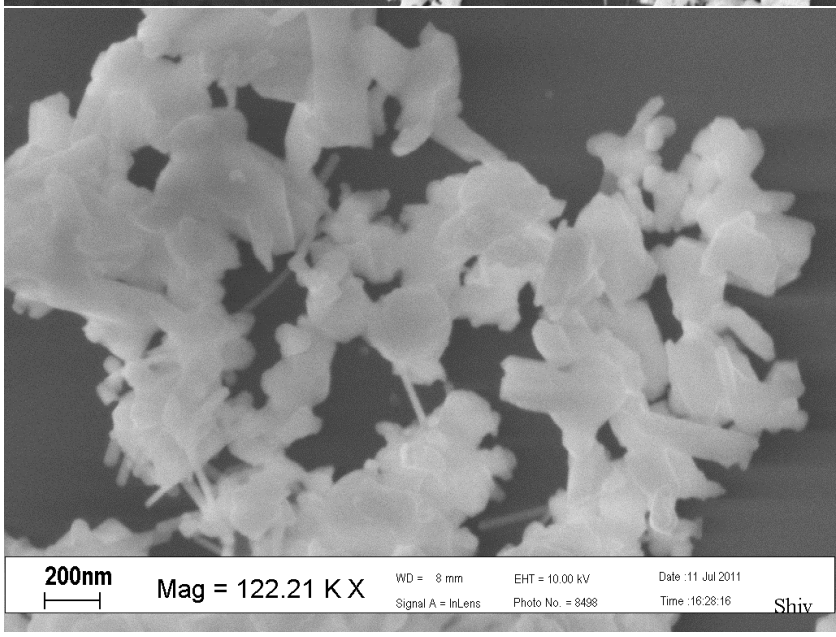




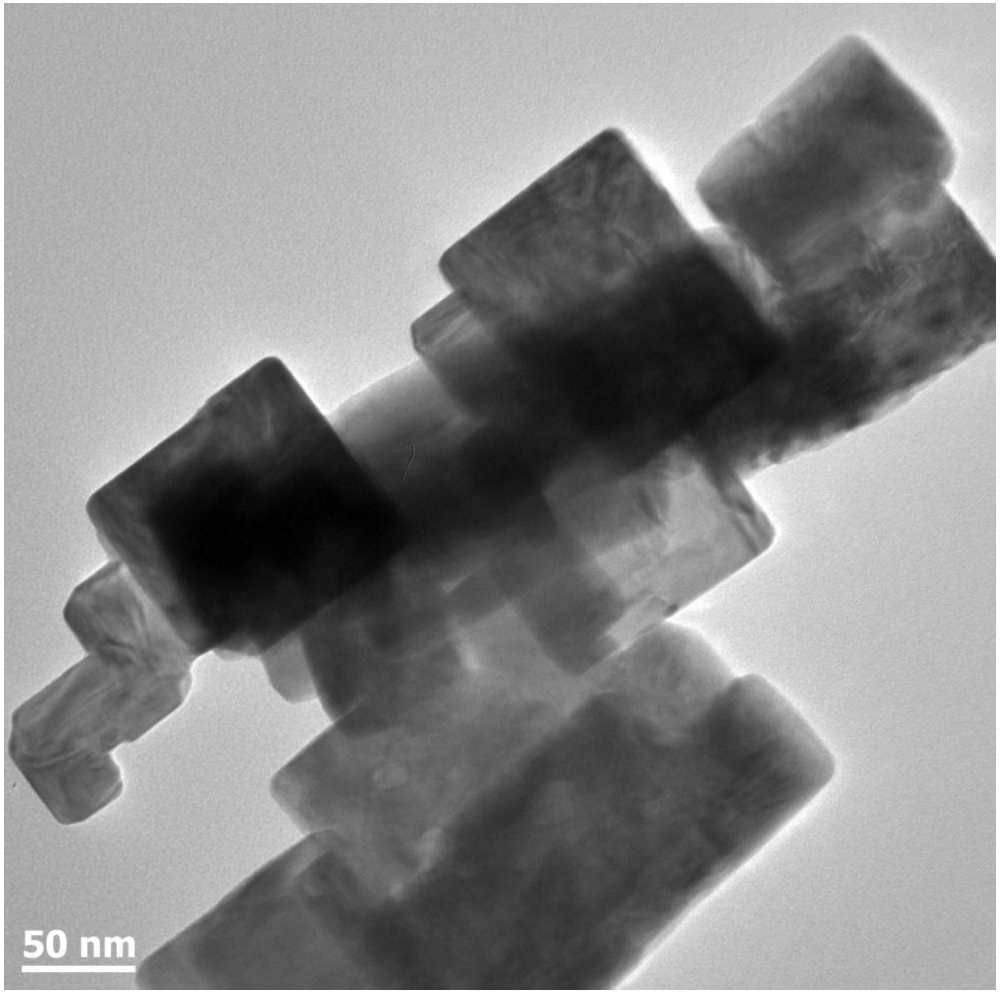
TEM images of the CFO nanoparticles

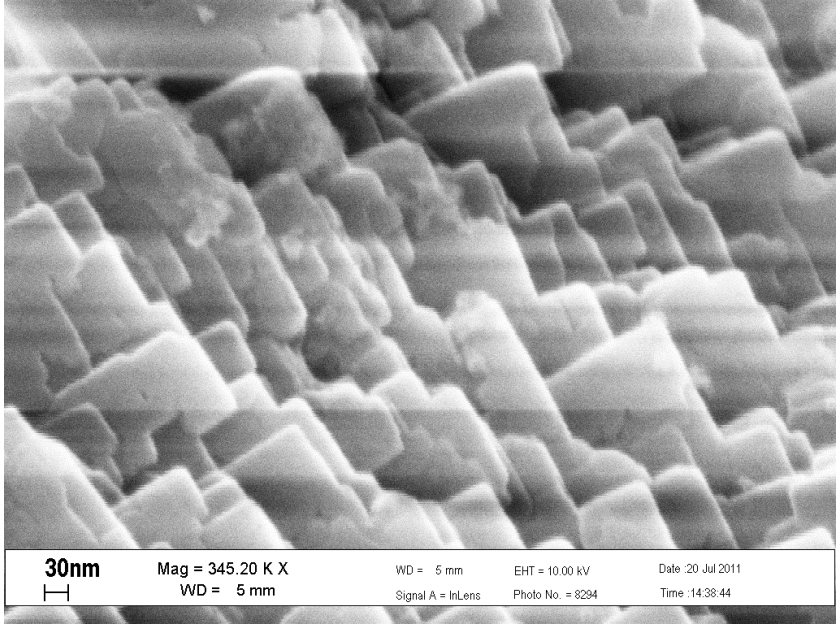


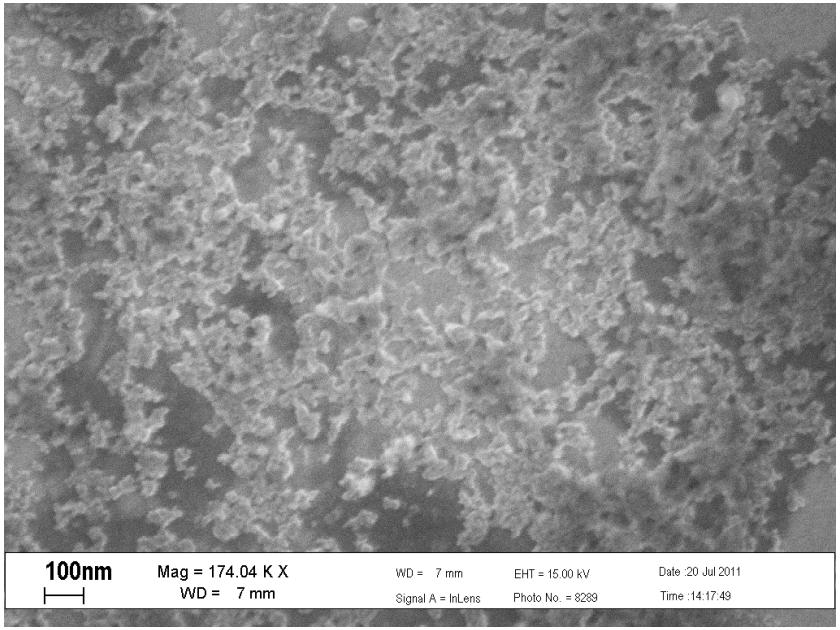




TEM and FE-SEM of PTO-CFO nanocomposites formed by LPD.

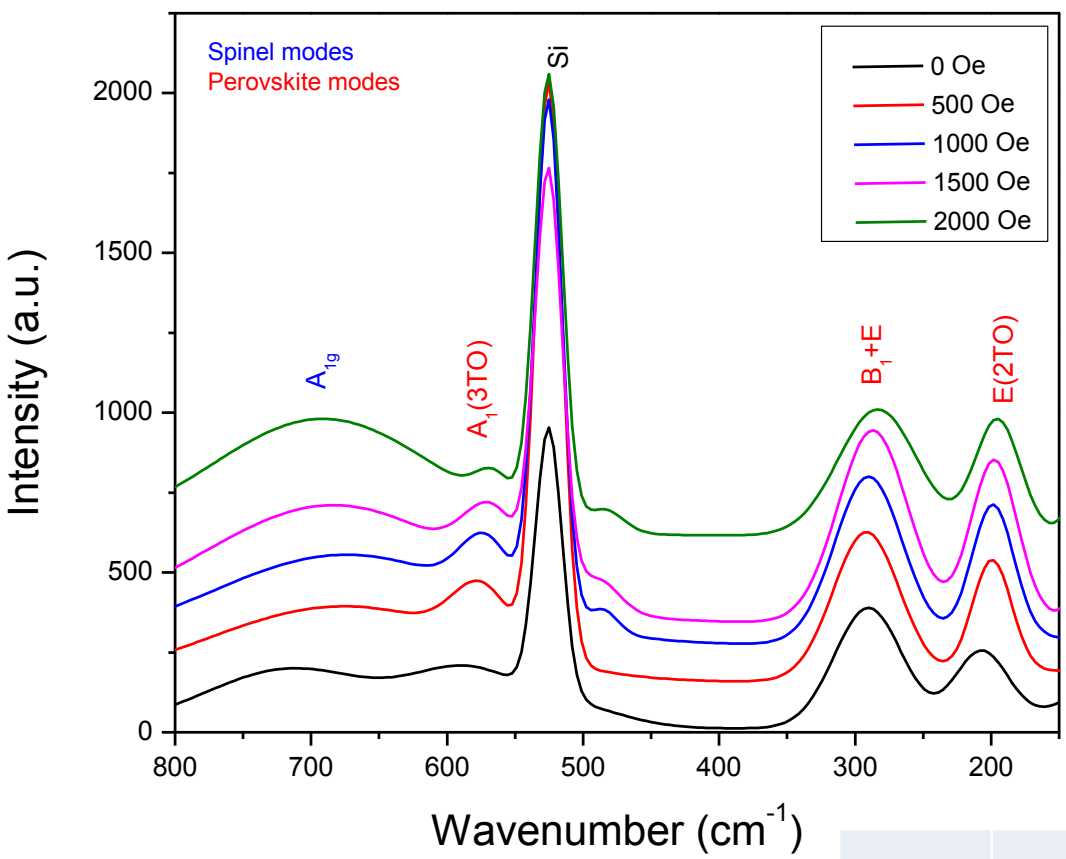






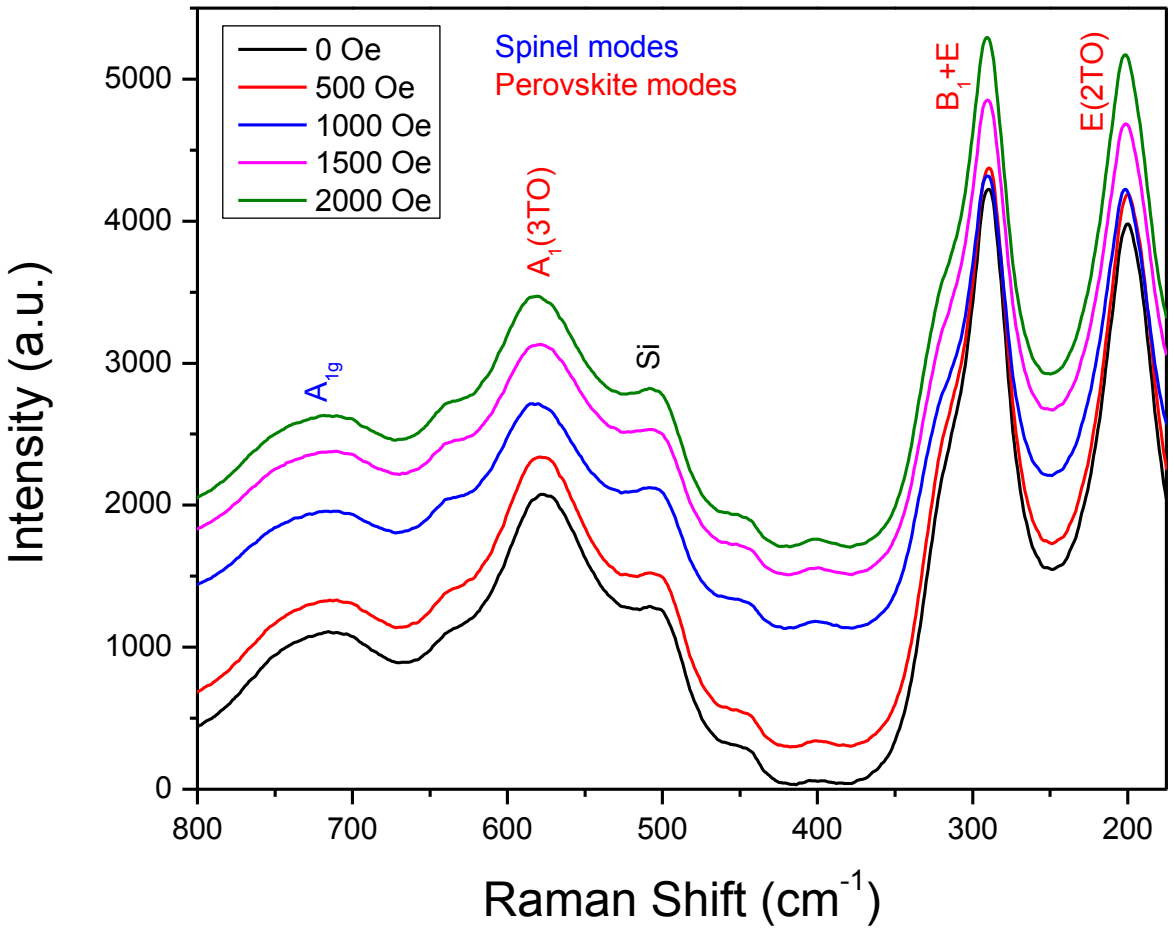
TEM and FE-SEM of PTO-CFO nanocomposites formed hdyrdothermally

Magnetic Field Assisted Raman



Raman Spectra of PTO-CFO powder prepared by LPD placed on a silicon wafer. Shifts in the perovskite modes suggest a coupling between the magnetic and piezoelectric phases.

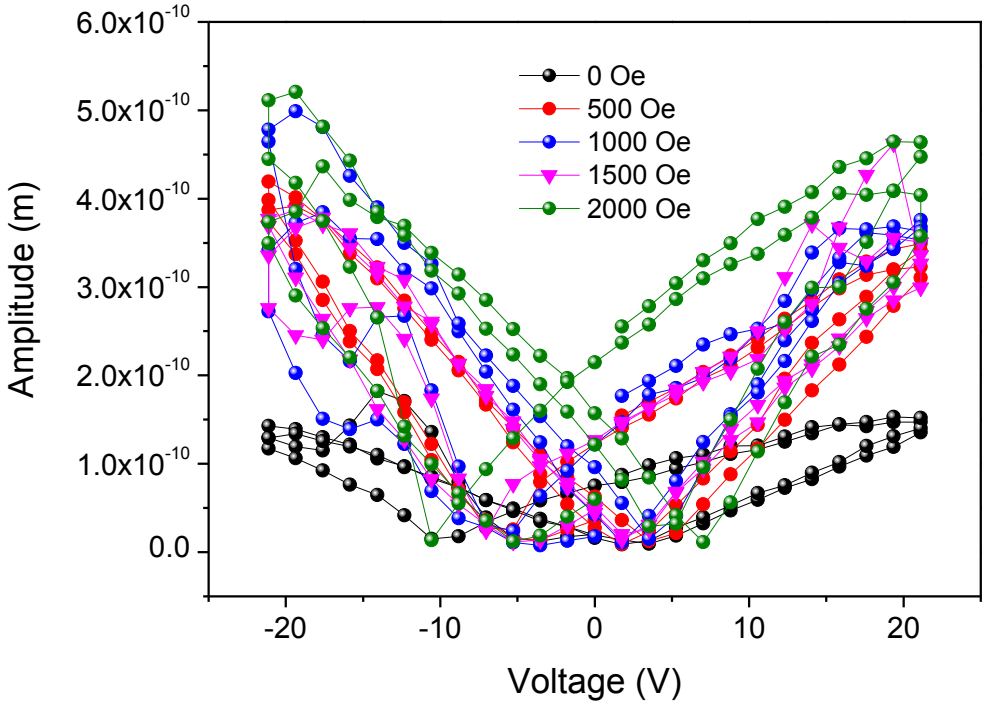
	Raman Bands				
	Ferrite	Perovskite			
Field (Oe)	A_{1g}	A_1(3TO)	B_1+E	E(2TO)	Si
0	713.5	584.2	290.3	207.1	525.2
500	677.3	574.8	291.9	199.4	525.3
1000	675.0	571.3	290.1	198.8	525.4
1500	684.0	566.5	287.1	197.7	525.4
2000	691.4	565.2	283.4	195.2	525.4

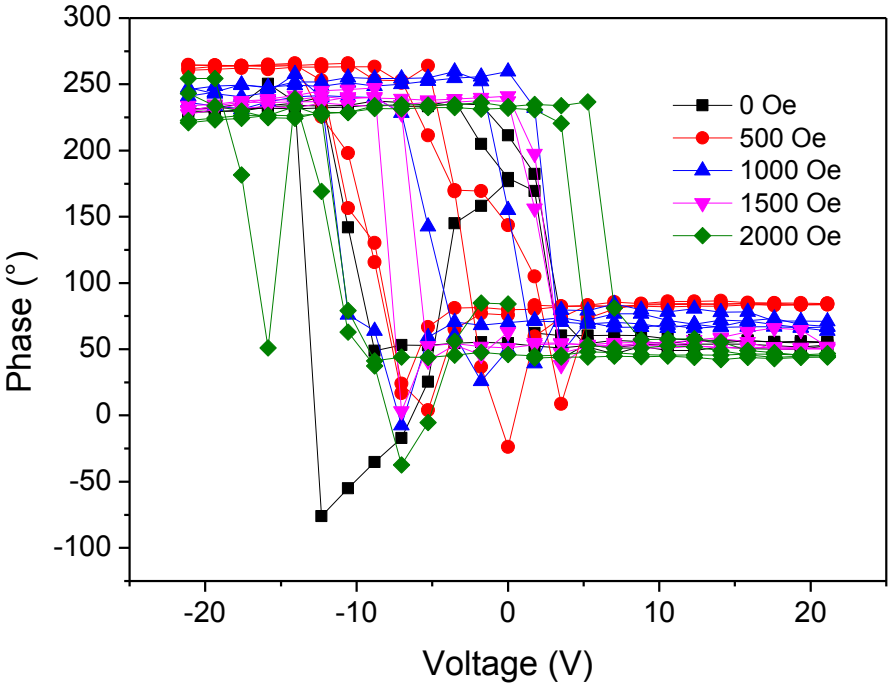


Raman Spectra of PTO-CFO powder prepared hydrothermally placed on a silicon wafer. Shifts in the perovskite modes suggest a coupling between the magnetic and piezoelectric phase.

	Raman Bands				
	Ferrite	Perovskite			
Field (Oe)	A_{1g}	A_1(3TO)	B_1+E	E(2TO)	Si
0	709.8	577.7	289.4	199.7	508.3
500	710.8	579.6	289.4	199.7	508.3
1000	709.8	580.6	290.4	201.7	508.3
1500	710.8	578.7	290.4	200.7	508.3
2000	710.8	580.6	290.4	201.7	508.3

Magnetic Field Assisted Piezoresponse Force Microscopy





PFM measurements of PTO-CFO nanocomposites synthesized by LPD method.

References

- Yourdkhani, A.; Perez, A.; Lin, C.; Caruntu, G. *Chem. Mater*. 2010, 22, 6075–6084 6075.
- Caruntu, D,; Caruntu, G,; Chen, Y.; O'Connor, C.; Goloverda, G.; Kolesnichenko, V. *Chem. Mater. 2004, 16, 5527-5534.*
- Liu, A.; Zhang, X.; Xu, Y.; Niu , X.; Zheng, X.; Ding, X. *Chemosphere* 59, 2005, 1367–1371.
- Wang, Y.; Xu, H.; Wang, X.; Zhang, X.; Jia, H.; Zhang, L.; Qiu, J.; *J. Phys. Chem. B* 2006, 110, 13835-13840.

Acknowledgements

This works was sponsored by Louisiana Board of Regents/National Science Foundation NSF(2010-15)-RII-UNO

Thanks also goes to Dr. Daniela Caruntu for her help in the CFO nanoparticle synthesis and to Denny Lenormand for help with the VSM measurements.