

# Structural and Magnetic Properties of $\text{Ca}_3\text{CoMnO}_6$ and Mn-Deficient $\text{Ca}_3\text{CoMn}_{1-x}\text{O}_6$ Multiferroic Ceramics

<sup>1</sup>Sunil Kumar, <sup>2</sup>Anupinder Singh, <sup>3</sup>Lakhwant Singh

<sup>1,2,3</sup>Multifunctional Materials Laboratory, Dept. of Physics, Guru Nanak Dev University, Amritsar, Punjab, India

## Abstract

$\text{Ca}_3\text{CoMnO}_6$  and Mn-deficient  $\text{Ca}_3\text{CoMn}_{1-x}\text{O}_6$  ( $x=0.02, 0.04, 0.06, 0.08$ ) solid solutions were synthesized by the solid state reaction route. XRD confirms the rhombohedral with space group R3c phase formation in all the samples. SEM micrographs clearly depicts that the grain size decreases as the Mn deficiency increases. Raman spectroscopy and FTIR analysis shows the bonding structure and different new vibration modes in Mn-deficient samples. Magnetic studies at room temperature revealed paramagnetic type behavior in all the samples.

## Keywords

X-Ray Diffraction, Raman Spectroscopy, FTIR, FESEM, VSM

## I. Introduction

Multiferroics are materials which have more than one ferroic (Ferroelectricity, Ferromagnetism and ferroelasticity) properties. The materials which have coexistence of ferroelectricity and magnetism are very important in these days due to their technical applications. The coupling between ferroelectric and magnetic orders is known as magnetoelectric coupling [1]. Type II multiferroics are those in which ferroelectricity appear even in collinear magnetic structure and these are also known as magnetically driven ferroelectrics systems [2].

$\text{Ca}_3\text{CoMnO}_6$  (Pure CCMO) is one of the new series of the complex oxides of  $\text{A}_3\text{MXO}_6$  (where A= Ca or Sr, M and X are the magnetic or nonmagnetic transition metal ions). It is quasi one dimensional compound which crystallizes into rhombohedral structure and spin chains are made up of alternatively placed  $\text{CoO}_6$  at trigonal prisms and  $\text{MnO}_6$  at the octahedra and structural unit lies along the hexagonal c-axis and are surrounded by six chains made of Ca antiprism [3-5]. The quasi one dimensional structure of the compound determines the anisotropic physical and magnetic properties [8].

Our purpose to study Mn-deficient  $\text{Ca}_3\text{CoMnO}_6$  is that the Mn deficiency favors Spin non frustration which is beneficial for the ferroelectricity.

## II. Experimental

Pure CCMO and Mn deficient solid solutions with general formula  $\text{Ca}_3\text{CoMn}_{1-x}\text{O}_6$  ( $x = 0, 0.02, 0.04, 0.06$  and  $0.08$ ) samples were prepared by conventional solid state reaction route. The raw materials  $\text{CaCO}_3$ ,  $\text{Mn}_2\text{O}_3$  and  $\text{Co}_3\text{O}_4$  with minimum 99% purity weighed in the stoichiometric proportions and mixed in ball milling (Zirconia balls used) in the propan-2-ol (as medium) for 24 hours. Then samples made dry and then calcined for 24 hours at  $950^\circ\text{C}$ . The calcined powder was mixed with 2% PVA as a binder. The pallets made with 10mm (diameter) and uniaxial hydraulic press and these pallets sintered at  $1200^\circ\text{C}$  for six hours. The structural characterization was done with XRD (SHIMADZU MAXima XRD-7000), Raman Spectroscopy (Reinshaw inVia) and FTIR (Parkin Elmer). The surface morphology was seen by FE-SEM (Carl ZEISS Supra 55) and Magnetic Studies were performed using Vibrating Sample Magnetometer (Microscience EZ9).

## III. Results and Discussion

Fig. 1 shows the room temperature XRD patterns of CCMO and (Mn deficient)  $\text{Ca}_3\text{CoMn}_{1-x}\text{O}_6$  samples. The room temperature XRD patterns are indexed according to rhombohedral structure with space group R3c. All Mn-deficient samples show slight peak shift in XRD patterns. This attributes to the defects that are created due to Mn-deficiency.

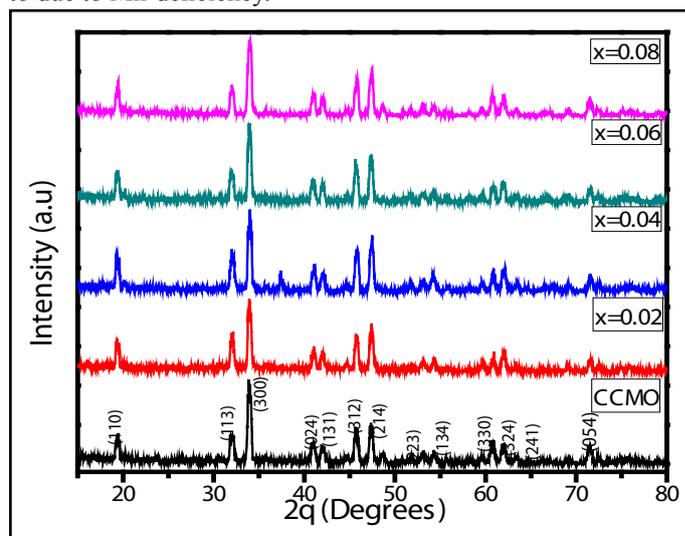
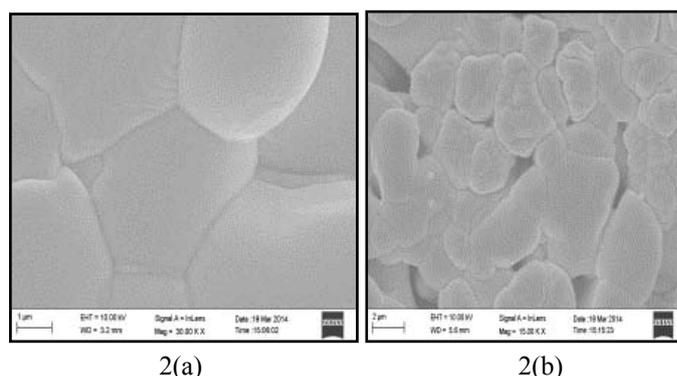


Fig. 1. XRD Pattern of CCMO and  $\text{Ca}_3\text{CoMn}_{1-x}\text{O}_6$  with  $x = 0.02, 0.04, 0.06$  and  $0.08$

Fig. 2 shows the SEM micrographs of all the samples. It is clear from the microstructure that grain size decreases with increase in the Mn deficiency in all the samples.

FTIR spectroscopy was performed by using Parkin Elmer FTIR spectrometer. There is appearance of some additional vibration modes at  $1022, 1261, 1384, 1460, 1632$  and  $1745\text{ cm}^{-1}$  in  $x = 0.08$  sample in comparison to the pure CCMO sample (shown in fig. 3).

Raman spectra of the samples were observed using Rainshaw inVia spectrometer with  $488\text{ nm}$  laser. Fig. 4 shows the Raman spectra of samples recorded at room temperature. The two prominent peaks have been found at  $510\text{ cm}^{-1}$  and  $659\text{ cm}^{-1}$  in samples with  $x = 0.02, x = 0.04$  and  $x = 0.08$ .



2(a)

2(b)

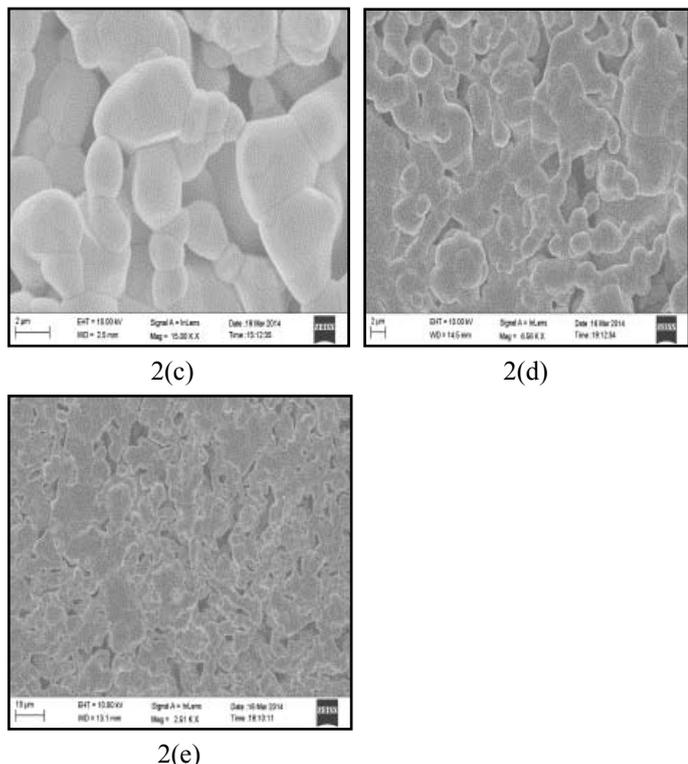


Fig. 2: SEM Micrographs of CCMO (pure) and  $\text{Ca}_3\text{CoMn}_{1-x}\text{O}_6$  (a) CCMO (pure) (b)  $x = 0.02$  (c)  $x = 0.04$  (d)  $x = 0.06$  (e)  $x = 0.08$

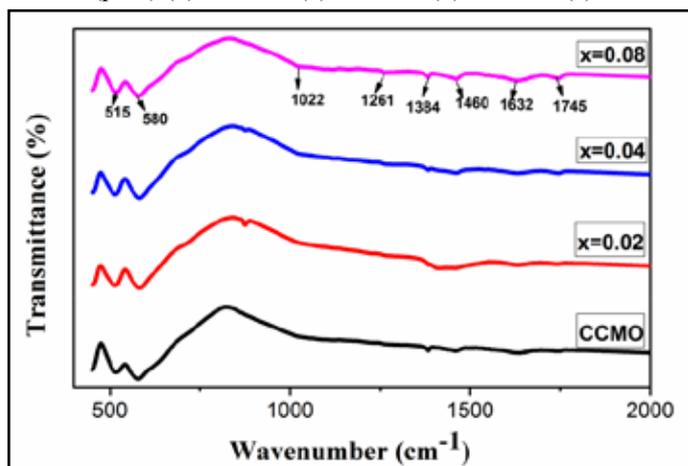


Fig. 3: FTIR Spectra of CCMO (pure) and  $\text{Ca}_3\text{CoMn}_{1-x}\text{O}_6$  with  $x = 0.02, 0.04, \text{ and } 0.08$

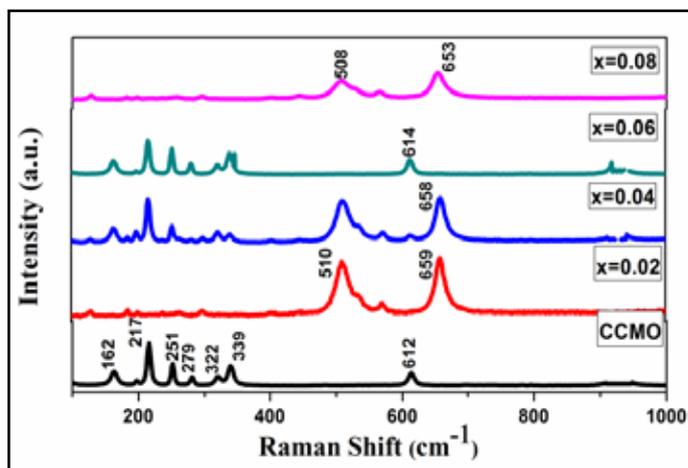


Fig. 4: Raman Spectra of CCMO and  $\text{Ca}_3\text{CoMn}_{1-x}\text{O}_6$  with (a)  $x = \text{CCMO}$ , (b)  $x = 0.02$ , (c)  $x = 0.04$ , (d)  $x = 0.06$  (e)  $x = 0.08$

The Raman vibration modes are not showing a proper trend. So there may be possibility of two types of deficiencies such as Mn and O. The different vibration modes may be attributed to these defects.

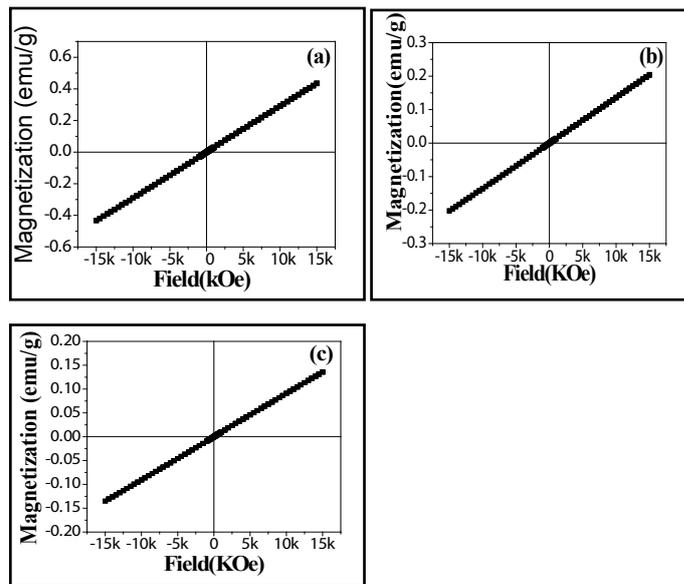


Fig. 5: M-H Curves at Room Temperature of Samples. (a) CCMO, (b)  $x = 0.02$  and (c)  $x = 0.08$

The M-H curves at room were performed with the Vibrating Sample Magnetometer (VSM) showing paramagnetic behavior at room temperature.

**IV. Conclusion**

XRD pattern revealed pure CCMO and Mn-Deficient  $\text{Ca}_3\text{CoMn}_{1-x}\text{O}_6$  with  $x = 0.02, 0.04, 0.06$  and  $0.08$  prepared by solid state reaction route technique showed rhombohedral phase formation. SEM micrographs decrease in grain size with increase in Mn-Deficiency. FTIR and Raman Spectra show appearance of additional vibration modes with Mn deficiency. The Room temperature M-H plots showed the paramagnetic behavior in all samples.

**References**

- [1] Singh A., Choudhary, I., Mehta, S., Dahiya, S., Walia, C., Raina, K.K., Chatterjee, R., "Optimal multiferroic properties and enhanced magnetoelectric coupling in  $\text{SmFeO}_3\text{-PbTiO}_3$  solid solution", Journal of Applied Physics, Vol. 107, 2010, pp. 084106.
- [2] Khomskii, D., "Classifying multiferroics: Mechanism and effect", Physics, Vol. 2, 2009, pp. 20.
- [3] Zubkov, V.G., Bazuev, G.V., Tyutyunnik, A.P., Berger, I.F., "Synthesis, crystal structure and magnetic properties of quasi one dimensional oxides  $\text{Ca}_3\text{CuMnO}_6$  and  $\text{Ca}_3\text{Co}_{1-x}\text{Mn}_x\text{O}_6$ ". Journal of solid state chemistry, Vol. 160, 2001, pp. 293-301.
- [4] Rayaprol, S., Sengupta, K., Sampathkumar, E.V., "Magnetic behaviour of Quasi-one-dimensional oxides  $\text{Ca}_3\text{Co}_{1-x}\text{Mn}_x\text{O}_6$ ", Solid state communications, Vol. 128, 2003, pp. 79-84.
- [5] Kaushik, S. D., Rayaprol, S., Saha, J., Mohapatra, N., Siruguri, V., Babu, P. D., Patnaik, S., Sampathkumar, E.V., "Magnetoelectric coupling in  $\text{Ca}_3\text{CoMnO}_6$ " Journal of Applied Physics, Vol. 108, 2010, pp. 084106.
- [6] Lin, L., Guo, Y.J., Xie, Y.L., Dong, S., Yan, Z.B., Liu, J.M., "Spin frustration destruction and ferroelectricity

- modulation in  $\text{Ca}_3\text{CoMnO}_6$ : Effect of Mn deficiency”, Journal of Applied Physics, Vol. 111, 2012, pp. 07D901.
- [7] Lin, L., Xie, Y.L., Liu, M.F., Guo, Y.J., Yan, Z.B., Liu, J.-M., “Multiferroicity in Mn-deficient  $\text{Ca}_3\text{CoMnO}_6$ : The consequence of Fe substitution”, Journal of Applied Physics, Vol. 114, 2013, pp: 027006.
- [8] Zubkov, V.G., Tyutyunnik, A.P., Berger, I.F., Bazuev, G.V., “Crystal structure and magnetic properties of quasi one dimensional oxide  $\text{Ca}_3\text{CuMnO}_6$ ” Doklady Chemistry. Vol. 376, 2001, pp. 20-24.



Sunil Kumar has received his B.Sc degree (in 2006) and M.sc degree in (Nanotechnology) in 2009 from Guru nanak dev university (GNDU), Amritsar, India. Author also received degree in M.tech (NS&NT) from Panjab University, Chandigarh, India. Presently Author is doing his Ph.D in the field of multiferroics from GNDU, India.