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Structural Analysis of Chromium Doped Mn_2O_3 Nanoparticles Prepared by Microwave Assisted Method

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Abstract

Chromium doped Mn2O3 nanoparticles prepared by microwave assisted method. The nanoparticles were prepared for various concentrations (0.2 M, 0.4 M, 0.6 M, and 0.8 M). The X-ray diffraction and Fourier transform infrared were employed to study the structural features and chemical composition of the nanoparticles. The structural studies confirmed that the prepared samples are in tetragonal and triclinic structure. The FTIR spectrum reveals the formation of Mn-O phase and Cr-O phase at specified location.

Keywords : FTIR, XRD and Microwave Assisted Method

INTRODUCTION

Nano scale material posses several unique properties such as large surface area, surface defects and fast diffusivities. Hence synthesis of nanoscale particle has received considerable attention in view of the potential for few materials with novel properties and the design of new devices for specific applications. This chapter summarizes various preparation methods of nanoparticles that are classified under physical, chemical and biological method. In the present work preparation of chromium doped Mn_2O_3 nanoparticles using the microwave assisted technique. In this work, we have studied the structural and phase identification of chromium doped Mn_2O_3. In addition to this, we have investigated the effect of doping of chromium on Mn_2O_3. The sample is prepared by using microwave method and characterized by using various instrumentation such as X-ray Difraction (XRD) and Fourier transform infrared spectroscopy (FTIR).

SYNTHESIS OF CrMnO NANO PARTICLE

In the present study $Cr_xMn_{(1-x)}O_3$ Nano powder were prepared from the aqueous solution of $MnCl_2$ and $CrCl_2$ solution reduced by NaOH. CrMnO-1 Nano powder were prepared from the aqueous solution of $CrCl_2$ (0.2 M), $MnCl_2$ (0.8 M) reduced by NaOH (0.5 M). In this process, required amount of $CrCl_2$ and $MnCl_2$ powder were added to 100 ml distilled water and the NaOH pellets were slowly added to the above resulted solution was kept under constant stirring for an hour to form a brown colour solution. The solution thus obtained was heated in a domestic Microwave oven (540W, 92°C) for 20 minutes. After the cooling process, the resultant brown precipitate was separated by the process of centrifugation. Following this, the mixture was washed with distilled water and absolute ethanol to remove the impurities and residual materials. After, washing the Nano particles were dried at 60°C. Finally the prepared materials were annealed at 500°C for three hours. The same procedure is repeated to dope with Cr in various proportions CrMnO-2 ($MnCl_2$ 0.60 and$CrCl_2$ 0.40), CrMnO-3 ($MnCl_2$ 0.40 and $CrCl_2$ 0.60)

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and CrMnO-4 ($MnCl_2$ 0.20 and $CrCl_2$ 0.80). Thus $Cr_xMn_{(1-x)}O_3$ powder was prepared for x=0.2, 0.4, 0.6 and 0.8. Prepared products were named as CrMnO-1, CrMnO-2, CrMnO-3 and CrMnO-4.

X-RAY DIFFRACTION

X-ray diffraction is very important tool used for extracting information recording microstructure like space groups, lattice type, unit cell, unit cell volume, structural imperfections, crystalline size etc. The crystalline size and lattice parameter are very important factor would be extracted from the XRD peak width analysis.

It reveals that the sample is a composite consisting of Mn_2O_3 and $MnCrO_3$ phase. This could understand on matching the peaks for the JCPDS standards 00-001-1127 and 00-026-1235. The Mn_3O_4 phase is tetragonal and the $MnCrO_3$ phase is triclinic lattice. Calculated unit cell parameters and the other structural parameters are listed in Table 4.1. The unit cell edge of both tetragonal (a=5.75963Å, b=5.75963Å and c=9.42933Å) and triclinic (a=5.41745Å, b=5.44698Å and c=4.95436Å) are almost equal and they are comparable with the standard JCPDS values (a=5.75Å and c=9.42Å) and (a=5.1130Å,b=5.3850Å and c=4.9910Å) other related structure like unit cell volume are calculated for both phase.

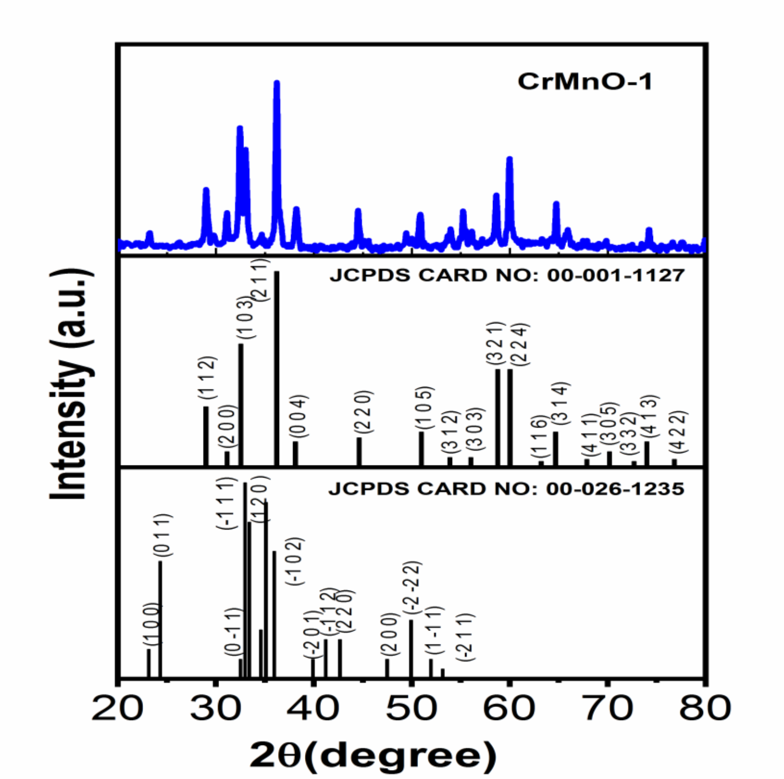

Fig. 3.1 X-ray diffraction pattern of $Cr_xMn_{(1-x)}O_3$ sample prepared with x=0.2

The role of dopant in individual nanostructure more significant in the doped sample.
CrMnO-1 with x=0 ($Cr_{0.2}Mn_{0.8}O_3$). Fig 3.2 shows the XRD pattern of CrMnO-1

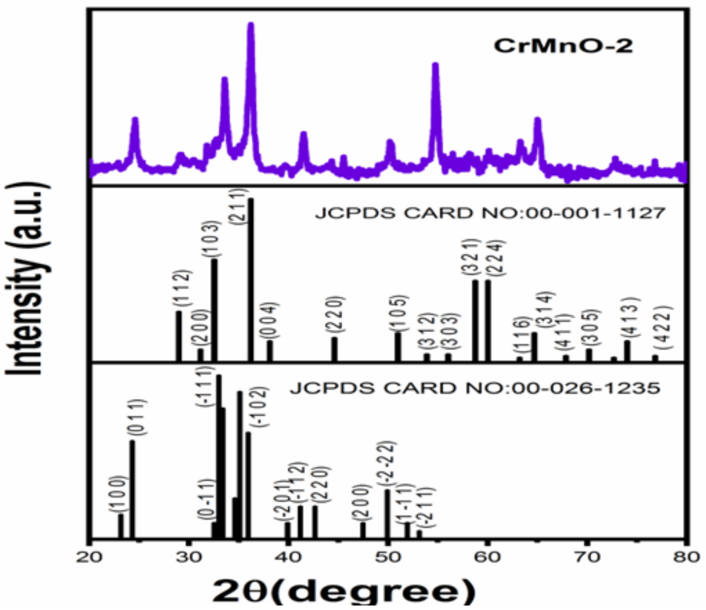

Fig 3.2 X-ray diffraction pattern of $Cr_xMn_{(1-x)}O_3$ sample prepared with x=0.4

The role of dopant in individual nanostructure more significant in the doped sample CrMnO-2 with x=0.4 ($Cr_{0.4}Mn_{0.6}O_3$). Fig 3.3 shows the XRD pattern of CrMnO-2 sample. It reveals that the sample is a composite consisting of Mn_3O_4 and $MnCrO_3$ phase. This could understand on matching the peaks for the JCPDS standards 00-001-1127 and00-026-1235.

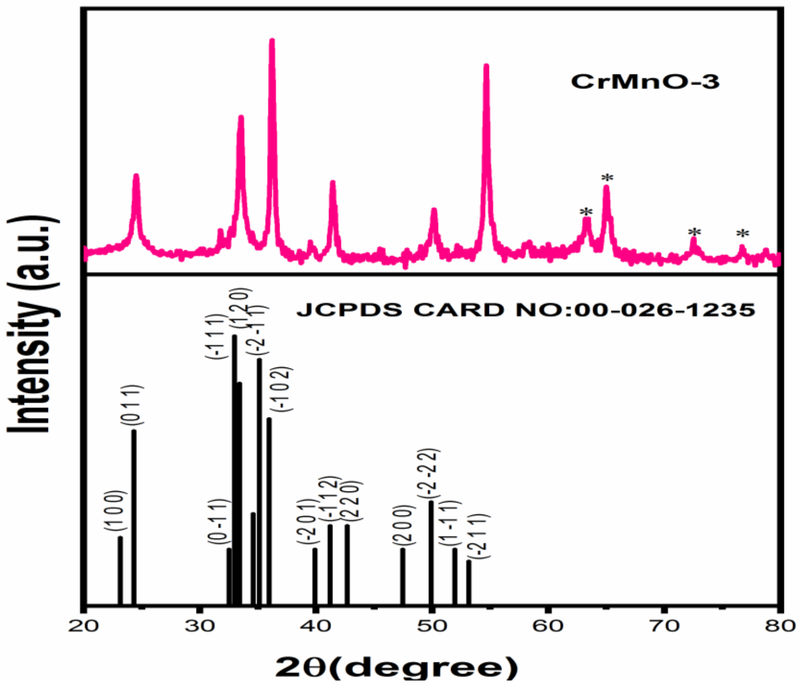

Fig 3.3 X-ray diffraction pattern of $Cr_xMn_{(1-x)}O_3$ sample prepared with x=0.4

The Mn$_3$O$_4$ phase is tetragonal and the MnCrO$_3$ phase is triclinic lattice. Calculated unit cell parameters and the other structural parameters are listed in Table 4.1. The unit cell edge of both tetragonal (a=5.71993, b=5.71993 and c=9.45715) and triclinic (a=5.15176, b=5.34968 and c=4.95189) are almost equal and they are comparable with the standard JCPDS values (a=5.75 and c=9.42) and (a=5.1130 ,b=5.3850 and c=4.9910) other related structure like unit cell volume are calculated for both phase. To increase the chromium doping concentration the mixed phase is slowly transformed the new peak is (-2 1 1). This is shown indicate in the figure 3.3.

The role of dopant in individual nanostructure more significant in the doped sample CrMnO-3 with x=0.6 (Cr$_{0.6}$Mn$_{0.4}$O$_3$). Fig 4.4 shows the XRD pattern of CrMnO-3 sample. The mixed phase is transferred to MnCrO$_3$ phase. This could understand on matching the peaks for the JCPDS standards 00-026-1235. The MnCrO$_3$ phase is triclinic lattice. Calculated unit cell parameters and the other structural parameters are listed in Table 4.1. The unit cell edge of both triclinic (a=4.62174, b=5.50969 and c=4.94623) are almost equal and they are comparable with the standard JCPDS values (a=5.1130,b=5.3850 and c=4.9910) other related structure like unit cell volume are calculated.

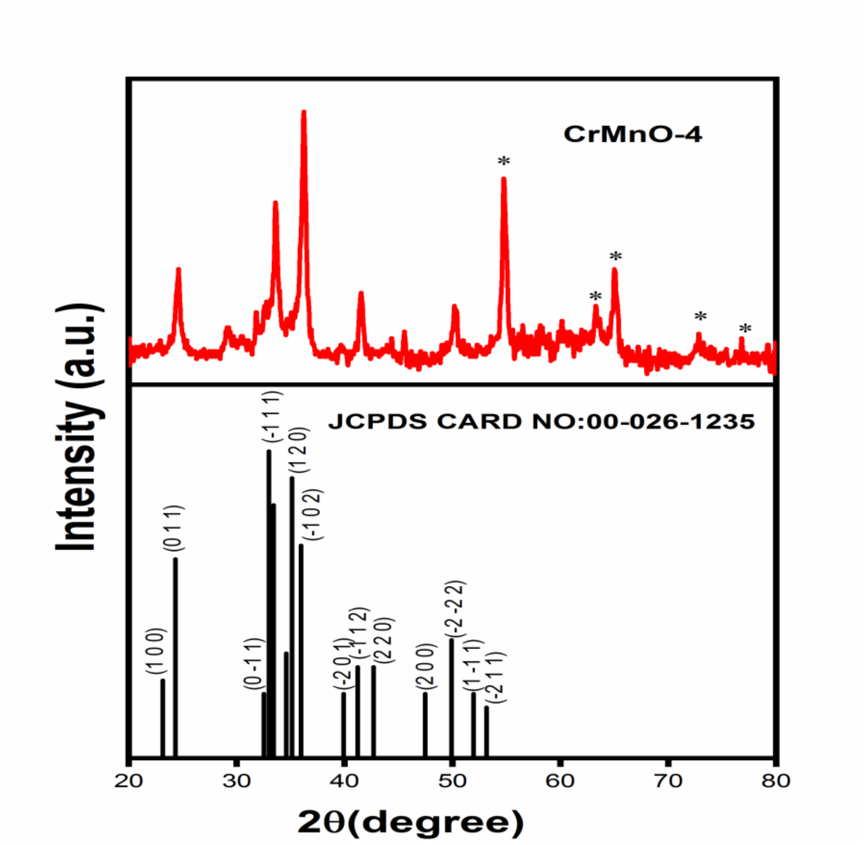

Fig 3.4 X-ray diffraction pattern of Cr$_x$Mn$_{(1-x)}$O$_3$ sample prepared with x=0.8

The role of dopant in individual nanostructure more significant in the doped sample CrMnO-4 with x=0.8 (Cr$_{0.8}$Mn$_{0.2}$O$_3$). Fig 4.5 shows the XRD pattern of CrMnO-4 sample. It reveals that the sample is a composite consisting of Mn$_3$O$_4$ and MnCrO$_3$ phase. This could understand on matching the peaks for the JCPDS standards 00-026-1235. The MnCrO$_3$ phase is Triclinic lattice. Calculated unit cell parameters and the other structural parameters are listed in Table 4.1. The unit cell edge of triclinic (a=5.04338, b=5.35158 and c=4.93705) are almost equal and they are comparable with the standard JCPDS values (a=5.1130, b=5.3850 and c=4.9910) other related structure like unit cell volume are calculated for both phase. In the CrMnO-4 is the most chromium doped sample has a single triclinic phase.

Tab 3.1 Structural parameter of Cr doped Mn_2O_3 nanoparticles

Sample Details	Lattice parameter (Å)		Volume (Å)		Crystalline size (nm)
	Exp	Std	Exp	Std	
CrMnO-1 (Tetragonal)	a=5.7596 c=9.4293	a=5.7500 c=9.4200	312.80	311.45	33.60
CrMnO-1 (Triclinic)	a=5.4174 b=5.4469 c=4.9543	a=5.1130 b=5.3850 c=4.9910	109.20	103.19	26.70
CrMnO-2 (Tetragonal)	a=5.7199 c=9.4571	a=5.7500 c=9.4200	309.41	311.45	21.19
CrMnO-2 (Triclinic)	a=5.1517 b=5.3496 c=4.9518	a=5.1130 b=5.3850 c=4.9910	105.34	103.19	26.79
CrMnO-3 (Triclinic)	a=4.6217 b=5.5096 c=4.9462	a=5.1130 b=5.3850 c=4.9910	95.66	103.19	25.05
CrMnO-4 (Triclinic)	a=5.0433 b=5.3515 c=4.9370	a=5.1130 b=5.3850 c=4.9910	101.51	103.19	30.61

In the present work, the study materials possessed tetragonal and triclinic structures. The lattice parameters 'a', 'b' and c are calculated utilizing the formulae connecting Miller indices 'h', 'k', 'l' and interplanar spacing 'd' as given below

For the tetragonal system

$$\frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}$$

For the triclinic system

$$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$$

A crystallite is a domain of solid-state matter that has the same structure as a single crystal. If the individual crystallites are oriented randomly, a polycrystalline structure is evolved and if they are oriented in a particular plane, a single crystalline structure is formed. The crystallite sizes of the samples are calculated using Debye Scherrer's formula by measuring FWHM (β) from the diffraction pattern. A perfect crystal with every atom of the same type in the correct position does not exist. All these structural parameters have been evaluated using the following formula

$$\text{Crystallite size } D = \frac{k\lambda}{\beta \cos\theta}$$

Where,

D – crystallite size
B_D - full width at half maxima
λ – wavelength
θ – Bragg peak position
k – Shape factor

IDENTIFICATION PHASE FORMATION USING FTIR

Fourier spectrum IR spectra were recorded for the prepared sample CrMnO-1 which is heat treated at 500°C. In the FTIR spectrum (fig.4.1) the peak at 412.31 cm^{-1} and 496.46^{-1} cm is due to the M-N and M-O mode [1]. The spectra shows, the Cr-O bond appear at 609.64 cm^{-1} and 950.01 cm^{-1} [2]. The band at 609.64 cm^{-1} and 950.01 cm^{-1} may be related with oxygen vacancy or oxygen deficiency in CrMnO. The peak at 1034.89 cm^{-1} and 1622.42 cm^{-1} shows the stretching and bending vibration of OH [3].

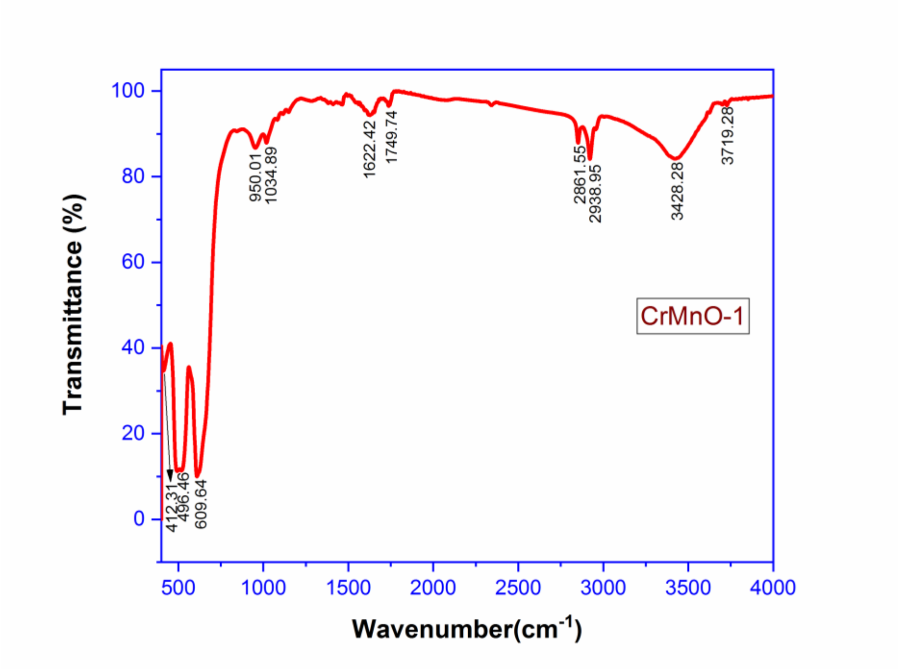

Fig .4.1 FTIR spectrum of CrMnO-1 Sample

The peak at 1749.74 cm^{-1} is due to the C=O stretching vibration. The sharp peak at 2861.55 cm^{-1} and 2938.95 cm^{-1} is due to the stretching vibration of CH. The peak at 3428.28 cm^{-1} and 3719.28 cm^{-1} reveals the OH stretching vibration in H_2O [4].

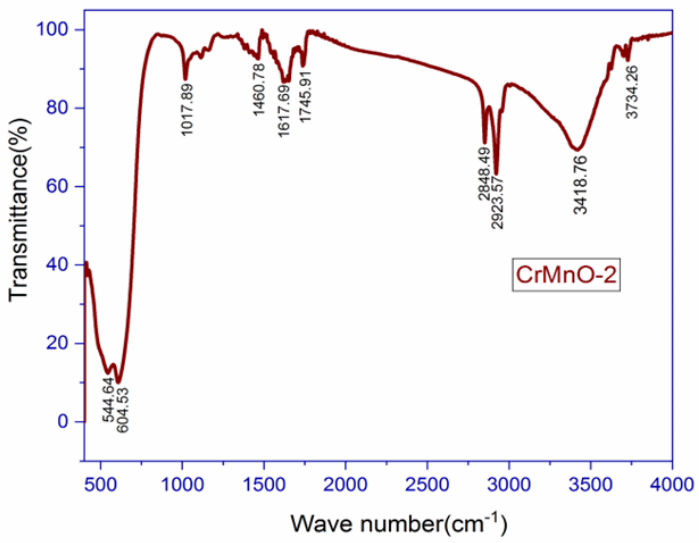

Fig. 4.2 FTIR spectrum of CrMnO-2 sample

Fourier Transform IR spectrum was recorded for as prepared sample CrMnO-2 which is heat treated at 500°C (fig 4.2). The peak at 544.64 cm^{-1} is due to the MnO stretching mode. The peak at 604.53 cm^{-1} is due to the Cr-O stretching mode of vibration. Thus Cr-O formation confirms the incorporation of chromium atoms in the CrMnO. The band at 1017.89 cm^{-1} reveals the C-O stretching. The band at 1617.69 cm^{-1} is due to the bending vibration of OH [5]. The peak at 1745.91 cm^{-1} is due to the C=O stretching vibration. The band at 2848 cm^{-1} and 2923cm^{-1} is due to CH stretching mode. The peak at 3418.76 cm^{-1} and 3734.26 cm^{-1} reveals the OH vibration in HO Of vibration [6].

Fourier Transform IR spectrum was recorded for as prepared sample CrMnO-3 which is heat treated at 500°C (fig 4.3). The peak at 543.63 cm^{-1} is due to the stretching mode of Mn-O [7]. The band at 1018.05 cm is due to the C-O stretching vibration. The peak at 1616.41 cm^{-1} is due to the bending vibration of OH in H_2O. The peak at 1741.17 cm^{-1} is due to the C=O stretching vibration.

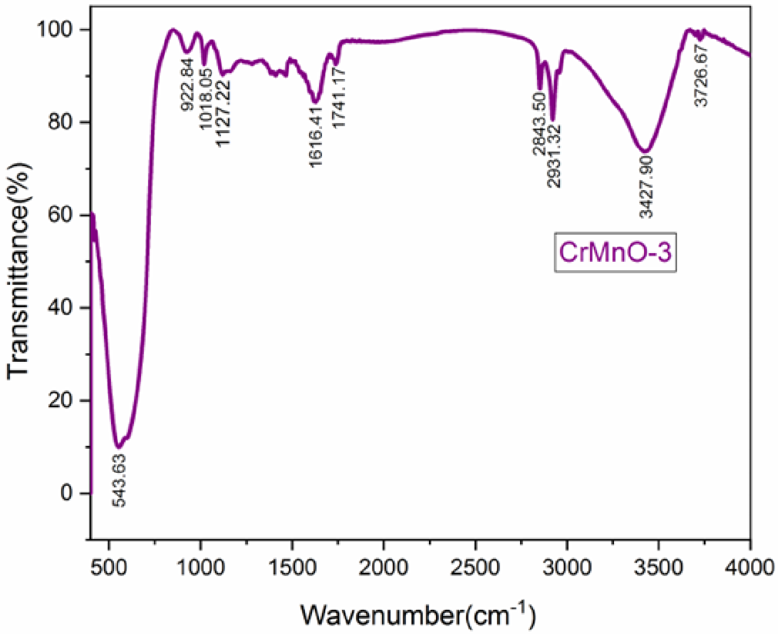

Fig. 4.3 FTIR spectrum of CrMnO-3 sample

The sharp peak at 2843.50 cm^{-1} and 2931.32 cm is due to the stretching vibration mode of CH. The band at 3427.90 cm^{-1} and 3726.67 cm^{-1} is due to the OH stretching vibration in H_2O.

Fourier Transform IR spectrum was recorded for prepared sample CrMnO-4 which is heat treated at 500°C (fig 4.4). The peak of 564.97 cm^{-1} and 623.25 cm^{-1} due to the stretching mode of Mn-O [22].The band at 886.73 cm^{-1} may be stretching vibration of Cr-O [8]. Thus, Cr-O formation confirms the incorporation of chromium atoms in CrMnO. The band at 1018.05 cm^{-1} is due to the stretching vibration of C-O [9].

The peak at 2923.93 cm^{-1} and 2850.88 cm-1 is due to the CH stretching mode of vibration [10]. The peak located around 3434.47 cm^{-1}, 3719.28 cm^{-1} and 1631.19 cm^{-1} shows the stretching and bending vibration of OH [11].

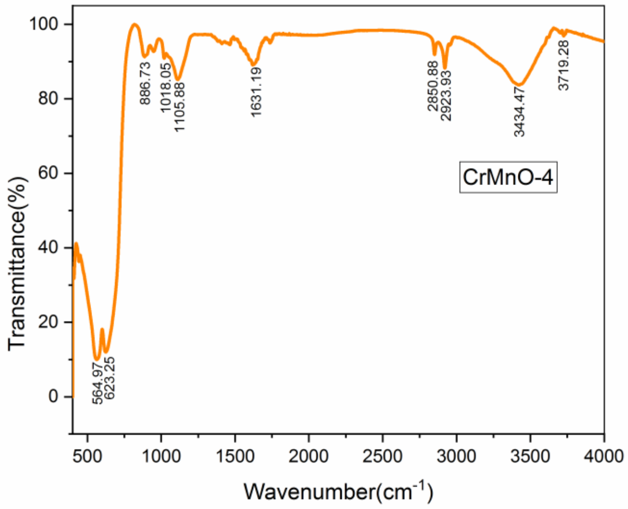

Fig. 4.4 FTIR spectrum of CrMnO-4 sample

CONCLUSION

In the present workchromium doped Manganese oxide was synthesized by microwave assisted method. The prepared nanomaterials were annealed at 5000c for three hours. The synthesized sample characterized by X-ray diffraction and FTIR. In X-ray diffraction unit cell volume, lattice parameter and crystalline size are calculated. These parameters are compared with the JCPDS value. The structural studies confirmed that the prepared sample is in tetragonal and triclinic structure. The CrMnO-1 and CrMnO-2 nanoparticles are in two phase.When chromium dopant increases it becomes single phase. The tetragonal phase confirmed that the manganese oxide. The triclinic phase confirms the chromium nanoparticles. The FTIR spectrum reveals the formation of Mn-O phase and Cr-O phase at specified location.

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