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RESEARCH ARTICLE

SYNTHESIS, STRUCTURAL AND MAGNETIC PROPERTIES OF MANGANESE SUBSTITUTED MAGNESIUM CHROMITE.

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Abstract

The nanocrystalline $Mg_{1-x}Mn_xCr_2O_4$ (X=0.0, 0.25, 0.50, 0.75 and 1.0) chromite were synthesized by sol-gel autocombution route. Thermal analysis of precursor after autocombution was carried out by TG-DTA. X-ray diffraction confirmed the formation of single cubic spinel lattice for all compositions. Lattice parameter shows increasing trend with an increase in Mn content. Formation of spherical nanoparticals were revealed by scanning electron microscopy (SEM).The elemental analysis obtained by EDAX is in close agreement with the expected composition from the stoichiometry of reactant used. The magnetic data indicate that, all compositions are ferrimagnetic in nature. The detailed results of XRD, thermal analysis, SEM, EDAX and magnetic properties indicating the role of substitution of manganese metal ions on the structural and magnetic properties of magnesium chromites are presented.

Introduction:-

Mixed metal oxides are an important class of compounds and among them chromites are most prominent by virtue or their spinel structure with high thermodynamic stability. The interest in these oxides emerges from their versatile applicability in telecommunication, power transformers, audio and video and many other applications involving electrical signals. Oxides spinel have been extensively studied by several workers [1-3] in order to elucidates the relationship between structure, bonding and magnetic properties because of technological potential of these materials. The benefit found in the oxides due to their structural and chemical variations on a nano scale, which are important for developing optimal magnetic properties [4-6].

Now a day fine particles of spinel oxides synthesized by chemical methods were shown to have magnetic properties markedly different from those prepared by the ceramic method. The various processing techniques, which are used for the synthesis of mixed metal oxides powders, include hydrothermal [7–8], microwave refluxing [9–11,], sol–gel [12–14], and co precipitation [15–17]. Among the Mn oxide spinel structured Ni-Mn, Cu-Mn oxides are referred to as negative temperature coefficient thermistors. Materials of mixed metal oxide with low Hc are called magnetically soft while those with higher values are called hard materials. The soft materials have high permeability and are used in applications at high frequencies [18].

The aim of present investigation is to synthesize the novel manganese substituted magnesium chromite nanoparticles by using sol–gel autocombution route. It is a simple process, which offers a significant saving in time and energy consumption over the traditional methods, and requires less sintering temperature. This method is employed to

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obtain improved powder characteristics, more homogeneity and narrow particle size distribution, thereby influencing the structural and magnetic properties of spinel $Mg_{1-x}Mn_xCr_2O_4$oxide.

Experimental Details:-

Synthesis Technique:-

The nanocrystalline mixed metal oxide system $Mg_{1-x}Mn_xCr_2O_4$ where x = 0.0, 0.25, 0.50, 0.75and 1.0 were prepared by sol-gel autocombution method. Analytical grade magnesium nitrate [$Mg(NO_3)_2.6H_2O$], manganese nitrate [$Mn(No_3)_2.4H_2O$], chromium nitrate [$Cr(NO_3)_3.9H_2O$], citric acid [$C_6H_8O_7.2H_2O$] and ammonia [NH_3] were used to prepare system compositions.Metal nitrates and citric acid were dissolved in minimum quantity of deionized water with 1:1 molar ratio for all compositions. The pH of the solution was adjusted to 9.5 using ammonia solution. This solution transforms to dry gel on heating to 353K. On further heating the dried gel undergo a self propagating combustion process and transform to floppy loose powder. The obtained powder was then calcined at 973 K for 6 h.

Characterization:-

Thermal analysis of precursor after autoccombution was carried out by TG-DTA. The phase formation of the sintered samples were confirmed by x-ray diffraction studies. The powder XRD patterns were recorded on a Philips PW-1710 x-ray diffractometer using CuKα radiation (λ=1.5406Å). Elemental analysis, surface morphology and average particle size were analyzed by EDAX spectroscopy and scanning electron microscope (SEM: Model JEOL-JSM6360).The room temperature magnetic measurements for all the compositions were performed by using a computerized high field vibrating sample magnetometer up to 15 kOe applied magnetic field.

Results and Discussion:-

Thermal Analysis;-

Thermal analysis was studied by using as synthesized precursor from room temperature to 1000°C in air atmosphere at the heating rate of 10°C /min and it is shown in **Fig. 1.** The TG curve shows that, the initial sample losses are about 12% weight of its original weight. Initially, the 20% loss in weight was observed by removal of absorbed water and water of crystallization up to 200°C. An exothermic peak at about 303 °C was observed due to evolution of heat by removal of absorbed water and water of crystallization. The decomposition of citrate complex was started at 250°C and it was completed at 700°C. During this decomposition, sample lost 60% weight. The DTA curve shows the formation of spinel oxides at about 700°C.

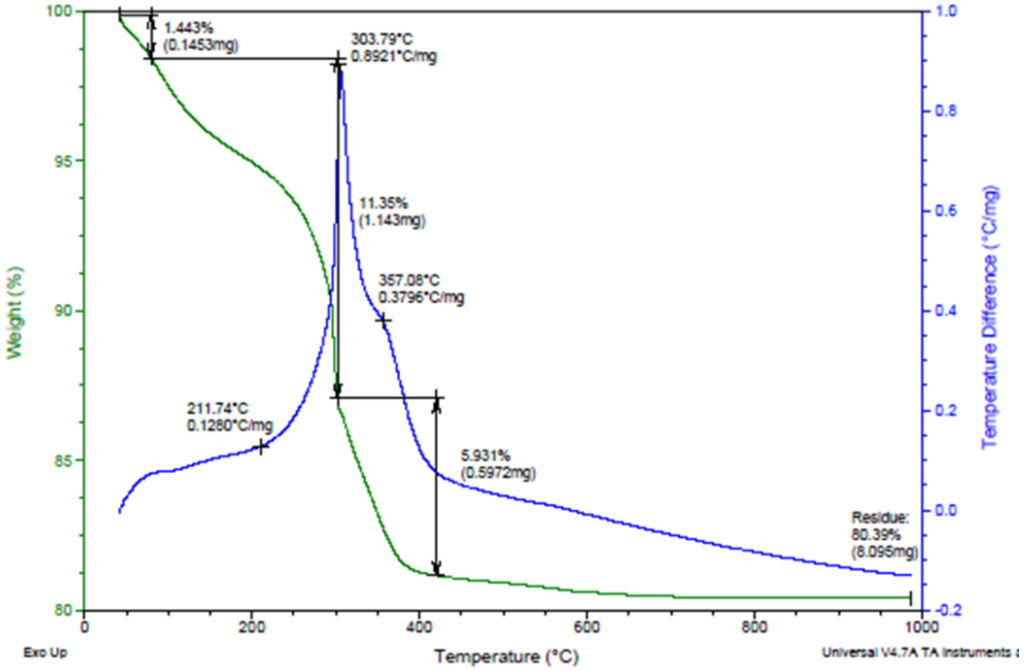


Fig.1:- TGA-DTA curves for $Mg_{0.5}Mn_{0.5}Cr_2O_4$samples

X-ray diffraction Study:-

Typical X-Ray diffraction patterns of samples $Mg_{1-x}Mn_xCr_2O_4$ obtained by gel combustion followed by annealing at 973 K are shown in **Fig. 2**. The diffraction pattern for all the chromate samples shows the crystalline nature. The diffraction data indicate that the samples have cubic spinel structure and well matched with JCPDS card no.77-0007 for $MgCr_2O_4$and JCPDS card on. 75-1614for$MnCr_2O_4$.The lattice parameters were calculated for the cubic phase using following relations:

$$1/ d^2 = h^2 + k^2 + l^2 / a^2 \quad (1)$$

Where a, is lattice parameter, (hkl) is the Miller indices and d is the interplanar distance. Reveals the linear increasing trend in the lattice parameter is attributed to the replacement of Mg^{2+} (0.65Å) ion by Mn^{2+}, a slightly larger ion with an ionic radius (0.80Å), in the system. From the X-ray diffraction peaks, crystallite size was estimated by using Debye Scherrer's formula [19]

$$t = 0.9\lambda/ \beta \text{ Cos } \theta \quad (2)$$

Where, symbols t = Particle size, λ = wave length of x-ray, β = full width at half maximum and θ = Bragg angle

The X-ray density (dx) was calculated using the following relation.

$$dx = 8M/Na^3 \quad (3)$$

Where, N= Avogadros number (6.023×10^{23} atom/mole)

M=Molecular weight

a = Lattice constant

The values of lattice constant (a), crystallite size (t) and X-ray density (dx) are summarized in **Table.1.** From the table it can be observed that the lattice parameter 'a' increases with increase in manganese content. Crystallite size't' and x-ray density 'dx' value varies with substitution of manganese metal ions concentration.

Table.1:- Lattice constant, crystallite size and x-ray density for the compositions

Compound	Lattice Constants (Å)	Crystallite Size (nm)	X – ray density (d_x) g/cm^3
x = 0.0	8.315	22.52	3.93
x = 0.25	8.347	22.86	4.13
x = 0.5	8.376	23.35	4.32
x = 0.75	8.392	24.48	4.47
x = 1.0	8.413	24.93	4.61

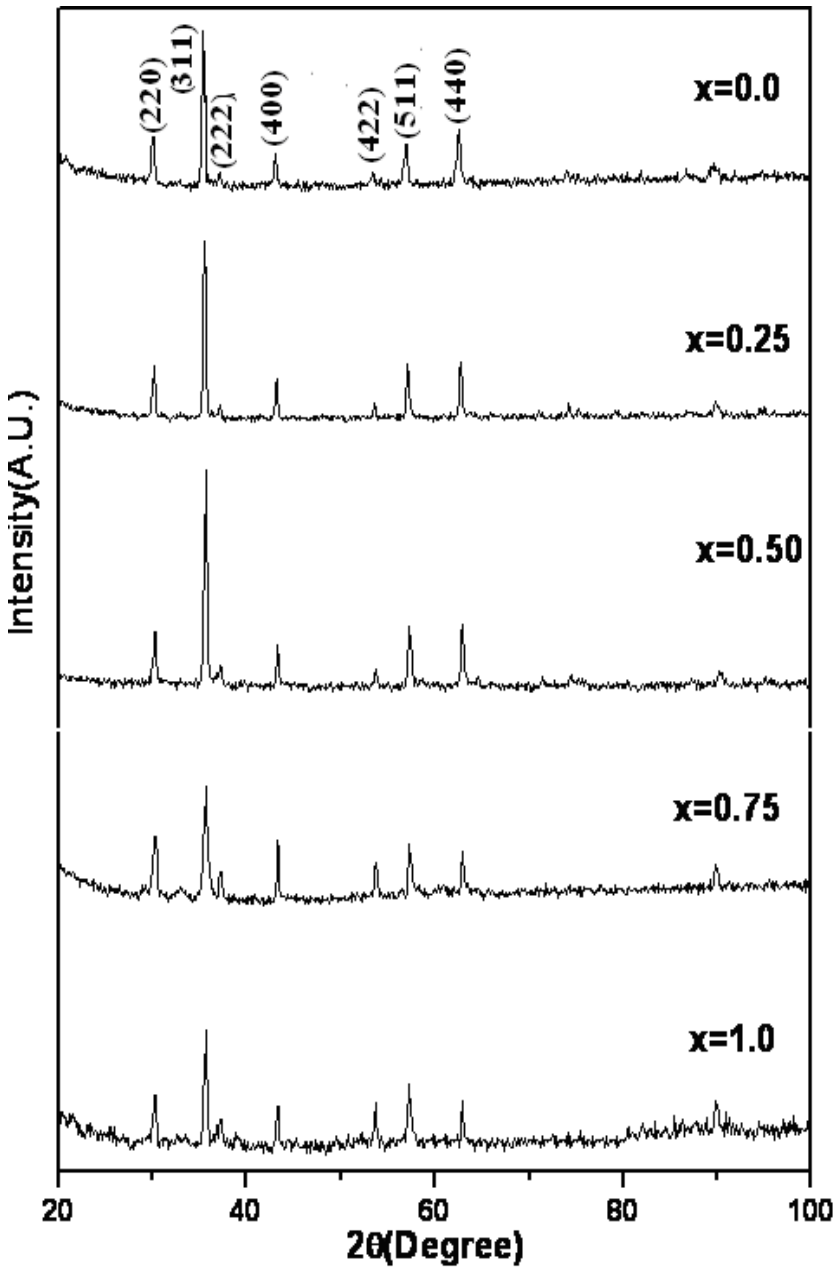
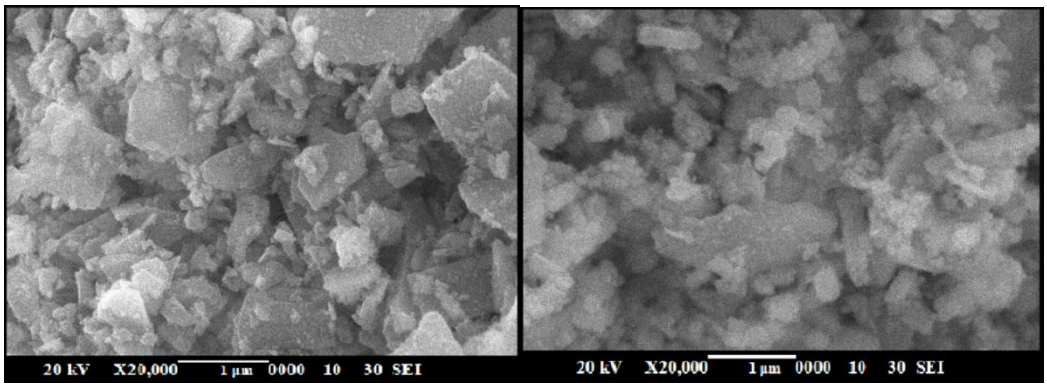


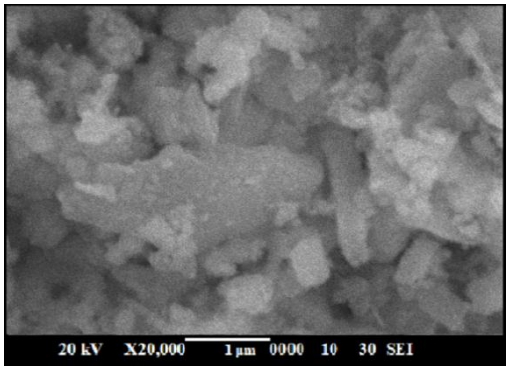
Fig.2:- X-ray diffraction patterns of $Mg_{1-x}Mn_xCr_2O_4$samples

Scanning electron microscopy:-

The surface morphology of system $Mg_{1-x}Mn_xCr_2O_4$ with x=0.0, 0.5 and 1.0 were examined by scanning electron microscopy. Typical micrograph of the samples treated at 973K for 6 h are shown in **Fig.3.** The SEM images of all the samples showed irregular microstructures with almost spherical small particles to the largest particles. Also, the all chromate powders possessed a uniform coarse structure with a well clear crystalline microstructure containing a spherical in nature.



(a) (b)

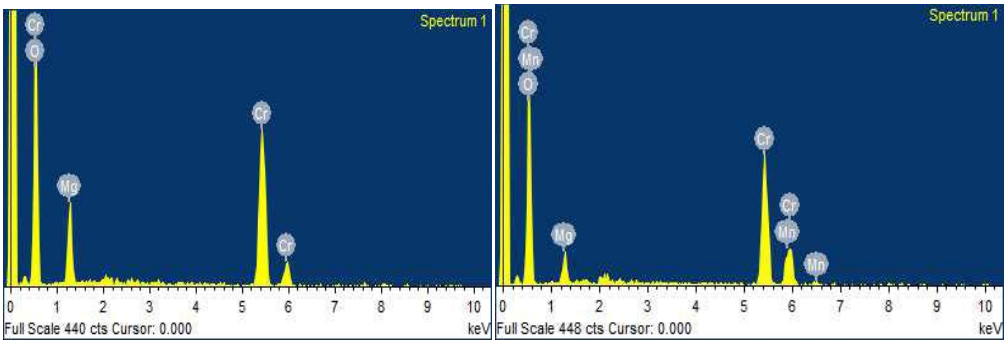


(c)

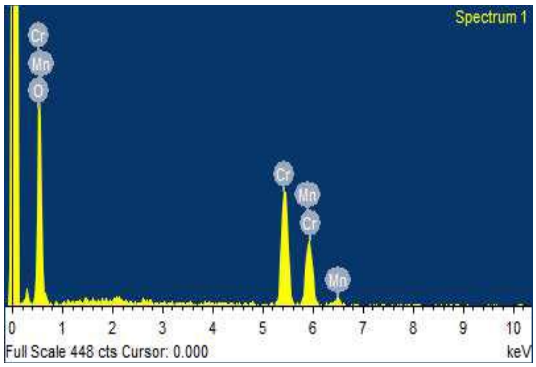
Fig.3:- SEM images of samples $Mg_{1-x}Mn_xCr_2O_4$ (a, x=0.0, b, x=0.5 and c, x=1.0)

Energy dispersion x-ray Analysis:-

The compositions of the nanocrystalline manganese substituted magnesium chromate were determined using the energy dispersion X-ray analysis (EDAX). The energy dispersion X-ray analysis spectrum of samples x =0.0, 0.50, 1.0 are shown in **Fig.4.** From the EDAX spectrum, the presence of Mg, Mn, Cr and O are confirmed in this sample. The quantitative analysis of EDAX spectrum revealed the relative atomic ratio of all elements is close to the expected values for theoretical values are given in **Table.2.**



(a) (b)



(c)

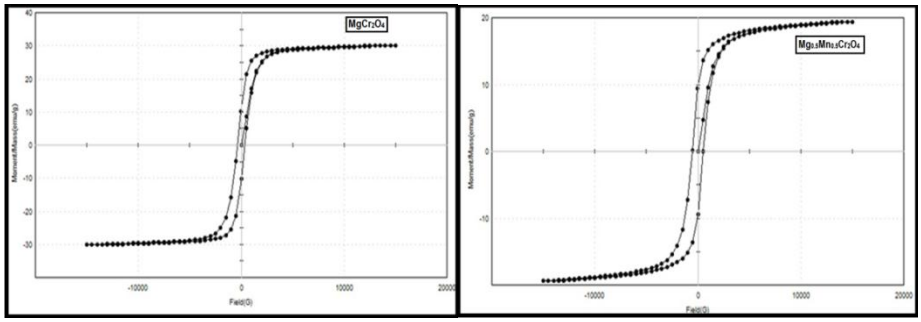
Fig.4:- EDAX patterns for the system $Mg_{1-x}Mn_xCr_2O_4$ (a, x=0.0, b, x=0.5 and c, x=1.0)

Table.2:- Atomic percentage value for x=0.0, 0.5 and 1.0 compositionsby EDAX analysis

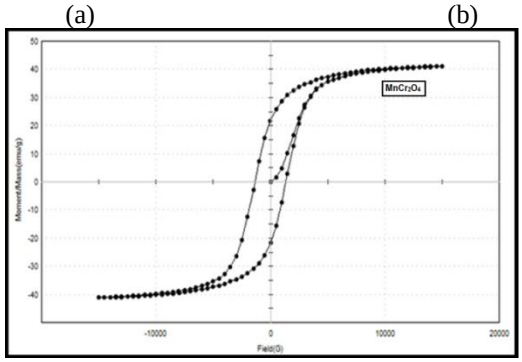
Compound	Expected (At %)			Observed(At %)		
	Mg	Mn	Cr	Mg	Mn	Cr
$MgCr_2O_4$	12.64	-	54.08	12.75	-	54.11
$Mg_{0.5}Mn_{0.5}Cr_2O_4$	5.85	13.23	50.09	5.83	13.26	50.07
$MnCr_2O_4$	-	26.64	46.64	-	26.67	47.62

Magnetic properties:-

The magnetization measurement for all compositions were carried out using a vibrating sample magnetometer (VSM) at room temperature with an applied magnetic field 15 kOe shown in **Fig.5.** The saturation magnetization (Ms), coercively (Hc), remnant magnetization (Mr) and magnetic moment (μB) of all the samples are listed in **Table.3.** Introduction of Mn^{2+} into Magnesium chromate greatly affect the magnetic properties. The magnetic study for all the samples indicates that, the variation in saturation magnetization, remnant magnetization, coercive force and magnetic moment (μB) due to substitution effect of Manganese on the $MgCr_2O_4$ and also, the sites preference energy also play important role in the magnetization.



(a) (b)



(c)

Fig. 5:- VSM plots of the system $Mg_{1-x}Mn_xCr_2O_4$ (a, x=0.0, b, x=0.5 and c, x=1.0)

Table.3:- Data for saturation magnetization (Ms), Corecievity (Hc), Remnant magnetization (Mr) and Magnetic moment (μB) for x=0.0, 0.5 and 1.0 samples.

Compound	Saturation Magnetisation (Ms) emu/gm	Coercive Field (Hc)	Remnant Magnetisation (Mr) emu/gm	Magnetic Moment (μ_B)
$MgCr_2O_4$	6.793	79.925	38.473	0.252
$Mg_{0.5}Mn_{0.5}Cr_2O_4$	11.357	34.929	36.254	0.391
$MnCr_2O_4$	16.648	6.513	11.829	0.664

Conclusion:-

The $Mg_{1-x}Mn_xCr_2O_4$ compositions were successfully synthesized by sol-gel autocombution technique. X-ray diffraction study reveals that, all compositionsare cubic phase. Thermal analysis indicates that required temperature for phase formation of metal oxides. The scanning electron microscopy study indicates that all compositions are well crystalline, uniform and homogeneous in nature. Magnetic study shows all samples were ferrimagnetic and magnetic properties increases with increase in manganese content.

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