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Synthesis, Structural And Magnetic Properties Of Cr Doped Magnetic Ferrite Nanoparticles

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Abstract

Nano-crystalline spinel ferrites system Mg FeCrO$_4$ with x=0.0-1.0 was prepared by sol-gel using 99.9% nitrates. The structural characterization of the sample was done by X-ray diffractometer and SEM technique. The XRD data was used to obtain lattice constant and particle size. The lattice constant decrease with chromium substitution. The analysis of XRD pattern clearly indiacate the single phase cubic spinel structure nation of the sample. Pulse field hysteresis loop technique is used to study the magnetization of the sample, the magnetization decrease with chromium substitution.

Keywords: Nanocystalline ferrite, Magnesium, Curie temperature .

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INTRODUCTION

Mixed metallic oxides specially spinel having the general formula A$_2$O$_4$ are very promising material for technologically important application. Spinel types ferrites are commonly used in the many electronic and magnetic devices due to their particular magnetic and electrical properties [1-2].The remarkable properties such as high magnetic permeability, low losses make them suitable in radio frequency region [3].Study of the nanosized spinel ferrite particles is of great importance to modern technologies including high density data storage, magnetic resonance imaging and magnetic carries for sites specific drug delivery [4].

The properties of spinel ferrites are dependent on their chemical composition and particle size. The method of preparation plays an important role in controlling the properties of spinel ferrites .Generally, spinel ferrites are prepared by standard ceramic technique. The method yields the particles of large size. There are various method available for production of nanosized ferrites materials such as vapour deposition [5],ball milling technique [6], reversed micelles [7],Langmuir-Blodget film [8], Self assembly monolayers [9], sol-gel method is a simple process which offer a significant saving in time and energy consumption with a need of very low sintering temperature. Morever, this method produces a homogenous product with narrow particles size disdurbation, which enchance the structural, magnetic and electrical properties of spinel ferrites [10]. MgFe$_2$O$_4$ is one of the most important magnetic oxides which reside in spinel structural and show good magnetic properties. MgFe$_2$O$_4$ have various application and can be used as catalyst [11], humidity sensor [12] and in hyperthermia treatment [13],With this background the present study aims at improvement of MgFe$_2$O$_4$ ferrites properties at nanoscale with Cr^{3+} substitution.

EXPERIMENT DETAIL

Nanocrstyalline powder of MgFe2O4 was prepared by sol-gel auto-ignation method. The A.R.Grade citric acid (C6hO3)3) and ferrite (Fe (NO3)3),(>99% sd-fine) were used as starting material. The molar ratio ratio of material nitrates to citric acid was taken 1:3 The metal nitrates were dissolved together in a minimum amount of double distilled water to get a clear solution of citric acid was mixed with metal nitrates solution, then ammonia solution was slowly added to adjust the pH at 7.The mixed solution was kept on a hot plate with continuous stirring at 90 C .During evaporation, the solution became viscous and finally formed a very viscous brown gel. When finally all water molecules were removed from the mixture, the viscous gel began frothing. After few minutes, the gel automatically ignited and burnt with glowing flints, the decomposition reaction would nonstop before the whole citrate complex was consumed. The auto-ignition was completed within a minute, yielding the brown-colored ashes

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termed as a precursor. The as-prepared of the sample were heat treated separated at 600 C to 4 h to get the final product .Phase analysis of the synthesized $MgFe_2O_4$ powder was conducted using primarily X-ray diffraction (XRD), employioing X-ray powder diffractometer (Philip X-ray diffractometer Model 3710) using CuKα radiation (λ=1.5405A□).the scanning step was 4.26□/min and scanning rate was 0.02□.The magnetic measurement viz .magnetization were carried out using pulse field hysteresis loop tracer (Magneta Company),applying 50Hz and r.m.s field of 100Oe was used record temperature variation susceptibility. The susceptibility and magnetization apparatus was calibrated with nickel prior to the measurements.

The XRD line width and particle size are calculated through the Scherrer's equation

$$t = \frac{0.9\lambda}{\beta cos\theta} \text{ Nm}$$

Where, t is diameter of crystal particle is wavelength of the X-ray radiation.θ_B is Bragg's angle. B is measure of broadening of diffraction due to size effect.

The bond length on tetrahedral (A) site (shortest distance between A-site cation and oxygen ion) and octahedral [B] site (shortest distance between B-site cation and oxygen ion) can be calculated. The values of tetrahedral and octahedral bond length d_{AX} and d_{BX} , tetrahedral edge, shared and unshared octahedral edge ($d_{AXE,}$ $d_{BXE,}$ d_{BXEU}) can be calculated by putting the experiment values of lattice parameter 'a' and oxygen position parameter 'u' of each sample in the equation given elsewhere[14].

The pellets in cylindrical shape were prepared using a die having bore radius 0.6 mm. The pressure of 6 ton was applied on the powder. Polyvinyl alcohol (2 wt %) was adder as binder, The measured density ρ_m Was determined using the formula [15]

$$dm = \frac{m}{\pi r^2 h}$$

Where ,m is the mass, r radius and h is the height of the pellet

The x-ray density of all the sample of the series $MgFe_2O_4$ have been calculated form the molecular weight and the volume of the unit cell using the formula [16],

$$dx \frac{8M}{N\alpha 3} \text{ gm/cm}^3$$

Where, M is the molecular weight, N is Avogadro's number and a is the lattice paramer. The porosity 'P' of the ferrite nano particle was then determined using the relation [15].

$$P = 1 \frac{dm}{dx}$$

Where dm and dx are the measured densities and X-ray respectively
The specific surface area was calculated from the measured diameter of the particle and density of the sample using the relation [17].

$$S = \frac{6000}{tdm}$$

Where, t is the particle of size and d_m is the measured density

3. RESULT AND DISCUSSION
3.1 Structural properties

Fig.1 depicts the X-ray diffraction (XRD) pattern of the typical composition x=0.0.0.6 and 1.0 of the series MgFe2CrO4 ferrites was concluded from the XRD pattern of the investigated samples. All diffraction peak are indexed to a spinel phase .The lattice parameter 'a' was calculated using the equation, a=d $= \sqrt{(h^2 + k^2 + l^2)}$ where, d is the inter-planer spacing and (hkl) is the index of the XRD reflection peak. For an accurate calculation of lattice constant 'a' lattice parameter for each peak of XRD pattern was calculated and then average of them is taken

The values of lattice parameter 'a' determined from the XRD data with an accuracy of ±0.002A☐ for all the sample are listed in Table 1 as a fuction of Cr^{3+}

Content x. Table 1indicate that the lattice constant decrease with the substitution of $Cr^{3+ \ ions}$ this behavior can be explained on the basis of difference in ionic radii. The decrease in the lattice consant is due to replacement of larger of larger Fe^{3+} ions (0.67 A☐) by similar Cr^{3+} ions (0.63 A☐). Usually, Ina solid solution of soft ferrite within the miscibility range, a range, a linear change in the lattice constant with concentration of the composition is observed [15].

The values of X-ray density (D_x), measured density (D_m),porosity (P),particle size (t), and specific surface area (S) as a function of Cr concentration 'x' .are given Table 1. The x-ray density decrease with the increasing Cr content 'x'. T his is related to the fact that, the increase in molecular weight overtake the increase in the volume of the unit cell. The porosity is an important with Cr concentration is tabulated in Table 1.It is observed that porosity increase as the concentration of Cr is increase. It is due to the smaller ionic radius of Cr as compared to Fe. The specific surface area value are calculated from the equation (5), and are given in Table 1.show that specific surface area values ranges from $36m^3/gm$ to $52 \ m^{3/}gm$.

Using the equation (1) the particle size has been calculated and some are listed in Table 1. Table 1 indicates that sol-gel autocumbustion method successfully yields nano-size ferrite particle. The particle size estimated show decreasing nature with increase in Cr content. This may be explained on the basis of hypothesis that the reaction condition, which favored the formation of new nuclei may vary regularly with Cr content.

The values of lattice parameter 'a' and oxygen postion parameter 'u' are used to calculate tetrahedral and octahedral bond length $(d_{AXE}$ and $d_{BX})$ tetrahedral edge, shared and unshared octahedral edge $(d_{AXE}, d_{BXE}, d_{BXEU})$ using the formula given elsewhere [14] and the values presented graphically in Giq.2(a) and Fif.2 (b). The Fig.2(a) indicate that the tetrahedral bond lenth d_{AX} decrease as Cr content x increase and octahedral bond length d_{BX} decrease.Fig.2(b) show that the tetrahedral edge d_{AXE} decreases, unshared octahedral edge d_{BXEU} does not vary much with composition while Shared octahedral edge d_{BXE} decreases. This could be related to the larger radius of Cr ions as compared to Fe ions and fact that Cr occupies strongly octahedral B-site. Fig.3 gives the typical SEM image for the sample x=0.2. The SEM micrograph show that grain growth is uniform and the grain size ranges from 0.5 to 0.7 μm

3.2 Magnetic properties

The magnetic properties like satuation magnetization (Ms) and coerciviy (Hc) were studied using the high field hysteresis loop technique [18]. Fig.4 show that the hysteresis curves of the sample at room temperature for the typical sample x=0.2 and 1.0. The reduction of saturation magnetization in the synthesized nanoparticles is attributed to the existence of 'a' dead surface layer for in which magnetic moments do not contribute to the magnetization in the applied field [19]. This particle exhibit super paramagnetic behavior at room temperature. The lower Ms Value associated to the particle with smaller size and also could be attributed to the fact that surface distortions due to interaction to the transition metal ions with the oxygen atom in the spinel ferrite lattice can be reduce the net magnetic moment in the particle. This effect is especially prominent for the ultrafine particle due to their large surface to volume ratio [20]. It is clearly observed from Fig.5 that the coecivity (Hc) increase as Cr^{3+} content x increase, this behavior is similar to that of porosity porosity. Porosity affects magnetization process because pores work as a generator of demagnetizing field. As the porosity increases high field is needed to push the domain wall and thus Hc increases. The satuation magnetization is related to H_c through Brown's relation [21].

$$H_c = \frac{2K1}{\mu 0 Ms}$$

μ According to the this relation H_c inversely proportion to M, Which is consistent with our experimental result .The coerciviy (H_c) increase slowly with Cr^{3+} content x up to x=0.6, but above x=0.6 a large value has been observed, This may be attributed to unquenched orbital angular momentum of Cr^{3+} and to large anisotropy value.

The magnetic momentum (nβ) per formula unit in Bohr magneton (μβ) was experimentally using the relation [22].

$$n_B = \frac{Molecular \ weight * \rho s}{5585 * \rho th}$$

Where, ρth is the bulk density of the sintered sample, Values of observed and calculated n_B are presented in Fig.6.The σs was calculated from M-H loops from the relation σs=(1-P) *Ms*d, where, P is the porosity, and Ms is

saturation magnetization. The variation of specific saturation magnetization decrease with the increasing substitution of Cr_{3+} ions.This can be attributed to the fall in density and increase in porosity. Since Cr_{3+} ions have a strong preference for octahedral [B] sites [24]. The magnetization moment per formula unit (nβ) calculated from Neel's sub two lattice model using the relation $n^N_{B=}M_{B(x)}$-$M_{A(x)}$ where M_B and M_A are the B and A sub lattice magnetic moment in μβ. It is evident from Fig.6 that the n_B decrease with increasing with suggesting a decrease in ferromagnetic behavior with increasing x.The calculated n^N_B values are in close agreement with experiment values. Conforming a collinear magnetic structure for B-sublattice dilution indicating strong A-B coupling (J_{AB}).

The thermal variation of a.c susceptibility of all polycrystalline samples was obtained using a double coil set up (25). From the plot of thermal variation inverse a.c magnetic susceptibility for x=0.0 to 0.4 and 1.0 are given in fig.7figure also shown an inset for variation of Curie tempreture (Tc) with composition. Curie temperature (T_c) determined from------versus temperature plot decreases with addition of –ions. It is well known that when ---ions are replaced by paramagnetic or diamagnetic ions, Curie temperature falls. When—ions of B-site replaced by paramagnetic –ions A-B interaction gets weakened. The observed fall in Curie temperature in the present system is attributed to this weaking of A-B exchange interaction.

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