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ORIGINAL ARTICLE

INCORPORATION OF LARGER Gd^{3+} RARE EARTH IONS INTO Mn-Cr-Fe NANOCRYSTALLINE POWDER ALLOYS

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Abstract:

Sol-gel auto combustion method is used to synthesize the rare earth Gd^{3+} incorporated Mn-Cr-Fe nanocrystalline powder. The synthesized powder samples were annealed at 600 ºC for 4 h. X-ray diffraction data were used to evaluate the structure of the prepared samples. X-ray diffraction pattern shows the presence of Gd^{3+} ions. Rare earth Gd^{3+} ions form the secondary phase as evidenced by the X-ray diffraction pattern. Lattice constant (a), X-ray density (d_x), Crystallite size (D_{XRD}), hopping lengths (L_A and L_B), allied parameters such as tetrahedral and octahedral bond length (d_{Ax} and d_{Bx}), tetrahedral edge, shared and unshared octahedral edge (d_{AXE}, dBXE and d_{BXEU}) were calculated were calculated using X-ray diffraction data. Hopping lengths and allied parameters varied with Gd^{3+} incorporation.

KEYWORDS:

Rare earth ion; Sol-gel method, hopping length

INTRODUCTION:

Magnetic nanoparticles are gaining importance due to their potential applications in high-density magnetic recording, magnetic fluid, biomedical and microwave applications etc. During the last few decades, ferrites have been studied extensively because of their importance in basic as well as in applied research [1,2].

Spinels with rare earth (RE) ions have attracted great attention in the material science field because of their interesting properties, such as infrared emission, catalytic, photoelectric, and magnetic properties [3,4]. It is known that the magnetic behaviour of the ferrimagnetic oxide compounds is largely governed by the Fe-Fe interaction (the coupling of the spins of the 3d electrons). By introducing R ions in the spinel lattice, the R-Fe interactions appear too (3d-4f coupling), which can lead to small changes in the magnetization and Curie temperature [5-7].

Many research groups have investigated to enhance the magnetic property of magnetic materials such as manganese ferrite. $MnFe_2O_4$ is a ferrimagnet (T_N = 560 K) having the spinel structure with two inequivalnt sublattices of tetrahedral (A) and octahedral [B] symmetries for the magnetic ions sites [8-11]. It is found that small substitution of Fe^{3+} ions by Gd^{3+} ions may favorably influence the electromagnetic

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properties of ferrites facilitating good magnetic characteristics for high frequency applications [12-15]. In this research we have made an attempt to study the effect of Gd3+ substitution on the structural properties of $MnCrGd_xFe_{1-x}O_4$ (x = 0.0, 0.05, 0.1 and 0.15)

EXPERIMENTAL

The ferrite powders were synthesized through sol-gel auto-combustion route to achieve homogeneous mixing of the chemical constituents on the atomic scale and better sinterability. AR grade manganese nitrate ($Mn(NO_3)_2 \cdot 6H_2O$), chromium nitrate ($Cr(NO_3)_3 \cdot 9H_2O$), gadolinium nitrate $Gd(NO_3)_3 \cdot 9H_2O$, iron nitrate ($Fe(NO_3)_3 \cdot 9H_2O$) and citric acid ($C_6H_8O_7 \cdot H_2O$),were used to prepare the $MnCrGd_xFe_{1-x}O_4$ (x = 0.0, 0.05, 0.1 and 0.15) ferrite compositions. Reaction procedure was carried out in air atmosphere without protection of inert gases. The molar ratio of metal nitrates to citric acid was taken as 1:3. The metal nitrates were dissolved together in a minimum amount of double distilled water to get a clear solution. An aqueous solution of citric acid was mixed with metal nitrates solution, then ammonia solution was slowly added to adjust the pH at 7. Then the solution was heated at 90 ºC to transform into gel. When ignited at any point of the gel, the dried gel burnt in a self-propagating combustion manner until all gels were completely burnt out to form a fluffy loose powder. The auto-ignition of gel was carried out in glass beaker upon a hot plate. The auto-combustion was completed within a minute, yielding the brown-colored ashes termed as a precursor. The as prepared powder then annealed at 600 ºC for 4 h.

Structural analysis of the powders were carried out on a Phillips X-ray diffractometer (Model 3710) using Cu-K radiation (=1.5405Å).

RESULTS AND DISCUSSION

The XRD patterns of typical composition $MnCrGd_{0.1}Fe_{0.9}O_4$ (x = 0.1) ferrite nanocrystals synthesized at room temperature is shown in Fig. 1. The XRD lines are appeared to be broad. Further, the increase in intensity of X-ray diffraction with Gd^{3+} doping shows improved crystallinity of the materials. The X-ray analysis indicated the presence of $GdFeO_3$ ortho phase in the resulting compound due to reactivity of Gd^{3+} and Fe^{3+} [16]. The presence of the second phase ($GdFeO_3$) is due to the higher activity of Fe^{3+} ions with Gd3+ ions on the grain boundaries.

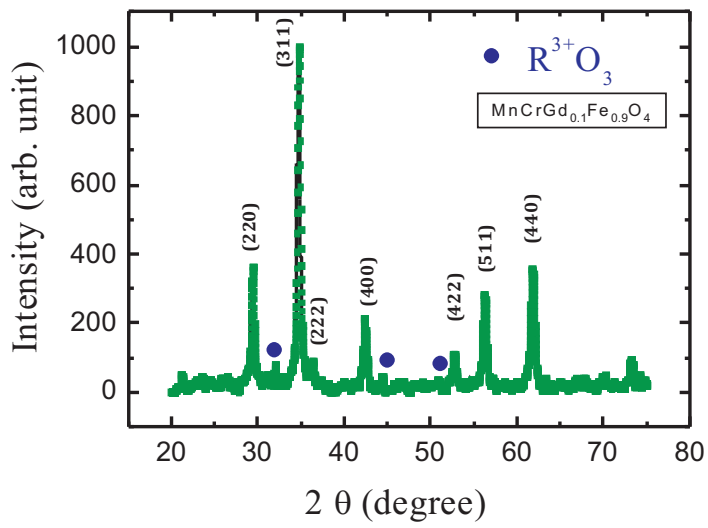

Fig. 1: X-ray diffraction pattern of the typical sample

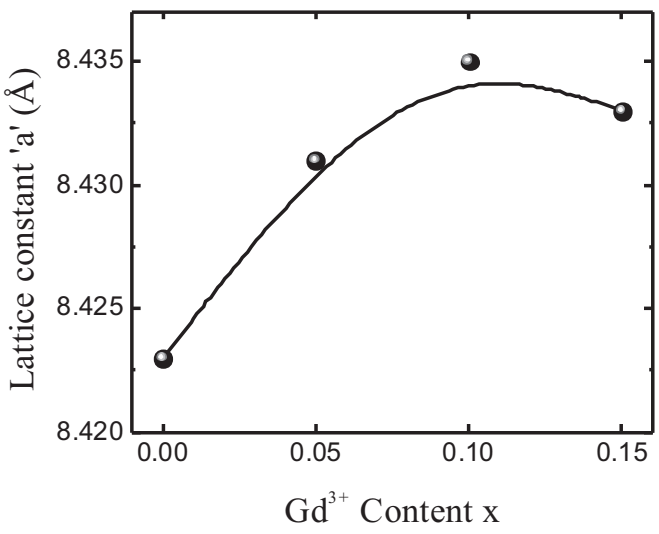

Fig. 2: Variation of lattice constant with Gd^{3+} content x

The lattice constants (a) are determined by using Bragg's law as a function of Gd^{3+} content [17]:

$$a = d\sqrt{(h^2 + k^2 + l^2)} \qquad \mathbf{1}$$

where d is the inter-planer spacing and (hkl) is the index of the XRD reflection peak. The dependence of the lattice parameter on the Gd^{3+} content x is shown in Table 1 and Fig. 2 and shows non-linear behavior.

The X-ray density (d_x) of all the samples of the series was obtained by the following relation:

$$dx = \frac{8M}{Na^3}$$

where 8 is the number of molecules per unit cell, 'M' is the molecular weight of sample, 'N' is the Avogadro's number and 'a' is lattice constant.

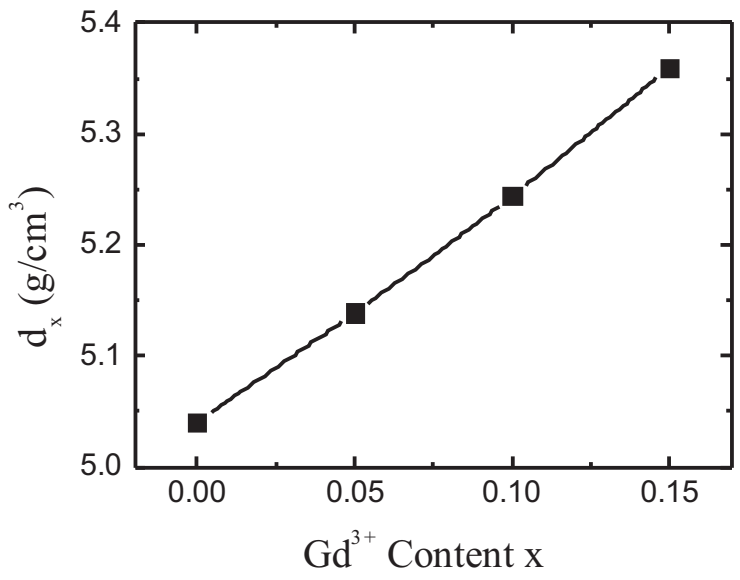

Fig. 3: Variation of X-ray density (dx) with Gd^{3+} content x

It is seen from Fig. 3 and Table 1 that the X-ray density increases linearly with the Gd^{3+} content x. Both the molecular weight and the volume of the unit cell for the doped ferrite increase with the Gd^{3+} content x, because of the replacement of larger Gd^{3+} for Fe^{3+} , and the molecular weight has more increment when compared to the volume of the unit cell, therefore, the X-ray density increases with the Gd^{3+} content x.

Table 1

Lattice constant (a), X-ray density (d_x) and crystallite size (D_{XRD}) of $MnCrGd_xFe_{1-x}O_4$

Comp. x	a (Å)	dx (g/cm^3)	D_{XRD} (nm)
0.00	8.423	5.041	12
0.05	8.431	5.139	15
0.10	8.435	5.244	20
0.15	8.433	5.360	17

The average crystallite diameter 'D_{XRD}' of powder estimated from the most intense (311) peak of XRD and using the Scherrer formula [17]:

$$D_{XRD} = \frac{0.9\lambda}{B\cos\theta}$$

where λ is the wavelength used in XRD, B is the full width of half maximum in (2), is the corresponding Bragg angle.

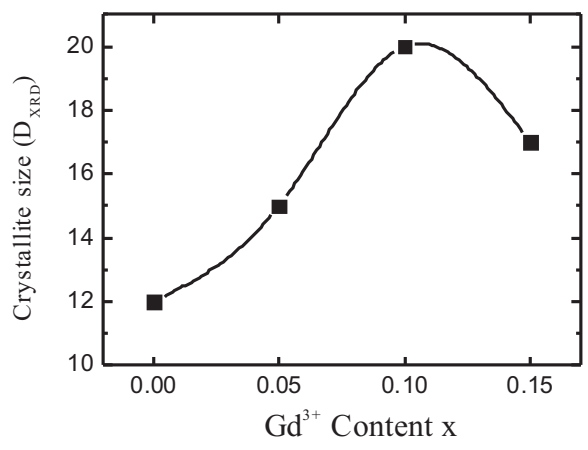

Fig. 4: Variation of crystallite size (D_{XRD}) with Gd^{3+} content x

Figure 4 and Table 1 shows that the crystallite diameter varies in the range of 12 to 20 nm with increase in Gd^{3+} substitution.

The allied parameters such as tetrahedral and octahedral bond length (d_{Ax} and d_{Bx}), tetrahedral edge, shared and unshared octahedral edge (d_{AXE}, d_{BXE} and d_{BXEU}) were calculated:

$$d_{Ax} = a\sqrt{3}\,(u-1/4) \quad \textbf{4}$$

$$d_{Bx} = a\,[3u^2-(11/4)u+43/64)]^{1/2} \quad \textbf{5}$$

$$d_{AxE} = a\sqrt{2}\,(2u-1/2) \quad \textbf{6}$$

$$d_{BxE} = a\sqrt{2}(1-2u) \quad \textbf{7}$$

$$d_{BxEu} = a\,[4u^2 - 3u + (11/16)]^{1/2} \quad \textbf{8}$$

Figure 5 and Table 2 show that all the allied parameter increased for x 0.1 with the increase in Gd^{3+} substitution.

Table 2

Tetrahedral bond (d_{AX}), octahedral bond (d_{BX}), tetra edge (d_{AXE}) and octahedral edge (d_{BXE}) (shared and unshared) of $MnCrGd_xFe_{1-x}O_4$

Comp. 'x'	d_{AX} (Å)	d_{BX} (Å)	Tetra edge (Å)	Octa edge d_{BXE} (Å)	
			d_{AXE}	Shared	unshared
0.00	1.911	2.059	3.120	2.835	2.986
0.05	1.913	2.061	3.123	2.837	2.988
0.10	1.914	2.062	3.125	2.839	2.990
0.15	1.913	2.061	3.124	2.838	2.989

The variation of allied parameters is related to the variation in lattice constant. In the present study smaller Fe^{3+} ions are replaced by the larger Gd^{3+} ion, this difference in the ionic radii is reflected in the lattice constant and also in the variation of all the allied parameters.

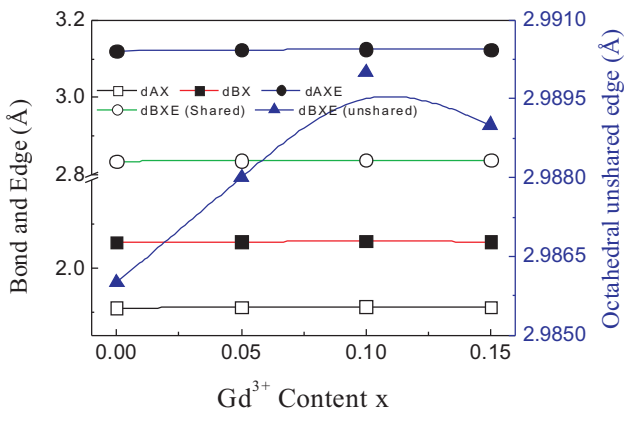

Fig. 5: Variation of Tetrahedral bond (d_{AX}), octahedral bond (d_{BX}), tetra edge (d_{AXE}) and octahedral edge (d_{BXE}) (shared and unshared) with Gd^{3+} content.

The hopping length for A-site (L_A) and B-sites (L_B) are calculated using the values of lattice constant.

$$L_A = a\sqrt{\frac{3}{4}} \quad \textbf{9}$$

$$L_A = a\sqrt{\frac{2}{4}} \quad \textbf{10}$$

Table 3 and Fig. 6 shows the variation of hopping lengths (L_A and L_B) with different concentration of Gd^{3+} ions substitution. The hopping length distance at both the available sites between the constituent ions in composition in increased with the Gd_{3+} substitution.

Table 3

Hopping length L_A and L_B of $MnCrGd_xFe_{1-x}O_4$

Comp. x	Hopping length	
	L_A (Å)	L_B (Å)
0.00	3.6473	2.9780
0.05	3.6507	2.9808
0.10	3.6525	2.9822
0.15	3.6516	2.9815

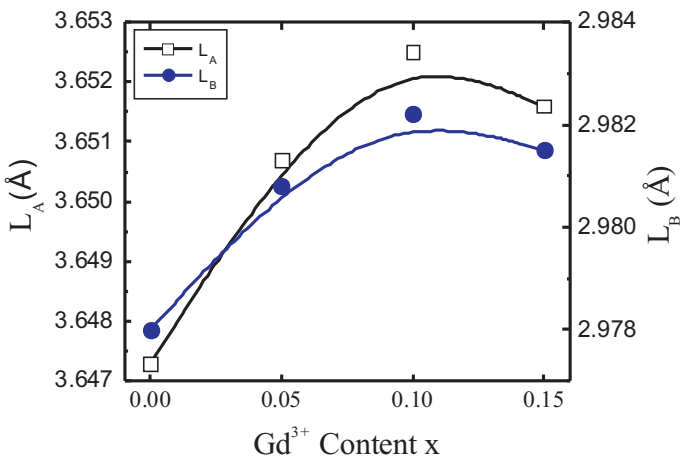

Fig. 6: Variation of hopping lengths (L_A and L_B) with Gd^{3+} substitution.

CONCLUSIONS

Rare earth Gd^{3+} substituted Mn-Cr ferrites nanoparticles with a chemical formula $MnCrGd_xFe_{1-x}O_4$ were successfully synthesized by the sol-gel auto combustion method. Variation of lattice constant is related to the difference in the ionic radii of Gd^{3+} and Fe^{3+} ions. X-ray density found to increase with the increase in Gd^{3+} ions, this increase in d_x is related to the molecular weight of Gd^{3+} ions. The average crystallite size initially increased followed by decreasing trend with Gd^{3+} substitution. Ion jump length of tetrahedral A- and octahedral B-sites and all the allied parameters shows dependence of Gd^{3+} substitution. Behaviour of ion jump lengths and allied parameters are related to the larger ionic radii of La^{3+} ions as compared to that of Fe^{3+} ions.

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