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ORIGINAL ARTICLE

Structural Development In Cr^{3+} Substituted Nano-particles Of $Co_{0.5}mg_{0.5}Fe_2O_4$ Ferrite

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Abstract:

Nano particles of $Co_{0.5}Mg_{0.5}Cr_xFe_{2-x}O_4$ *were synthesized by sol-gel auto-combustion method at relative low annealing temperature. The obtained samples were characterized by X-ray diffraction (XRD) technique. Cr3+ ions induced the change in lattice constant and other structural parameters of* $Co_{0.5}Mg_{0.5}CrxFe_{2-x}O_4$*. Hopping lengths of tetrahedral A-site (LA) and octahedral B-site (LB) found to decrease with increases* Cr^{3+} *ions. The allied parameters such as tetrahedral bond (dAX), octahedral bond (dBX), tetra edge (dAXE) and octahedral edge (dBXE) shows decreasing behaviour with increasing* Cr^{3+} *ions.*

KEYWORDS:

Ferrite; Sol-gel method; XRD; Hopping lengths

1. INTRODUCTION

Mg-Co nanomaterials are potential candidates to miniaturize the size of antennas. The excellent combination of the magnetic and dielectric properties of these materials can be used to fulfill the future demands of high frequency applications. As the technology advances, the miniaturization of electronic devices and the increase of operational frequency are in demand. To improve the performance of these materials and size miniaturization, the current focus is on nantechnology. Co-Mg ferrite compound found good correlation between structure and magnetic interaction [1, 2].

The presence of Co^{2+} could improve the coercivity of the ferrite compound. Due to the antiferromagnetic nature of Cr^{3+} ions, there is a possibility of achieving control over magnetic parameters like remanence and coercivity in developing technologically important materials by simple substitution of the A ions in AFe_2O_4 by Cr [3]. Moreover, substitution of Cr^{3+} at the B-site should be effective in enhancing the electrical resistivity. In the present work, the aim of Cr^{3+} substitution combined with Fe^{3+} replacement to maintain the overall electroneutrality, to reduce dielectric loss and to improve dc-electrical resistivity and magnetic properties. The MgCrO is a normal spinel and all the chromium ions are bound mostly to octahedral sites. The magnesium ferrite belongs to the partially inverse spinel, and it can be considered as a collinear ferrimagnet whose degree of inversion depends on the thermal history of the sample.

Keeping the importance of above discussion in mind, in the paper we reports our results on the

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structural properties of Cr^{3+} substituted $Co_{0.5}Mg_{0.5}Fe_2O_4$ ferrite with a chemical formula $Co_{0.5}Mg_{0.5}Cr_xFe_{2-x}O_4$

2.EXPERIMENTAL

Nano-particles of $Co_{0.5}Mg_{0.5}Cr_xFe_{2-x}O_4$ (x = 0.0, 0.25, 0.50, 0.75, 1.0) were synthesized by sol-gel auto-combustion method. Analytical grade citric acid ($C_6H_8O_7{\cdot}H_2O$), Magnesium nitrate (Mg(NO3)2·6H2O), cobalt nitrate (Co(NO3)2·3H2O), chromium nitrate ($Cr(NO_3)_3{\cdot}9H_2O$) and iron nitrate ($Fe(NO_3)_3{\cdot}9H_2O$) were used as starting materials. 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. The mixed solution was kept on to a hot plate with continuous stirring at 90 ºC. 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 not stop before the whole citrate complex was consumed. 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. The samples were powdered for X-ray investigations. Part of the powder was X-ray examined by Phillips X-ray diffractometer (Model 3710) using Cu-K radiation (=1.5405Å).

3.RESULTS AND DISCUSSION

The broad XRD line indicates that the ferrite particles are of nano-size (Fig. 1).

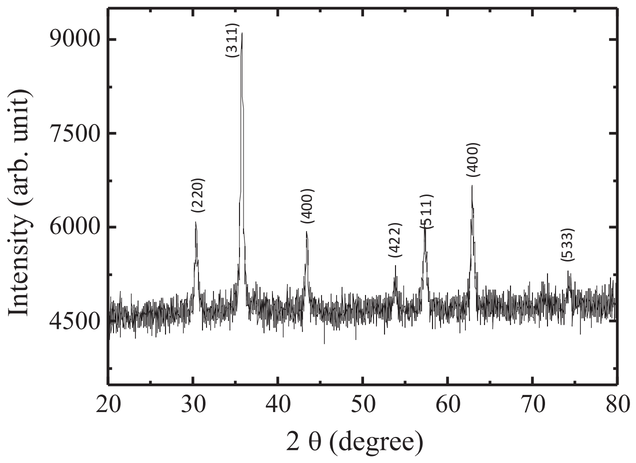

Fig. 1. Typical XRD pattern of $Co_{0.5}Mg_{0.5}Cr_xFe_{2-x}O_4$ (x = 0.25)

The XRD patterns exhibit peaks corresponding to Cr^{3+} substituted Co-Mg ferrites and the absence of any other impurity phases. The data reveals single-phase spinel structure with cubic symmetry. No extra lines indicate the existence of secondary phases, and the data were compared and indexed with ICDD card no 22-1086. The lattice parameter 'a' was calculated using the following equation [4],

$$a\ \theta\ d\sqrt{(h^2\ \theta\ k^2\ \theta\ l^2)}$$

where d is the inter-planer spacing and (hkl) is the index of the XRD reflection peak. It is observed that the lattice constant 'a' decreases from 8.381 - 8.364Å with increase in Cr^{3+} substitution in Co-Mg alloys. The decrease in lattice constant is related to the ionic radii of the respective ions. In the present ferrite system smaller Cr^{3+} of 0.63 Å ionic radii replaces larger Fe^{3+} ions with 0.67 Å ionic radii.

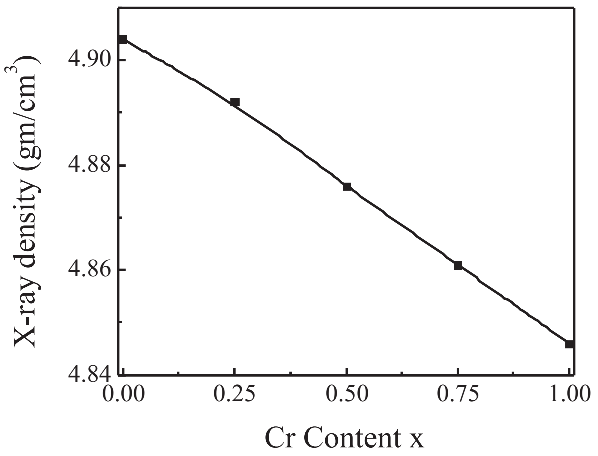

Fig. 2. X-ray density plot of $Co_{0.5}Mg_{0.5}Cr_xFe_{2-x}O_4$

The X-ray densities (dx) of the samples have been calculated from the molecular weight and the volume of the unit cell.

$$dx\ \theta\ \frac{8M}{Na^3} \qquad 2$$

where M is molecular weight of sample, N is the Avogadro's number and a is the lattice constant. Fig. 2 shows the variation of X-ray density with Cr^{3+} substitution. It can be noted from Fig. 2 that the X-ray density decreases with increase in Cr^{3+} substitution. The X-ray density decreases slowly with increase of Cr concentration this is because; the decrease in mass overtakes the decrease in volume of the unit cell.

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

$$L_A\ \theta\ a\sqrt{\frac{3}{4}} \qquad 3$$

$$L_B\ \theta\ a\sqrt{\frac{2}{4}} \qquad 4$$

The variation of hopping lengths with Cr content x is shown in Table 1 and Fig. 3.

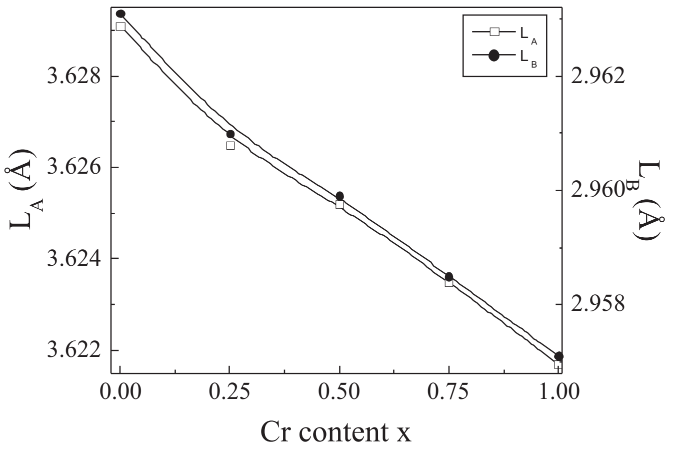

Fig. 3. Hopping lengths (L_A and L_B) of $Co_{0.5}Mg_{0.5}Cr_xFe_{2-x}O_4$

Table 1

Hopping length LA and LB of Co0.5Mg0.5CrxFe2-xO4

Comp.	**Hopping length**	
x	**L_A (Å)**	**L_B (Å)**
0.0	3.6291	2.9631
0.25	3.6265	2.9610
0.5	3.6252	2.9599
0.75	3.6235	2.9585
1.0	3.6217	2.9571

It is observed from Table 1 and Fig. 3 that the distance between the magnetic ions (hopping length) decreases as Cr substitution increases. This behavior of hopping length with x is analogous with the behavior of lattice constant with Cr^{3+} substitution. This variation may be attributed to the deference in the ionic radii of the constituent ions, which makes the magnetic ions become smaller to each other and the hopping length decreases. Using the experimental values of lattice constant 'a', oxygen positional parameter 'u' and substituting using the following equations, the allied parameters such as tetrahedral and octahedral bond length (dAx and dBx), tetrahedral edge, shared and unshared octahedral edge (dAXE, dBXE and dBXEU) were calculated.

$$d_{Ax} = a\,\theta 3\,(u-1/4) \quad 5$$

$$d_{Bx} = a\,[3u^2-(11/4)u+43/64)]^{1/2} \quad 6$$

$$d_{AxE} = a\,\theta 2\,(2u-1/2) \quad 7$$

$$d_{BxE} = a\,\theta 2(1-2u) \quad 8$$

$$d_{BxEu} = a\,[4u^2 - 3u + (11/16)]^{1/2} \quad 9$$

Table 2 and Fig. 4 indicate that all the allied parameter decreases as Cr^{3+} substitution increases. This could be related to the smaller ionic radius of Cr^{3+} ions as compared to Fe^{3+} ions and the site occupancy of the constituent ions in the present ferrite system.

Table 2

Tetrahedral bond (d_{AX}), octahedral bond (d_{BX}), tetra edge (d_{AXE}) and octahedral edge (d_{BXE}) (shared and unshared) of $Co_{0.5}Mg_{0.5}Cr_xFe_{2-x}O_4$

Comp. 'x'	**d_{AX} (Å)**	**d_{BX} (Å)**	**Tetra edge (Å)**	**Octa edge d_{BXE} (Å)**	
			d_{AXE}	**Shared**	**unshared**
0.0	1.902	2.048	3.105	2.820	2.971
0.25	1.900	2.047	3.103	2.818	2.969
0.5	1.900	2.046	3.102	2.817	2.968
0.75	1.899	2.045	3.100	2.816	2.966
1.0	1.898	2.044	3.099	2.815	2.965

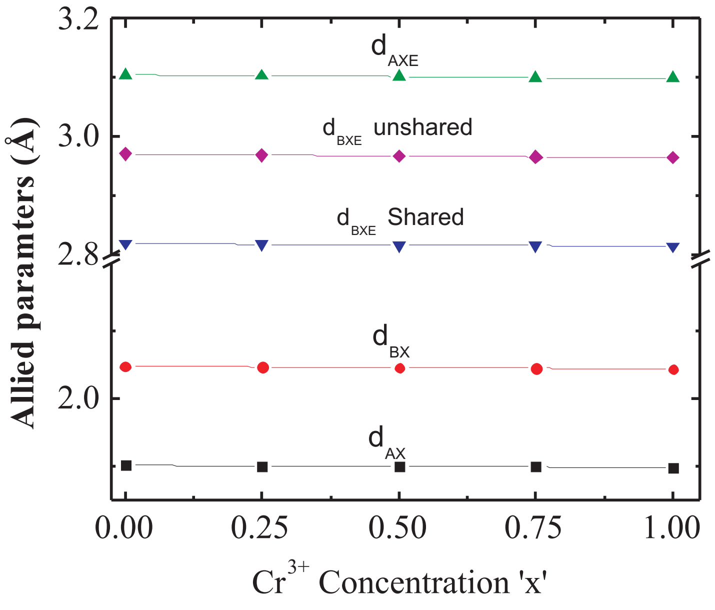

Fig. 4. Variation of Tetrahedral bond (d_{AX}), octahedral bond (d_{BX}), tetra edge (d_{AXE}) and octahedral edge (d_{BXE}) (shared and unshared) with La content x of $Co_{0.5}Mg_{0.5}Cr_xFe_{2-x}O_4$

1.CONCLUSIONS

A ferrite series with a chemical formula $Co_{0.5}Mg_{0.5}Cr_xFe_{2-x}O_4$ were successfully synthesized via the sol-gel method. Due to the smaller ionic radii of Cr^{3+} ions induce the decrease in lattice constant of the system. X-ray density is also decreased with the increase in Cr^{3+} ions, this decreased in dx is attributed to the smaller molecular weight of Cr^{3+} ions. The difference in ionic radii between Cr^{3+} and Fe^{3+} ions also causes the change in ion jump and allied parameters of $Co_{0.5}Mg_{0.5}Cr_xFe_{2-x}O_4$

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