



Ion Jump Lengths Of MN-ZN-AL-FE And MG-ZN-CR-FE Nano-particles

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Abstract:

Al³⁺ substituted Mn-Zn-Fe with a chemical formula $Mn_{0.5}Zn_{0.5}Al_xFe_{2-x}O_4$ and Cr³⁺ substituted Mg-Zn-Fe with a chemical formula $Mg_{0.5}Zn_{0.5}Cr_xFe_{2-x}O_4$ were synthesized by sol-gel auto-combustion method. The samples were obtained by annealing at relatively low temperature at 600 °C and characterized by X-ray diffraction (XRD). Lattice constant is decreased in both the system with the increasing substitution of Al and Cr ions. Ion jump length found to decrease with the increase of Al³⁺ in Mn-Zn-Fe, similar results were observed for Cr³⁺ substituted Mg-Zn-Fe. All the allied parameters such as tetrahedral bond (dAX), octahedral bond (dBX), tetra edge (dAXE) and octahedral edge (dBXE) shows decreasing trend in both the Mn-Zn-Al-Fe and Mg-Zn-Cr-Fe systems.

KEYWORDS:

Ferrites; Sol-gel method, Ion jump length.

1. INTRODUCTION

Soft ferrites are widely used in electronic equipment, and recently, the demand for highly inductive materials has increased so as to lower prices. MgZn ferrite is used in large quantities because it is highly cost effective. In general, copper and manganese oxides are added to MgZn ferrites in order to achieve high quality [1-3]. The parameters related to the ionic charge and radius, crystal fields play an important role in the site preference of the cations. The effect of Cr³⁺ substitution for Fe³⁺ in spinel ferrites has been studied extensively [4-6]. Though there is no reports are found to us in which Cr³⁺ substituted in Mg-Zn ferrite.

The Mn-Zn ferrites are preferred over other ferrites because of their high initial permeability, low losses, high saturation magnetization and relatively high Curie temperature [7]. These ceramics have spinel structure based on a face-centered cubic lattice of oxygen ions with functional units of $(ZnFe^{x-1-x})[Mn_{1-x}Fe_{1+x}]O_4$ [8]. Mn-Zn ferrites have different behaviors of saturation magnetization; the addition of nonmagnetic zinc ferrite to the inverse spinel manganese ferrite raises the saturation magnetization. Leading to this non-magnetic substitution it could be interesting to see the effect of Al³⁺ ions in Mn-Zn ferrite.

The aim of the present research report is to study the effect of Cr³⁺ and Al³⁺ substitution for Fe³⁺ on

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the ion jump length and allied parameters of the $Mg_{0.5}Zn_{0.5}CrFe_{2-x}O_4$ and $Mn_{0.5}Zn_{0.5}AlFe_{2-x}O_4$ spinel system.

2. EXPERIMENTAL PROCEDURE

The Analytical grade citric acid ($CH_2O \cdot HO$), manganese nitrate ($Mn(NO)_3 \cdot 6H_2O$), zinc nitrate ($Zn(NO)_3 \cdot 6H_2O$), aluminum nitrate ($Al(NO)_3 \cdot 9H_2O$) and iron nitrate ($Fe(NO)_3 \cdot 9H_2O$), were used to synthesize the $Mn_{0.5}Zn_{0.5}Al_xFe_{2-x}O_4$ ($x = 0.0-0.5$) samples by sol-gel auto combustion method. A series of Mg-Zn ferrite substituted by Cr, $Mg_{0.5}Zn_{0.5}CrFe_{2-x}O_4$ ($x = 0.0-1.0$) were prepared using the sol-gel auto-combustion method, in which high purity nitrates of A.R. grade citric acid ($CH_2O \cdot HO$), magnesium nitrate ($Mg(NO)_3 \cdot 6H_2O$), zinc nitrate ($Zn(NO)_3 \cdot 6H_2O$), chromium nitrate ($Cr(NO)_3 \cdot 9H_2O$), and iron nitrate ($Fe(NO)_3 \cdot 9H_2O$) were used.

The weighed amounts of these metal nitrates were completely dissolved in distilled water and the solution was stirred for half an hour. This solution was then added to citric acid in such a way that in the final sample, the molar ratio these nitrates and citric acid become 1:3. A small amount of ammonia was drop-wise added to achieve pH of the solution 7 with stirring the solution simultaneously. The detail of sol-gel synthesis method was reported in our previous reports [9-11]. Using Cu-K α radiations with wavelength 1.5406 Å, X-ray diffraction investigations was analyzed at room temperature to confirm the crystallographic phase formation of nanocrystalline ferrite material.

3. RESULTS AND DISCUSSION

Figure 1 shows the X-ray diffraction (XRD) patterns of the typical samples of Mg-Zn-Cr-Fe and Mn-Zn-Al-Fe ($x = 0.2$).

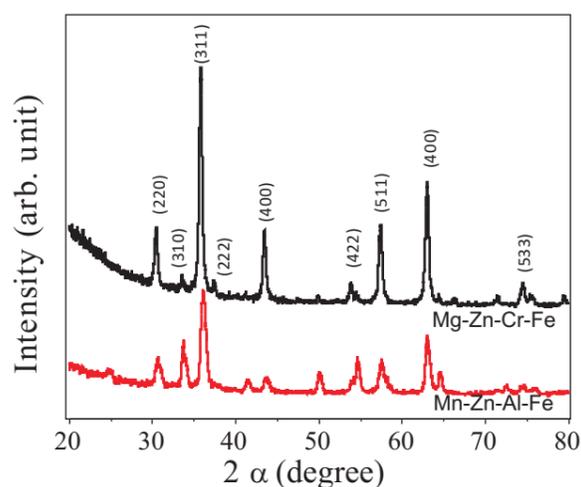


Figure 1. The XRD pattern of the typical samples ($x = 0.2$) of Mg-Zn-Cr-Fe and Mn-Zn-Al-Fe

The X-ray diffraction study has revealed the crystal structure to be cubic. The XRD pattern of the typical samples, showing well-defined reflections without any ambiguity, exhibits the formation of $Mg_{0.5}Zn_{0.5}CrFe_{2-x}O_4$ and $Mn_{0.5}Zn_{0.5}AlFe_{2-x}O_4$. The broad nature of the XRD shows the synthesized samples are in nanometer dimensions.

The lattice parameter 'a' was calculated using the following equation [12],

$$a = \frac{a_0}{\sin \alpha} \sqrt{\frac{h^2 + k^2 + l^2}{\sin^2 \alpha}}$$

where (hkl) are the Miller indices and α is the diffraction angle corresponding to the (hkl) plane.

It is observed that the unit cell parameter of the Al³⁺ substituted Mn-Zn ferrite phase gradually decreases from 8.445 to 8.385 Å with increasing Al³⁺ substitution in the composition obeying Vegard's law. The slow linear decreasing trend in the lattice parameter is attributed to the replacement of Fe³⁺ (0.67 Å) ion by Al³⁺, a smaller ion with the ionic radii of 0.51 Å. Similarly, lattice constant also decreased from 8.412 to 8.381 Å with the increase in Cr³⁺ content x. The decrease in the lattice constant is related to the difference in ionic radii of Fe³⁺ and Cr³⁺. In the present ferrite system Fe³⁺ ions (0.67Å) ions are replaced by the relatively small Cr³⁺ ions (0.64Å).

Using the values of lattice constant 'α', the distance between magnetic ions (jump lengths) available in tetrahedral A-site and octahedral B-site i.e. 'LA' and 'LB' respectively was calculated by using the relations,

$$L_A = \alpha \cdot 3/4 \tag{2}$$

$$L_B = \alpha \cdot 2/4 \tag{3}$$

Figs. 3 and 4 shows the relation between the hopping lengths in octahedral (A) and tetrahedral [B] sites.

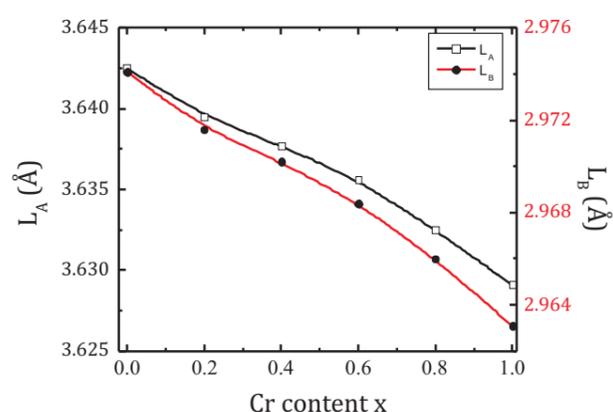


Figure 2: Variation of hopping lengths (LA and LB) with Cr content x.

Table 1

Hopping length LA and LB of MgZn_{0.5}CrFe_{2-x}O₄

Comp. x	Hopping length	
	LA (Å)	LB (Å)
0.0	3.6425	2.9741
0.2	3.6395	2.9716
0.4	3.6377	2.9702
0.6	3.6356	2.9684
0.8	3.6325	2.9660
1.0	3.6291	2.9631

The variation of ion jump lengths (LA and LB) as a function of Al and Cr content 'x' is shown in

Figs. 2 and 3 and the values are given in table 1 and 2, which shows that ion jump lengths decreased with the increases in Al and Cr content. The results can be explained by the variation in the lattice constant with increasing Al and Cr content.

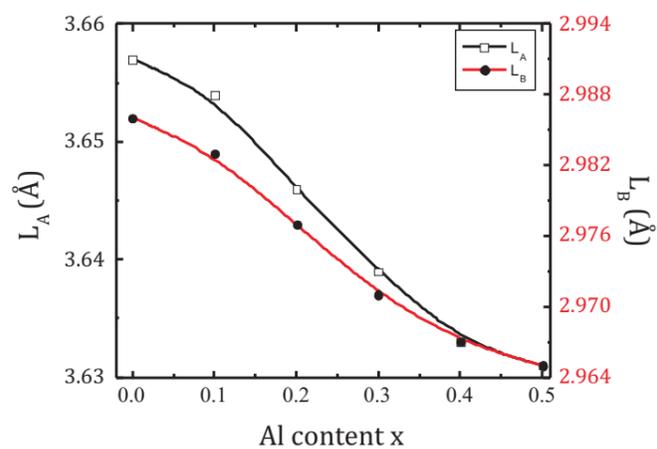


Figure 3: Variation of hopping lengths (L_A and L_B) with Al content x.

Table 2

Hopping length L_A and L_B of $Mn_3Zn_{0.5}Al_xFe_{2-x}O_4$

Comp.	Hopping length	
	L_A (Å)	L_B (Å)
x		
0.0	3.657	2.986
0.1	3.654	2.983
0.2	3.646	2.977
0.3	3.639	2.971
0.4	3.633	2.967
0.5	3.631	2.965

The bond length of tetrahedral A-site and octahedral B-site i.e. shortest distance between site cations and oxygen ions along with tetrahedral edge, shared and unshared octahedral edge, are calculated using the formulae given below [13] by inserting the values of lattice constant and oxygen position parameter in to these formulae.

$$d_{AX} \propto a \sqrt{\frac{3}{4}} \frac{\alpha}{u} \propto \frac{1}{4} \frac{\alpha}{\alpha} \quad (4)$$

$$d_{BX} \propto a \frac{\alpha}{\alpha} \frac{3u^2}{\alpha} \propto \frac{\alpha}{\alpha} \frac{11\alpha}{4\alpha} \frac{1}{\alpha} \propto \frac{43\alpha^2}{64\alpha} \quad (5)$$

$$d_{AE} \propto a \sqrt{2} \frac{\alpha}{\alpha} \frac{2u}{\alpha} \propto \frac{1}{2} \frac{\alpha}{\alpha} \quad (6)$$

$$d_{BEshared} \propto a \sqrt{2} \frac{\alpha}{\alpha} \frac{2u}{\alpha} \quad (7)$$

$$d_{BEunshared} \propto a \frac{\alpha}{\alpha} \frac{4u^2}{\alpha} \propto \frac{3u}{\alpha} \frac{11\alpha^2}{16\alpha} \quad (8)$$

The variations of these structurally important parameters are shown in the Figs. 4 and 5.

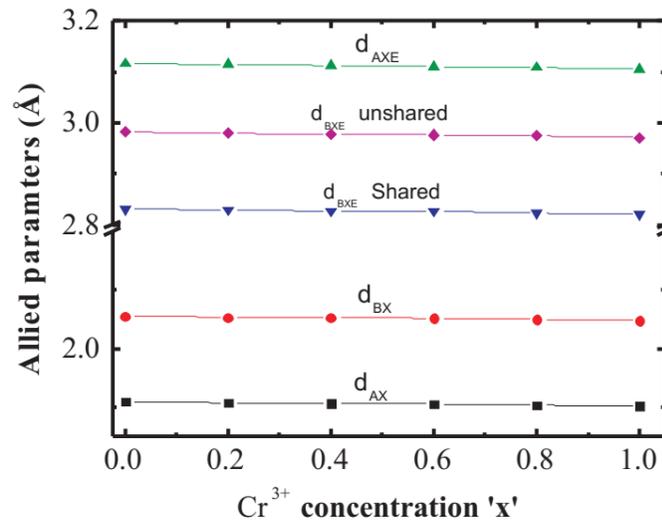


Figure 4. Allied parameters with concentration 'x' for MgZn_{0.5}CrFe_{2-x}O₄

It can be observed from Figs. 4 and 5 that the tetrahedral bond (d_{AX}), octahedral bond (d_{BX}), tetra edge (d_{AXE}) and octahedral edge (d_{BXE}) in both the ferrite systems are decreased with increase in Al³⁺ and Cr³⁺ substitution. Figs. 4 and 5 indicates that the tetrahedral and octahedral bond lengths decreases as Al³⁺ and Cr³⁺ ion substitution increases. The tetrahedral edge and shared and unshared octahedral edges decrease as Al³⁺ and Cr³⁺ content increases. This trend could be related to the smaller radius of Al³⁺ and Cr³⁺ ions compared to Fe³⁺ ions.

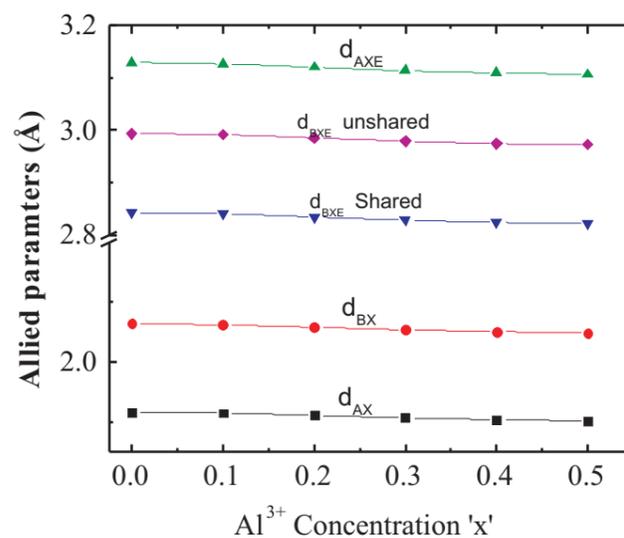


Figure 6. Allied parameters with concentration 'x' for $Mn_{0.5}Zn_{0.5}Al_xFe_{2-x}O_4$

4.CONCLUSIONS

$Mn_{0.5}Zn_{0.5}Al_xFe_{2-x}O_4$ and $Mg_{0.5}Zn_{0.5}Cr_xFe_{2-x}O_4$ were successfully synthesized by sol-gel method. Lattice constant is decreased with increasing Al and Cr³⁺ substitution. Ion jump lengths are decreased with increasing Al³⁺ and Cr³⁺ substitution, which suggests that the length between the magnetic particles of the constituent ions in the respective systems is decreases. Allied parameters are also shows similar trend to that of lattice constant suggesting the strong relation of its variation with ionic radii of the substituted ion.

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