

## Study of Cation Distribution in $\text{Cu}_{0.7}(\text{Zn}_{0.3-x}\text{Mg}_x)\text{Fe}_{1.7}\text{Al}_{0.3}\text{O}_4$ by X-ray Diffraction Using Rietveld Method

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A series of ferrite samples of the chemical composition  $\text{Cu}_{0.7}(\text{Zn}_{0.3-x}\text{Mg}_x)\text{Al}_{0.3}\text{Fe}_{1.7}\text{O}_4$  ( $x=0.05, 0.1, 0.15, 0.2$  and  $0.25$ ), prepared by ceramic technique at  $1000^\circ\text{C}$ , were found to have cubic spinel structure. On applying the full pattern fitting of Rietveld method using FullProf program, exact coordinates of atoms, unit cell dimensions, atom occupation factors, interatomic distances as well as crystallite size and residual microstrain have been determined. It was found that the lattice parameter decreases with increasing the Mg content, which may be attributed to the influence of the difference between the ionic radius of Mg and Zn cations. Also, the variation of the cation distribution has been discussed on the basis of site preference, size and valence of the substituting cations. The low values of the isotropic microstrain may be attributed to the method of the preparation in which the samples after the last sintering were treated by annealing.

### Introduction:

Copper ferrite crystallizes as a spinel structure. The spinel ferrite unit cell is based on a closed packed oxygen lattice, where metal cation reside on 8 of 64 tetrahedral sites (A-sites) and 16 of the 32 octahedral sites (B-sites). Spinel copper ferrite shows a remarkable variation in its atomic arrangement depending critically on the thermal history of the preparation [1,2] and may be attributed to the distribution of Cu and Fe cations between the two nonequivalent lattice A- and B-sites. Accordingly, the molecular formula of that ferrite can be written as [3]



where  $\delta=1$  for normal spinel, i.e. the divalent metal ion occupies the tetrahedral site and the trivalent ion occupies the octahedral site;  $\delta=0$  for inverse or distorted spinel and  $\delta$ =fraction for random distribution. The obtained type, depends on the method of preparation and is variable with the preparation temperature and type of cations. It has been pointed out that the distribution and the valence of the metal cations on these sites determine the material magnetic and electric properties.

The aim of the present work is to study the effect of type, and content of the replacing cations on their distribution, between two lattice sites (A&B) in copper ferrite spinel structure. Also, the microstructural characteristics (crystallite size and microstrain) will be investigated using X-ray diffraction and program for full pattern structure refinement of Rietveld method. In this respect, the Cu cation is replaced partially by two types of divalent atoms and the Fe atom by a trivalent cation in order to prepare a ferrite with general formula  $\text{Cu}_{0.7}(\text{M}^{\text{II}}_{3-x} \text{M}^{\text{III}}_x)\text{Fe}_{1.7} \text{M}^{\text{III}}_{0.3}\text{O}_4$ . This structure study will be correlated with the magnetic and electrical properties of the investigated ferrites in future.

### Experimental and Computational Work:

The divalent atoms that selected to partially substitute Cu in the corresponding ferrite were Mg and Zn, and the trivalent atom Al to substitute partially was. The proposed ferrite samples were prepared by ceramic technique using highly pure materials CuO,  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, Al(OH)<sub>3</sub>, MgO and ZnO. Weighted materials, mixed well in molar ratios, were ground to very fine powder in corundum mortar in order to prepare compounds with the chemical formula,  $\text{Cu}_{0.7}(\text{Zn}_{0.3-x} \text{Mg}_x) \text{Al}_{0.3}\text{Fe}_{1.7}\text{O}_4$  [ $x = 0.05, 0.1, 0.15, 0.2$  and  $0.25$ ].

The mixtures were calcined at 800 °C for 6 hours in air, followed by grinding, pressing into disks under pressure of 15 tons/cm<sup>2</sup> and sintered in air at different temperatures (900, 950, 1000, 1050 and 1100 °C) for 6 hours rate of heating 4°C/min. The sintered samples at each temperature were tested by X-ray diffraction to ensure the formation of one phase of spinel structure. Among these samples only those sintered at 1000 °C gave a one phase spinel structure. Then all the proper samples were ground, pressed in the same manner and sintered at 1000 °C for 14 hours in air. All the diffraction patterns were indexed using (Treor) program to calculate the accurate unit cell dimension.

Powder X-ray diffraction data were collected on computer controlled X-ray diffractometer (formely made by Diano corporation, USA) using step scanning mode and filtered Co  $k_{\alpha}$ -radiation. The scanning range was 15-128.5° (2 $\theta$ ), with step size=0.02° (2 $\theta$ ) and counting time=8 second per step.

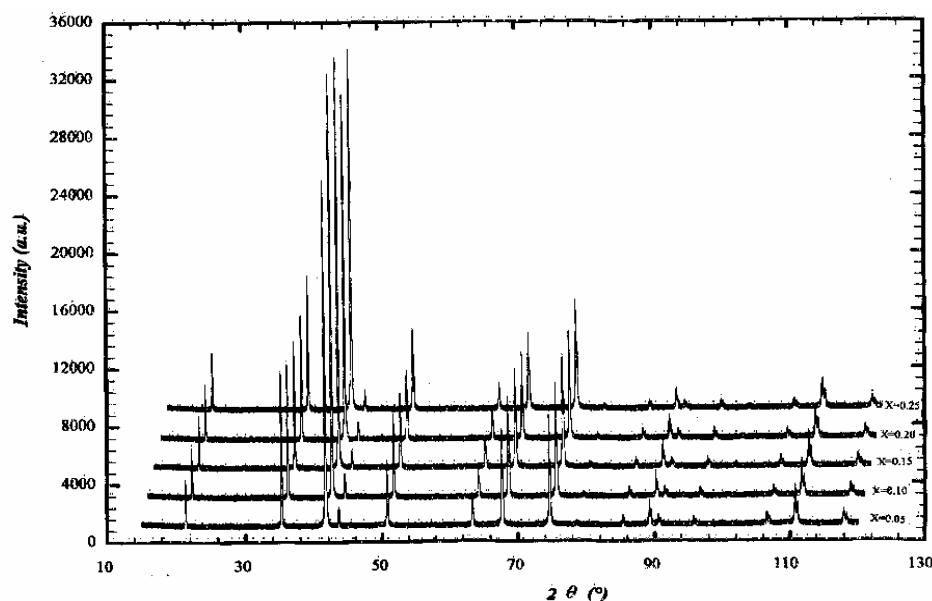


Fig. (1): X-ray powder diffraction patterns of the substituted Cu-ferrite compounds

Using FullProf program [4], the refinement of the first sample was started using a model taken from literature [5], in which the space group is  $Fd\bar{3}m$ ; its origin is at  $\bar{4}3m$  at  $-1/8, -1/8, -1/8$  from the centre  $\bar{3}m$ , and the oxygen anions occupy position 32b, while the tetrahedral and octahedral sites occupy the positions 8f and 16c, respectively. This model was not succeeded to refine the structure because of the absence of the calculated (400) reflection and high discrepancy factor obtained after many unsuccessful trials, have been

done to refine the structure. Therefore, the alternative origin of the space group was taken for the model which has the origin at the centre  $\bar{3}m$ , at  $1/8, 1/8, 1/8$  from  $\bar{4}3m$  in which, the oxygen atom occupies the 32e position with fractional coordinates,  $1/4, 1/4, 1/4$ ; A-site at 8f and B-site at 16c positions. The experimental profile was fitted by modified THOMPSON COXHASTING PESUDO-VOIGT function [6,7], recommended by the international union of crystallography [8]

$$H_G = (U \tan^2 \theta + V \tan \theta + W + Z / \cos^2 \theta)^{1/2} \quad \text{and} \\ H_L = X \tan \theta + Y / \cos \theta$$

where:  $H_G$  is the Gaussian component of the peak width,  
 $H_L$  is the Lorentzian component of the peak width,  
 $U$  is the Gaussian isotropic microstrain parameter,  
 $V$  and  $W$  are refinable peak width parameters,  
 $Z$  is the Gaussian isotropic crystallite size parameter,  
 $X$  is the Lorentzian isotropic microstrain parameter, and  
 $Y$  is the Lorentzian isotropic crystallite size parameter.

In the first step of the refinement the global parameters (2 $\theta$ -zero, instrumental profile, profile asymmetry, background, specimen displacement) were refined. In the next step, the structure parameters (atomic coordinates, specimen profile breadth parameter, lattice parameter, preferred orientation and site occupancy) were refined in sequence mode. The site occupancy in the two positions (octahedral and tetrahedral sites) were constrained in order to keep the sum of the same cations in the two sites always have its stoichiometric value.

In the last cycle, when the discrepancy factor  $R_{wp}$  (R-weight patterns) has reached its minimum value, all the parameters (global and structural) were refined simultaneously giving the goodness of fit, which is given in Table(1). Fig. (2) illustrates observed and calculated X-ray patterns as well as their difference for sample (1) as an example.

It is worth mentioning, that the crystallite size was treated in the refinement process as it only has Lorentzian in character, which is independent on the order of reflection. While the microstrain has Gaussian in character.

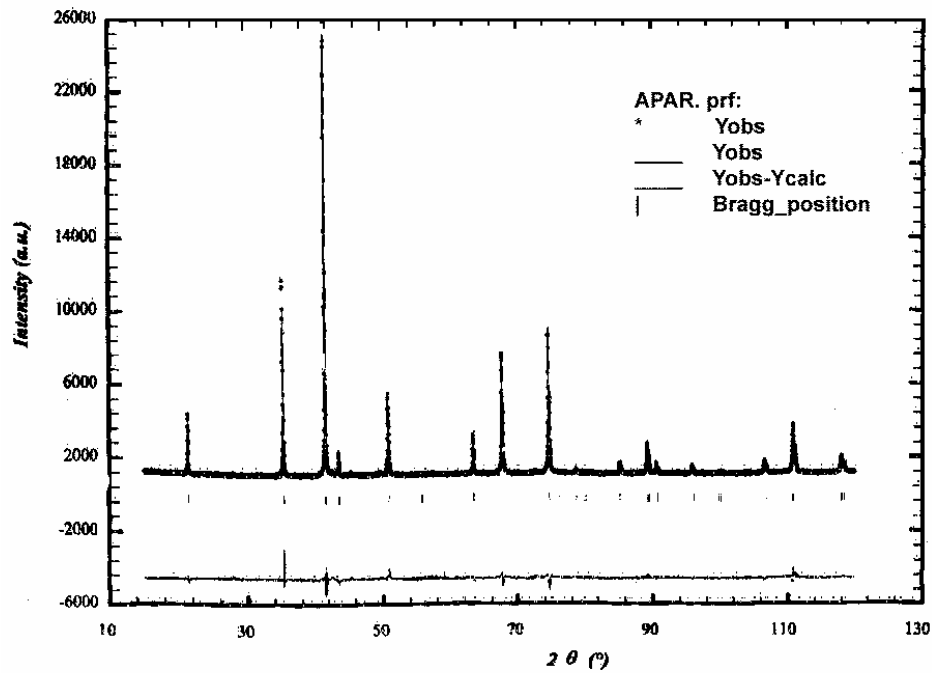


Fig. (2) : The relation between observed and calculated X-ray patterns as well as their difference for sample (1).

### Results and Discussion:

All the results obtained from the refinement of the structure are correlated with the  $x$ -parameter. Table (2) shows the variation of the lattice parameter of the investigated samples as a function of magnesium concentration, which is represented graphically in Fig.(3). It is clearly shown, that the lattice parameters exhibit a continuous decrease with increasing magnesium content, i.e. decreasing zinc content. This may be logically attributed to the difference between the ionic radius of Zn and magnesium cations, where the Mg concentration of radius ( $0.71 \text{ \AA}$ ) increases on the expense of Zn concentration of radius ( $0.74 \text{ \AA}$ ) results in the reduction of the unit cell volume.

The refined values of atomic coordinates and occupancy in addition to the inversion parameter  $\delta$  (Fe occupancy in the tetrahedral site) are given in Table (3). The final results of Rietveld refinement show that  $\text{Al}^{3+}$  ions that substitute  $\text{Fe}^{3+}$  preferentially occupy the octahedral site (B-site), in consistent with the work given elsewhere [9-11], that  $\text{Al}^{3+}$  ions have a strong B-site

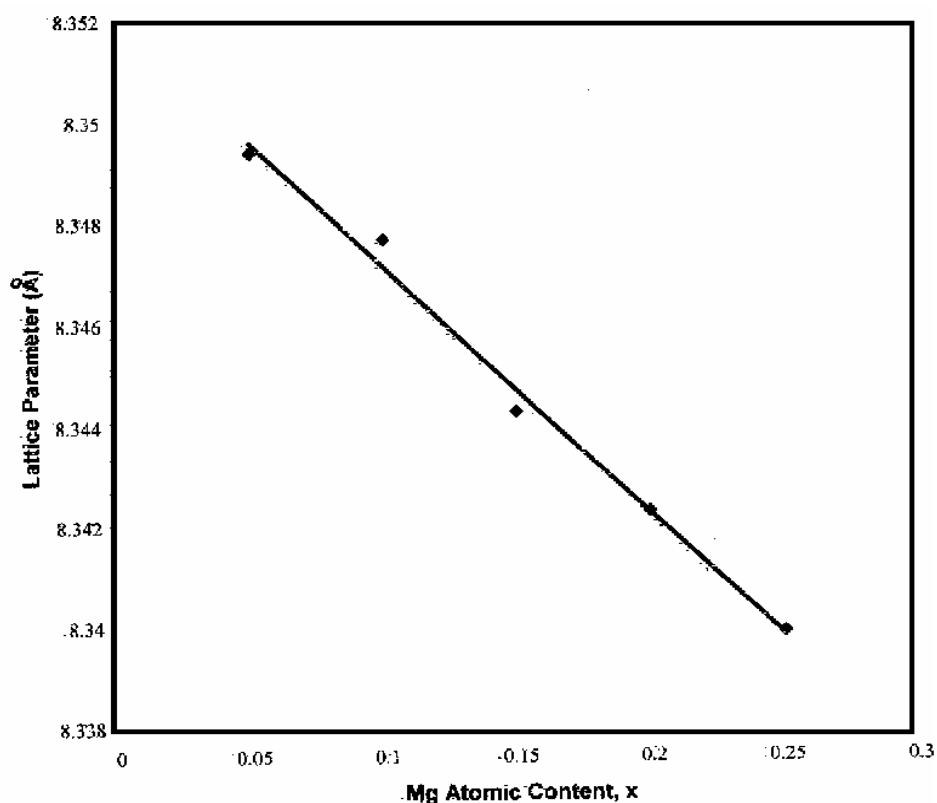


Fig. (3): The relation between lattice parameter and magnesium atomic content.

preference. As a result some  $\text{Cu}^{2+}$  ions migrate from B-site to A-site, as demonstrated in Table (3) sample number (1). On the other hand, it is well known that  $\text{Zn}^{2+}$  [12] and  $\text{Mg}^{2+}$  [13] have a strong A-site preference. Only  $\text{Cu}^{2+}$  and  $\text{Fe}^{3+}$  are distributed randomly between the two sites in such a way governed by the presence of different concentrations of  $\text{Zn}^{2+}$  and  $\text{Mg}^{2+}$  ions. It is clearly shown that  $\text{Cu}^{2+}$  ions have its maximum occupancy value at B-site when the Mg content is low (sample No.1) and then continuously migrate from B-site to the A-site with increasing the Mg content. While, Cu occupancy reaches minimum value in sample No. 5, where the Mg content has its maximum value. At the same time, some of  $\text{Fe}^{3+}$  ions transfer from the A-site to the B-site in order to balance the relative occupancy given by the space group. In other words, the increase of the Mg content forced the structure of these compounds to be normal spinel. This is clearly shown from many parameters obtained during the refinement of the structures, Particularly, the degree of inversion which is linearly decreased with increasing Mg content, as shown in Fig.(4).

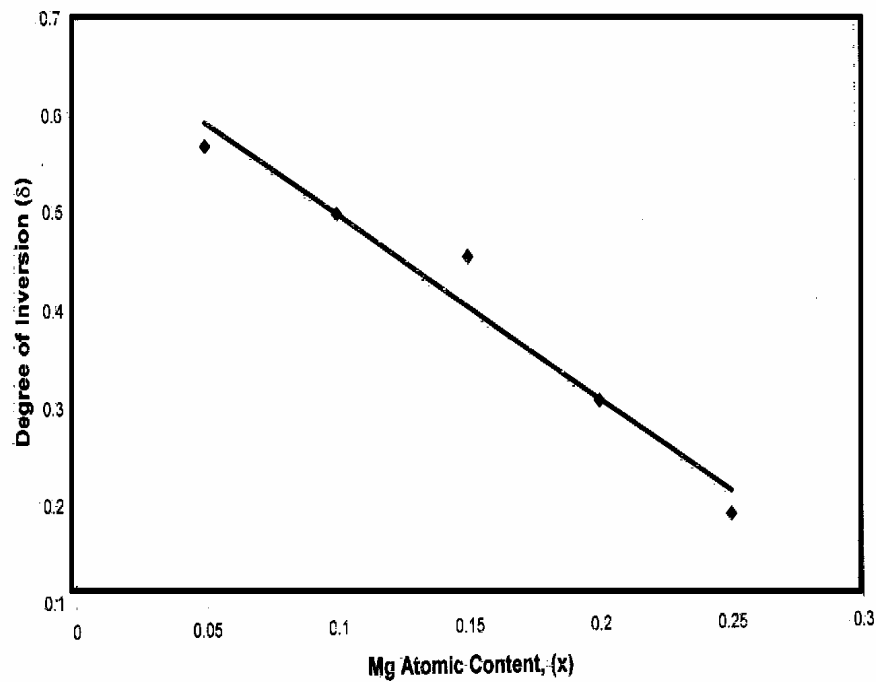


Fig. (4): The relation between Mg content and degree of inversion (iron content at tetrahedral site).

The tendency of Zn cation to occupy its preference site is consistent with that Blasse [14] where its electronic configuration has marked preference for the tetrahedral site, since their 4s and 4p or 5s and 5p electrons can form covalent bond with the 2p electron of oxygen ion. On other hand, it may suggested, that the increase of the Mg content will increase the tendency of the structure to a normal spinel, because the size and the valency of the cations are the important factors to fulfil this tendency. Another reason for this behaviour is that large divalent cations, in our case Mg and Zn, tend to occupy the tetrahedral site as this is favoured by polarization effects of the oxygen atoms intermediate between A and B sites [15]. This means that the tetrahedral sites are expanded by an equal displacement of the 4 oxygen ions outwards along the body diagonal of the cube. At the same time the oxygen ions connected with the octahedral sites move in such a way as to shrink the size of the octahedral site by the same amount as the tetrahedral site expands. This behaviour is reflected in the enlargement of the bond length of the tetrahedral polyhedron as given in Table (4) and depicted in Fig.(5). The discrepancy in the increase of the tetrahedron or the decrease in the octahedron bonds may be attributed to the relative value of the occupancy of both Mg and Zn in the tetrahedral site and particularly to the degree of inversion ( $\delta$ ).

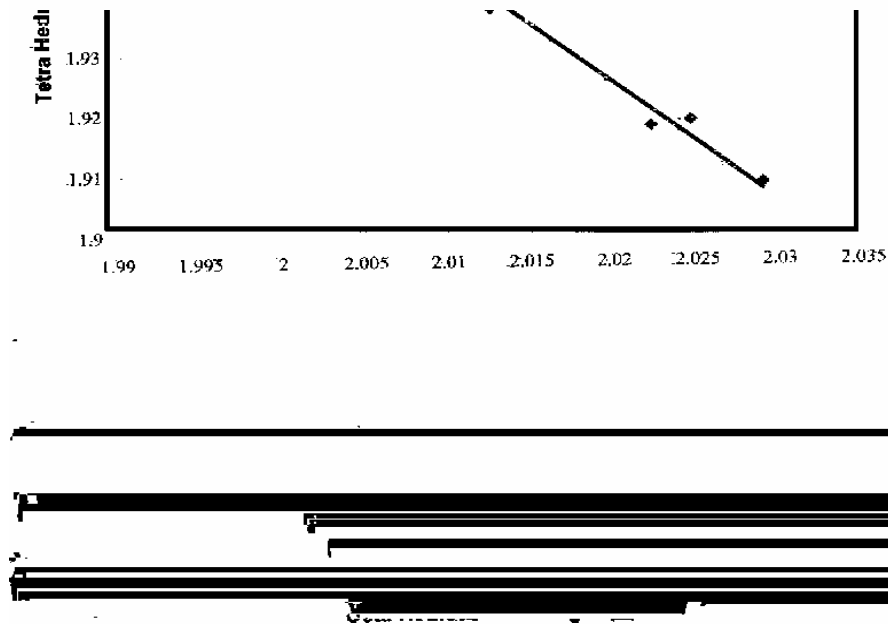


Fig. (5): The relation between tetrahedral bond length and octahedral bond length.

The refinable values of the crystallite size and microstrain of the investigated samples that given in Table (5), indicating large crystallite size and low strain. This may be attributed to the method of preparation, in which the samples after last sintering were subjected to furnace cooling. Comparing with Table(3), it is clearly shown that the crystallite size gradually tends to decrease as the degree of inversion decreases. In contrary , the estimated microstrain value decreases as the degree of inversion increases and this may be attributed not only to annealing process but also to the variation in the substituted cations .

### Conclusions:

**From the refined parameters it can be concluded that**

- 1- The lattice parameter decreases with increasing magnesium content and may be attributed to the small ionic radius of Mg relative to that of Zn.
- 2- The increase in the magnesium content forced the structure of these samples to be normal spinel.
- 3- The bond length increase of the tetrahedral site and the decrease of the octahedral site may be attributed to the relative value of the occupancy of magnesium to zinc in the tetrahedral site and to the degree of inversion.



- 4- The isotropic microstrain introduced in the crystal lattice is due to the variation in ionic radii of the substituting cations.
- 5- The crystallite size tends to decrease as the degree of inversion decreases.

**Table (1):** The values of the discrepancy factor and expected values.

Samples	R <sub>wp</sub>	R <sub>expected</sub>	Chi <sup>2</sup>
1	14.6	9.83	2.210
2	13.6	9.52	2.030
3	14.8	9.61	2.130
4	13.1	10.19	1.650
5	13.6	9.92	1.890

Chi<sup>2</sup> is the goodness of fit index  $Chi^2 = (R_{wp}/R_{expected})^2$ .

**Table (2):** Lattice parameters of the samples.

Magnesium (atomic content., x)	Lattice Parameter (Å)
0.05	8.3494
0.10	8.3477
0.15	8.3443
0.20	8.3423
0.25	8.3399

**Table (3):** Values of atomic coordinates (x,y,z), temperature factor (B), occupancy (g) and degree of inversion (δ).

Atom	Sample (1)		Sample (2)		Sample (3)		Sample (4)		Sample (5)	
	x=y=z	g	x=y=z	g	x=y=z	g	x=y=z	g	x=y=z	g
O	0.2620	4.0000	0.2577	4.0000	0.2570	4.0000	0.2591	4.0000	0.2578	4.0000
Al	0.5000	0.3000	0.5000	0.3000	0.5000	0.3000	0.5000	0.3000	0.5000	0.3000
Fe	0.5000	1.1330	0.5000	1.2049	0.5000	1.2500	0.5000	1.3990	0.5000	1.5174
Cu	0.5000	0.5670	0.5000	0.4951	0.5000	0.4500	0.5000	0.3010	0.5000	0.1826
Zn	0.5000	0.0000	0.5000	0.0000	0.5000	0.0000	0.5000	0.0000	0.5000	0.0000
Fe	0.1250	0.5670	0.1250	0.4951	0.1250	0.4500	0.1250	0.3010	0.1250	0.1826
Cu	0.1250	0.1330	0.1250	0.2049	0.1250	0.2500	0.1250	0.3990	0.1250	0.5174
Zn	0.1250	0.2500	0.1250	0.2000	0.1250	0.1500	0.1250	0.1000	0.1250	0.0500
Mg	0.1250	0.0500	0.1250	0.1000	0.1250	0.1500	0.1250	0.2000	0.1250	0.2500
δ	0.5670		0.4951		0.4500		0.3010		0.1826	

**Table (4):** Bond lengths obtained from powder cell program.

Bond Length Å	Samples				
	1	2	3	4	5
Tet-Tet cation (A-A)	3.6154	3.6146	3.6132	3.6123	3.6113
Tet-Octa cation (A-B)	3.4615	3.4607	3.4593	3.4585	3.4575
Octa-Octa cation (B-B)	2.9520	2.9513	2.9501	2.9494	2.9486
Tetrahedral bond (A-O)	1.9815	1.9186	1.9083	1.9374	1.9177
Octahedral bond (B-O)	1.9921	2.0247	2.0290	2.0127	2.0223

**Table (5):** Microstructural characteristics.

<i>Samples</i>	<b>Microm Strain</b>	<b>Crystallite Size Å</b>
1	0.001152	1573
2	0.001345	1772
3	0.001075	1653
4	0.001334	1548
5	0.001648	1345

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