
Structural Studies in Al^{3+} substituted Cd ferrites

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Abstract

The spinel ferrite series of $Cd_1Al_xFe_{2-x}O_4$ where x varies from $x=0.0$ to 0.5 in the steps of 0.1 were prepared by the conventional ceramic method. The structural characterization was carried out using X-ray diffraction method. The single phase spinel structure was confirmed from XRD patterns. Lattice parameter, X-ray density, porosity, particle size and intensities of diffracted lines were calculated. The intensity ratios of structure sensitive planes have been estimated and considered for cation distribution.

The SEM micro-graph were taken and it showed that grain growth is non-uniform. The percentage compositions of the elements present in the sample were estimated from EDAX. The TEM images of all the ferrite samples have been recorded by ultrasonically agitating the ferrite samples.

Introduction:-

The spinel ferrites have gained enormous importance because of their novel combined electric and magnetic properties. Ferrites are widely used in transformers, ultrasonic generators, modulators, phase shifters, isolators, memory devices, recording devices, sensors etc. nickel ferrite has a inverse spinel structure with collinear ferrimagnetic order. The investigations on the addition of trivalent cations for Fe^{3+} influence the magnetic and electrical properties. In spinels the intra sub-lattice interactions are weaker than the inter sub-lattice interactions. Due to this there are unsatisfied bonds in the ferrimagnetic region which brings various exchange interactions. These exchange interactions in spinels allows variety of magnetic orders. The magnetic order can be controlled by proper cation substitution.

The substitution of magnetic and non-magnetic cations can be done in order to get particular properties resulting from cation distribution in crystal lattice. The substitution for Fe^{3+} by another trivalent cation is one of the most effective means to control saturation magnetization. The effect of cadmium substitution on structural and magnetic properties of nickel ferrite has been studied by K. M. Jadhav et. al. [1]. Electrical Properties of Cadmium Substitution in Nickel Ferrites has been studied by Ande Ashok et. al. [2]. Effects of cadmium on physical and magnetic properties of Co-Cd ferrites has been studied by Sarout Noor et. al. [3].

In the survey of reported work so far, there is no information available to our knowledge about the systemic study of the structural and magnetic properties of mixed magnetic oxides $CdFe_{2-x}Al_xO_4$. Therefore, view of this fact, it is proposed in the present investigation to study the effect of substitution of non-magnetic cation Al^{3+} on the structural and magnetic properties of these mixed ferrites.

Experimental:-

Synthesis:- The spinel ferrite series of $Cd_1Al_xFe_{2-x}O_4$ where x varies from $x=0.0$ to 0.5 in the steps of 0.1 were prepared by the conventional ceramic method. The chemicals for ferrite systems were of analytical grade high purity oxides CdO , Al_2O_3 & Fe_2O_3 were mixed in proper proportion so as to yield the desired stoichiometry composition. Each of these compositions was ground for half an hour in an agate mortar. This mixture was then presintered at $850\text{ }^\circ\text{C}$ for 24 hours then slowly cooled to room temperature. The presintered samples were gain milled to fine powder. The powder was then pressed at around 5 tones/square inch of pressure to form pellets of about 1 cm in diameter. Pellets of good quality were obtained by using poly vinyl alcohol as binder & maintaining the pressure for about ten minutes each time. The pellets were finally sintered at $900\text{ }^\circ\text{C}$ for 24 hours and naturally cooled to room temperature.

Structural study

To study the structural aspects of the prepared ferrite samples the X-ray powder diffraction method was employed. The X-Ray diffraction patterns for all the powdered samples were recorded on X-ray diffractometer by using CuK radiation with wavelength 1.542 \AA . The recorded XRD were used to determine lattice parameter, X-ray density and crystalline size of all the samples. Intensity calculation were carried out and cation distribution was determined using intensity ratios of structure sensitive planes.

The SEM micro-graph of the prepared ferrite samples were taken to know about the nature of grain growth. The percentage compositions of the elements present in the sample were estimated from EDAX. The TEM images of all the ferrite samples have been recorded by ultrasonically agitating the ferrite samples.

Results and discussion:-

Structural Studies

The X-ray diffraction patterns of all the six samples of the $\text{Cd}_1\text{Al}_x\text{Fe}_{2-x}\text{O}_4$ system are shown in figures (1). The X-ray diffraction patterns confirm the single phase spinel formation. The reflections from different planes in the XRD pattern indicate the cubic spinel structure of the samples. The Lattice parameter ' a_{cal} ' of each of the sample was calculated using the X-ray data and the same is listed in table (1). The lattice parameter is found to decrease with increase in Al^{3+} concentration in the composition. The ionic radius is found to influences the lattice parameter. The ionic radii r_A & r_B (of the tetrahedral site & octahedral site respectively) have been calculated considering the cation distribution. Theoretical values of the lattice parameter ' a_{th} ' have been determined using the following relation [4]

$$a_{\text{th}} = \frac{8}{3\sqrt{3}} [(r_A + R_0) + \sqrt{3}(r_B + R_0)] \quad \text{----- 1}$$

Where is r_A is the ionic radii of the tetrahedral site, r_B is the ionic radii of octahedral site and R_0 is the radius of oxygen ion [5].

The lattice parameter ' a_{th} ' calculated using relation 1 is listed in table (1). The ionic radii r_A of tetrahedral site, r_B of octahedral site and the average ionic radii have been calculated and are listed in table (2). The decrease in r_B with increase in Al^{3+} is due to the replacement of larger Fe^{3+} (0.64 \AA) by smaller Al^{3+} (0.51 \AA) on the B- site [6]. The octahedral site plays a dominant role in influencing the lattice parameter. The average ionic radius decreases with increase in Al^{3+} content. This accounts for the decrease in lattice parameter with (x). Thus the decrease in lattice parameter with increase in Al^{3+} content may be attributed to the replacement of larger Fe^{3+} (0.64 \AA) by smaller Al^{3+} (0.51 \AA) ions. The values of theoretical and observed lattice parameter are listed in table (1). These values are comparable with the values reported in literature [7,8].

The X-ray densities (d_x) of all the samples were calculated by using the formula [9]

$$d_x = \frac{ZM}{NV} \text{ gm/cm}^2 \quad \text{----- 2}$$

where 'Z' is number of molecules per unit cell (here $Z=8$), 'M' is molecular weight of the sample, 'N' is Avogadro's number and 'V' is volume of the unit cell.

The X-ray densities (d_x) are tabulated in the table (3). It can be seen from the table that the X-ray density decreases with increasing Al^{3+} . The bulk density also reflects the same behavior as X-ray density. This decrease in density with increase in Al^{3+} content can be ascribed to the atomic weight and density of Al^{3+} ($27, 2.79 \text{ gm/cm}^3$), which is lower than that of Fe^{3+} ($55.8, 7.87 \text{ gm/cm}^3$).

The crystalline size of all the samples was calculated by using Scherer's formula [10]. The crystalline size of all the samples is given in table (3). It can be observed from the table that the crystalline size varies in the range of 225 \AA to 375 \AA with average crystalline size 297 \AA which is consistent with the crystalline size of ceramically prepared systems.

The percentage porosity (%P) of all the samples have been calculated by using the formula given by Standly K.J. [11]. The values of percentage porosity (%P) are d listed in table (3). From the table it can be seen that porosity is found to be 30% to 40%, which is in good agreement with the values reported by R.G.Dorie etal. [12].

The cation distribution was determined on the basis of X-ray intensities and the saturation magnetization. The X-ray intensities were calculated by using the formula given by Burger [13].

$$I_{hkl} = \left| F_{hkl} \right|^2 \cdot P \cdot L_p \text{ ----- } 5$$

Where, F_{hkl} is structure factor, P is multiplicity factor and L_p is Lorentz polarization factor.

The distribution of divalent and trivalent ions among the tetrahedral and octahedral sites in the $Cd_1Al_xFe_{2-x}O_4$ system are determined by considering the ratios of intensities for structure sensitive planes [14-17]. The intensity ratios of the planes : I(220)/I(400), I(422)/I(400) and I(440)/I(422) are structure sensitive [18]. These ratios have been considered to determine cation distribution besides saturation magnetization. The estimated cation distributions are given in table (4). It is evident from the table that the trivalent Al^{3+} ion replaces Fe^{3+} ion in the octahedral B site. The divalent Cd^{2+} occupies the tetrahedral A site as it has strong preference for A site. The same trend is reported by number of researchers.

Scanning electron micrograph for the all samples are shown in figure (2) The SEM micro-graph shows that grain growth is non-uniform. The structure is crystalline in nature which is typical of spinel ferrites prepared by ceramic method. The percentage compositions of the elements present in the sample were estimated from EDAX. Typical EDAX pattern of $Cd_1Al_xFe_{2-x}O_4$ for $x = 0.2$ is shown in figures. (3). It is evident from the values given in Table (5) that all the samples were formed with the desired stoichiometry and purity within experimental errors.

The TEM images of all the ferrite samples have been recorded by ultrasonically agitating the ferrite samples. Figure (4) shows typical TEM micrograph of the prepared system. It can be seen from the figure that there is a formation of highly agglomerated particles. The agglomeration of the particles might have resulted during annealing from the driving force provided by the net decrease in the solid–solid and the solid–vapour interface free energy.

Conclusions

The system $Cd_1Al_xFe_{2-x}O_4$ with $x = 0.0$ to 0.5 (with step of 0.1) has a single phase spinel structure. The Lattice parameter decreases with increase in Al^{3+} content. The cation distribution indicates that Al^{3+} has preference for B-site. The X-ray density decreases with increasing Al^{3+} . The bulk density also reflects the same behavior as X-ray density. The crystalline size varies in the range of $225A^\circ$ to $375A^\circ$ with average crystalline size $297 A^\circ$. The porosity is found to be 30% to 40%. The cation distribution shows that the trivalent Al^{3+} ion replaces Fe^{3+} ion in the octahedral B site. The divalent Cd^{2+} occupies the tetrahedral A site as it has strong preference for A site. The SEM micro-graph shows that grain growth is non-uniform. The TEM images show that there is a formation of highly agglomerated particles.

References

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Figures

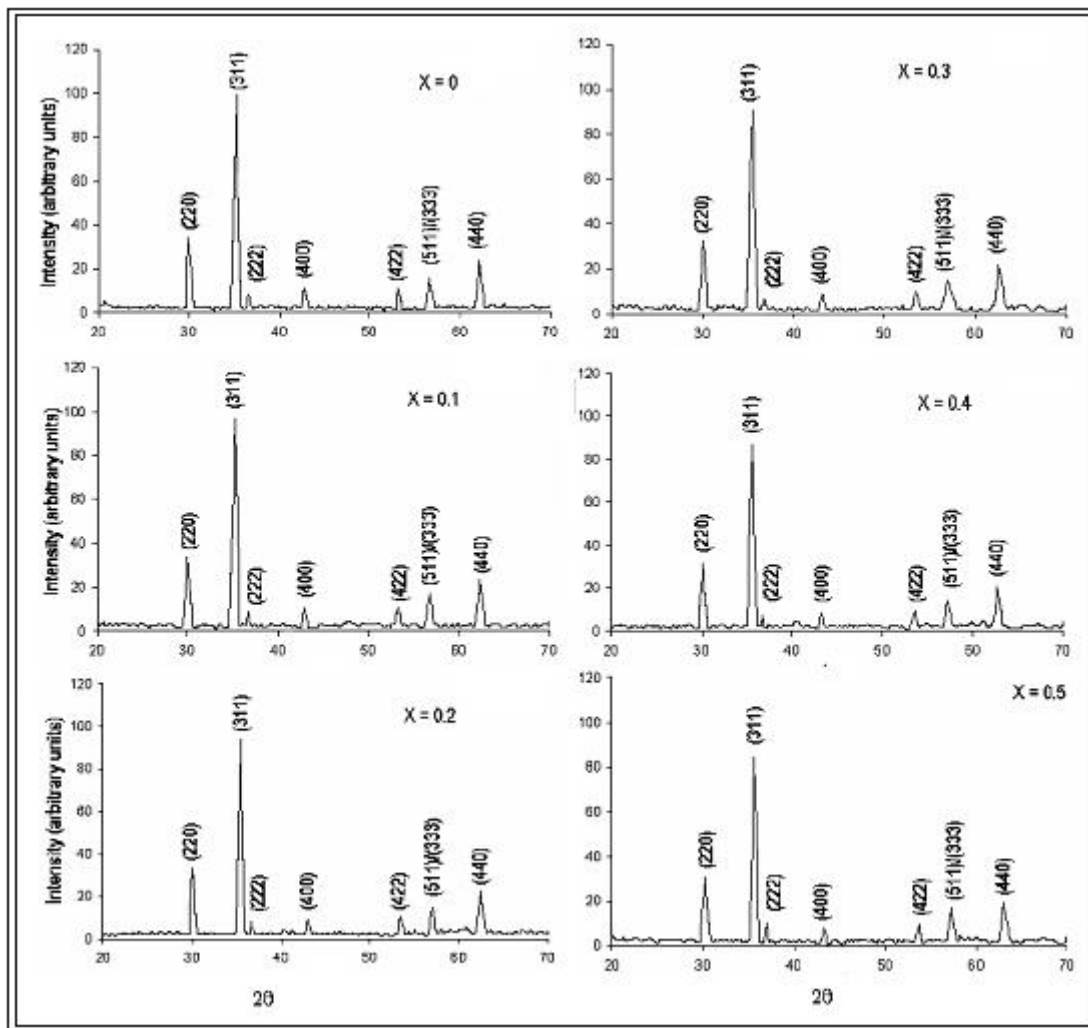


Fig. 1. Typical X-ray diffractograms of the $\text{Cd}_1\text{Al}_x\text{Fe}_{2-x}\text{O}_4$ system.

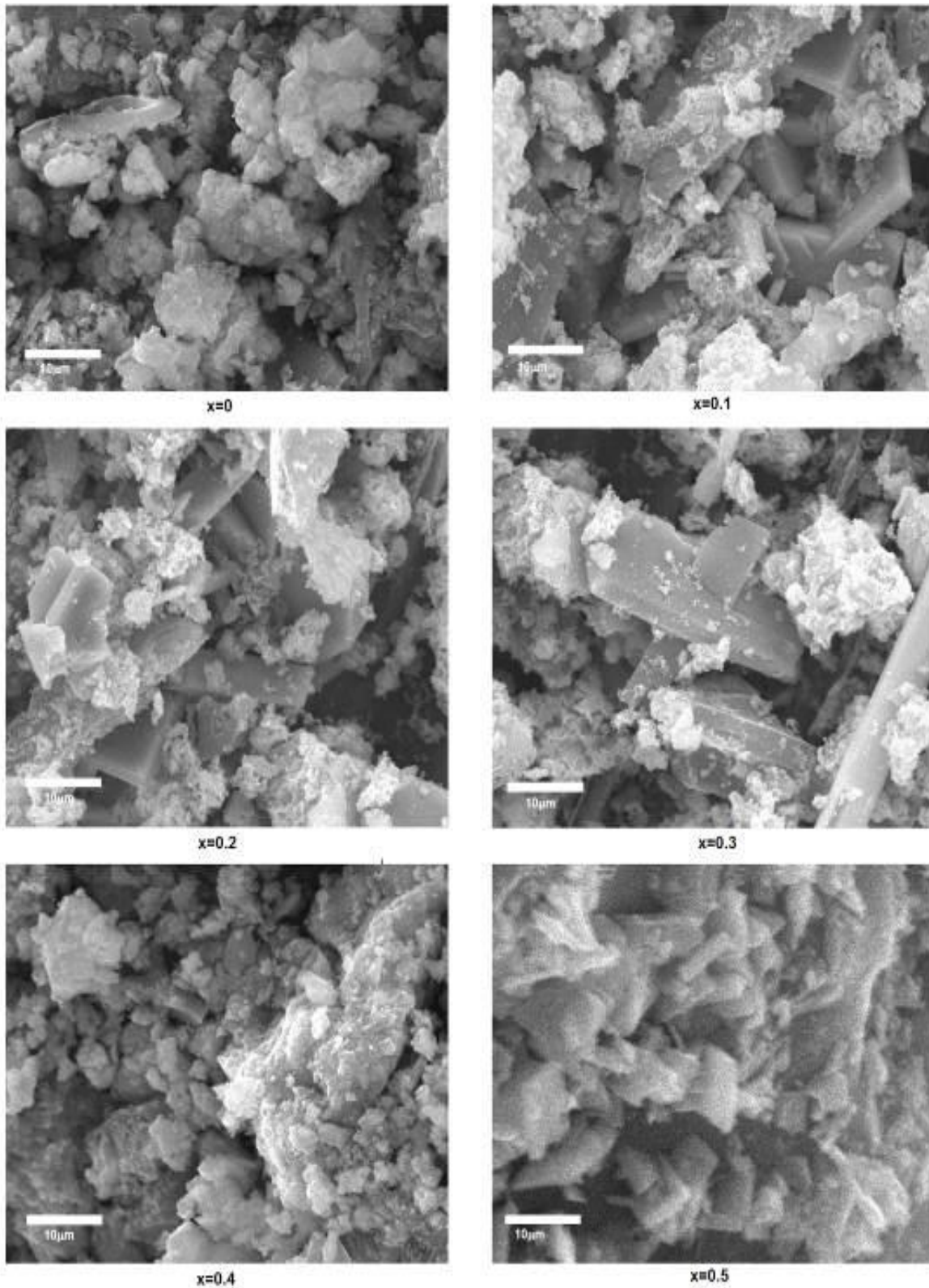


Figure 2 Typical SEM images of Cd₁Al_xFe_{2-x}O₄

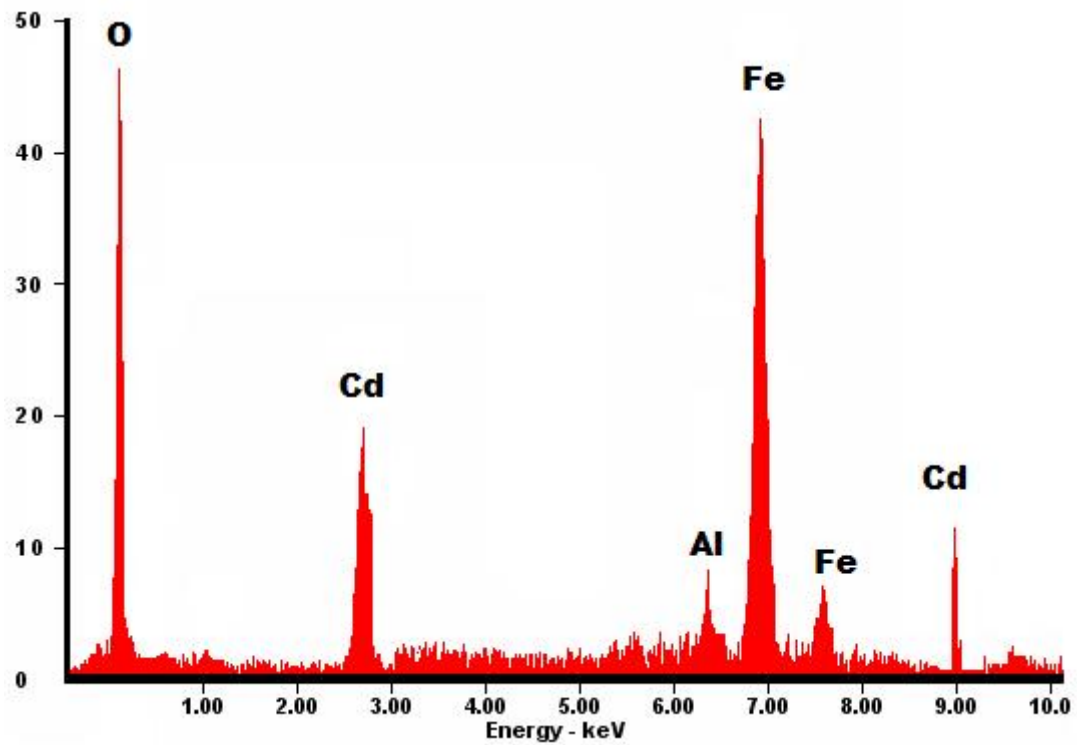


Figure 3. Typical EDAX pattern of $Cd_1Al_xFe_{2-x}O_4$ for $x = 0.2$ 3

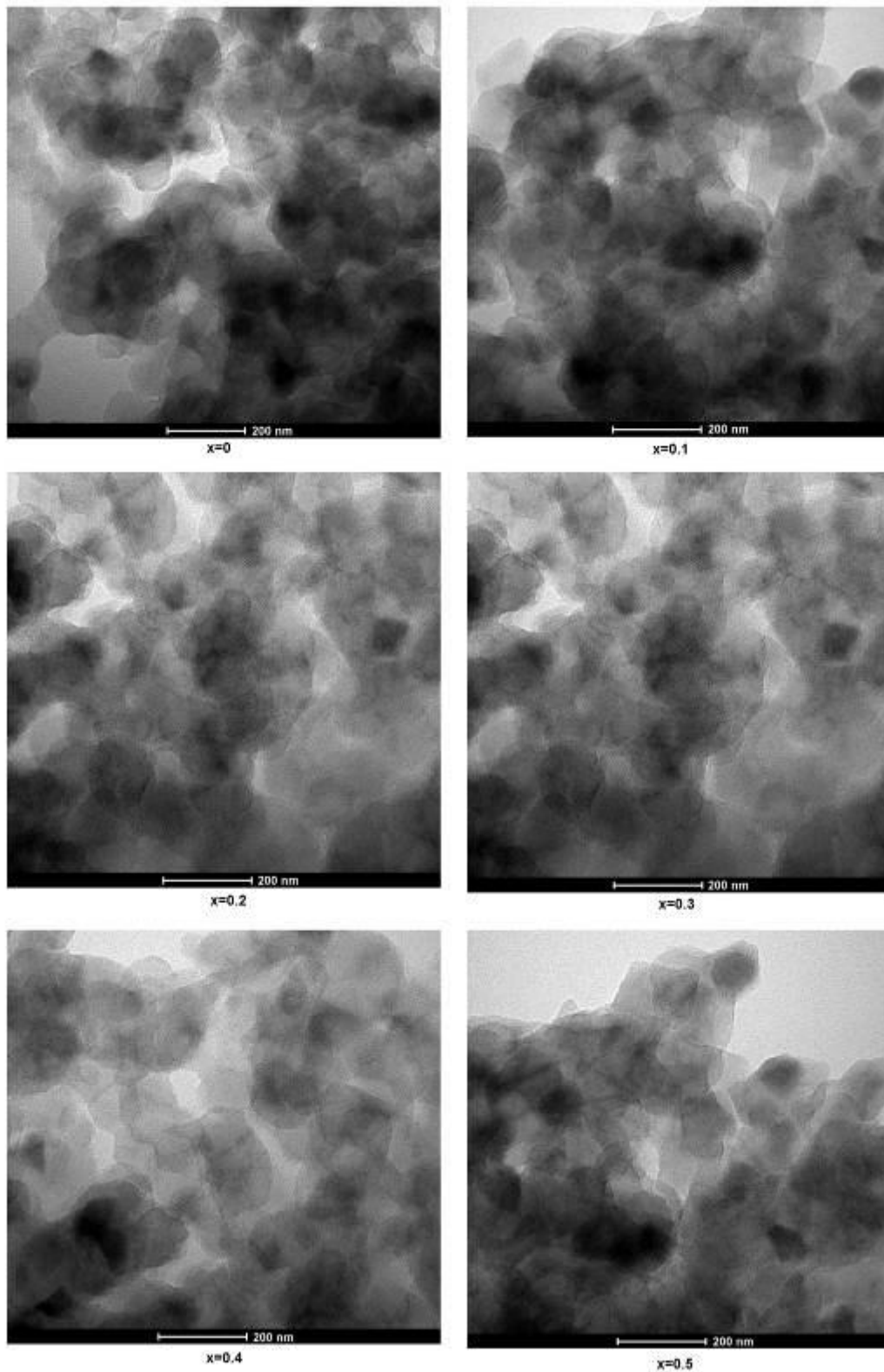


Figure 4. Typical TEM images of $Cd_1Al_xFe_{2-x}O_4$

Tables

Composition (x)	Lattice parameter	
	a _{th.} Å	a _{cal.} Å
0	8.74	8.73
0.1	8.73	8.71
0.2	8.71	8.69
0.3	8.69	8.67
0.4	8.67	8.65
0.5	8.65	8.63

Table 1. Variation of Lattice parameter with Al concentration.

Composition (x)	r _A (Å)	r _B (Å)	r (Å)
0	0.97	0.64	0.805
0.1	0.97	0.634	0.802
0.2	0.97	0.627	0.799
0.3	0.97	0.621	0.796
0.4	0.97	0.614	0.972
0.5	0.97	0.608	0.789

 Table 2. Variation of ionic radii r_A of A-site, r_B of B-site and r the average ionic radii with Al concentration.

Composition (x)	X-ray density dx.gm/cm ³	Bulk density d gm/cm ³	Particle Size t. Å	Porosity %
0	5.774	3.906	333.7	32
0.1	5.775	3.765	303.4	35
0.2	5.736	3.623	371	37
0.3	5.717	3.511	238	39
0.4	5.697	3.491	256.9	39
0.5	5.677	3.408	278.4	40

Table 3. Variation of X-ray density, particle size and %porosity

(x)	Cation Distribution	
	A-Site	B-Site
0	(Cd ₁)	(Fe ₂)
0.1	(Cd ₁)	(Al _{0.1} Fe _{1.9})
0.2	(Cd ₁)	(Al _{0.2} Fe _{1.8})
0.3	(Cd ₁)	(Al _{0.3} Fe _{1.7})
0.4	(Cd ₁)	(Al _{0.4} Fe _{1.6})
0.5	(Cd ₁)	(Al _{0.5} Fe _{1.5})

Table 4. Cation distribution and intensity ratios.

Composition x	O %	Fe %	Al %	Cd %
0.0	22.21	38.76	0	39.02
0.1	22.44	37.19	0.94	39.41
0.2	22.67	35.58	1.93	39.81
0.3	22.90	33.98	2.88	40.23
0.4	23.14	32.31	3.90	40.63
0.5	23.37	30.60	4.94	41.07

Table 5. Percentage compositions of the elements from EDAX for $Cd_1Al_xFe_{2-x}O_4$ system.