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Evaluation of Structural Properties of Calcium Hexaferrites on the Basis of Synthesis Method

Ch. Mamatha

Department of Physics, Sri Venkateshwara College of Engineering, Bangalore, India

ABSTRACT

In the new age of technologies, the necessity of new magnetic materials inspired researchers to carry the study on hexagonal ferrites largely due to their extensive applications as magnetic materials. Ferrites have become vital for both commercial and technological usages. Their applications are based on very basic properties viz., saturation magnetization, high electrical resistivity, low electrical losses and chemical stability. Diminution to nanosize, unique and technologically thought-provoking properties have been obtained. On the other hand, nanoparticles could be modified with various structures by different synthesis methods and substitutions to enhance their properties. Most common applications are magnetic recording, data storage materials, ferrofluids and drug delivery. In the present work, aluminum substituted calcium hexaferrite nanoparticles were successfully synthesized in two different methods visualized as solution combustion and hydrothermal synthesis to attain elite results. Structural properties are characterized by XRD, SEM and TEM. XRD data of all the samples have confirmed the formation of single-phase M-type hexagonal ferrites with the space group of $P6_3/mmc$. Grain size, lattice parameters and volume of the samples are calculated. SEM analysis revealed that the particles are of uniform grain morphology and nano in size. Although the compound is same, based on the synthesis method structural properties are found to be different. Particle size and shape are different in two methods.

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KEYWORDS
Hexaferrite; combustion; hydrothermal

1. Introduction

Ferrites are large class of oxides with excellent magnetic properties, which have been investigated and applied for the past few decades. The formation of the hexagonal ferrites is an extremely complex process. Methodologies to formulate hexagonal ferrites are pretty complex in nature. Despite several investigations by many researchers over the years, the right and simplified methods have not been derived [1–4]. Currently, to prepare hexagonal ferrite nanoparticles, various synthesis methods such as chemical co-precipitation [5], hydrothermal [6], sol–gel [5–7], solution combustion synthesis [8], etc. have been developed. In the present work, calcium hexaferrites substituted with trivalent Al ions are synthesized in two different methods such as hydrothermal and solution combustion. Their structural properties are studied and reported.

CONTACT Ch. Mamatha mamathasree@yahoo.co.in
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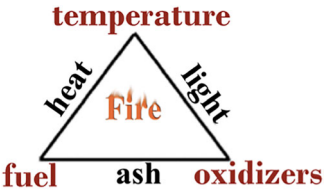

Figure 1. Combustion process.

Ferrimagnetic oxides or ferrites are ceramic ferrimagnetic materials which are dark brown or gray in appearance and very hard and brittle in character. They are prepared by heat-treating the various transition metal oxides or alkaline earth oxides with the ferric oxides. The magnetic behavior exhibited by the ferrites is called ferrimagnetism, which is quite different from ferromagnetism that is exhibited by metallic substances. Substituted hexaferrites belonging to the family of magnetoplumbite with general formula M ($Fe_{12}O_{19}$) where M is usually barium, strontium, calcium or lead, are fascinating due to their specific magnetic behavior. The basic structure consists of 38 oxygen ions occupying the interstitial sites forming a close packed hexagonal structure. Twenty-four ferric ions occupy five different locations in the unit cell in which 2a, $4f_2$ and 12k are octahedral, $4f_1$ is tetrahedral and 2b is bi-pyramidal [9,10].

In the current scenario, hydrothermal synthesis is gaining significance as a relatively convenient way of making hexaferrite nanoparticles. In hydrothermal synthesis a solution of metal salts and a base are autoclaved under pressure to give the final product. The product is often a mixed phase containing unreacted precursors, and sometimes a-Fe_2O_3, which are removed by washing with dilute HCl [11].

Combustion synthesis is also known as self-propagating high temperature synthesis (SHS). To ignite the process, an oxidizer, a fuel, and the right temperature are needed. All these three essentials make up a fire triangle as shown in Figure 1. Fire can be described as an abandoned combustion, which produces heat, light, and ash [1]. The process makes use of highly exothermic redox chemical reactions between an oxidizer and a fuel [11].

2. Experimental

A series of M-type aluminum substituted calcium hexaferrites with general formula $CaAl_xFe_{12-x}O_{19}$ ($x = 0, 1, 2, 3, 4$) are prepared successfully in two different methods, hydrothermal and combustion, to study structural properties.

2.1. Hydrothermal Synthesis

To prepare samples in hydrothermal method, stoichiometric quantities of the AR grade $Ca(NO_3)_2{\cdot}4H_2O$, $Fe(NO_3)_3{\cdot}9H_2O$, $Al(NO_3)_3{\cdot}9H_2O$ and NaOH were used as reactants. Reactants were dissolved in deionized water under vigorous stirring. The solution was poured into Teflon liner held in a stainless steel autoclave, sealed and kept in the oven at 160 °C. Same temperature was maintained for 18 h. After cooling the autoclave to room temperature in natural process, the precipitate obtained was separated by centrifugation gives the calcium ferrite, ionic state of sodium nitrate and water. By repeatedly

washing with ethanol and deionized water in sequence removes the sodium and nitrate ions. The solution was then dried in hot air oven at 80 °C for 3 h. Figure 2 shows the flow of hydrothermal synthesis.

2.2. Solution Combustion Synthesis

The flow of the combustion synthesis is shown in Figure 3. Samples are prepared with AR grade calcium nitrate $Ca(NO_3)_2{\cdot}4H_2O$, iron nitrate $Fe(NO_3)_3{\cdot}9H_2O$, aluminum nitrate $Al(NO_3)_3{\cdot}9H_2O$ and freshly prepared oxalyl dihydrazide ODH ($C_2H_6N_4O_2$)

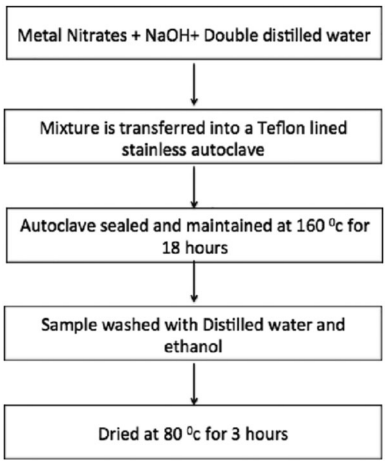

Figure 2. Flow of hydrothermal synthesis.

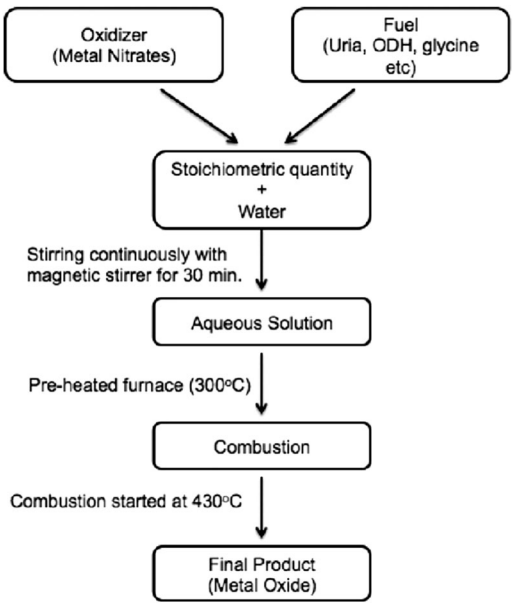

Figure 3. Flow of combustion synthesis.

[12,13]. In solution combustion method, stoichiometric amounts of metal nitrates act as an oxidizing agent and fuel (oxalyl dihydrazide (ODH) [$C_2H_6N_4O_2$]) acts as reducing agent with exothermic reaction. Metal nitrates along with ODH dissolved completely in double distilled water to form an aqueous solution. Combustion process is performed in a muffle furnace and samples are calcined at 900 °C [14].

3. Structural Studies

Structural studies are carried out on powder X-ray diffractometer with step size of 02° in 2° range of 20°–80° at RT. The PXRD pattern of Calcium hexaferrites substituted with aluminum is shown in Figures 4 and 5. X-ray diffraction studies confirm the formation of hexaferrites with the space group $P6_3/mmc$.

The average particle size, *D*, was determined from line broadening of (1 0 7) reflection using Scherrer [3] formula given by

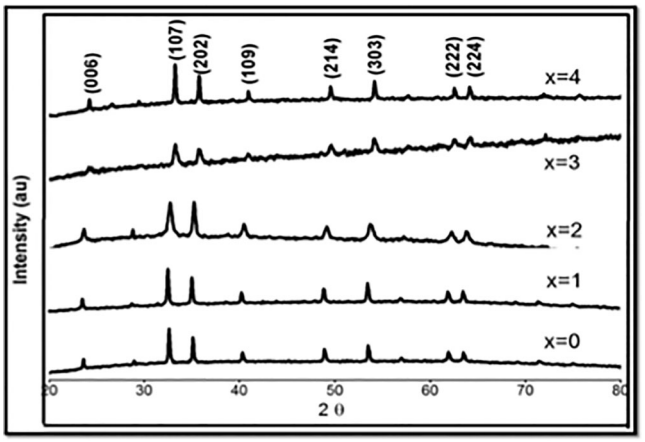

Figure 4. XRD spectrum of samples prepared in hydrothermal synthesis.

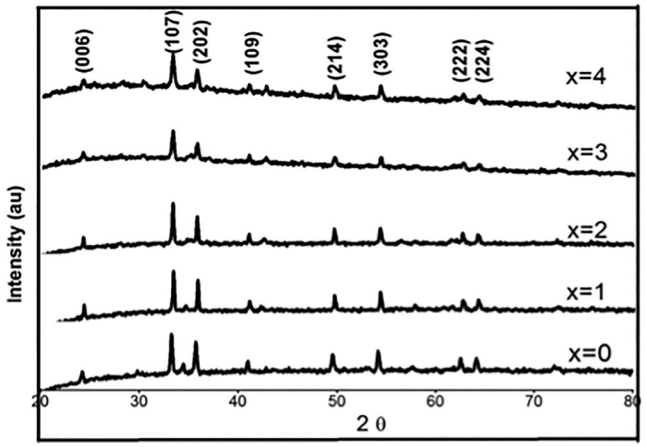

Figure 5. XRD spectrum of samples prepared in combustion synthesis.

Table 1. Structural parameters the samples prepared in combustion synthesis.

Sample	Grain size, D (nm)	Lattice parameters		Volume of the cell, V (Å^3)	c/a
		a (Å)	c (Å)		
$CaFe_{12}O_{19}$	33.43	5.809	22.342	652.89	3.85
$CaFe_{11}AlO_{19}$	30.47	5.803	22.287	649.94	3.84
$CaFe_{10}Al_2O_{19}$	32.59	5.805	22.253	649.39	3.83
$CaFe_9Al_3O_{19}$	30.8	5.986	21.823	677.18	3.64
$CaFe_8Al_4O_{19}$	23.4	5.979	21.949	679.50	3.67

Table 2. Structural parameters the samples prepared in hydrothermal synthesis.

Sample	Grain size, D (nm)	Lattice parameters		Volume of the cell, V (Å^3)	c/a
		a (Å)	c (Å)		
$CaFe_{12}O_{19}$	41.38	5.998	22.856	712.08	3.81
$CaFe_{11}AlO_{19}$	37.61	5.995	22.851	711.22	3.81
$CaFe_{10}Al_2O_{19}$	19.53	5.993	22.844	710.52	3.81
$CaFe_9Al_3O_{19}$	13.36	5.806	22.394	653.74	3.86
$CaFe_8Al_4O_{19}$	38.2	5.816	22.368	655.23	3.85

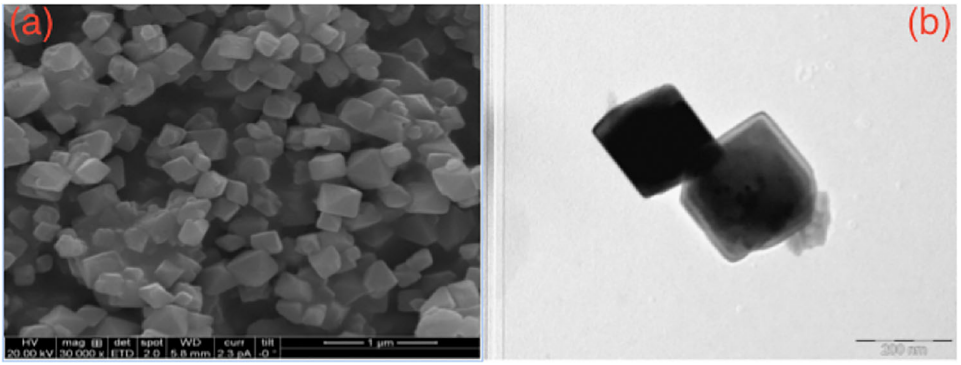

Figure 6. (a) SEM and (b) TEM images of $CaFe_{12}O_{19}$ prepared in hydrothermal synthesis.

$$D = \frac{\mathrm{K}\ \lambda}{\beta\ \cos\theta} \tag{1}$$

where β is the angular line width at half maximum intensity and θ the Bragg angle of the height peak. Structural properties, such as lattice parameters (a, c), particle size (D), volume (V) and c/a ratios are calculated by using following equations [15].

$$\frac{1}{d^2} = \frac{4(h^2 + hk + k^2)}{3a^2} + \frac{l^2}{c^2} \tag{2}$$

$$V_{\text{cell}} = 0.866a^2c \tag{3}$$

4. Results and Discussions

X-ray diffraction spectrum for all the samples prepared in both hydrothermal synthesis and combustion synthesis are shown in Figures 4 and 5. X-ray diffraction studies

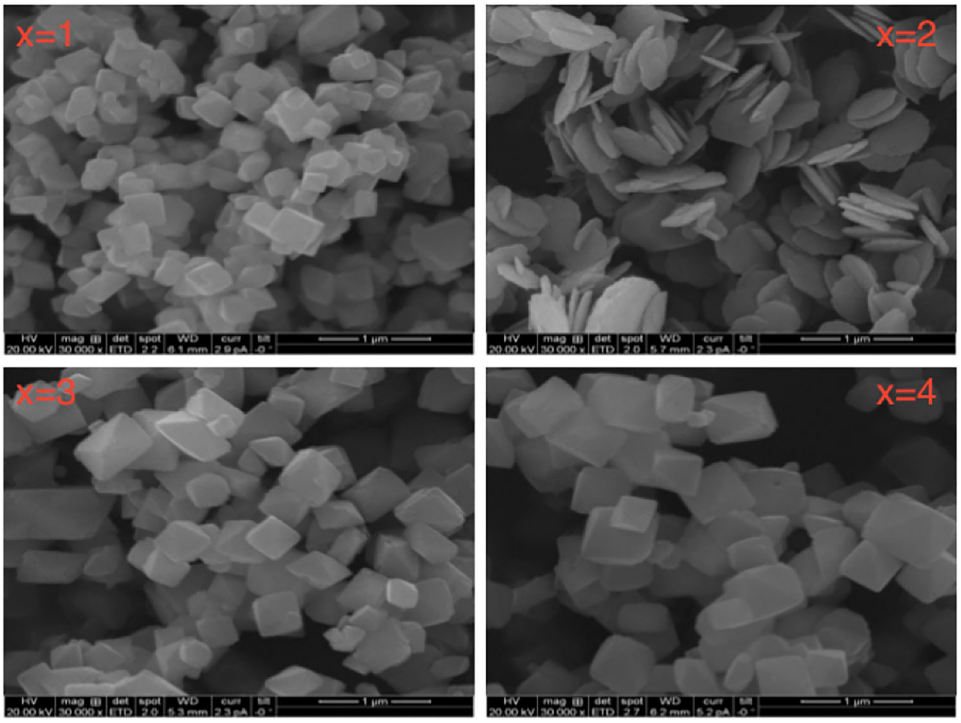

Figure 7. SEM images of $CaAl_xFe_{12-x}O_{19}$.

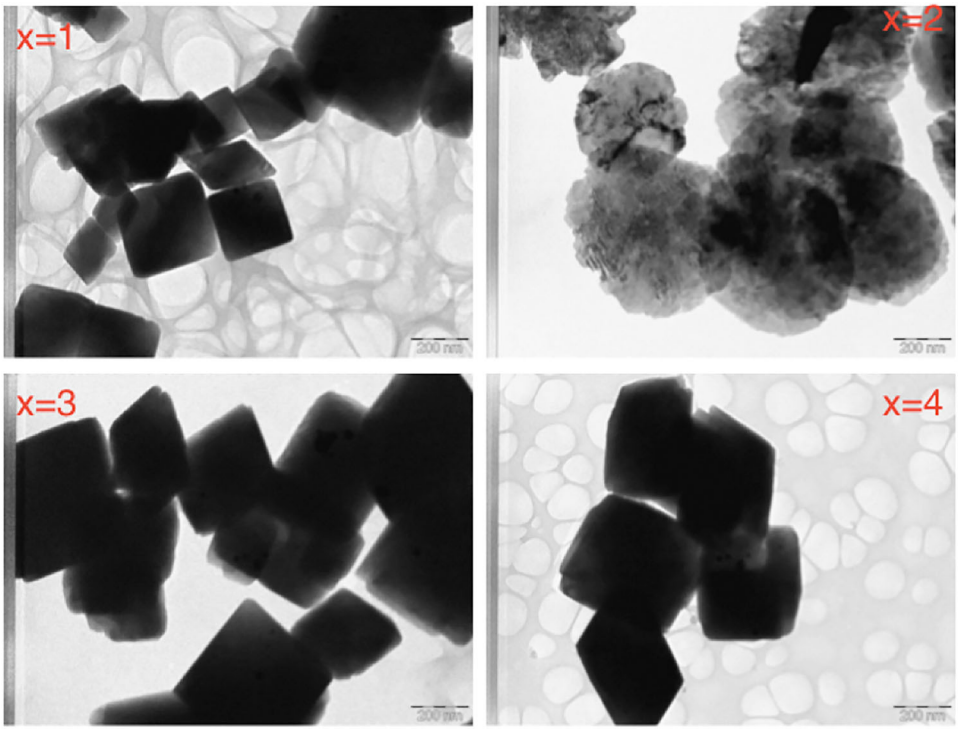

Figure 8. TEM images of $CaAl_xFe_{12-x}O_{19}$.

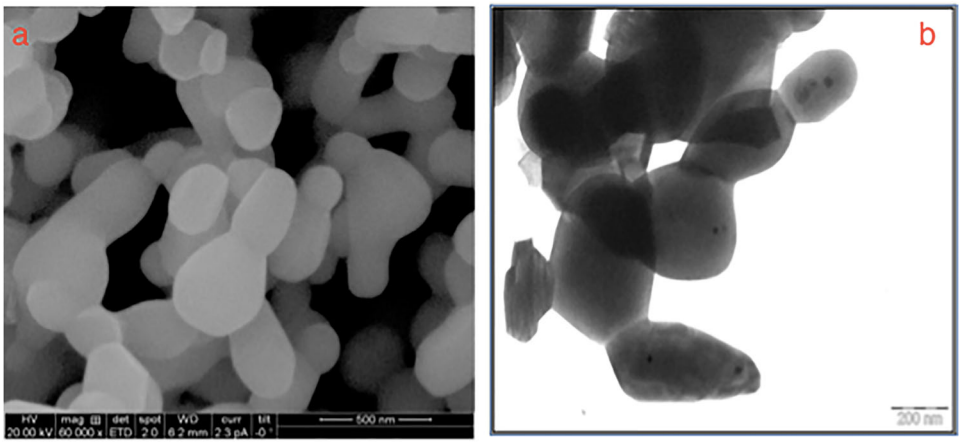

Figure 9. (a) SEM and (b) TEM images of $CaFe_{12}O_{19}$ prepared in combustion synthesis.

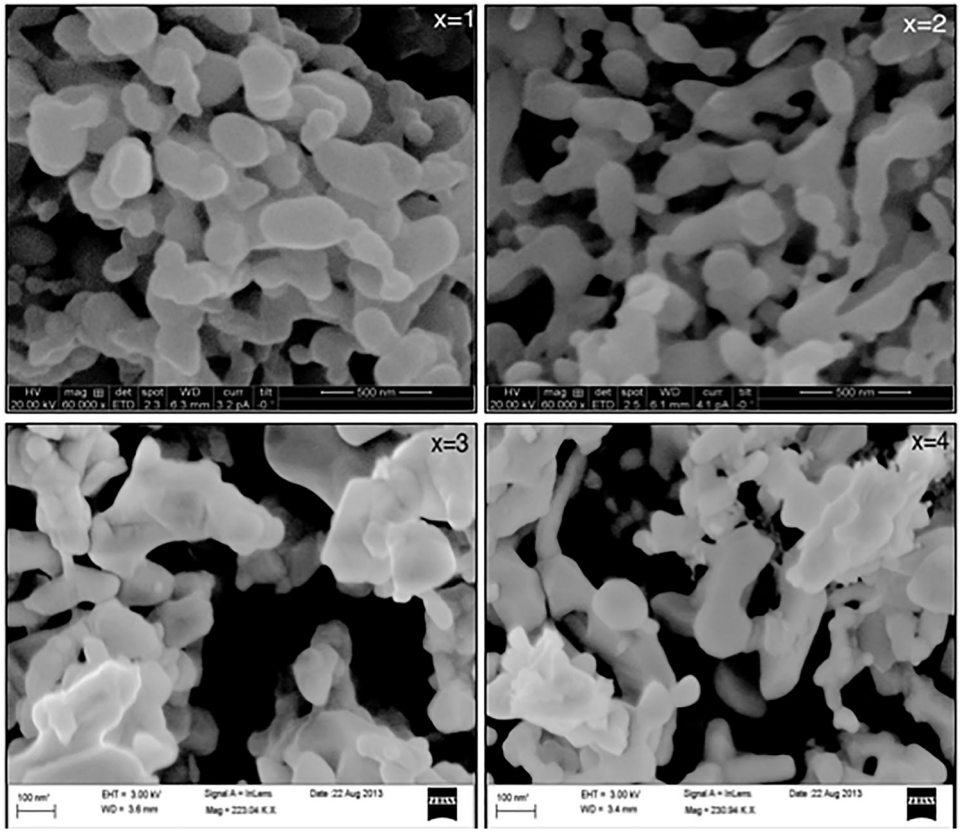

Figure 10. SEM images of $CaAl_xFe_{12-x}O_{19}$ prepared in combustion.

confirm the formation of hexaferrites with the space group $P6_3/mmc$. The major intensity diffraction peaks of samples have been found at (0 0 6), (1 0 7), (2 0 2), (1 0 9), (2 1 4), (3 0 3), (2 2 2) and (2 2 4) orientations as mentioned in Figures 4 and 5. All peaks

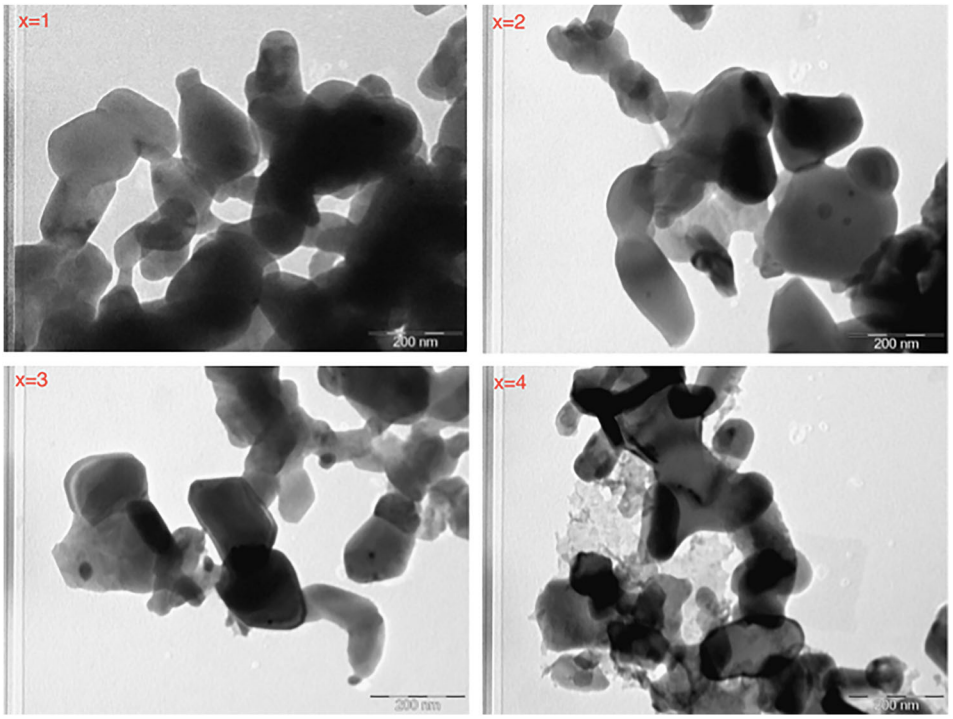

Figure 11. TEM images of $CaAl_xFe_{12-x}O_{19}$ in combustion.

match perfectly with Bragg reflections of the hexagonal structure with space group $P6_3/mmc$ and matching with the PCPDF no. 49-1586. A close examination of the PXRD pattern indicates slight variation in the parameters such as peak intensities, peak positions and peak width, with the increase in the aluminum content due to the small ionic radius of Al^{3+} ion (0.54 Å) than Fe^{3+} (0.65 Å). Al^{3+} Substitution for Fe^{3+} causes the shrinkage of crystal lattice [9,16–18]. Structural properties, such as lattice parameters (*a*, *c*), particle size (*D*), volume (*V*) and *c*/*a* ratios are given in Tables 1 and 2. There is a variation in the particle size with different substitution. The lattice parameters ratio *c*/*a* lies in the range from 3.67 to 3.85 for the samples prepared in combustion synthesis and 3.81 to 3.85 for samples prepared in hydrothermal synthesis, exhibited the formation of M-type hexagonal structure [9,16]. Consequently, the aberrance of the crystal lattice leads to the changes in the crystal lattice parameters *a*, *c* and variation in the radius of the crystal grains. M-type hexaferrite structure is assumed if the lattice parameters ratio is observed to be lower than 3.98 [17–19].

Figures 6–8 show SEM and TEM images of the samples prepared in hydrothermal synthesis. Figures 9–11 show SEM and TEM images of the samples prepared in combustion synthesis. From figures it is evident that particles are in nanosize. Agglomeration increases with the increase of substitution. It clearly shows that particle size and shape are entirely different for the same compound in two different methods.

5. Conclusions

Series of Al substituted calcium hexaferrites with general formula $CaAl_xFe_{12-x}O_{19}$ ($x = 0, 1, 2, 3, 4$) have been prepared by two different synthesis methods, hydrothermal synthesis and combustion synthesis. The role of synthesis method in structural properties and substitution of Al^{+3} in place of Fe^{+3} are studied and summarized.

Powders are characterized by XRD, SEM and TEM. X-ray diffraction patterns reveal the formation of M-type hexagonal structure with space group $P6_3/mmc$. Though the compound $CaAl_xFe_{12-x}O_{19}$ is same, structural properties are varied widely as the methodologies are different. The average particle size is found to be in the nano range in both methods. Size and shape of the particles are more effective in hydrothermal synthesis as compared to combustion synthesis.

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