



PROPERTIES OF SUBSTITUTED NANOSIZE CALCIUM HEXAFERRITES

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ABSTRACT

The samples of various combinations of Y-type aluminium substituted calcium hexaferrite with composition $\text{Ca}_2\text{Zn}_2\text{Fe}_{12-x}\text{Al}_x\text{O}_{22}$ ($0 \leq x \leq 1$) were synthesized by sol-gel auto-combustion route by blending metal nitrates as oxidants accompanied with fuel like urea as reducing agent. The structural property is being analyzed by XRD and TEM. The synthesized samples are found to be in nanorange. The X-ray diffraction pattern at room temperature showed the prepared samples have a single Y-type hexagonal ferrite. The magnetic properties of the samples were studied by using Vibrating Sample Magnetometer (VSM). The magnetic properties are observed to be improved upon those of the samples reported earlier. This confirms the more viability of such samples in the various applications of such as permanent magnet, microwave device materials and magneto-optic recording media.

Key words: Y-type hexagonal ferrite, structural property, magnetic property, Sol-gel auto-combustion route etc.

1. Introduction

In modern techno scientific era, the industrial application of nonmaterial has grabbed a paramount importance owing to their improved characteristics. Hexagonal ferrites especially Y-type ferrites have been proved to be the promising candidate for nonmaterial. The structure of Y-type ferrite as a stacking of hexagonal T and spinal S- blocks along the hexagonal c axis... (TS)(TS)*(TS)** where S is two oxygen-layered block, while T is four oxygen-layered block. The symbol * indicates rotation of corresponding blocks through 120° , about the c-axis [1-3].

In current research, the samples of Y-type aluminium substituted calcium hexaferrite have been synthesized by sol-gel auto-combustion route. The influence of substitution of Al^{3+} ion for Fe^{3+} ion on



structural and magnetic properties of substituted calcium hexaferrite have been investigated.

2. Experimental

2.1. Sample preparations

The aluminium substituted calcium hexaferrite powders have been synthesized by sol-gel auto-combustion route. The synthesis route involved the combustion of redox mixtures, in which metal nitrates acted as an oxidizing reactant and urea as a reducing reactant. The initial composition of solution containing metal nitrates and urea was based on the total oxidizing and reducing valences of the oxidizer and the fuel using the concept of propellant chemistry [4].

The stoichiometric amounts of AR grade $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Zn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and urea $\text{CO}(\text{NH}_2)_2$, dissolved in a minimum quantity of water, were placed in a beaker. The beaker containing the solution was introduced into a microwave oven. Initially the solution boils and undergoes dehydration followed by decomposition with the evolution of a large volume of gases (N_2 , NH_3 , and H_2CO). After the solution reaches the spontaneous combustion, it begins burning and releases lots of heat, vaporizes all the solution instantly and becomes a solid burning at temperatures above 100°C . The entire combustion process which produces aluminium substituted calcium hexaferrite powders in microwave oven takes only 15 min.

2.2 Characterization

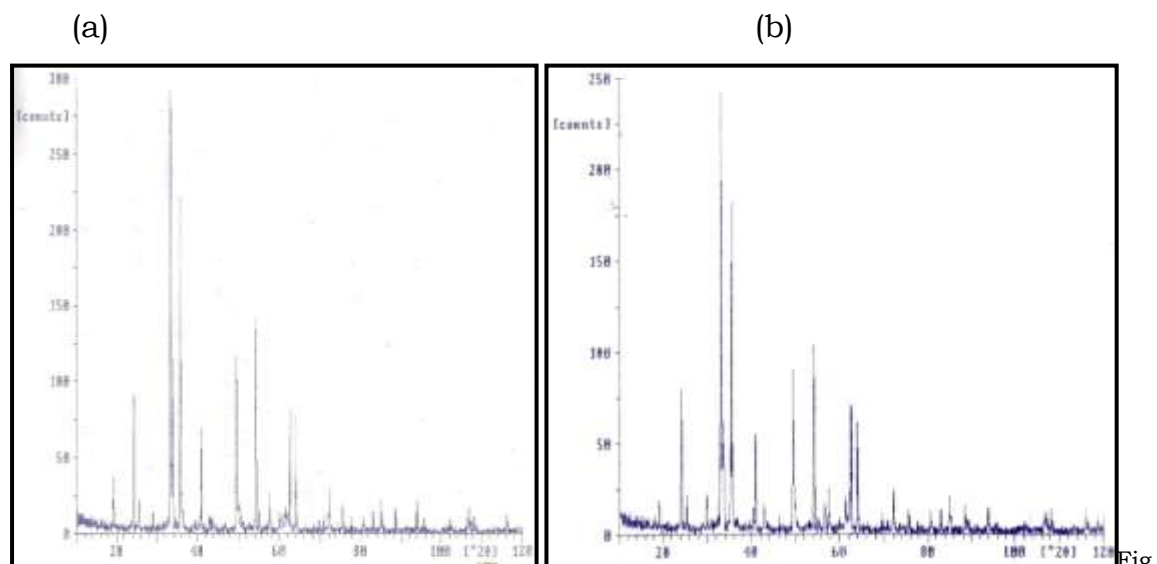
The samples were analyzed using a Philips X-ray diffractometer (PW-1710) and Cu-K α radiation with the wavelength $\lambda = 1.54056 \text{ \AA}$. The X-ray pattern showed a single crystalline phase of Y-type hexagonal ferrite without any impurity. The space group for the samples was observed to be $R\bar{3}m$ (SG no. 166). The particle morphology of synthesized samples was examined by a transmission electron microscope (TEM).

The magnetic properties of the prepared sample were measured by a Vibrating Sample Magnetometer (VSM) with a maximum applied field of 20 KOe.

3. Results and discussion

3.1. XRD analysis

The XRD patterns of the samples are shown in Fig 1. The crystallographic data are tabulated in Table 1. The data is analyzed by using computer software PCPDF Win, Powder-X and Full proof Suite. By comparing the patterns with JCPDS, the phases in the different samples are determined. It is being observed that most of the hexagonal grains are of same size. Using 2θ , observed d -values and intensity calculations, d - values is recalculated and (h k l) planes are finalized. The value shown in Table 1 and 2 confirm the formation of single phase hexagonal ferrites. The lattice parameters a and c are found to be in the range 5.0452 Å and 44.2512 Å for samples. The XRD pattern confirms the formation of single phase Y-type hexagonal ferrites. The space group of the sample is found to be $(R\bar{3}m)$.



1.(a) sample $\text{Ca}_2\text{Zn}_2\text{Fe}_{11.5}\text{Al}_{0.5}\text{O}_{22}$ and (b) $\text{Ca}_2\text{Zn}_2\text{Fe}_{11}\text{AlO}_{22}$: X-ray diffraction spectra.



Table 1:XRD data of $\text{Ca}_2\text{Zn}_2\text{Fe}_{11.5}\text{Al}_{0.5}\text{O}_{22}$ compound $a = 5.0452\text{\AA}$, $c = 44.2512\text{\AA}$

2θ	d_{obs} (\AA)	d_{cal} (\AA)	I/I_o	h k l
24.175	3.6876	3.6876	39.7	0 0 12
33.180	2.7245	2.7657	100	0 0 16
35.305	2.5465	2.5609	21.7	1 0 14
35.650	2.5226	2.5226	81.7	1 1 0
40.870	2.2106	2.2126	24.3	0 0 20
49.485	1.8450	1.8438	41.50	0 0 24
54.100	1.6980	1.6987	43.2	1 0 24
57.645	1.6017	1.5978	12.2	2 1 7
62.485	1.4888	1.4886	34.70	2 1 24
64.030	1.4566	1.4556	23.00	3 0 1
71.985	1.3140	1.3110	9.90	2 0 27
75.490	1.2615	1.2613	6.80	2 2 0
84.970	1.1433	1.1429	12.2	3 0 24
108.12	0.9538	0.9535	6.10	4 1 0

Table 2: XRD data of $(\text{Ca}_2\text{Zn}_2\text{Fe}_{11}\text{AlO}_{22})$
 compound $a = 5.0446\text{\AA}$, $c = 44.2056\text{\AA}$

2θ	d_{obs} (\AA)	d_{cal} (\AA)	I/I _o	h k l
24.200	3.6838	3.6838	29.9	0 0 12
29.915	2.9918	3.1073	39.2	1 0 10
32.38	2.7645	2.7629	97.1	0 0 16
33.36	2.6713	2.6834	41.9	1 0 13
35.03	2.5510	2.5591	100	1 0 14
35.56	2.5233	2.5233	74.5	1 1 0
40.870	2.2117	2.2103	23.2	0 0 20
42.850	2.1240	2.1206	18.0	2 0 5
49.505	1.8443	1.8419	34	0 0 24
53.88	1.6980	1.6972	41	0 0 26
56.625	1.6281	1.6232	23.2	2 1 5
62.145	1.4961	1.4875	43.1	1 1 24
71.995	1.3138	1.3171	15.1	1 0 32

Table 3: Lattice constants (a), (c), c/a ratio and cell volume
 (V) of samples

Sample	a (\AA)	c (\AA)	c/a ratio	V (\AA) ³
$\text{Ca}_2\text{Zn}_2\text{Fe}_{11.5}\text{Al}_{0.5}\text{O}_{22}$	5.0452	44.25	8.770	1245.1
		12	9	1
$\text{Ca}_2\text{Zn}_2\text{Fe}_{11}\text{AlO}_{22}$	5.0446	44.20	8.762	1244.8
		56	9	9

Other parameters such as lattice constants (a & c) and cell volume (V) are enumerated in Table 3. The lattice parameter 'a' and 'c' and 'V' slightly changes with substitution of Al^{3+} ion in calcium hexaferrite sample. This is due to relatively large ionic radius of Al^{3+} ion (0.53\AA) comparing to that of Fe^{3+} ion (0.64\AA) for six fold coordination. Kuhikar [5] reported the values of 'a' and 'c' as 5.884\AA and 43.938\AA for $\text{Ca}_2\text{Co}_2\text{Fe}_{11}\text{LaO}_{22}$ sample. Moharkar

[6] also reported the values 'a' and 'c' as 5.0418 (Å) and 44.1876 (Å) for $\text{Ca}_2\text{Zn}_2\text{Fe}_{12-x}\text{Co}_x\text{O}_{22}$ sample.

3.2 TEM analysis

Fig 2 shows TEM photographs of aluminium substituted calcium hexaferrite. The average particle size of the samples is in nanorange with an average diameter of 50 nm. The TEM analysis shows remarkable changes in the microstructure, grain size and homogeneous particle size distribution. Therefore it could be attributed that these remarkable changes are observed as a perturbation of many dependant parameters like time of synthesis, temperature, process of annealing, intermittent quenching and grinding etc [7-8].

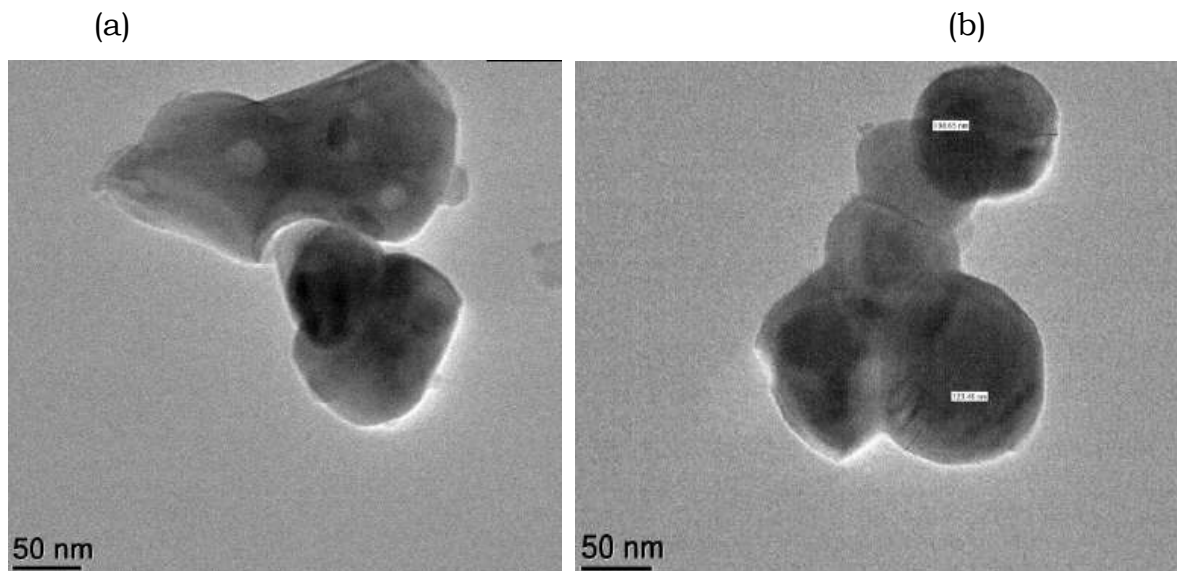


Fig.2: TEM micrographs of samples:

(a) $\text{Ca}_2\text{Zn}_2\text{Fe}_{11.5}\text{Al}_{0.5}\text{O}_{22}$ and

(b) $\text{Ca}_2\text{Zn}_2\text{Fe}_{11}\text{AlO}_{22}$

3.3 VSM analysis

The magnetization of the substituted calcium hexaferrite samples were measured on a VSM at room temperature under an applied field of 20 kOe. Fig. 3 shows the hysteresis loops of the samples at room temperature. Table 4 shows the values of magnetic parameters such as saturation magnetization (M_s), retentivity (M_r) and coercivity (H_c) of the samples obtained from the hysteresis loops. In table, the values of saturation

magnetization (M_s) and retentivity (M_r) decreases where as coercivity (H_c) increases for replacement of Fe^{3+} ion by Al^{3+} ion. The magnetic behaviour of the ferrite compounds can be possibly explained on the basis of interaction of these six sites- $6c_{vi}$, $6c_{iv}$, $6c^*_{vi}$, $3b_{vi}$, $18h_{vi}$ and $3a_{vi}$ due to several possible distribution of ions Enz [9], Sizov [10].

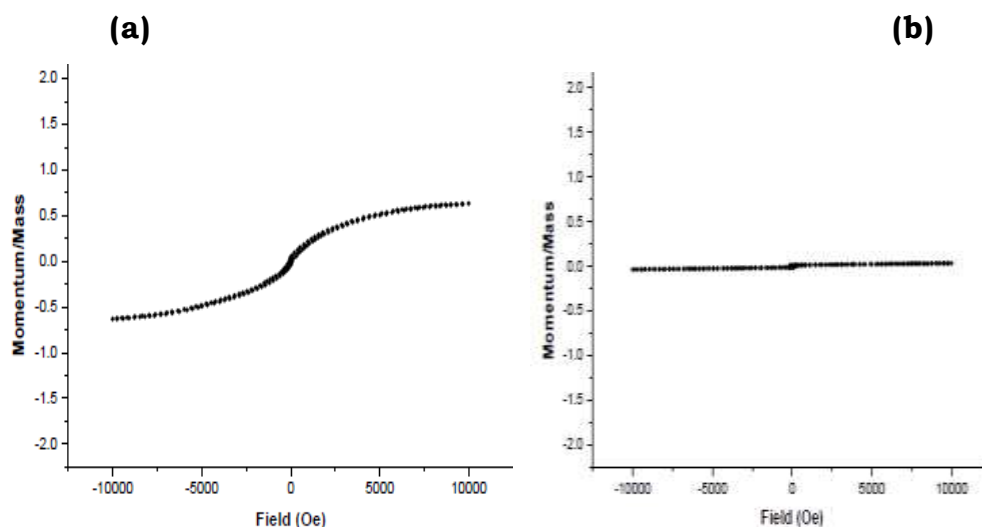


Fig. 4: Hysteresis loops at room temperature:

(a) $Ca_2Zn_2Fe_{11.5}Al_{0.5}O_{22}$ and

(b) $Ca_2Zn_2Fe_{11}AlO_{22}$

Table 4: Magnetic parameters of the $Ca_2Zn_2Fe_{12-x}Al_xO_{22}$ samples

Sample	Saturation Magnetization M_s (emu/g)	Retentivity M_r (emu/g) $\times 10^{-2}$	Coercivity H_c (Oe)
$Ca_2Zn_2Fe_{11.5}Al_{0.5}O_{22}$	0.632	4.309	68.310
$Ca_2Zn_2Fe_{11}AlO_{22}$	0.034	1.063	105.321

4. Conclusion

The aluminium substituted calcium hexaferrite samples were synthesized by the sol-gel auto-combustion route. The XRD data have confirm the formation of Y-type hexaferrites and the values of a and c of the sample supports this confirmation. TEM studies reveal the synthesized samples are in the nanorange. The magnetic properties of the samples were improved by substitution of Al^{3+} for Fe^{3+} in calcium hexaferrites.



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