CALCIUM HEXAFERRITE POWDERS PREPARED BY A MICROWAVE-INDUCED SOL-GEL COMBUSTION ROUTE AND STUDY OF SOME OF THEIR PROPERTIES

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Abstract

Powders of calcium hexaferrites doped with Zirconium - Cobalt $CaFe_{11}(ZrCo)O_{19}$ and $CaFe_{10}(ZrCo)_2O_{19}$ have been synthesized. The nitrates are used as oxidants accompanied with urea as a fuel. Conventional Sol-gel technique is improved by replacing conventional heating furnace by a microwave source, hence the method is named as *'The Microwave Induced sol-gel combustion route'* [1,2]. Structural analysis of the synthesized powders have been carried out using X-ray diffraction spectroscopy (XRD)& Morhological study is done using Transmission electron microscopy (TEM). Values of Lattice parameters (a, c) confirms the formation of Hexaferrite unit cell [3]. TEM imaging demonstrate the formation of nanosize particles. Variatoin of loss tangent (tan δ) is studied as a function of frequency using precision impendence Analyser. Value of DC electrical resistivity (ρ) is also determined for the samples. Response to the external applied magnetic field is studied using Vibrating sample magnetometer (VSM), which show the moderate values of saturation magnetization (Ms), Remenace (Mr) and Coercivity (Hc). These nano sized materials with high resistivity are reported to be useful specially for the many Microwave absorbing applications. Also the reduction of particle size of hexaferrites to nanorange helps to improve magnetic and electric properties mentioned earlier.

1.Introduction

In modern technoscientific era, the industrial application of nano materials has grabbed a principal importance owing to their improved electric and magnetic characteristics. Hexagonal ferrites especially M-type ferrites have been proved to be the promising candidates for nano materials due to their ease of applicability in high density recording media, microwave absorption devices, magneto-optic recording media, etc. Ferrite is a very important class of magnetic oxides which contains

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magnetic ions arranged in such a manner that it produces spontaneous magnetization while maintaining good dielectric properties. The present module of research aims to develop a systematic method which facilitates the production of ultra fine hexagonal ferrite particles especially in nano scale and to find possible ways of improving their behavioral characteristics. Many efforts have been devoted to control structural M-type magnetoplumbites merely by the substitution of trivalent or coupled divalent & tetravalent cations into the mother base of these ferrites. Substituted magnetoplumbites with Ca^{2+} for Ba^{2+}, trivalent metallic ion for Fe^{3+} or a combination of divalent and tetravalent ions for Fe^{3+} have been reported[4]. The calcium hexaferrits [5] attracted the attention as they have been less studied and have magnetic properties comparable to BaM or SrM.

There are many procedures for synthesis. The known sol-gel technique is reported to have many advantages for structural, electrical and magnetic parameters over old techniques like solid state method, co-precipitation, Hydro-thermal synthesis, Glass crystallization, etc. [6]. The magnetic particles produced by conventional methods are reported to be larger than those produced by this technique. This technique is improved by replacing conventional heating furnace by scientific microwave source of specific frequency, hence the name *'The Microwave Induced sol-gel combustion route'*.

In this module, samples synthesized by Microwave Induced sol-gel combustion route with varying concentrations of dopants are described and their structural, electric and the magnetic properties are discussed.

2. Experimental

The synthesis of powders of $CaFe_{11}(ZrCo)O_{19}$ and $CaFe_{10}(ZrCo)_2O_{19}$ is done using the sol–gel route [7]. The reactive oxidants such as $Ca(NO_3)_2$, $Fe(NO_3)_2.9H_2O$, $Co(NO_3)_2.6H_2O$, $ZrO(NO_3)_2.H_2O$ were dissolved into an unionized distilled water at the temperature of 50^oC for 15-20min, urea

is used as fuel which gives requisite energy to initiate exothermic reaction. The gel produced is then kept for an hour in the room temperature and then it is heated in the digitally controlled microwave oven of 2.54GHz for 15-20 min. The gel get burnt and finally gets converted in homogeneous powder. The sample is then sintered by giving sporadic moderate heat treatments for further few minutes with further grinding. The samples so produced are then kept in humidity free atmosphere in air tight compartment. Pellets of diameter 15mm are formed using hydraulic press. Polyvinyl acetate (PVA) is used as binder for pellets and the sintering is done at 400oC for 2 hours by sequentially increasing and decreasing temperature at the moderate rate of 4oC/min.

3. Result and discussion

Table 1 gives the values of the Structural, Electric and Magnetic properties of the samples.

3.1 Structural Properties

The diffraction patterns of samples are taken with Philips X'pert Diffractometer, using Cu Kα radiation with wavelength λ=1.542 A.U.
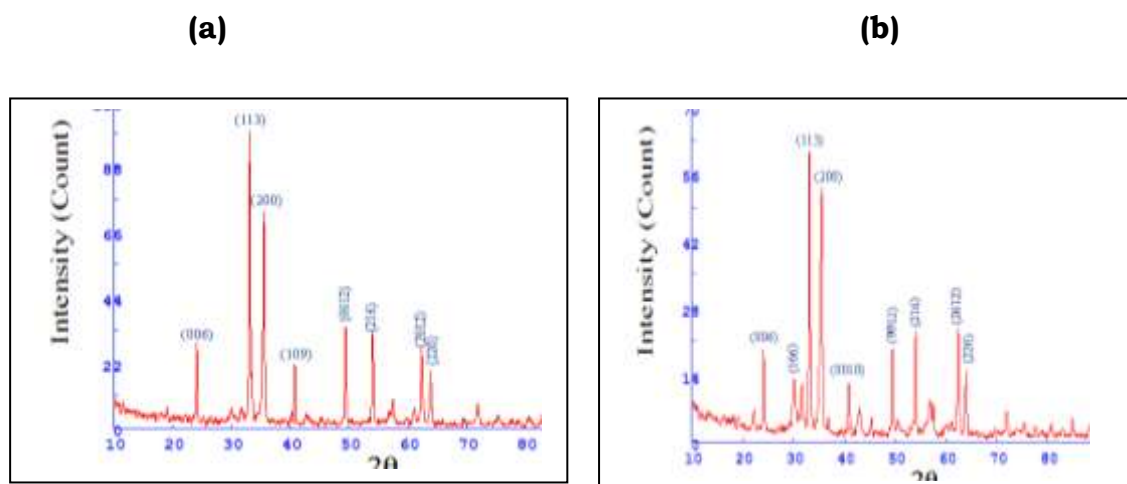
Fig 1 . X-ray powder diffraction patterns of samples

(a)   (b)

Fig 1 (a-b) shows the intensity graphs for samples $CaFe_{11}(ZrCo)O_{19}$ and $CaFe_{10}(ZrCo)_2O_{19}$ respectively. By comparing the diffraction patterns with JCPDS standards, using 2θ values, observed d-values and intensity

variations, d-values are recalculated and (hkl) planes are finalized. Values of lattice parameters confirms the formation of single phase hexagonal ferrites. Lattice parameters a and c are found to be 5.8256 **(Å)**. and 22.1244 **(Å)**. respectively for $CaFe_{10}(ZrCo)_2O_{19}$ and 5.8234 **(Å)**. and 22.1286 **(Å)**. for $CaFe_{10}(ZrCo)_2O_{19}$ respectively. The space group of samples is observed to be *P63/mmc.*

Nanosize confirmation is done by TEM analysis using Philips CM200, Fig 2 (a-b) shows the TEM images of the samples. The particle size is found to on an average 100nm. The grains are found to have sharp edges.
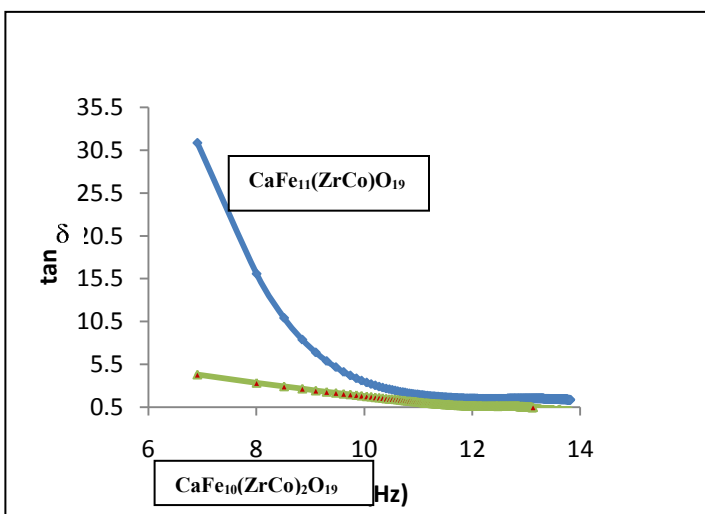
$CaFe_{10}(ZrCo)_2O_{19}$ $CaFe_{11}(ZrCo)O_{19}$

(a)   (b)
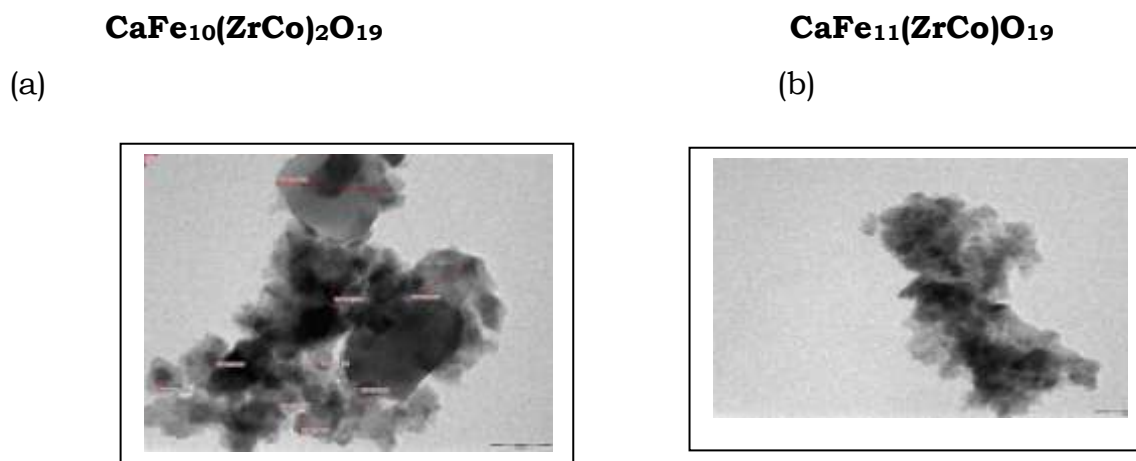
Fig. 2 (a-b) Transmission electron micrographs of the samples

3.2 Electric & Dielectric Properties

The variation of Resistivity, loss tangent(tan δ), with respect to frequency, temperature and composition are studied using precision impendence Analyser 6500B, Waynekerr Electronics. For controlled temperature variation, the sample is kept in a digitally controlled furnace. Four probe method is used to measure dielectric properties of the samples in palletized form.

From Table 1 it is observed that resistivity at room temperature decreases from, $1.2292*10^7$ Ω-m to $1.7718*10^6$ Ω-m with increase in

substitution of cations. Electric and dielectric properties of the hexaferrites are explained on the basis Verwey's hopping mechanism [8] The dielectric loss ($\tan\delta$) gives energy loss within the material during conduction of electrons. Variation of dielectric loss ($\tan\delta$) with frequency is shown in Fig 3 at constant temperature. The value of loss tangent is observed to decrease with increasing concentration of substitution. Lagging of the polarization with applied ac electric field is the main cause of the dielectric loss [9]. In low frequency region more energy is required for the electron exchange between Fe^{3+} and Fe^{2+} ions due to which loss is higher. But at higher frequencies lesser energy is required for the exchange and therefore dielectric loss decreases rapidly.

Fig 3 : Variation of dielectric loss ($\tan\delta$) with frequency for CaFe$_{11}$(ZrCo)O$_{19}$ and CaFe$_{10}$(ZrCo)$_2$O$_{19}$

3.3 Magnetic Properties

Fig. 4 shows hysteresis curves for the sample depicting magnetic behavior of the sample in the presence of external magnetic field.

Values of saturation magnetization Ms, remnant magnetization Mr and coercivity Hc found to decreases with the substitution of cations as mentioned in Table 1. Decrease in the values of Ms, Mr with increase in values of substitution is due to the substitution of diamagnetic ions not

only into the spin-down sublattices $4f_1$ of Fe^{3+} ions but also into other octahedral spin-up sublattices 12k, 2a, 2b of Fe^{3+} ions. Decrease in the value of coercivit Hc with increase in the value of substitution is due to lowering of magneto crystalline anisotropy[10] .

Also the area under hysteresis curves decreases with increase in substitution level which indicates that the ferrite become soft with increasing degree of substitution.
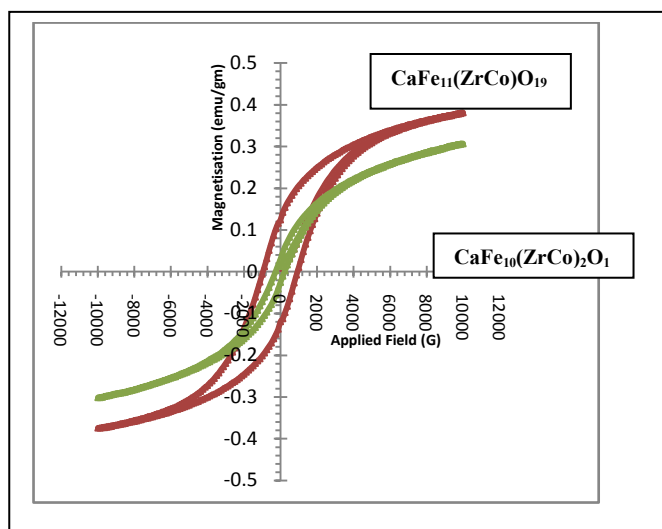
Fig. 3 Hysteresis curves for the samples $CaFe_{10}(ZrCo)_2O_{19}$ and $CaFe_{11}(ZrCo)O_{19}$

Table 1 : Lattice parameters (a and c) , Bulk Density(D_B), X-ray Density (D_x), % Porosity (P%), Values of saturation magnetization M_s , remnant magnetization M_r and coercivity H_c

Samples	a (Å)	c (Å)	ρ at 373K (Ω-m)	tan δ at 1 kHz	Ms (emu/gm)	Mr (emu/gm)	Hc (G)
$CaFe_{11}(ZrCo)O_{19}$	5.8256	22.124	$1.2292*10^7$	2.6238	0.3805	0.1245	875
$CaFe_{10}(ZrCo)_2O_{19}$	5.8234	22.128	$1.7718*10^6$	0.1314	0.3055	0.0305	250

4. Conclusion

The new combustion route using Microwave found to be successful for the synthesis of nanosized Co^{2+}–Zr^{4+} substituted calcium hexaferrites with added advantage of sol-gel method which gives the nanosized hexaferrite

particles. The X-ray diffraction studies confirm the formation of hexaferrites and the a & c values of the sample supports this confirmation. From TEM data, particle size is found to be in nano range. Dielectric losses are observed to decrease with increase in frequency. With high values of electrical resistivity and low values for dielectric loss tangent, the synthesized calcium hexaferrites dopped with Zr^{4+} and Co^{2+} can prove to be a promising material in the microwave absorbing , EMI shielding applications. Hysteresis curves of the samples depicts the moderate values of coercivity and large values of saturation magnetization. The variation in the values of magnetic parameters shows the possibility of tailoring of the magnetic properties according to the requirement for different utilities[8 ,11]. The average particle size will determine the background noise in the recording media. Nano size of the particles helps to reduce the noise produced in magnetic data storage devices which occur due to displacement of domain boundaries[2]. Thus the reduction of particle size of hexaferrites to nanorange helps to improve magnetic and electric properties.

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