

Influence of aluminium ions substitution on microstructure, electrical conductivity and drift mobility of nanocrystalline CaY ferrite.

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Manuscript Details

Available online on <http://www.irjse.in>

ISSN: 2322-0015

Cite this article as:

Gawali SR and Moharkar PR. Influence of aluminium ions substitution on microstructure, electrical conductivity and drift mobility of nanocrystalline CaY ferrite, *Int. Res. Journal of Science & Engineering*, February, 2020, Special Issue A7: 209-217.

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ABSTRACT

In modern technoscientific era, the industrial application of nanomaterials has grabbed a paramount importance owing to their improved characteristics. Hexagonal ferrites especially Y-type ferrites have been proved to be the promising candidates for nanomaterials by virtue of their ease of applicability in the solid-state electronic devices and microwave to radio frequency devices.etc. Keeping this view, the series of samples of aluminium substituted calcium hexaferrites with compositions $\text{Ca}_2\text{Zn}_2\text{Fe}_{12-x}\text{Al}_x\text{O}_{22}$ (where $x = 0, 0.5$ and 1) were prepared by sol-gel auto-combustion method. The microstructure of synthesized samples is being analyzed by XRD and TEM. The X-ray diffraction pattern at room temperature showed the prepared samples have a single phase Y-type hexagonal ferrite. The TEM study has confirmed the ultrafine nano range particle with diameter of 29-36 nm. The influence of substitution of Al^{3+} ion for Fe^{3+} ion on the unit cell parameters, density and porosity has been investigated. The DC electrical conductivity was measured as a function of temperature from 300 K to 800 K using two probe techniques. The phenomenon of conduction was explained on the basis of a Verwey hopping model. The influence of aluminium ion substitution on drift mobility has been investigated.

Keywords: Y-type hexagonal ferrite, microstructure, sol-gel auto-combustion method, electrical conductivity, drift mobility, etc.

INTRODUCTION

The Y-type hexagonal ferrite possesses electrical properties like conductivity, dielectric constant and loss tangent etc., which are useful in the solid-state electronic devices and microwave to radio frequency devices Simmons [1], Popa et al.[2] The low electrical conductivity results into low losses, which are useful for microwave application. The electrical properties give information about the defects in crystal structure conduction mechanism and grain boundaries, which depends on the chemical composition of material, the charges and distribution of ions amongst the various sites. Most of the hard ferrites, either cubic or hexagonal, possess semiconducting properties with low mobility of charge carries and variation in electrical conductivity with temperature Hadj Farhat and Joubert [3], Smit and Wijn.[4] As the semiconducting materials have very low conductivity at room temperature, they have high frequency applicability in various areas.

In current research, the series of samples of CaY ferrite have been synthesized by sol-gel auto-combustion method. The influence of substitution of Al^{3+} ion for Fe^{3+} ion on microstructure, electrical conductivity and drift mobility of substituted calcium hexaferrite have been investigated.

METHODOLOGY

Sample preparations

The synthesis process 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 Jain et al.[5] The calcium nitrate $Ca(NO_3)_2 \cdot 4H_2O$, iron nitrate $Fe(NO_3)_3 \cdot 9H_2O$, aluminum nitrate $Al(NO_3)_3 \cdot 9H_2O$, zinc nitrate $Zn(NO_3)_2 \cdot 4H_2O$ and urea $CO(NH_2)_2$ (analytical reagent grade) was used as raw components. Nitrate/urea ratio considerably affects the combustion process and the grain size of prepared ferrite powder. The sufficient quantity of hot water was added to dissolve the metal nitrates and urea in a borosil

beaker. The beaker containing solution was introduced into a microwave oven. Initially, the solution boils. Then, the urea and metal nitrates decompose and give flammable gases such as NH_3 , $HNCO$, O_2 and NO respectively. After the solution reaches the point of spontaneous combustion, it begins burning and becomes a solid which burns at a temperature above $1000\text{ }^\circ\text{C}$. The combustion is not completed until all the flammable substances are consumed and the resulting material is a loose, highly friable substance exhibiting voids and pores formed by escaping gases during combustion reaction Mali and Ataie[6], Gawali and Moharkar[7]. The ashes obtained after combustion were brown and voluminous. The burned ashes formed were crushed in the agate mortar to fine calcium hexaferrites powder. Further these synthesized powdered were pelletized and subjected to heating of 2hr and 800°C in order to remove any unburned impurity and produce the unperturbed crystal structure expected out of the process.

Characterization

The crystalline phase determination of the samples were carried out on Philips Holand XRD unit (PW 1710) operating at 42.5 kV and 18.00mA with Copper $K\alpha$ -radiation with wavelength 1.54056 \AA . The values of lattice constant 'a' and 'c', the unit cell volume (V), X-ray density ($\rho_{x\text{-ray}}$), bulk density (ρ_m) and porosity (P) were calculated by using following equations.

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

$$V = 0.8666a^2c \quad (2)$$

$$\rho_{x\text{-ray}} = \frac{zM}{N_A V} \quad (3)$$

$$\rho_m = \frac{m}{(\pi r^2)h} \quad (4)$$

$$P = 1 - \frac{\rho_m}{\rho_{x\text{-ray}}} \quad (5)$$

Where, 'a' and 'c' are lattice constants, 'M' is the molar mass, 'm' is the mass of pellet, 'r' is radius of the pellet, 'N_A' is Avogadro's number and 'V' is the unit cell volume.

The average particle size of synthesized samples were determined by a Transmission Electron Microscope (TEM) of make PHILIPS (model CM200) having operating voltage 20-200kV and resolution of 2.4 Å.

The four probe method was employed to study DC electrical resistivity of the said ferrites system in the temperature range 300 K to 800 K. The DC electrical resistivity of all the samples decreases with increasing temperature in accordance with Arrhenius equation Kasap [8].

$$\rho = \rho_0 \exp\left(\frac{\Delta E}{k_B T}\right) \quad (6)$$

Where, ' k_B ' is the Boltzmann constant, ' T ' is temperature and ' ΔE ' is the activation energy, which is the energy needed to release an electron from the ion for a jump to neighbouring ion, giving rise to the electrical conductivity.

The activation energy of the aluminium substituted calcium hexaferrites have been determined from the slope of plots of $\ln(\sigma)$ versus temperature ($1000/T$) above and below the transition temperature (T_t).

The drift mobility (μ_d) of all synthesized hexaferrite samples were calculated using the relation.

$$\mu_d = \frac{1}{ne\rho} \quad (7)$$

Where, ' e ' is the charge on the electron, ' ρ ' is the D.C. electrical resistivity at a given temperature and ' n ' is the concentration of charge carriers and can be calculated from the relation

$$n = \frac{N_A \rho_m P P_e}{M} \quad (8)$$

Where ' N_A ' is the Avogadro's number, ' ρ_m ' is the bulk density, ' M ' is the molecular weight of the sample, ' P_{Fe} ' is the number of iron atoms in the chemical formula.

RESULTS AND DISCUSSION

XRD analysis

The XRD patterns of the samples are shown in Fig. 1. The crystallographic data are tabulated in Table 1. The XRD data analysis was done using computer software PCPDF Win, Powder-X and fullproof software suite. XRD study showed that the prepared samples are found to have Y-type hexagonal structure belonging to the space group $R\bar{3}m$ (no. 166).

The lattice parameter ' a ' and ' c ' show decreasing trend with increase in concentration of Al^{3+} ions. This variation is relatively small but can be considered due to smaller ionic radii of Al^{3+} ions (0.53Å) compared to that Fe^{3+} ions (0.64Å) for six fold coordination. As a result, the cell volume of CaY ferrites found to have contraction after being doped with Al^{3+} ions. This is in agreement with the fact that all the hexagonal types exhibit variation in lattice constant after being substituted by variable size ions as reported by Haneda and Kojima[9], Ounnunkad and Winotai[10], Gawali et al.,[11], Rewatkar et al.,[12] reported the similar values of lattice constants a and c . The X-ray density is higher than the bulk density (ρ_m) which indicates the presence of pores in the synthesized samples. The porosity decreases with increase in the Al^{3+} ions content in calcium hexaferrites. These results agree well to that reported by M. B Solunke et al., [13].

Table 1: Lattice constants (a) and (c), cell volume (V), X-ray density ($\rho_{x\text{-ray}}$), Bulk density (ρ_m) and Porosity (P) of Aluminium substituted Calcium hexaferrite.

Sample	x	A (Å)	c (Å)	V (Å) ³	Mol. Weight M (gm)	$\rho_{x\text{-ray}}$ (gm/cm ³)	ρ_m (gm/cm ³)	Porosity P (%)
Ca ₂ Zn ₂ Fe ₁₂ O ₂₂	0	5.0490	44.2672	1249.27	1233.61	4.2239	3.0982	36.67
Ca ₂ Zn ₂ Fe _{11.5} Al _{0.5} O ₂₂	0.5	5.0452	44.2512	1245.11	1219.18	4.1507	2.7761	33.11
Ca ₂ Zn ₂ Fe ₁₁ AlO ₂₂	1.0	5.0446	44.2056	1244.89	1204.75	4.1067	2.1255	23.90

Table 2 : Electrical conductivity and activation energy in Para and Ferri magnetic regions of aluminium substituted calcium ferrite.

Sample	Elect. Cond.(σ) At Room Temp. ($\Omega^{-1}\text{cm}^{-1}$) $\times 10^{-9}$	Activation Energy ΔE (eV)	
		Ferri	Para
$\text{Ca}_2\text{Zn}_2\text{Fe}_{12}\text{O}_{22}$	11.13	0.25	0.37
$\text{Ca}_2\text{Zn}_2\text{Fe}_{11.5}\text{Al}_{0.5}\text{O}_{22}$	8.25	0.27	0.38
$\text{Ca}_2\text{Zn}_2\text{Fe}_{11}\text{Al}\text{O}_{22}$	6.26	0.24	0.35

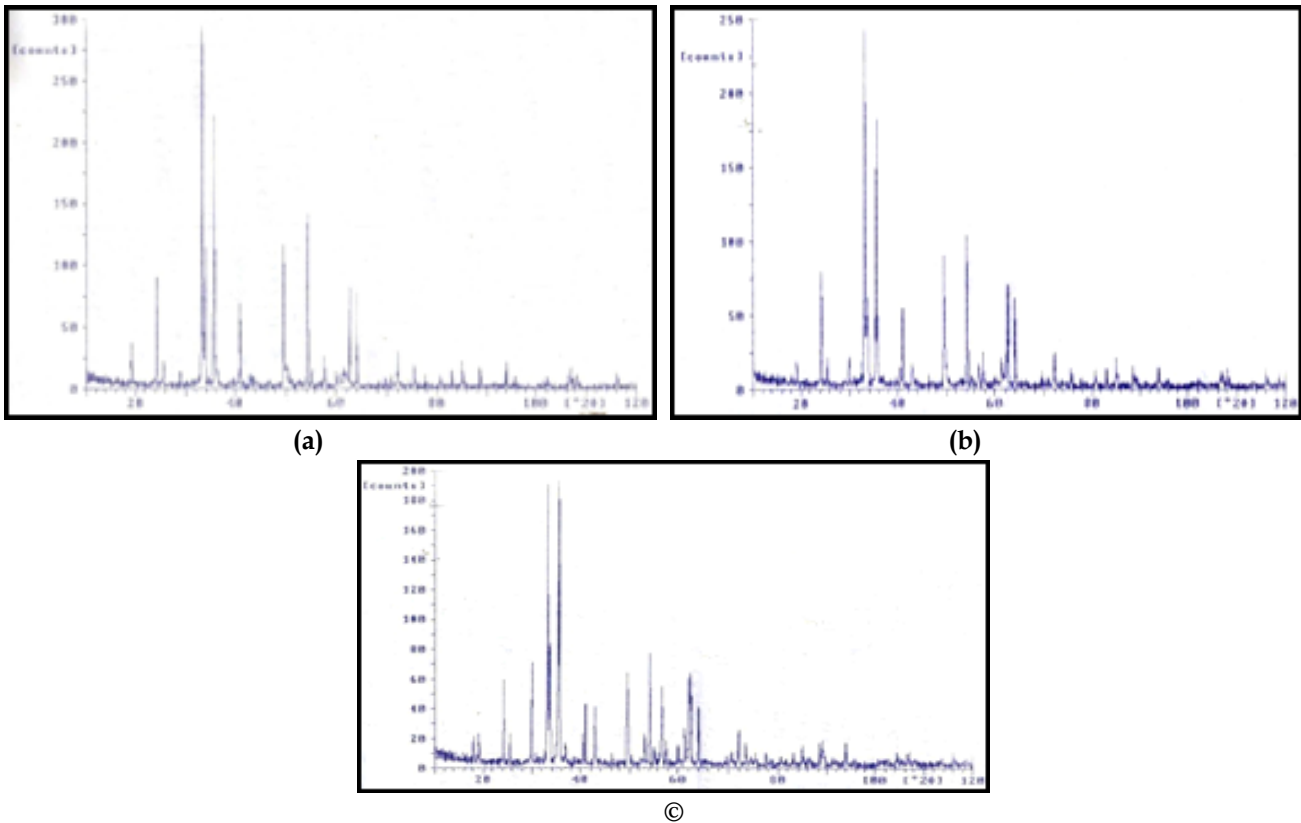
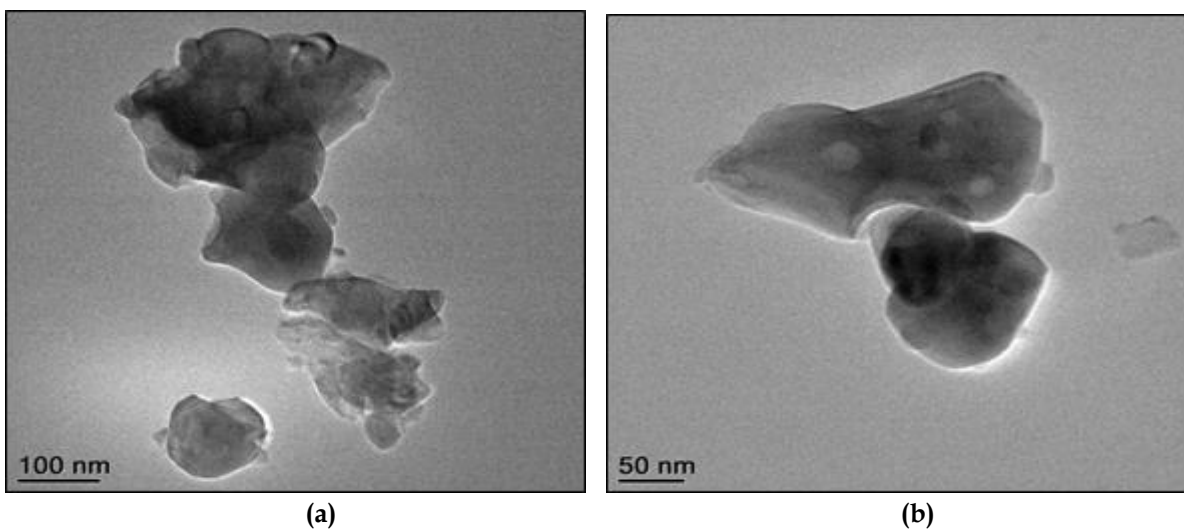
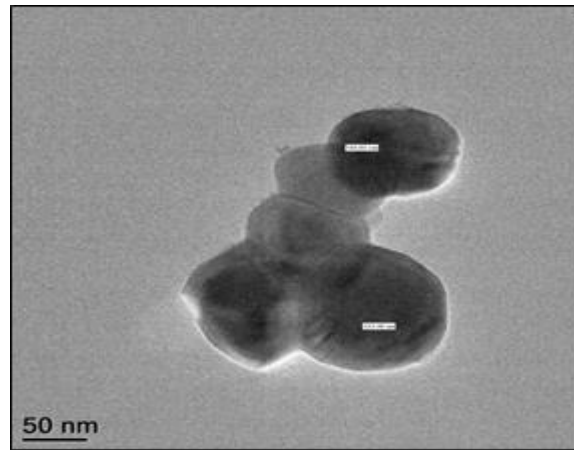


Fig. 1. : X-ray diffraction spectra (a) $\text{Ca}_2\text{Zn}_2\text{Fe}_{12}\text{O}_{22}$, (b) $\text{Ca}_2\text{Zn}_2\text{Fe}_{11.5}\text{Al}_{0.5}\text{O}_{22}$ and (c) $\text{Ca}_2\text{Zn}_2\text{Fe}_{11}\text{Al}\text{O}_{22}$





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Fig.2: TEM micrographs of samples: (a) $\text{Ca}_2\text{Zn}_2\text{Fe}_{12}\text{O}_{22}$, (b) $\text{Ca}_2\text{Zn}_2\text{Fe}_{11.5}\text{Al}_{0.5}\text{O}_{22}$ and (c) $\text{Ca}_2\text{Zn}_2\text{Fe}_{11}\text{AlO}_{22}$

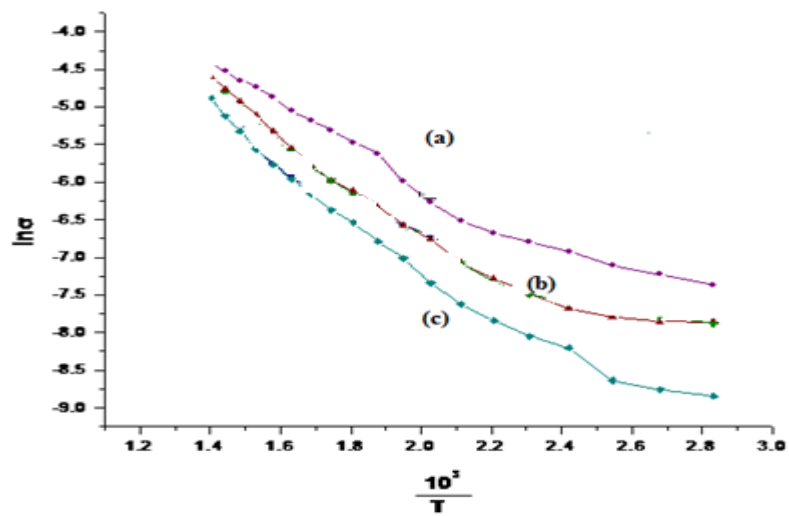


Fig.3 : Variation of $\ln(\sigma)$ with temperature ($10^3/T$): (a) $\text{Ca}_2\text{Zn}_2\text{Fe}_{12}\text{O}_{22}$, (b) $\text{Ca}_2\text{Zn}_2\text{Fe}_{11.5}\text{Al}_{0.5}\text{O}_{22}$ and (c) $\text{Ca}_2\text{Zn}_2\text{Fe}_{11}\text{AlO}_{22}$

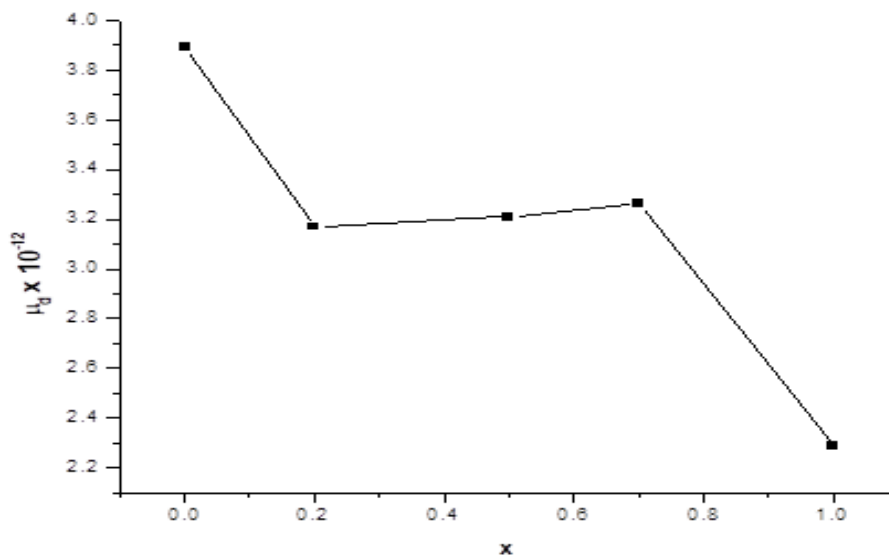


Fig. 5.4: Variation of μ_d with x of $\text{Ca}_2\text{Zn}_2\text{Fe}_{12-x}\text{Al}_x\text{O}_{22}$ (x = 0, 0.5 and 1.0)

TEM analysis

Fig. 2 shows TEM micrographs of aluminium substituted calcium hexaferrite. The average particle size of the sample is in the range of 29-36 nm. These observations are strongly supported by the results observed by Teh et al.[14]

DC conductivity

Fig. 3 shows the graph of electrical conductivity $\ln(\sigma)$ verses temperature ($10^3/T$) for all ferrites sample

It has been observed from the graphs that the value of $\ln \sigma$ declines almost linearly with increasing of reciprocal temperature up to a certain temperature known as transition temperature (T_t). where there is a change in slope (kink) occurs in plots. The temperature where kink is observed for the various composition of Al^{+3} ions in CaY ferrites is in neighborhood of magnetic transition temperature (Curie temperature T_c). This reveals that the kink observed in the aluminium substituted CaY ferrite can be attributed to the ordered to disordered transitions.

The electronic conduction in ferrite at room temperature is mainly due to hopping of electrons between ions of the same elements present in more than one valency state, distributed randomly over lattice sites as explain by Verway *et al.*,[15] Ferrite shows semiconducting behaviour at high temperature. The activation energy is the energy required to release an electron from ion for a transition to neighbouring ions. The activation energies calculated from slopes of plots of $\ln \sigma$ vs $10^3/T$ temperature above and below transition temperature (T_t) are depicted in Table 2.

It is seen from the observations that the activation energy in ferrimagnetic region (below transition temperature) is less than that of paramagnetic region. These are supported by the result seen in case of Co-Zn Tawfik [16], Ni-Zn ferrites by Pan'kov and Bashikov [17] and Co-Zn ferrites by Sable[18].

Drift mobility

The drift mobility is found to be decreasing with increasing doping concentration 'x' of Al. the

decreasing of drift mobility is due to change in resistivity by doped Al ions shown in Fig. 4.

Shahid Hussain and Asghari Maqsood[19] observed same behavioral trend. In the drift mobility with increasing amount of Pb in Sr ferrites. Muhammad Ashiq[20] reported the decreasing pattern in the drift mobility with increasing substituent of Al and Ga in strontium ferrites.

CONCLUSION

The aluminium substituted calcium hexaferrite samples were synthesized by the sol-gel auto-combustion method. The XRD data have confirm the formation of single phase Y-type hexaferrites and the values of a and c of the sample supports this confirmation. TEM studies showed the synthesized samples are in the nano-range. The synthesized samples are semiconductors. The dc electrical conductivity, activation energy as well as drift mobility decreased with increasing concentration of Al^{3+} ions. The phenomenon of conduction was explained on the basis of a Vervey hopping model. The decrease in conductivity of the sample with the substitution of Al^{3+} ion for Fe^{3+} ion has potential applications in microwave devices.

Acknowledgement: I am very much thankful to Prof. K. G. Rewatkar, Head, Department of Physics, Dr. Ambedkar College, Nagpur for providing laboratory for my research work.

Conflicts of interest: The authors stated that no conflicts of interest.

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