



EFFECT OF RARE EARTH IONS (Sm^{3+}) ON HUMIDITY SENSING PROPERTIES OF NANOCRYSTALLITE CADMIUM FERRITES

Ashok B Gadkari¹, T. J. Shinde² and P. N. Vasambekar³

¹Gopal Krishna Gokhale, College, Subhash Road, Kolhapur-416012

²KRP Mahavidyalaya, Isalmpur-415409, (MS) India

³Shivaji University, Kolhapur-416004, (MS) India

ashokgadkari88@yahoo.com

Abstract

The nanocrystallite powders of Sm-Cd ferrites were prepared by oxalate co-precipitation method. The structural analysis was done by XRD, SEM and FT-IR techniques. The X-ray diffraction study reveals the nanostructure material with crystallite size of range of 29.56 to 30.40nm. The grain size obtained from SEM study is in the range of 0.7 to 1.2 μm . The grain size of Sm^{3+} added cadmium ferrite is smaller than Cadmium ferrite. FT-IR show two absorption band in high and low frequency region. The resistivity of the samples decreases with increase in percentage relative humidity (%RH). The decrease is found to be exponential for 40 to 80 %RH and linear for 80 to 90%RH. All the samples are humidity sensitive at low humidity range of 40 to 80%RH. The sensitivity of Sm-Cd sensor is higher than Cd sensor. The response and recovery time of Sm-Cd sensor shorter than Cd sensor.

Keywords: Cd ferrites; Grain size; Humidity sensitivity; Response time.

Introduction

Humidity is an important environmental factor that affects wide range of technologies including biomedical, pharmaceutical, food, chemical, textile, computer and many others. It plays an important role in human life in many ways, drastically influencing the working efficiency. It strongly affects the amount of infrared energy penetrating in the air, providing infrared shield for earth. Therefore the measurement and the control of humidity is quite necessary [1]. An accurate control, monitoring of water content estimate are practically essential in various fields, including air quality detection, inflammable gas inspection, food, healthcare, clinical, biological sectors and defense [2]. There are some major requirements for a good humidity sensor like sensitivity, fast response time, long life time, and selectivity, chemical and thermal stability. Some polycrystalline ferrites can be used as good humidity sensor elements. The porosity of ferrites is advantageous when they are used as humidity sensors. They can give the change in resistivity of about three orders of magnitude with changes in the surrounding humidity [3]. In this communication, we report effect of Sm^{3+} ions addition on humidity sensing properties of Cd ferrites.

Material and Methods

Synthesis and Characterization
Polycrystalline powders 5wt% rare earth element Sm^{3+} added CdFe_2O_4 samples were prepared by the oxalate co-precipitation method using sulphates. The detail method of synthesis for sample under investigation is reported elsewhere [4]. The polycrystalline ferrite powder under investigation, were characterized by X-ray powder diffraction on Philips PW-3710 X-ray

diffractometer with $\text{CuK}\alpha$ radiation ($\lambda = 1.5424 \text{ \AA}$). Each sample was scanned in range 200 to 800 with a step size of 0.020. The X-ray tube was excited at 40 kV and 0.03 A. The SEM micrographs of fractured were recorded on scanning electron microscope, JEOL – JSM 6360 model, Japan. The FT-IR absorption spectra of powdered samples were recorded in the range 350 cm^{-1} – 800 cm^{-1} , on a Perkin-Elmer model: Spectrum one FT-IR spectrometer by KBr pellet technique. Humidity Sensing Characteristic The humidity testing of samples was conducted in a microprocessor controlled humidity chamber (Aditi Associate make, Model ASC-10, Mumbai) in the range of 40%RH to 90%RH in steps of 10%RH. The sensor elements (pellets) about 2mm thickness and 13mm diameter were fixed in conducting cell. For good electrical contact silver contacts were made on sensor element. DC voltage was applied across the sensor element with the help of constant potential voltage source. The resistance of sensor (pellet) was measured by two probe method with a picometer. The measurement was performed at the temperature 270C.

Result and Discussion

Characterization
The structural analysis (XRD, SEM and FT-IR) of 5wt% Sm^{3+} added Cd ferrites under investigations is already reported [4]. The typical XRD patterns of 5wt% Sm^{3+} added CdFe_2O_4 confirms the formation of cubic spinel with orthoferrite secondary phase. The rare earth ions induce second phase which corresponds to orthoferrite phase [5]. The average crystallite size of the samples is in the range of 29.87 to 30.40nm. The lattice constant, crystallite size and grain size of all the samples under investigation is listed in table I. From this

table, it is observed that lattice constant of prepared by oxalate co-precipitation method are very close to those reported for samples prepared by ceramic method [5]. Such reduction in the lattice constant in rare-earth ions substituted ferrites has been reported by E. Rezlescu and N. Rezlescu [6], suggesting the occupancy of rare earth ion on B-sites. Similar results for rare-earth element added ferrites have been reported [5-7]. The X-ray density (ρ_x), physical density (ρ_p) and porosity of all the samples are given in table I. The physical densities of the samples are 85.56% to that of X-ray densities. The density of rare earth added Cd ferrites is higher than Cd ferrites. This is attributed to formation of the secondary phase which favors the inhabitation of grain growth [4]. The microphotographs of 5wt% Sm³⁺ ions added CdFe₂O₄ is presented in Fig. 2. The average grain size lies in the range of 0.70 μ m to 1.2 μ m. The grain size obtained for the samples under investigation is smaller than that for ferrites prepared by ceramic method [7]. From table I it is further observed that the average grain size decreases with addition of rare earth elements in Cd ferrites. Typical Infrared absorption spectra of 5wt% Sm³⁺ added CdFe₂O₄ is presented in Fig. 3. The figures show two major absorption bands in the frequency range 350–800cm⁻¹. The high and low frequency absorption bands (ν_1 , ν_2) are observed in frequency range 467 to 587cm⁻¹ and 411 to 472 cm⁻¹ respectively. These bands are common characteristics of spinel ferrites [8]. Humidity sensing Variation of resistivity with humidity (%RH) of ferrite sensors is presented in Fig. 4. All the samples exhibit a significant decrease in the electrical resistivity with increased relative humidity in the range of 40 to 90%RH. The highest decrease in resistivity is observed between 40 to 70% RH. The resistivity of these sensor elements follows the equation [9], (1) where, S - humidity sensitivity and RH - relative humidity. The humidity is surface adsorption phenomenon in which higher humidity sensitivity is attributed to higher surface area of the samples. At low humidity, water adsorption on surface is dominant factor for electrical conductance. The higher surface area would provide more sites for water adsorption and produce more charge carriers for electrical conductance [10]. At low humidity levels chemisorption takes place leading to formation of two hydroxyl group with charge transports occurring by hopping mechanism [11]. At higher %RH physisorption of water molecules and electrolytic conduction takes

place. The adsorption of humidity on the surface decreases the resistivity due to the increase of charge carriers, protons, in the ferrite and water system. The adsorption of water on the surface of the material leads to the dissociation of hydrogen ions. These hydrogen ions bonded with the surface lattice oxygen atom, forms the hydroxyl groups [12] as, (2) where, - corresponds to oxygen at lattice sites. These hydroxyl groups are bonded with the lattice iron atoms and liberate the free electrons [13] giving increase in conductivity as, (3) Thus the conductivity increases with increased humidity [8]. The sensitivity of humidity sensor has been defined as the change in resistivity ($\Delta\rho$) of sensing element per unit change in relative humidity (%RH). It is seen from table that, the sensitivity of all the samples increases with increase in radius of rare earth ions which is attributed to increase in porosity. Kotnala et al. [14] reported increase in sensitivity for lithium substituted magnesium ferrite in the range 10-80%RH. All the samples are humidity sensitive in lower humidity range. The large decrease in resistivity with increased %RH is related to adsorption of water molecules on the surface and condensation in capillary pores. These samples have smaller grain size. This smaller grains leads to much more grain boundaries and thus to more active sites available for water adsorption. The decreased resistivity at higher %RH of the samples is due to lesser porosity of the samples. At higher %RH the adsorbed water molecules condense in capillary pores, resulting electrolytic conductance. Rezlescu et al [9] reported compositional dependence of humidity sensitivity of Ga and La substituted Mg-Cu ferrites. The response/recovery time of all samples lies between 160-285 s. The Sm-Cd ferrite sensor is having shortest response time. The sensors show shorter response time than Cd ferrite sensors [15]. This is because of the decrement in the grain size due to formation of secondary phase on grain boundaries of these sensors and highest of porosity in this sensor. The recovery time of these sensors is also smaller than that of Cd ferrite sensors.

Conclusion

The nanocrystallite powders of Sm-Cd ferrites were prepared by oxalate co-precipitation method. The X-ray diffraction study reveals the nanostructure material having cubic spinel structure with orthoferrite secondary phase. The crystallite size of range of 29.56 to 30.4 nm. The grain size of Sm³⁺ added cadmium ferrite is smaller than Cadmium

ferrite. FT-IR show two absorption band in high and low frequency region. All the samples are humidity sensitive at low humidity range of 40 to 80%RH. The sensitivity of Sm-Cd sensor is higher than Cd sensor. The response and

recovery time of Sm-Cd sensor shorter than Cd sensor. The gas sensitivity depends largely on microstructure, working temperature, type of substitution and test gas.

Table 1. Grain size of 5 wt% rare earth element (R) added CdFe₂O₄ systems (R = Sm³⁺).

Rare earth ion	Crystallite Size D (nm)	Lattice Constant a (Å)	Grain Size (µm)	X-ray Density ρ _x (gm/cc)	Physical Density ρ _p (gm/cc)	Porosity P (%)	Humidity Sensitivity (MΩ/%RH)	Response and Recovery time (sec)	
								Res	Reco
Cd	30.40	8.71	1.2	5.78	4.74	17.99	58.03	170	285
Sm ³⁺	29.56	8.69	0.70	6.27	5.64	19.58	1116.66	160	279

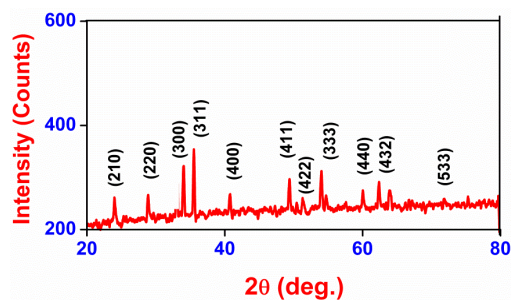


Figure 1: Typical X-ray diffraction patterns of 5 wt% Sm³⁺ ions added CdFe₂O₄

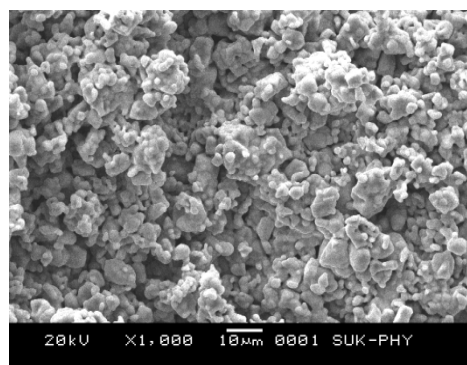


Figure 2: SEM micrograph of CdFe₂O₄

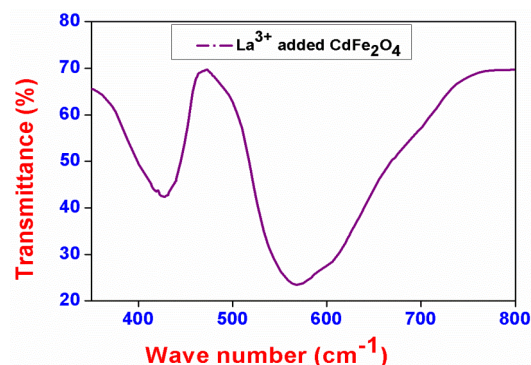


Figure 3: Typical FT-IR spectra of 5wt% Sm³⁺ ions added CdFe₂O₄

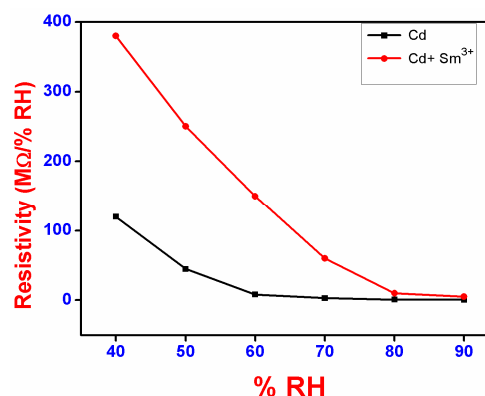


Figure 4: Variation of resistivity (ρ) – (%RH) characteristics for R- Cd ferrite

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