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Investigation of magnesium substituted nano particle zinc ferrites for relative humidity sensors

S.N. Patil*, A.M. Pawar, S.K. Tilekar, B.P. Ladgaonkar*

Post Graduate Department of Electronics, Shankarrao Mohite Mahavidyalaya, Akluj, Dist., Solapur 413 101, Maharashtra, India

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ABSTRACT

Nano particle Spinel ferrites, the magnetic semiconductor, are exhibiting remarkable surface phenomenon, wherein the process of adsorption is most significant. Humidity sensing is the realization of adsorption mechanism. Therefore, ferrites would be suitable for humidity sensing applications. Considering this fact into account, the compositions of polycrystalline Mg-Zn ferrites have been prepared by chemical route and characterized by standards tools like X-ray powder diffraction and FTIR spectroscopy. From the results of X-ray diffraction investigation, formation of single phase compositions is confirmed. The resulted structure is FCC with 311 as a prominent reflection. Average particle size obtained by using Scherrer method is within the range from 40 nm to 48 nm. The existence of the nanoparticles results into increase of the surface area required to favour adsorption mechanism. The significant absorption bands were observed for higher range of frequencies in FTIR, which are attributed to the modes of vibration of water molecules. Therefore, it can be used for development of the humidity sensor. The relative humidity sensor is designed by depositing thick film of the materials under investigation on ceramic substrate. Electrical resistance of the sensor (R_H) reveals decreasing trend with increase in the relative humidity. Relative deviation in the resistance (RDR) with humidity depicts two significant regions attributed to the existence of protonic conduction mechanism. The sensor, developed from x = 0.40, reveals good linearity over wide range of humidity from 40%RH to 75%RH, which suggests its suitability for sensor development. Moreover, the features of the composition for x = 0.40 is suitable for design of electronic interfaces required for instrumentation. The sensitivities of the compositions less than 1 s for 10% variation in the relative humidity. This confirms that the humidity sensors developed by employing compositions of ferrite on ceramic substrate are very fast and reliable.

1. Introduction

Humidity, a concentration of water vapors in the air, is most significant parameter to be measured. Precise measurement of humidity exhibits prime importance in various sectors such as sugar and paper based industries, chemicals and medicine industries, automotive industries, climatology, HVAC systems, agriculture etc. [1]. Recently, the term precision agriculture is evolving, wherein crops are grown in controlled environment. The humidity of polyhouse environment should be monitored and controlled to the deterministic level. For meteorological applications the collection and processing data, in real time, regarding humidity of the environment is most essential, which may help to predict about the precipitation, Dew or Fog [2]. The information can be suitably availed to avoid catastrophic disaster due to heavy precipitation. To have desirable surrounding atmosphere, it is essential to monitor and control the ambient humidity under various conditions related to the temperature and concentration of other environmental gases [3]. In paper manufacturing industry, the humidity of environment plays significant role on the quality of the paper. Furthermore, in hardboard manufacturing industries, the finishing paper sheet is laminated in controlled humidity condition. It is found that, for food processing industries, the controlling of humidity of the environment plays vital role on the quality of the food product [1,21]. To realize the preciseness in the measurement, the humidity sensor should be of prominent features. The sensing material and sensing principle play a key role on the specification of the sensor. For deployment of the sensor for electronic system design, the parameters such as ambient resistance, range of investigation, linearity, response timing, recovery timing, cost, realiability etc should be optimum. In present investigation, it is

* Corresponding authors.
E-mail addresses: suhas.patil05@gmail.com (S.N. Patil), bladgaonkar@yahoo.com (B.P. Ladgaonkar).

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attempted to optimize above parameters. The major objective of the present research work is to synthesize the materials suitable for humidity sensing and fabrication of the humidity sensor, which may realize the greater applicability. Therefore, compositions of polycrystalline Mg-Zn nanoferrite material were synthesized and results of investigation are interpreted.

The synthesis and characterization of materials, suitable for humidity sensing, was carried out by many researchers and the results obtained are reported. It is known that variety of materials, classified as polymers, electrolytes, porous ceramics, organic polymers, acoustics and optics [4,5] can be suitably deployed for development of humidity sensors. It was suggested that, the ceramic and polymer materials are most suitable for humidity sensor [5]. The research work, reported by the researchers, is reviewed and briefly discussed. On literature survey, it is found that, the polycrystalline spinel ferrite materials of nano particle size exhibit humidity sensing properties. Lipare et al. have investigated the effect of LiCl substitution on humidity dependent electrical properties of CuZn spinel ferrites [6]. They reported that, substitution of LiCl results into enhancement of the performance of the materials to the humidity. Wang et al. [7] have studied lanthanum ferrite/polymer quarternary acrylic resin composite materials for humidity dependent electrical properties. They reported improvement in the response timing due to addition of polymer in lanthanum ferrites. They also reported the hysteresis effect and relaxation behavior in dielectric response of the material under investigation. The effect of substitution of multivalent cations (Sn & Mo) in Mg ferrites was investigated by Rezlescu et al. [8]. They synthesized the materials by sol-gel auto combustion method and reported nanocrystallite structure. They reported that, the Sn ion enhances the humidity sensitivity of the magnesium ferrite. Emphasizing the features of ceramic materials, Faia et al. [9] investigated the humidity sensing properties of thick film titania prepared by spin deposition technique. The behavior of the materials to the humidity is attributed to the existence of protonic conduction mechanism. Kotnala et al. studied the humidity response of Li Mg ferrites [10]. They claimed that, substitution of lithium causes to enhance humidity sensitivity of magnesium ferrites. Deploying self combustion method the compositions of magnesium copper ferrites have been synthesized by Rezlescu et al. [11] and effect of Y^{3+}, Ga^{3+} and La^{3+} on performance of sensitivity for humidity is investigated. They reported that, substitution of Ga in MgCu ferrites results into increase in the range of humidity. Humidity sensing properties of α-Fe_2O_3 have been studied by Tulliani and Bonville [12] and reported the results on investigation of humidity dependent electrical properties of the screen printed thick film sensor. They suggested the suitability of doping of alkali and alkaline earth oxides for improvement in the performance of the sensors. Bagum et al. [13] have synthesized compositions of CuZn nano ferrites with doping of 0.05 wt% of $MgCl_2$ and deployed to study resistance humidity characteristics of the same. Electrical properties of the compositions are attributed to the microstructure and porosity of the compositions. Nanocrystallite Mg-Cd spinel ferrite samples were prepared by Gadkari et al. by oxalate co-precipitation method [14]. They investigated the humidity sensitive electrical properties and reported good performance for wide range of humidity. Emphasizing the applicability of the ferrite materials for development of humidity sensor, Petrila and Tudorache have synthesized nanostructured tungsten substituted CuZn ferrites [15]. The exponential behavior of the resistance against humidity attributed to the conduction mechanism. They reported the expression $R = Ro\ Exp(-K_{RH}t)$ for resistance curve and $C{=}Co\ Exp(K_{CH}t)$ for capacitance curve. Cavalieri et al. [16] studied effect of substitution of small amount of Cu in place of Fe^{3+} ion in LaSr ferrites and reported improvement in response of the samples for water vapour proving its suitability for development of humidity sensor. The compositions of nanostructure MgZn ferrites were synthesized by Rezlescu et al. using standard ceramic method and the results regarding humidity dependent electrical characteristics are reported [17]. The behavior of electrical conductivity is attributed to the microstructure of the samples. A thick film of Mn Zn spinel ferrite was deposited on ceramic substrate by Arshaka et al. [18]. They prepared thick film sensors, wherein two layers; one of interdigitated electrode and second of sensing element, have been deposited. The investigation regarding their performance for humidity proves its suitability for sensor based applications. It was also reported that, the accuracy of capacitive sensor is more than that of resistive type sensor. However, the response times of capacitive sensor is large than that of resistive sensor. The complex electronic circuit is required to interface capacitive sensor [19,20]. Köseoglu et al. [21] intensively studied the humidity sensing properties of MnNi ferrites prepared by chemical route using nitrides of the constituents. They reported that the $Mn_{0.2}Ni_{0.8}Fe_2O_4$ is sensitive for ethanol, acetone LPG and some oxidizing gases as well. However, the sensitivity of this material for water vapour is significantly high than other gases. Hence, these materials are suitable for humidity sensor. From literature survey, it is found that the electrical properties of the materials have been investigated. However, reports on development of the sensors and optimization of its features are rather rare. Therefore, present paper communicates results of sensor development.

2. Mechanism of humidity dependent electrical conduction

Polycrystalline spinel ferrite, the semiconducting oxides, due to its microstructural properties such as porosity, nanoparticles, larger surface area, uniform grain size etc, are most suitable for electrochemical sensor applications [22]. It is known that, the current through ferrite sample is temperature dependent. However, the electrical conduction through the ferrite compositions also depends upon humidity of the atmosphere. In fact, electrical conduction in the ceramic can be classified as ionic conduction, electronic conduction and solid-electrolyte, wherein surface phenomenon is realized. From FTIR studies, it is also found that, the ferrites are hygroscopic in nature, supported by existence of absorption band at higher domain of frequencies.

In ferrites, humidity dependent electrical conduction depends upon the phenomenon of water vapour adsorption based on chemical adsorption (chemisorption), physical adsorption (physisorption) and capillary condensation processes [23]. It is surface phenomenon. When ferrites are exposed to atmospheric moist air, in the first stage of the interaction a few water vapour molecules are chemically adsorbed (chemisorption) at the neck of the crystalline grains on activated sites of the surface, which is accompanied with a dissociative mechanism of vapour molecules to form hydroxyl groups (two hydroxyl ions per water molecule) as shown in Fig. 1. The H^+ ion is referred as proton. As an interaction between the surface ions of the grain necks and the adsorbed water, the hydroxyl group of each water molecule is adsorbed on metal cations, which are present in the grains' surfaces and possess high charge carrier density and strong electrostatic fields, providing mobile protons. The proton transfer takes place. The protons migrate from site to site on the surface. The released H^+ ion immediately combines with another H_2O molecule to form hydronium ion H_3O^+. This transfer mechanism is called Grotthus mechanism and can be illustrated as

$$H_2O = H^+ + OH^-$$

$$H^+ + H_2O = H_3O^+$$