Highly Sensitive Carbon Doped Magnesium Ferrite Humidity Sensor

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Abstract—Carbon doped magnesium ferrite has been explored for the resistive type humidity sensor.. Magnesium ferrite is a highly resistive $10^8 \Omega$ material carbon doping has significantly to reduce the base resistance of ferrite. By doping 0.4 wt % carbon its resistivity reduced to $10^7 \Omega$ at ambient humidity. Magnesium ferrite is a resistive type humidity sensor and its resistance decreased from $3x10^9 \Omega$ at 11 %RH to $73x10^6 \Omega$ at 86% relative humidity. While 0.4 wt% carbon doped ferrite exhibited decreased in resistance from $5x10^8 \Omega$ to $4.7x10^6 \Omega$ for 11 to 86%RH. A linear decrease in log resistance with increasing humidity has been observed carbon doped ferrite. Spinel phase formation of carbon doped magnesium ferrite has been confirmed by X-ray diffraction pattern. Carbon doping in ferrite has significantly enhanced the porosity of the ferrite confirmed by scanning electron microscopy. The properties of the sensor studied in this work make it beneficial as an instrument for environment monitoring of humidity.

Keywords: Carbon doped magnesium ferrite, Resistive humidity sensor, Relative humidity.

1. INTRODUCTION

Relative humidity is an important parameter for all of the measurement and characterization system, chemical processing, pharmaceuticals, biological products, which can induce structural changes, chemical changes and toxicity in different ceramic oxide materials and food products, polymers, organic compounds, not only inorganic and this superconducting phenomenon are also highly influenced by the humidity [1-5]. Therefore, in aspect of materials science, it is important to monitor humid environment with the help of highly precise humidity sensor[6]. Magnesium ferrite is a porous material possessing large surface area and having electrical resistance of the order of $10^7 \Omega$. If the sensing material has low electrical conductivity, it is difficult to measure the resistance in low humidity environment. On the other hand, if it has high electrical conductivity, the humidity dependence becomes relatively too small to be measured conventionally. In order to reduce the base resistance of the ferrite various doping/substitutions have been explored [7-12]. The interest of sensing materials consists the change in electrical properties in presence of water vapors. The fundamental mechanism that enables ceramic sensors to sense humidity is the interaction of water molecules, with surface cations, defects, inherent oxygen and pores on the surface of the sensor materials. In present paper humidity sensing property of undoped and carbon doped magnesium ferrite has been studied.

2. EXPERIMENTAL

Carbon doped magnesium ferrite has been synthesized by solid state reaction method. Analytical grade precursors MgCO₃, Fe₂O₃ and graphite has been taken in stochiometric ratio. All precursors have been wet grinded in pestle and mortar for 1h. Homogenized powder mixture was pre-sintered at 800°C in argon atmosphere for 8h. Pre-sintered powder then grinded and pelletized in rectangular shape 15 mm x 8 mm of 1 mm thickness with hydraulic press. Rectangular pellets were kept for sintering at 900°C for 2h in argon atmosphere. Sintered pellet were then silver pasted at the cross-sectional edge followed by heating. Copper wires were soldered at the pellet edges. Different relative humidity has been generated by making saturated solution of salts LiCl, MgCl₂, K₂CO₃, Mg(NO₃)₂.6H₂O, CuCl₂, KCl and BaCl₂ in a sealed glass vessel at ambient temperature, which yielded 11%, 33%, 43%, 54%, 67%, 86% and 90% relative humidity, respectively. The change in resistance of pellet in different relative humidity has been measured by Keithley 6541 electrometer. Porous microstructure has been observed by Scanning electron microscopy LEO 404. Spinel phase formation has been confirmed by Bruker X-ray diffractometer.

3. RESULTS AND DISCUSSION

Crystal phase of pure and carbon doped magnesium ferrite has been analysed by X-ray diffraction pattern as shown in Fig. 1. The fivepeaks appeared t $2\theta = 30.14^{\circ}$, 35.49° , 43.16° , 57.05° and 62.65° correspond to (220) (311) (400) (422) and (333) planes of spinel structure. There was no extra phase found in undoped magnesium ferrite. Very small peaks identified as Fe₂O₃ phase appeared in the carbon doped magnesium ferrite. This may be due to formation of CO₂ during sintering which leads to slightly reduced peaks of magnesium ferrite.



Fig. 1: X-ray diffraction pattern of undoped magnesium ferrite and 0.4 wt% carbon doped magnesium ferrite.

Grain size, pores size distribution, surface morphology of magnesium ferrite and carbon doped ferrite has been analyzed by SEM images as shown in Fig. 2 (a, b). Grain size distribution is uniform and symmetric throughout the surface of undoped magnesium ferrite. SEM image shows the impression of nucleation of small crystals on the bigger crystallites and the cluster like formation on grains. Nano to micropores are distributed uniformly and connected via grain neck in magnesium ferrite. The average pore size distribution is 30 nm to 360 nm. Carbon doping of 0.4 wt% in magnesium ferrite with 20 nm to 660 nm pores has been observed in fig. 2(b). Porous structure due to defects formation by carbon doping offers a high surface area for water vapor adsorption.



Fig. 2: SEM images of (a) undoped magnesium ferrite and (b) 0.4 wt% carbon doped ferrite.

Effect of carbon doping on water vapor sensing has been determined compared to undoped ferrite for the humidity range 11% to 86%RH as shown in Fig. 3. It has been clearly

observed, that the base resistance of undoped magnesium ferrite has been decreased to 2 order by carbon doping. This is beneficial to bring its resistance to measurable range by ordinary multimeter. Undoped magnesium ferrite resistance decreased from $3 \times 10^9 \Omega$ at 11 %RH to $73 \times 10^6 \Omega$ at 86% relative humidity. While 0.4 wt% carbon doped ferrite exhibited decreased in resistance from $5x10^8 \Omega$ to $4.7x10^6 \Omega$ for 11 to 86%RH. A linear decrease in log resistance with increasing humidity has been observed in carbon doped ferrite which is quite desirable for any sensor. Linear response of carbon doped ferrite may be due to increased pores which provide high surface area and capillary for water vapor condensation. Besides this, all the grain boundaries are well connected through neck of the grains, hence providing fast transport for protonation across the grain boundaries also. The association of the water vapors involves exchange of electrons between the adsorbed species and the material surface because of local surface charge density on the sensor surface. Thus exchange of electron leads to the chemisorptions process to dissociate water vapors in H⁺ and OH⁻ ions to chemically adsorb on an activated site to form an adsorption complex. Then, because of high electrostatic field in the chemisorbed layer another water molecule comes to be adsorbed through hydrogen bonding on the hydroxyl groups of chemisorbed layer known as first physisorbed water layer. Further adsorption of water vapors rise to the formation of a hydronium ion (H_3O^+) and release the proton to neighboring water molecule as indicated in following reaction [11]:

$$2 \text{ H}_2\text{O} \leftrightarrow \text{H}_3\text{O}^+ + \text{OH}^-$$

which gives further formation of proton to hydration process:

$$H_3O^+ \leftrightarrow H_2O + H^+$$

Thus the proton starts conduction in a chain to from second physisorbed layer, as the protonic conduction starts, the reduction in potential barrier height at the surface leads to the drops in electrical resistance of sensor.

Besides this, all the grain boundaries are well connecting through neck of the grains, hence providing fast transport for protonation across the grain boundaries also.



4. CONCLUSIONS

Humidity sensing property of undoped and 0.4 wt% carbon doped magnesium ferrite has been measured. Porosity of the ferrite has been found to increase by carbon doping in ferrite. This may be due to defect creation by CO₂ formation during sintering process. Carbon doped magnesium ferrite showed decrease in base resistance than undoped ferrite. Linear response in resistance has been observed for the entire humidity range 11%RH to 86%RH by carbon doping in magnesium ferrite. The properties of the sensor studied in this work make it beneficial as an instrument for environment monitoring of humidity.

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