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Zinc(II) Oxide–Yttrium(III) Oxide Composite Humidity Sensor

A. M. Edwin Suresh Raj*), C. Maria Magdalane, and K. S. Nagaraja[1])*)

Department of Chemistry, Loyola Institute of Frontier Energy (LIFE), Loyola College, Chennai 600 034, India

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A dc mode compatible $ZnO–Y_2O_3$ composite humidity sensor operating at room temperature was fabricated by the conventional solid state route. The base matrix was doped with Li^+ to enhance the sensitivity. The activation energy for dc conductance was found to be 0.75 eV. Thermoelectric power measurements revealed the nature of the materials to be of n-type. Resistance measurements were made on the composites at different relative humidities, generated by using different water buffers. The firing temperature was varied and the $ZnO–Y_2O_3$ composite sintered at 1273 K showed maximum sensitivity, which is attributed to an increase in porosity.

1. Introduction

Humidity is a significant environmental factor, which has to be monitored and controlled for a comfortable living. Various materials have been developed for humidity sensing of which the oxide based ones are reported to be potential candidates [1–4]. Ceramics have some attractive properties like stability of their chemical composition even at high temperatures, wear resistance, corrosion resistance and microstructure which renders the materials to be highly promising [5]. Metal oxides, especially ZnO and Y_2O_3, are known to be potential materials from both take fundamental and technical point of view [6–8]. In this article we report the electrical and humidity sensing properties of a novel $ZnO–Y_2O_3$ composite. A dc mode of operation was preferred throughout the investigation for the ease of compatibility with electronic circuitry.

2. Experimental

ZnO (Reachim, 99.9%) and Y_2O_3 (Koch-Light, 99.9%) were used as the starting materials. Equimolar quantities of ZnO and Y_2O_3 were mixed together for the fabrication of $ZnO–Y_2O_3$ composite. The mixture was milled for 12 h for homogeneity in a vibromill and was subsequently ground under absolute ethanol for 2 h in an agate mortar. This intimate mixture was then dried and pressed into pellets of about 10 mm diameter and 5 mm thickness in a hydraulic press at a pressure of 100 MPa. The pellets were then heated in a high purity alumina support in the uniform temperature zone of a tubular furnace in ambient air. Different heating rates were employed for better sintering and tensile strength. The sample was heated at a rate of 10 K/min up to 673 K, 2 K/min up to 973 K, and followed by 1 K/min up to the target temperature at which the sample was maintained for 12 h. The phases present in the sintered samples were ascertained

[1]) Corresponding author; ksnagi@vsnl.net
*) Present address: Department of Materials, Imperial College of Science, Technology and Medicine, London SW7 2BP, UK

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by a powder X-ray diffractometer (Rigaku Rotaflex, Japan) using Cu-K_α radiation within a 5 mass percent limit of its detection of impurity phases.

The dc resistance and temperature dependence of conductance measurements on the samples were carried out using a two-probe method. The electrodes of the sample were connected to the dc power supply and the picoamperemeter in series. Given the high resistivity of the materials under investigation, the potential inaccuracy due to contact resistance is assumed to be negligible. For thermoelectric power (TEP) measurements, the sample disk along with the hot junction of two K-type thermocouples pressed against the flat surfaces was sandwiched between the two flat ends of one-end-closed concentric quartz tubes. Two circular platinum discs sandwiched between thermocouple and sample on either face served as electrodes. The necessary mechanical pressure was exerted by two springs which pulled the tubes together near their open ends at the mouth of the furnace. A resistance wound tubular furnace of vertical configuration was used for these measurements. The thermo-emf as well as the thermocouple output was measured using a high impedance digital multimeter (Solartron DMM 7150). The hot end was kept as positive and the cold end as negative. The thermo-emf was measured in ambient air by connecting the identical chromel leads of the two thermocouples. The other technical details are given elsewhere [9].

The controlled humidity environments were achieved using anhydrous P_2O_5 and different saturated aqueous salt solutions in a closed glass vessel at an ambient temperature of 298 K. These relative humidity (RH) levels were independently monitored by using a Barigo hygrometer. Heat cleaning of the samples was found to be a must for better sensitivity. Hence the samples were heated to 473 K, followed by cooling in humidity free atmosphere before and after the sensitivity measurements especially when the sensors were operated at higher RH.

3. Results and Discussion

The powder XRD pattern (Fig. 1) of the sample sintered at 1273 K indicated the presence of only ZnO and Y_2O_3. Since dc mode is used for resistance measurements at various relative humidities, the activation energy for electrical conduction was determined in inert atmosphere in the temperature range of 373–673 K by using a dc two-probe method. The plot of $\ln S$ (conductance) against $10^3/T$ is found to be a straight line, from the slope of which the activation energy was calculated to be 0.75 eV.

The thermoelectric power (θ) was measured by a differential technique using the formula $\theta = \Delta V/\Delta T$, where ΔV and ΔT are the thermoelectric voltage and temperature gradient, respectively. The chromel/Pt correction was done using the formula [9],

$$E(\text{chromel, Pt})/\text{mV} = -10.43 + 0.03371T.$$

The coefficient of TEP at 673 K was found to be 940 μV/K for the composite sintered at 1273 K. The sign convention is that ΔV is positive when the hot end is at a positive potential with respect to the cold end, so that the sign of θ and that of the charge carriers are opposite to each other [10]. From the positive value of θ it can be inferred that the material is of n-type. One salient feature of most of the commercial humidity sensors is that these materials are n-type semiconductors as those presently investigated. Moreover, the conductivity of n-type sensors increases with increase in water vapor pressure while that of a p-type sensor decreases. The adsorption of electron do-

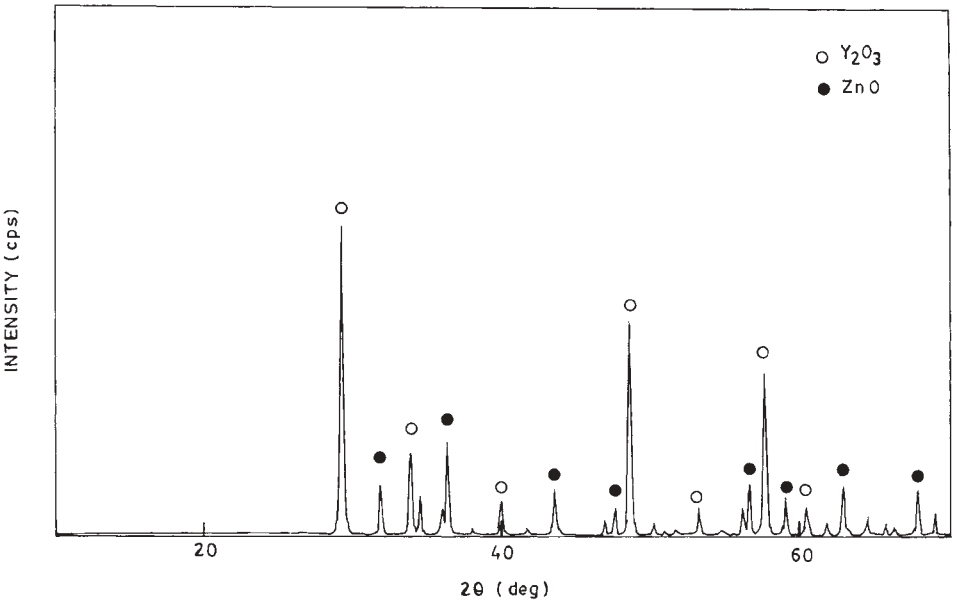

Fig. 1. Powder XRD pattern of the $ZnO–Y_2O_3$ composite sintered at 1273 K

nor molecules (water) results in a conductivity change that is larger for n-type semiconducting oxides than for p-type oxides, which makes n-type oxides more desirable. The high value of the coefficient of TEP can be explained from the low thermal conductivity of ceramics. The thermal conductivity of $ZnO–Y_2O_3$ at an ambient temperature of 673 K will be low and hence the coefficient of TEP, which is measured by monitoring the thermo-emf on both faces of the pellet, will be high.

The results of resistance measurements as a function of RH at a fixed ambient temperature of 298 K are presented in Fig. 2. The sensitivity factor S_f was calculated using the formula $S_f = R_{5\%}/R_{98\%}$ where $R_{5\%}$ and $R_{98\%}$ are the dc resistance at 5% and 98% RH, respectively. Two target temperatures, viz. 1173 and 1273 K, were chosen for finding out the effect of porosity on the humidity-sensing behaviour. Salt doping in ceramics is known to enhance the humidity sensitivity [11]. Since pure $ZnO–Y_2O_3$ ceramics show less sensitivity, the base matrix was doped with Li^+. Increase in sensitivity with Li^+ doping may be due to the high charge density of Li^+ ions, which highly polarize/dissociate the adsorbed water molecules. It can be observed from Fig. 2 that the variation of dc resistance against relative humidity was negligible for undoped ceramic sintered at both 1173 and 1273 K. The sample sintered at 1273 K and doped with Li^+ shows the maximum sensitivity with a S_f of 2800, and the value of S_f corresponding to the doped sample sintered at 1173 K is only 30.

Decrease in density with increase in sintering temperature was reported for ZnO ceramics, which is attributed to an increase in grain coalition with increasing temperature, which ultimately leads to an increase in the porosity [12]. But taking into account the vapour pressure of ZnO, the vapour pressure at 1173 and 1273 K is 7.3×10^{-4} and 1×10^{-2} Torr, respectively [13]. It is evident from the vapour pressure data that the vapour pressure increases by about a factor of 14 when the temperature is increased

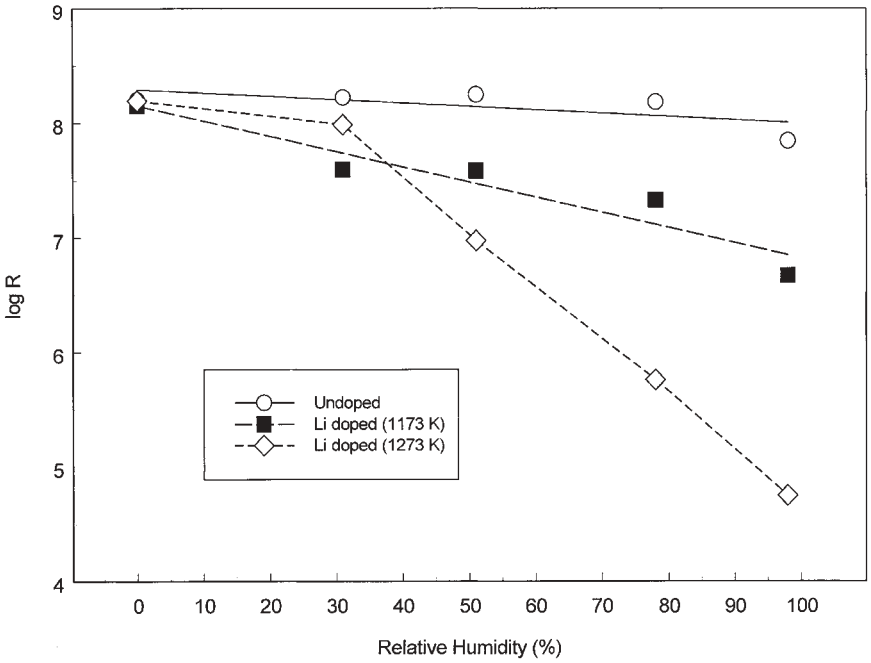

Fig. 2. Relative humidity vs. dc resistance plot of the $ZnO–Y_2O_3$ composites at 298 K

from 1173 to 1273 K. Hence the contributions towards the pore formation arising from the increase in the vapour pressure of ZnO with increase in temperature also cannot be ruled out. When the pore size is large, it becomes easier for water vapour to diffuse into or out of relatively bigger pores, and as a result the sample sintered at 1273 K has the maximum sensitivity. The Li^+ doped sample sintered at 1273 K shows linear behaviour in the resistance versus relative humidity plot in the humidity range of 51–98% RH. But the Li^+ doped sample sintered at 1173 K shows linear behaviour in the entire humidity range of 5–98% RH, however with only a sensitivity factor of 30. The linear behaviour is a prerequisite for commercial humidity sensors, which allows the sensors to be exploited in the range of study.

Charging of the electrodes was observed when the dc measurements were made on the samples by lodging the samples over the respective salt solutions in closed chambers, especially at higher RH. However, when online measurements were carried out to check the response and recovery behaviour, that is by purging air saturated with water vapour through a glass tube of about 200 cm^3 volume containing the sample, the charging effect on the electrodes was found to be minimum. To calculate the recovery and response time of the sensor, the Li^+ doped sample sintered at 1273 K was chosen. Within approximately 7 min of purging with moist air, the dry resistance of the material (on the order of 10^8 Ω) drops to the order of 10^5 Ω. However, when dry air was again introduced to monitor the recovery characteristics, the recovery was rather very slow. Most of the ceramic materials devised for humidity sensing applications require constant heat cleaning. Hence for better response and recovery characteristics, the sensors were repeatedly heat-refreshed at 473 K before and after the measurements.

It should be mentioned that the sensitivity of neither ZnO nor Y_2O_3 is appreciable towards moisture. Our earlier studies on ZnO–$ZnMoO_4$ composites indicated [14] that the sensitivity factor of pure ZnO is negligible ($S_f = 2$), and the current studies inferred the sensitivity factor of pure Y_2O_3 to be 10. This clearly indicates that an optimum blend on ZnO and Y_2O_3 is necessary for maximizing the sensitivity. Further, all the measurements were carried our in air ambient in the absence of any oxidizing/reducing gases. In the presence of such gases, cross-sensitivity measurements should be made which, however, is beyond the scope of the present investigation.

4. Conclusions

Novel ceramic humidity sensors were developed by co-firing ZnO and Y_2O_3 at 1173 and 1273 K. The sintering temperature could not be raised further since XRD patterns show a distortion in the ZnO and Y_2O_3 lines and the sensitivity decreases. The effect of porosity and relative humidity on the sensing characteristics has been studied. The sensitivity factor is found to be around 2800 for the ceramic composite sintered at 1273 K. The sign of the Seebeck coefficient indicated the n-type nature of the materials. In view of this, the samples under investigation would merit to be commercial candidate materials for humidity sensing.

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