Humidity sensing properties of Li^+ doped $BiVO_4$–V_2O_5 composites prepared by a sol-gel method

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ABSTRACT - This paper reports electrical conductivity and humidity sensing properties of BiVO4 (BV) and V2O5 (VO) composites prepared by a sol-gel method and sintered at 773 K in the form of cylindrical discs. Sintered polycrystalline discs of composites made in the mole ratios 80:20, 60:40, 40:60 and 20:80 are doped with 2 mole % of Li^+ were studied. The composites were characterized by powder XRD, SEM and BET surface adsorption studies. The composites were subjected to DC resistance measurements as a function of relative humidity in the range of 5–98% RH, achieved by different water vapour buffers thermostated at room temperature. The composites were subjected to DC resistance measurements as a function of relative humidity in the range of 5–98% RH, achieved by different water vapour buffers thermostated at room temperature. The sensitivity factor Sf (R5%/R98%) measured at 25°C revealed that BVVO-46 has the highest humidity sensitivity factor of 15535 (±380). BVVO-46 composite exhibits excellent humidity sensing characteristics such as fast response time (40s), rapid recovery (75s), linearity, hysteresis within 5%, excellent repeatability, good stability and broad range of operation (5-98% RH).

Key words: Bismuth vanadate, Humidity sensors, Vanadium pentoxide, Composites, sol-gel technique.

I. INTRODUCTION

Humidity is a significant environment factor, which has to be monitored and controlled for a comfortable living [1]. Over the last decade, considerable interest has been received to synthesize novel material with potential humidity sensing characteristics for the fabrication of low cost, rapid and stable humidity sensors [2-5]. An excellent humidity sensor should have high response value, quick response and fast recovery, good reproducibility, broad range of operation and low cost [6]. Ceramic and polymaterials have commonly been used as sensing materials for the construction of humidity sensors [7-11]. Ceramics have some attractive properties like thermal stability, water resistance, corrosion resistance and microstructure, which renders the materials to be highly promising [12] as humidity sensors. Ceramic materials based on various metal oxides offer several advantages over polymeric materials such as high chemical and mechanical stability, high response, rapid recovery dynamics and broad range of operation.

Bismuth vanadate is a well-known photocatalyst material [13-15], has received great interest in the past few years due to its application potential in many technological areas such as gas sensors, electronic devices, plating additives, posistors, solid-state electrolytes and positive electrode materials for lithium rechargeable batteries [16]. Different methods including solid-state [17], sonochemical [18], organic decomposition [19], precipitation [20], hydrothermal [21] and sol-gel [22] methods have been employed to synthesize $BiVO_4$ with various morphologies. The sol-gel method has been established as an effective route due to its operational simplicity, cost-efficiency and continuous production potential compared with other methods. Bismuth phosphate [23] and Bi_2MO_6 (M= W or Mo) [24] have been synthesized and investigated the humidity sensors exhibited high sensitivity, fast response and short recovery time towards moisture. However, there is no report on the application of $BiVO_4$-V_2O_5 composites for the detection of humidity. The present study reports, for the first time, on humidity sensor featuring $BiVO_4$-V_2O_5 composites as the sensitive layer. In this study, the $BiVO_4$-V_2O_5 composites were synthesized by a sol-gel method.

II. EXPERIMENT

The experimental procedure [25] for preparing $BiVO_4$–V_2O_5 composite by sol-gel method is schematically shown in [Fig. 1]. Bismuth nitrate ($Bi(NO_3)_3.5H_2O$) and ammonium vanadate (NH_4VO_3) were used as the starting precursors with 1:1 molar ratio. 4.8g of bismuth nitrate dissolved in 50 mL of 4M nitric acid and 1.2g of ammonium vanadate dissolved in 50 mL of 4M ammonium hydroxide were mixed together with constant stirring for 30 min. After these two solutions were mixed, yellow solution was obtained. The yellow sol solution was then added with 100 mL ethanol and heated 70^0 C with constant stirring for 1 hour. The yellow sol solution was obtained. Sol was changed to the yellow gel after addition 50 mL of deionized water and 5 mL of 1M acetic acid. Finally, the yellow gel was

dried in oven at 100^0C for 48 h and calcined in furnace at 500^0C for 1 hour. The different mole ratios of $BiVO_4$ and V_2O_5 were mixed together for the fabrication of $BiVO_4$ – V_2O_5 composite. As lithium was shown to enhance the sensitivity of humidity sensors, the base matrices were doped with 2 moles % of Li^+ as LiOH. H_2O. 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. After drying, the mixtures were compacted into cylindrical disc of about 10 mm diameter and 5 mm thickness in a hydraulic press at a pressure of 100 Mpa. These 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 samples were heated at a rate of 10 K min^{-1} up to 673 K, 2 K min^{-1} up to 773 K, and followed by 1 K min^{-1} up to the target temperature 873 K at which the sample was maintained for 12 h.

The prepared composites were characterized by powder XRD method. The phases present in the sintered samples were ascertained by a powder X-ray diffractometer (Rigaku Rotaflex, Japan) using Cu–Kα radiation within a 5 mass percent limit of its detection of impurity phases. The SEM analysis was carried out with a Hitachi SEM S415 A microscope. The surface area of the composite, $BiVO_4$ – V_2O_5 was determined employing BET equations in a Carlo Erba Sorptometer using N_2 adsorption at 77 K. All the samples were preheated at 473 K at 20 μ vacuum before measurements. The composites were characterized by solid-state electrical temperature dependent (373-673K) measurement have been [26] carried out.

The Li^+ doped $BiVO_4$–V_2O_5 composites were used for the evaluation of humidity sensing performance. The different relative humidity (RH) levels were generated in closed bottles by the different saturated salt solutions at room temperature. The bottles were made of glass having 19cm height and 6 cm diameter. The nine different controlled humidity environments standard saturated aqueous salt solutions of CH_3COOK 5 (± 0.10 % RH), 20 (± 0.20 % RH), 31 (± 0.10 % RH), 42 (± 0.15 % RH), 51 (± 0.23 % RH), 66 (± 0.18 % RH), 79 (± 0.16 % RH), 88 (± 0.24 % RH), 98 (± 0.30 % RH) were used to act as humidity source [26]. The saturated salt solutions were placed in the bottles for 12 h to ensure that the air in the bottle reached to equilibrium state. The $BiVO_4$–V_2O_5 was placed successively into the bottles with different RH levels at room temperature and the impedance of the film was measured as a function of RH. A humidity probe (Model 6517 – RH Humidity probe, Keithley Instruments, USA) was also placed into the bottles along with the $BiVO_4$–V_2O_5 composites to monitor the RH during the measurement.

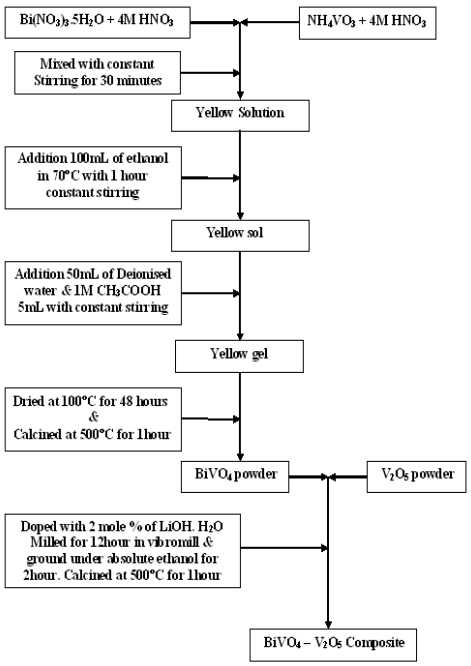

Fig.1. Flow chart of the preparation of $BiVO_4$ – V_2O_5 composites by sol-gel method.

III. RESULT AND DISCUSSION

A. Materials characterization

The powder XRD patterns of as-prepared $BiVO_4$–V_2O_5 composite [Fig. 2] exhibits the diffraction peaks corresponding to $BiVO_4$–V_2O_5. The relative intensity ratios of individual peaks agree with the data reported by JCPDS data card 14-0688 ($BiVO_4$) and 65-0131 (V_2O_5). No other peaks were observed, indicating that no impurities were present and confirming that the adopted synthesis route gives pure $BiVO_4$–V_2O_5 composite.

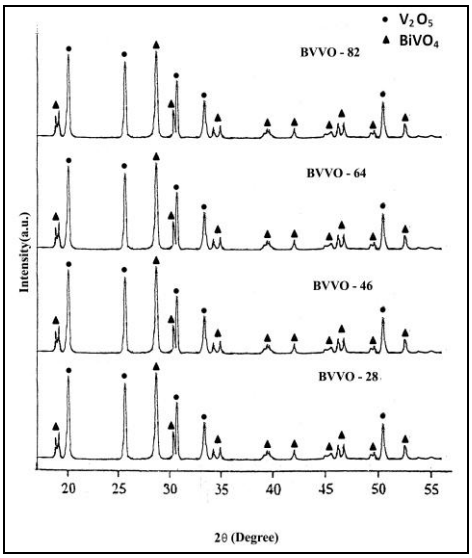

Fig.2. Powder XRD patterns of $BiVO_4$ – V_2O_5 composites (a) BVVO-82 (b) BVV-64 (c) BVVO-46 (d) BVVO-28.

The samples showed the linear current–voltage curves and thus the electrical conductivity was calculated from the slope by curve fitting using the least square method. Since DC mode is used for resistance measurements at various relative humidities, the activation energy for electrical conduction was determined in air atmosphere in the temperature range 373–673 K by using a DC two-probe method [26]. The potential inaccuracy due to contact resistance could be assumed to be negligible owing to the high resistivity of the materials under investigation. The DC measurements were carried out to measure chiefly the electronic conduction which could be used in humidity sensing measurements. Due to variation in electrical conductance because of the donation of electrons by water molecules either into the conductance band or positive holes of the composite materials, the sensitivity of the material varies. A polarization effect at the electrodes, if any, may be overlooked as the measurements were made uniformly and graphical methods of evaluation and comparison have been resorted.

B. SEM and BET measurement

SEM photograph of the sensor materials indicated that the porosity and grain size of the materials significantly increases and revealed qualitatively that BVVO-46 [Fig. 3] composition has greater and larger number of pores compared to the other composites.

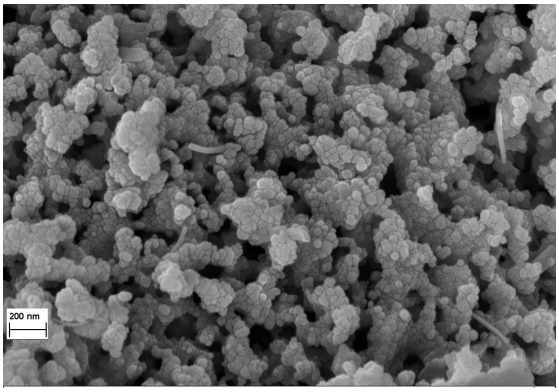

Fig.3. SEM photographs of BVVO-46 composite.

The BET surface adsorption studies revealed that the pore size of the samples were distributed [Fig. 4] between 10 and 45 Å in radius, and the specific volume of the pore was 0.01 cm^3 gm^{-1} which can easily trap the water molecules into it. The sensitivity factor of the composition should be indicative of the extent of moisture condensation in the pores. The pore size, grain size of the two phases, and the distribution of the pores should in turn govern the extent of moisture sorption.

C. Humidity generation measurement

The dependence of the resistance of $BiVO_4$–V_2O_5 composite measured at different relative humidities is shown in [Fig. 5]. The drop in DC resistance with increase in RH is smaller in the terminal phases BVVO-10 and BVVO-01 than that of the composites. The sensitivity factor $S_f = R_{5\%}/R_{98\%}$, where $R_{5\%}$ and $R_{98\%}$ are the DC resistances [Table. 1] at 5 and 98% RH is used for a better appreciation of the material characteristics towards moisture. The greater is the value of Sf, the higher is the sensitivity of the material towards moisture. The maximum sensitivity occurs in BVVO-46 where the resistance drops by more than three orders of magnitude and there is a non-monotonic trend in S_f as a function of composition. This implies that the BVVO–46 composite is humidity sensitive. The linearity of the humidity response in the humidity range (5-98% RH) suggests that the $BiVO_4$–V_20_5 composite based humidity sensor can be reliably used to monitor the RH over this range.

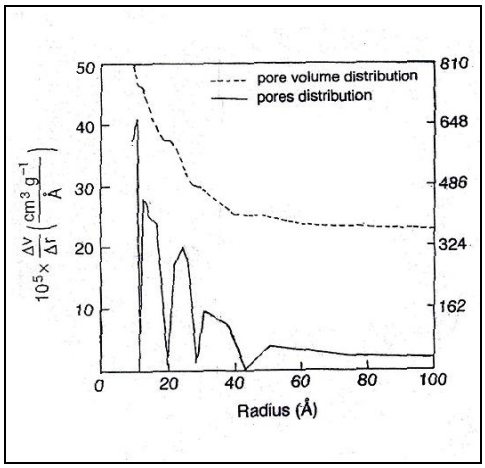

Fig.4. Pore size and pore volume distribution in BVVO–46 composite.

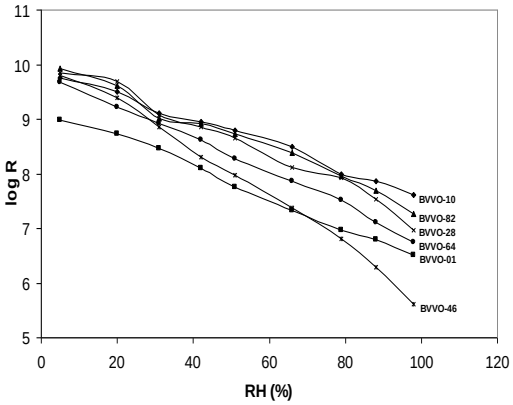

Fig.5. Dependence of resistance on the RH (%) for $BiVO_4$ – V_2O_5 composites.

D. Hysteresis studies

As the composites are placed in the higher humid environment, the pores in the composite will be saturated and the condensation of the moisture will take place. As a result, the conductivity increases where as the resistance decreases. Thus this could explain the variation of S_f with different composition of the composite, but no regular trend could be observed. It should be mentioned that the sensitivity of neither $BiVO_4$ nor V_2O_5 is appreciable towards moisture. In order to examine the repeatability, the impedance of $BiVO_4$–V_20_5 composite film was measured for three

time by exposing it from the low (11% RH) to high (97% RH) humidity atmospheres. Further, all the measurements were carried out 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. The humidity hysteresis characteristic of the composite based humidity sensor is shown in [Fig. 6].

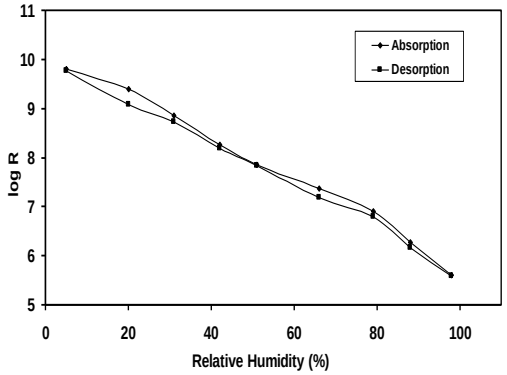

Fig. 6. Humidity hysteresis characteristics of BVVO–46 composite.

The humidity hysteresis error ($\gamma H = \pm \Delta RH_{max}/2F_{FS}$) was calculated using the expression [27]. Were ΔRH_{max} is the difference in output of forward and back-ward operations and $2F_{FS}$ is the full scale output. During the whole adsorption-desorption process, the maximum adsorption value of γH is found to be 3.5% RH in the range of 5-98% RH indicating a good reliability of the sensor.

E. Response and recovery characteristics

BVVO–46 composite was chosen [Fig. 7] to evaluate the recovery and response time of the sensor. Within approximately 40s of purging with moist air, the dc resistance of the material (10^9 ohm) under dry condition drops to 10^6 ohm. However, when dry air was again introduced to monitor the recovery characteristics, the recovery time was around 75s. When online measurements were carried out to check the response and recovery behavior, the charging effect on the electrodes was found to be minimal. 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 353 K before and after the measurements

F. Stability measurement

To investigate the stability, the $BiVO_4$-V_2O_5 composite based humidity sensor was exposed in air

TABLE 1 SENSITIVITY FACTOR AND ACTIVATION ENERGY FOR Li^+ DOPED $BiVO_4$–V_2O_5 COMPOSITES.

No. of moles		Sample code	Resistance $R_{5\%}$ (Ω)	Resistance $R_{98\%}$ (Ω)	S_f ($R_{5\%}/R_{98\%}$)	Activation energy Ea (eV)
B_iVO_4	V_2O_5					
100	0	BVVO-10	$5.6 \times 10_9$	4.05×10^7	138 (±40)	0.69
80	20	BVVO-82	$8.5 \times 10_9$	1.85×10^7	459 (±76)	0.42
60	40	BVVO-64	$4.7 \times 10_9$	5.65×10^6	827 (±135)	0.56
40	60	BVVO-46	$6.4 \times 10_9$	4.11×10^5	15535 (±380)	0.88
20	80	BVVO-28	$7.2 \times 10_9$	9.17×10^6	785 (±186)	0.48
0	100	BVVO-01	$9.6 \times 10_9$	3.24×10^6	296 (±64)	0.69

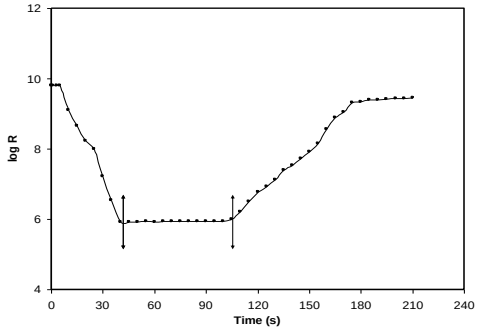

Fig.7. Response and recovery characteristics of BVVO–46 composite.

for 30 days and a measurement of the resistances once in every 5 days was performed at 5-98 % RH. As shown in [Fig. 8] there are almost no changes in the resistances, which directly confirm the good stability of the sensors.

IV. CONCLUSION

Composites having different mole ratios of $BiVO_4$ and V_2O_5 were fabricated by sol-gel method and studied for humidity sensing applications. The composites were subjected to DC conductance measurements over the temperature range 373–673 K from which the activation energies were determined. The activation energy values for DC conductance were found to be in the range of 0.42-0.88eV.

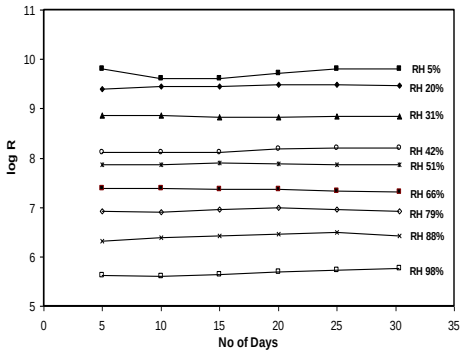

Fig. 8. Stability of the sensor measured at 5 – 98 % RH.

The composites were identified by powder XRD data. The BET surface adsorption studies showed that the radius of the pore sizes was found to be distributed from 10–45 Å. The pore specific volume was calculated to be 0.01 cm^3 gm^{-1}. As the composite having micropores are preferred for humidity sensing properties. The SEM studies were carried out to study the surface and pores structure of the sensor materials. The SEM revealed that the BVVO–46 composite has larger and greater number of microscopic pores hence is a good candidate for humidity sensor, which was further evidenced by the surface studies and its sensitivity factor higher than 15×10^3. The sensor exhibits excellent humidity sensing characteristics such as linearity, fast response and recovery behavior, hysteresis with in 5%, good repeatability, stability and broad range of operation (5-98% RH). Therefore, Li^+ doped $BiVO_4$–V_2O_5 composites are quite promising for the fabrication of a practical humidity sensor.

V.ACKNOWLEDGEMENT

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