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Studies of Electrical and Humidity Sensing Properties of Ternary Mixture of Some Transition Metal Oxides

S.Manivannan[a]* R.Karthikeyan[b] and Crystal Y.Wilson[c]
a*b Department of Chemistry, Dr.Ambedkar Government Arts College
Vyasarpadi, Chennai-600039, India.
c Department of Chemistry, Anna Adharsh College for Women
Anna Nagar, Chennai-600040, India.
e-mail: sembanuran@gmail.com: karthiakash@gmail.com

Abstract— **The ternary mixture of transition metal oxides [nickel (II), zinc (II) and copper (II)] NZC, and [nickel (II), manganese (JV) and tungsten (VI)] NMW were prepared with different mole ratios of their component oxides and sintered at 850K in the form of cylindrical discs. Experimental results on NZC and NMW for humidity sensing are described. The mixture of metal oxides having highest sensitivity were subjected to dc conductance measurements over the temperature range 518K to 623K from which activation energies was determined. The activation energy values for dc conductance were found to be in the range of 0.172 – 0.244 eV. The mixtures of metal oxides having highest sensitivity were identified by powder XRD and FT-IR data. The metal oxide mixture were subjected to dc resistance measurement as a function of relative humidity in the range of 5-98% RH, achieved by different water vapour buffers thermo stated at room temperature. The sensitivity factor ($S_r = R_{5\%}/R_{98\%}$) measured at 298K revealed that NMW-211 metal oxides mixture has the highest humidity sensitivity factor of 147242.**
Keywords- **Sensor; humidity; Sensitivity factor; Metal oxide**

I. INTRODUCTION

Monitoring and controlling environmental humidity is receiving ever-wider attention mainly for physical comfort and for industrial processes [1]. For this purpose, humidity sensors making use of electrical parameters are preferable. Particularly in recent years, the use of humidity control in production processes and products in a wide range of industries like manufacturing electronic devices, precision instruments, textiles and processes food has gained momentum [2]. Sometimes it is necessary to monitor the absolute humidity or the dew point, but more often it is important to control the relative humidity (RH). Numerous materials have been utilized for humidity sensing of which the metal oxides that are physically and chemically stable have been extensively investigated [3-6]. Sensors based on changes in resistance and capacitance is preferred to the conventional ones owing to their small size and compatibility with electronic circuits [7]. Transition metal oxides constitute one of the most fascinating classes of inorganic solids exhibiting a very wide variety of structures, the properties and phenomena due to the unique nature of the outer d electrons and the metal-oxygen bonding varying from nearly ionic to metallic [8-10]. Hence transition metal oxides were chosen for study. We hereby report the humidity dependent electrical resistance characteristics of [NiO-ZnO-CuO]-NZC, and [NiO-MnO_2–WO_3] - NMW ternary mixtures.

II. SAMPLE PREPARATION AND EXPERIMENTAL

All reagents employed for the synthesis were of Analar grade. The metal oxides NiO,MnO_2 , WO_3 ,ZnO, and CuO were used as received. The ternary mixture of metal oxide sensors were synthesized from different mole ratio of ZnO, CuO and NiO or MnO_2 , WO_3, and NiO; the exact details are presented in Table 1. The mixture was vibromilled and ground mechanically for 5 hours in the presence of pure acetone. The samples were compacted in a form of the cylindrical disc of about 10mm diameter and 2mm thickness. These pellets were then heated at a rate of 10Kmin^{-1} up to 850K and kept at this temperature for 12 hours to facilitate sintering followed by furnace cooling of the samples. The experiments were repeated at least thrice to ensure good crystalline of the metal oxide mixture. The metal oxide mixtures were characterized by powder XRD and FI-IR measurements. The phases present in the sintered samples were ascertained by a powder X-ray diffractometer (Philips X'lerator detector) using Cu-K_α radiation at λ = 1.54Ǻ. Perkin Elmer Infrared Spectrometer was used for the determination of the surface functional groups.

TABLE 1 MOLE RATIOS, RESISTANCE, SENSITIVITY FACTOR AND ACTIVATION ENERGY DATA FOR NZC AND NMW METAL OXIDE MIXTURES.

NiO (No.of Moles)	M1 M1=ZnO or MnO_2 (No.of Moles)	M2 M2=CuO or WO_3) (No.of moles)	Sample Code	Résistance*(n Ω) $R_{5\%}$	$R_{98\%}$	S_f ($R_{5\%}/R_{98\%}$)	E_a (eV)
1	1	0	NZC-110	3.406×10^8	1.693×10^8	2.015	
1	0	1	**NZC-101**	2.826×10^9	5.310×10^5	**5652**	0.244
0	1	1	NZC-011	1.341×10^9	3.443×10^7	38.98	
1	1	1	NZC-111	2.860×10^9	9.470×10^6	3178	
2	1	1	NZC-211	5.914×10^{10}	1.153×10^9	51.29	
1	2	1	NZC-121	1.904×10^{11}	1.439×10^9	132.31	
1	1	2	NZC-112	1.658×10^9	3.480×10^5	5527	
1	1	0	NMW-110	1.072×10^7	7.620×10^5	14.08	
1	0	1	NMW-101	2.769×10^9	6.681×10^6	415	
0	1	1	NMW-011	2.376×10^9	7.544×10^6	317	
1	1	1	NMW-111	4.440×10^9	2.027×10^9	2.2	
2	1	1	**NMW-211**	6.478×10^{10}	4.460×10^5	**147242**	0.1724
1	2	1	NMW-121	3.723×10^9	2.570×10^5	14892	
1	1	2	NMW-112	2.170×10^9	3.220×10^5	67813	

* R5% and R98% stand for dc resistances measured at 298K corresponding to RH 5 and 98% respectively

The samples were scanned in the spectral range of 4000-400cm^{-1}. The electrical contacts were made on the surface of the pellet by means of two thin copper wires affixed with silver point. The pellet was inserted in the middle of the pyrex tube of 5cm diameter on which the Kanthal wire was uniformly wounded externally. The Kanthal wire ends were connected to a Varian to vary the temperature and a copper-Constantine thermocouple kept at the pellet was used to measure the temperature of the sample. The electrodes were connected to a dc power supply and a Pico ammeter in series. The applied field (V/d), where V is the voltage and d is the distance between the electrodes, was varied and the corresponding current at room temperature was measured. A plot of current versus applied field was obtained. The dc resistance and its temperature dependence (318 – 623K) were carried out using a two-probe method [11-12]. The controlled humidity level was achieved by using anhydrous P_2O_5 and saturated aqueous solutions of $CaCl_2.6H_2O$, $Ca(NO_3)_2.4H_2O$, NH_4Cl and $CuSO_4.5H_2O$ in a closed glass vessel at an ambient temperature of 298K, which yielded approximately 5,31,51,79 and 98% relative humidity respectively and was exactly measured with Barigo hygrometer. After heating the metal oxide mixtures were placed inside the controlled humidity environment for 2 hours. The change in current was measured by varying the voltage from 2 to 32 volts. Prior to the saturation of the pellets in the above buffers the pellets were heat cleaned at 393K, by cooling in humidity free atmosphere to remove adsorbed water. The sensitivity factor was calculated from the ratio of the resistance of 5% to 98% of relative humidity

$$\text{Sensitivity Factor } S_f = R_{5\%}/R_{98\%} \quad (1)$$

”.

III. RESULTS AND DISCUSSION

The powder XRD patterns of the ternary mixture of metal oxides for NZC-101 corresponding to (400), (220), (222), (440) reflection characteristics of NiO of JCPDS value 895881 and peaks (111), (011), (200), (002) characteristics of CuO having JCPDS value 895899 and NMW-211corresponding to (400), (220), (222), (440) of JCPDS value 895881 of NiO. The peaks of JCPDS value 822169 corresponds to (110), (111), (201), (311) of MnO_2, the peaks (200),(002),(020),(202) corresponds to WO_3 having JCPDS value 894480 implying that there are no impurity peaks. The FT-IR spectrum of NMW-211 exhibit a common broad band near 3400cm^{-1} due to the OH^- stretching vibrations of free and hydrogen bonded hydroxyl groups and at 1600cm^{-1} is assigned to the deformative vibration of water molecules which is most probably due to water absorption during the compaction of the powdered specimens with KBr [13-14]. The bands from 400 to 1000cm^{-1} belong to metal oxide absorption and also indicate that the mixtures of metal oxides are not amorphous. 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. The data and the plot presented is an average resistance made on these samples in order to check the reliability. The potential inaccuracy due to contact resistance could be assumed to be negligible owing to the high resistivity of the materials under investigation. The humidity measurement studies showed that the resistance of mixture of metal oxides ranges from $10^{-5}$to 10^{-11}ohms. The metal oxide mixtures showed a decrease in the resistance as the humidity increased implying that the conduction at the grain surface occurred. At low humidity level, the conduction occurs due to physisorption and chemisorptions of water molecules which dissociates into hydroxyl and hydronium ion,

$$2H_2O \rightarrow H_3O^+ + OH^- \qquad (2)$$

Whereas at high humidity level the conduction increased due the formation of pores of sintered material and electrolytic conduction takes place in addition to the adsorbed layers [15].

The results of resistance measurements as a function of RH at a fixed ambient temperature of 298K are presented in Fig.1 and 2. There is no systematic trend in the magnitude of drop in resistance against the increasing NiO, ZnO, MnO_2, CuO and WO_3 contents. For a better appreciation of the material characteristics towards moisture, the ratio of resistance, $R_{5\%}$ and $R_{98\%}$ where $R_{5\%}$ and $R_{98\%}$ are the dc resistances at 5 and 98% RH, respectively, are measured(Table 1). This ratio is referred to as the sensitivity factor, S_f. The greater the S_f , the higher is the sensitivity of the material towards moisture[16]. It is observed that a maximum sensitivity occurs in the sample, NZC-101(5652) among NZC mixtures and NMW-211(147242) among NMW mixtures in which the resistance drops by more than four orders of magnitude. The metal oxides mixtures showing the maximum sensitivity were chosen for temperature dependence study. The activation energies in Fig.3 and 4 for the samples in the temperature range of 318 – 623K were obtained (Table 1) using the Arrhenius equation

$$I = I_0 e^{-Ea/kT} \qquad (3)$$

Where I is the current, Ea the activation energy, k the Boltzmann constant and T the temperature. Since

$$\ln I = \ln I_0 - Ea/kT \qquad (4)$$

the plot of lnI versus 1/T gives a linear curve. The activation energy was calculated from the slope (-Ea/kT). From the results it was found to have a low values which shows (0.172 – 0.244 eV) small polaron mechanism is operating in this temperature range. It shows that only lower energy is required to cross the energy band for conduction [17].

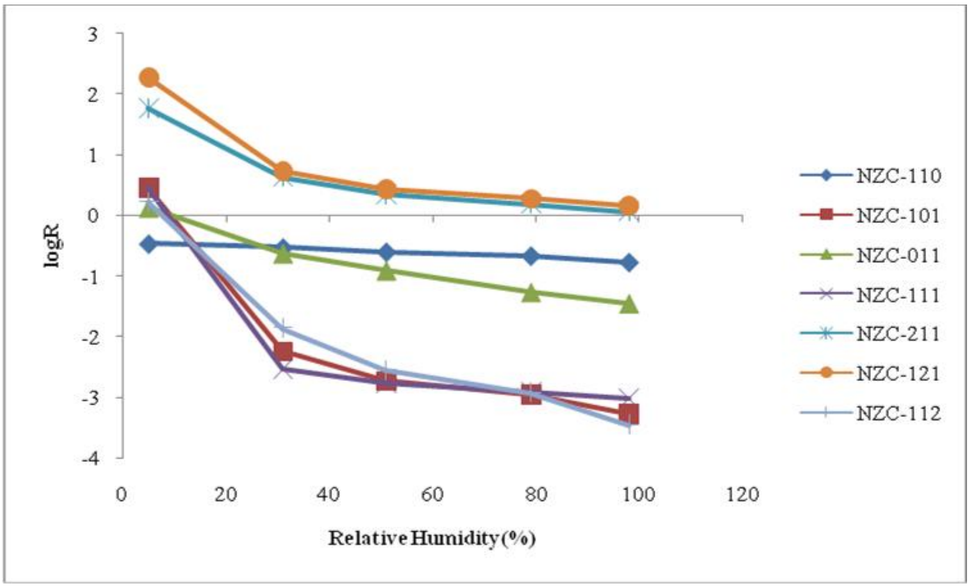

Fig. 1 Relative humidity versus log resistance plots at 298K for NZC composites

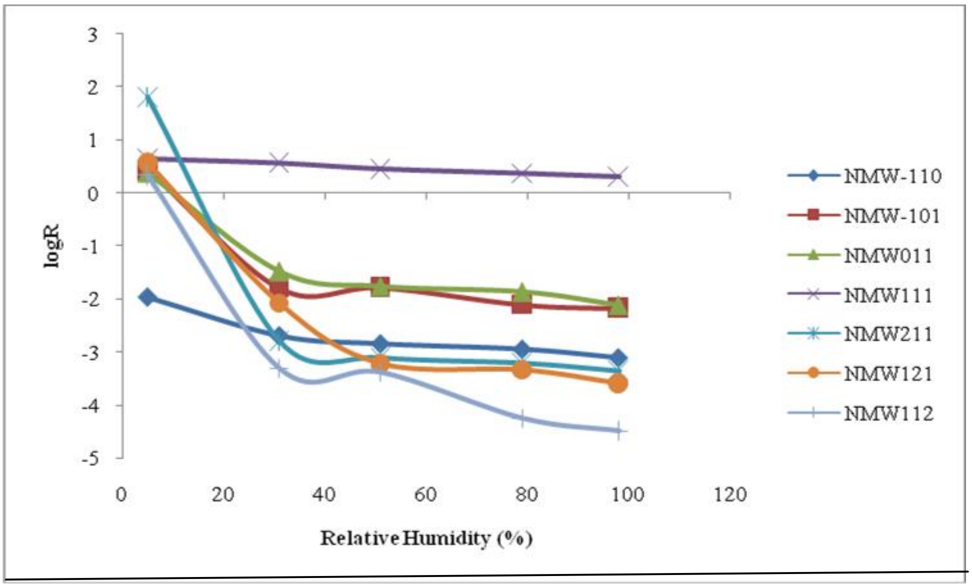

Fig. 2 Relative humidity versus log resistance plots at 298K for NMW composites

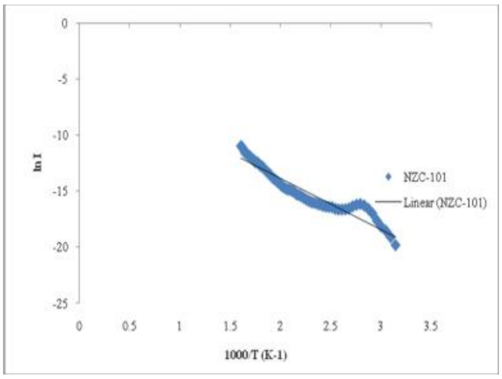

Fig. 3 Temperature dependent dc conductance plot of NZC-101

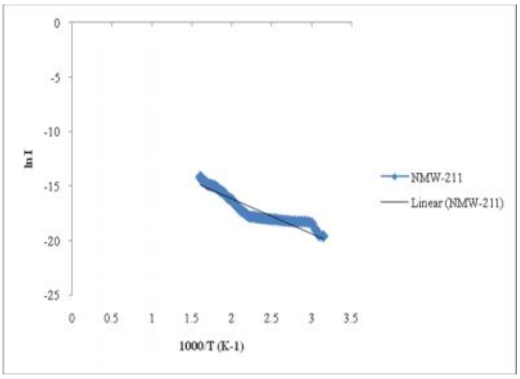

Fig.4 Temperature dependent dc conductance plot of NMW-211

IV. CONCLUSION

Ternary mixture of transition metal oxides with seven different mole ratios NZC (NiO- ZnO-CuO) and NMW (NiO-MnO_2-WO_3) were fabricated and studied for humidity sensing properties. The X-ray diffraction studies showed that no new phase has been formed and confirmed the presence of the individual metal oxides in the solid mixture. In all the two systems a decrease in resistance with increase in humidity was observed, this was explained using Grothus chain mechanism. Comparing the two systems the solid mixture NMW-211 has got the highest sensitivity factor. These ternary mixtures of metal oxides can be used as commercial thick film humidity sensor because of their humidity sensing factors.

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