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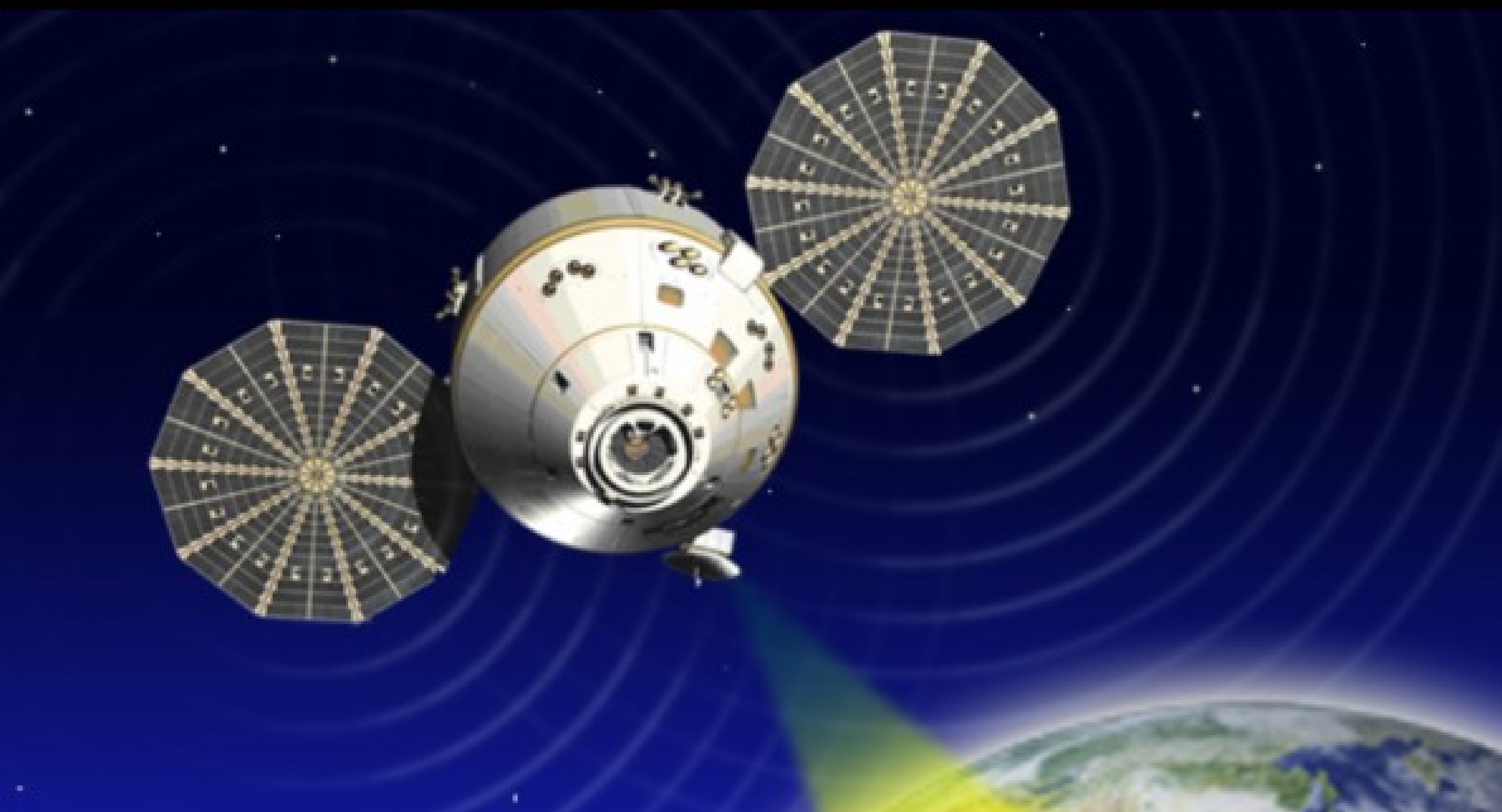

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New Solid State Sensor for Detection of Humidity, Based on Ni, Co, and Mn Oxide Nano Composite Doped with Lithium

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Abstract: The lithium doped metal oxide nano composite was fabricated by sol-gel method. The metal oxide nano composite was then sintered at 700 °C for 6 h. The metal oxide nano composite was characterized by solid-state electrical measurement, AAS, XRD, fr-IR, SEM, BET, AFM and TEM studies to analyze activation energy for conduction, surface morphology and pore structure of the sensor materials, respectively. The humidity sensing properties of metal oxide nano composite was measured by employing the sensor configuration of a cylindrical disk. The micropores of nano composite have a crucial role in humidity sensing. The materials was subjected to water vapor of different humidity achieve by various water buffers at room temperature and the electrical conductivity was measured as a function of relative humidity (RT). The electrical resistively drastically decreases with increase in humidity and hence proving the materials to be a good water vapor sensor. The sensitivity factor (S_f) of Li doped metal oxide nano composite has been increased 9.2 times as compare to the undoped metal oxide nano composite sensitivity factor. The response and recovery time of sensor was also measured. *Copyright © 2008 IFSA.*

Keyword: Nano composite, Solid state, Synthesis, Humidity sensor, Element and Nano technology

1. Introduction

The measurement and control of humidity is important in many area including meteorology, medicine, food production, agriculture and domestic environment.

Various methods are employed for the measurement of humidity of which the measurement of relative humidity seems to be very convenient [1-2]. Metal nano oxides, which are physically and chemically stable, have been widely investigated at for humidity sensing both elevated and room temperature [3-5]. Measurement of relative humidity (RH) is the most convenient way [6] among the various methods [7]. The electrical conductivity of hubnerite ceramic materials exhibits a high sensitivity to humidity changes [8]. Various humidity sensor materials have been developed based on several composite with or without lithium doping. In this study, metal oxide nano composite doped with lithium was synthesized by sol-gel method in order to investigate the humidity sensing of material. The incorporation of Ni, Co, Mn and Li was made to improve humidity sensitivity and increase electrical resistivity. The sensor elements have been characterized and tested in atmosphere of different relative humidity. The recovery and response characteristics of sensor have been determined by its resistance measurement. The effect of Li was studied in the sensor performance.

2. Experimental

A know amount of Ni $(NO_3)_2.6H_2O$ (1 molar) was dissolved in distilled water and the two drop of Tyron was added to the solution. The solution was introduced into citric acid (1 molar) solution drop wise, which was used as ligand.

HNO_3 or NH_4OH was used to adjust the PH of mixed solution to pH=2. The completely homogeneous and transparent solution was subjected to stirring and slow evaporation at 70 °C until a highly viscous residual was obtained. After it was dried at 110 °C, the precursor was then milled and calcined in muffle furnace. Five grams of AR-grade Co $(NO_3)_2.6H_2O$ and NH_4HCO_3 were put in an agate mortar with Co $(NO_3)_2.6H_2O$ molar ratio to NH_4HCO_3 equal to 2:5.

The materials were mixed and milled at room temperature until the color of the milled powder kept unchanged, and then the powder was thoroughly washed with distilled water and dried at 100 °C in air. The powder was calcined at 300 °C in air and porcelain crucible for 2 h. $MnCl_2.H_2O$ (3g), NiO (2g), CoO_3 nano particle and 0.1 g of Li_2CO_3 were dissolved in 20 ml of deionized water and two drop of Tyron added. The solution was then mixed together followed by the addition of ammonia by drop wise and stirred from solution for more than an hour. The green color precipitate was filtered and then washed with deionized water several times. It was then dried, ground well, pressed into pellet under a pressure of 0.7 tons and sintered to 700° C in 6 h with controlled heating rate. The sintered pellet were grounded well and compacted into pellets of 10 mm diameter and thickness 2 mm using acetyl alcohol as a binder at pressure 100 MPa, which were then heated to 500° C. The percentage composition of the metal was measured by atomic absorption spectroscopy. Nature of the sample was studied by X-ray diffraction (XRD) recorded in powder form, using $K_\alpha Cu$ radiation. The fr-IR spectrum of the sample was recorded in a spectrophotometer in the region of 100-450 cm^{-1} using polyethylene film.

Magnetic susceptibility measurement was done at room temperature. The corrected magnetic moment was obtained after incorporation of the necessary diamagnetic correction for oxygen. The sample was observed on a scanning electron microscopy (SEM) operating at accelerating voltage of 25 KV. The surface area of the nano composite was measured by BET porosimetry (Micromeritices Auto pore) using N_2 adsorption at 77° K. In order to study the Hall effect, the powder sample was compacted into cylindrical discs of 10 mm diameter and 2 mm thickness in hydraulic press at pressure of 100 MPa and subsequently heated to 500 ^{0}C for 1 hr and cooled to room temperature. The electrical contacts were made on the surface of the pellet by the means of two thin copper wires affixed with silver paint. The pellet was inserted in the middle of the hall-effect instrument. A plot of current versus applied fielded was obtained. Their dc resistance and its temperature dependence (rage 298 - 600° K) were measured using a two-probe method.

The electrical conductivity of pellets was measured by a DC power supply using two-probe method. The applied field was increased from 0.77 to 15.5 V/Cm in steps and the corresponding current was measured (I-V curve). In order to study the temperature dependence of conductivity, the sample was kept inside a pyres cylinder of 5 Cm diameter and 75 Cm length and kanthel Aluminum wire uniformly wound around it. The end of the kanthel wires was connected to a variac for heating. The controlled humidity environments were achieved using anhydrous P_2O_5 powder and saturated an aqueous solution of Potassium acetate, calcium chloride and etc. in a closed glass vessel at an ambient temperature of 25 °C, which yield approximately a range of relative humidity from 5 to 98 %. Heat cleaning of the sample was done at 200° C for better sensitivity, followed by cooling in humidity – free atmosphere before and after the sensitivity measurements especially when the sensor was operated at higher RH. The resistance measurement in dry air as well as in moist air alternatively helped to establish the recovery and response characteristics for moisture sensing.

3. Results and Discussion

The chemical composition of the mixed metal nano oxides drive from AAS data, Mn (19.9%), Co (33.6%), Ni (17.33%) and Li (0.005%), based on the XRD pattern the chemical composition of the metal nano composite correspond to $Mn_{0.36}Co_{0.56}Ni_{0.29}O_{1.84}$, upholding the fact there are no impurity phases. The d-value from X-ray patterns (Fig.1) along with their intensities are 1.256 (11), 1.399 (1), 1.457 (36), 1.524 (2), 1.587 (35), 1.683 (10), 2.062 (23), 2.486 (100) and 2.919 (27). The d-value are compared with the JCPDS –ICD data cards against the various nano oxides of Mn, Co, Ni such as MnO_2, Mn_2O_3, Mn_3O_4, NiO, Co_3O_4. The XRD indicated the absence of any of the above oxides and further evidenced the formation of nano metal oxides.

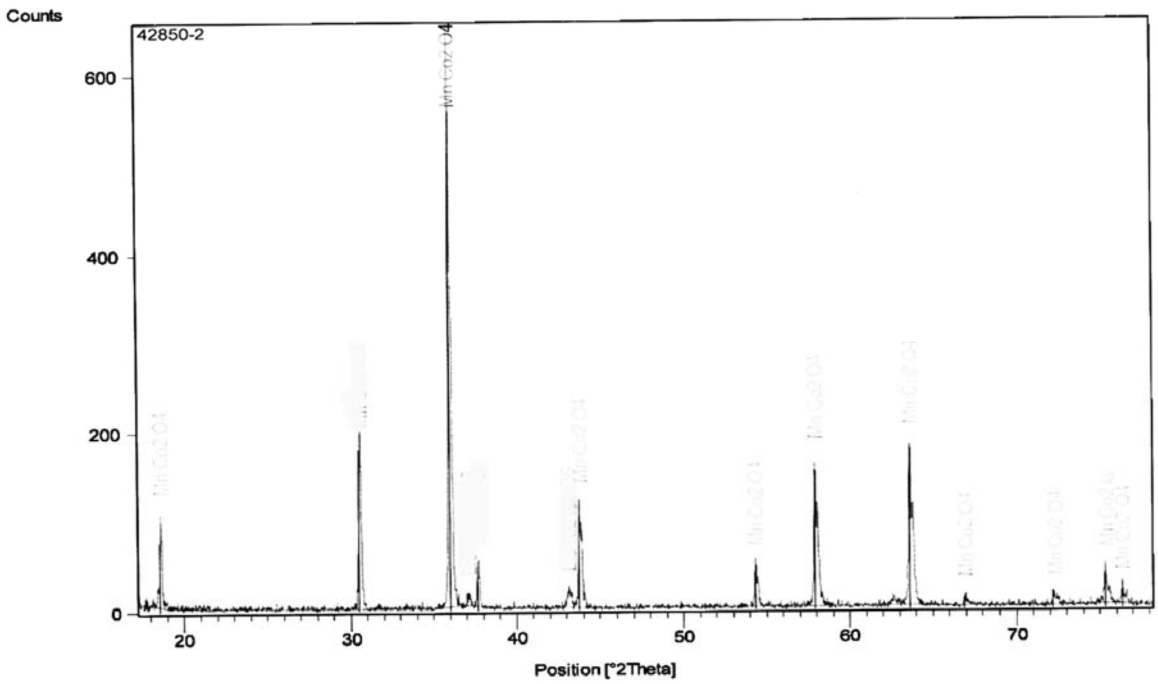


Fig. 1. Powder XRD pattern of $Mn0_{.36}Co_{0.56}Ni_{0.29}O_{1.84}$ nano composite.

The far infrared spectral band at 345-415 cm^{-1} could be attributed to the (Co-O) and (Ni-O). The band at 166 cm^{-1} suggested [9] the presence of (Mn-Mn) bond and the bond at 362 cm^{-1} could be attributed to (Mn-O) multiple bonding. The bond at 436 Cm^{-1} is due to ν (Co-O).

The resistance of the materials and the conductance at the ambient temperature were calculated using the ohm lams. The resistance at 25° C was found to be 7.1 × 10^{11} ohm from which the conductance was calculated to be ohm $^{-1}$. The temperature dependence of electrical conductivity was carried out in the temperature rang (298- 600 °K) (Fig. 2).

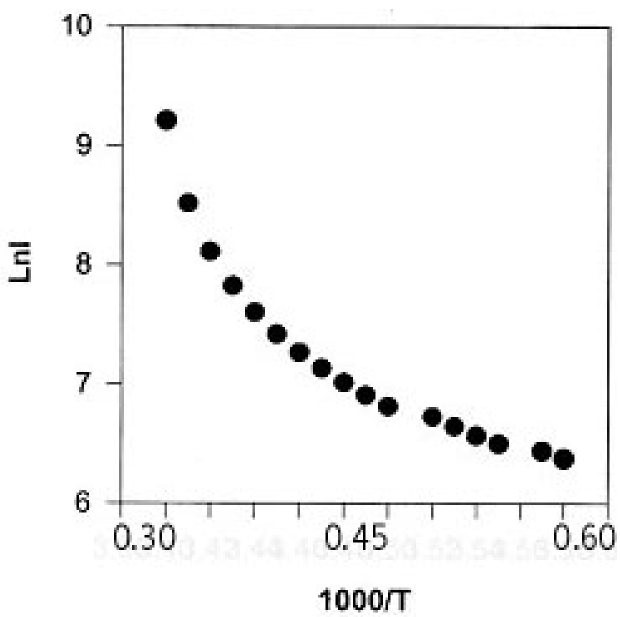


Fig. 2. Ln I Vs 1000/T plots of Mn$0_{.36}$$Co_{0.56}$$Ni_{0.29}$$O_{1.84}$ nano composite.

In I-V curve study, the electrical field was varied from 0.77 – 15.5 V/cm and the corresponding current was recorded. The current was formed to vary linearly (Fig. 3 I-V curve) with the applied field suggesting the Ohmic nature of the sample. The Hall effect measurements were shown in Table1.

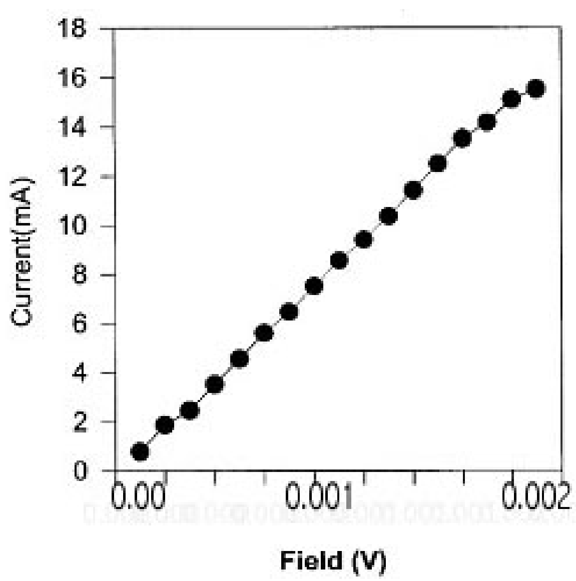


Fig. 3. Field Vs current studies of Mn$0_{.36}$$Co_{0.56}$$Ni_{0.29}$$O_{1.84}$ nano composite.

Table. 1. Sensitivity factor and activation energy for conduction of Li doped and undoped nano composite.

NO.	Sample Code	Doped With Li^+ R5%	Doped With Li^+ R98%	S_f (5%/98%)	Undoped With Li^+ R5%	Undoped With Li^+ R98 %	S_f (5%/98%)	E_a
1	NCML1	$7.1x10^{-11}$	$1.2x10^{-4}$	591666	$8.3x10^{-8}$	$1.3x10^{-4}$	63846	52.15
2	NCML2	$3.5x10^{-9}$	$1.7x10^{-4}$	205882	$7.4x10^{-9}$	$1.7x10^{-5}$	43529	51.85
3	NCML3	$4.3x10^{-10}$	$1,5x10^{-5}$	286666	$3.8x10^{-9}$	$1,5x10^{-5}$	25333	51
4	NCML4	$5.8x10^{-10}$	$1.3x10^{-5}$	446153	$5.8x10^{-9}$	$1.9x10^{-5}$	30526	51.18
5	NCML5	$4.5x10^{-10}$	$1.7x10^{-5}$	264705	$7.6x10^{-8}$	$1.8x10^{-5}$	42222	51.65
6	NCML6	$5.3x10^{-9}$	$1.3x10^{-5}$	407692	$8.2x10^{-8}$	$1.2x10^{-5}$	68333	52.10

From the temperature dependence conductivity data, LnI verses 1000/T plot was drawn to determine the activation energy. The activation energy calculated for nanocomposites were 51 eV respectively.

The results of resistance measured as a function of relative humidity at a fixed ambient temperature of 298 K are present in (Fig. 4). The resistance of the nano composites is in order of 10^{11} ohms under dry condition (RH 5%). The plot of Log R vs. RH (%) shows that sensitivity toward moisture of the nanocomposite. As the humidity is increased the Log R value drops and the sensitivity of the elements toward humidity increase. The nanocomposite is found to have the highest sensitivity factor S_f =591666 as inferred from the ratio $R_{5\%}/R_{98\%}$. The variation in Log R with RH (%) is almost linear in the entire range of humidity, prerequisite for commercial humidity sensor.

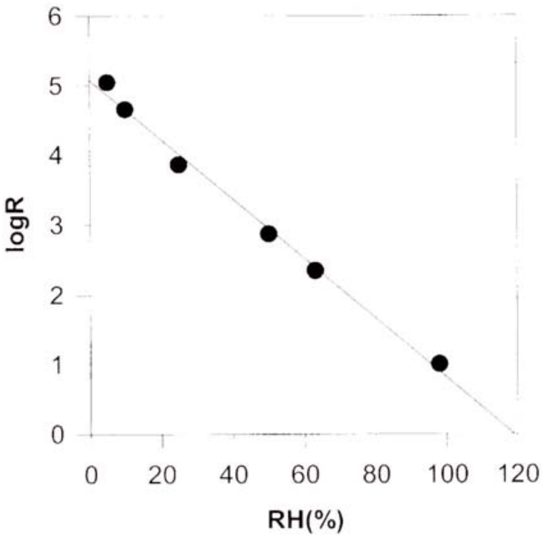
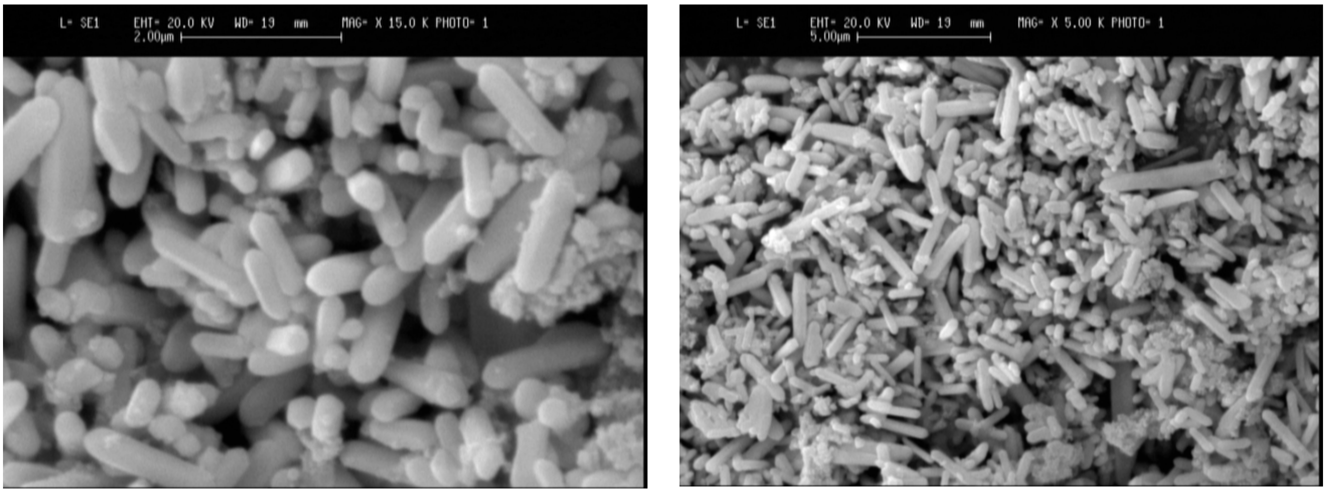


Fig. 4. Log R Vs RH (%) plot of $Mn0_{.36}Co_{0.56}Ni_{0.29}O_{1.84}$ nano composite.

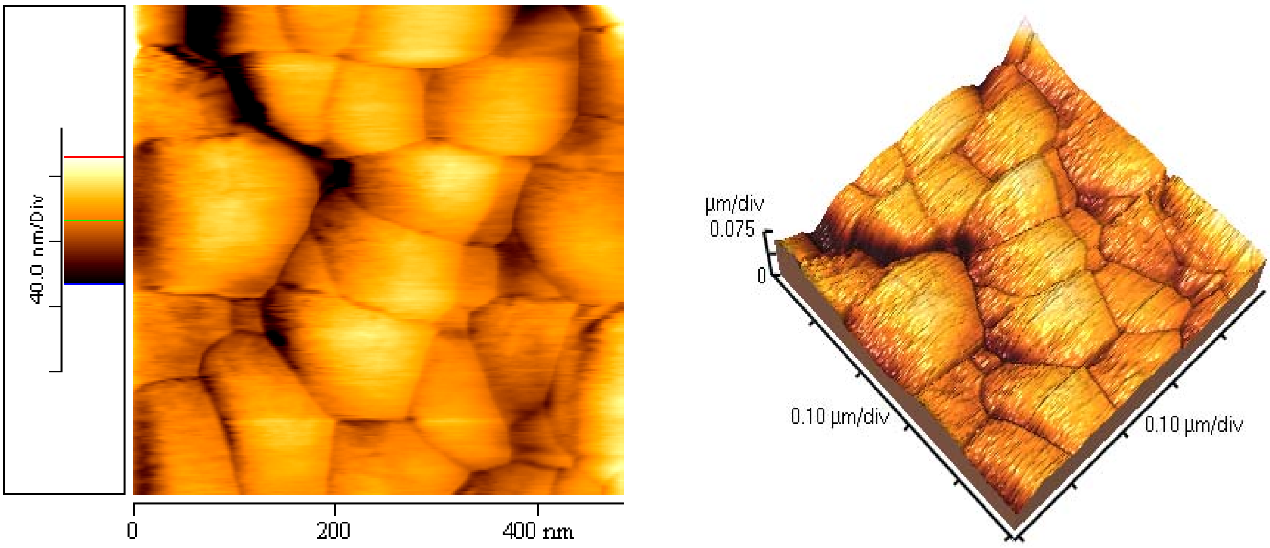
The (BET) surface absorption studies revealed that the pore size of the sample were distributed between 0.12 – 50 Å in radius; and the specific volume of the pore 50 m^2/gr which can easily trap the water molecules to it.

The scanning electron microscopy (SEM) photograph of the sensor materials sintered at 700° C for the 5 h indicated that the porosity and grain size of the materials signification increases. SEM photographs revealed (Fig. 5) qualitative that nano composite has greater and larger number of pores. The AFM photograph (Fig. 6) from the AFM image of nanocomposite in the layer. By taking image from different parts of the surface and driving the average size of nano composite particles in each image by foregoing software and averaging over these sizes, the average size of nano composite in each sample was calculated, and the mean particle size is about 40 nm. The particle are packed closely and well distributed on the disk.



(a) (b)

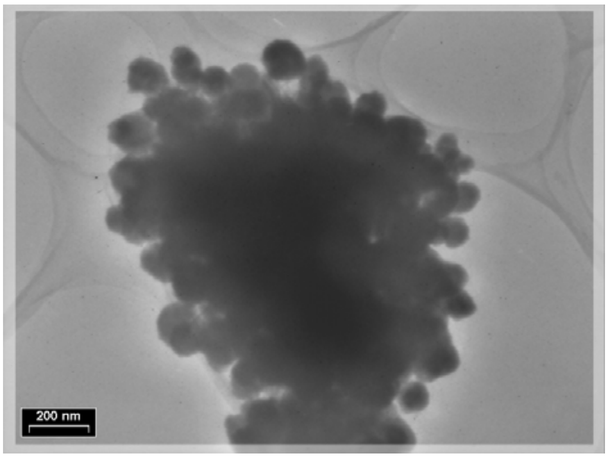
Fig. 5. SEM photograph of $Mn0_{.36}Co_{0.56}Ni_{0.29}O_{1.84}$ nano composite.



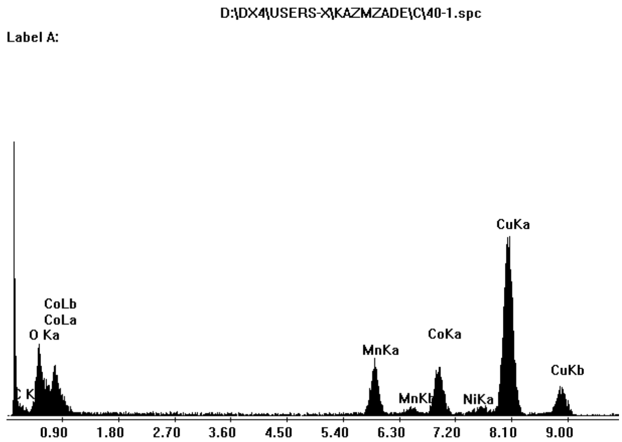
(a) (b)

Fig. 6. AFM photograph of $Mn0_{.36}Co_{0.56}Ni_{0.29}O_{1.84}$ nano composite.

The size and morphology of the nanocomposite particles were characterized by TEM As shown in (Fig. 7 a, c, d, e, f) the uniformity of nano powder was confirmed by TEM observation and point EDX analysis of sample was shown in (Fig.7 b).



(a)



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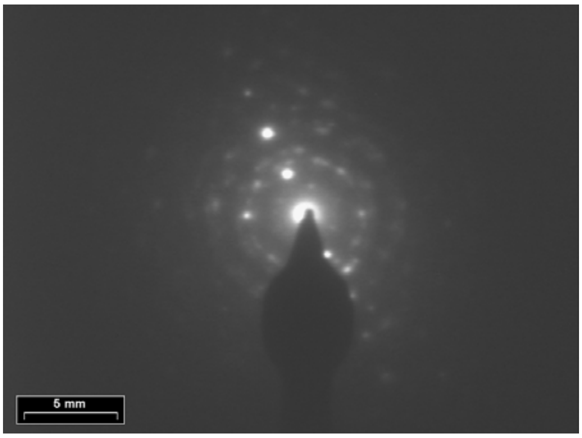

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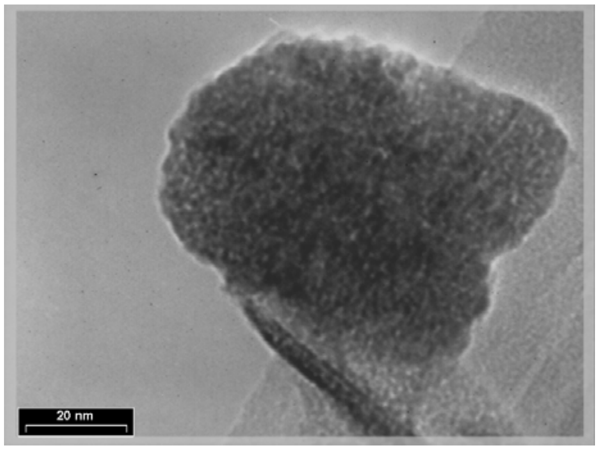

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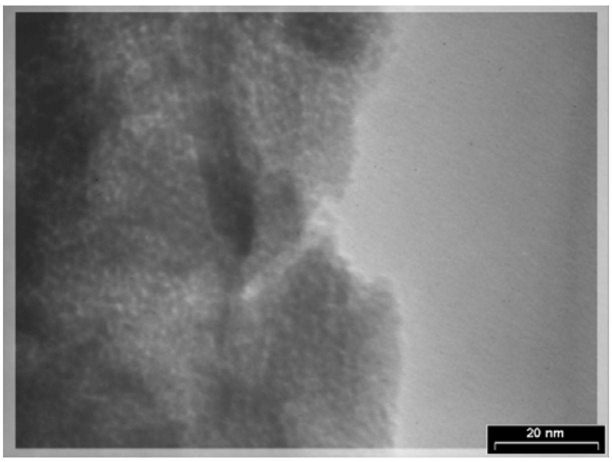
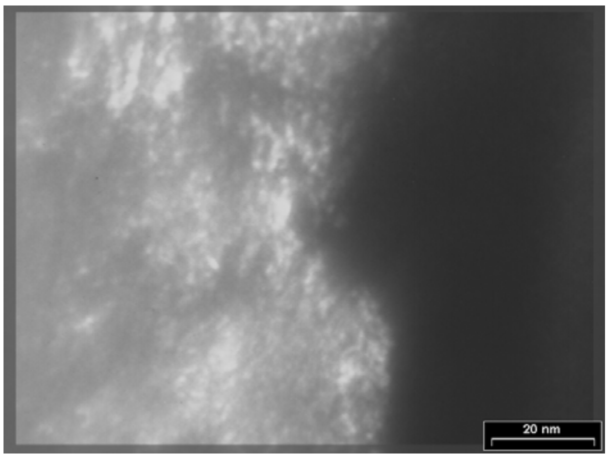


(e)



(f)

Fig. 7. TEM photograph of $Mn0_{.36}Co_{0.56}Ni_{0.29}O_{1.84}$ nano composite.

The evaluation of the response and recovering characteristics has been carried out. The dc resistance in dry air as well as in moist air alternatively helped to establish the response and recovering characteristics. The results (Fig. 8) show that the invariant resistance in dry air in the order of

10^{11}ohms. Within about 4 minutes of paring with moist air, the resistance drops by four or five orders of magnitude to reach a constant value of approximately 10^5 ohms. However, when dry air was again introduced to monitor the recovering characteristics, the recovering time was around 5 min. hence for better response and recovering characteristics, the sensors were repeatedly heated at 200°C to refresh it before and after the measurement.

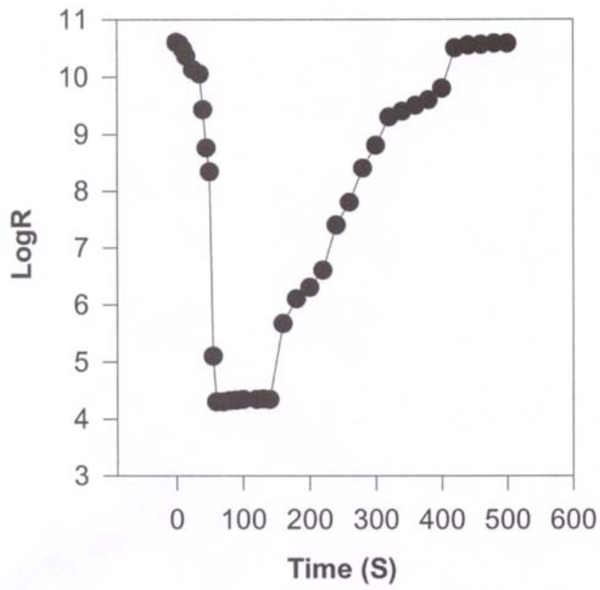


Fig. 8. Invariant resistance in dry air.

4. Conclusion

Nano composites with equimolar molar of $MnCl_2.H_2O$, $NiCl_2$. H_2O, Co $(No_3)_2.6H_2O$ and Li_2CO_3 as a doping agent were fabricated and studied for humidity sensing applications. The scanning Electron Microscope revealed that the Mn-Co-Ni with Li^+ nano oxides has large and greater number of microscopic pores hence is a good candidate for humidity sensor, which was further evidenced by the TEM, AFM and surface studies and its sensitivity factor higher than 5.9×10^5. It can be concluded then in the present system the electrical conductivity change as a function of RH, good response time and recovering characteristics were another proof for a good humidity sensor. The Li doped metal oxide nanocomposite sensor has shown promising characteristic to be used in industrial applications. The addition of Li to the nano structure of metal oxide composite sensor increases its sensitivity 10 times more than un doped one. This was not reported in earlier studies.

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References

[1]. M. K. Jain, M. C. Bhatnager, G. L. Sharma, Effect of Li^+ doping ZrO_2-TiO_2 humidity sensor, *Sens. Actuators B*, 55, 1999, pp. 180-185.
[2]. C. N. Xu. K. Miyasaki, T. Watanabe, Humidity sensor using Manganese oxides, *Sens. Actuators B*, 46, 1998, pp. 87-96.

[3]. C. Cosentino, E. N. S. Muccillo, R. Muccillo, Development of zirconia-titania porous ceramics for humidity sensors, *Sens. Actuators B*, 96, 2003, pp. 677-683.

[4]. T. Seiyama, N. Yamazoe, H. Arai, Ceramic humidity sensors, *Sens. Actuators*, 4, 1983, pp. 85-96.

[5]. M. Bayhan, T. Hashemi, A. W. Brinkman, Sintering and humidity sensitive behavior of the $ZnCr_2O_4$-K_2CrO_4 ceramic system, *J. Mater. Sci*., 32, 1997, pp. 6619-6623.

[6]. C. Catalini, M. Faccio, G. Ferri, M. Pelino, The influence of water vapour on carbon monoxide sensivity of d-Fe_2O_3 micro porous ceramic sensors, *Sens. Actuators B*, 19, 1994, pp. 437-442.

[7]. E. Traversa, Ceramic sensors for humidity detection: the state of the art and future developments, *Sens. Actuators B*, 23, 1995, pp. 135-140.

[8]. W. Qu. W. Wlodlarsi, J. Meyer, Comparative study on micro morphology and humidity sensitive properties of thin-film and thick film humidity sensors based on semi conducting $MnWO_4$, *Sens. Actuators B*, 64, 2000, pp. 76-82.

[9]. K. Nakamotto, Infrared and Raman spectra of inorganic and coordination compound (L4 ed.), *Wiley Interscience*, London, 1986.

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Sensors & Transducers Journal (ISSN 1726-5479) provides an advanced forum for the science and technology of physical, chemical sensors and biosensors. It publishes state-of-the-art reviews, regular research and application specific papers, short notes, letters to Editor and sensors related books reviews as well as academic, practical and commercial information of interest to its readership. Because it is an open access, peer review international journal, papers rapidly published in *Sensors & Transducers Journal* will receive a very high publicity. The journal is published monthly as twelve issues per annual by International Frequency Association (IFSA). In additional, some special sponsored and conference issues published annually.

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Contributions are invited on all aspects of research, development and application of the science and technology of sensors, transducers and sensor instrumentations. Topics include, but are not restricted to:

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