

Humidity and Gas Sensitivity of Ni and Co Ferrites pellets with nanoscale grain size at Room Temperature

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Abstract

Ni and Co ferrite pellets were prepared by co-precipitation method at 100 °C as a reaction temperature and then sintered at 400 °C for the phase formation. The identified phase was confirmed by x-ray diffraction analysis in which all intensity peaks of Ni and Co ferrites were observed which clearly indicates that the single phase of inverse spinel ferrite. Surface morphology of pellet was studied by Scanning Electron Microscopy (SEM), which shows high reacting surface area due to small grain size \approx 32 to 40 nm. The pellets were prepared as gas sensor elements. We have studied humidity sensing with Ni and Co ferrite in pellet form. Also with Ni and Co ferrite, sensing to NH_4 and acetone gas has been studied. It has been found that the gas sensing for test gases is found to be in the order of humidity, NH_4 , acetone and Cl_2 . Here it is shown that $CoFe_2O_4$ acts as a good sensor as compared to $NiFe_2O_4$ especially for acetone and ammonia gases.

key word: co- precipitation method; x-ray diffraction; gas sensor.

الرطوبة وحساسية الغاز لعينات فرايت النيكل والكوبلت مع الحجم الحبيبي عند درجة حرارة الغرفة

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الخلاصة

تم تحضير جسيمات فرايت النيكل والكوبلت النانوية بطريقة الترسيب بدرجة حرارة 100°C (درجة حرارة التفاعل) وبعد ذلك تم تليدها عند درجة حرارة 400°C لغرنتشكيل الطور. وتم التأكد من تشكيل الطور بواسطة تحليل حيود الاشعة السينية والذي أظهر ان شدة جميع القمم لكل من فرايت النيكل وفرايت الكوبلت والتي بينت وبشكل واضح الطور المنفرد للفرايت عكسي اليرم. تمت دراسة مورفولوجية سطوح العينات المحضرة باستخدام المجهر الالكتروني الماسح والتي بينت وجود مساحة تفاعل سطحي عالية نتيجة لصغر الحجم الحبيبي تقريبا من 32 nm الى 40 nm نانومتر. وان العينات التي هي على هيئة حبات حضرت لتكون عناصر لمتحسس غازي. دراسة حساسية الرطوبة باستخدام فرايت النيكل والكوبلت على هيئة حبات (كريات). وتمت دراسة حساسيتها لغاز الامونيا والاسيتون. وجد ان التحسس الغازي للغازات المفحوصة هو ضمن حدود الرطوبة وغازات الامونيا والاسيتون والكور. هنا وجد ان المركب $CoFe_2O_4$ يعمل كمتحسس جيد بالمقارنة مع المركب $NiFe_2O_4$ ويلاحظ للاسيتون و غازات الامونيا .

الكلمات الدالة: طريقة الترسيب، حيود الاشعة السينية، متحسسات الغاز

Introduction

Now-a-days the vast growing industries, various machines and an increasing large number of vehicles are responsible for spoiling the healthy life of human beings and all living organisms. Air pollution is found to be very dangerous as it is related to the respiratory system. Some gases like acetone, NH_4 , Cl_2 and humidity evolved are found to be very toxic and create allergic and

respiratory diseases like asthma, allergic bronchial asthma, and rhinitis [1- 4]. Gas sensors based on metal oxides are commonly used in the monitoring of toxic pollutants and can provide the necessary sensitivity, selectivity and stability required by such systems [5]. Spinel of the type $M^{2+}M_2^{3+}O_4$ attract research interest because of their versatile practical applications [6–8]. In the case of $M^{3+} = Fe$, the resulting spinel ferrites having a general chemical composition of MFe_2O_4 ($M = Mn, Mg, Zn, Ni, Co, Cd, etc.$) are widely used as magnetic materials. Currently it is a topic of increasing interest to study the gas sensing properties of ferrites [9–13]. Gas sensing at room temperature is of great interest; most of the currently available sensors, expect a few types of polymer-based gas sensor operate at elevated temperature [14-15].

Experimental

The $NiFe_2O_4$ and $CoFe_2O_4$ samples were synthesized distinctly using Ni nitrate, Co acetate and Fe nitrate as precursors, by dissolving them in distill water in the required mole proportion. The clear solution was co-precipitated with 1 molar NaOH solution at fixed temperature of 100 °C. Samples at this stage are refereed ‘as prepared’. The precipitate was filtered and then washed several times with distilled water until the pH of the filtered water becomes 7 (i.e. neutral). The filtrate was then dried at 100°C overnight. The dried powder was milled to convert into fine powder and was pressed under load of 5-6 tones for 5 minutes to make the pellets. The diameter of the 2-3 mm thick pellet was 1cm. These pellets were sintered at different sintering temperatures for time interval of 8hr. Finally it is observed that at 400°C crystalline single phase of ferrite is formed. The single-phase formation of the materials was confirmed by powder X-ray diffraction technique. X – Ray diffractogram of all the samples was recorded using an X-ray diffractometer (model Bruker D8 Advance). Micrographs of the samples were recorded using a scanning electron microscope (JEOL, Analytical Scanning Electron Microscope, Model JSM-6360A). Using two-probe method carried out the resistivity measurements. Keithley’s multimeter (model 2000) was used to record resistance of the sample at room temperature.

Gas sensing setup

A specially designed gas sensing system was used for sensing of various toxic gases. The sensing setup consisted of a dome vessel of a 20L volume made of thick glass having 12 in. diameter. The dome vessel was kept on a circular metallic base. There was a gas-handling unit attached to the system, which measured the exact amount of gas inserted in the vessel. Also one

can insert gas with the help of a syringe through a valve provided on a vertical wall of the metallic base of the system. The connections from the sensor were drawn as discussed in the fabrication of sensors. The sensor was placed in the vessel and outputs were connected to a Keithley (2000 Multimeter) meter. Commercially available gases of 99% purity were used to study the sensing response, while Cl₂ gas was prepared by the reaction of HCl and bleaching powder with some water vapour. The gas HCl mixture with water vapours was passed through a cold trap for the water vapour to get condensed. Thus, we obtained pure Cl₂ gas of 99.9% purity [16]. A known amount of the gases namely Cl₂, ammonia and acetone, was inserted with the help of a syringe and the change in resistance was noted for a fixed concentration of a gas as a function of time. The sensor response to an analyte gas is defined as the ratio of the change in resistance of a sensor in the analyte to the resistance in air [17]:

$$S(\%) = \left(\frac{\Delta R}{R_a} \right) \times 100 = \left(\frac{|R_a - R_g|}{R_a} \right) \times 100$$

Where R_a and R_g are the resistance in air and in gas, respectively, and ΔR is the change in resistance.

Results and discussion

Ni and Co ferrite powders were characterized at several stages of synthesis using X-ray diffraction technique. The X-ray diffraction patterns of each Ni and Co ferrite treated at 400° C is shown in the figure 1. The positions of all the Bragg's peaks were used to obtain the interplaner spacing and these values are used to index the peaks. The peaks were indexed by comparing the interplanar distance with the JCPDS data [18]. Both samples show formation of single spinel cubic phase. No any extra peak was observed in x-ray diffraction patterns.

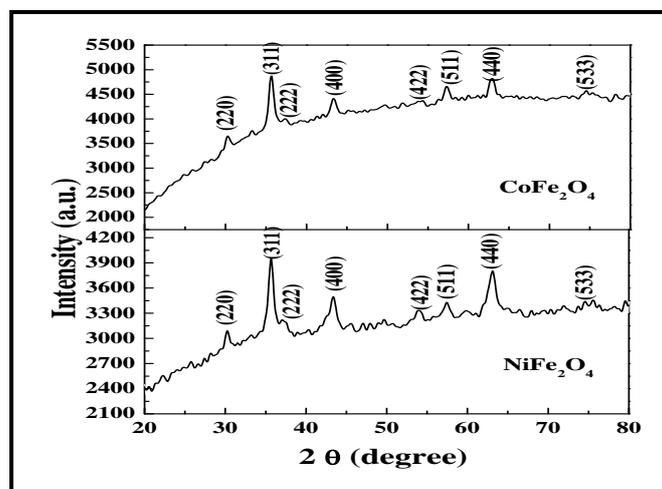


Fig. 1: X-ray diffraction patterns of Ni and Co Ferrites.

The scanning electron micrographs of the Ni-ferrite and Co-ferrite are shown in Figs. 2, respectively. It is clearly seen in the micrographs that the grains of the Ni ferrite and Co ferrite are at nano-scale. This is very advantageous for gas sensing applications as smaller grains have a larger specific area and as a result a higher response to analyte gases. Both samples show formation of single spinel cubic phase. The average grain size determined from SEM was noted as 32 nm for Co-ferrite and 40 nm for Ni-ferrite .

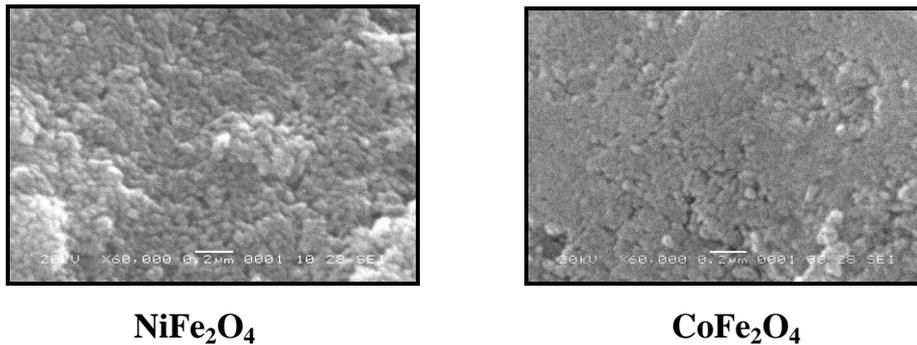


Fig. 2: Scanning Electron Micrographs of Ni and Co Ferrites.

To get elemental analysis, The Ni ferrite powder annealed at 400°C was characterized by EDAX. Fig. 3 shows the EDAX technique results for NiFe₂O₄. It show overall elemental distribution in the matrix which confirms formation of stoichiometric compound. The expected weight % are O = 68.0436%, Fe = 24.24% , Ni = 8.7243% and the observed weight % are O = 65.3338 % , Fe = 24.37% , Ni = 10.2962 % which is slightly varying from the expected weight % . The weight percentage chemical composition of NiFe₂O₄ pellet are tabulated in Table 1.

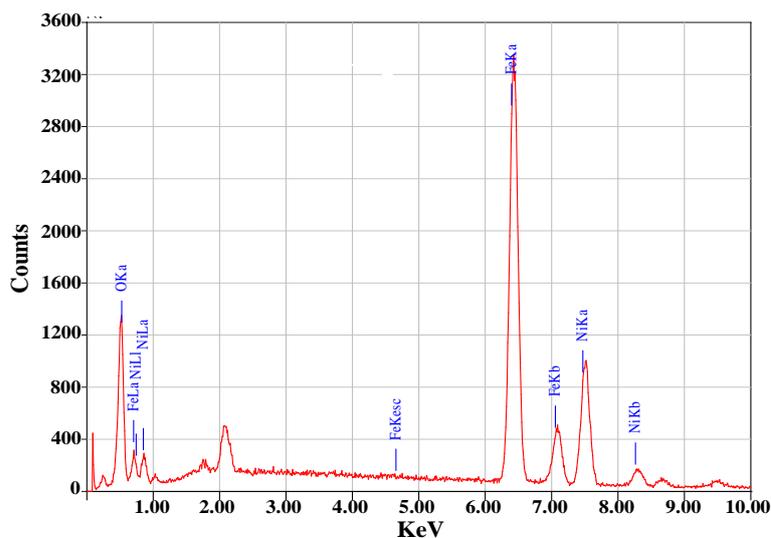
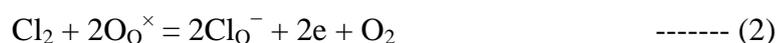
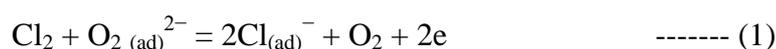


Fig.3: Quantitative analysis of elemental distribution using EDAX pattern in SEM image.

Table 1 Measure of wt. % chemical composition of NiFe₂O₄ pellet by EDAX.

| Element | Line(Ka) | mass% | Error% | At% |
|---------|----------|--------|--------|--------|
| O K | 0.525 | 65.38 | 0.72 | 46.81 |
| Fe K | 6.398 | 24.37 | 1.25 | 36.60 |
| Ni K | 7.471 | 10.29 | 2.17 | 16.59 |
| Total | | 100.00 | | 100.00 |

Initially, we studied the gas sensing of NiFe₂O₄ and CoFe₂O₄ sensor for acetone, NH₄ and Cl₂ gas. The variation in response of the NiFe₂O₄ and CoFe₂O₄ pellets to these gases of 1000 ppm with time is shown in Fig 3 (a-b). The resistance of the pellet sensor was measured in air atmosphere before introducing any gas in the dome chamber. Then a quantity of 20 ml of these gases was inserted in the chamber of 20 Lit, so that the concentration of gases became 1000 ppm. As soon as these gases were inserted, the NiFe₂O₄ and CoFe₂O₄ pellet showed an increase in the sensor response. The response increased up to 70% within 5 min and it reached to a steady value around 8 min. After reaching to the steady response, gases were removed from the closed chamber. The change in response was found to be insignificant. It took several hours to recover the original resistance after removal of gases from the closed chamber. The poor recovery observed at room temperature is due to the bulky nature of the sensing element. When the NiFe₂O₄ and CoFe₂O₄ pellets are exposed to NH₄ gas it goes deeper into the pellet and it comes out very slowly. This results into a longer recovery time. The Cl₂ gas sensing response of oxides involve mainly four kind of adsorption behavior in the reactions below [19-20].



where subscripts, ad and O, mean the species adsorbed on the surface and the species occupying lattice oxygen sites, respectively. V_O'' is an oxygen vacancy. In reactions (1) and (2), chlorine substitutes for adsorbed oxygen and lattice oxygen to form Cl_(ad)⁻ and ClO⁻, respectively, inducing electron donation into the oxide. On the other hand, in reactions (3) and (4), chlorine is adsorbed on the surface and occupies the oxygen vacancy to form Cl_(ad)⁻ and ClO⁻, respectively. In these cases, electrons are drawn from the oxide, resulting in an increase in resistance. At room temperature there would be no oxygen adsorption as observed in the case of other oxide

semiconductor gas sensors [21]. Therefore, the oxygen adsorption-desorption mechanism is not employed to sense the Cl₂ gas, and hence in the present case chlorine adsorption on the surface of the sensor is favorable mechanism. The sensing mechanism can be understood in a similar line to that of Cl₂ sensing.

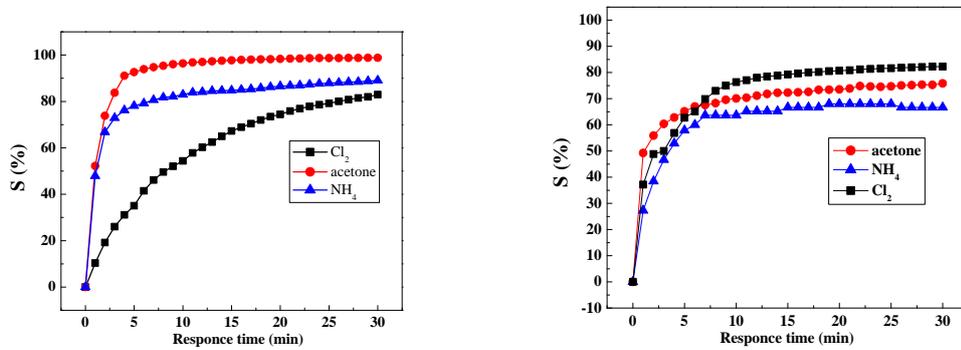


Fig. 4: Sensing response of (a) Co ferrite and (b) Ni ferrite pellet to different gases [acetone, NH₄, Cl₂].

Fig.5 shows the comparison data for maximum response of NiFe₂O₄ and CoFe₂O₄ to all gases. From the chart it can be clearly observed that CoFe₂O₄ shows maximum sensitivity for NH₄ and acetone as compared to NiFe₂O₄. But NiFe₂O₄ and CoFe₂O₄ show near about same sensitivity for Cl₂ gas.

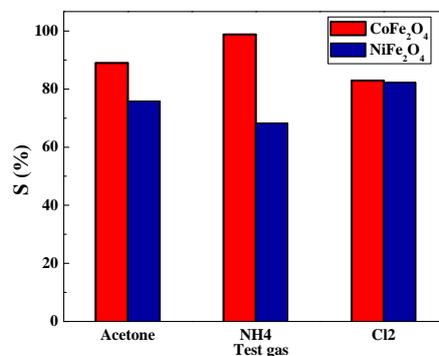


Fig. 5: comparison of sensing response between Co and Ni ferrites.

Fig.6 shows variation in sensitivity response with change in humidity. It is observed that in low humidity region the sensing response for both NiFe₂O₄ and CoFe₂O₄ is more and it gets saturated in higher humidity region indicating that all the porous surface of the samples were filled by H₂O molecules.

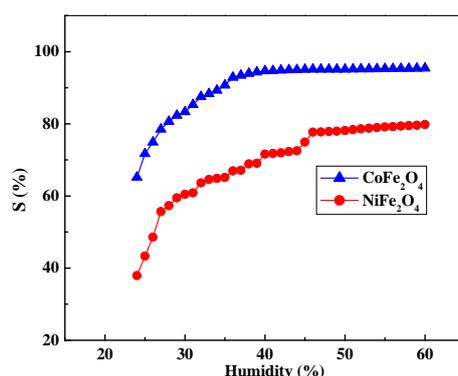


Fig. 6: Variation of sensing response of Co ferrite and Ni ferrite pellet to humidity.

Conclusions

NiFe₂O₄ and CoFe₂O₄ in bulk form has been successfully synthesized and characterized for their structural and morphological properties. The morphological and structural studies proved the nanocrystalline nature of the samples. EDAX shows stoichiometric formation of Ni-ferrite and Co-ferrite. The NiFe₂O₄ and CoFe₂O₄ sensor showed a large response to all gases in a short time and better recovery. The present study explored the possibility of making use NiFe₂O₄ and CoFe₂O₄ for sensing for ammonia, acetone and Cl₂ gases at room temperature. It can be concluded that CoFe₂O₄ acts as a good sensor as compared to NiFe₂O₄ specially for acetone and ammonia gases.

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