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Synthesis, Characterization of $ZnCr_2O_4$ Nanoparticles and their Application for Ammonia Gas Sensing

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Abstract: The research work reported about preparation of nanocrystalline$ZnCr_2O_4$ through sol -gel method and characterization of their microstructural and gas sensing properties. The structural properties investigated by X-ray diffraction revealed with $ZnCr_2O_4$ cubic structure. crystallite size was found to be 15-35 nm. The morphological study characterized by scanning electron microscopy (SEM). The sensor fabricated from these nanocrystalline$ZnCr_2O_4$ exhibits high sensitivity and rapid response/recovery to ammonia gas at 250^0C. The sensitivity was up to 59.23% when the sensor was exposed to 50 to 200 ppm ammonia gas and the response and recovery time is about 40 and 50 s respectively. The linear dependence of sensitivity on the ammonia concentration was found in the range 50-200 ppm.

Keywords: $ZnCr_2O_4$, Ammonia gas, Nanocrystalline, Gas response

1. Introduction:

The recent emergence of concern over environmental pollution and accidental leakages of explosive gases have increased awareness for efficient detection and constant monitoring of such gases. To meet this demand, considerable research into the development of sensors with novel design using tailored material properties is under-way.Metal oxides have been known for decades as good gas sensing materials, which have been used for environmental monitoringand industrial applications. On the other hand, nanostructuredmaterials have been used extensively as sensitive layers in gas sensors because very large surface-to-volume ratios can significantlyimprove the gas sensitivity due to interaction gas-nanostructure,which primarily occurs on the surface [1–6]. Therefore, nanostructured metal oxides are shown in the literature to be among themost promising gas sensing materials.

Spinal of the type $M^{2+}M_2^{3+}O_4$ attract the research interest because of their versatile practical application [7-8]. Spinel compounds have a general formula AB_2O_4, in which the A-site is tetrahedrally coordinated and generallyoccupied by divalent cations (Mg, Mn, Ni, and Zn) and the B-site is octahedrally coordinated and occupied bytrivalent cations (Al, Cr, and Fe). Metal oxides with spinel structures are some of the most studiedcompounds due to their wide range of applications [9].

$ZnCr_2O_4$is one of the most important ferrites. It has a cubic structure of normal spinel-type and is an n type semiconducting material, which finds a number of applications in heterogeneous catalysis, adsorption, sensors, and in magnetic technologies [10-11].

Current years have been increased interests in study the gas sensing properties of ferrites [12-14]. Gopalreddy et al. reported the response of copper ferrite ($CuFe_2O_4$) and zinc ferrite ($ZnFe_2O_4$) for hydrogen sulfide (H_2S) and that of nickel ferrite ($NiFe_2O_4$) for chlorine gas (Cl_2) [12]. One of the present authors (Y-L.Liu) also confirmed that $ZnFe_2O_4$ possessed gas sensing properties for H_2S [15]. $ZnCr_2O_4$ is one of the important ferrites with spinel structure and gas sensing application [13].

In this paper, we have synthesized $ZnCr_2O_4$ nanoparticles by sol gel method. One of our aims is to develop a general synthesis method and explore the gas sensing properties of the $ZnCr_2O_4$nanopowder. We found that the process is a convenient, environment friendly, inexpensive and efficient. Furthermore, the $ZnCr_2O_4$ obtained possesses excellent gas-sensing responses to reducing gas and grain size is about 15-35 nm.

2. Experimental:

2.1. Synthesis of Materials:

For the present study, polycrystalline $ZnCr_2O_4$ powder was prepared by sol gel route using citric acid as fuel. The materials used as precursors wereZinc nitrate$Zn(NO_3)_2{\cdot}6H_2O$, Chromium Nitrate nonahydrate$Cr(NO_3)_2 9H_2O$ and Citric acid. Citric acid possesses a high heat of combustion. It is an organic fuel and provides a platform for redox reactions during the course of combustion. Initially the Copper nitrates, Iron nitrates and Citric acid are taken in the 1:1:4 stoichiometric amounts and dissolved in 250 ml beaker slowly string with glass rod clear solution was obtained. Solution formed was evaporated on hot plate in temperature range 80^0C gives thick gel. Gel was obtained by constant stirring and heating the solution at 120^0C temperature in pressure vessel. The gel was subjected to calcinations at 650^0C for 6 hours in a furnace to obtain the combusted flake form material. By grinding the flakes in mortar and pestle, powdered form of material was obtained.

2.2. Structural and Sensing Measurement:

Structural analysis of synthesized powdered samples was carried out using X-ray diffractometer (Philips 3710, PAN anytical) using Cu-Kα radiation with wavelength (λ = 1.5406 ˚A), and the surface morphology of the samples was investigated with a Scanning Electron Microscope (JEOL-JXA-8100 SEM). The 10mm diameter size of pellet was made using polyvinyl alcohol (PVA) as binder of each sample for ferrite powder. Two-gram powder sample was uniformly mixed with 5 wt% by weight of PVA. The mixture was pressed in a die and punch arrangement using a hand press machine. The prepared pellets were sintered at 300^0C for 3 hours to removeorganic PVA. The gas-sensing characteristics were recorded with reference to time at different operating temperatures and as a function of gas concentration. The sensing response was calculated using the given formula :

$$S\,(\%) = [(Ra - Rg)/Ra] \times 100, \qquad (1)$$

whereRa and Rg are the resistance in the air and in the presence of tested gas, respectively.

3. Results and Discussion:

The crystallographic structure of the synthesized $ZnCr_2O_4$nanoparticles was identified by powder X-Ray Diffraction (XRD) measurement. The powder XRD patterns of $ZnCr_2O_4$ are presented in Fig.1. All of the main peaks are indexed as the spinel $ZnCr_2O_4$ in the standard data (JCPD No: 22-1107).The average crystallite sizes of $ZnCr_2O_4$ samples were calculated from X-ray line broadening of the reflections of (111), (202), (311), (105), (400) ,(333) and (404) using Scherrer's equation (i.e., D = 0.89k/(β cosθ), where k is thewavelength of the X-ray radiation, K is a constant taken as 0.89, h the diffraction angle, and b is the full width at half-maximum. The estimated crystallite size is about 15-35nm.

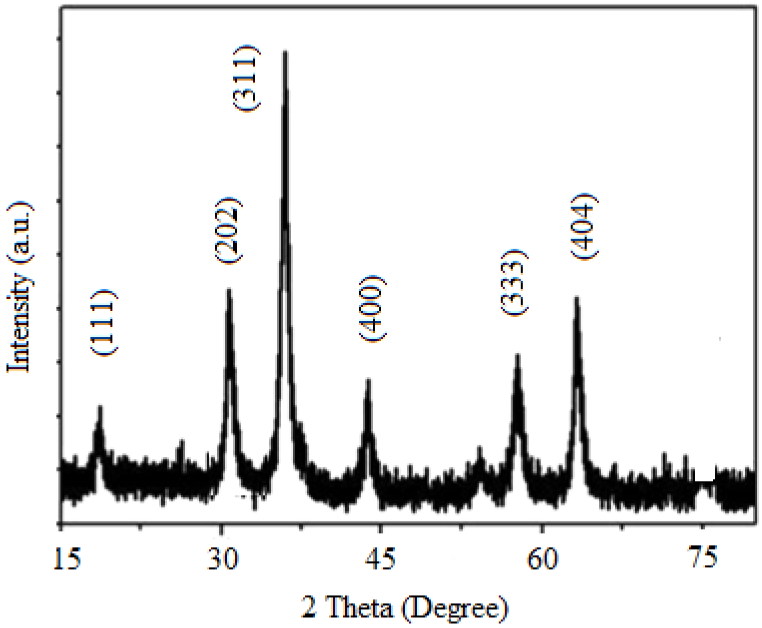

Figure (1) : X-ray diffraction patterns of $ZnCr_2O_4$ as synthesized Powder

Figure 2 shows the SEM image of the as synthesized $ZnCr_2O_4$nanopowder. It is observed that $ZnCr_2O_4$have uniformed size. The surface was smooth, spongy and pores were shown in the micrograph.

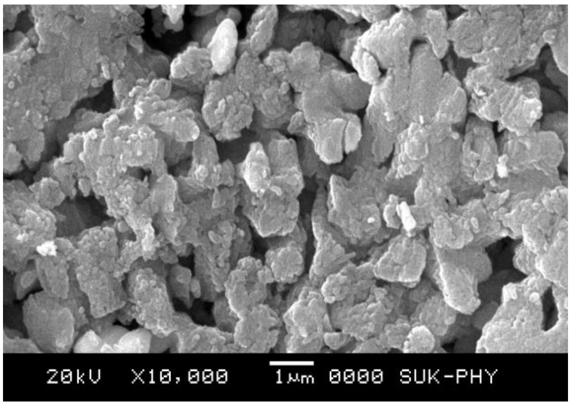

Figure (2) :SEM images of the $ZnCr_2O_4$nanopowder

Our investigations focus on the ammonia gas sensing properties of the $ZnCr_2O_4$. The $ZnCr_2O_4$exhibit high sensitivityand rapid response / recovery characteristics toammonia gas at 250°C, as shown in Figure (3).These results reveal that the sensor can detect ammonia gas at different concentrations and down to 10 ppm. Furthermore, it can also be seen that the electrical signal from the sensor becomes stable within 40 s after it is exposed to ammonia gas, and returns to the original values within 50 s after the tested ammonia gas is replaced with air. The rapid response and recovery of the sensor is based on products can facilitate fast mass transfer of the analyze molecules, from the interaction region and also require charge carriers to traverse the barriers introduced by molecular recognition along the nanofilm. Simultaneously, comparing with nano films, the interfacial areas between the active sensing region of the nanofilm and the underlying substrate is greatly reduced. Those advantages lead to significant gain in the sensing performances of prepared nanofilm. The sensitivity of the $ZnCr_2O_4$ versus ammonia gas concentration is shown in Figure (3). The sensitivity rapidly increases with increasing ammonia gas concentration below 200 ppm. Above 200 ppm, the sensitivity slowly increases with the ethanol vapor concentration, indicating the sensor becomes more or less saturated. Finally the sensitivity reaches saturation at about 200 ppm. Moreover, in Figure (3) shows the linear calibration curve in the range of 150–200 ppm, which further confirms that the $ZnCr_2O_4$can be used as a promising material for ammonia gas sensors.

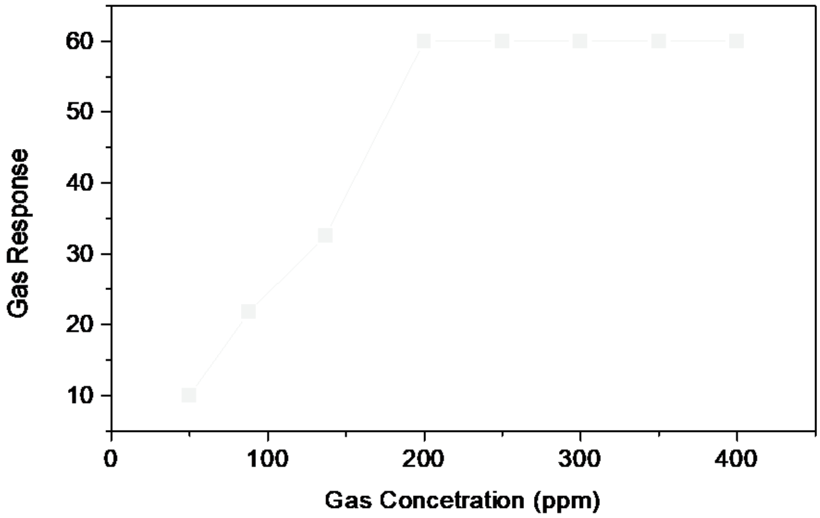

Figure (3) :Response characteristics of the $ZnCr_2O_4$ film to ammonia gas at 250^0C.

The mechanism of gas sensing can be explained on the basis of gas adsorption and the chemical reactions occurs on the surface of the materials [16]. When $ZnCr_2O_4$nanomateials are exposed to the air, their surface will be surrounded by oxygen molecules. These oxygen molecules will extract electrons from the conduction band of the materials and ionize to O^{2-}, O^- and O_2^-. This will lead to conductivity decreasing of martial. However, when $ZnCr_2O_4$nanomateials are exposed to ammonia gas, the surrounding NH_3 molecules will react with these ionized oxygen species and release the trapped electrons back to the materials. Thus increase the conductivity of $ZnCr_2O_4$nanomateials.

4. Conclusions:

We have successfully prepared $ZnCr_2O_4$nanocrystalite by using sol gel method. $ZnCr_2O_4$ with an average diameter of 15-35 nm are synthesized. The structure of $ZnCr_2O_4$was spinel confirmed by XRD and their ammonia gas sensing properties are also investigated by exposing the corresponding sensor to different concentrations of ammonia gas at 250°C. High sensitivity and rapid response/recovery was observed in investigation, suggesting that $ZnCr_2O_4$ are act as good candidates for fabricating high performance gas sensors.

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