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The Preparation of $ZnGa_2O_4$ Nano Crystals by Spray Coprecipitation and Its Gas Sensitive Characteristics

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Abstract: $ZnGa_2O_4$ nano crystals were prepared by an improved coprecipitation method, which we call 'spray coprecipitation'. XRD results shows the resulting crystal size using the new method is under 10nm, whereas the powder prepared by ordinary coprecipitation is about 30nm. XRD results also shows ZnO peaks exists in $ZnGa_2O_4$ powder prepared by traditional coprecipitation, but disappears in $ZnGa_2O_4$ nano crystal prepared by spraying coprecipitation. SEM and TEM were used to analysis the structural characteristics of $ZnGa_2O_4$ nano crystals. The gas sensitive characteristics of $ZnGa_2O_4$ nano crystals are reported.

Keywords: Coprecipitation, Nano crystals, Spray, Gas sensitive.

Introduction

ZnO and Ga_2O_3 have been used as gas sensors for decades due to their high sensitivity. Although the ZnO-Ga_2O_3 system offers a great potential for sensing applications there is a relative dearth of literature on the subject. Recent publications report the preparation of the films of spinel zinc gallate [1-5], with the materials recently investigated for application to vacuum fluorescent displays (VFDs) [6]. Bulk single crystals of $ZnGa_2O_4$ spinel, with an edge length of up to 10 mm, have been successfully synthesized by slowly cooling a PbF_2-free, PbO-B_2O_3 [6]. Satyanarayna and Reddy have prepared $ZnGa_2O_4$ powders [7] via a thick film preparation technique using a paste composed of $ZnGa_2O_4$ powder and a polyvinyl alcohol solution; the resulting films were then investigated

establishing a relationship between method of synthesis, crystal structure and the gas sensing properties.

In this paper $ZnGa_2O_4$ nano crystals were prepared by an improved spray coprecipitation method. XRD results shows the crystal size is under 10nm, whereas the powder prepared by ordinary coprecipitation is about 30nm. XRD results also shows ZnO peaks exists in $ZnGa_2O_4$ powder prepared by traditional coprecipitation, but disappears in $ZnGa_2O_4$ nano crystals prepared by spraying coprecipitation. The gas sensitive characteristics of $ZnGa_2O_4$ nano crystal were tested.

Experimental

$Ga_2(SO_4)_3 \cdot 18H_2O$ and $ZnCl_2$ were taken in a Zn:Ga=1:2 mole ratio and dissolved in de-ionized water. The mixture was coprecipitated with urea under constant stirring. The precipitate was washed several times. Finally the mixture was dried, then calcined at 750°C for 6 hours.

In order to reduce particles size and improve size distribution, we developed a spraying coprecipitation method. Fig.1 shows a schematic drawing of the spraying coprecipitation apparatus. In the scheme, compressed air drives reactants (ammonia and reagent containing Zn^{2+} and Ga^{2+}) quickly through the pipeline. Passed through respective flowmeters, the reactants mix and react in the tee junction. The resulting mixture in then sprayed into a beaker. Typical experimental settings in spraying coprecipitation method are as follows: diameter of pipe 4mm, flow rate 10m/s.

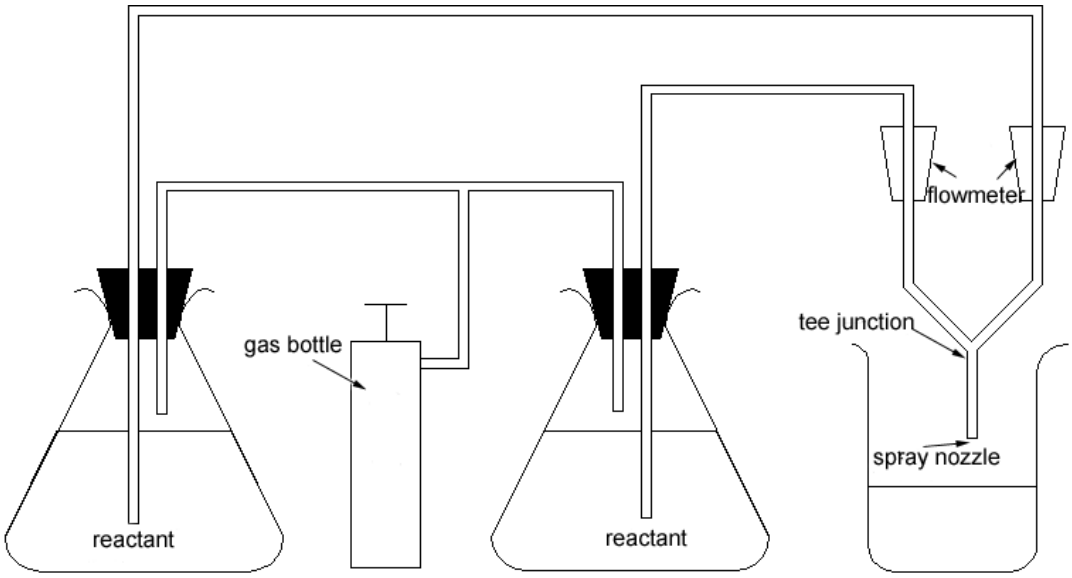


Figure 1. Scheme of spraying coprecipitation.

$ZnGa_2O_4$ powder is used to fabricate a gas sensor in the following way. A total of 2.5wt.% poly-vinyl alcohol(PVA) was used as a binder to form a paste and the materials were then coated onto aluminum tube substrates provide with platinum wire electrodes for electrical contacts. Finally the sensor is sintered at 650°C for 2 hours to make it rigid and impart ceramic properties. The resistance of sensor element was measured in the presence and absence of test gases. The sensitivity, S is defined as the ratio of resistance of the sensor in air, R_a, to resistance of the sensor in the presence of gases, R_g.

Results and Discussion

Fig.2 is XRD pattern of the resulting powder. The powder is spinel structure $ZnGa_2O_4$, JCPDS file 3-1155. The $ZnGa_2O_4$ in Fig.2(a) is prepared by coprecipitation, and Fig.2(b) by spray coprecipitation.

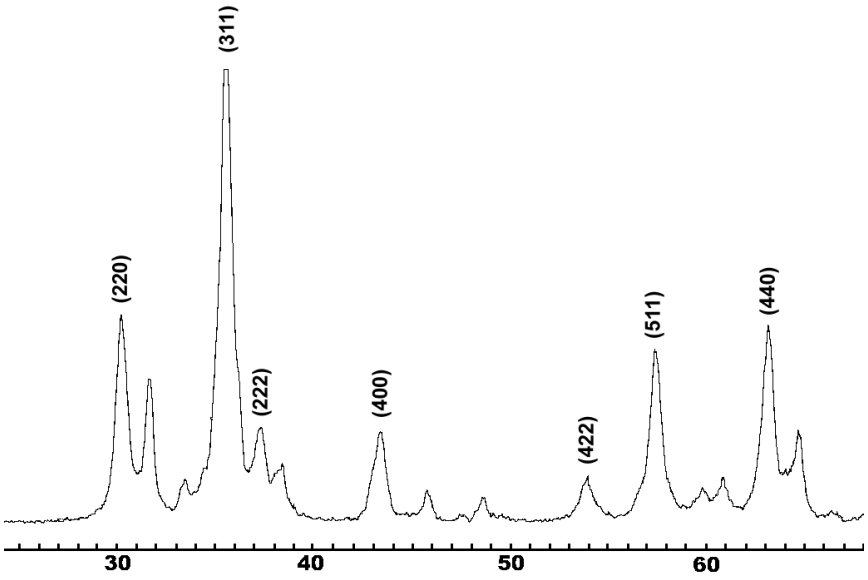


Figure 2(a) prepared by coprecipitation.

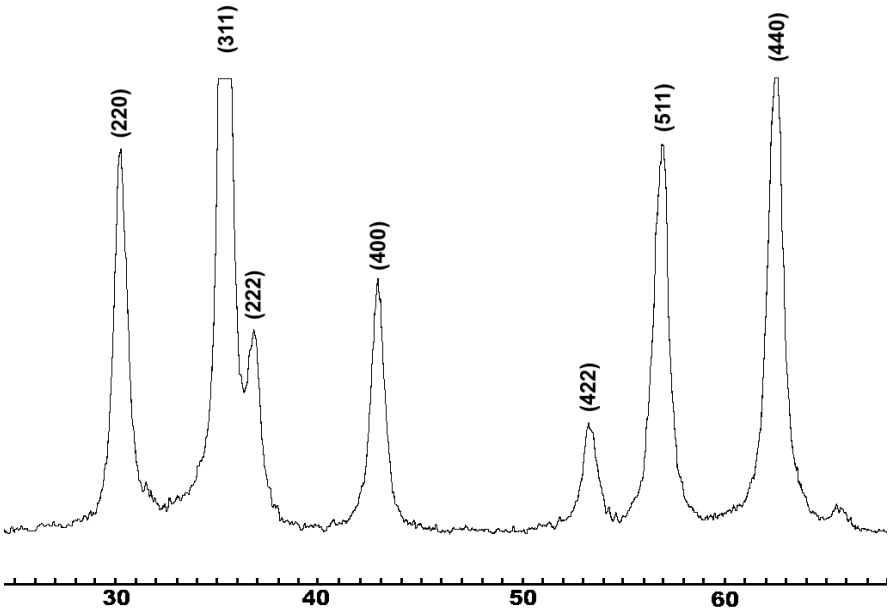


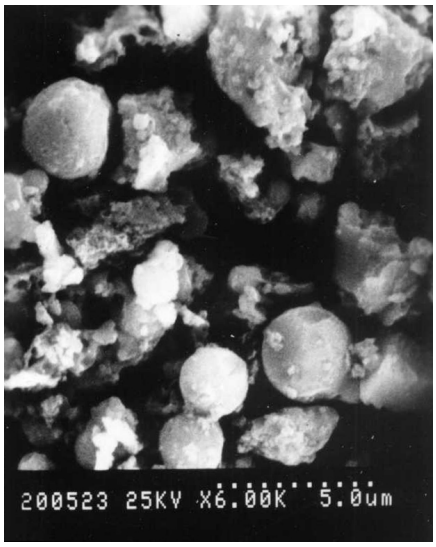
Figure 2(b) prepared by spraying coprecipitation.

Figure 2. XRD pattern of $ZnGa_2O_4$ powder.

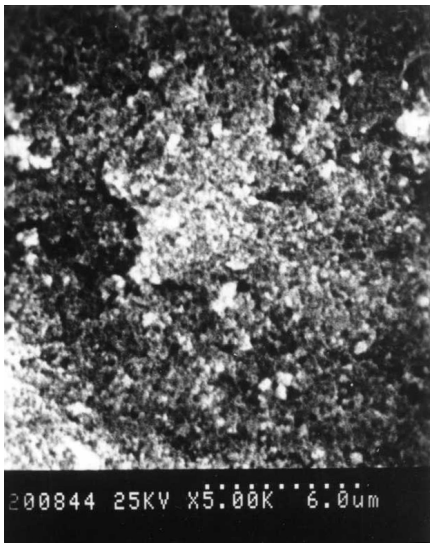
In Fig.2(a) ZnO Peaks can be found, while no Ga_2O_3 peaks exist, which means a small quantity of ZnO exists outside the crystal lattice of $ZnGa_2O_4$. While in Fig.2(b) no ZnO peaks exists, all Zn^{2+} are

in $ZnGa_2O_4$ crystals. Peaks in Fig.2(b) are wider than those in Fig.2(a); the crystallite sizes were evaluated from the line width. In Fig.2(a) the average size of $ZnGa_2O_4$ particles was 30nm while in Fig.2(b) the average size was less than 10nm. These results demonstrate that spray coprecipitation produces smaller particle sizes and purer nano powders.

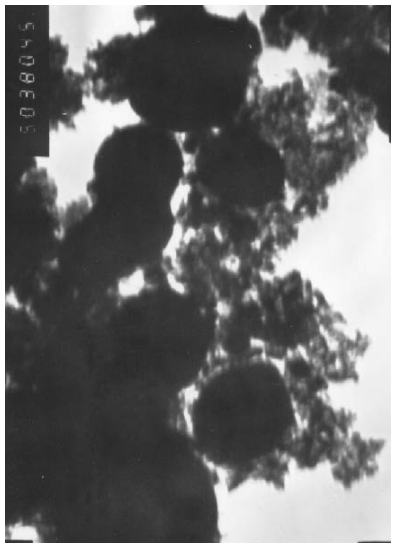
SEM and TEM images of $ZnGa_2O_4$ powder are shown in Fig.3. Fig.4 is an electron diffraction image of $ZnGa_2O_4$. Comparing Fig3(a) and Fig.3(b), It can be found that the $ZnGa_2O_4$ particles prepared by spray coprecipitation are smaller and more uniform. The particle size in Fig3(a) is about 20nm, while in Fig.3(b) 10nm. In Fig.3(c) there are many particles less than 5nm. In Fig.4 the $ZnGa_2O_4$ powder is crystalline.



(a) SEM image, prepared by chemical coprecipitation



(b) SEM image, prepared by spraying coprecipitation.



(c) TEM image, prepared by spraying coprecipitation.

Figure 3. SEM and TEM image of ZnGa2O4 powder.

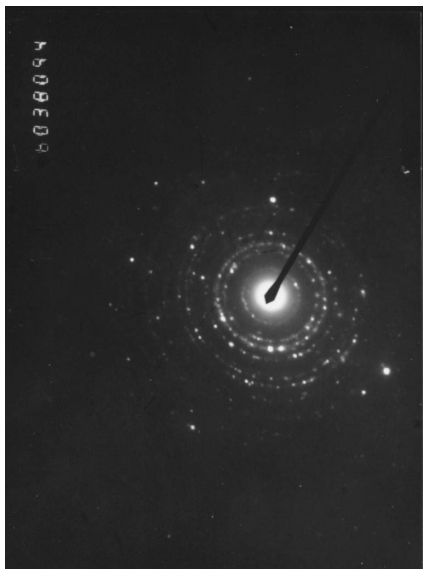


Figure 4. Electron diffraction image of $ZnGa_2O_4$.

According to the report of Nakatani et al. [8], the small grain size plays an important role in gas-sensing properties. Therefore, the thick film sensors based on $ZnGa_2O_4$ prepared by spray coprecipitation, which have a larger specific surface area, will have excellent gas sensitivity.

The adsorption activation energy of surface oxygen can be determined from the slope of the conductance-temperature line seen in Fig.5, which is 1.02eV.

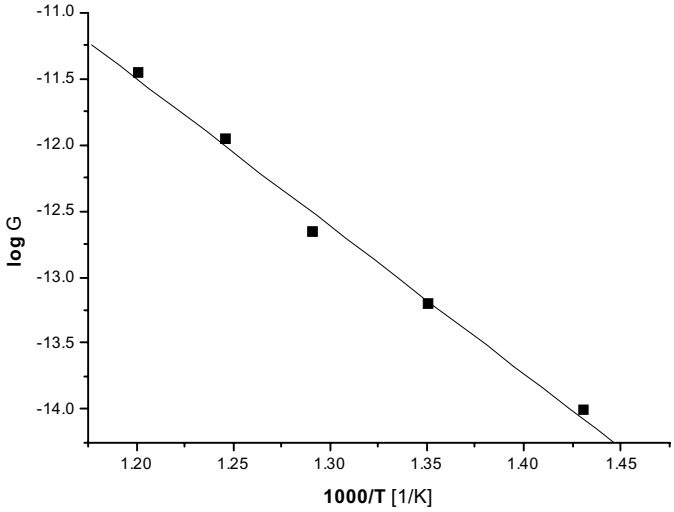


Figure 5. Conductance-temperature relationship of $ZnGa_2O_4$ gas sensor.

Fig.6 shows the change in electrical resistance with time; as indicated by the figure $ZnGa_2O_4$ gas sensors have excellent stability.

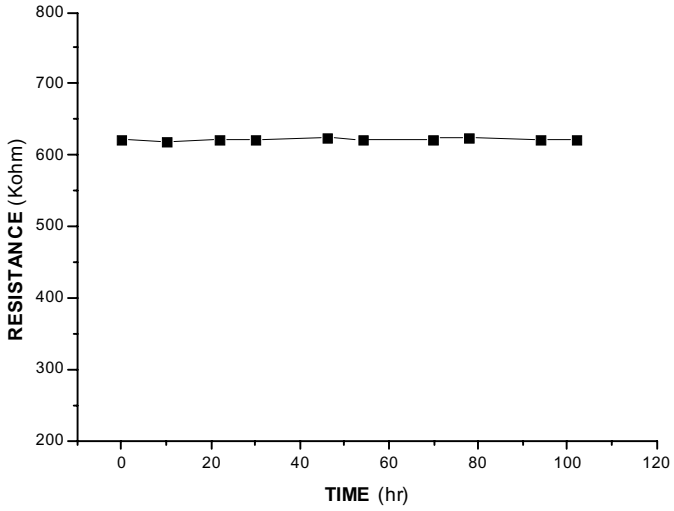


Figure 6. Resistance stability of $ZnGa_2O_4$ gas sensor measured in air.

Fig.7 shows relationships between gas sensitivity and working temperature of a $ZnGa_2O_4$ gas sensor exposed to a 500ppm LPG atmosphere. Maximum sensitivity to liquid petroleum gas (LPG) is achieved at an operating temperature of 410°C.

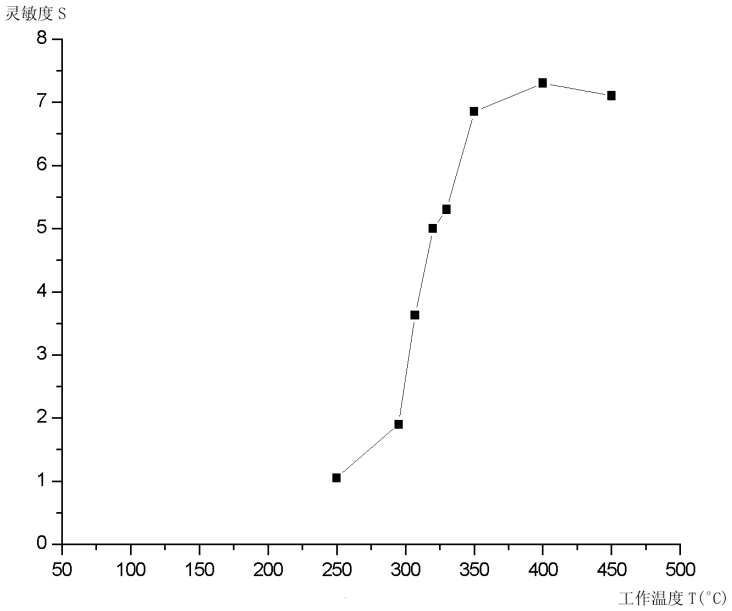


Figure 7. Relationships between gas sensitivity and working temperature of $ZnGa_2O_4$ gas sensor (500ppmLPG).

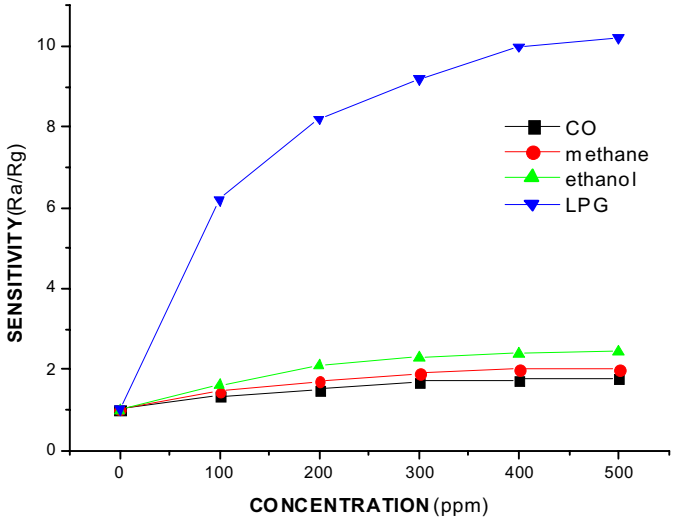


Figure 8. Sensitivity of $ZnGa_2O_4$ gas sensor to different gases.

Fig.8 shows change in sensitivity of a $ZnGa_2O_4$ gas sensor to different gases. Obviously, the element is more sensitive to LPG than to CO, C_2H_5OH and CH_4. When LPG concentration is 500ppm, the sensitivity to LPG already reaches 10, while sensitivity to CO, C_2H_5OH and CH_4 are only 1.6, 2.0 and 1.4 respectively.

Fig.9 shows the time dependent response of a $ZnGa_2O_4$ gas sensor to LPG. The response time is on the order of a few seconds, with a recovery time of approximately 60s.

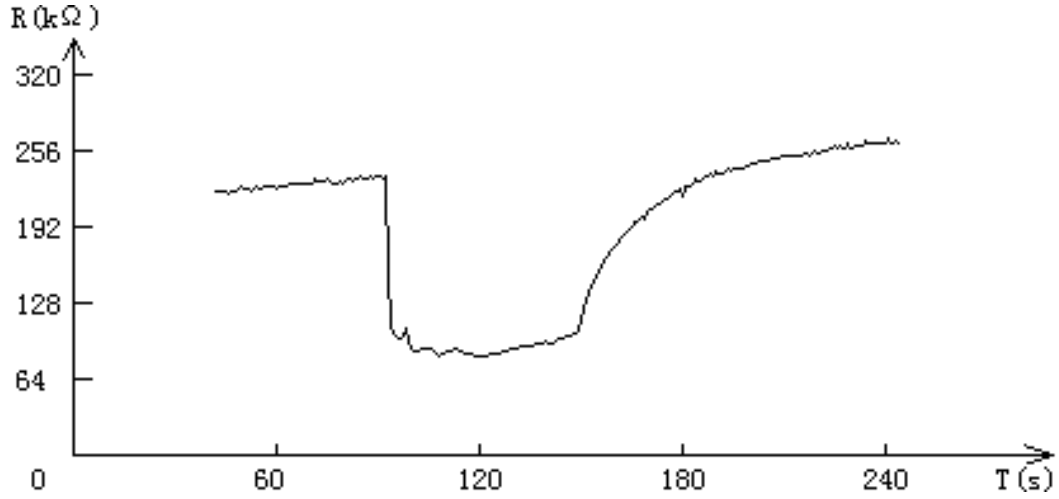


Figure 9. Response of a $ZnGa_2O_4$ gas sensor to a nitrogen/ 500 ppm CO/nitrogen environment.

Per sensing mechanism, as highlighted by works on metal oxides [9-13], the occurrence of different types of ionosorbed oxygen species like O_2^-, O^-, or O^{2-} is a function of temperature and prevailing atmospheric conditions. Electron exchange between the test gas and the oxide surface upon adsorption is suggested, i.e. a surface charge layer is formed when the test gas is adsorbed at the oxide surface, so that the bulk charge is generated and the energy band changes near its surface. For gases such as CH_4 and CO, it can be inferred that the conductance of nanocrystalline $ZnGa_2O_4$ elements will change greatly when reducing gases are allowed to react with the surface-adsorbed species releasing electrons. Consequently, the selectivity and sensitivity of the sensors can be controlled via modification of the conditions at which the reactions take place on the surface [14-16].

Conclusions

$ZnGa_2O_4$ nano crystals were prepared by spray coprecipitation. XRD results show the crystal size is under 10nm, whereas the powder prepared by ordinary coprecipitation is about 30nm. XRD results show that while ZnO peaks exist in $ZnGa_2O_4$ powder prepared by traditional coprecipitation, they disappear in $ZnGa_2O_4$ nano crystals prepared by spray coprecipitation. SEM and TEM were used to analyze the structural characteristics of $ZnGa_2O_4$ nano crystals. The spray coprecipitation fabrication route was presented, and the gas sensitive characteristics of $ZnGa_2O_4$ reported.

Acknowledgements

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Sample Availability: Available from the authors.