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Synthesis characterization and electrical properties of nanocrystalline ZnMgO by combustion route

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ABSTRACT

Nano structured $Zn_{(0.5)}Mg_{(0.5)}O$ *was synthesized by self combustion method using glycine as a fuel. The nanomaterial ZnMgO mixed oxide was characterized by TG-DTA, XRD, SEM, EDX and TEM. The average particle size of the nanomaterial ZnMgO calculated from XRD was found in the range 34 nm .It was good agreement with TEM .Electrical properties of the synthesized nanoparticles are studied by AC conductivity measurement. Electrical conductivity of the nanomaterial ZnMgO was increased with the temperature.*

Keywords: TG/DTA, XRD, SEM, EDX, TEM, Combustion method, Nano materials,

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INTRODUCTION

Recently, there is great deal of interest in the physical properties of diluted magnetic semiconductors for their potential technological application to optoelectronics, magneto electronics and microwave devices. The development of magnetic semiconductors with practical ordering temperatures could lead to new classes of device and circuits, including spin transistors and ultra dense nonvolatile semiconductors memory [1-4].Semiconducting metal oxide such as Zinc oxide, Tin oxide and Tungsten oxide have been widely studied for their gas sensing application, presently many other oxides also have been explored for the gas sensing devices. Gases form auto and industrial exhausts are polluting the environment. The sensors are required basically for measurement of physical quantities and for monitoring working environment. Inflammable gases such as gobar gas and Liquefied Petroleum Gas (LPG) are widely used for domestic purposes. Some of the well known materials for LPG sensors are SnO_2-Ru (thin film) [5], SnO_2-Ru (nano wire) [6], SnO_2 sulfuric acid (pellet) [7], $ZnSnO_3$ (pellet) [8], $ZnGa_2O_4$-Pd (paste applied on alumina tube) [9] etc. To monitor and control these gases has led to the research and development of a wide variety of sensors using different semiconducting oxide in bulk ceramic [9-10], thick film [11], has been studied from candidate sensors elements for gas sensing spinel type oxide semiconductors and cubic crystalline structures of the incomplete inverse spinel type.

The Wurtzite-type MgZnO alloy possesses attractive properties for possible applications in optoelectronic and display devices. Alloying of wurtzite ZnO [12] with cubic MgO [13], spectroscopic ellipsometry (SE) studies of MgZnO in the transparency and E_0-band-gap region were reported by Kang et al [14]. In order to extend the band gap energy so as to achieve the true blindness, the Mg content in ZnMgO must be high. Magnesium oxide (MgO) has a band gap of 7.8 eV and cubic crystal structure. The ionic radius of Mg^{2+} (0.57A^0) is similar to that of Zn^{2+} (0.60 A^0) . So replacement of Zn by Mg should not cause a significant change in lattice constants. Dropping suitable Mg into ZnO, it may be possible to obtain a ternary ZnMgO alloy with a wide band gap. However, the large crystal structure dissimilarity between wurtzite-hexagonal ZnO and rock-salt cubic MgO can cause unstable phase mixing. Hydrogen is considered as an efficient and clean fuel for the future due to its abundance it is easy to synthesis, and is in non-polluting nature.[15] The hydrogen storage materials require[16].high volumetric/gravimetric capacity [17] fast sorption kinetics at relatively low temperatures, and high tolerance to recycling. Recently, carbon nanotubes as well as metal hydrides have attracted extensive attention as promising hydrogen storage materials [18].Additionally,TiS_2 [19] and MoS_2[20] have been investigated as possible hydrogen storage materials [21].Hydrogen storage of ZnO and Mg doped ZnO nanowires[22].

Present works prepare ZnMgO by preparation of combustion techniques as a nanostructure of zinc magnesium oxide. The rapid heating and cooling during self combustion reaction can produce materials.

MATERIALS AND METHODS

Powder preparation

In this study polycrystalline $Zn_{(0.5)}Mg_{(0.5)}O$ powder was prepared using combustion synthesis method using glycine as fuel [23-24].

The materials used as precursors were zinc nitrate hexahydrate Zn $(NO_3)_2.6H_2O$, magnesium nitrate hexahydrate Mg $(NO_3)_2.6H_2O$ (all these were purchased from AR Grade of Qualigen fine Ltd.India) and glycine (Nuclear band). All of them were of high purity (99.9%, 98%, and 99.9% respectively). Glycine 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 Zinc nitrate and Magnesium nitrate in the proportion 0.5M and 0.5M respectively. Two moles of glycine were dissolved in a beaker then slowly stirring by using glass rod then clear solution was obtained. Then the formed Solution was evaporated on hot plate in temperature range 70^0C to 80^0C gives thick gel. The gel was kept on a hot plate for auto combustion and heated in the temperature range 170^0C to 180^0C. The nanocrystalline ZnMgO powder was formed within few minutes. And then sintered at about, 800^0C for about 4 hours then we get white colour shining powder of nanocrystalline ZnMgO.

Characterization Technique

The as –prepared samples were characterized by TG/DTA thermal analyzer (SDT Q600 V 20.9 Build 20), XRD Philips Analytic X-ray B.V. (PW-3710 Based Model diffraction analysis using Cu-K_α radiation), scanning electron microscope (SEM, JEOL JED 2300) coupled with an energy dispersive spectrometer (EDS JEOL 6360 LA), A JEOL JEM–200 CX transmission electron microscope operating at 200 kV analysis.

RESULT AND DISCUSSION

$$2C_2NH_3O_2 + (9/2)\,O_2 \rightarrow N_2\uparrow + 4CO_2\uparrow + 5H_2O \qquad (1)$$

$$Zn\,(NO_3)_3 + Mg\,(NO_3)_3 + 4C_2H_5NO_2 \rightarrow ZnMgO + 8H_2O + 10H_2O + 5N_2\uparrow \qquad (2)$$

TG-DTA analysis was performed at a heating rate of 10 K min^{-1} to investigate the thermal properties of ZnMgO. The TG spectrum and its 1st derivative presented in Fig. 1, show the thermal decomposition of ZnMgO is the curve indicates that the slight weight loss of about 32.66 % at temperature up to 275^{0}C in ZnMgO powder due to little loss of moisture, carbon dioxide and nitrogen gas. The DTA curve of ZnMgO recorded in static air and in shown in Fig. 1, the curve shown that ZnMgO did not decompose, but weight loss was due to dehydrogenation, decarboxylation and denitration. Further weight loss of about 9.33 % between the temperature range 400^{0}C and continuous loss in weight about 39 % up to 600^{0}C is attributed to loss of organic materials and yield final product at 650^{0}C, this weight loss and weight gained was very negligible. This weight change was in the range of 650^{0}C these indicating that the synthesized powder was almost stable from the begging. The formation temperature in the present work is found to be comparatively similar than that reported for corresponding solid state reaction route.

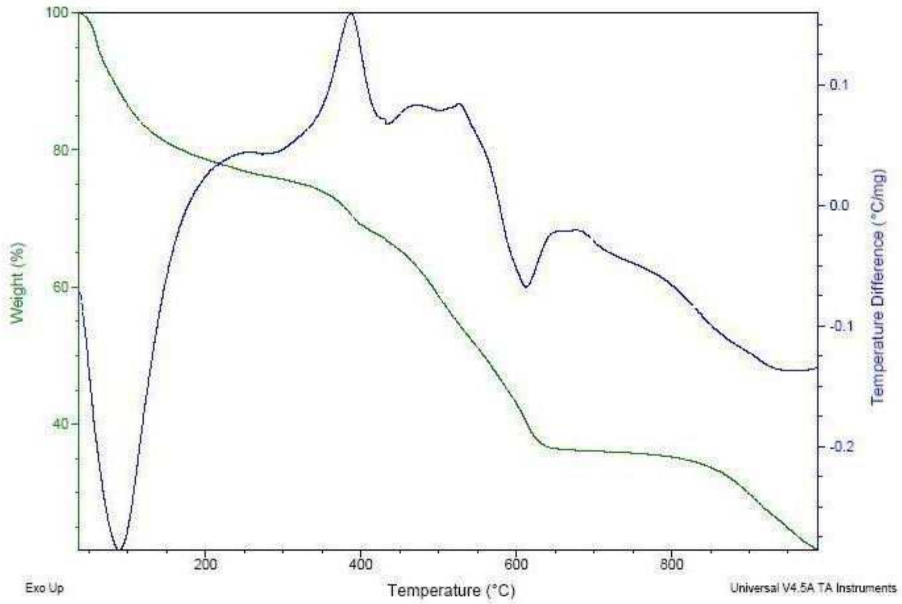

Fig.1 DTA-TG prepared ZnMgO nominal composition

The structure possesses the cubic may be attributed to the different preparation method which may yield different structural defects. The crystalline size was determined from full width of half maximum (FWHM) of the most intense peak obtained by scanning X-ray diffraction pattern. The grain size was calculated by using following Scherrer's formula [25-26].

$$d = 0.9\lambda / \beta\cos\theta$$

Where, d is the crystalline size, λ is the X-ray wavelength of the Cu K_{α} source (λ=1.54056 A^0), β is the FWHM of the most predominant peak at 100 % intensity, θ is the Braggs angle at which peak is recorded. The grain size was found to be 34nm.

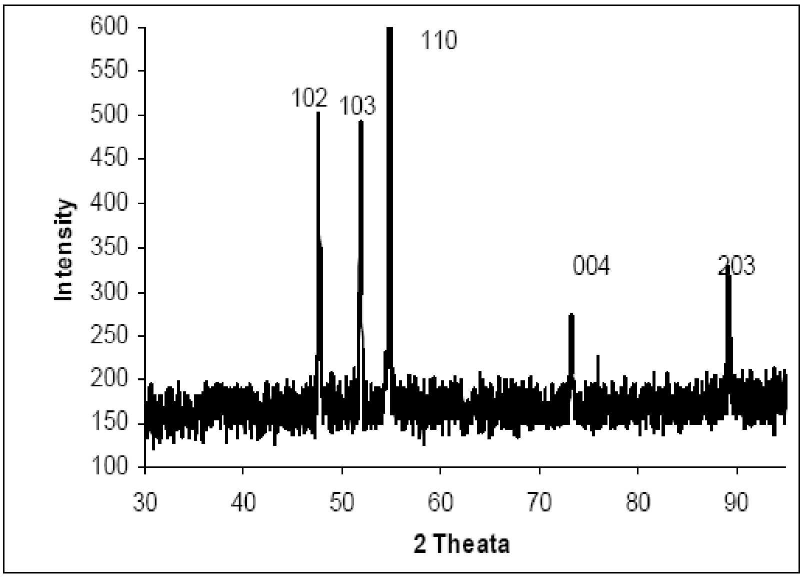

Fig.2 XRD pattern of ZnMgO as synthesized powder.

Powder morphology of as-synthesized powders was characterized by SEM techniques. It exhibited foamy agglomerated particles with homogeneous distribution and presence of random distribution of voids in their structure. This highly porous, foam-like structure was formed due to the inherent nature of the chemical reaction associated with the evolution of large volume of gas, and short reaction period followed by fast quenching which prevented further agglomeration/sintering of particles. Fig.3 (a, b,) showed the SEM micrography of as-formed foamy structured power. All photography showed clearly discrete spherical shaped nano-particles and their foam like agglomeration. Fig. 3 (a, b) exhibited the SEM photography of as-formed voluminous mass obtained from mixed fuel batches. The highly porous configuration was observed in case of second photography (Figure 3 b).During the combustion reaction, the release of extensive gaseous by-products and the instantaneous reactions inhibit the particles sintering and create the porous in the structure of resultant powder.

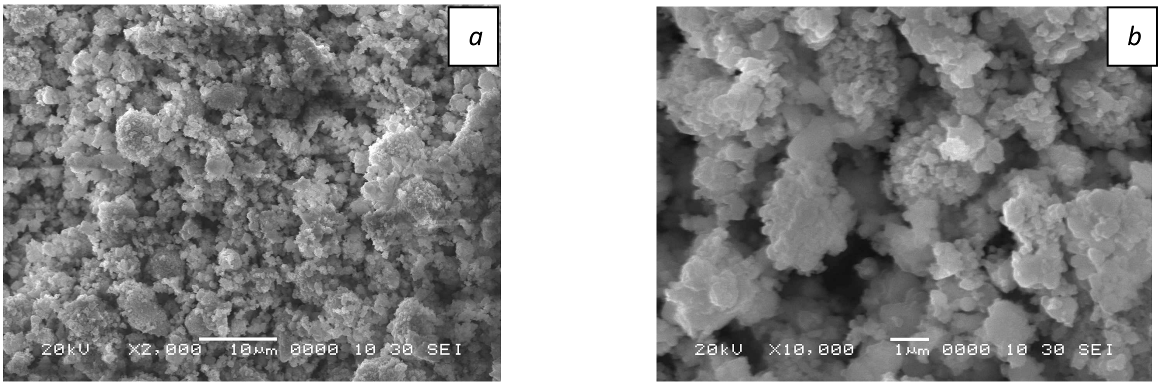

Fig.3 SEM images of mixed precursor at 800^{0}C in air for 4 h (a) low resolution and (b) high resolution

Fig.4 shows the energy dispersive X-ray spectrum of ZnMgO. This was carried out to understand the composition of zinc, magnesium and oxygen in the material. There was no unidentified peak observed in EDX. This confirms the purity and the composition of the ZnMgO nanomaterial.

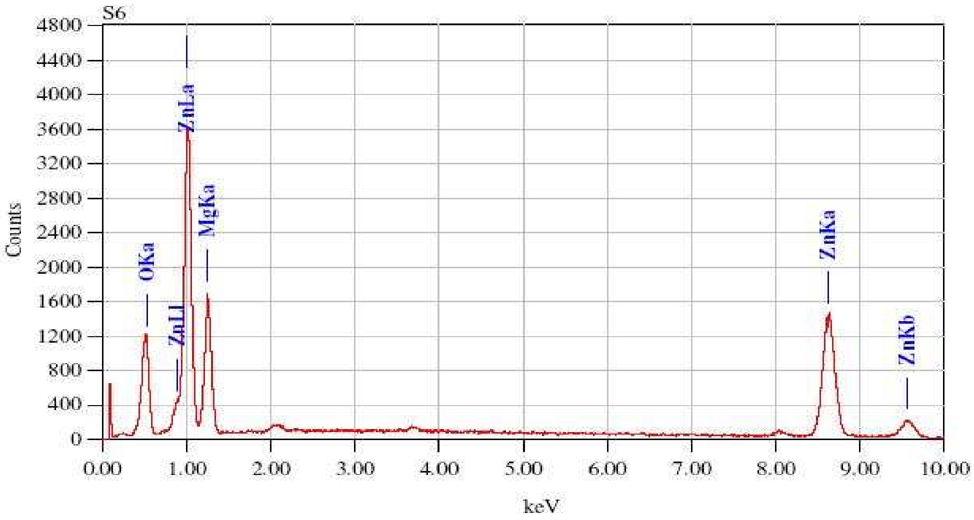

Fig.4 EDX pattern of ZnMgO.

The TEM image of the mixed precursor calcined at 800^{0}C for 2h are shown in Fig. 5(b) It indicates the presence of ZnMgO nanoparticles with size 30-50 nm which form beed type of oriental aggregation throughout the region. The selected area electron diffraction (SAED) pattern Fig. 5 (a) shows the spot type pattern which is indicative of the presence of single crystalline particles. No evidence was found for more than one pattern, suggesting the single phage nature of the material.

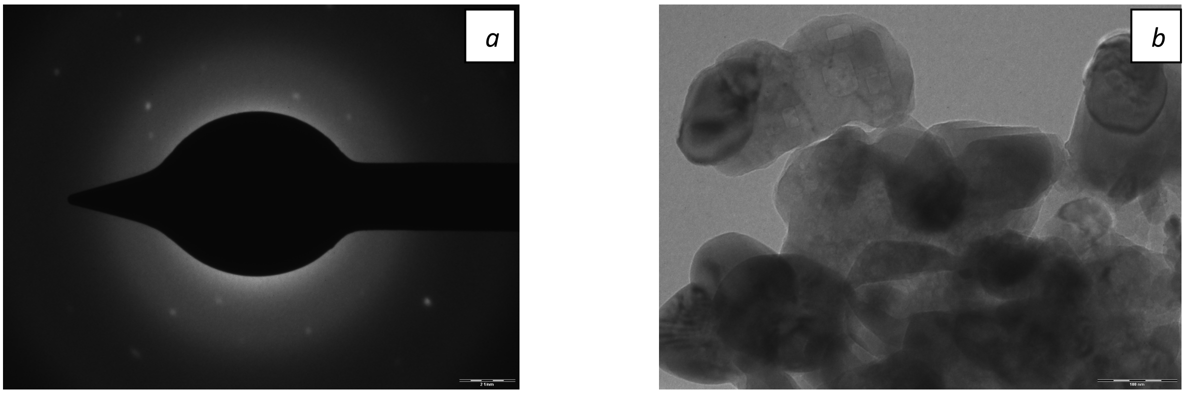

Fig.5. TEM (b) images of nanostructured ZnMgO (a) SAED pattern

Electrical properties

Fig. 6 of the ZnMgO film. It is clear from the symmetrical I-V characteristics that the silver contact on the film was ohmic in nature.

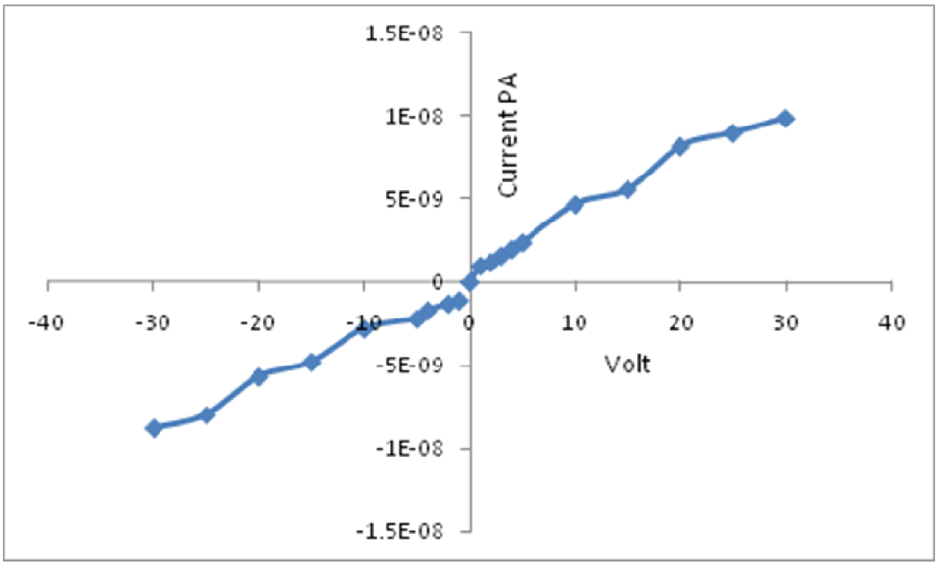

Fig.6. *I-V* characteristics of the ZnMgO.

Electrical conductivity

The semiconducting nature of ZnMgO is observed from the measurements of conductivity with temperature. The semiconductivity in ZnMgO may be attributed to oxygen deficiency in it. The material would then adsorb oxygen species at higher temperature $(O_2^- \rightarrow 2O^- \rightarrow O^{2-})$. The adsorption chemistry of the pure ZnMgO thick film surface. The ZnMgO misfits on the surface enhance the oxygen adsorption capability of the surface. The ZnMgO misfits distributed evenly on the surface would have made it possible to adsorb the oxygen ions even at low temperatures. From Fig.7 it was clearly noted that the conductivities of ZnMgO films increase with an increase in operating temperature. This behavior confirmed the semiconducting nature of ZnMgO. The increase in the charge-carrier generation mechanism resulted from the electronic defects. These generated electrons and the donor level in the energy band gap of ZnMgO will contribute to an increase in conductivity [27-28].

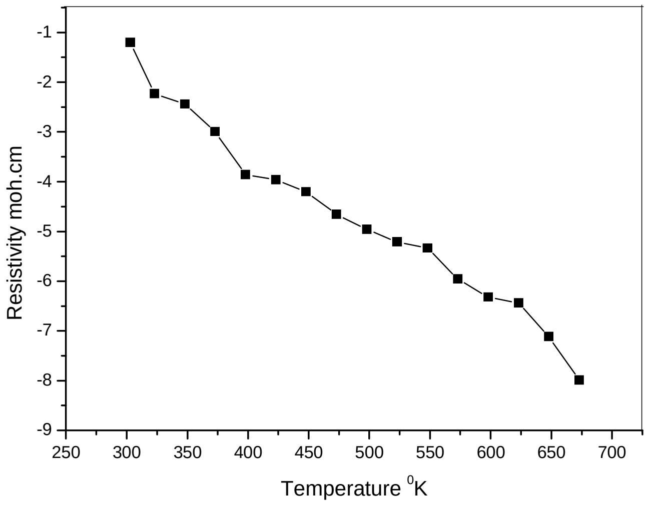

Fig.7. Variation of log (conductivity) with reciprocal operating temperature (K^{-1})

CONCLUSION

Nanocrystalline ZnMgO has been successfully synthesized by self combustion route. TG-DTA analysis indicates the phase formation was carried out at 650^0C. The route may be used for the synthesis of other metal oxide. XRD technique was shown the average crystal size of the ZnMgO nanoparticles about 34 nm at 800^0C respectively. Elemental analysis confirmed by using EDX. SEM micrographs show the material is porous in nature. TEM image shows grain size of the material was 30-50 nm. The material possesses good electrical conductivity. Electrical conductivity increases with increasing temperature of the material.

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