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Controllable growth of Zn_2SnO_4 nanostructures by urea assisted microwave-assisted solution combustion process

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Nanoparticle powders of zinc stannate indate spinel (Zn_2SnO_4) were prepared with a single step process. The first nano-oxides of ZnO and SnO_2 were obtained by microwave-assisted combustion of aqueous solution of metal nitrates (as the oxidizer) and urea (as fuel). This method is rapid, effective, cheap and convenient. In this paper, different combinations of fuel to oxidant ratio was used to prepare Zn_2SnO_4 nanoparticle and its effect on structural, morphological and optical characteristics were investigated using powder X-ray diffractometer, scanning electron microscope, Fourier transform infrared spectra meter and UV-Vis absorbance spectroscopy, respectively. The structural parameters were calculated from XRD pattern which confirmed the spinel structure of Zn_2SnO_4. The SEM investigations evidenced the presence of homogeneous distribution of spherical nanoparticles.

Key words: Nanoparticles, Zinc stannate, Microwave-assisted combustion synthesis, Optical studies.

Introduction

Considerable developments have been witnessed in many fields due to the implication of nanotechnology and also due to the employment of novel materials with desired properties. The nanosized mixed metal oxides have much interest in cutting edge technologies due to their size and shape dependent properties, which are tuneable by varying the experimental parameters. In the recent years, fabrication of transition conducting oxides (TCO) with nano structure has been the target of scientific interests because of their unique properties and fascinating applications in optoelectronics, devices and biomedical science [1]. Among these materials, zinc tin oxide (ZTO) which is sometimes referred to as zinc stannate, has recently received attention as an alternative TCO materials and has attracted considerable interest in many areas of chemistry, physics and material science. They have extra attention due to their broad range of applications in sensors [2], catalysts [3], solar cells [4], transparent conductive oxides [5], optoelectronic devices [6] piezoelectric devices [7] and additive in many industrial products. Therefore the researchers make much effort to focus on investigating them for technological applications due to their unusual physical and chemical properties, which differ significantly from those of conventional bulk materials. Generally nanoscale particles possess different physical, chemical properties, better sinter ability, larger catalytic activity and other unique properties may be expected because of their nano-sized particle are high surface area with different surface defect properties etc. So the technological importance of zinc stannate (Zn_2SnO_4) has motivated several studies on the synthesis of this material using various methods. Few research accomplishments have been reported on the synthesis of zinc stannate by various synthetic methods. However there is no attempt has been made to study the Zn_2SnO_4 by microwave-assisted combustion synthesis (MACS) method to the best of our knowledge. Belliard et al. prepared Zn_2SnO_4 NPs by mixing stoichiometric amounts of SnO_2 and ZnO and ball milled for 12 hrs. Then it was calcinated at 1000 °C for 48 hrs and the product can be used as an anode material for lithium battery [8]. Powder mixtures of zinc oxide and tin oxide in the molar ratio, $ZnO:SnO_2 = 2 : 1$, were prepared prior to the sintering process as well as to optimize the processing route for the advanced mechanochemical synthesis of zinc-stanate spinel [9]. Among the synthetic approaches MACS method is considered to be one of the best techniques to prepare nanomaterials because of its short reaction time, high purity, high yield, better homogeneity and high surface area in a single step. The aim of this study is to prepare Zn_2SnO_4 nanoparticles by microwave-assisted combustion method. Its structural, optical and electrical properties are also explored.

Experimental Procedure

All the chemicals and reagents used in the experiments

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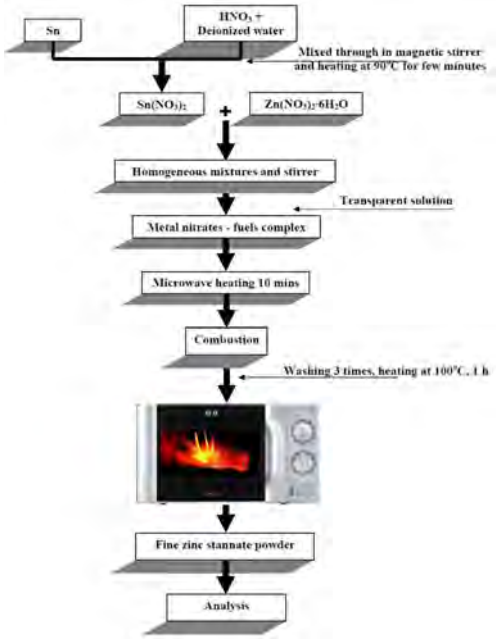

Fig. 1. Flowchart for sample preparation of zinc stannate by microwave-assisted combustion method.

were analytically pure and were purchased from MERCK Company, and were used as received without further purification. For the preparation of Zn_2SnO_4 nanoparticles, zinc nitrate, tin nitrate and urea was used as starting materials. Deionized water was used for preparing solutions. Zn_2SnO_4 nanoparticles were prepared by MACS method, containing stoichiometric amount of corresponding metal nitrate and a suitable fuel. A schematic representation of the synthesis process used in the current study is graphically shown in Fig. 1. The stoichiometric composition of solution components (oxidizer to fuel) was calculated according to the principle of propellant chemistry. The stoichiometric amounts (2 : 1) of zinc nitrate and tin nitrate (oxidizer) were dissolved in a minimum amount of deionized water to get clear solution. Then, urea was added in this solution and poured into a quartz container and could be mixed well by magnetic stirring for 1 hr, which made them almost as homogeneous mixtures, which was placed in a domestic microwave-oven. Initially, the solution boils and undergoes dehydration followed by decomposition with the evolution of large amount of gases with white fumes occurs coming out from the exhaust opening provided on the top of the micro oven. After the solution reaches the point of spontaneous combustion, it begins burning and releases lots of heat, vaporizes all the solution instantly and becomes a foamy white solid powder.

The synthesized Zn_2SnO_4 powders was identified the phase formation, structural and crystallite size estimation by powder X-ray diffraction (PXRD) method using a X-Pert PRO PANalytical diffractometer using nickel filtered Cu-Kα radiation (λ = 0.15418 nm) as source and operated at 40 kV and 30 mA. The sample was

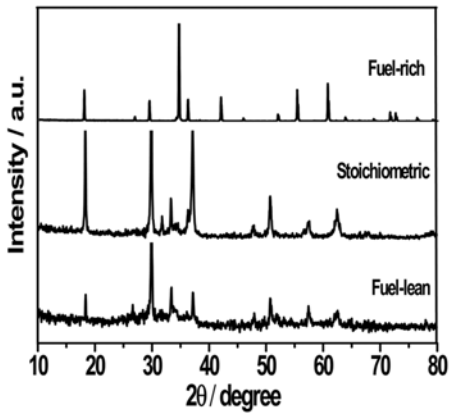

Fig. 2. XRD patterns of Zn_2SnO_4 synthesized by a microwave-assisted combustion method.

Table 1. XRD structure parameters and Rietveld refined of urea used Zn_2SnO_4.

Parameters	From XRD results	From Rietveld refinements results
Crystal size (nm)	18	24
a (Å)	8.626	8.7235
Cell volume ($Å^3$)	648.53	642.11
Crystal density ($g.cm^3$)		6.451
R_{exp} (%)		4.51
R_{wp} (%)		9.33
R_p (%)		6.31
R_{Bragg} (%)		3.1
DW (%)		3.61
S (%)		2.06

scanned in the 2θ ranging from 10 to 80° in θ-θ scan mode. The observed peak positions were compared with the standard JCPDS data and Miller indices were assigned to the Bragg peaks. The structure of the prepared Zn_2SnO_4 powders was solving using PXRD method with refinement by Rietveld method. SEM micrographs of samples were obtained using Hitachi S4800 scanning electron microscope. Infrared spectra were recorded using Nicolet Avatar 360 FTIR spectrometer with KBr pellets and UV-Vis absorption spectra were recorded using Shimadzu UV-2550 spectrophotometer.

Results and Discussion

The structure of the prepared Zn_2SnO_4 nanocrystallites has been investigated by powder X-ray diffraction (PXRD) analysis. Fig. 2 shows a typical PXRD pattern of urea as fuel-lean, stoichiometric and fuel-rich conditions of Zn_2SnO_4. The reaction of the components completes and transform to a face-centered cubic spinel structural of fuel stoichiometric and fuel rich conditions. From

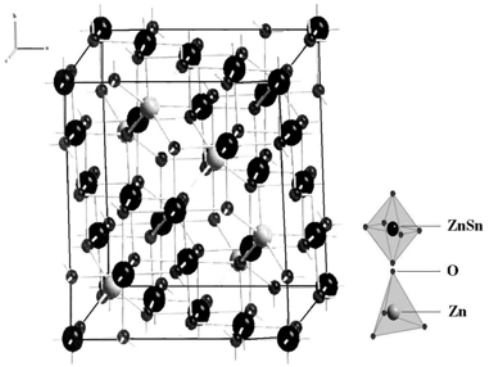

Fig. 3. The results of Rietveld analysis for the rhombohedral structure of Zn_2SnO_4 synthesized using urea as fuel.

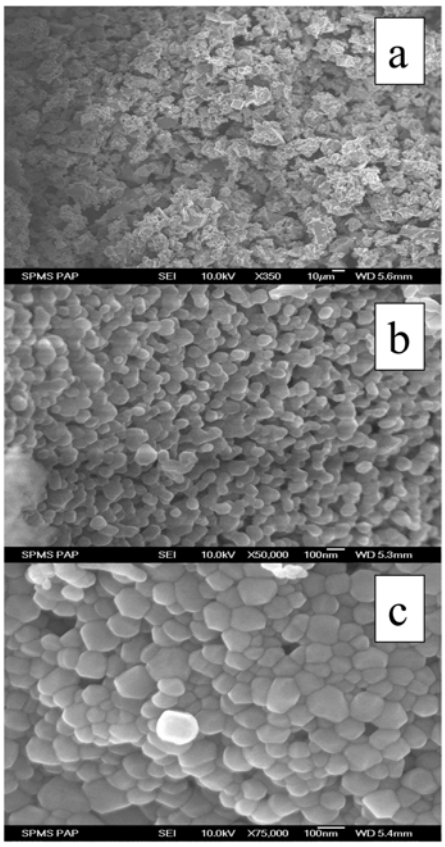

Fig. 4. SEM micrograph of (a) fuel in lean, (b) stoichiometric and (c) rich condition of Zn_2SnO_4 powders.

this conditions, the XRD clearly depicts the peaks corresponding to the (111), (220), (311), (222), (400), (422), (511), (440), (531), (533), (622) and (444) Miller planes, which suggest the face-centered cubic spinel structural of Zn_2SnO_4 as per the JCPDS (File no. 74-2184). The lattice constant "a" was calculated using multiple peaks by least squares method which is consistent with the standard value (JCPDS File no. 74-2184). No impurities are detected from this pattern, indicating that the products are pure and high crystalline spinel oxide. This indicates that pure Zn_2SnO_4 was obtained under the present synthesis method. The average crystallite size (D) of the

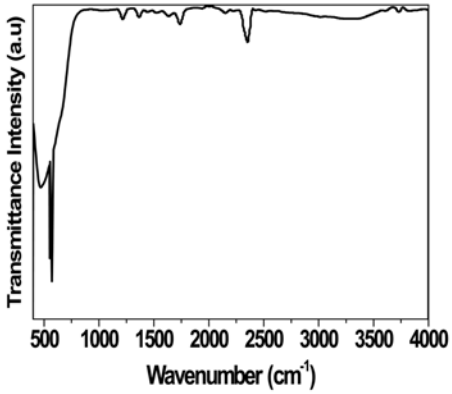

Fig. 5. FTIR spectra of Zn_2SnO_4.

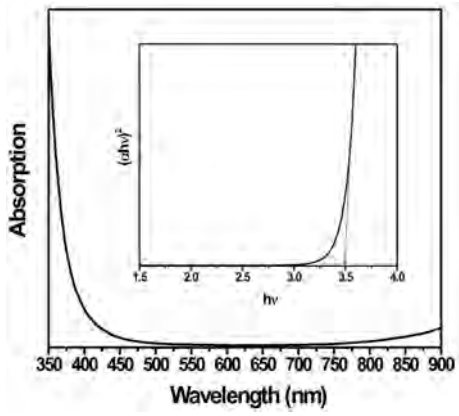

Fig. 6. UV-Vis spectra of Zn_2SnO_4.

Zn_2SnO_4 was calculated using the Debye-Scherrer formula and other crystal structure parameters are in good agreement with the reported JCPDS data.

The Rietveld refinements for the investigated Zn_2SnO_4 are summarized in Table 1. As it can be seen, the calculated lattice crystal parameters of stibnite are in good agreement with the observed one (Table 1). The results of Rietveld analysis demonstrate the cubic spinel structure form for glycine used Zn_2SnO_4 as shown in Fig. 3. In general, R_p, R_{wp} and S show a decreasing trend with the increase of the weight fraction of albite suggest that the pattern fitting was accurate. The phase of Zn_2SnO_4 Rietveld fit was performed the cubic spinel structure with space group $Fd3^-m$ (227). The positions of Zinc atoms are located in 16(c) for Zn_1 and 8(b) for Zn_2, tin (Sn) atoms in the 16(c) positions and oxygen (O) atoms are located in 32(e) special Wyckoff positions in the occupancies sites of Zn at (0, 0, 0) and (0.372, 0.372, 0.372), Sn at (000) and O at (0.241, 0.241, 0.241). Rietveld refinement is probably the method of choice for determining accurate unit-cell parameters.

Fig. 4 shows the SEM micrographs of urea as fuel-lean, stoichiometric and fuel-rich conditions of Zn_2SnO_4. The product is foamy and porous in nature formed by the escaping gases during the combustion process. The particle size of Zn_2SnO_4 was observed in

stoichiometric condition, it is in nanometer scale compared to the other conditions.

Fig. 5 shows the FTIR spectrum of the stoichiometric condition of Zn_2SnO_4, a broad absorption peak at ~ 572 and 555 cm^{-1} is due to symmetric stretching vibration of ZnO and SnO_2 groups respectively and this band could be assigned to the Sn-O-Zn bonding of the Zn_2SnO_4 inverse spinel. An absorption band at ~ 1630 and 3500 cm^{-1} indicates the presence of hydrogen bonds and absorption at ~ 1429 and 2350 cm^{-1} were assigned to C-H vibration modes attributed to the organic trace residuals. The peak at ~ 1740 cm^{-1} band is the possible bonding of Zn in ZnO and ~ 1219 cm^{-1} is attributed to Sn-O stretching vibrations group. The small absorption at ~ 1000 cm^{-1} is due to the deformation vibration of C = O.

The UV-Vis spectrum of stoichiometric condition of Zn_2SnO_4 is shown in Fig. 6. The absorption peak shoulder onset peaks are located at 355 nm corresponding to the band gap of 3.5 eV. Compared with the other methods, nanocrystalline Zn_2SnO_4, obtained by this microwave-assisted combustion method has larger band gap energy. The linear part of the $(\alpha h\upsilon)^2$ versus $h\upsilon$ axis is extrapolated to cut the $h\upsilon$ axis. This is the absorption edge of the spectrum which gives the band gap of the material.

Conclusions

The spherical shape Zn_2SnO_4 powders are successfully synthesized by microwave-assisted combustion reaction by using urea as a fuel. The structural parameters calculated from XRD pattern confirm Zn_2SnO_4 nano crystalline possessing face-centered cubic spinel structure. Nanocrystalline Zn_2SnO_4 powder was confirmed for the stoichiometric condition. SEM micrograph revealed the nano particles in the order of 50 to 60 nm, which was estimated from the gaussian distribution of particles graph. The chemical structure of the Zn_2SnO_4 powders was investigated by FTIR. From the optical spectrum, absorption edge corresponding to the band gap energy of Zn_2SnO_4 was shifted towards blue region and suggested that the materials become nano size. It has potential applications in gas-sensing.

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