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Preparation, Wettability properties of perovskite-type composite oxides nanocrystals by Combustion Route

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ABSTRACT

The aim of said study was to obtain nanostructured La_2ZnO_4 through self combustion synthesis using lanthanum nitrate, znic nitrate as precursors and glycine as a fuel, without the subsequent heat treatments after synthesis. The temperature variation with respect to a sample with constant molar ratio was investigated. The crystallinity (phases present and crystallite size: estimated by single-line method) of the product obtained was determined by X-ray diffraction (XRD) measurement, thermogravimetric analysis(TG-DTA),scanning electron microscope(SEM),and transmission electron microscopy (TEM). The synthesis method facilitated the production of Perovskite La_2ZnO_4 with crystallite size between 18-40 nm. The superhydrophilicity of the sintered oxides was investigated by wetting experiments, by the sessile drop technique, were carried out at room temperature in air to determine the surface and interfacial interactions.

Keywords: La_2ZnO_4 nanostructure, XRD, TG/DTA, EDX, SEM, TEM.

INTRODUCTION

Combustion synthesis is an easy and convenient method for the preparation of a variety of advanced ceramics, catalysts and nanomaterials.[1] In this technique, based on the principles of the propellant chemistry,[2] a thermally induced redox reaction takes place between an oxidant and a fuel. Many types of combustion synthesis exist which differ mainly in the physical state of the reactants or in the combustion modality.1,[3-7] By combustion-based methods it is possible to produce monophasic nanopowders with homogeneous microstructure, at lower temperatures or shorter reaction times, if compared with other conventional methods like solid-state synthesis[8,9] or nitrate method[10,11]. Citrate–nitrate auto-combustion synthesis (CNA) is a very popular solution combustion method,[12,14] where the fuel is citric acid and metal nitrates are used as metal and oxidant source. CNA method shows high similarities with the very well known Pechini process [15,16] and it can be more properly described as a "sol–gel combustion method"[17]. Perovskite-type ABO_3 and related compounds have been reported to be of importance due to their wide uses in fuel cells[18], catalysts[19,20],membranes in syngas production[21], sensors[22,23]and environmental monitoring applications[24]. Gas sensing application [25,26] etc. Among the chemical sensors $LaCoO_3$, $BaTiO_3$, $LaFeO_3$, $LaMnO_3$ etc. are perovskite-type materials of general formula ABO_3 are extensively studied owing to their notable gas sensitivity for different poisonous gases in addition to their magnetic, catalytic and other physical properties. The perovskite-type metal oxide including the d-block and rare earth elements has attracted the attention of many researchers due to their homogeneity, interesting structural, catalytic and gas sensing properties. There is an increasing interest in finding new materials in order to develop high performance solid state gas sensors.Several studies have reported that by finely controlling the micro/nanostructure or chemical composition of a surface, the adhesion between the superhydrophobic surface and water can be

changed. Such superhydrophobic sur-faces show potential in a variety of applications from antisticking, anticontamination and selfcleaning to anticorrosion and low friction coatings and gas sensing.

The present research, analyze the synthesis of an Perovskite La_2ZnO_3 by the combustion method with an average crystalline size of 45 nm.The superhydrophilicity of the sintered oxides was investigated by wetting experiments by the sessile drop technique was carried out at room temperature in air to determine the surface and interfacial interactions.

MATERIALS AND METHODS

In this study polycrystalline La_2ZnO_4 powder was prepared using combustion technique. The materials used as precursors were lanthanum nitrate hexahydrate La $(NO_3)_2.6H_2O$, zinc nitrate hexahydrate Zn $(NO_3)_2.6H_2O$ and glycine (all these were purchased from AR Grade of Qualigen fine Ltd.India). 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 providing a platform for redox reactions during the course of combustion. Initially the lanthanum nitrate and znic nitrate are taken in the proportion 1:1:4 stoichiometric amount respectively and two moles of glycine were dissolved in a beaker slowly stirring by using glass rod clear solution was obtained. Then the formed solution was evaporated on hot plate in the temperature range of 70^0C to 80^0C resulting into a gives thick gel. The gel was kept on a hot plate for auto combustion and heated in the temperature range of 170^0C to 180^0C. The nanocrystalline La_2ZnO_4 powder was formed within a few minutes. And it was sintered at about 500 ^{0}C about 4 hours then we got a white colour shining powder of nanocrystalline La_2ZnO_4.

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.

RESULTS AND DISCUSSION

6.1 TG-DTA analysis:

The TG cure recorded for thermal decomposition of La_2ZnO_4 is shown in (1). The cure indicates that the slight weight loss in La_2ZnO_4 powder due to little loss of moisture, carbon dioxide and Nitrogen gas. The DTA curve of La_2ZnO_4 recorded in static air and is shown in Figure-1. The curve shows that La_2ZnO_4 did not decompose, but weight loss was due to dehydrogenation, decarboxylation and denitration and yield final product at 800^0C. This weight change was in the synthesized powder was almost remain stable from the beginning.

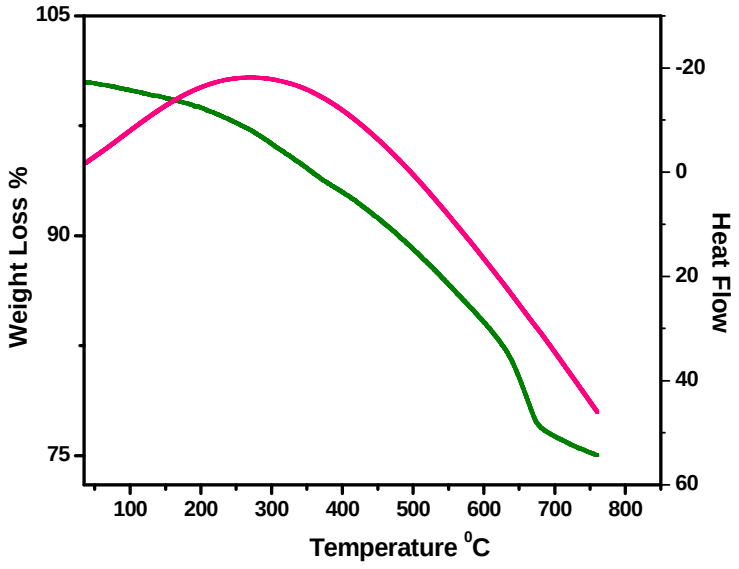

Figure -1.TG-DTA curve of mixed precursor.

6.2 X-ray Diffraction analysis:

The X-ray diffraction pattern of La_2ZnO_4 powder is shown in Figure- 2. This material is novel so no JCPDS match is found. We are reported this first time the structure possesses may be the Perovskite structure 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 shown scanning of X-ray diffraction pattern. The grain size was calculated by using Scherer's formula[27,29].

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

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(110), θ is the Braggs angle at which peak is recorded. It was similar to TEM 18-40 nm.

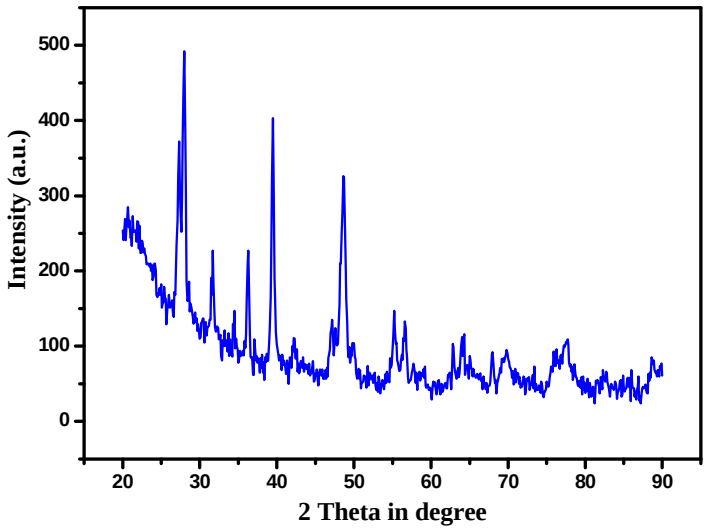

Figure - 2. XRD pattern of calcinied mixed precursor La_2ZnO_4 at 800^{0}C, in air for 4 h.

6.3 Energy dispersive X-ray microanalysis analysis (EDX):

Figure-3 shows the energy dispersive X-ray spectrum of La_2ZnO_4. This was carried out to understand the composition of Lanthanum, zinc and oxygen in the material. There was no unidentified peak observed in EDX. This confirms the purity and the composition of the La_2ZnO_4 nanomaterial.

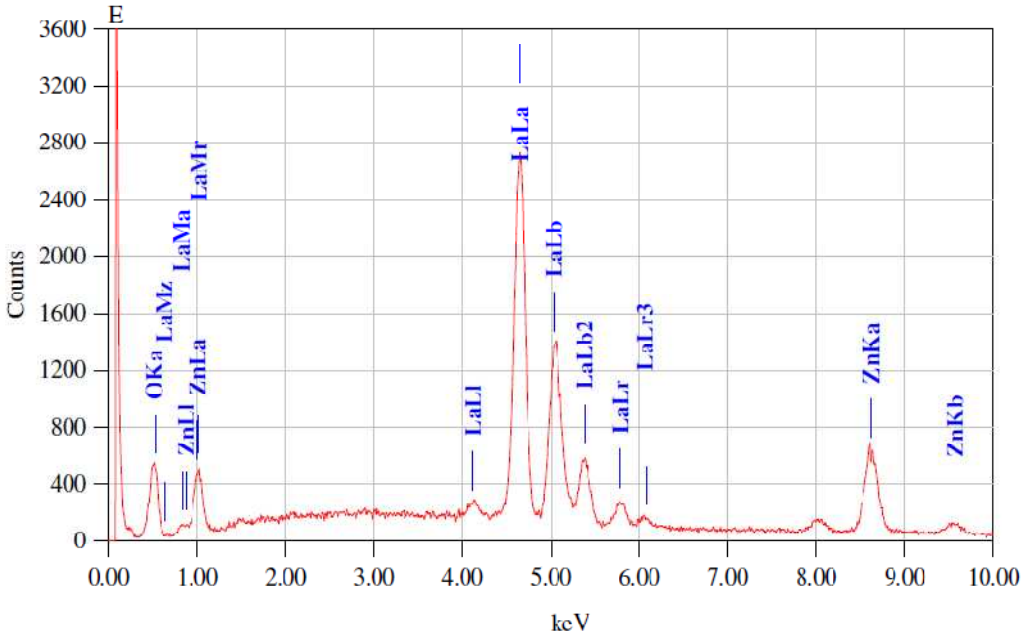

Figure - 3. EDX pattern of mixed precursor La_2ZnO_4 at 800^{0}C in air for 4 h.

6.4 Scanning electron micrograph analysis:

The microstructure of the sintered samples can be visualized from scanning electron microscope (SEM) tool. Figure - 4 shown the particle morphology of high resolution, the particle are most irregular in shape with a Nanosize range. Some particles are found as agglomerations containing very fine particles the particles shapes are not defined porous nature and small and large core, spongy pores are seen in the micrograph.

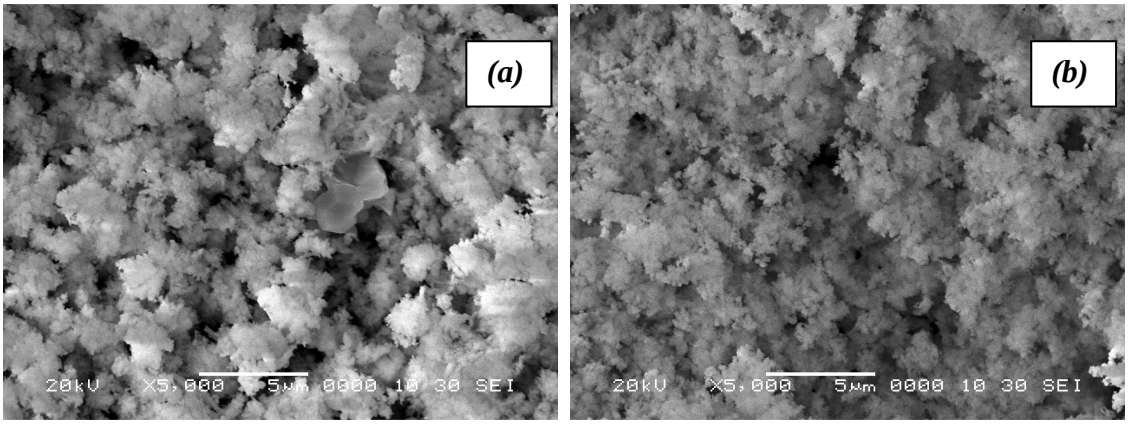

Figure - 4. SEM images of mixed precursor La_2ZnO_4 at 800^{0}C in air for 4 h (a) low resolution and (b) high resolution.

6.6 Superhydrophilic Test:

Wet ability of pallet shows behavior of water droplet on upper surface of material depends on surface energy and surface roughness of material. Thomas Young had described the force acting on a liquid droplet spreading on surface so-called contact angle (θ) is related to interfacial energies acting between the solid-liquid (γ_{SL}), solid-vapor (γ_{SV}) and liquid-vapor (γ_{LV}) given by following relation.

$$\cos\theta = \frac{(\gamma_{SV} - \gamma_{SL})}{\gamma_{LV}} \quad \text{..... (2)}$$

The expression given by Equation 2 is strictly valid only for surfaces that are atomically smooth, chemically homogeneous and those that don't change their characteristics due to interactions of the probing liquid with the substratum or any other outside force. Wenzel regime liquid wets the surface but the measured contact angle θ* differs from the "true" contact angle θ by Wenzel's equation for rough surface r > 1.

$$\cos\theta^* = r\cos\theta \quad \text{..... (3)}$$

Where r is the roughness factor of the 9/surface. The wet ability nature of our synthesized material is super hydrophilic in the Wenzel because of highly rough surface nature was clearly seen from SEM images with consideration given to the surface roughness. Figure - 6 (a-b) shows the image of contact angle on rough surface of lanthanum zinc oxide material. It was seen that contact angle of material is θ =0 hence material in superhydrophilic θ≤5 may be due to high energy surface and their porous nature.

In to characterization

Wetting experiment of synthesized pure lanthanum zinc oxide evaluated by contact angle measurement were performed by the sessile drop method using advanced goniometer apparatus (Model110, Ram hart Instrument Co., USA) and distilled water droplets of 0.01ml were delivered to surface of lanthanum cobalt oxide pellet material at different points.

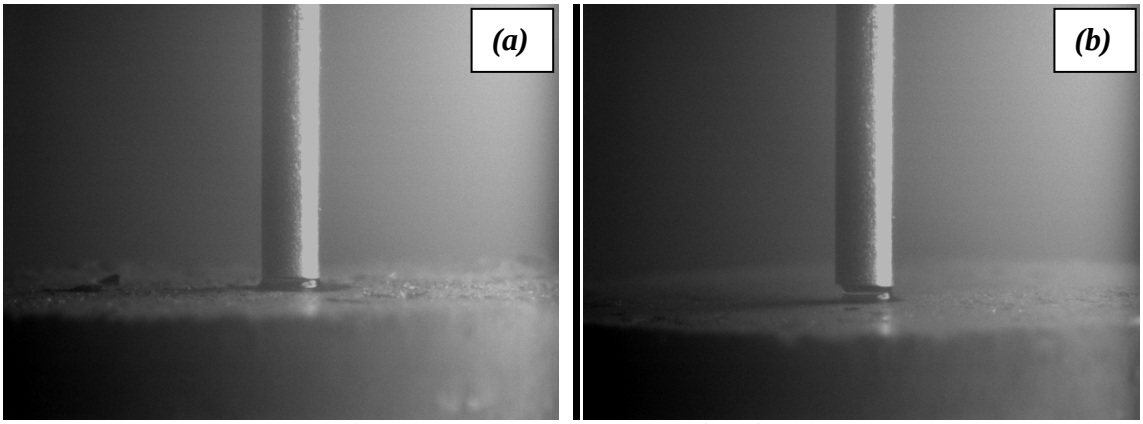

Figure - 6 (a-b) Photograph of measured contact angle on rough surface of lanthanum cobalt oxide (pellet) material.

CONCLUSION

Nanocrystalline La_2ZnO_4 has been successfully synthesized by self combustion route. TG-DTA analysis indicates the phase formation was carried out at 800^0C. The route may be used for the synthesis of other metal oxide. XRD technique was shown the average crystal size of the La_2ZnO_4 nanoparticles ranges from about 45 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 40-50 nm. Wetability of this material obtained from contact angle goniometer. The contact angle θ was zero, which indicates that oxide material was superhydrophilic in nature.

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