Nanocrystalline LaFeO$_3$ Perovskite Oxide Prepared at Lower Temperature with Improved Ethanol Gas Sensoring

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Abstract—Nanocrystalline LaFeO$_3$ perovskite oxide were synthesized by the co-precipitation method. The products were characterized with X-ray spectrometer (XRD), an Scanning Electron Microscope (SEM). The XRD patterns confirmed the formation of perovskite phase. The SEM micrographs indicated that perovskite samples were nanosized particles with morphology of likely high concentration of inter particle porosity. The application as ethanol gas sensor was investigated and found from the lower calcinations temperature the LaFeO$_3$ showed great enhancement of sensitivity toward ethanol giving results that were much better than many sensors ever reported.

Keywords—Perovskite, LaFeO$_3$, Co-Precipitation method and Ethanol gas sensor.

I. INTRODUCTION

ETHANOL gas sensors may find application in many fields such as the control of fermentation processes, safety testing of food packaging, monitoring drunken drivers, etc. Recently, plastic substrate based ethanol sensors have attracted considerable attention, owing to their attractive characteristics including flexibility, lightness, shock resistance, and softness. However, most plastics will deform or melt at temperature of only 100 – 200 °C causing severe limitations on sensor application as many gas sensors are required to operate at high temperature (> 200 °C) [1].

Perovskite-type oxides (ABO$_3$, A= a rare earth cation , B = a transition metal cation) constitute an important class of strategic materials due to their outstanding properties such as electrical, mechanical, optical, magnetic, and catalytic properties, hence these materials find numerous technological uses. These oxides have been used in solid oxide fuel cells (as electrode materials), chemical sensors, oxygen-permeating membranes, thermoelectric devices, and as catalyst for combustion of CO, hydrocarbons, and NO$_x$ decomposition. For these applications, it is important to prepare high-quality and homogeneous powders with controlled stoichiometry and microstructure. In most cases, the presence of secondary phases may reduce the functional properties, so the single-phase materials are preferred [2-4].

Many methods of synthesizing nanostructured materials are available: reverse microemulsion nanoreactor method [5], solid state reaction or thermal decomposition [6-7], sol-gel method [8-9], combustion process [10-11], electrospinning method [12-13], biotemplate method [14], glycine nitrate method [15], nanocasting method [16], citrate method [17], polymerizable complex method [18], and co-precipitation method [19-20]. All methods are standout from the efficiency and scale up perspectives.

These techniques, however, have some disadvantages with the preparation of high specific surface area perovskites. The temperature required to induce the perovskite structure in the conventional ceramic methods is usually high. The high temperature can be lowered slightly in the above mentioned methods due to the finely dispersed oxides in the precursors. Nevertheless, this “low” temperature is still high enough (> 600 °C) to enhance grain growth and, hence, to reduce the specific surface area [3].

The aim of this work is to find a simple route to prepare nano-LaFeO$_3$ through low calcination temperature that yields high purity perovskite phase and study for possible application as ethanol gas sensing material. In the first stage, the precursor for LaFeO$_3$ will be synthesized by co-precipitation from metal nitrate and carbonate salts. The precursor then will be calcined at high temperature (conventional method) and at varied lower temperatures to obtain the desired perovskites LaFeO$_3$. The resulting perovskites obtained from the lower temperature treatment exhibited better performance as ethanol sensor than the ones from high temperature. This route has several advantages such as simplicity, low cost, no waste, and no environmental pollution compared with other routes.

II. EXPERIMENTAL

A. Preparations of LaFeO$_3$ Powders by Conventional Method

LaFeO$_3$ perovskites were prepared based on the co-precipitation method reported previously [21] with some modifications. For LaFeO$_3$

, La(NO$_3$)$_3$$\cdot$$6H_2O$ and Fe(NO$_3$)$_3$$\cdot$9$H_2O$ were used as starting materials. A specific amount of each was dissolved in distilled water to make 1 M solutions. Both solutions (equal volume) were mixed together with vigorous stirring. Then aqueous solution of K$_2$CO$_3$$\cdot$1.5$H_2O$ (2 M) – same volume as one of
and 80 °. The Debye-Scherrer equation was used to calculate the diffractometer. The X-ray diffraction (XRD) was performed using Cu Kα (λ = 0.154 nm) radiation source in a X'Pert MPD, PHILIPS X-ray diffractometer. The diffraction angle (2θ) ranged between 20 ° and 80 °. The Debye-Scherrer equation was used to calculate the average crystallite size (D),

\[
D = \frac{K \lambda}{B \cos \theta}
\]

where D is the average crystallite size, K is a dimensionless shape factor with a value close to unity. The shape factor has a typical value of about 0.89, but varies with the actual shape of the crystallite. λ is the X-ray wavelength, B is the line broadening at half the maximum intensity (FWHM) after subtracting the instrumental line broadening in radians, θ is the Bragg angle.

The specific surface area and pore size distribution of LaMO\textsubscript{3} were determined by nitrogen sorption isotherm using BET method (Coulter, model SA 3100, USA).

D. Sensors Fabrication and Gas Sensing Measurement

The powdered LaFeO\textsubscript{3} was mixed with organic binder (mixture of α-terpineal and ethyl cellulose) to make a paste which was dropped onto the alumina substrate (3×2 mm) - with gold interdigitated electrodes - to form films. The LaMO\textsubscript{3} film was then annealed at 450 °C for 2 h to remove organic content.

In a gas testing chamber, the electrode of the LaMO\textsubscript{3} sensor was connected with the probe on a heating state. Voltage was applied to two Ni-Cr coils and the operating temperature of 350 °C was monitored by thermo couple. For the gas testing, the resistance of the film was measured in air (R\textsubscript{a}) and various concentrations of ethanol gas (50, 100, 200, 300, 500, and 1000 ppm) were continuously flowed into the chamber using a mass flow controller and the gas sensor resistance (R\textsubscript{g}) was measured. The sensitivity of the LaMO\textsubscript{3}-based sensor to ethanol gas was expressed in term of response (R) defined as

\[
R = \frac{R_g}{R_a}
\]

III. RESULTS AND DISCUSSION

A. Preparations by Conventional Method and characterization Of Products

The precursor first obtained was a mixture of La\textsubscript{2}(CO\textsubscript{3})\textsubscript{3} and Fe\textsubscript{2}(CO\textsubscript{3})\textsubscript{3} which later was subjected to calcination. As the temperature rose the carbonates decomposed to the corresponding oxides and subsequently merged to form the corresponding perovskites at higher end of calcination temperature. Phase analyses of all samples were studied by powder X-ray diffraction (Fig 1). The XRD pattern of LaFeO\textsubscript{3} matched with the JCPDS file number 37-1493 of perovskite having orthorhombic structure.

Using the Debye-Scherrer equation and the XRD peak informations yielded the average crystallite sizes of 79 nm. The appearances of all three XRD patterns are sufficiently clean from other unwanted peaks such that they can be considered as high purity perovskites.

![XRD Pattern of LaFeO\textsubscript{3} Powder After Being Calcined At 900 °C for 2h](image)

B. Morphologies of Products

The scanning electron micrographs of the LaFeO\textsubscript{3} sample was shown in Fig.2. The images of LaFeO\textsubscript{3} perovskites exhibit distinct grain growth into large particles having almost-spherical shape for the latter.

![SEM Image of LaFeO\textsubscript{3} Powder After Being Calcined At 900 °C for 2h](image)

The sensitivities of LaFeO\textsubscript{3} film-based sensors were tested against some common gases (CO\textsubscript{2}, SO\textsubscript{2}, H\textsubscript{2}, and EtOH) at 350 °C with the gas concentration range 50 - 1000 ppm. All sensors showed no response to CO\textsubscript{2}, SO\textsubscript{2}, and H\textsubscript{2} gases but exhibited some positive signs with ethanol gas the results of which are shown in Fig.3. The response increased with an increase of ethanol gas concentration. The response exhibited by LaFeO\textsubscript{3} film gas was low (response = 1.3 / 1000 ppm) and immeasurable response (~ 0) with CO\textsubscript{2} gas. Wang and co-worker prepared LaFeO3 and measured with CO\textsubscript{2} gas, their result was also low (1.5 / 1000 ppm) but ethanol gas was not mentioned in their report [4]. In other reports for LaFeO\textsubscript{3} as ethanol sensor, for example, Sathitwitayakul et al. showed that LaFeO\textsubscript{3} prepared from self-propagating high temperature synthesis ( > 1000 °C ) exhibited response toward ethanol.
about 2.6 with 20 ppm ethanol at 550 °C [13], and Chu et al. with the response ~ 10 for 1000 ppm EtOH at 350 °C using LaFeO$_3$ prepared from solid-state reaction [8].

C. Better Products from Lower Calcination Temperatures

C.1. Products Characterization

The desired properties of perovskites believed to exhibit good performance as gas sensors should have high surface area and smaller crystallite sizes compared with those prepared from the conventional method. This is why the lower calcination temperature comes into focus. The high temperature tends to give good crystallinity and larger crystallite sizes which reduces the surface area.

In this part, we attempted to vary the calcination temperatures for the lowest possible temperature to obtain the perovskite structures. The precursors were still prepared by the same method these precursors were then subjected to different calcination temperatures to locate the lowest temperature that each precursor would transform to perovskite phase.

The XRD patterns of LaFeO$_3$ at various temperatures are shown in Fig.4., the product obtained from calcination at 800 °C was indeed LaFeO$_3$ perovskite (matched with JCPDS file no. 37-1493) having orthorhombic structure with particle size of 68 nm. If the calcination temperature was lower than 800 °C, sample powder existed only as mixture of La$_2$O$_3$ and Fe$_2$O$_3$.

C.2. Better Gas Sensors

The efficiencies as gas sensors exhibited by LaFeO$_3$ perovskites prepared at lower calcination temperatures (< 900 °C) to ethanol gas are displayed graphically in Fig.6. The responses to EtOH at 2.26, 7.5, 45.50, 52.60, 56.10, 180, and 259 (units of Re/Ra). The experiment was carried out under the same conditions. Comparing Fig. 3 and Fig. 6, one can see that the efficiencies as gas sensors of LaFeO$_3$ were dramatically increased several folds (199 folds for LaFeO$_3$ at 1000 ppm of EtOH) and varied linearly with increasing ethanol concentrations.
One interesting point is that LaFeO$_3$ prepared by this method showed dramatic enhancement of response compared with that prepared at 900 °C (Fig. 4). In all, the two perovskites prepared at temperature below 900 °C in this work are worth being considered as highly sensitive sensors.

Fig. 6 The Sensor Sensitivity of LaFeO$_3$ Based Sensor From This Work

IV. CONCLUSION

LaFeO$_3$ perovskite samples in powder form were prepared using the co–precipitation method. XRD, and SEM techniques revealed the significant difference in physical properties of the samples. The responses of LaFeO$_3$ to various concentrations of ethanol gas were measured at 350 °C. From the Lower calcinations temperature the LaFeO$_3$ showed great enhancement of sensitivity toward ethanol giving results that were much better than many sensors ever reported.

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