Comparison of Nanocrystalline $LaMO_3$ (M = Co, Al) Perovskite Oxide Prepared by Co-Precipitation Method

Wankassama Haron, Anurat Wisitsoraat, and Sumpun Wongnawa

***Abstract*—Nanostructured perovskites with formula $LaMO_3$ (M = Co, Al) were synthesized by the co-precipitation method and characterized with X-ray Diffraction (XRD), Energy Dispersive X-ray Spectrometry (EDX), X-ray Fluorescence spectrometry (XRF) and Scanning Electron Microscopy (SEM) techniques. The XRD pattern confirmed that all samples are perovskite oxide. Elemental compositions of $LaMO_3$ were investigated by EDX. The EDX pattern of $LaCoO_3$ showed the presence of La, Co, and O while La, Al, O and K (as impurity) were detected in $LaAlO_3$. SEM micrographs indicated that all perovskite samples were nanosized particles having difference morphologies.**

***Index Terms*—Perovskite, $LaCoO_3$, $LaAlO_3$, co-precipitation method.**

I. Introduction

Recent advances in synthesis and manufacturing techniques of nanomaterials have created considerable opportunities for the development of gas sensors. Nanostructured materials are especially attractive in the field of metal oxide gas sensors to improve their sensitivity and response time. The expected improvements are basically due to the higher surface area and smaller crystallite size compared with those offered by conventional microcrystalline materials [1], [2].

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 will suppress the functional properties, so the single-phase materials are preferred [3]-[6].

Among perovskite-type oxides, $LaCoO_3$ and related materials exhibit interesting electrical and electrocatalytic properties. The $LaCoO_3$ perovskite is an effective oxidation monoxide and unburned hydrocarbons. Depending upon the reaction temperature, it could oxidize the CO and ethanol while leaving methane intact since methane is the most stable hydrocarbon and its catalytic combustion usually takes place at high temperatures [4]-[6]. The properties of this material are strongly dependent on the preparation method which affects its numerous applications [5].

Most of the published reports on gas sensing properties of perovskites have been reviewed by Fergus [2]. A variety of perovskite oxides, including titanates , ferrites and cobaltates have been studied as sensors for different gases such as CO, NO_2, CH_4. Among the perovskite-based materials, $LaCoO_3$ has shown good sensitivity in CO detection [3]. Catalytic activity also has been detected in $LaCoO_3$, for example, in the decomposition of NO_x, the combustion of methane and propane, and the oxidation of CO [6]-[8].

Lanthanum aluminate ($LaAlO_3$) was widely used as the substractes of high-temperature superconder and ferroelectric thin film due to their low dielectric loss and minorlattice perameter mismatch between the substrates and film [7]-[9].

The $LaAlO_3$ has attracted a great attention in recent years because of its variety of applications. $LaAlO_3$ with perovskite-type structure has good dielectric characters: high relative permittivity, high quality factor ($Q \times f$ = 68000; Q =1/tan δ; f = measuring frequency and tan δ = dissipation factor), and very small temperature coefficient of resonant frequency. This material can be used for microwave dielectrics, high-frequency capacitors, catalyst or catalyst support, substrate and insulating buffer for high temperature superconducting microwave device, electrolyte or electrode for solid oxide fuel cells, etc [7]-[9].

A lot of work has focused on improving synthesis methods to achieve nanostructured perovskites with high specific surface area (SSA) and low crystallite size. Recently, relatively complex and expensive techniques were used to obtain nanostructured $LaCoO_3$ with low calcination temperatures.

Among a wide variety of techniques capable of synthesizing nanostructured materials, sol–gel, impregnation, and precipitation are the most promising ones from efficiency and scale up perspectives. Although these techniques are excellent for synthesizing nanocrystalline simple oxides or supported catalysts, they have some disadvantages when preparing high SSA perovskites. The precipitate or gel must be heated to enhance solid state diffusion in order to form a perovskite structure [7]-[9].

The aim of this work is to find a simple route to prepare nano-$LaCoO_3$ and $LaAlO_3$ through low calcination temperature but yielding high purity of perovskite phase.

All compounds can be synthesized by co-precipitation from metal nitrate and carbonate salt then calcine the

Manuscript received May 2, 2013; revised November 26, 2013.

Wankassama Haron and Sumpun Wongnawa are with the Department of Chemistry, Faculty of Science, Prince of Songkla University, Hat Yai, Songkhla 90112, Thailand (e-mail: w_asmah@hotmail.com, sumpun.w@psu.ac.th).

Anurat Wisitsoraat is with the Nanoelectronics and MEMS Laboratory, National Electronics and Computer Technology Center (NECTEC), Bangkok12120, Thailand (e-mail: anurat.wisitsoraat@nectec.or.th).

precursor at 900 ℃ for 2 hours. This route is simple and low cost, no waste and no environmental pollution compared with other routes.

The $LaCoO_3$ and $LaAlO_3$ synthesized from this work will be studied in the next stage for other possible applications such as gas sensing material and catalytic activity in certain reactions. The content in this report concentrates on synthesis and characterization of the as-synthesized products. A brief preliminary study results on gas sensing is also given.

II. Experimental

$LaMO_3$ (M = Co, Al) was prepared by the co-precipitation method [7]. For $LaCoO_3$, $La(NO_3)_3{\cdot}6H_2O$ and $Co(NO_3)_2{\cdot}6H_2O$ were used as starting materials. A specific amount of each was dissolved in distilled water to obtain 1 M solution. Both solution were mixed together under vigorous stirring. Then aqueous solution of 2M $K_2\ CO_3{\cdot}1.5H_2O$ and 1 M NaOH were rapidly added. After filtering, the precipitate was washed with distilled water several time until pH =7. The product was then dried at 110˚C for 4 h and calcined at 900˚C for 2 h.

For $LaAlO_3$, $La(NO_3)_3{\cdot}6H_2O$ and $Al(NO_3)_3{\cdot}6H_2O$ were used as starting materials and the same procedure was applied.

The structural characterization was carried out by powder X-ray diffraction (XRD) using Cu/K_α (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.

Microstructure and morphology of the synthesized powders were investigated using scanning electron microscope (SEM). The metal constiuents of $LaMO_3$ (M = Co, Al) perovskite oxide were detected by EDX using ISIS 300, Oxford Energy Dispersive X-ray Spectrometer. The portable X-ray fluorescence (XRF) spectrometer was used to investigate the purity of the products over a wide range. The spectra from the portable XRF was recorded with a multi-chanel analyzer (MCA) set at the energy 25.0 kv.

Fabrication and gas sensing measurement of $LaCoO_3$ and $LaAlO_3$ were carried out as follows. The $LaCoO_3$ film (or $LaAlO_3$) was deposited on alumina substrate (3×2 mm) with gold interdigitated electrodes. The powder of $LaCoO_3$ (or $LaAlO_3$) was mixed with organic binder (mixture of α-terpineal and ethyl cellulose). The paste was dropped onto alumina substrate to form film. The film was then annealed at 450 ℃ for 2 h to remove organic content. In a gas testing chamber, the electrodes of the $LaCoO_3$ and $LaAlO_3$ sensors was connected with the probe on a heating state. Voltage was applied to two Ni-Cr coils and operating temperature of 350 ℃ was monitored by thermo couple. For gas testing, the resistance of the film was measured in air (R_A) then various concentrations of ethanol gas (50, 100, 200, 300, 500, and 1000 ppm) were continuously allowed to flow into the chamber using a mass flow controller and the gas sensor resistance (R_E) was measured. The sensitivity of the $LaCoO_3$ (or $LaAlO_3$) – based sensor to ethanol gas was expressed in term of response defined as $R= R_E / R_A$.

III. Results and Discussion

Fig. 1 shows photographs of the powders of $LaMO_3$ precursor and $LaMO_3$ perovskite oxide. When M = Co the precursor was violet powder which after being calcined at 900˚C for 2h turned to black powder perovskite. For M = Al, both the precursor and the perovskite were off-white powders.

Phase analysis of all samples were studied by powder X-ray diffraction (Fig. 2). The XRD pattern of $LaCoO_3$ is in good agreement with JCPDS file no. 48-0123 and confirms the presence of rhombohedral pure $LaCoO_3$ perovskite oxide phase with average crystallite size about 70 nm. For $LaAlO_3$, the pattern indicates the presence of a small amount of $La(OH)_3$ with the majority of the product as $LaAlO_3$ perovskite phase having hexagonal structure (JCPDS file no 82-0478) with average crystallite size about 75 nm.

Fig. 1. The powder of $LaMO_3$ precursor prepared by the co -precipitation method and $LaMO_3$ perovskite oxide after being calcined at 900˚C for 2 h : A1) $LaCoO_3$ precursor, A2) $LaCoO_3$ perovskite, B1) $LaAlO_3$ precursor, and B2) LaAlO perovskite.

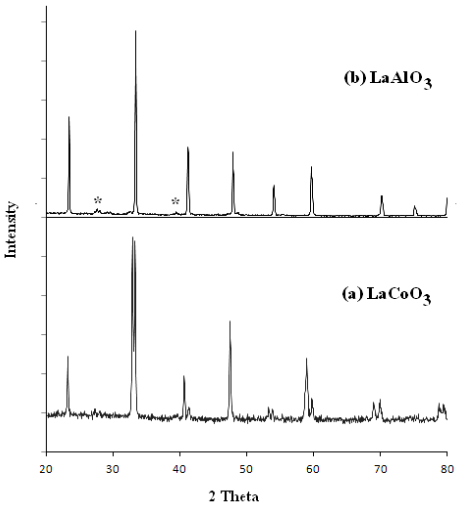

Fig. 2. XRD-pattern of $LaMO_3$ powder after being calcined at 900˚C for 2 h: a) $LaCoO_3$ and b) $LaAlO_3$ (* $La(OH)_3$).

The wide scan inspection by portable XRF analysis for possible contamination by other elements is shown in Fig. 3. The XRF spectra of $LaCoO_3$ show only La (L line) and Co (K line) and only La (L line) for $LaAlO_3$.

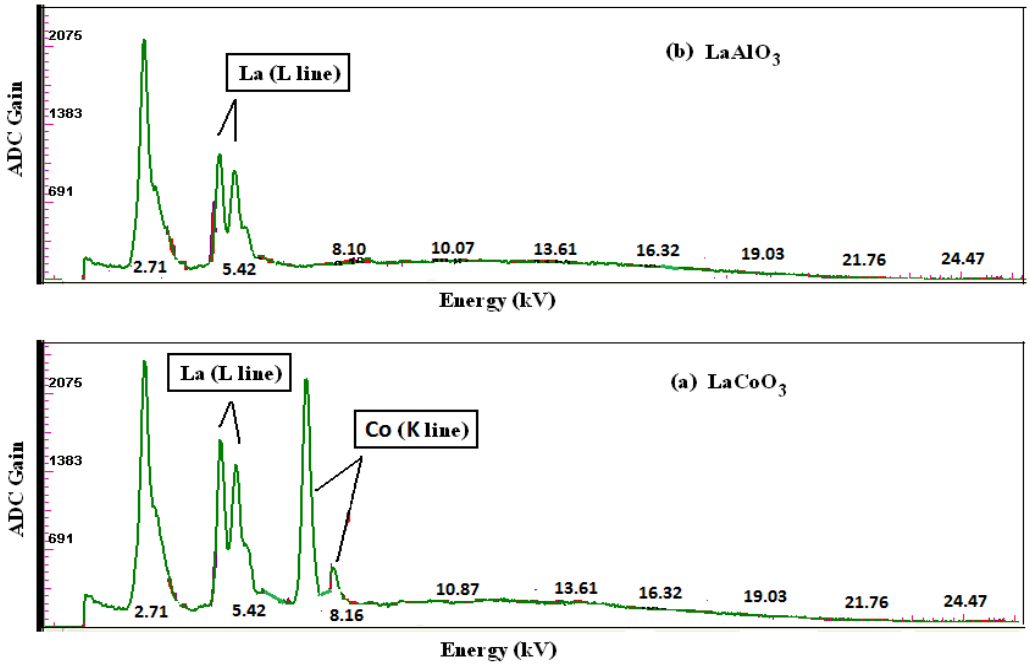

Fig. 3. XRF-spectra of $LaMO_3$ powder after being calcined at 900˚C for 2 h : a) $LaCoO_3$ and b) $LaAlO_3$.

For more details, the EDX which has higher sensitivity was used to confirm the elemental composition of $LaCoO_3$ and $LaAlO_3$ perovskite samples (Fig. 4). The EDX pattern of $LaCoO_3$ shows only three elements La, Co and O while the $LaAlO_3$ pattern shows five elements : La, Al, O, C and K. (The element C arises from glue which was used to fix the sample. $LaAlO_3$ compound had K as impurity but it did not show up in XRD pattern. K may also arise from glue.)

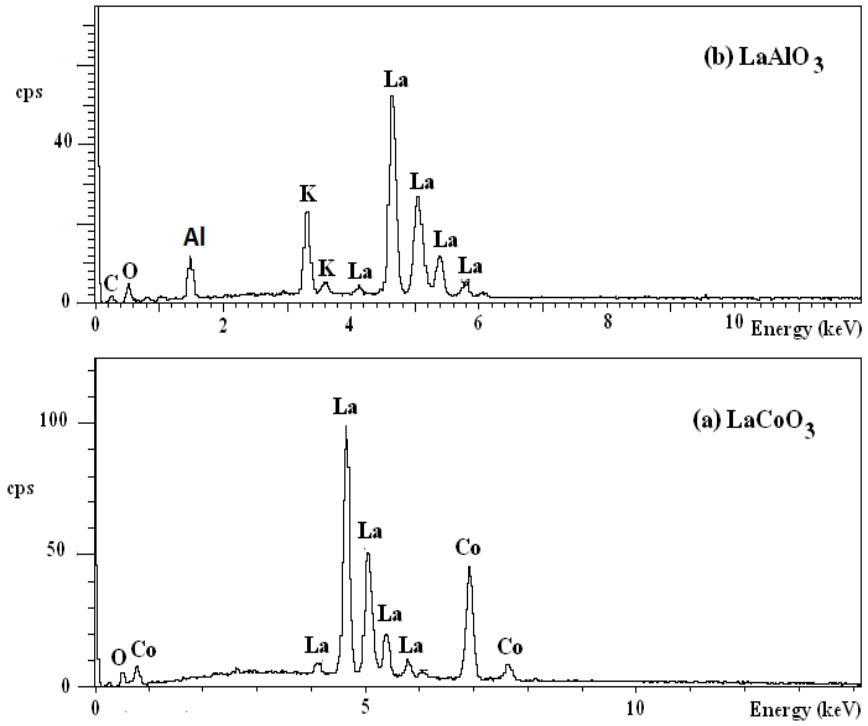

Fig. 4. EDX-patterns of $LaMO_3$ powder after being calcined at 900˚C for 2 h : a) $LaCoO_3$ and b) $LaAlO_3$.

The SEM micrographs of the samples are shown in Fig.5. It can be clearly seen that the particle morphologies of both samples are different. The $LaCoO_3$ perovskite sample is nanosized particles with high concentration of inter-particle porosity while the image of $LaAlO_3$ perovskite sample exhibits distinct grain growth into large particles having cubic shape.

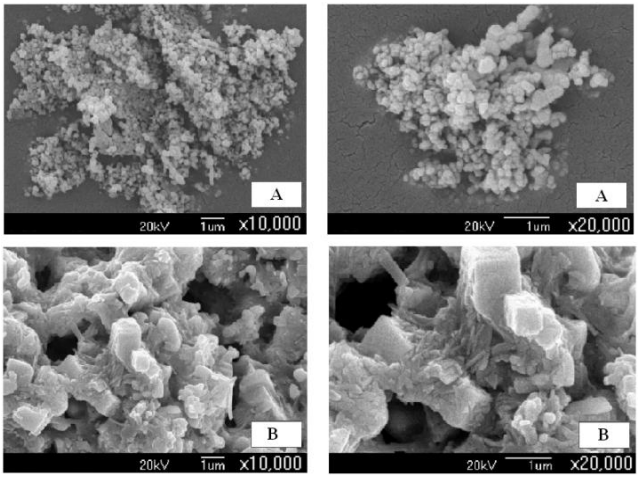

Fig. 5. SEM image of $LaMO_3$ powder after being calcined at 900˚C for 2 h : A) $LaCoO_3$ and B) $LaAlO_3$.

The responses of $LaCoO_3$ and $LaAlO_3$ to various concentration of ethanol gas were determined at 350 ˚C. The sensor responses as a function of concentration are given in Fig. 6. It can be seen that the response of $LaCoO_3$ sensor increased significantly with increasing ethanol concentration while the response of $LaAlO_3$ sensor was very low throughout the range of ethanol concentration. The better performance of $LaCoO_3$ may be due to its grains are smaller than $LaAlO_3$. The $LaCoO_3$ from this work will be further studied for possible application as gas sensing material.

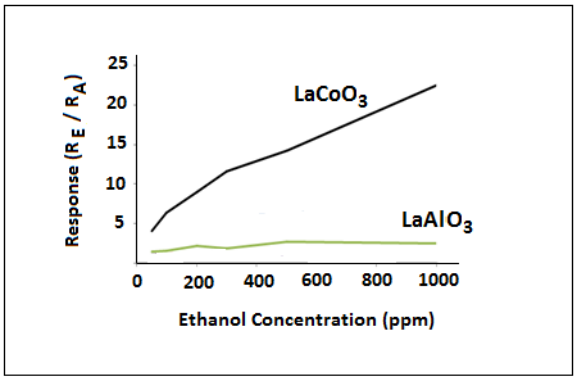

Fig. 6. The effects of ethanol concentration on the sensitivity of $LaCoO_3$ and $LaAlO_3$–based sensor at 350˚C.

IV. Conclusion

$LaMO_3$ (M = Co, Al) perovskite samples in powder form were prepared using the co-precipitation method. X-ray diffraction, EDX, XRF techniques and SEM images revealed the significant differences in physical properties of the samples.

The co-precipitation method gaved the pure phase of $LaCoO_3$ while in the $LaAlO_3$ perovskite oxide small amount of $La(OH)_3$ was detectd as shown in the XRD pattern.

Acknowledgment

The authors wish to acknowledge the Office of the Higher Education Commission of Thailand (OHEC) for financial support of this work.

References

[1] M. Ghasdi and H. Alamdari, "CO sensitive nanocrystalline $LaCoO_3$ perovskite sensor prepared by high energy ball milling," *Sensors and Actuators B: Chemical*, vol. 148, pp. 478-485, 2010.

[2] M. M. Natie, E. Ugel, C. Maccato, and A. Glisenti, "$LaCoO_3$: Effect of synthesis conditions on properties and reactivity," *Applied Catalysis B: Environmental*, vol. 72, pp. 351-362, 2007.

[3] S. Farhadi and S. Sepahvand, "Microwave-assisted solid-state decomposition of $La[Co(CN)_6]$ $5H_2O$ precursor: A simple and fast route for the synthesis of single-phase perovskite-type $LaCoO_3$ nanoparticles," *Journal of Alloys and Compounds*, vol. 489, pp. 586-591, 2010.

[4] J. W. Fergus, "Perovskite oxide for semiconductor – based gas sensor," *Sensor and Actuators B*, vol. 123, pp. 1169-1179, 2007.

[5] S. Ajami, Y. Mortazavi, A. Khodadadi, F. Pourfayaz, and S. Mohajerzadah, "Highly selective sensor to CH_4 in presense of CO and ethanol using LaCoO3 perovskite filter with Pt/SnO_2," *Sensor and Actuators B*, vol. 117, pp. 420-425, 2006.

[6] Z. Tian, W. Huang, and Y. Liang, "Preparation of spherical nanoparticles of $LaAlO_3$ via the reverse microemulsion process," *Ceramics International*, vol. 35, pp. 661-664, 2009.

[7] M. Ghasdi and H. Alamdari, "CO sensitive nanocrystalline $LaCoO_3$ perovskite sensor prepared by high energy ball milling," *Sensor and Actuators B*, vol. 148, pp. 478-485, 2010.

[8] O. Haas, R. P. W. J. Struis, and J. M. McBreen, "Synchrotron X-ray absorption of $LaCoO_3$ perovskite," *Journal of Solid State Chemistry*, vol. 177, pp. 1000-1010, 2004.

[9] H. F. Yu, J. Wang, S. S. Wang, and Y. ManKuo, "Thermochemical behavior of metallic citrate precursors for the production of pure $LaAlO_3$," *Journal of Physics and Chemistry of Solids*, vol. 70, pp. 218-223, 2009.

Wankassama Haron was born in Pattani, Thailand on August 29, 1981. She completed her undergraduate work in Chemistry (B.Sc.Chemistry) from Thaksin University, Songkhla, Thailand, in Political Science (B.P.Sc. Political Science) from Sukhothai Thammathirat Open University, Nonthaburi, Thailand, and Master degree in Inorganic Chemistry (M.S. Chemistry) from Kasetsart University, Bangkok, Thailand. Presently, she is the Ph.D. candidate in Inorganic Chemistry at Prince of Songkla University, Hat Yai, Songkhla, Thailand. She is studying toward the Ph.D. degree under the scholarship from the Office of the Higher Education Commission of Thailand (OHEC).

Anurat Wisitsoraat was born in Bangkok, Thailand. He received B.S. degree in Electrical Engineering from Chulalongkorn University, Bangkok, Thailand, M.S. and Ph.D. in Electrical and Computer Engineering from Vanderbilt University, USA. Presently, he is researcher at Nanoelectronics and MEMS laboratory, National Electronics and Computer Technology Center, Bangkok, Thailand. His research interests are in Fabrication of Micro-Electro-Mechanical System (MEMSs), Gas and pressure sensors, and Microelectronic devices and Integrated circuits.

Sumpun Wongnawa was born in Chanthaburi, Thailand on February 3, 1950. He received B.S. degree in Chemistry from Michigan Technological University, USA, M.S. and Ph.D. in Inorganic Chemistry from Ohio State University, USA. Presently, he is associate professor in Inorganic Chemistry at Department of Chemistry, Faculty of Science, Prince of Songkla University, Hat Yai, Songkhla, Thailand. His research interests are in metal oxides and photocatalysts, complex formation between transition metals and herbal natural products, oxalato complexes of aluminum and transition metals, nano-materials and inorganic chemistry.