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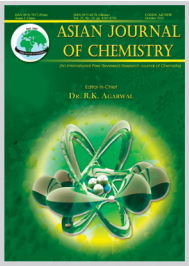

Synthesis and Properties of $La_2Mo_2O_9$ Nano-Powder Prepared *via* Sol-Gel Combustion Route†

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In this study, ultrafine $La_2Mo_2O_9$ powders have been successfully prepared by a novel sol-gel combustion route using a unique combination of citric acid. A range of analyzing techniques including XRD, TG-DSC and BET were employed to characterize the experimental powders. From the result of XRD patterns, we found that well-crystalline cubic structure $La_2Mo_2O_9$ was obtained by calcining the precursor gel at 600 ºC for 2 h. The as-synthesized powders have an average crystallite size of 30 nm.It has also been found that the powders produced by sol-gel combustion method have fine sinterability, it can be sintered close to theoretical density at 950 ºC for 4 h.

Key Words: $La_2Mo_2O_9$, Electrolyte, Sol-gel combustion, SOFC, Synthesis.

INTRODUCTION

The development of new oxide-ion conducting materials is a pressing scientific and technological need as they form the basis of a range of important environmentally friendly applications such as sensors, gas separation membranes and solid oxide fuel cells (SOFCs). This latter example in particular is being intensively studied, as the high efficiency of SOFCs and their ability to act as a bridging technology between hydrocarbon and hydrogen-fuel technologies makes them prime candidates for next generation power production.

To date, oxide materials exhibiting the fluorite or perovskite structures, such as doped ZrO_2, doped CeO_2 and doped $LaGaO_3$, have dominated research in this area[1-3]. Recently, however, a new family of oxides based on $La_2Mo_2O_9$ has been proposed as alternative solid electrolyte materials for intermediate temperature (600-800 ºC) solid oxide fuel cells (IT-SOFCs) due to their excellent oxygen-ion conductivity compared to yttria-stabilized zirconia (YSZ)[4,5].

$La_2Mo_2O_9$ powder has been reported to be synthesized by various wet chemical routes, such as, high-energy ball milling, sol-gel, co-precipitation, hydrothermal, polymeric precursors, freeze-drying, solid-state reaction, spark plasma sintering, ultrasonic assisted spray-pyrolysis process and solution combustion route[4,5]. Among the above-mentioned processes the solution combustion method is characterized by fast reaction rate and low cost. In this paper, we use sol-gel combustion method to synthesize ultrafine $La_2Mo_2O_9$ powders. The synthesis process, the characterization and the sintering properties of this nano-sized $La_2Mo_2O_9$ powder are evaluated.

EXPERIMENTAL

Powdered samples with the general formula of $La_2Mo_2O_9$ were synthesized by the sol-gel combustion method. Analytically pure $La(NO_3)_3{\cdot}6H_2O$ and $(NH_4)Mo_7O_{24}{\cdot}4H_2O$ were used as starting materials. $La(NO_3)_3{\cdot}6H_2O$ and $(NH_4)Mo_7O_{24}{\cdot}4H_2O$ were dissolved in deionized water under continuous stirring at room temperature. Citric acid was subsequently added as a chelating and a reducing agent, with the Mo and La-to-citric acid molar ratio of 1:2. The pH value of the final solution was adjusted to the desired value by adding $NH_3{\cdot}H_2O$ in order to achieve the complete complexation of citric acid with metallic ions without precipitation. A homogeneous sol formed. The sol was heated and stirred at 80 ºC to form the gel complexes. The gel was placed in an oven at 105 ºC for 24 h to dry. Powders were prepared by thermal treatment the dried gel at different temperatures for 2 h. The powders were pressed into pellets of 14 mm in diameter and 1-2 mm in thickness under 200 MPa of pressure using a 5 % poly(vinyl alcohol) (PVA) solution as the binder. Finally, the pellets were sintered at different temperatures in air for 4 h. The densities of the sintered samples were determined using Archimedes method.

The thermal analysis was done using differential scanning calorimetry (DSC) and thermo-gravimetric analysis (TG)

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techniques with a heating rate of 10 ºC/min in air environment to study the different reaction steps and temperatures of the $La_2Mo_2O_9$ precursor gel. The phase identification of the as-synthesized products was recorded by X-ray diffractometer (XRD) with CuK_α radiation (λ = 0.15406 nm).

RESULTS AND DISCUSSION

Auto-combustion behavior of dried gel: Differential thermal analysis (DTA-TG) of the dried gel was performed in order to study the decomposition and crystallization of the precursor. The TG-DSC curves for the $La_2Mo_2O_9$ dried gel is shown in Fig. 1. This feature indicates the occurrence of combustion reaction. The combustion reactions start at around 373 ºC. No weight loss was observed after the combustion reaction when citric acid was used as the fuel. This indicates complete combustion reaction giving a product free of residual reactants and carbonaceous matter. In case of fuel weight loss continues up to 400 ºC. This indicates incomplete combustion of oxidant and fuel. Based on the TG result the powder prepared by combustion route has calcining at 400 ºC.

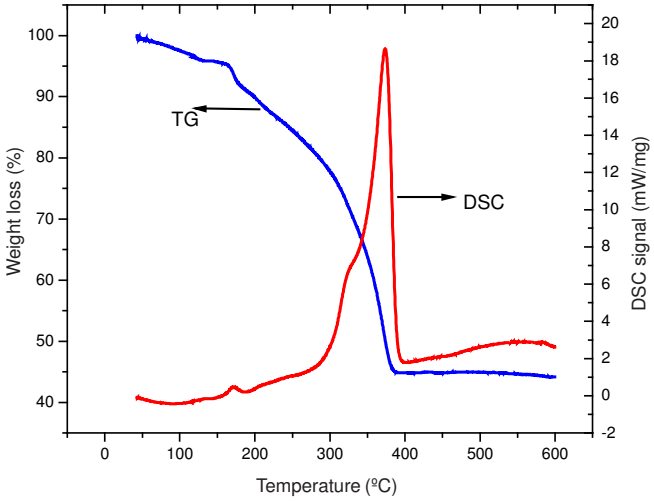

Fig. 1. TG-DSC curves of the dried gel

XRD analysis of samples: The phase development in the sol-gel combustion method has been closely examined by studying the XRD patterns of $La_2Mo_2O_9$ powders at 500 ºC and 600 ºC as illustrated in Fig. 2. The XRD patterns of $La_2Mo_2O_9$ precursor powders have been recorded at different temperatures in order to understand the phase evolution. The precursor powders as dried at 500 ºC for 2 h reveal high background counts without any reflections indicating the amorphous nature of the powder. The pattern of the powders calcined at 600 ºC for 2 h marks the initialization of crystallization and matches with those reported in the International centre for diffraction data (ICDD) database (ICDD No. 28-509), confirming a single phase of cubic-type crystal structure formation.

Specific surface area and sintering character of powders: The specific surface area of the as-synthesized $La_2Mo_2O_9$ powder was determined using N_2 adsorption by means of a Micromeritics ASAP 2000 instrument at 77 K. The samples were out gassed at 150 ºC for 20 h before the analyses. The BET surface area of $La_2Mo_2O_9$ powder was calculated to be

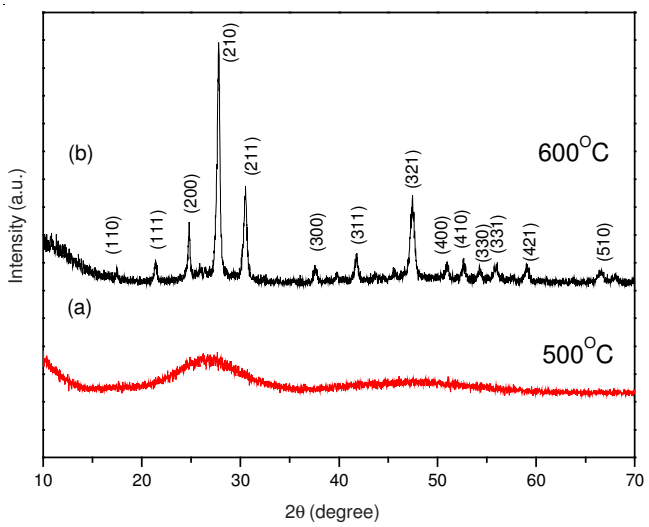

Fig. 2. X-Ray diffraction of the powders

36.23 m^2/g according to the BET method. The average particle sizes (d) of as-synthesized powders were calculated to be 29.8 nm employing the following equation:

$$d = \frac{6000}{\rho s} \quad (1)$$

where ρ is the theoretical density (5.560 g/cm^3) of $La_2Mo_2O_9$ and s is the specific surface area. The calculated results indicate that $La_2Mo_2O_9$ powders with an average particle size about 30 nm can be directly prepared by sol-gel auto-combustion method.

The nano-sized $La_2Mo_2O_9$ powders via the sol-gel combustion method have fine sinterability. Fig. 3 shows the relative densities of the sintered specimens at different temperature. It was seen that the specimens sintered at 950 ºC for 4 h had relative density of 98.6 %, which in fact could assist co-firing of other cell components of SOFCs at low temperatures.

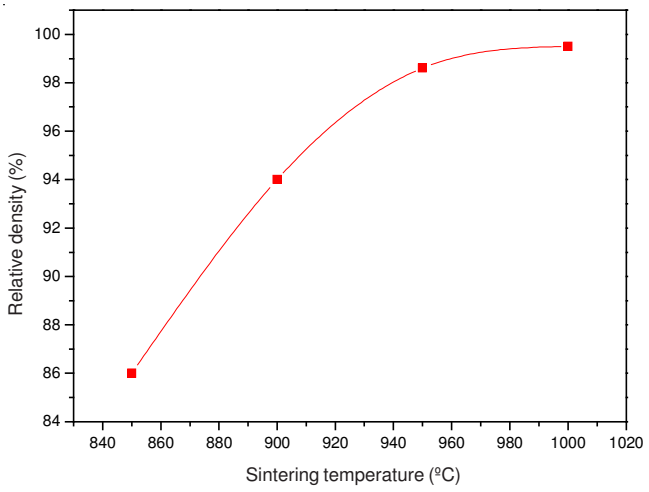

Fig. 3. Effect of sintering temperature on the density

Conclusion

Single phase $La_2Mo_2O_9$ ultrafine powders of cubic-type crystal structure with average size of *ca.* 30 nm can be synthesized by the sol-gel combustion method. More than 98.6 % of

theoretical density was obtained for $La_2Mo_2O_9$ sintering at 950 ºC for 4 h. The sol-gel combustion process is proved to be a simple and effective method in preparing $La_2Mo_2O_9$ for solid electrolyte application.

ACKNOWLEDGEMENTS

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REFERENCES

1. C.M. Lapa, D.P.F. de Souza, F.M.L. Figueiredo and F.M.B. Marques, *Int. J. Hydrogen Energy*, **35**, 2737 (2010).
2. R. Chockalingam, S. Chockalingam and V.R.W. Amarakoon, *J. Power Sources*, **196**, 1808 (2011).
3. G.-B. Jung and T.-J. Huang, *J. Mater. Sci*., **38**, 2461 (2003).
4. S. Georges, R.A. Rocha and E. Djurado, *J. Phys. Chem. C*, **112**, 3194 (2008).
5. L. Malavasi, H. Kim, S.J. Billinge, T. Proffen, C. Tealdi and G. Flor, *J. Am. Chem. Soc*., **129**, 6903 (2007).