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Effect of Heat Treatment on the Phase Formation of $La_{0.6}Sr_{0.4}CoO_{3-\alpha}$

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Abstract**—**Powder of $La_{0.6}Sr_{0.4}CoO_{3-\alpha}$ (LSCO) was synthesized by a combined citrate-EDTA method. The as-synthesized LSCO powder was calcined, respectively at temperatures of 800, 900 and 1000 °C with different heating/cooling rates which are 2, 5, 10 and 15 °C min^{-1}. The effects of heat treatments on the phase formation of perovskite phase of LSCO were investigated by powder X-ray diffraction (XRD). The XRD patterns revealed that the rate of 5 °C min^{-1} is the optimum heating/cooling rate to obtain a single perovskite phase of LSCO with calcination temperature of 800 °C. This result was confirmed by a thermogravimetric analysis (TGA) as it showed a complete decomposition of intermediate compounds to form oxide material was also observed at 800 °C.

Keywords**—**$La_{0.6}Sr_{0.4}CoO_{3-\alpha}$, heat treatment, perovskite-type oxide, XRD.

I. INTRODUCTION

PEROVSKITE-type oxide with general formula of ABO_3 (A is usually a rare earth element, B is a transition metal) such as $La_{0.6}Sr_{0.4}CoO_{3-\alpha}$ (LSCO) is a good mixed electronic and ionic conductor (MIEC). LSCO is deemed to be one of the most promising cathode candidates for intermediate temperature solid oxide fuel cells (IT-SOFCs) since it has shown very low polarization resistance, higher electronic conductivity and good catalytic activity at intermediate temperatures (500-800 °C) [1].

In the field of ceramics, synthesis routes are well known to play an important role on the properties of final materials. LSCO and related $LaCoO_3$-based perovskites powders have been synthesized by numerous methods including solid-state reaction (SSR) methods, mechanical-synthesis, co-precipitation, solution combustion or thermal decomposition, hydro-thermal and Pechini method. Among them, Pechini or modified-Pechini method has received the most attention as it offers low processing temperature with the ability to control the stoichiometry and purity by forming a gel of complex metals precursor. Pyrolysis of the precursor creates a final product with high purity, homogeneous morphology and ultrafine particle size. In this method, chelating agents play an important role in the evolution of crystalline phase and properties of final product. They used to chelate various metal ions to form metal complexes in solution with uniform distribution at atomic level. Citric acid, urea and ethylenediaminetetraacetic acid (EDTA) and a polyalcohol are usually used as chelating agents [2], [3].

Another crucial stage in the preparation of ceramic materials is calcination process. It is also can significantly affect the properties of produced materials, in terms of phase formation, microstructural properties and chemical composition. Traditionally, calcination process usually carried out at relatively high temperatures in order to obtain the desired ceramic materials. This process undeniably increases energy consumption and lead to the loss of some easily evaporated elements. Moreover, uncertainty will be introduced to the elemental composition and undoubtedly may affect the stability and performance of the materials [4], [5]. Investigations often relate the effect of chelating agents [3], [6], [7] and calcination temperatures [8], [9] on the phase formation of perovskite-type oxides materials. However, the role of heating/cooling rate on phase formation of these materials has been less extensively studied. It is common for ceramic microstructure to undergo phase evolution, grain growth and densification during the calcination process. Therefore, the rate of heating/cooling during calcination process should be carefully controlled as it determines the level of in-situ oxidant available to participate in the organic oxidation/decomposition reaction [10].

Within this context, the present work aims to examine the effect of calcination temperatures with different heating/cooling rates on the phase formation of the LSCO perovskite. For this purpose, LSCO was synthesized by a combined citrate-EDTA method. This technique allows the preparation of crystalline materials with excellent control of its stoichiometry and homogeneous composition along with relatively large surface area after thermal treatment.

II. MATERIALS AND METHODS

A. Powder Synthesis

The materials used in the synthesis were $La(NO_3)_3.6H_2O$ (99.999% purity, ACROS), $Sr(NO_3)_2$ (99+% purity, ACROS), $Co(NO_3)_2.6H_2O$ (99+% purity, ACROS), citric acid monohydrate (CA) (99.5% purity, MERCK), EDTA (99%

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purity, ACROS) and ethylene glycol (EG) (99.97% purity, ACROS). CA and EDTA were used as chelating agent to chelate the metal cations to form metal complexes while EG was used as surfactant for the process of polymerization. A summarized route for the synthesis of LSCO ceramic powders by a combined citrate-EDTA method is shown in Fig. 1. To yield 5 g of the final LSCO powder, a stoichiometric amount of the metal nitrates were dissolved in 100 mL deionized water. The metal nitrates solution was stirred and heated in a water bath at 75 °C for an hour. Calculated amounts of CA and EDTA with ratio to overall metal cations content of 1.5:0.5:1 were added into the solution. The initially red color solution turned to transparent red coloration after CA was added and changed to dark violet color solution few minutes later after dissolving EDTA in the solution as shown in Fig. 2. After that, the pH of the solution was adjusted to be 0.5 by adding appropriate amount of ammonia hydroxide solution. Then, EG with ratio to overall metal cation of 3:1 was added to adjust the viscosity of the solution. The solution was continuously heated and stirred for several hours to evaporate the water. The resulting viscous gel was dried at 150 °C for 12 hours and then dried at 250 °C for 5 hours. The as-synthesized powder was calcined at selected temperatures (800, 900 and 1000 °C) with different heating/cooling rates (2, 5, 10 and 15 °C min^{-1}) for 5 hours, to yield black LSCO powder (Fig. 3).

B. Powder Characterization

In order to clarify the influence of heating/cooling rate on the phase formation of calcined LSCO powders, powder X-ray diffraction (XRD) analysis was carried out. Powder XRD patterns were recorded at room temperature on an X-ray diffractometer (XRD 6000 Shimadzu) with Ni-filtered and Cu-K$_\alpha$ radiation source ($\lambda = 0.1540558$ nm) operating at 40 kV and 30 mA using a step scan procedure of 0.02^o s^{-1} for the 2θ range from 20^o to 80^o.

The percentage of perovskite phase present in the calcined samples was calculated by using equation (1) as proposed by Swartz and Shrout.

$$\text{Perovskite phase (wt\%)} = \left[\frac{I_p}{I_p + I_m}\right] \times 100\% \qquad (1)$$

where, I_p and I_m refer to the maximum intensity of the perovskite phase and impurities phase, respectively [11].

Thermal decomposition behavior of the gel precursor dried at 150 °C was studied using thermal analysis (TA) instrument (model SDT Q600) on 16-18 mg of sample with an air flow of 100 mL min^{-1}. The heating/cooling rate was set at 5 °C min^{-1} for temperatures range from 25 °C up to 1000 °C. The weight changes were recorded as a function of temperature.

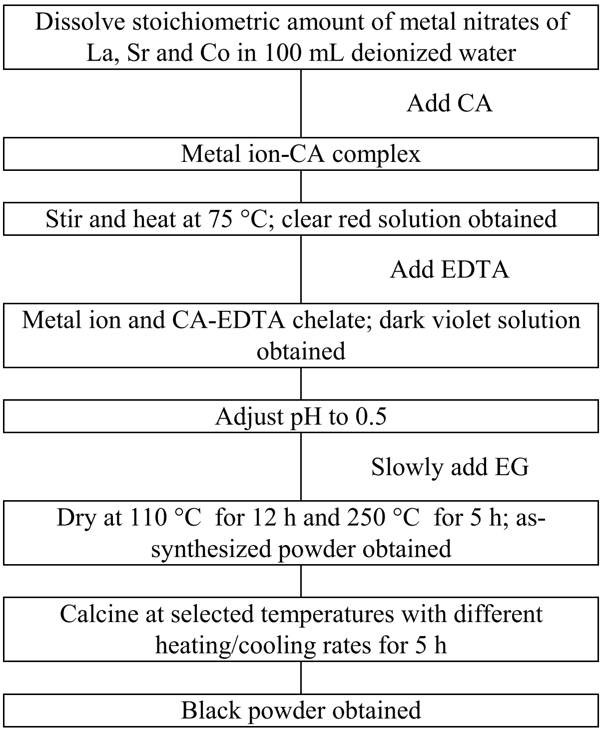

Fig. 1 Steps of LSCO powder synthesis by a combined citrate-EDTA method

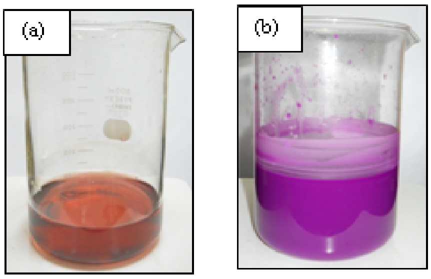

Fig. 2 Photographs of solution color changes during synthesizing process: after CA was added (a) and after EDTA was added (b)

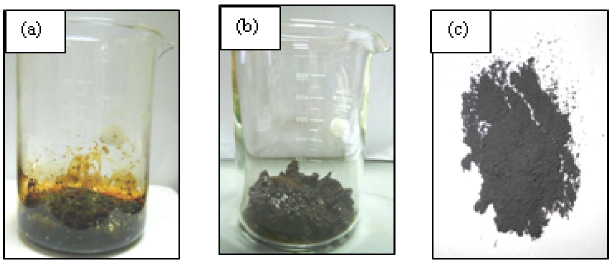

Fig. 3 Photographs of the gel precursor dried at: 110 °C (a); 250 °C (b) and black LSCO powder obtained after calcination process (c)

III. RESULTS AND DISCUSSIONS

A. XRD Analysis

Fig. 4 shows the XRD patterns of LSCO powders calcined at selected temperatures for 5 hours with different heating/cooling rates. The strongest reflections of the XRD patterns that matched with JCPDS file 48-0121 were found in all the spectra which indicate the formation of perovskite phase. However, some additional reflections those correlate to the trace of impurity phases such as cobalt oxide (CoO) (JCPDS file 43-1004), strontium oxide (SrO) (JCPDS file 6-0520) and strontium cobalt oxide ($SrCoO_x$) (JCPDS file 49-0692) are presence in some of the XRD spectrum. The XRD results along with the calculated relative percentages of the perovskite and impurity phases formed are tabulated and summarized in Table I.

TABLE I
SUMMARY OF POWDER XRD PATTERNS ANALYSIS OF LSCO POWDERS AFTER CALCINED AT SELECTED TEMPERATURES WITH VARIOUS HEATING/COOLING RATES

Heating/ cooling rate (°C min^{-1})	Calcination temperature (°C)	Crystalline phases	Amount of each phase (wt%)	
			Perovskite	Impurity
2	800	$La_{0.6}Sr_{0.4}CoO_{3-\alpha}$ $SrCoO_x$, SrO, CoO	67.63	32.37
	900	$La_{0.6}Sr_{0.4}CoO_{3-\alpha}$	100.00	-
	1000	$La_{0.6}Sr_{0.4}CoO_{3-\alpha}$ SrO, CoO	71.86	28.14
5	750	$La_{0.6}Sr_{0.4}CoO_{3-\alpha}$ $SrCoO_x$, CoO	71.34	28.66
	800	$La_{0.6}Sr_{0.4}CoO_{3-\alpha}$	100.00	-
	900	$La_{0.6}Sr_{0.4}CoO_{3-\alpha}$	100.00	-
	1000	$La_{0.6}Sr_{0.4}CoO_{3-\alpha}$ SrO, CoO	72.00	28.00
10	800	$La_{0.6}Sr_{0.4}CoO_{3-\alpha}$ $SrCoO_x$, CoO	91.55	8.45
	900	$La_{0.6}Sr_{0.4}CoO_{3-\alpha}$ $SrCoO_x$, CoO	93.44	6.56
	1000	$La_{0.6}Sr_{0.4}CoO_{3-\alpha}$	100.00	-
15	800	$La_{0.6}Sr_{0.4}CoO_{3-\alpha}$ $SrCoO_x$, SrO, CoO	65.70	34.30
	900	$La_{0.6}Sr_{0.4}CoO_{3-\alpha}$ SrO, CoO	70.67	29.33
	1000	$La_{0.6}Sr_{0.4}CoO_{3-\alpha}$ SrO, CoO	71.57	28.43

Intensity of the peaks in all XRD spectra is increased as the calcination temperatures increase. However, this trend is not observed for the XRD patterns in Fig. 4(a) with heating/cooling rate of 2 °C min^{-1}. The intensity of the peaks dramatically decreases as the calcination temperatures increased from 800 °C to 900 °C. This might due to distort of perovskite lattice structure in the presence of large oxygen vacancy [12]. Besides that, an increase of calcination time is also brings to decrease of the intensity of the peaks, which is an evidence of product amorphization or the beginning of perovskite decomposition [13]. Another reason is might due to the partial substitution of La by Sr in the LSCO system [14] as we observed that $SrCoO_x$ disappeared after LSCO was calcined at temperature of 1000 °C. The optimum calcination temperature to obtain a single phase perovskite of LSCO at heating/cooling rate of 2 °C min^{-1} is found at 900 °C.

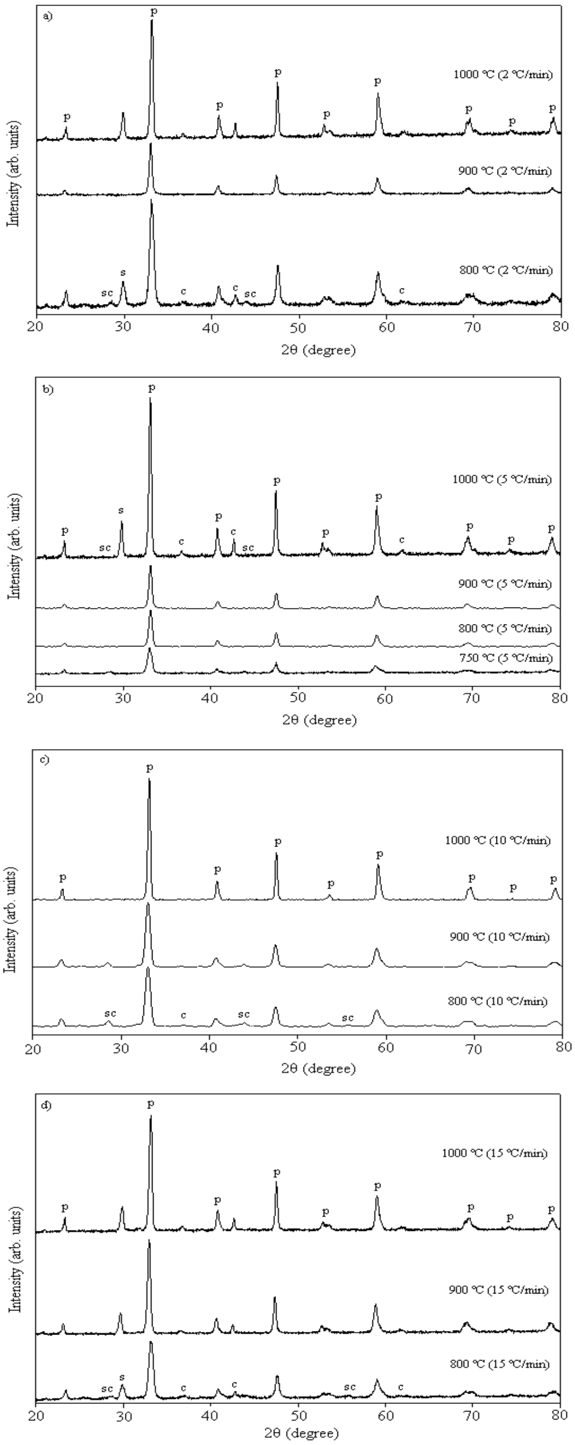

Fig. 4 Powder XRD patterns of LSCO powders calcined at selected temperatures with heating/cooling rate of: 2 °C/min (a); 5 °C/min (b); 10 °C/min (c) and 15 °C/min (d)
(p = perovskite, c = CoO, s = SrO, sc = $SrCoO_x$)

Based on the XRD patterns show in Fig. 4(b), it is found that the calcination temperatures of 800 °C and 900 °C are the optimum temperatures for the formation of a single perovskite phase of LSCO with heating/cooling rate of 5 °C min^{-1}. An amount of impurity phases such as CoO, SrO and $SrCoO_x$ appeared after calcination temperatures increased to 1000 °C. This indicates the decomposition of LSCO perovskite phase as the powder was calcined beyond the optimum condition [5].

The perovskite formation of the calcined LSCO powders with heating/cooling rate of 10 °C min^{-1} was started at calcination temperature of 800 °C and completed at 1000 °C as observed by XRD patterns in Fig. 4(c). Fig. 4(d) depicts there is no complete formation of calcined LSCO powders at heating/cooling rate of 15 °C min^{-1}. The XRD patterns show weak crystallinity of the LSCO perovskite phase formed since the traces of impurity phase appear for all the samples. However, the amount of calculated percentages of perovskite phase formed was increased when the calcination temperatures increase at this heating/cooling rate. This is due to the disappearance of $SrCoO_x$ impurity phases for the LSCO powders calcined at temperatures of 900 °C and 1000 °C. The powders should be calcined at temperature above 1000 °C as suggested by Tao *et al.* [4] and Bansal *et al.* [7] in order to obtain a single perovskite phase of LSCO.

By comparing the XRD data obtained, it is obvious that the formation of a single perovskite phase of LSCO is favoured by heating/cooling rates as shown in Fig. 5. At low heating/cooling rates, 2 °C min^{-1} and 5 °C min^{-1}, the formation of a single perovskite LSCO is desirably at relatively low temperature which is at 800 °C and 900 °C, respectively. It is because the slowest heating/cooling rate offers sufficient energy and longer time for samples to react during heating up period at optimum calcination temperatures [15]. However, when the calcination temperature increases over the optimum condition, the perovskite phase is easily decomposes. At high heating/cooling rates, 10 °C min^{-1} and 15 °C min^{-1}, the formation of a single perovskite LSCO requires relatively high calcination temperature which is at 1000 °C or possibly above 1000 °C. The high heating/cooling rates allow direct nucleation of the impurity phase from the amorphous powder which retards the formation of a single perovskite phase at low calcination temperatures [16]. Therefore, high calcination temperatures are needed to eliminate the impurity phase formed as a consequence of transitory non-equilibrium state in the beginning of the reaction until the complete formation of a single perovskite LSCO. Additionally, insufficient energy and short time for the samples to react during the heating up period at high heating/cooling rates are also bring to incomplete calcination process to obtain single perovskite phase at low calcination temperatures [17].

B. TGA Analysis

Thermogravimetric Analysis (TGA) was carried out in order to study thermal decomposition of the as-synthesized LSCO precursor heated at 150 °C using optimum heating/cooling rate of 5 °C min^{-1}. The TGA signal was registered from 25 °C to 1000 °C and three weight loss steps are observed in the TG curve between 25-150 °C, 150-550 °C and 550-800 °C as shown in Fig. 6.

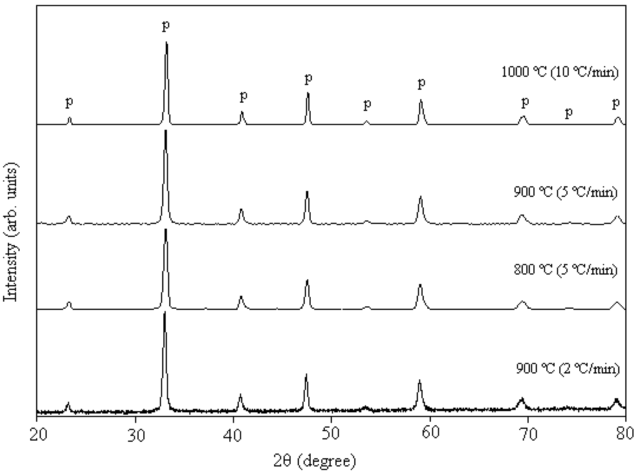

Fig. 5 Powder XRD patterns of a single perovskite phase of calcined LSCO powders obtained at different calcination temperatures with different heating/cooling rates

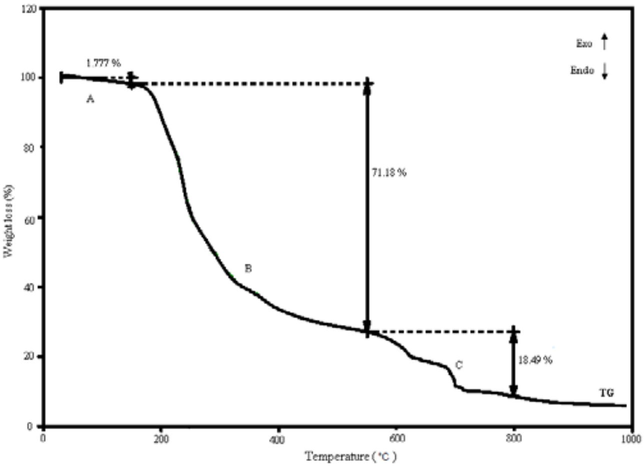

Fig. 6 TG curve of the as-synthesized LSCO precursor heated at 150 °C

At the first temperature region up to 150 °C (A), a small weight loss of about 1.8% is attributed to the dehydration process of adsorbed moisture, traces of structural hydroxide in the powder and decomposition of of nitrates. Since the boiling point of water is 100 °C, all moisture was decomposed at this stage. The large decrease in weight (71.18%) observed at temperature region of 150 °C until 550 °C (B) is corresponding to the oxidation and combustion of metal-chelate complex. The combustion of metal complexes results into the releasing of H_2O, CO_2 and NO_x gaseous as the chelating agents used are sources of carbon, hydrogen and nitrogen. This result is also in agreement with the work done by Doorn *et al.* [6]. They found that the exothermic heats are attributed to the burnout of carbon and nitrogen for the sample $La_{0.3}Sr_{0.7}CoO_{3-\alpha}$. Fey *et al.* [18] also reported that the exothermicity of the combustion processes triggered the calcination of the oxide product. The thermal transformation was about to complete in the final stage at 550 °C to 800 °C with the reduction of weight loss of about 18.49%. This is related to the decomposition of carbonaceous residue and the beginning of crystallization as well as the structural transformation to form oxides. From 800-1000 °C, TG curve showed very little weight loss was observed which indicates that the possibility perovskite phase is formed. This result is in line with the XRD results discussed before that revealed a single perovskite phase of LSCO obtained at calcination temperature of 800 °C with heating/cooling rate of 5 °C min^{-1}.

IV. CONCLUSION

The optimum heating/cooling rate to obtain a single perovskite phase of LSCO is found at 5 °C min^{-1} with calcination temperature of 800 °C. This result is consistent with the TGA signal which indicates a complete decomposition of intermediate compounds was also observed at 800 °C using 5 °C min^{-1} heating/cooling rates. The formation of a single perovskite phase of LSCO at high rates (10 °C min^{-1} and 15 °C min^{-1}) requires relatively high calcination temperatures and the optimum temperature is 1000 °C at heating/cooling rate of 10 °C min^{-1}. Even though the impurity phases are always formed at the beginning of the process, but they transform into a single perovskite LSCO quickly at low heating/cooling rates as compared to high heating/cooling rates. Further work on the chemical compatibility of this material co-sintering with cerate-zirconate electrolyte to be used as cathode and electrolyte materials, respectively for IT-SOFCs has been extensively investigated and the progress will be reported elsewhere.

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REFERENCES

[1] A. V. Berenov, A. Atkinson, J. A. Kilner, E. Bucher, and W. Sitte. "Oxygen tracer diffusion and surface exchange kinetics in $La_{0.6}Sr_{0.4}CoO_{3-\alpha}$." *Solid State Ionics 181*, 2010: 819-826.

[2] J. Shao, Y. Tao, J. Wang, C. Xu, and W. G. Wang. "Investigation of percursors in the preparation of nanostructured $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\alpha}$ via a modified combined complexing method." *Journal of Alloys and Compounds 484*, 2009: 263-267.

[3] Y. Tao, J. Shao, J. Wang, and W. G. Wang. "Synthesis and properties of $La_{0.6}Sr_{0.4}CoO_{3-\alpha}$ nanopowder." *Journal of Power Sources 185*, 2008: 609-614.

[4] R. Ran, Y. Guo, D. Gao, S. Liu, and Z. Shao. "Effect of foreign oxides on the phase structure, sintering and transport properties of $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\alpha}$ as ceramic membranes for oxygen separation." *Separation and Purification Technology 81*, 2011: 384-391.

[5] I. Kashif, A. Abdelghany, and R. El-said. "Effect of sintering and milling time on lead magnesium niobate nanocrystallite phase." *Materials Chemistry and Physics 115*, 2009: 309-312.

[6] R. H. E. van Doorn, H. Kruidhof, A. Nijmeijer, L. Winnubst, and A. J. Gurggraaf. "Preparation of $La_{0.3}Sr_{0.7}CoO_{3-\alpha}$ perovskite by thermal decomposition of metal-EDTA complexes." *J. Mater. Chem 8(9)*, 1998: 2109-2112.

[7] N. P. Bansal, and Z. Zhong. "Combustion synthesis of $Sm_{0.5}Sr_{0.5}CoO_{3-\alpha}$ and $La_{0.6}Sr_{0.4}CoO_{3-\alpha}$ nanopowders for solid oxide fuel cell cathodes." *Journal of Power Sources 158*, 2006: 148-153.

[8] K. Rida, A. Benabbas, F. Bouremmad, M. A. Pena, E. Sastre, and A. Martinez-Arias. "Effect of calcination temperature on the structural characteristics and catalytic activity for propene combustion of sol-gel derived lanthanum chromite perovskite." *Applied Catalysis A: General 327*, 2007: 173-179.

[9] K. Rida, M. A. Pena, E. Sastre, and A. Martinez-Arias. "Effect of calcination temperature on structural properties and catalytic activity in oxidation reactions of $LaNiO_3$ perovskite prepared by Pechini method." *Journal of Rare Earths, Vol. 30, No. 3*, 2012: 210-216.

[10] H. W. Wang, D. A. Hall, and F. R. Sale. "A thermoanalytical study of the metal nitrate-EDTA precursors for lead zirconate titanate ceramic powders." *Journal of Thermal Analysis, Vol. 41*, 1994: 605-620.

[11] Wongmaneerung, R., R. Yimnirun, and S. Ananta. "Effect of two-stage sintering on phase formation, microstructure and dielectric properties of perovskite PMN ceramics derived from a corundum Mg4Nb2O9 precursor." *Materials Chemistry and Physics 114*, 2009: 569-575.

[12] Z. H. Yang, and Y. S. Lin. "Synergetic thermal effects for oxygen sorption and order-disorder transition on perovskite-type oxides." *Solid State Ionics 176*, 2005: 89-96.

[13] E. Avvakumov, M. Senna, and N. Kosova. "Chapter 6: Mechanochemical Synthesis of Double Oxides."

[14] R. Pereniguez, J. L. Hueso, F. Gaillard, J. P. Holgado, and A. Caballero. "Study of oxygen reactivity in $La_{1-x}Sr_xCoO_{3-\alpha}$ perovskites for total oxidation of toluene." *Catal Lett 142*, 2012: 408-416.

[15] P. Bomlai, N. Sirikulrat, and T. Tunkasiri. "Effect of heating rate on the properties of Sb and Mn-doped barium strontium titanate PTCR ceramics." *Materials Letters 59*, 2005: 118-122.

[16] P. Duran, F. Capel, J. Tartaj, D. Gutierrez, and C. Moure. "Heating-rate effect on the $BaTiO_3$ formation by thermal decomposition of metal citrate polymeric precursors." *Solid State Ionics 141-142*, 2001: 529-539.

[17] Yi-Cheng. "Effect of heating rate on properties of $Pb(Mg_{1/3}Nb_{2/3})O_3$ ceramics produced by the reaction-sintering process." *Materials Letters 58*, 2004: 944-947.

[18] G.T.K.Fey, J. G. Chen., Z. F. Wang, H. Z. Yang, and T. P. Kumar. "Saturated linear dicarboxylic acid as chelating agents for the sol-gel synthesis of $LiNi_{0.8}Co_{0.2}O_2$." *Materials Chemistry and Physics. 87*, 2004: 246-255.