

# Low-temperature chemical synthesis of lanthanum copper oxide

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Lanthanum copper oxide ( $\text{La}_2\text{CuO}_4$ ) precursors for superconductors were synthesized by acetate/nitrate self-propagating combustion synthesis (SPCS) in the presence of urea at different ratio of O/F. Phase-pure  $\text{La}_2\text{CuO}_4$  powder could be obtained by calcining the as-prepared precursors at temperature as low as  $600^\circ\text{C}$ . It was demonstrated that the ratio of O/F strongly influenced the composition and morphology of the precursors as well as the samples calcined at various temperatures. We have studied the synthesis conditions, demonstrating the existence of a relationship between the calcination temperature and the calcination time needed to obtain the pure phase. An interesting stereoscopic network structure was observed on the samples synthesized at the ratio of  $\text{O/F} = 0.20$ , morphology evolution of the samples was also investigated. The emission of  $\text{H}_2\text{O}$  as well as  $\text{CO}_2$  was responsible for the formation of the structure during the calcination process.

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## 1. Introduction

Since the discovery of high- $T_c$  superconductors in cuprate systems,  $\text{La}_2\text{CuO}_4$  and related compounds with  $\text{K}_2\text{NiF}_4$  structure appear as model materials for studying superconductivity phenomena because of their simple formulation and structure, a great number of studies have been performed in order to understand their properties. For this purpose, it is necessary to have high-quality samples in order to obtain reliable results. Moreover, recent studies [1, 2] on  $\text{La}_2\text{CuO}_4/\text{ZnO}$  *p-n* heterocontacts revealed that it could be used as humidity sensor with outstanding properties, such as a response of 4 orders of magnitude in the whole relative tested humidity (RH) range, and a fast response time. The preparation of  $\text{Ln}_2\text{MO}_4$  ( $\text{Ln} = \text{rare earth}$ ,  $\text{M} = \text{Co}$ ,  $\text{Ni}$ ,  $\text{Cu}$ ) with  $\text{K}_2\text{NiF}_4$  structure is usually carried out using the conventional synthesis method [3] which requires several cycles of heating and grinding treatments to obtain the desired product. Such a method is a batch process, time consuming and results in mixed phases. Other chemical methods used include decomposition of nitrates [4], homogeneous precipitation of oxalates [5], etc. Synthesis of  $\text{La}_2\text{CuO}_4$  was also studied [6] by the combustion synthesis method. The desired phase was obtained by rapidly heating a saturated aqueous solution containing stoichiometric amounts of corresponding metal nitrates (oxidizer) and MH ( $\text{C}_2\text{H}_4\text{N}_2\text{O}_2$ , fuel) at  $350^\circ\text{C}$  in a muffle furnace. The product of the combustion process was amorphous phase, which needs further calcination.

Recently, a sol-gel method or self-propagating combustion synthesis in the presence of urea has received

increasing attention in the synthesis of multicomponent oxides, such as  $\text{La}_2\text{CuO}_4$  [7],  $\text{Gd}_2\text{CuO}_4$  [8], and  $\text{LaAlO}_3$  [9]. With this method, the desired phases could be obtained at relatively low temperatures. However, all water-soluble metal salts used in these experiments were nitrates. As a result, the gel obtained from the initial solutions containing metal salts and urea combusted at high temperature with rapid emission of gases in a very short time. The disadvantages of very high combustion temperature and rapid emission of gases make it almost impossible to control the combustion process because nitrate and urea are strong oxidizer and reducer, respectively. In order to make the combustion process easy to control, soluble lanthanum acetate was used in the synthesis of  $\text{La}_2\text{CuO}_4$ . The partial substitution of acetate for nitrate can also decrease the amount of urea used due to the fact that acetate is neither oxidizer nor reducer.

In this paper, the preparation of  $\text{La}_2\text{CuO}_4$  powders from the starting lanthanum acetate and copper nitrate water-soluble salts, via sol-gel process with  $\text{CH}_4\text{N}_2\text{O}$  decomposition, is described as a promising technique for powder synthesis. The decomposition of  $\text{CH}_4\text{N}_2\text{O}$  in aqueous solutions is accompanied by the slow and controlled supply of ammonia and carbon dioxide into the solution [10]. The smooth increase of pH obtained by the steady supply of  $\text{OH}^-$  and  $\text{CO}_3^{2-}$  ions, typically lead to the precipitation of metal hydroxycarbonates with controlled particle morphology [11–13].

The substitution of lanthanum acetate for lanthanum nitrate provided an advantage of lower combustion

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temperature and less amount of urea used in the combustion process. Medium combustion temperature through adjusting the ratio of O/F makes it possible to synthesize pure-phase  $\text{Ln}_2\text{MO}_4$  ( $\text{Ln}$  = rare earth,  $\text{M}$  = Co, Ni, Cu) with  $\text{K}_2\text{NiF}_4$  structure at low temperature and on a large scale. An interesting stereoscopic network structure, which is useful in porous materials, was observed on the samples synthesized by acetate/nitrate SPCS process at the ratio of  $\text{O/F} = 0.20$ .

## 2. Experimental procedure

### 2.1. The synthesis of precursor

The lanthanum source was lanthanum acetate ( $\text{La}(\text{CH}_3\text{COO})_3$ ). It was prepared by a reaction of acetic acid solution and lanthanum oxide ( $\text{La}_2\text{O}_3$ , purity 99.99%) pre-calcined for 2 h in air at  $1000^\circ\text{C}$ . The reaction was made in a 400-ml-capacity glass beaker with continuous magnetic stirring. The final 200 ml of lanthanum stock solution containing 0.12 mol lanthanum acetate was clear and colorless. Copper nitrate ( $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ , purity 99.5%) of 0.06 mol was added into the lanthanum stock solution, followed by the dissolution of reagent-grade urea of 0.50 mol in the solution. The final lanthanum and copper stock solution was blue.

According to the concepts used in propellant chemistry [14], the elements of C, H, Cu are considered as reducing elements with the corresponding valences of +4, +1, +2, respectively. The element oxygen is considered as an oxidizing element with the valence  $-2$ . The valence of nitrogen is considered to be zero. Accordingly, the oxidizing and reducing valences of the compounds used in the combustion mixtures can be calculated. In the present work, copper nitrate,  $\text{Cu}(\text{NO}_3)_2$ , and urea were used as oxidizer and fuel, respectively. The total reducing and oxidizing valences of the fuel (F) and oxidizer (O) serve as numerical coefficients for stoichiometric balance so that the equivalence ratio ( $\Phi_e$ ) is unity, i.e.,  $\text{O/F} = 1$ , and the energy released is at a maximum [14]. In order to lower the combustion temperature, excessive fuel was used in the reaction in which the ratio of  $\text{O/F}$  was 0.20. In order to study the influence of the ratio of  $\text{O/F}$  on the composition and morphology of the precursors and the samples calcined at various temperatures, less fuel was also used at the ratio of  $\text{O/F} = 0.83$ .

The glass beaker containing the solution was placed in a drying oven kept at  $120^\circ\text{C}$  in order to evaporate the water of the solution. The solution was concentrated with the evaporation of water accompanied by the slow decomposition of urea to ammonia and carbon dioxide. At the end of the evaporation, the solution became turbid and viscous. The glass beaker containing viscous liquid was taken out and then placed rapidly in a muffle furnace kept at  $500^\circ\text{C}$ . Initially, the mixture undergoes dehydration followed by decomposition, with swelling and frothing, resulting in foam that ruptures with a flame. The entire combustion process was complete in less than 10 min. The product of combustion was a voluminous, foamy, and amorphous precursor.

### 2.2. The preparation of $\text{La}_2\text{CuO}_4$ powder

The  $\text{La}_2\text{CuO}_4$  powder was prepared by calcining the ground precursor powder in air. The furnace temperature increased to various pre-set temperatures in the range of  $550$ – $1000^\circ\text{C}$  at a heating rate of  $10^\circ\text{C}/\text{min}$  and kept for 2–18 h, followed by cooling in air, to yield the crystalline- and pure-  $\text{La}_2\text{CuO}_4$ .

### 2.3. Powder sample characterization

Powder X-ray diffraction (XRD) patterns were obtained for the precursor powders, as well as for the samples calcined at  $550$ – $1000^\circ\text{C}$ . A diffractometer (Model D/MAX-RA, Rigaku Co., Tokyo, Japan.) was used with monochromatic  $\text{Cu K}\alpha$  radiation at the step size of  $0.02^\circ$  for phase-characterization purposes. Prior to XRD examination, the samples were slightly ground in an agate mortar.

Particle-size and morphology characteristics of the samples were assessed from scanning electron microscopy (SEM) (Model JSM6301, JEOL, Tokyo, Japan.) and transmission electron microscopy (TEM) (Model EM-420, Phillips, Holland). Prior to SEM examination, the powder samples were sputter-coated with a layer of gold.

## 3. Results and discussion

### 3.1. The crystallization of $\text{La}_2\text{CuO}_4$ obtained from the precursors synthesized at the ratio of $\text{O/F} = 0.20$ via XRD

The product of combustion was a voluminous and foamy amorphous precursor. This foamy precursor could be easily ground in an agate mortar to fine dark green powders. The calcination and phase-evolution characteristics of these precursor powders were studied under isothermal calcination ( $600^\circ\text{C}$ ) in air at various calcination times by powder X-ray diffraction.

Fig. 1 displays the time dependence of the  $\text{La}_2\text{CuO}_4$  phase formation for samples calcined at  $600^\circ\text{C}$ . The

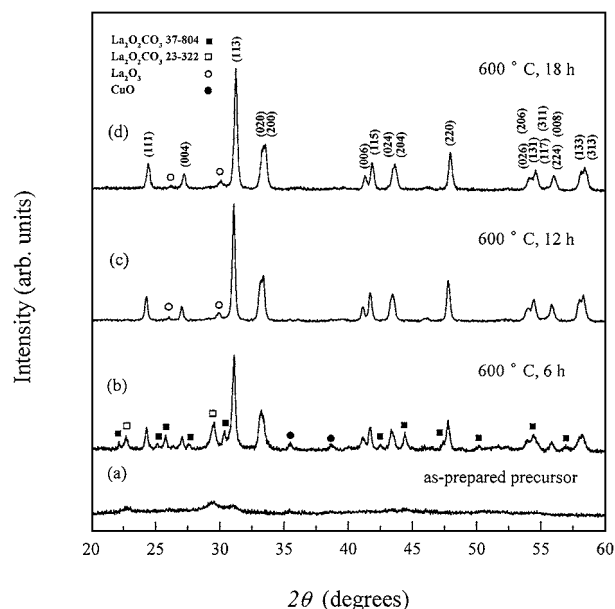
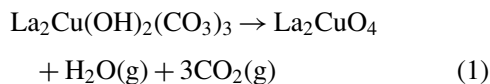


Figure 1 X-ray diffraction patterns of the precursor powders synthesized by acetate/nitrate SPCS process at the ratio of  $\text{O/F} = 0.20$ , followed by calcining at  $600^\circ\text{C}$  for different times. The indexed peaks correspond to  $\text{La}_2\text{CuO}_4$  phase.

diffraction pattern for the precursor shows no exact evidence of Bragg peaks, as shown in Fig. 1a, which is typical of a non-crystalline solid. This result was confirmed by electron diffraction, which showed the non-crystalline solid. Because our energy dispersive spectroscopy (EDS) analysis showed the presence of lanthanum and copper in the precursors, the as-prepared precursor may supposedly belong to  $\text{La}_2\text{Cu}(\text{OH})_2(\text{CO}_3)_3$ , whose weight loss is 27% after calcination at 900 °C for 6 h. This weight loss is very close to that of 26% in the precursor synthesized by acetate/nitrate SPCS process at the ratio of O/F = 0.20, according to the following reaction.



Although somehow premature at this stage, without having the quantitative chemical analysis data of the precursors, assuming that the samples have a stoichiometry and structure resembling  $\text{La}_2\text{Cu}(\text{OH})_2(\text{CO}_3)_3$  seems to be, at least logical.

In Fig. 1b, the X-ray diffraction pattern of the precursor calcined at 600 °C for 6 h revealed the presence of  $\text{La}_2\text{CuO}_4$ , CuO and a lanthanum oxide carbonate. The lanthanum oxide carbonate was identified as  $\text{La}_2\text{O}_2\text{CO}_3$  (JCPDS Powder Diffraction File card 23-322 and 37-804). The reflections associated with the lanthanum oxide carbonate disappear in the powder calcined at 600 °C for 12 h. However, low-intensity reflection peaks associated with  $\text{La}_2\text{O}_3$  remained, as shown in Fig. 1c. With prolonged calcination time of 18 h, the reflection peaks of  $\text{La}_2\text{O}_3$  were still detectable, as shown in Fig. 1d. The presence of  $\text{La}_2\text{O}_3$  after calcination of 18 h is probably because of the formation of it during the combustion process. Once  $\text{La}_2\text{O}_3$  phase forms, higher calcination temperatures are needed to obtain phase-pure  $\text{La}_2\text{CuO}_4$  phases.

The crystallization behavior of  $\text{La}_2\text{CuO}_4$  obtained from the precursors at the ratio of O/F = 0.20 is given in Fig. 2. The crystallization of  $\text{La}_2\text{CuO}_4$  was noted to begin at temperature as low as 600 °C. The peaks of  $\text{La}_2\text{O}_2\text{CO}_3$  (JCPDS Powder Diffraction File card 37-804) were detected after the precursor was calcined at 700 °C for 6 h. It may result from low combustion temperature at low ratio of O/F. Fig. 2 shows that 800 °C ( $\times 6$  h) was the lowest temperature necessitated for the formation of phase-pure  $\text{La}_2\text{CuO}_4$  powders by the acetate/nitrate SPCS method at the ratio of O/F = 0.20. The EDS analysis performed on all the samples displayed in Fig. 2 revealed that the atomic ratio of La/Cu is 2 : 1. This fact also confirms that the phase purity of these samples, and proves acetate/nitrate SPCS process a successful method to synthesize multicomponent oxide with  $\text{K}_2\text{NiF}_4$  structure at low temperature.

### 3.2. The crystallization of $\text{La}_2\text{CuO}_4$ obtained from the precursors synthesized at the ratio of O/F = 0.83 via XRD

The crystallization behavior of  $\text{La}_2\text{CuO}_4$  obtained from the precursors synthesized at the ratio of O/F = 0.83 is

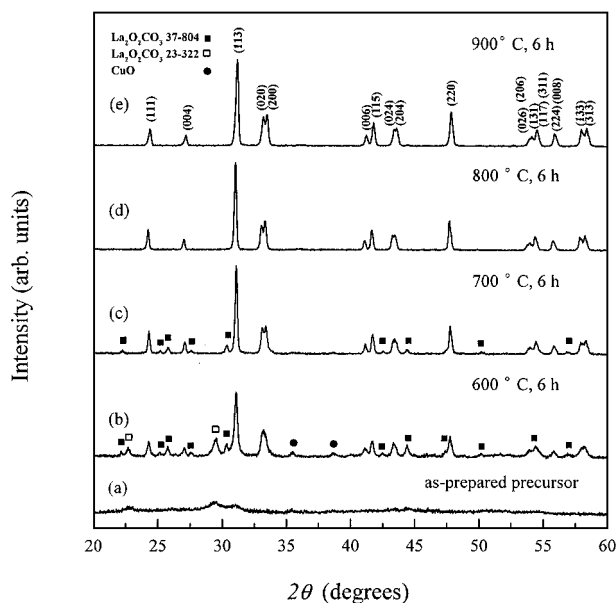


Figure 2 Monitoring of the phase-evolution characteristics in  $\text{La}_2\text{CuO}_4$  precursor powders synthesized by acetate/nitrate SPCS process at the ratio of O/F = 0.20. The indexed peaks correspond to  $\text{La}_2\text{CuO}_4$  phase.

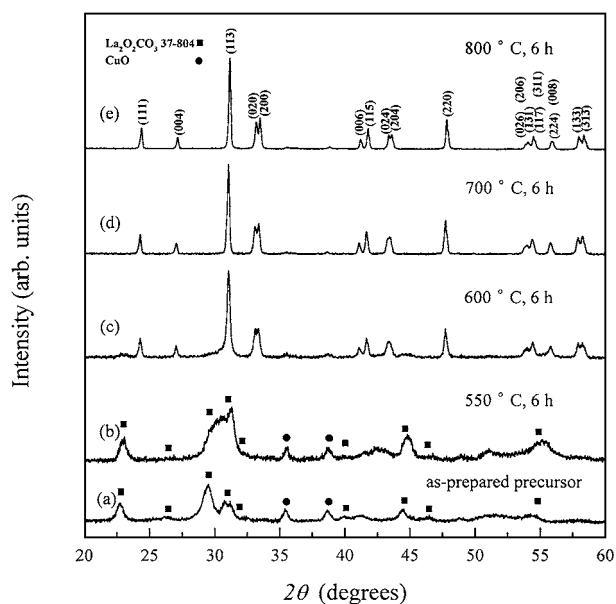


Figure 3 Monitoring of the phase-evolution characteristics in  $\text{La}_2\text{CuO}_4$  precursor powders synthesized by acetate/nitrate SPCS process at the ratio of O/F = 0.83. The indexed peaks correspond to  $\text{La}_2\text{CuO}_4$  phase.

given in Fig. 3. The XRD pattern of the as-prepared precursor displayed broad peaks that were identified to be a mixture of  $\text{La}_2\text{O}_2\text{CO}_3$  and CuO, in terms of the d-spacings. These exact Bragg peaks associate with higher combustion temperature than that synthesized at low ratio of O/F (0.20). At the calcination temperature of 550 °C, the diffraction peaks for the precursor calcined at the temperature for 6 h are similar to that of the as-prepared precursor, the absence of the diffraction peaks of  $\text{La}_2\text{CuO}_4$ , demonstrating that it did not begin to crystallize. As the calcination temperature increased to 600 °C,  $\text{La}_2\text{CuO}_4$  became the dominant phase. Fig. 3 shows that 700 °C ( $\times 6$  h) was the lowest temperature necessitated for the formation of phase-pure  $\text{La}_2\text{CuO}_4$ . This temperature is lower than that at low ratio of O/F

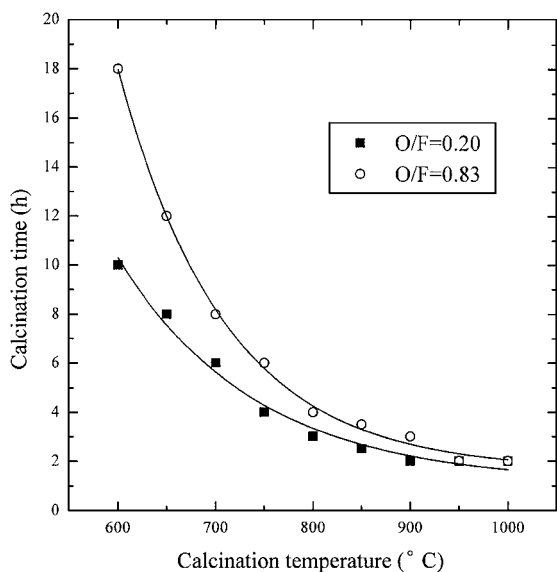


Figure 4 Calcination time necessary to obtain phase-pure  $\text{La}_2\text{CuO}_4$  as a function of the calcination temperature at different ratio of O/F.

(0.20). It may result from high combustion temperature at high ratio of O/F. The crystallization of  $\text{La}_2\text{CuO}_4$  was also noted to begin at temperature as low as  $600^\circ\text{C}$ .

### 3.3. Relationship between calcination time and calcination temperature

Fig. 4 shows the calcination time needed to obtain the  $\text{La}_2\text{CuO}_4$  phase as a function of the calcination temperature at the ratio of O/F = 0.20 and 0.83, respectively. For the samples obtained from the precursors synthesized at the ratio of O/F = 0.20, the time necessary to obtain the pure phase decreases exponentially as the calcination temperature increases. Thus, while more than 18 h is needed at  $600^\circ\text{C}$ , 12 h at  $650^\circ\text{C}$ , 8 h at  $700^\circ\text{C}$ , 6 h at  $750^\circ\text{C}$ , less time at higher temperatures (800, 850, 900, 950,  $1000^\circ\text{C}$ ) is required to obtain phase-pure  $\text{La}_2\text{CuO}_4$ . For the samples synthesized at the ratio of O/F = 0.83, only 10 h is needed at  $600^\circ\text{C}$ , 8 h at  $650^\circ\text{C}$ , 6 h at  $700^\circ\text{C}$ , 4 h at  $750^\circ\text{C}$ , less time at higher

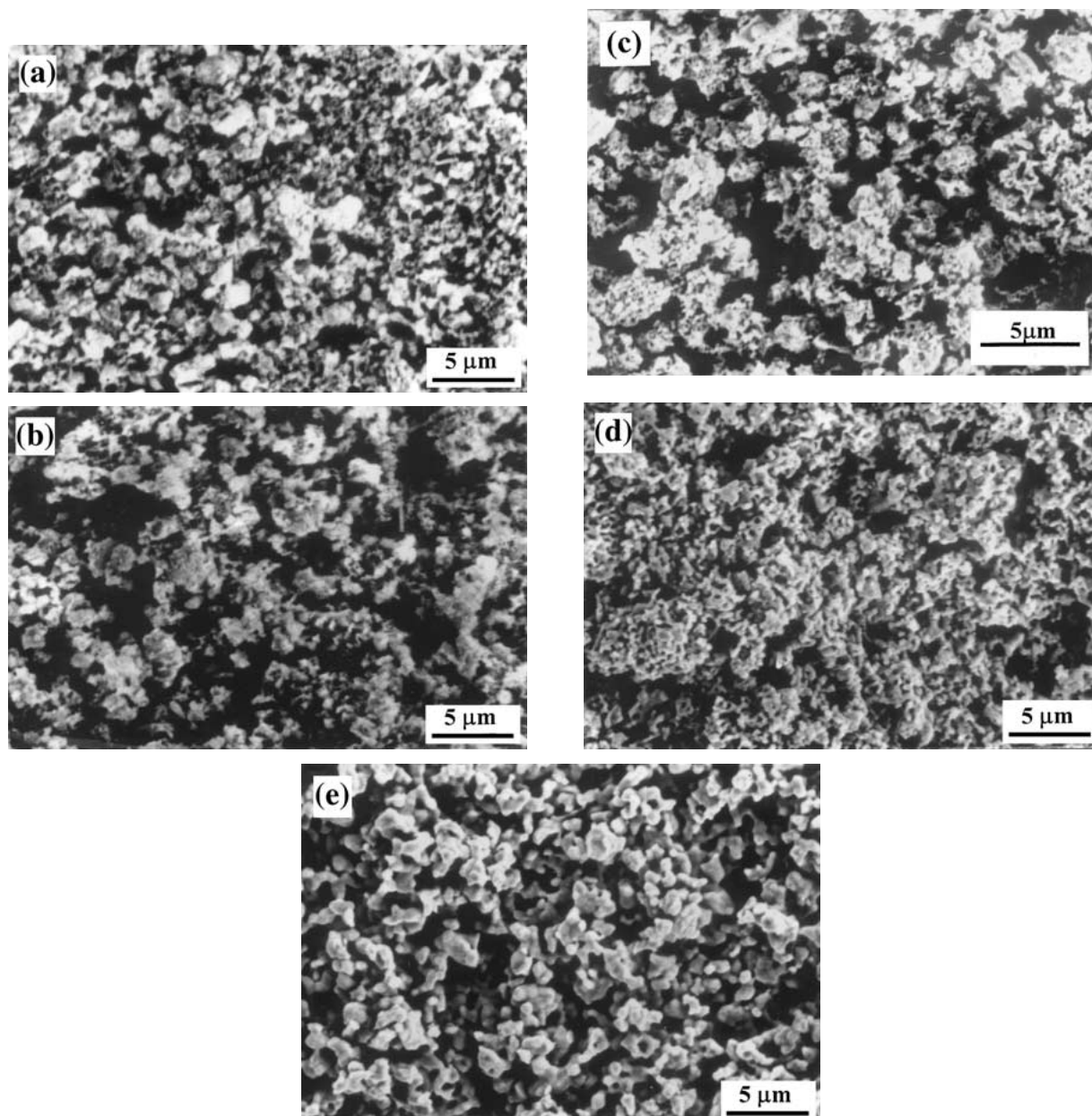


Figure 5 SEM micrographs of the as-prepared precursor powder (a) synthesized at the ratio of O/F = 0.20, and the samples prepared by calcining the as-prepared precursor powders at  $600^\circ\text{C}$  (b),  $700^\circ\text{C}$  (c),  $800^\circ\text{C}$  (d), and  $900^\circ\text{C}$  (e) for 6 h.

temperatures (800, 850, 900, 950, 1000 °C). At low calcination temperatures, less times were needed to obtain phase-pure  $\text{La}_2\text{CuO}_4$  for the precursors synthesized at the ratio of  $\text{O/F} = 0.83$  than those synthesized at the ratio of  $\text{O/F} = 0.20$ .

### 3.4. SEM investigations

Fig. 5 shows the SEM morphology-evolution characteristics in  $\text{La}_2\text{CuO}_4$  precursor powders synthesized by acetate/nitrate SPCS method at the ratio of  $\text{O/F} = 0.20$ . The particles of the precursor powders are well dispersed, as shown in Fig. 5a. Fig. 5b shows a morphology of a representative powder sample obtained by calcining the precursor at 600 °C for 6 h, in which  $\text{La}_2\text{CuO}_4$  phase present, as proved by the result of XRD. There is no exact evidence of pores on the particles; this is probably because the calcination temperature is relatively low. However, small pores were observed on the particles of the samples calcined at 700 °C for 6 h, which makes a network structure, as shown in Fig. 5c. As the calcination temperature increases, the pores on the particles grows bigger, as can be observed on the micrographs of the samples calcined at 800 °C, and 900 °C for 6 h, as shown in Fig. 5d and e, respectively. The reason for the stereoscopic structure of network is probably because of the emission of  $\text{H}_2\text{O}$  and  $\text{CO}_2$  during the calcination process, and  $\text{H}_2\text{O}$  plays a more important role than  $\text{CO}_2$  in the formation of the net structure. This can be confirmed by the result that no network structure was observed on the samples that were obtained at the ratio of  $\text{O/F} = 0.83$  following the calcination in the temperature range of 600–900 °C. The precursor prepared by acetate/nitrate SPCS method at the ratio of  $\text{O/F} = 0.83$  were a mixture of  $\text{La}_2\text{O}_2\text{CO}_3$  and  $\text{CuO}$ , which has no emission of  $\text{H}_2\text{O}$  during the calcination process. Spherical particles of the network structure also grow bigger as the calcination temperature increases.

Fig. 6 shows the micrograph of the precursor synthesized at the ratio of  $\text{O/F} = 0.83$ , followed by calcining at 900 °C for 6 h. The particle size of the sample (5–10  $\mu\text{m}$ ) is larger than that (0.5–3  $\mu\text{m}$ ) of the sample synthesized at the ratio of  $\text{O/F} = 0.20$ , followed by calcining at 900 °C for 6 h, as shown in Fig. 5e.

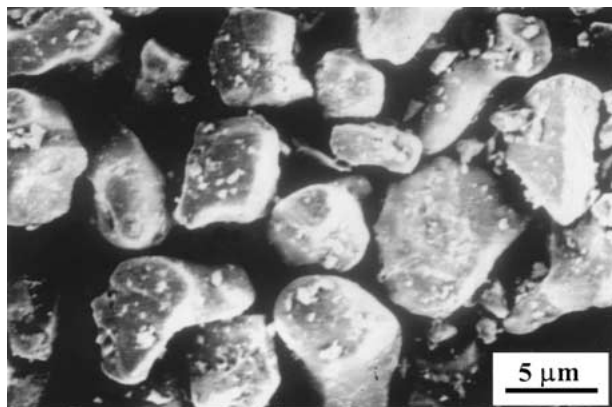


Figure 6 SEM micrographs of the precursor powders synthesized at the ratio of  $\text{O/F} = 0.83$ , followed by calcining at 900 °C for 6 h.

## 4. Conclusions

1. Acetate/nitrate SPCS process is an easy-control, pollution-free and efficient method to synthesize lanthanum copper oxide ( $\text{La}_2\text{CuO}_4$ ). The crystallization of  $\text{La}_2\text{CuO}_4$  began at temperature as low as 600 °C and the pure phase could be synthesized at that temperature.

2. The ratio of  $\text{O/F}$  strongly influences the composition and state of the precursors. The as-prepared precursor synthesized at the ratio of  $\text{O/F} = 0.20$  was non-crystalline solid with the tentative chemical formula of  $\text{La}_2\text{Cu}(\text{OH})_2(\text{CO}_3)_3$ . However, the precursor synthesized at the ratio of  $\text{O/F} = 0.83$  was a mixture of  $\text{La}_2\text{O}_2\text{CO}_3$  and  $\text{CuO}$ .

3. The calcination time necessary to obtain phase-pure  $\text{La}_2\text{CuO}_4$  decreases considerably as the calcination temperature increases. The ratio of  $\text{O/F}$  makes a notable impact on the calcination times necessary to obtain phase-pure  $\text{La}_2\text{CuO}_4$ . At low calcination temperatures, they are shorter at high ratio of  $\text{O/F}$ . Medium combustion temperature through adjusting the ratio of  $\text{O/F}$  is favorable for the easy control of the synthesis process and shorter calcination time.

4. The ratio of  $\text{O/F}$  also influences the morphology of the products after calcination treatment. At the ratio of  $\text{O/F} = 0.20$ , an interesting stereoscopic network structure was observed on the samples calcined at 700, 800, 900 °C for 6 h. This network structure is useful in the porous materials. At the ratio of  $\text{O/F} = 0.83$ , the products after calcination treatment were non-porous. As the calcination temperature increases, the diameter of the pore on the stereoscopic structure of network grows bigger. The emission of  $\text{H}_2\text{O}$  as well as  $\text{CO}_2$  is responsible for the formation of the structure during the calcination process.

5. The particle size of the calcined samples synthesized at low ratio of  $\text{O/F}$  (0.20) is considerably smaller than that synthesized at high ratio of  $\text{O/F}$  (0.83).

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