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Combustion synthesis of γ-lithium aluminate by using various fuels

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Abstract

Combustion synthesis, which is a quick and straightforward preparation process to produce homogeneous, crystalline and unagglomerated multicomponent oxide ceramic powders without the intermediate decomposition and/or calcining steps, was used to prepare γ-lithium aluminate. Lithium nitrate and aluminium nitrate were used as the starting materials and various organic compounds, such as citric acid, urea, carbohydrazide, glycine and alanine, as the fuels. The mixture of nitrate and fuel could be ignited at 450 °C, but only urea and carbohydrazide could be reacted with the mixed nitrates to result in dry, loose and white γ-$LiAlO_2$ powders. In this study, the effects of fuel type and ratio of fuel to nitrates on the phase formation of γ-$LiAlO_2$ powder were investigated and also discussed. Additionally, the phase and morphology of the γ-$LiAlO_2$ powder synthesized by the combustion reaction were compared with that by the conventional solid state reaction.

1. Introduction

Lithium aluminate ($LiAlO_2$) seems to fulfill the required thermophysical, chemical and mechanical stability as well as the favorable irradiation behavior to be used as a tritium-breeding blanket in fusion reactors [1–3]. It is also the state-of-art material used as ceramic matrix for molten carbonate fuel cells [4]. $LiAlO_2$ presents three crystalline phases: α-, β-, and γ-$LiAlO_2$ with hexagonal, monoclinic and tetragonal structures, respectively [5]. The γ-$LiAlO_2$ is most stable among the three forms and the α- and β-$LiAlO_2$ can transform to γ-$LiAlO_2$ at an elevated temperature. For these kinds of applications, this ceramic needs a highly pure phase with well-defined stoichiometric composition and homogeneous grain size.

Conventionally, γ-$LiAlO_2$ powder is prepared by solid state method [6]. Later, some wet chemical methods, such as sol–gel and polymeric precursor methods are known to be better than the solid state reaction method in intimate mixing of reactants, high product purity and low processing temperature [7,8]. Kwon et al. prepared pure phase γ-$LiAlO_2$ by sol–gel method starting with long chain alkoxides such as lithium butoxide and aluminum butoxide [8]. However, the expensive and unstable reactants and many precisely controlled steps restricted the use of this method. They also synthesized γ-$LiAlO_2$ via polymeric precursor routes, such as amorphous citrate process, Pechini process and PVA-assisted process [9], but all the methods required long time to prepare the precursor and high fired temperature (about 800 °C).

In comparison with above methods, the combustion synthesis seems to be much more advantaged for the preparation of γ-$LiAlO_2$. This method explores an exothermic, generally very fast and self-sustaining chemical reaction between the desired metal salts and a suitable organic fuel, which is ignited at a temperature much

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lower than the actual phase formation temperature. Its key feature is that the heat required to drive the chemical reaction and accomplish the compound synthesis is supplied by the reaction itself and not by an external source [10–12].

Jain et al. [13] devised a simple method of calculating the oxidizing to reducing character of the mixture according to the thermochemical concepts used in the field of propellants and explosives. This method consists on establishing a simple valency balance, irrespective of whether the elements are present in the oxidizer or in the fuel components of the mixture, to calculate the stoichiometric composition of the redox mixture, which corresponds to the release of the maximum energy for the reaction. The usual combustion gas products are CO_2, H_2O and N_2, so the carbon and hydrogen are regarded as reducing elements with corresponding valencies of $+4$ and $+1$, respectively, nitrogen is considered as having a valency of zero, while oxygen is oxidizing element with corresponding valency of -2. The metal elements contained in ceramic oxides are also considered as reducing elements with the valencies they have in the corresponding oxides.

In this study, the combustion behavior of various fuels and the effect of ratio of fuel to nitrates on the structural properties of the as-burnt γ-$LiAlO_2$ were investigated. Additionally, the phase and morphology of the γ-$LiAlO_2$ powder synthesized by combustion method were compared with that by solid state reaction method.

2. Experimental procedure

γ-$LiAlO_2$ powder was prepared according to the procedure shown in Fig. 1. A stoichiometric amount of lithium nitrate ($LiNO_3$) and aluminum nitrate ($Al(NO_3)_3 \cdot 9H_2O$) with the cationic ratio of Li:Al = 1:1 and the fuel, such as citric acid ($C_6H_8O_7 \cdot H_2O$), urea ($CO(NH_2)_2$), carbohydrazide ($CO(N_2H_3)_2$), glycine ($C_2H_5NO_2$) or alanine ($C_3H_7NO_2$), were dissolved in distilled water. The resulting solution was heated on a hot plate until most of water evaporated. Then the precursor mixture with a small amount of water was transferred into a muffle furnace that was preheated to 450 °C and spontaneously ignited by burning of the metal nitrates and fuel with the release of gases like N_2, CO_2 and H_2O. The combustion reaction was completed within a few minutes and the white powder was obtained from some of the redox reaction systems of fuel-nitrate. All the chemicals used were of analytical reagent grade.

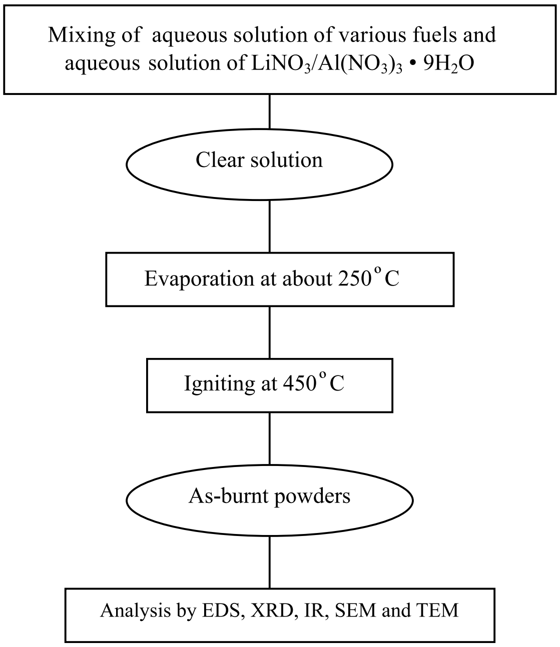

Fig. 1. Preparation procedure of γ-$LiAlO_2$ powder by combustion process.

The structural and morphological properties of $LiAlO_2$ powder were characterized by several techniques. The crystalline phases of the as-burnt powders were determined by X-ray diffractometry (XRD, D/max-3A) with radiation of CuKα at the scanning speed of 4°/min. An infrared spectroscopy technique (IR) was also used to determine the structure of the as-burnt powders. Vibrational spectra in the region of infrared were obtained in a galaxy 3030 Mattson spectrometer using the KBr disk technique in the transmission mode. Scanning electron microscopy (SEM, Philips 515) and transmission electron microscopy (TEM, JEM 2010) were used to study the morphology of the synthesized γ-$LiAlO_2$ powders. Energy dispersive spectrum (EDS) was used to analyze the composition of the final products.

To compare the characteristics of combustion synthesized powders with those of solid state reacted ones, other powders were also prepared by the mechanical mixing of Li_2CO_3 and ultra-fine γ-Al_2O_3 and calcined at 200–1000 °C in air for 2 h.

3. Results and discussion

In general, a good fuel used in a combustion process should react non-violently, produce non-toxic gases, and act as a complexant for metal cations [14]. Complexes increase the solubility of metal cations, thereby preventing preferential crystallization as the water in the precursor solution evaporates [15]. For different metal cations, various organic fuels with different ligand groups, i.e. caboxylic group and/or amine group may exhibit different complex power, which is one of the important factors that affect the phase formation and morphology of the final product. In addition, the chemical energy released from the exothermic reaction between various metal nitrates and various fuels is different. This is another important factor that affects the phase formation of the final product because high temperature is in favor of the stable phase formation and particle aggregation of the final product.

In consideration of the above factors, the effects of fuel type in the initial combustion mixture on the combustion behavior and phase formation of the γ-$LiAlO_2$ were investigated. Experimental observation showed that all of the nitrate–fuel systems could be ignited at 450 °C with obvious flame and large amount of smoke. However, the similar combustion behavior did not lead to the same products. The final brown product obtained by the combustion of citric acid was a mixture of the pyrolytic products of citric acid, namely aconitic acid or citraconic acid [16]. The final products obtained by the combustion of glycine and alanine with mixed nitrates were gray and black powders, respectively, which contained some carbon from the pyrolysis of the two fuels during combustion, as shown in their EDS patterns (Figs. 2(d) and (e)). However, the dry, loose and white powders could be easily obtained by igniting the urea-nitrate or carbohydrazide–nitrate mixture precursors. The EDS patterns of the as-burnt powders prepared by using urea and carbohydrazide as fuels indicated that no carbon contained in the final white powders.

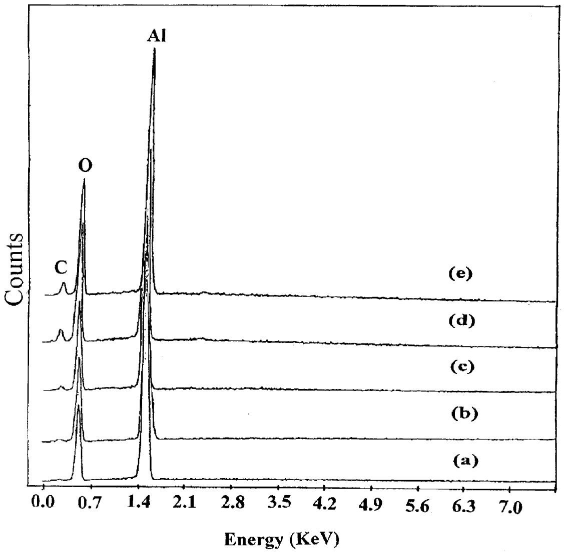

Fig. 2. EDS patterns of the as-burnt powders prepared by using various fuels: (a) citric acid, (b) urea, (c) carbohydrazide, (d) glycine and (e) alanine.

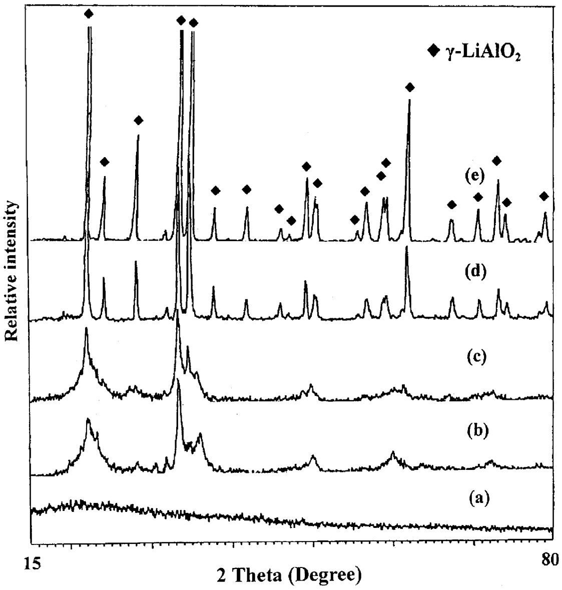

Fig. 3. XRD patterns of the as-burnt powders prepared by using various fuels: (a) citric acid, (b) alanine, (c) glycine, (d) carbohydrazide and (e) urea.

Fig. 3 shows the XRD patterns of the as-burnt powders by various fuels. When stoichiometric citric acid was used as fuel, the amorphous phase was found in the as-burnt powder (Fig. 3(a)), which was consistent with the experimental result of Kim et al. [17]. When stoichiometric glycine or alanine was used as fuel, the weak peaks of γ-$LiAlO_2$ phase as well as some peaks of impurities, can be seen from the XRD patterns (Figs. 3(b) and (c)). Contrastively, when carbohydrazide or urea was used as fuel, very intense peaks of a pure γ-$LiAlO_2$ phase can be seen from the XRD patterns (Figs. 3(d) and (e)). This indicates that single γ-$LiAlO_2$ phase could be easily obtained without any impurity by the combustion reaction of the mixed nitrates with urea or carbohydrazide.

Kim et al. [17] have reported that γ-$LiAlO_2$ could not be synthesized using lithium nitrate/aluminium nitrate as starting materials and urea as fuel by the combustion process. However, in our study, the pure γ-$LiAlO_2$ could be easily synthesized using urea as fuel by the similar combustion process. In order to further testify our experimental result, infrared spectroscopy technique was used to analyze the as-burnt powders by using various fuels. The IR spectra are shown in Fig. 4. In the spectra of the powders prepared by the fuels except citric acid, the strong bands at 650, 810 cm^{-1} are related to the stretching frequencies of AlO_4 tetrahedra [18,19] and the weak bands at 450, 520 and 550 cm^{-1} refer to the AlO_4–LiO_4 lattice, respectively [20]. So the γ-$LiAlO_2$ phase is well defined in the infrared spectrum.

From the above results, we can see that citric acid is not an effective fuel in our combustion system. This might be due to that lithium/aluminum nitrate and citric

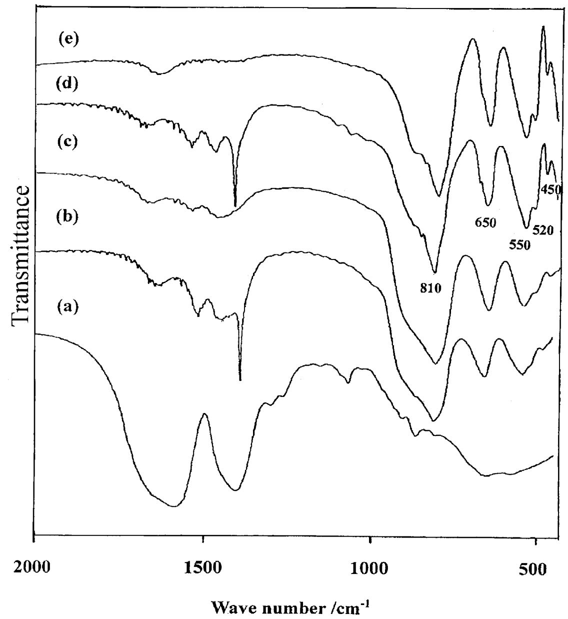

Fig. 4. Infrared spectra of the as-burnt powders prepared by using various fuels: (a) citric acid, (b) alanine, (c) glycine, (d) carbohydrazide and (e) urea.

acid could not decompose at close temperatures and the exothermic redox reaction did not easily occur (the former decomposes at about 200 °C [21] and the later at about 500 °C [22]) under our experimental conditions. The other four fuels, not like citric acid, all contain amine group, which could not only complex with metal cations but also decompose at a relative low temperature giving ammonia (NH_3). The redox reaction Eq. (1) between ammonia and the oxides of nitrogen (NO_x) from the decomposed nitrates occurred to give water and nitrogen:

$$4x\mathrm{NH}_{3(g)} + 10\mathrm{NO}_{x(g)} \rightarrow (5+2x)\mathrm{N}_{2(g)} + 6x\mathrm{H}_2\mathrm{O}_{(g)} + 2x\mathrm{O}_{2(g)}. \quad (1)$$

The energy released from the redox reaction accelerated the phase formation of γ-$LiAlO_2$.

The as-burnt powders by using urea, carbohydrazide, glycine and alanine were studied by SEM. It can be seen from Fig. 5 that the micrograph of the synthesized γ-$LiAlO_2$ powder using urea shows clear elongated faceted crystals, just as that reported by Takahashi et al. [23]. The synthesized powders using glycine and alanine have morphology similar to that using urea, but the size of the particles was smaller than the latter. However, the

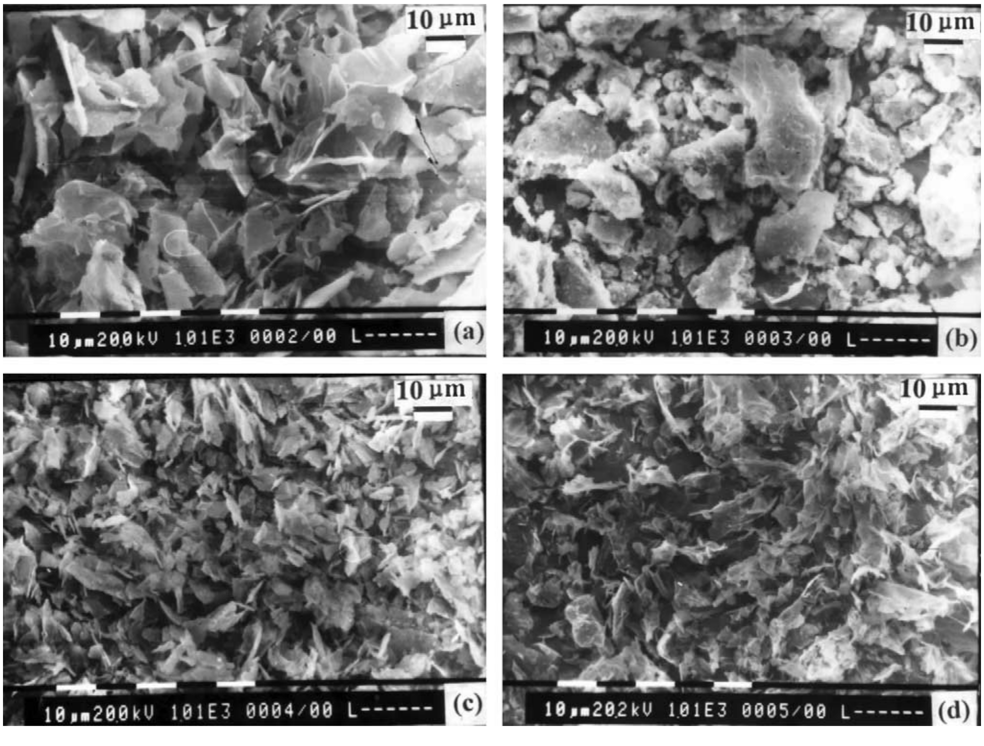

Fig. 5. SEM images of as-burnt powders prepared by using (a) urea, (b) carbohydrazide, (c) glycine and (d) alanine.

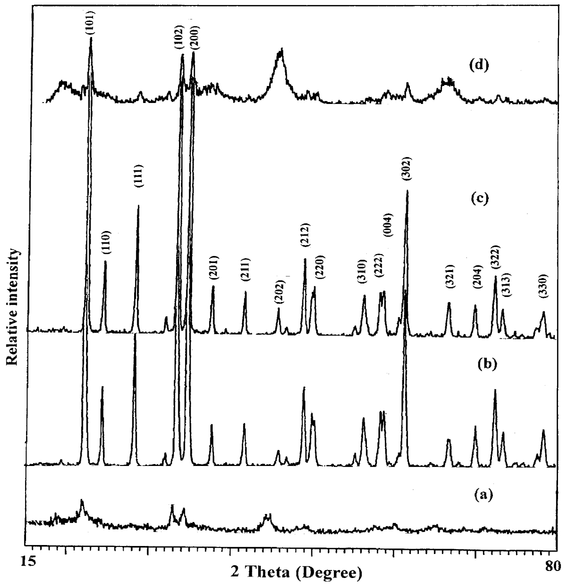

Fig. 6. XRD patterns of the as-burnt powders prepared by various amounts of urea as fuel: (a) 50% stoi., (b) stoi., (c) 200% stoi. and (d) 300% stoi.

micrograph of that using carbohydrazide shows irregular flakes. Therefore, the morphology of the resulting γ-$LiAlO_2$ crystals also seems to depend upon the fuel type.

It is well known that one of the major parameters that determine the phase formation of the synthesized powder is the ratio of fuel to metal nitrate in the combustion reaction. In this study, the effects of ratio of fuel to metal nitrates on the characteristics of the synthesized powder were investigated in a precursor solution consisting of urea as a fuel and a mixed nitrate of lithium and aluminium. Fig. 6 shows the XRD patterns of the γ-$LiAlO_2$ produced at four different ratios of urea to nitrates. Four different ratios were 50% stoi., stoi., 200% stoi. and 300% stoi., which denoted the precursor solution contained urea with one-half, one, two, and three times of stoichiometric urea. The synthesized powder prepared using 50% stoi. of fuel consisted with insufficiently developed crystalline $LiAlO_2$ and some impurity because the absent fuel could not react completely with the mixed nitrate of lithium and aluminium to release heat enough to accelerate the phase formation of γ-$LiAlO_2$. However, the as-burnt powders prepared by using stoi. and 200% stoi. fuels consisted with the well-developed phase of γ-$LiAlO_2$. When 300% stoi. fuel was used

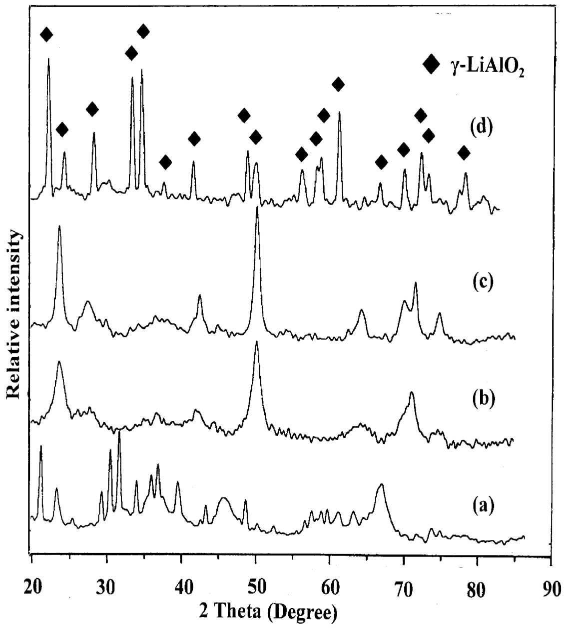

Fig. 7. XRD patterns of the powders prepared by solid state reaction: (a) after oven-drying, (b) after calcining at 600 °C for 2 h, (c) after calcining at 800 °C for 2 h and (d) after calcining at 1000 °C for 2 h.

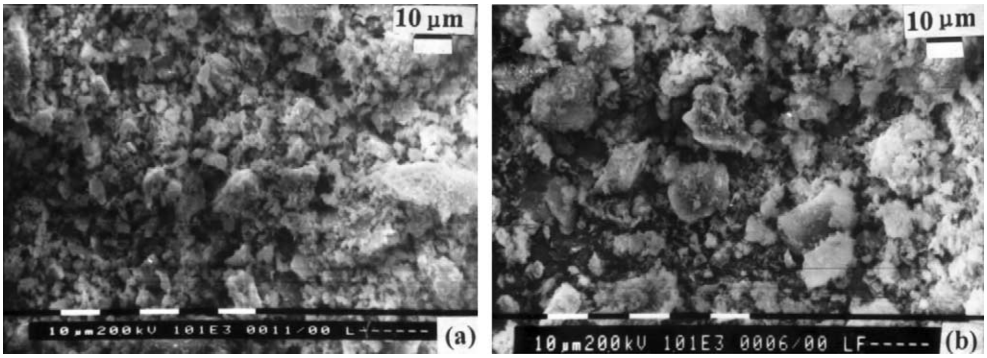

Fig. 8. SEM images of (a) the combustion synthesized γ-$LiAlO_2$ powder after being milled and (b) the γ-$LiAlO_2$ powder prepared by solid state reaction method.

in the combustion synthesis, very weak γ-$LiAlO_2$ peaks can be checked in the XRD pattern of the as-burnt powder. This experimental result means that the ratio of fuel to mixed nitrates of lithium and aluminium is important in obtaining the pure crystalline γ-$LiAlO_2$ powder by combustion reaction.

The solid state reaction process is the most conventional method for synthesis of the oxide ceramics including $LiAlO_2$. In this study, $LiAlO_2$ powder was produced by the solid state reaction of Li_2CO_3 and γ-Al_2O_3 in order to compare the characteristics of the combustion synthesized powders. Fig. 7 shows the XRD patterns of as-dried powders with various calcination temperatures. The as-dried powder without calcination did not contain the $LiAlO_2$ phase but did contain the starting materials including Li_2CO_3 and γ-Al_2O_3. When being calcined at the temperature range of 600–800 °C, the powders were mainly composed of α-$LiAlO_2$. When the calcination temperature reached 1000 °C, the observed phase was attributed to γ-$LiAlO_2$ as well as a small amount of $LiAl_5O_8$. These experimental results were consistent with the previous report [24]. Fig. 8 shows the morphologies of the synthesized γ-$LiAlO_2$ powders by two methods. As shown in Fig. 8(a), the laminar shape (see Fig. 5(a)) of the as-burnt powder was dramatically changed to grain shape after being milled with an agate mortar and dispersed with an ultrasonic facility for 5 min. This indicates that the as-burnt powder was very loose to be broken easily, although the primary crystal of the powder still maintained the faceted shape, which can be seen from Fig. 9. By contrast, the particle shape of the power synthesized by solid state reaction method looked like that of the milled powder prepared by combustion process, but in fact, the crystallite shape of the former was also laminar according to the literature [21].

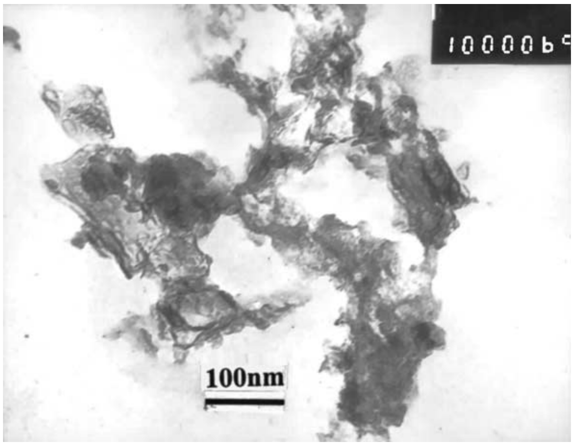

Fig. 9. TEM image of the combustion synthesized γ-$LiAlO_2$ powder.

4. Conclusions

Combustion synthesis is an efficient, quick and straightforward method for the preparation of dry, loose and white γ-$LiAlO_2$ powders without further calcination. The fuel type and the ratio of fuel to nitrates dramatically influenced the phase formation of the final products. By contrast with citric acid, glycine and alanine, urea and carbohydrazide were efficient fuels to react with the mixed nitrates and result pure γ-$LiAlO_2$. When the ratio of fuel to nitrates was stoichiometric or 200% stoichiometric, the final products were mainly attributed to γ-$LiAlO_2$, but much less (50% stoi.) or much more (300% stoi.) fuel was not reacted completely with the nitrates to result γ-$LiAlO_2$. The morphology of the as-burnt powders was elongated faceted or laminar particles, which was similar to that prepared by solid state reaction, as reported by previous work. In this work, the γ-$LiAlO_2$ phase could be obtained until the calcination temperature reached 1000 °C by a solid state reaction, which means that combustion synthesis is a more efficient, quick and economic method for the preparation of γ-$LiAlO_2$ than conventional solid state reaction method.

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