

Synthesis of Li_2TiO_3 ceramic breeder powders by the combustion process

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Abstract

The synthesis of the ultra-fine Li_2TiO_3 powder by the combustion reaction of lithium nitrate, titanium nitrate and specific fuels was investigated. Ultrafine Li_2TiO_3 powders could be synthesized using glycine or a mixture of urea and citric acid. A pure Li_2TiO_3 phase was obtained by the simple process without further calcination reaction. The specific surface area of the as-synthesized powder was 10 to 14 m^2/g and the primary particle size was about 30 nm. The Li_2TiO_3 body sintered at 800°C for 3 h had dense agglomerates which were formed by the inter-agglomerate sintering process. Each of the agglomerates consisted of very fine grains with a size of 0.3 to 0.5 μm . © 1998 Elsevier Science B.V.

1. Introduction

The choice of a suitable breeding material for D–T fueled fusion reactors is very important in view of the effective power conversion, tritium release behaviors and safety considerations [1]. Lithium-based ceramics such as Li_2O , $\gamma\text{-LiAlO}_2$, Li_4SiO_4 , Li_2ZrO_3 and Li_2TiO_3 have been considered as candidates for tritium breeding materials in D–T fusion reactors [2,3].

Li_2TiO_3 is known to be a low-activation ceramic material for use in tritium breeding. To date, however, very little work has been done on the fabrication of the Li_2TiO_3 ceramic powder, the sintering behavior, the tritium release behavior and the properties database [4]. Finn et al. [5] performed preliminary research which indicated that Li_2TiO_3 possessed attractive properties. Li_2TiO_3 has the same lithium density as that for Li_2ZrO_3 and its melting point is similar. The thermal conductivity is better than that for lithium aluminate or lithium zirconate. Long-term waste problems should be low because titanium is the low activation element. In addition, Li_2TiO_3 appears to possess excellent tritium release behaviors at temperatures below 300°C [4].

In this study, a novel method for preparing fine-crystalline Li_2TiO_3 powders, that is based on the combustion reaction, is reported. Several conventional powder synthesis techniques including solid state synthesis, co-precipitation and sol–gel process are available [6]. However, these reactions are complicated and require multi-step reaction routes with long term reactions. Therefore, a simple process is needed. One of the simplest powder preparation processes is combustion synthesis [7,8]. This process is an exploitation of an exothermic and usually very rapid chemical reaction to form final reaction products [9]. A key feature of this process is that the heat required to maintain the chemical reaction is supplied from the reaction itself (internal source) and not from an external source.

Many advantages of this technique have been demonstrated in the past as follows. (1) The method needs little heating to start a rapid reaction. (2) The method requires little or no further processing such as calcination and milling. There is a considerable savings in time, energy and equipment compared with the conventional techniques. (3) The process can be applied to prepare novel-oxides containing dopant elements, low-temperature compounds and cermets which are difficult to synthesize by the conventional methods. (4) The process uses the heat generated by the chemical reaction between fuel and metal nitrates to convert the metal ions to the target ceramics materials [10].

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(5) The combustion synthesized powders with wet chemical techniques have good sinterability because most of them are produced in ultrafine form. This wet chemical route allows the degree of mixing of the reactants to be better than by directly blending the solid reactants.

In this study, the combustion behavior of various fuels and fuel composition on the phase formation were investigated to synthesize the ultra-fine Li_2TiO_3 powder by the combustion reaction. Additionally, the sintering behavior of the combustion synthesized powder will also be discussed.

2. Experimental procedure

The combustion process is a self-sustaining combustion synthesis technique that produces fine homogeneous metal-oxide powders. Aqueous precursor solutions containing metal nitrates and fuel such as urea, citric acid and glycine were heated until the water was evaporated. After evaporation of the water, the precursor mixture auto-ignited and underwent combustion spontaneously to form the metal-oxides.

Titanium nitrates were used as a source material of titanium because the water soluble Ti(IV) ion exists only in a strong acid media. Titanium nitrate is not commercially available and was prepared according to the path shown in Fig. 1. It was prepared by dissolving hydrated titania in nitric acid. The hydrated titania was obtained by adding TiCl_4 aqueous solution to ammonia solution. Hydrated titania was carefully washed with distilled water until the chloride ions were fully removed. After these

metal salts (LiNO_3 and $\text{TiO}(\text{NO}_3)_2$) and fuel were dissolved in water, this precursor solution was heated with stirring. As soon as the water was evaporated, the precursor mixture spontaneously ignited by burning of the metal nitrate and fuel and fine Li_2TiO_3 powder was formed with the release of gas like N_2 , CO_2 and H_2O . The composition of fuel and metal nitrates was calculated according to the method of Jain et al. [11]. A 'stoichiometric' composition denotes a fuel-to-nitrate ratio in which the fuel can react completely with all of the metal nitrates in the same mixture, such that no residual fuel or nitrate remains in the product materials.

The combustion synthesis for Li_2TiO_3 was done according to the flow sheet shown in Fig. 1. The combustion reaction was completed within 20 s. The crystalline phases of as-synthesized powders were determined by X-ray diffractometry with radiation of $\text{Cu K}\alpha$ (Rigaku) at the scan speed of $1^\circ/\text{min}$. Scanning electron microscopy (SEM, JEOL) and transmission electron microscopy (TEM, JEOL 2000FX-2, 200 keV), were used to observe the morphology and size of the synthesized powders. Simultaneous thermogravimetric and differential thermal analysis (TG/DTA) and differential scanning calorimetry (DSC) were performed to analyze the thermal behaviors of the precursor solution and the synthesized powders. The specific surface area of the synthesized Li_2TiO_3 powders was measured with BET method.

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 TiO_2 and calcined at 400 to 1000°C for 3 h.

3. Results and discussion

3.1. Phase formation with fuel type and composition

The type and the composition of fuels in the combustion synthesis can strongly influence the reactivity of the combustion reaction and the phases formed in the synthesized powders. If only nitrates were dissolved in a precursor solution without any fuels, then hard lumps remained without any combustion reaction during heating. But when fuels were mixed along with nitrates, the precursor solution could be reacted with or without a flame present. The reactivity of the combustion reaction is dependent upon the ligand groups of the fuel molecule and the compositional ratio of fuel to nitrates.

Therefore, the reactivity and the product phases from metal (Li, Ti) nitrates with various fuels were investigated before the synthesis of Li_2TiO_3 powder by the combustion reaction was undertaken. These results are summarized in Table 1. LiNO_3 is reacted with citric acid or glycine. However, the produced phase is not Li_2O but Li_2CO_3 , which seems to be due to the CO_2 adsorption character-

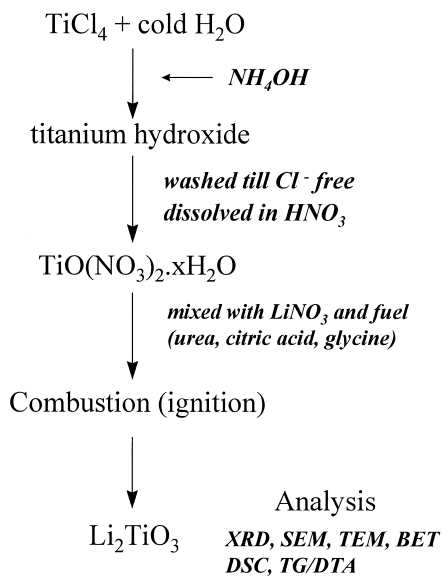


Fig. 1. Flow sheet of the combustion process for synthesis of the Li_2TiO_3 powder.

Table 1
Combustion behavior of LiNO_3 and $\text{TiO}(\text{NO}_3)_2$ with various fuels

Reactant composition (stoichiometric)		Reactivity	Phase
LiNO_3	urea	no reaction	$\text{Li}_2\text{CO}_3 + \text{LiNO}_3$ crystalline
	citric acid	very explosive	Li_2CO_3 crystalline
	glycine	very explosive	$\text{Li}_2\text{CO}_3 + \text{LiNO}_3$ crystalline
$\text{TiO}(\text{NO}_3)_2$	urea	no reaction	anatase
	citric acid	weak reaction	anatase
	glycine	weak reaction	anatase

istics of Li-compounds from glycine or citric acid during the combustion reaction and atmosphere [12]. Although glycine reacts on lithium nitrate with flame, not all phases are Li_2CO_3 . This seems to result from the excess amine group which is not complexed with lithium ions. $\text{TiO}(\text{NO}_3)_2$ is not reacted with urea but weakly reacted with glycine or citric acid. However, all the phases are anatase which is the low temperature phase of titanium oxide, i.e. the heat from the combustion reaction seems to be too small to produce the rutile phase. The reactivity of the mixture of LiNO_3 – $\text{TiO}(\text{NO}_3)_2$ was different from that of each of the nitrates. The fuels consisted of both the carboxylic acid group and amine group like glycine or a mixture of urea and citric acid were strongly reacted with mixed metal (Li, Ti) nitrates. The reactivity of this system was strongly dependent on the composition of fuels. The strong reaction occurred only at the stoichiometric ratio of fuel and nitrates. The reactivity and the produced phases are summarized in Table 2. Among various compositions of fuels, the stoichiometric composition of glycine or a mixture of urea and citric acid produced the Li_2TiO_3 phase with a strong reaction. The powders prepared by the combustion process had the specific surface area of 10 to 20 m^2/g which was dependant on the type and composition of the fuel.

The self-sustaining nature of the combustion can be explained as follows. The precursor mixture contains, a strong oxidizer, metal nitrate, and also contains glycine or

citric acid, a readily combustible fuel. On heating, the precursor mixture, after evaporating water, nitrate decomposes giving oxides of nitrogen (NO_x). The gaseous NO_x reacts with the fuel (glycine or citric acid) generating heat (flame) and more gases. The homogeneous gas-phase exothermic oxidation–reduction increases the temperature of the intact viscous mixture immediately adjoining to the combustion zone, causing it to react. The reaction process proceeds rapidly and sustainably until all of the intact zone is consumed. The rapid temperature increase with the orange flame and the volume of gas generated during the reaction depend on the fuel type, composition and content; in general, a higher fuel content or stoichiometric composition gives rise to higher temperature and to more evolved gas.

XRD patterns of the synthesized powder prepared by various fuels are shown in Fig. 2. When pure urea (mark A in Fig. 2) or mixed fuel of urea and citric acid with composition of urea/citric acid equal to 12 (mark B) was used as a fuel, LiNO_3 and TiO_2 (anatase) phases were found in the synthesized powders. This observation seems to be related to heat produced from the combustion reaction. When pure glycine (mark F) and mixed fuels of urea and citric acid with the same ratio (mark C) or excess of citric acid (mark D) were used as fuels, Li_2TiO_3 could be easily obtained. However, an unreacted residue phase seemed to exist along with Li_2TiO_3 in the excess citric acid fuel. Similar results were observed with mixed fuel

Table 2
Effects of fuel type and composition on the synthesis of Li_2TiO_3 powder

Composition of the fuel (mol) (for 1 mol of Li_2TiO_3)			Reactivity	Phase (XRD)	Remark	BET (m^2/g)
urea	citric acid	glycine				
10/3	–	–	no reaction	LiNO_3 , TiO_2 (anatase)	A	–
8/3	2/9	–	no reaction	LiNO_3 , TiO_2 (anatase)	B	–
5/3	5/9	–	strong reaction	Li_2TiO_3	C	17.01
2/3	8/9	–	moderate reaction	Li_2TiO_3 (impurity)	D	19.23
–	10/9	–	weak reaction	Li_2TiO_3 (impurity)	E	28.49
–	–	20/9	very strong reaction	Li_2TiO_3	F	13.50

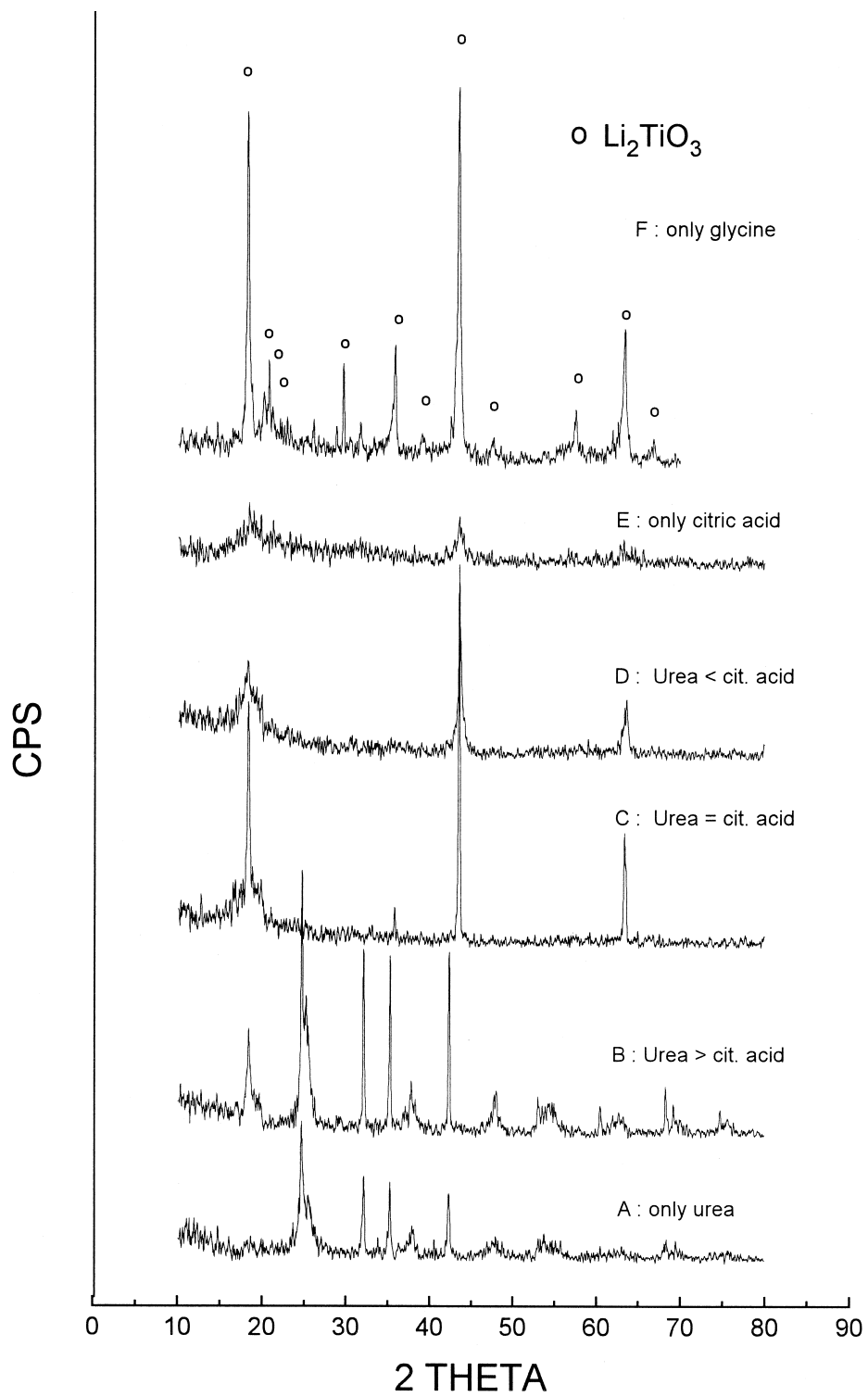
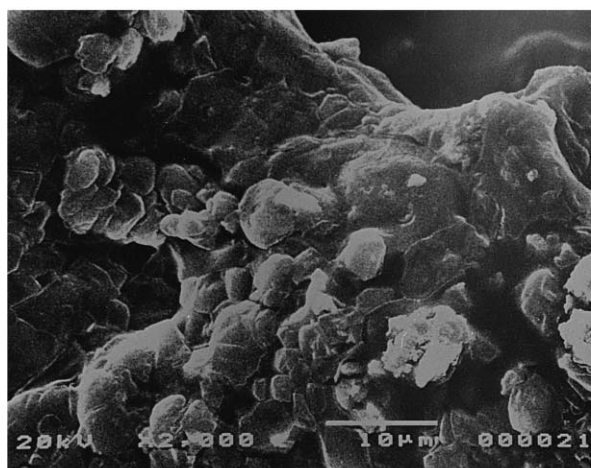
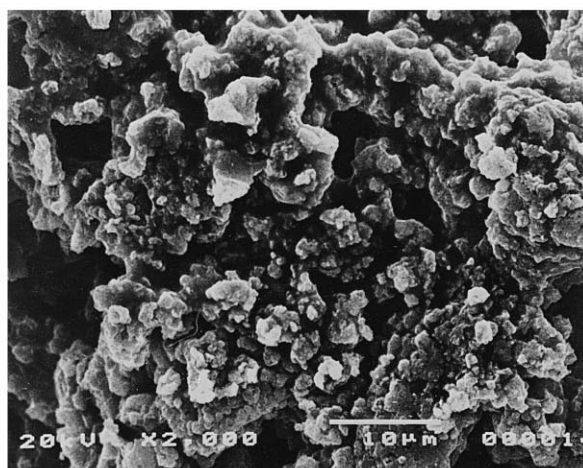


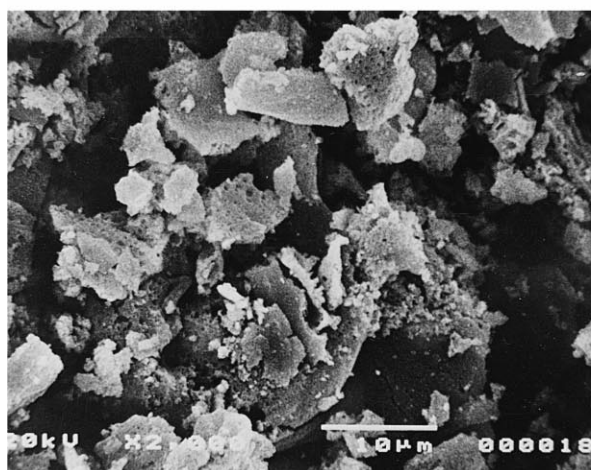
Fig. 2. XRD patterns of as-synthesized powders with various fuel types and compositions.



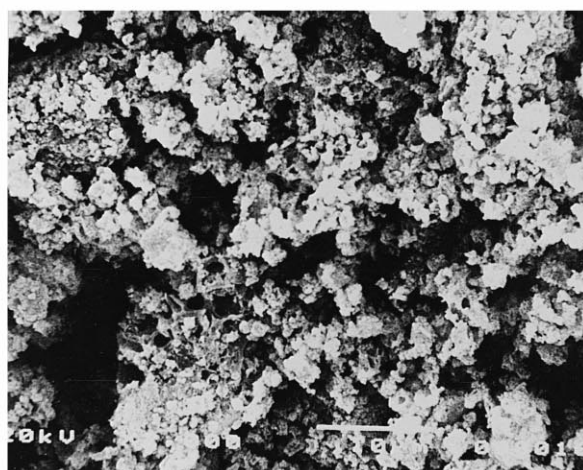
(a)



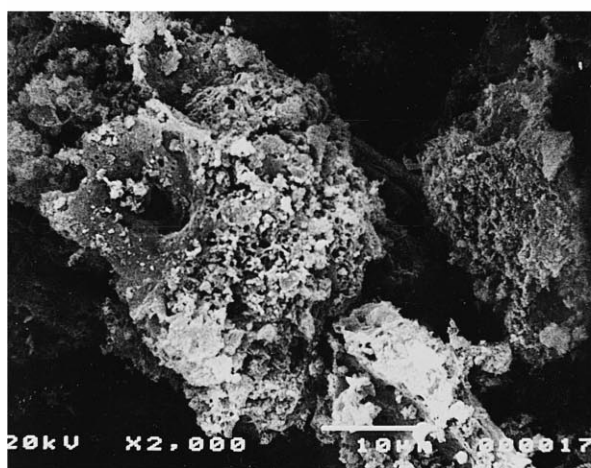
(b)



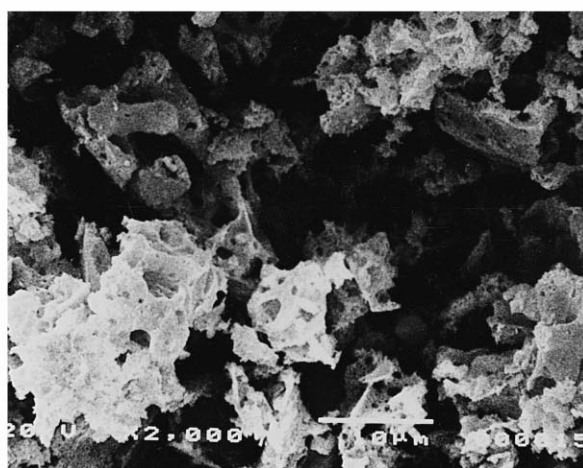
(c)



(d)



(e)



(f)

Fig. 3. SEM photographs of as-synthesized powders with fuel type: (A) urea, (B) urea > citric acid, (C) urea = citric acid, (D) urea < citric acid, (E) citric acid and (F) glycine.

with excess citric acid in the case of pure citric acid as a fuel. The reactivity of pure citric acid was lower than mixed fuel with excess citric acid, i.e. to synthesize Li_2TiO_3 powder by combustion reaction, a fuel must possess both the carboxylic acid group and amine group.

The microstructures of the synthesized powders using various fuels were observed. A typical micrograph of the synthesized powders is shown in Fig. 3. The powders prepared from pure urea (A in Fig. 3) and a mixed fuel with excess urea composition (B in Fig. 3) had a cluster of aggregates, which were LiNO_3 , TiO_2 (anatase) and unreacted fuels. In both cases, the reaction is very weak. By contrast, the synthesized Li_2TiO_3 powders using glycine (F in Fig. 3) formed the foamy agglomerated particles.

A lot of pores were found on the surface of the synthesized powders, which seems to result from the evolved gas during the combustion reaction. The SAD (selected area diffraction) pattern and the microstructure of as-synthesized powder observed by TEM are shown in Fig. 4. While the morphology of secondary particles was a porous skeleton, the primary particles were ultra-fine and equiaxed crystalline with a particle size of about 20 nm. The SAD pattern shows clear rings, which means that the synthesized powder is very fine crystalline.

Considering the above results, the Li_2TiO_3 powder could be easily synthesized by the combustion reaction with glycine or a mixed fuel of urea and citric acid which is consisted of both of amine group and carboxylic group.

3.2. Phase formation with ratio of fuel to nitrate

It is known that one of the major parameters that determines the phase formation and the morphology of the synthesized powder is the ratio of fuel to metal nitrate in the combustion reaction [9,10]. When a precursor solution has the stoichiometric ratio of fuels to metal nitrates, the reactivity and the phase formation are the most desirable. In this study, effects of the ratio of fuels to metal nitrates on the characteristics of the synthesized powder were investigated in a precursor solution consisting of glycine as a fuel and a mixed nitrate of lithium and titanium.

Fig. 5 shows XRD patterns for Li_2TiO_3 produced at three different ratios of glycine to nitrates. Three different compositions are fuel-lean which denotes the precursor solution contains glycine with one-half of the stoichiometric ratio, fuel-rich which denotes the precursor solution contains two times of glycine and fuel-stoichiometric. The

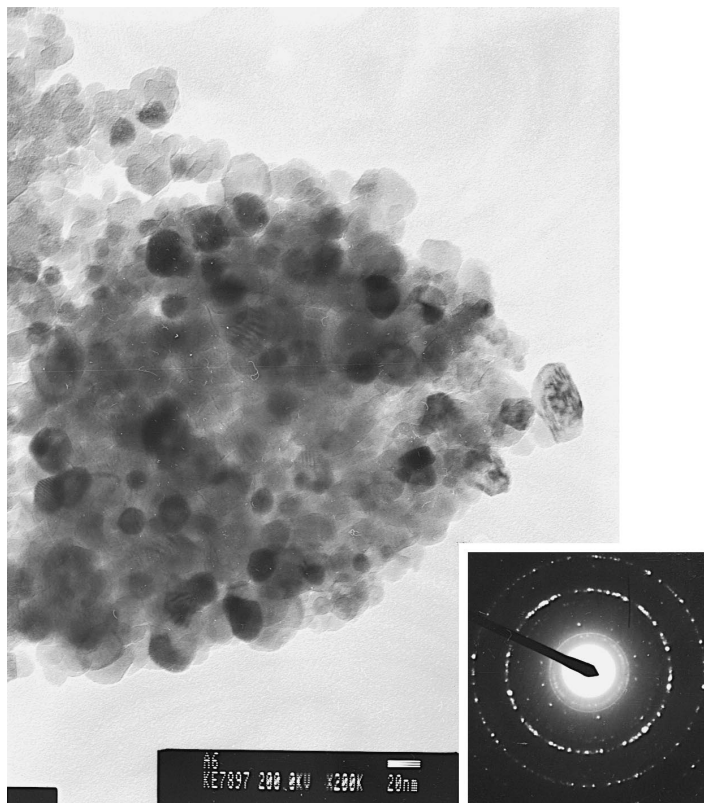


Fig. 4. Bright-field TEM image and SAD pattern of as-synthesized Li_2TiO_3 powders.

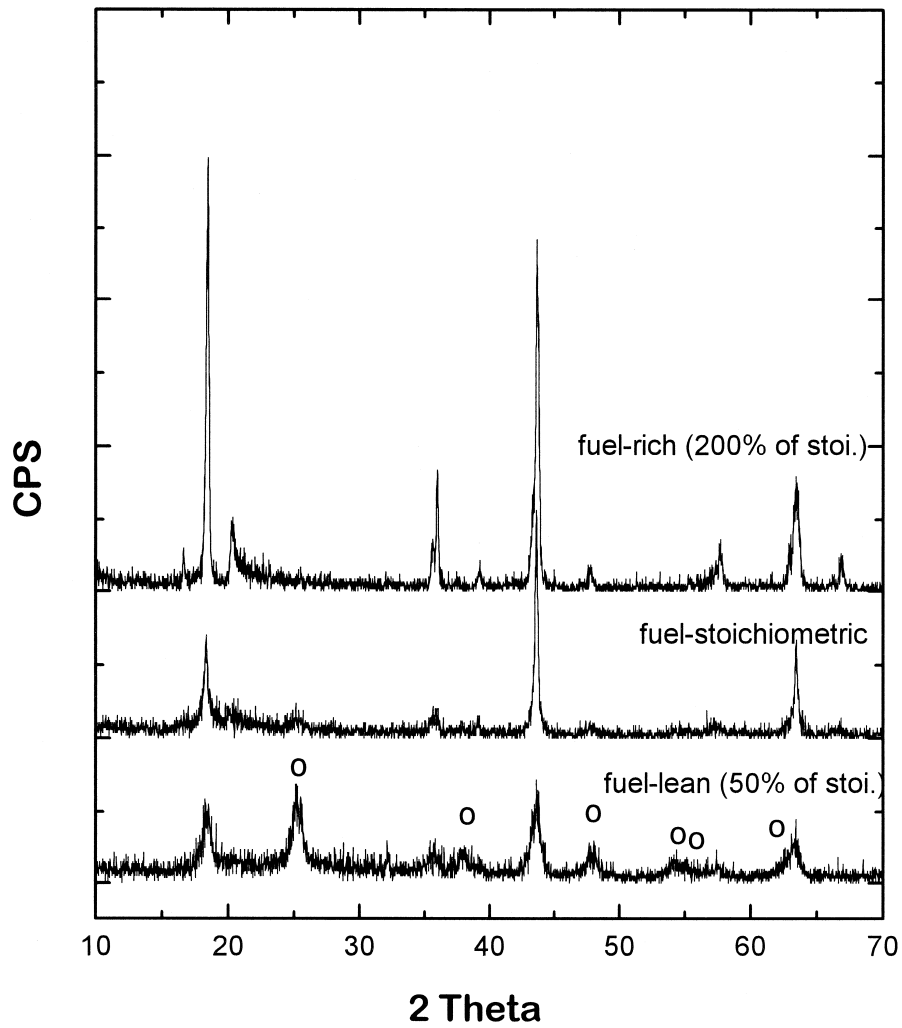


Fig. 5. XRD patterns for Li_2TiO_3 synthesized by the combustion reaction with three different ratios of glycine to nitrate (open circle: anatase).

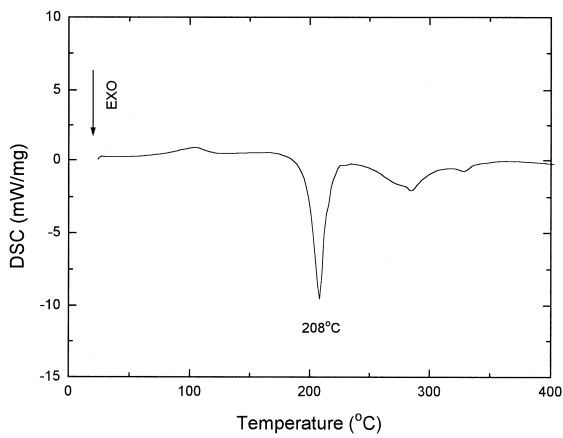


Fig. 6. DSC curve of precursor mixture with glycine and (Li and Ti) nitrates.

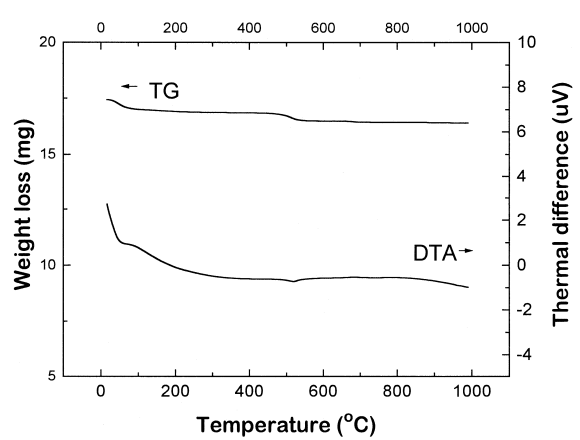


Fig. 7. DTA/TG analysis curves of as-synthesized Li_2TiO_3 powder by the combustion reaction.

synthesized powders prepared using the fuel-stoichiometric and fuel-rich consisted of fully crystalline Li_2TiO_3 with an average primary crystalline size of about 30 nm which is determined by XRD line broadening analysis. However, unreacted residues co-existed in the synthesized powder prepared by the fuel-rich precursor solution. Most of the crystalline phases produced by the precursor solution with the fuel-lean process are anatase and small amounts of unreacted residue also co-existed. This observation means that the ratio of glycine to mixed nitrates of lithium and titanium is important in obtaining the fine crystalline Li_2TiO_3 powders by the combustion reaction.

Variations of heat (or calorie) produced from the reactions during the heating of a precursor solution were

analyzed by DSC. The small lump sample was prepared by pre-drying of the precursor solution with a fuel-stoichiometric composition before the combustion reaction. The measured DSC curve was shown in Fig. 6. The exothermic peak occurs at 208°C which is associated with the redox reactions of burning the chemical groups involved in glycine. Up to 400°C, the decomposition was completed and the total weight loss was about 95%. The TG and DT analysis were also performed to investigate the existence of an unreacted residue in the as-synthesized powder prepared by glycine with fuel-stoichiometric composition. Fig. 7 shows that weight losses were less than 5% and no thermal peaks were observed up to 1000°C, which indicated that pure Li_2TiO_3 powder without a further calcina-

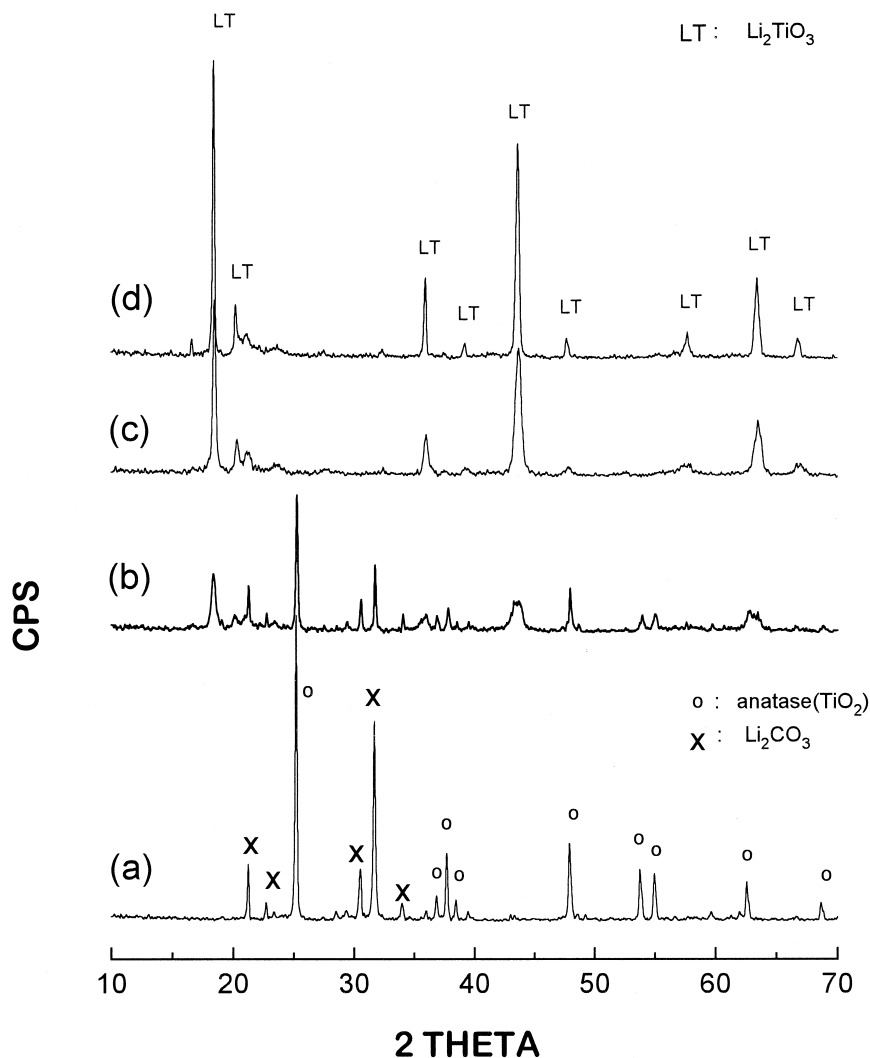


Fig. 8. XRD patterns of the Li_2TiO_3 powder prepared by solid state reaction; (a) after oven-drying, (b) after calcining at 550°C for 3 h, (c) after calcining at 700°C for 3 h and (d) after calcining at 1000°C for 3 h.

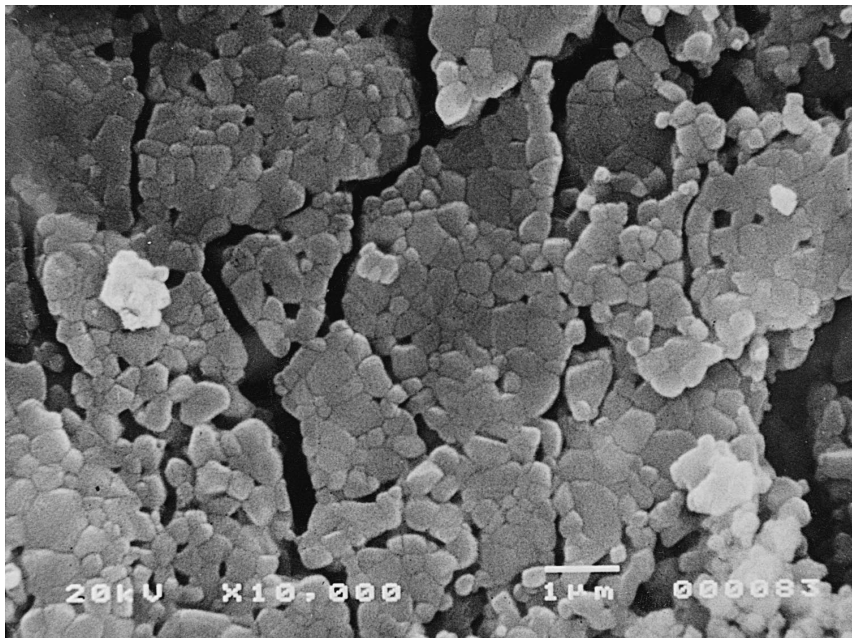


Fig. 9. The surface microstructure of Li_2TiO_3 body sintered at 800°C for 3 h using the combustion synthesized powder.

tion process could be easily synthesized by this simple combustion process.

3.3. Comparison of solid-state process with combustion process

A powder synthesis process by the solid state reaction is the most well known method for synthesis of the oxide ceramics including Li_2TiO_3 . Li_2TiO_3 powder was produced by the solid state reaction of TiO_2 (anatase) and Li_2CO_3 in order to compare the characteristics of the synthesized powders. A 1:1 stoichiometric mixture of titania and lithium carbonate was prepared by mixing together with a zirconia ball in ethanol. Then, the mixed powder was dried at 100°C for 24 h and calcined in the range 400 to 1000°C for 3 h.

Fig. 8 shows the XRD patterns of as-dried powders with various calcination temperatures. The as-dried powder did not contain the Li_2TiO_3 phase but did contain TiO_2 (anatase) and small amounts of Li_2CO_3 . A Li_2TiO_3 phase appeared at 550°C , but TiO_2 (anatase) and small amounts of Li_2CO_3 were also observed along with Li_2TiO_3 phase at that temperature. When the calcination temperature reached 700°C , the observed phase was only Li_2TiO_3 . These phenomena can be confirmed by the TG/DT analysis. The DTA curve shows a broad endothermic peak in the range of 400 to 700°C , which is in agreement with the calcining results above. Although Li_2TiO_3 is produced at 700°C in the solid state reaction, this reaction required a long reaction time.

The shrinkage curves of the combustion synthesized powder were shifted toward a lower temperature than those of the solid state reacted one. Fig. 9 shows the surface microstructure of a sintered Li_2TiO_3 body using the combustion synthesized powder which was sintered at 800°C for 3 h. This Li_2TiO_3 sintered body has dense agglomerates which are formed by the inter-agglomerate sintering process. Each of the agglomerates consist of very fine grains with a size of 0.3 to $0.5 \mu\text{m}$. Large pores present at the intra-agglomerates in the sintered body decrease the sintered density of the Li_2TiO_3 powder compact. Therefore, an additional de-agglomeration process would be necessary to increase the packing density and thus the sintering density.

4. Conclusion

Ultrafine Li_2TiO_3 powders could be easily synthesized by a combustion reaction in a short time using glycine or a mixture of urea and citric acid with a stoichiometric composition. A pure Li_2TiO_3 phase was obtained by the simple process without further calcination reaction. The synthesized powder was very fine and equiaxed. The specific surface area of the as-synthesized powder is 10 to $14 \text{ m}^2/\text{g}$ and the primary particle size is about 30 nm .

A Li_2TiO_3 body sintered at 800°C for 3 h has dense agglomerates which were formed by an inter-agglomerate sintering process. Each of agglomerates consist of very fine grains with a size of 0.3 to $0.5 \mu\text{m}$.

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