

Synthesis of Lanthanides Doped CaTiO₃ Powder by the Combustion Process

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Lanthanides such as La, Gd and Ce have recognized as elements of high level radioactive wastes immobilized by forming solid solution with CaTiO₃. For easy forming solid solution between CaTiO₃ and lanthanides, the combustion synthesis process was applied and the powder characteristics and sinterability were investigated. The proper selection of the type and the composition of fuels are important to get the crystalline solid solution of CaTiO₃ and lanthanides. When glycine or the mixtures of urea and citric acid with stoichiometric composition was used as a fuel, the solid solution of CaTiO₃ with La₂O₃ or Gd₂O₃ or CeO₂ was produced very well by the combustion process. The combustion synthesized powder seemed to have a good sinterability with the linear shrinkage of more than 25% up to 1500 °C, while that of the solid state reacted powder was less than 10% at the same condition.

Key words: CaTiO₃, Lanthanide, Combustion, HLW

I. Introduction

CaTiO₃ is one of the promising materials for the disposal of high level radioactive wastes because it can immobilize lanthanides and actinides by forming solid solutions with them.^{1,2)} The solid state reaction between lanthanides and CaTiO₃ is the most well known process to form the solid solution.³⁾ In the solid state reaction process, high temperatures and long reaction times are required to obtain the solid solution because the diffusion of atoms or ions between different phases is generally the rate-limiting step.⁴⁾

Synthesis of oxide powders using exothermic oxidation and reduction reaction between dissolved metal nitrate and fuel in water has been reported.^{5,6)} Generally most of the radioactive wastes elements were treated as a nitrate form. Therefore, if the combustion process which used metal nitrates as reactant materials is applied to immobilize the lanthanide-based radioactive wastes elements, crystalline (solid solutions) immobilizing them are can be easily formed.

During the combustion process, externally initiated redox reaction is self-sustained due to the exothermic reaction. A significant volume of gas evolved during combustion reaction and led to loosely agglomerated particles. The high temperature inherent to the highly exothermic nature of the redox reaction leads to well-crystallized powder in a short time. By using this method, various kinds of single and multi-component oxides with fine and homogeneous crystalline phases could be produced.⁷⁻¹²⁾ Patil et al. reported that Synroc B including

CaTiO₃ perovskite, zirconollite and hollandite, which is the waste free composition proposed for the immobilization of nuclear wastes, could be prepared by the combustion and calcination processes using carbohydrazide and tetraformal trisazine as fuels.¹³⁾

In this study, the combustion process was applied to easily form the solid solution of lanthanides such as La, Gd and Ce doped CaTiO₃. Urea, citric acid, glycine and their mixtures which consist of carboxylic acid group and/or amine group were used as fuels in order to investigate the effect of organic fuel on the combustion reaction. The effects of the type and the composition of fuels on the phase formation were also investigated. Additionally, the sinterability of the synthesized powders was characterized.

II. Experimental Procedures

Ca(NO₃)₂ · 6H₂O (Aldrich), La(NO₃)₃ · 6H₂O (Aldrich), Ce(NO₃)₃ · 6H₂O (Aldrich), Gd(NO₃)₃ · 6H₂O (Aldrich) and TiO(NO₃)₂ · xH₂O were used as source materials of nitrate. Because titanium nitrate was not commercially available, it was prepared from TiCl₄ with NH₄OH and distilled water according to the previous reported procedures.¹⁴⁾ To investigate the effect of fuel type on the combustion reaction, four types of fuels were prepared; urea, citric acid, glycine and the mixture of urea and citric acid. The stoichiometric composition of fuel and nitrate was calculated according to the method of Jain et al.¹⁵⁾ The stoichiometric composition denotes a fuel to metal nitrate ratio at which the fuel can react completely with all of the metal nitrates in the mixture, such that no residual fuel or

nitrate remains in the product material. Lanthanides nitrate with equivalent amounts of up to 50 mol.% of lanthanides doped CaTiO_3 was mixed with $\text{Ca}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{TiO}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$, respectively.

The mixed solution was heated to evaporate water. As soon as the evaporation of water was completed, ignition of the mixture was initiated and spontaneously underwent combustion with exothermic reaction to form lanthanides doped CaTiO_3 powders.

X-ray diffraction analysis was performed on the synthesized powders to confirm the formed phases using CuK_α radiation with 2θ in the range of 20 to 80°. The morphology and the particle size of the synthesized powders were investigated using scanning electron microscopy (SEM: JEOL JSM-5200) and transmission electron microscopy (TEM: JEOL 2000 FX2) with selected area diffraction (SAD) pattern.

The as-synthesized powders were ball-milled for 24 h using zirconia balls in ethanol as a liquid medium. After drying, the powder was uniaxially pressed to obtain a cylindrical pellet with diameter of 10 mm in a steel die followed by cold isostatic pressing with an applied pressure of 200 MPa. The linear shrinkage of the specimens was measured by the dilatometric method. In order to compare the sintering behavior of the combustion synthesized powder with that of the solid state reacted powder, commercial La_2O_3 (Aldrich), CaCO_3 and TiO_2 (Aldrich) powders were reacted at 1000 °C for 2 h and it was pro-

cessed and sintered by the same route to the combustion synthesized powder. Microstructures of the sintered specimens were observed by SEM.

III. Result and Discussion

1. Formation of CaTiO_3 by the combustion process

The type and the composition of fuels used 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 known to be dependent upon the ligand groups of the fuel molecule and the compositional ratio of fuel to nitrates.⁹⁾

The self-sustaining nature of the combustion can be explained as follows. The precursor mixture contains, strong oxidizers, metal nitrate and also contains glycine or citric acid, a readily combustible fuel. On heating the precursor mixture, after evaporating water, nitrate decomposes to release NO_x gas. The gaseous NO_x reacts with the fuel 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

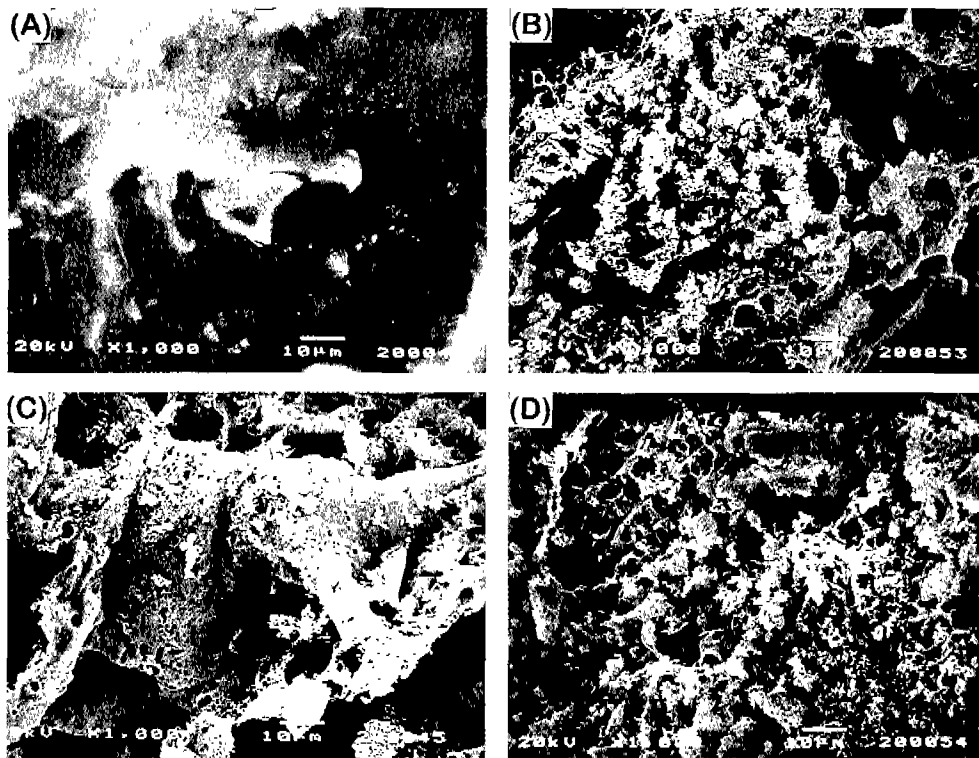


Fig. 1. Scanning electron micrographs of the combustion synthesized CaTiO_3 powders using various fuels; (A) urea, (B) citric acid, (C) glycine and (D) mixture of urea and citric acid.

to react. The reaction process proceeds rapidly and sustainedly until the entire intact zone is consumed. The temperature increase and the volume of gas evolved during the reaction depend on the fuel type, composition and content; in general, a rich or stoichiometric fuel composition results in higher combustion temperature and more gas evolution.

During the synthesis of CaTiO_3 powder by the combustion process, pure glycine or the mixture of urea and citric acid strongly reacted with nitrates, while pure urea brought rare reaction and pure citric acid brought weak reaction without flame and with gas evolution. The microstructures of the synthesized powders using various fuels were observed. Fig. 1 shows the typical microstructures of the synthesized powders. The synthesized CaTiO_3 powders using citric acid ((B) in Fig. 1), glycine ((C) in Fig. 1) and mixture of urea and citric acid ((D) in Fig. 1) had the foamy agglomerated particles while the powders prepared using pure urea ((A) in Fig. 1) had a cluster of aggregates. The porous microstructure of the synthesized powders seemed to be due to the large amount of gas evolution during the combustion reaction. The resulting phases of the combustion reaction with various fuels were confirmed by X-ray diffraction analysis and their results are shown in Fig. 2. When pure glycine or mixture of urea and citric acid with the same composition was used as a fuel, the pure CaTiO_3 phase was obtained. On the other hand, when pure urea was used as a fuel, CaTiO_3 phase was not found but other phases such as $\text{Ca}(\text{NO}_3)_2$, CaCO_3 and TiO_2 (anatase) phase were observed. The reactivity of pure citric acid was lower than that of the mixed fuel or glycine as shown in Fig. 2. That is, to synthesized CaTiO_3

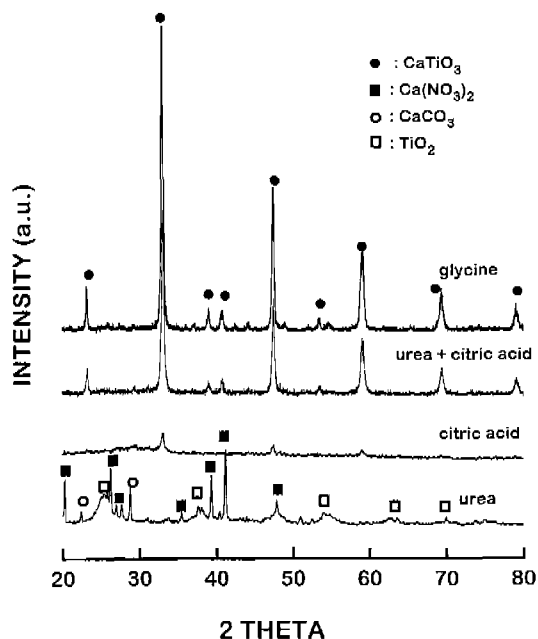


Fig. 2. X-ray diffraction patterns of the combustion synthesized CaTiO_3 powders using various fuels.

powder by combustion reaction, a selection of fuel type (or group) is very important, which means that the reaction is dependent on the reaction groups of fuel as reported by Chick et al.⁵⁾ This is considered to be related to the bonding of groups with metal ions during heating of precursor nitrate solutions. If excess groups without bonding with metal ions are existed in the precursor solution, the combustion reaction seems to be not strong enough to form the crystalline phase. To produce the CaTiO_3 phase, the fuel must possess both the carboxylic acid group and amine group. If a fuel has pure carboxylic acid group or

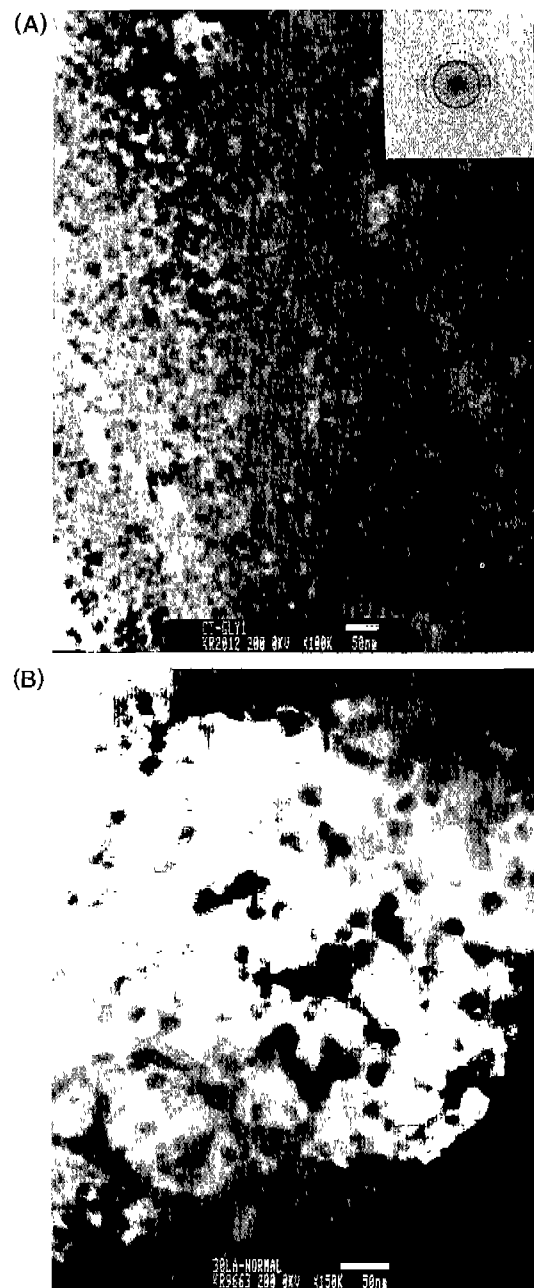


Fig. 3. Transmission electron micrograph with selected area diffraction pattern of the combustion synthesized (A) CaTiO_3 powders and (B) 30 mol.% La doped CaTiO_3 powders.

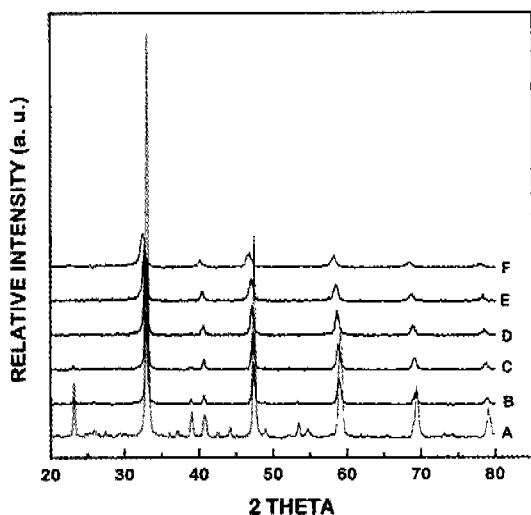


Fig. 4. X-ray diffraction patterns of the combustion synthesized La doped CaTiO_3 powders; (A) pure CaTiO_3 , (B) 5 mol.% La, (C) 10 mol.% La, (D) 20 mol.% La, (E) 30 mol.% La and (F) 50 mol.% La doped CaTiO_3 powders.

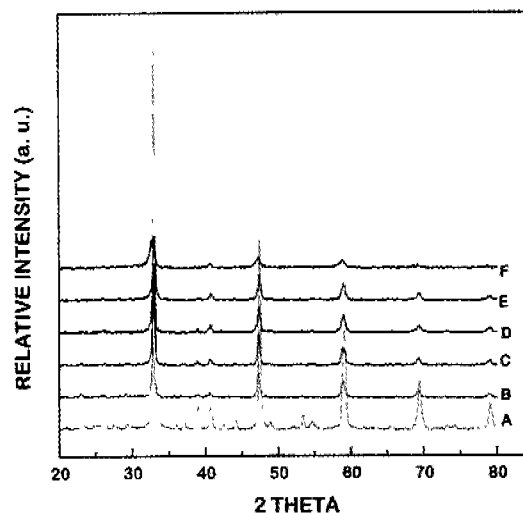


Fig. 6. X-ray diffraction patterns of the combustion synthesized Gd doped CaTiO_3 powders; (A) pure CaTiO_3 , (B) 5 mol.% Gd, (C) 10 mol.% Gd, (D) 20 mol.% Gd, (E) 30 mol.% Gd and (F) 50 mol.% Gd doped CaTiO_3 powders.

pure amine group, the combustion reaction may not generate the heat enough to form the CaTiO_3 phase.

The SAD pattern and the microstructure of as-synthesized powder using glycine observed by TEM are shown in Fig. 3. While the morphology of secondary particles was a porous skeleton (as shown in Fig. 1(C)), 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 the synthesized powder is very fine crystalline.

Considering above results, the CaTiO_3 powder could be easily synthesized by the combustion reaction using fuel

having both of amine group and carboxylic group such as glycine or mixture of urea and citric acid.

2. Formation of solid solution and sinterability of lanthanides doped CaTiO_3

To form the solid solution of CaTiO_3 with lanthanides, the combustion reaction of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ [or $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ or $\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$], $\text{Ca}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{TiO}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ was performed and the crystalline phases in resulting product were analyzed by X-ray diffractometry. Fig. 4, 5 and 6 show X-ray diffraction patterns of the combustion synthesized La or Ce or Gd doped CaTiO_3 powder, respectively. No evidence of the existence of pure lanthanides or second phases was observed at composition of up to 50 mol.% of La or Gd and up to 30 mol.% Ce. It means that solid solution of CaTiO_3 with lanthanides have been formed during the combustion reaction without any calcination step.

CaTiO_3 containing 30 mol.% La powder was also synthesized by solid state reaction of lanthanides, CaCO_3 and TiO_2 at 1000 °C for 2 h to compare the powder characteristics with those of the combustion synthesized powder. The solid state reacted 30 mol.% La doped CaTiO_3 powder shows dense agglomerates (Fig. 7 (B)). Because of a large amount of evolved gas during the combustion reaction, however, the combustion-synthesized powder has a foamy and porous structure as shown in Fig. 7 (A), which is a typical microstructure of the powders prepared by the combustion process.

In Fig. 3(B), The primary particle size and the morphologies of the combustion synthesized 30 mol.% La doped CaTiO_3 powder observed by TEM microstructure were a diameter of 20–30 nm and equiaxed crystalline, which seemed not to be influenced by the addition of the second

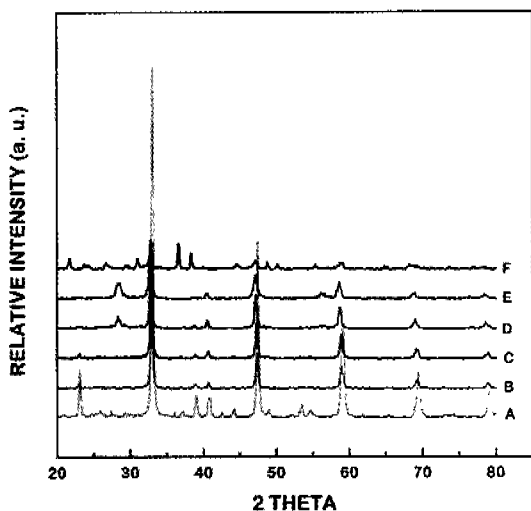


Fig. 5. X-ray diffraction patterns of the combustion synthesized Ce doped CaTiO_3 powders; (A) pure CaTiO_3 , (B) 5 mol.% Ce, (C) 10 mol.% Ce, (D) 20 mol.% Ce, (E) 30 mol.% Ce and (F) 50 mol.% Ce doped CaTiO_3 powders.

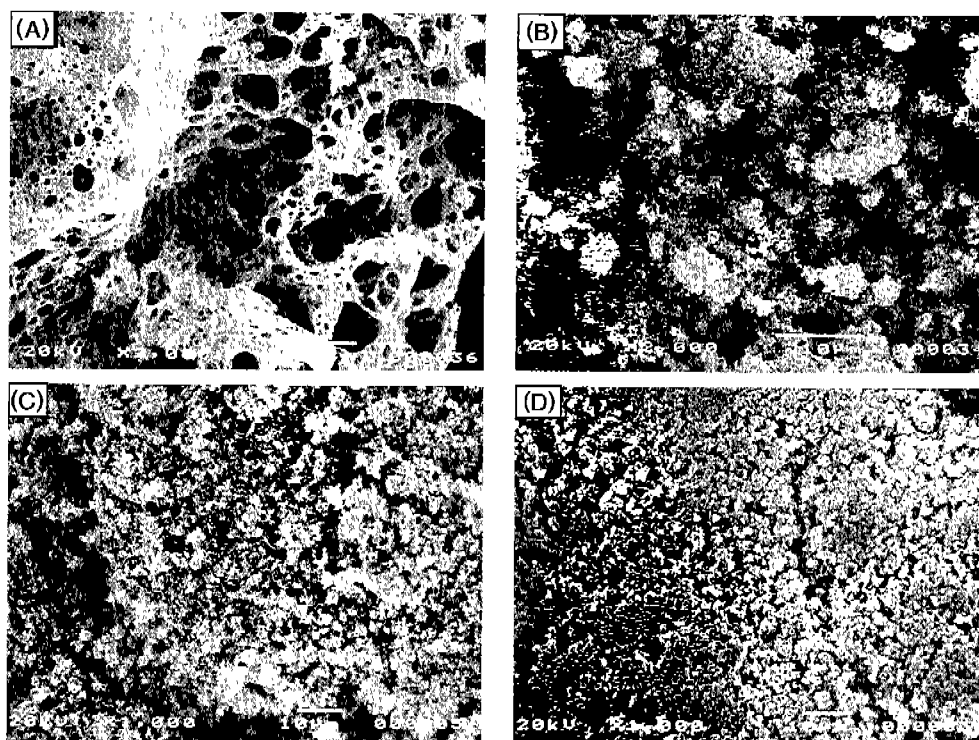


Fig. 7. Scanning electron micrographs of 30 mol.% La doped CaTiO_3 powders prepared by different process; (A) as-combustion synthesized, (B) as-solid state reacted, (C) as-milled for 24 h after combustion synthesis and (D) as-milled for 24 h after solid state reaction.

phases to form the solid solution. The combustion-synthesized and the solid state reacted powders were ball milled for 24 h to break down the agglomerates, respectively. In the case of the combustion-synthesized powder, most of the foamy agglomerates were easily broken down and the individual particles showed equiaxed shape with the size of submicrometer (Fig. 7(C)). In contrast, the solid state reacted powder was hard to mill and showed an irregular shape with larger particle size (Fig. 7 (D)). These differences of the particle sized and the morphologies of the milled powders are expected to result in the different sintering behavior.

In order to compare the sinterability of the powders prepared by the combustion synthesis with that of solid state reacted one, the dilatometric measurements were performed up to 1500 °C for 30 mol.% La doped CaTiO_3 powder. The variations of the linear shrinkage are shown in Fig. 8. The combustion-synthesized powder had a good sinterability showing the linear shrinkage of more than 25% up to 1500 °C, while that of the solid state reacted powder was less than 10% at the same condition. The sintered density of the solid state reacted powder was limited to 3.73 g/cm^3 at 1400 °C for 2 h whereas the combustion-synthesized powder was sintered to a density of 4.19 g/cm^3 at the same sintering temperature and time. Fig. 9 shows the microstructures of the specimen sintered at 1400 °C for 2 h. As already mentioned in the dilatometric analysis, it could be known that the sintering process of the

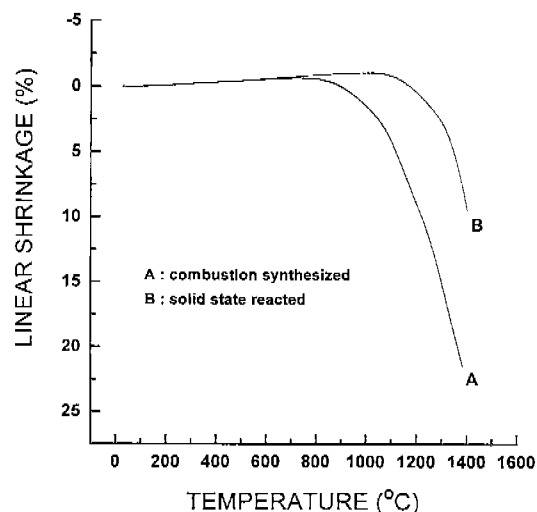


Fig. 8. Linear shrinkage curves of 30 mol.% La doped CaTiO_3 powders prepared by different methods.

specimen using the combustion synthesized powder had been more progressed than that using the solid state reacted powder. The sintered specimen using the combustion-synthesized powder (Fig. 9(A)) showed a large amount of the shrinkage, which resulted in the densification, the change in pore shape and the intragranular fracture mode. On the other hand, only neck growth with a little shrinkage was observed in the specimen using the solid

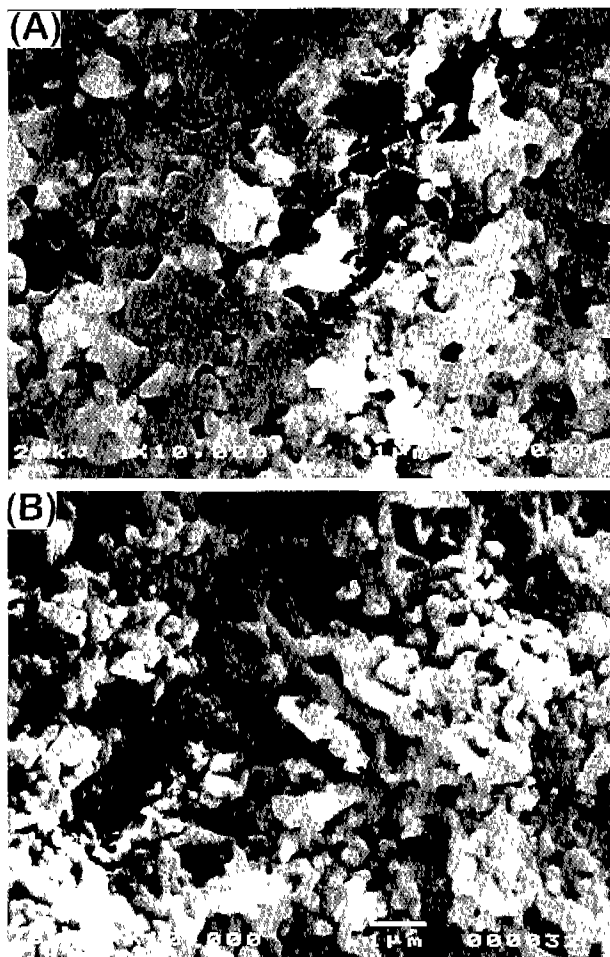


Fig. 9. Microstructures of 30 mol.% La doped CaTiO_3 , prepared by different powder process and sintered at 1400°C for 2 h; (A) combustion reaction and (B) solid state reaction.

state reacted powder (Fig. 9 (B)).

IV. Conclusions

The solid solutions of CaTiO_3 with lanthanides were easily obtained by the combustion process. In this process, up to 50 mol.% of La or Gd and 30 mol.% Ce were formed the solid solution with CaTiO_3 . The combustion synthesized powder had a good sinterability with the linear shrinkage of more than 25% up to 1500°C , while that of the solid state reacted powder was less than 10% at the same condition. The combustion process using nitrates form as starting materials was proven to be a simple approach to prepare a solid solution of CaTiO_3 with lanthanides for immobilizing the lanthanides elements of high level radioactive wastes.

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