

Fabrication of Nano-sized Titanate Powder via a Polymeric Steric Entrapment Route and Planetary Milling Process

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ABSTRACT

Pure and nano-sized TiO_2 and CaTiO_3 powders were fabricated by a polymeric steric entrapment route and planetary milling process. An ethylene glycol was used as a polymeric carrier for the preparation of organic-inorganic precursors. Titanium isopropoxide and calcium nitrate were dissolved in liquid-type ethylene glycol without any precipitation. At the optimum amount of the polymer, the metal cations were dispersed in solution and a homogeneous polymeric network was formed. The dried precursor ceramic gels were turned to porous powders through calcination process. The porous powders were crystallized at low temperatures and the crystalline powders were planetary milled to nano size.

Key words : Titanate powder, Planetary milling, Ethylene glycol, Precursor

1. Introduction

In recent, solution-polymerization technique using PVA (Polyvinyl Alcohol), PEG (Polyethylene Glycol) or EG (Ethylene Glycol) as a polymer carrier has been developed to make easier and high productive soft solution processing.¹⁻⁹⁾ The technique also has an advantage over other sol-gel methods in that it is more simple and cheaper. The PVA ensures the homogeneous distribution of the metal ions in its polymeric network structure and inhibits their segregation and/or precipitation from the solution. Water is able to diffuse through the polymer and stretch it because of the acetate clusters. In the solution, the long chain polymer prevents contact between cations and limits their agglomeration and precipitation. In particular, the amount of polymer and its molecular length can affect the distribution of cations in the solution. The PVA process also produces carbonaceous material that gives heat through its combustion, so that fine and single-phase powders can be formed at a relatively low external temperature.^{1-5, 8, 10-11)}

The method used in this experiment is based on the steric entrapment using Ethylene Glycol (EG, $\text{HOCH}_2\text{CH}_2\text{OH}$), as an organic carrier. The PVA method only works with systems that are water soluble. However, by using only the polymerizing agent this process can be extended to chemicals that decompose in water, such as titanium isopropoxide. In particular, the ethylene glycol can act as an effective solvent for wet chemical synthesis of titanate powder because water-soluble titanium salt is not available in commercial.^{12,13)} The polymerization agent, ethylene glycol in this method, acts to capture the metal ions through a

polymerization-complexation mechanism like the PVA method. This serves to decrease the mobility of metal ions and constrain the system to prevent precipitation of cation species and agglomeration. It involves mechanical, steric entrapment, and not just/necessarily chemical chelation.^{14,15)} At the optimum amount of polymer, the metal ions are dispersed in solution and a homogeneous polymeric network is formed. Titanium isopropoxide is not soluble in water, so other water soluble chemical routes such as sol gel methods and PVA methods can not be used with the chemical. BaTiO_3 and Ba_2TiO_4 powders have been successfully synthesized by the ethylene glycol method.¹²⁾

In this study, as one and two component titanate powders, TiO_2 and CaTiO_3 powders were prepared by the ethylene glycol method, and the effects of polymer content on crystallization and powder morphology were examined. In addition, synthesized, porous powders were planetary milled to break agglomeration and to reduce particle size. The effects of planetary milling on porous powder were also examined.

2. Experimental

2.1. Powder Synthesis

Titanium (IV) isopropoxide ($\text{Ti}(\text{OC}_3\text{H}_7)_4$, reagent grade, Alfa Aesar Chem. Co., Ward Hill, MA) or titanium (IV) isopropoxide and calcium nitrate ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, reagent grade, Aldrich Chem. Co., Milwaukee, WI) were dissolved in stoichiometric proportions in liquid-type ethylene glycol (Fisher Chemical, FW:62.07, Fair Lawn, NJ). The amount of ethylene glycol was calculated using a ratio of total weight of metal ions from cation sources to weight of ethylene glycol. Several ratios were tried to each powder for examination of the effect of ethylene glycol amount. The transparent solutions were then allowed to gel for 48 h in a

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drying oven at 80°C. The dried gels were then calcined at various temperatures. The calcined and crystallized powders were planetary milled with ϕ 5 mm zirconia ball media for 20 h. Isopropyl alcohol was used as a solvent for wet milling and milling speed was 200 rpm.

2.2. Characterization

The crystallization behavior of the gel-type powders was examined as a function of ethylene glycol content, using a X-ray diffractometer (Dmax 2200, Rigaku/USA, Danvers, MA) with $\text{CuK}\alpha$ radiation (40 kV, 30 mA). The measurements were made with a scanning speed of 10°C/min and a sampling interval of 0.02°C at room temperature. Five-point BET analysis from nitrogen gas absorption (Model Autosorb-1, Boynton Beach, FL) was used to obtain the BET specific surface areas of the porous, crystalline powders and planetary milled powders. The morphologies of the porous, crystallized powders and planetary milled powders were examined by Scanning Electron Microscopy, (SEM, Hitachi S3500N, Hitachi, Japan) and Transmitted Electron Microscopy (TEM, Hitachi H-600, Hitachi, Japan). The planetary milled powders were dispersed in alcohol by ultrasonicator

for TEM examination. The average particle size of the planetary milled powders were monitored by electrophoretic light scattering spectrophotometer (ELS-8000, Photal, Tokyo, Japan). The pyrolysis and decomposition behavior of the organic/inorganic precursors were monitored by simultaneous Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA) (DSC/TGA, Model STA 409, Netzsch GmbH, Selb, Germany) up to 1200°C, at a heating rate of 20°C/min, in an air atmosphere.

3. Results and Discussion

After dissolving titanium isopropoxide and calcium nitrate in ethylene glycol, the solution was pale yellow and transparent. During the drying process at 80°C, the transparent sol turned to a yellow-colored, soft solid gel.

3.1. TiO_2 Powder

Fig. 1 shows the XRD results of the calcined TiO_2 powders at different ethylene glycol content. At 800°C, all powders were fully crystallized to rutile phase except the powder prepared by 1:1 ratio. It is speculated that the not enough

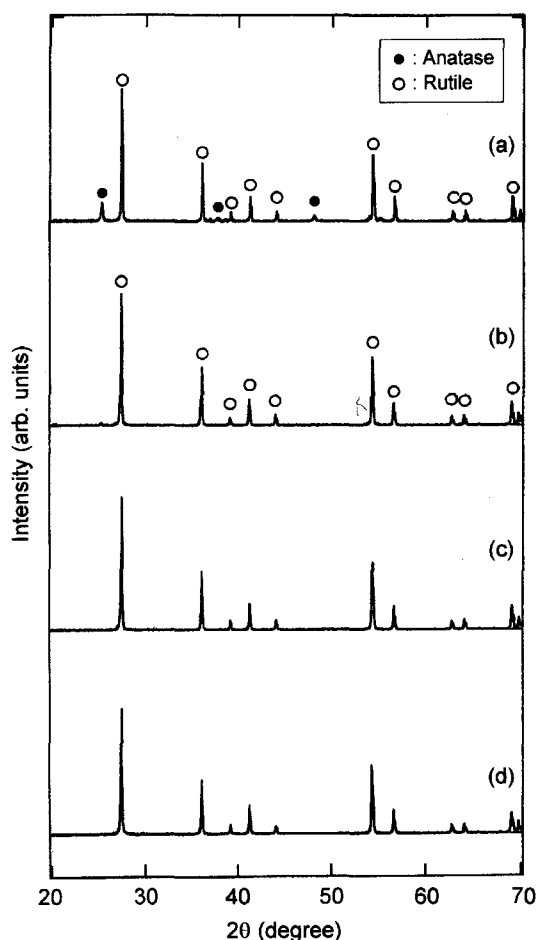


Fig. 1. XRD patterns of synthesized TiO_2 powder calcined at 800°C for 1 h. Ratio of weight of metal ions from cation source to weight of ethylene glycol of (a) 1:1, (b) 1:3, (c) 1:5 and (d) 1:7.

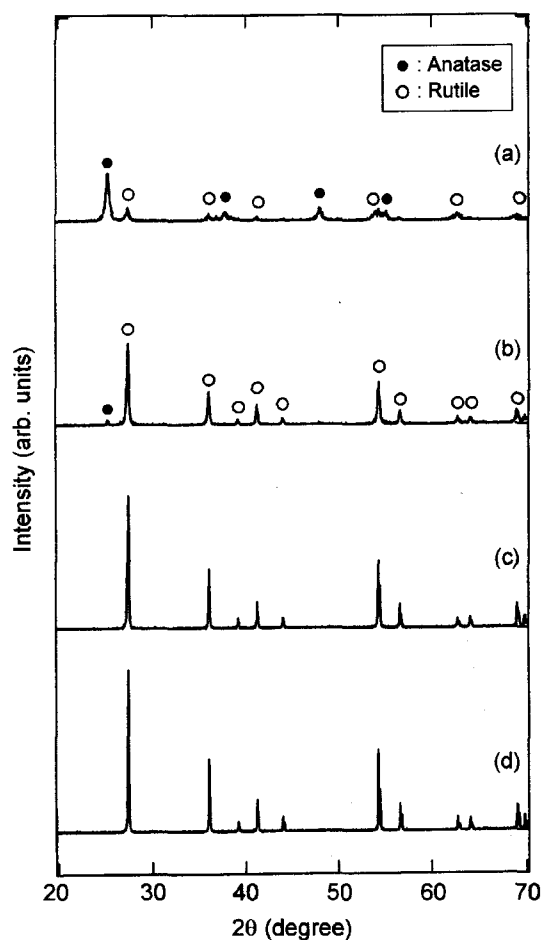


Fig. 2. XRD patterns of synthesized TiO_2 powder, derived from ethylene glycol content of 1:5 ratio, calcined at (a) 500°C, (b) 600°C, (c) 800°C and (d) 1000°C for 1 h.

polymer caused inhomogeneity in the precursor due to deficiency of steric entrapment in the polymer chain and metallic cation system. This resulted in hard agglomerated powder after calcination and higher temperature for crystallization to rutile. In the case of the powder from 1:7 ratio, the crystallization behavior was consistent with 1:3 and 1:5 cases. However, the excess amount of EG made longer burn-out time and waste of polymer. The crystallization behavior for the powder from 1:5 ratio is shown in Fig. 2. At 600°C, the main phase was rutile having some anatase phase. In general, the anatase phase, low temperature form, transforms to the rutile form, high temperature form, at about 800°C through rearrangement transformation in the TiO_2 polymorphism.¹⁶⁾ The crystallization to rutile at about 200°C lower temperature than the normal case is due to low activation energy for crystallization caused by the fine crystalline size and low energy barrier of nuclei creation.¹⁷⁾ In the XRD patterns obtained at 800°C and 1000°C, the stable and pure rutile phase was detected.

Fig. 3 shows the result of planetary milling of the crystalline TiO_2 powder. At the first beginning of 5 h milling, the powder size was significantly decreased to 2.1 μm . In the ethylene glycol method, the pyrolysis and oxidation of the polymer carrier, and removal of free organics from metal ion source made release of various gases, such as CO , CO_2 and N_xO_y during calcination.^{4,12)} It resulted in soft and porous powder structure, and maximized the milling effect. Finally, planetary milled TiO_2 powder was ground to ultra-fine size, which has a BET specific surface area of about 38 m^2/g , by 20 h milling.

The powder morphologies of the crystalline and planetary milled powders are shown in Fig. 4. The SEM micrograph of the TiO_2 powder prepared from the 1:5 ratio presented soft, porous and large agglomerated particles. In the TEM micrograph of the 20 h planetary milled powder, significantly reduced particles of about 100-50 nm in size were observed.

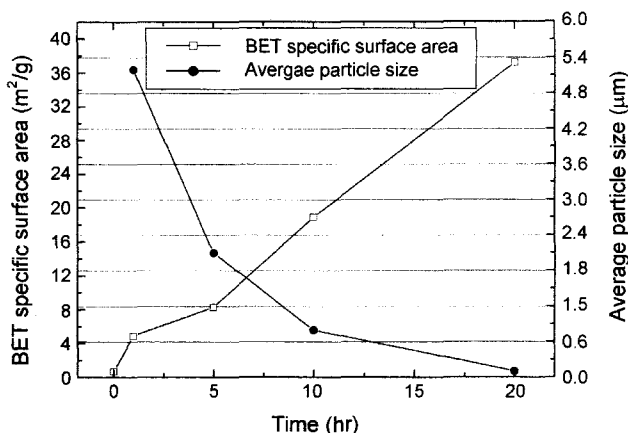


Fig. 3. BET specific surface areas and average particle sizes of planetary milled TiO_2 powder (1:5 ratio and calcined at 600°C) as a function of milling time.

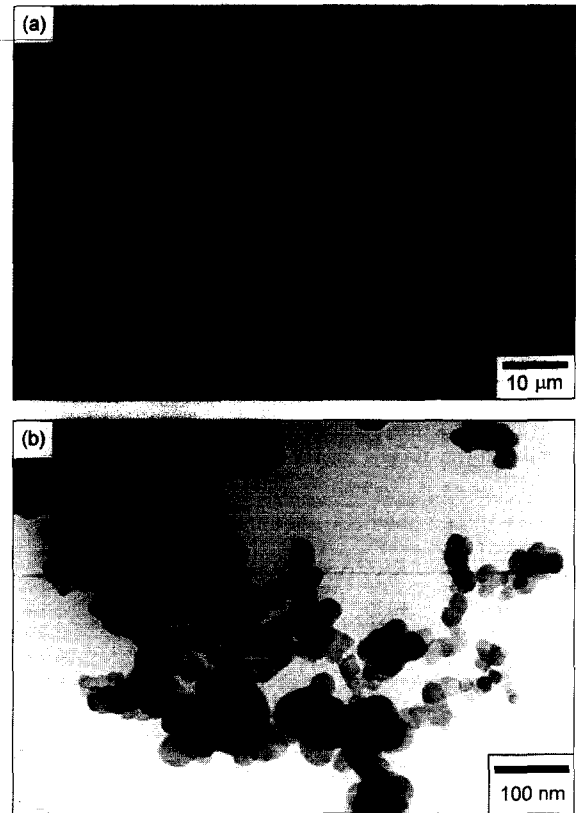


Fig. 4. (a) SEM micrograph of TiO_2 powder as calcined at 600°C and (b) TEM micrograph of TiO_2 powder planetary milled for 20 h.

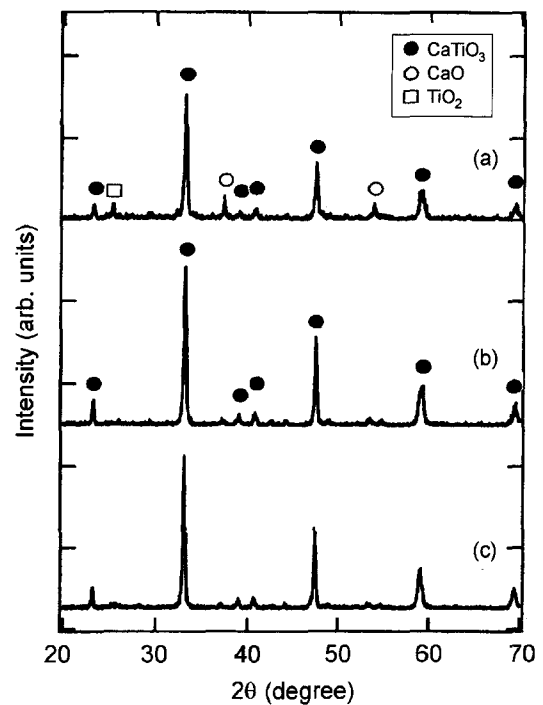


Fig. 5. XRD patterns of synthesized CaTiO_3 powder calcined at 800°C for 1 h. Ratio of weight of metal ions from cation source to weight of ethylene glycol of (a) 1:1, (b) 1:5 and (c) 1:7.

Table 1. Summary of CaTiO_3 Powder Prepared by Ethylene Glycol Method

Amount of EG [§]	Calcination temp. (°C)	Crystallization temp. (°C)	Specific surface area [§] (m ² /g)
1:1	600	950	10.6
1:5	600	800	19.7
1:7	650	800	21.2

[§]total weight of metal ions from cation sources : weight of ethylene glycol

[§]crystalline powder

3.2. CaTiO_3 Powder

Fig. 5 shows the crystallization behavior of the CaTiO_3 precursors at different ethylene glycol content. Like the result of TiO_2 , all powders were fully crystallized to CaTiO_3 at 800°C, except the powder from 1:1 ratio. In the 1:1 ratio, free CaO and TiO_2 were observed. It may be also because of the insufficient ethylene glycol content. This resulted in agglomerated metal ions in solution and residual free CaO and TiO_2 after heating at 800°C. In case of the 1:7 ratio powder, the crystallization behavior was consistent with 1:5 case.

The summary of CaTiO_3 powders prepared by different ethylene glycol content are listed in Table 1. The powder derived from 1:1 ratio crystallized to CaTiO_3 at 950°C without free CaO and TiO_2 phases. In the other two cases, only CaTiO_3 phase was observed at 800°C. The polymer content also affected the surface area of crystallized powders. The BET measurement of crystalline powder prepared from 1:1 ratio had a lowest specific surface area of 10.6 m²/g in comparison with the 1:5 and 1:7 cases. These results mean that the insufficient polymer caused inhomogeneity in the precursor as a result of agglomeration of the metal cations. This resulted in increase of crystallization temperature and low specific surface area caused by the serious agglomeration.

The CaTiO_3 precursors showed a distinct calcination behavior. The crisp, dried precursor gels were quite hydrophilic and had a vigorous exothermic reaction on continuous heating. This reaction was occurred in all the precursors, regardless the ethylene glycol content. After the reaction, the precursor gel changed to a solid like fluffy dust, having a

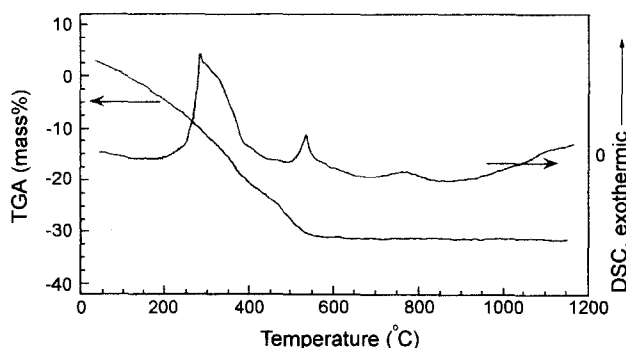


Fig. 6. TGA/DSC curves for the CaTiO_3 precursor made by the EG method (ethylene glycol content was 1:5).

volume expansion. In the precursor derived from 1:5 ratio, the thermal analysis plot is shown in Fig. 6. In the TGA curve, the mass loss occurred in the range of 100°C ~ 550°C indicated the release of the N_xO_y gases from the nitrate salt and burn out of the ethylene glycol.¹²⁾ The DSC spectrum showed two exothermic peaks at about 280°C and 540°C. The first exothermic peak was caused by decomposition of the metal salts and degradation of the polymeric structure by pyrolysis of ethylene glycol, which is then followed by oxidation of residual carbon. The second peak at 550°C means the oxidation of residual carbon. The vigorous exothermic reaction involving volume expansion was also occurred at about 250°C ~ 300°C. It is speculated that the exothermic peak by the explosive oxidation reaction was overlapped with the first exothermic peak at 280°C and the reaction

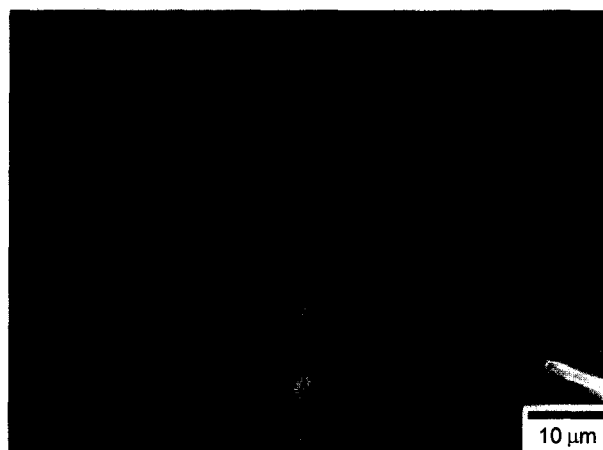


Fig. 7. SEM micrograph of crystalline CaTiO_3 powder (ethylene glycol content was 1:5).

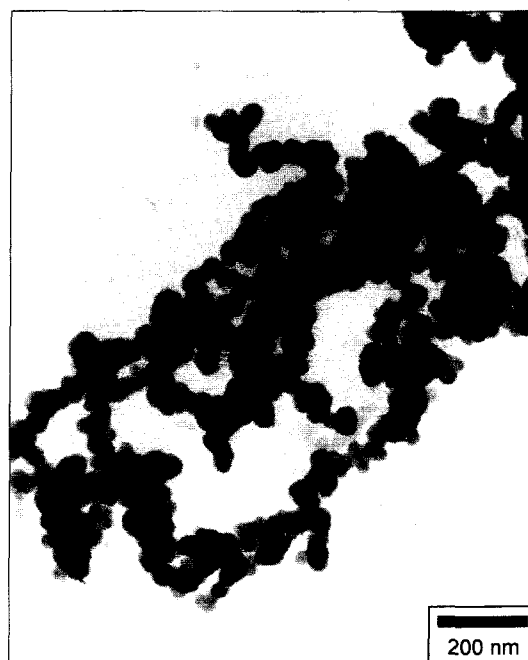


Fig. 8. TEM micrograph of nano-sized CaTiO_3 powder planetary milled for 20 h.

was caused by oxidation of unstable Ca salt form.⁸⁾ The explosive oxidation reaction will be examined in more detail by FTIR study¹⁸⁾ in the near future.

The powder morphologies of the porous crystalline and planetary milled powders are shown in Fig. 7 and Fig. 8. The SEM micrograph of the CaTiO₃ powder prepared from the 1:5 ratio revealed soft, porous and agglomerated particles. In the TEM micrograph of the 20 h planetary milled powder, significantly reduced particles of about 60-50 nm in size were observed.

4. Conclusion

TiO₂ and CaTiO₃ powders were successfully synthesized by ethylene glycol method employing water-insoluble chemicals as a source of titanium ions. The simple, processable precursors could be synthesized on steric entrapment of cations by ethylene glycol polymer to avoid selective precipitation and produces homogeneous mixing on a molecular scale. In the calcination process, polymer decomposition and explosive reaction caused by oxidation of calcium ions resulted in soft and porous crystalline powders. The porous powders were ground to nano size by powerful planetary milling technique. The ethylene glycol method followed by planetary milling process is expected for making nano-sized titanate powders because of its merits, such as cheap and simple process, and easy control of porous, stable crystalline form and particle size by effective milling.

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REFERENCES

1. M. A. Gülgün and W. M. Kriven, "A Simple Solution-polymerization Route for Oxide Powder Synthesis," pp. 57-66 in *Ceramic Transactions*, Vol. 62. Ed. by J. J. Kingsley, C. H. Schilling and J. H. Adair, American Ceramics Society, Westerville, 1995.
2. M. A. Gülgün, M. H. Nguyen and W. M. Kriven, "Polymerized Organic-inorganic Synthesis of Mixed Oxides," *J. Am. Ceram. Soc.*, **82** [3] 556-60 (1999).
3. M. H. Nguyen, S. J. Lee and W. M. Kriven, "Synthesis via a Polymeric Steric Entrapment Precursor Route," *J. Mater. Res.*, **14** [8] 3417-26 (1999).
4. M. H. Nguyen, "A New Polymer Route to the Synthesis of Mixed Oxide Ceramics," in M.S. Thesis, University of Illinois at Urbana-champaign, Urbana, 1997.
5. S. J. Lee and W. M. Kriven, "Crystallization and Densification of Nano-size, Amorphous Cordierite Powder Prepared by a PVA Solution-polymerization Route," *J. Am. Ceram. Soc.*, **81** [10] 2605-12 (1998).
6. I. Nettleship, J. L. Shull and W. M. Kriven, "Chemical Preparation and Phase Stability of Ca₂SiO₄ and Sr₂SiO₄ Powders," *J. Euro. Ceram. Soc.*, **2** 291-98 (1993).
7. M. A. Gülgün, O. O. Popoola and W. M. Kriven, "Chemical Synthesis and Characterization of Calcium Aluminate Powders," *J. Am. Ceram. Soc.*, **77** [2] 531-39 (1994).
8. S. J. Lee, E. A. Benson and W. M. Kriven, "Preparation of Portland Cement Components by Poly (vinyl alcohol) Solution Polymerization," *J. Am. Ceram. Soc.*, **82** [8] 2049-55 (1999).
9. S. J. Lee and W. M. Kriven, "A Submicron Scale Duplex Zirconia and Alumina Composite by Polymer Complexation Processing," *Ceram. Eng. Sci. Proc.*, **20** [3] 69-76 (1999).
10. P. Praminik and A. Pathak, "A New Chemical Route for the Preparation of Fine Particles of Mixed Oxide Systems," *Mater. Sci. Bull.*, **17** [6] 967-75 (1994).
11. D. A. Fumo, M. R. Morelli and A. M. Segadaes, "Combustion Synthesis of Calcium Aluminates," *Mater. Res. Bull.*, **31** [10] 1243-55 (1996).
12. S. J. Lee, M. D. Biegalski and W. M. Kriven, "Powder Synthesis of Barium Titanate and Barium Orthotitanate via an Ethylene Glycol Complexation Polymerization Route," *J. Mater. Sci.*, **14** [7] 3001-06 (1999).
13. C. H. Jung, J. Y. Park, M. Y. Lee, S. J. Oh, H. Y. Kim and G. W. Hong, "Synthesis of Lanthanides Doped CaTiO₃ Powder by the Combustion Process," *Kor. J. Ceram.*, **6** [1] 47-52 (2000).
14. M. Pechini, "Method of Preparing Lead and Alkaline-earth Titanates and Niobates and Coating Method Using the Same to Form a Capacitor," U.S. Pat., No., 3 330 697, July 11, 1967.
15. L. W. Tai, H. U. Anderson and P. A. Lessing, "Mixed-cation Oxide Powders via Resin Intermediates Derived from a Water-soluble Polymer," *J. Am. Ceram. Soc.*, **75** [12] 3490-94 (1992).
16. K. Kiss, J. Madger, M. S. Vukasovich and R. J. Lockhart, "Ferroelectric of Ultrafine Particle Size: I. Synthesis of Titanate Powders of Ultrafine Particle Size," *J. Am. Ceram. Soc.*, **49** [6] 291-94 (1996).
17. M. J. Lee, H. Kim, C. T. Lee and B. H. Choi, "Studies on Preparation of TiO₂ Powder with High Purity and Fine Particle A Study of High Purifying (I)(in Kor.)," *J. Kor. Ceram. Soc.*, **37** [10] 933-37 (2000).
18. B. M. Lee, D. Y. Shin and S. M. Han, "Synthesis of Hydrous TiO₂ Powder by Dropping Precipitant Method and Photocatalytic Properties(in Kor.)," *J. Kor. Ceram. Soc.*, **37** [4] 308-13 (2000).