

Preparation of Fine Ceramic Powders by Direct-Wet and Hydrothermal Process

Kyung-Hee Lee and Byung-Ha Lee

Dept. of Inorganic Materials Engineering
Myung Ji University

Since it is necessary to make good performance and reliable ceramic materials for practical application specially in the electro ceramic field, the reproducible manufacturing processes have to be established. For this reason the forming and sintering process of selected powder are of course important. Because the powder characterization can determine final product's properties, the powder property characterization is the most critical.

In this study we have examined the direct-wet process and hydrothermal process which can be applied to prepare high purity and ultra-fine powder.

We applied the direct-wet process for the preparation of BaTiO_3 , SrTiO_3 , and $(\text{Ba-Sr})\text{TiO}_3$ of perovskite structure which are remarkable as high dielectric and semi-conducting materials. The main advantage of direct-wet process is that various powders can be easily synthesized in water solution at the temperature range from 20°C to 90°C with good control of particle size distribution.

Another characteristic of this process is that the desired materials can be made at low temperature and needs not to synthesize metallic alkoxide like sol-gel process. In this process selected soluble metal salts are solved into a certain pH alkaline water solution to react for the given period of time. (Fig. 1) BaTiO_3 powder (Fig. 2), SrTiO_3 powder (Fig. 3) and $(\text{Ba, Sr})\text{TiO}_3$ powder (Fig. 4) were synthesized by this method at our laboratory. To study the reaction mechanism of this synthesis, SrTiO_3 case was selected and tested through the method shown in Fig. 5. Judging from the test results, followings are concluded.

Table 1. Chemical composition of $\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$

Starting materials System	$\text{Pb}(\text{NO}_3)_2$	TiCl_4	$\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$	PbO	TiO_2
1	1	0.48	0.52	.	.
2	.	0.48	0.52	1	.
3	1	0.48	.	.	0.52
4	.	0.48	.	1	0.52

1) About 40% noncrystalline SrTiO_3 coexists with about 60% crystalline SrTiO_3 in the final products which was prepared at pH 13.8 by this method. In this case, Ti-O infrared absorption of noncrystalline SrTiO_3 in FT-IR appeared at 1630cm^{-1} and those of Sr-Ti-O appeared at 1512cm^{-1} , 1370cm^{-1} and 1057cm^{-1} (Fig. 6)

2) Above pH13 crystalline SrTiO_3 was formed and noncrystalline SrTiO_3 was formed at the pH higher than 7. This coincides with the neutral point of reactants by KOH solution. Noncrystalline SrTiO_3 which was formed over pH 7 was crystallized by calcination with crystallizing temperature of 370°C .

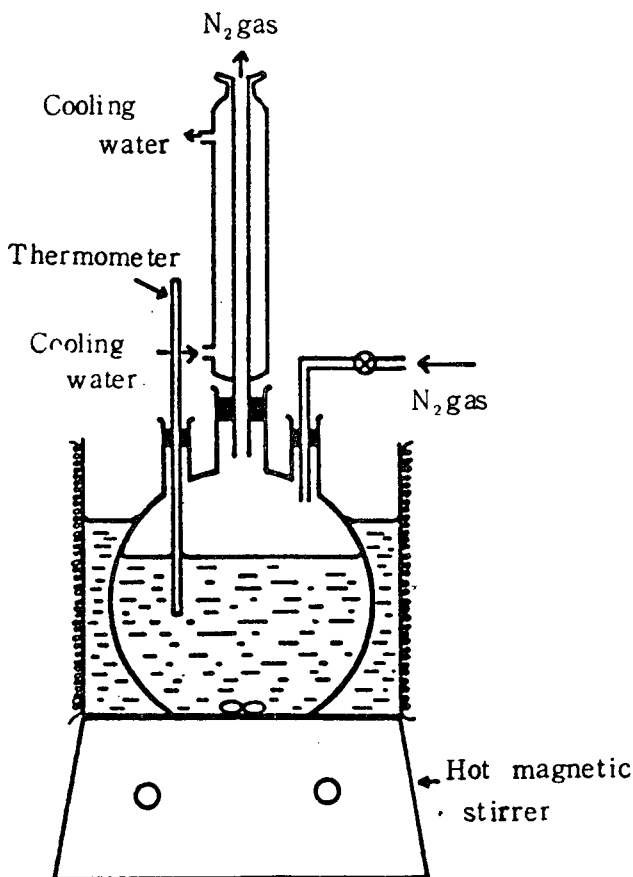


Fig. 1. Preparation of BaTiO_3 , SrTiO_3 and $(\text{Ba,Sr})\text{TiO}_3$ from aqueous solution.

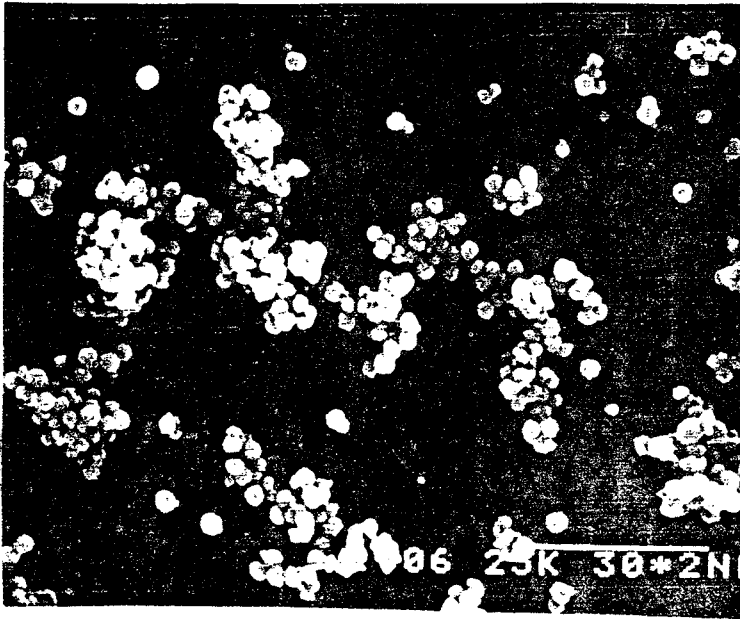


Fig. 2. SEM Microphotographs of BaTiO₃ powders prepared at 90°C by Direct-Wet process.

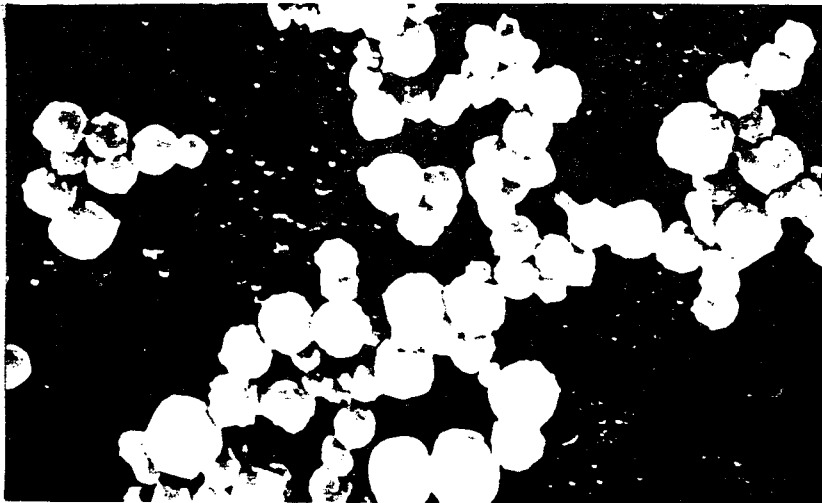


Fig. 3. SEM Microphotographs of SrTiO₃ powder prepared at 60°C by Direct-Wet process.

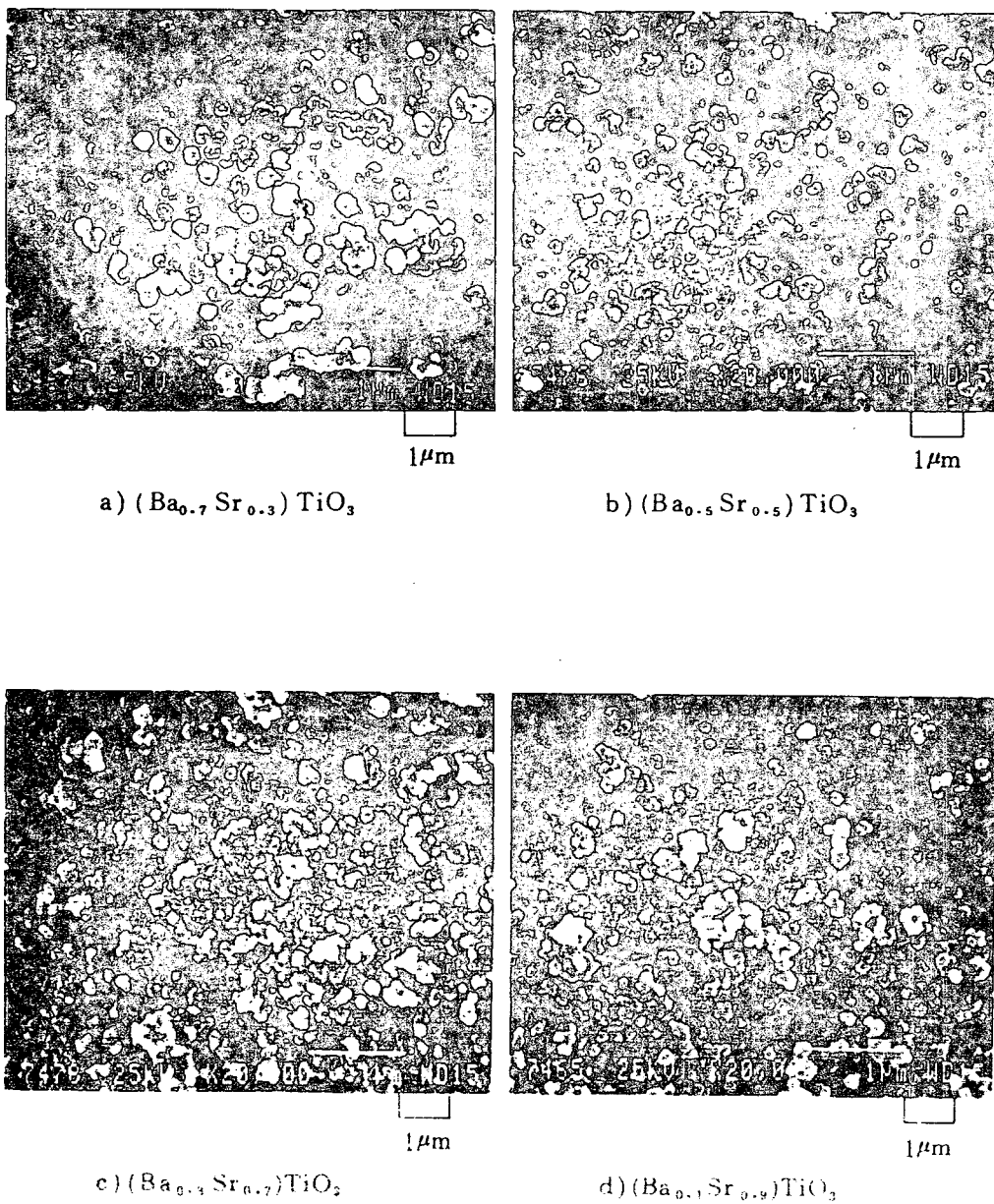


Fig. 4. SEM Microphotographs (Ba,Sr)TiO₃ powder at 90°C by Direct-Wet process.

3) Crystallization of noncrystalline SrTiO₃ increases its bonding energy and weakens the absorption vibration spectra, such as 1630cm⁻¹, 1512cm⁻¹ and 1057cm⁻¹ were almost fades out and the absorption spectrum of crystalline SrTiO₃ bonding, 578cm⁻¹, becomes distinctive.

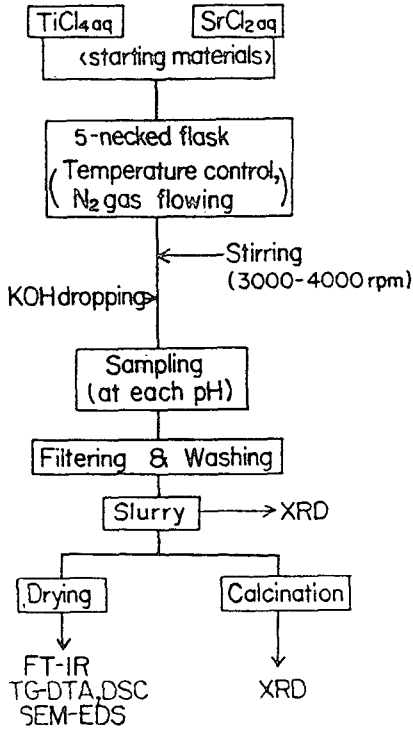


Fig. 5. Schematic diagram of reaction process for SrTiO₃ synthesis.

At our laboratory Ba-ferrite (Fig. 7), Sr-ferrite (Fig. 8) and Pb (Zr_{0.52}Ti_{0.48})O₃ powders (Fig. 9) were prepared by hydrothermal synthesis. Among them PZT powder synthesis is described hereinafter. Using soluble salts such as Pb(NO₃)₂, TiCl₄ and ZrOCl₂·8H₂O along with necessary oxide such as PbO and TiO₂ as starting materials, PZT powder was hydrothermally synthesized at the temperature range between 150°C and 200°C. Starting materials were classified into four systems as shown in Table 1.

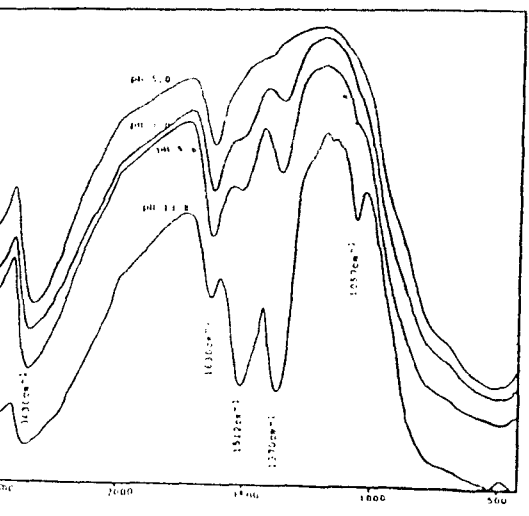
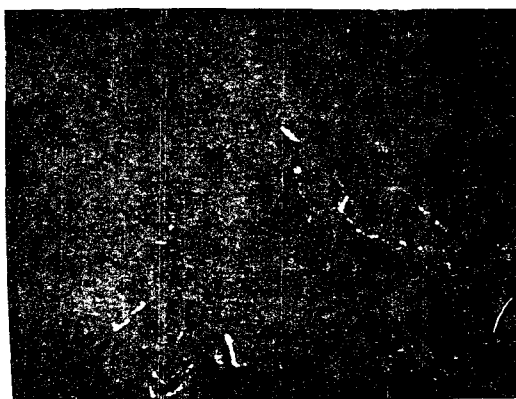


Fig. 6. FT-IR spectra of samples with the variation of pH (Dried at 105°C, 24hrs)

Fig. 7. SEM Microphotographs of Ba-ferrite powders prepared at 200°C by hydrothermal process.



Fig. 8. SEM Microphotographs of Sr-ferrite powders prepared at 250°C by hydrothermal process.



(x10.000)

Fig. 9. SEM Microphotographs of Pb (Zr_{0.52}Ti_{0.48})O₃ powder prepared at 150°C by hydrothermal process.

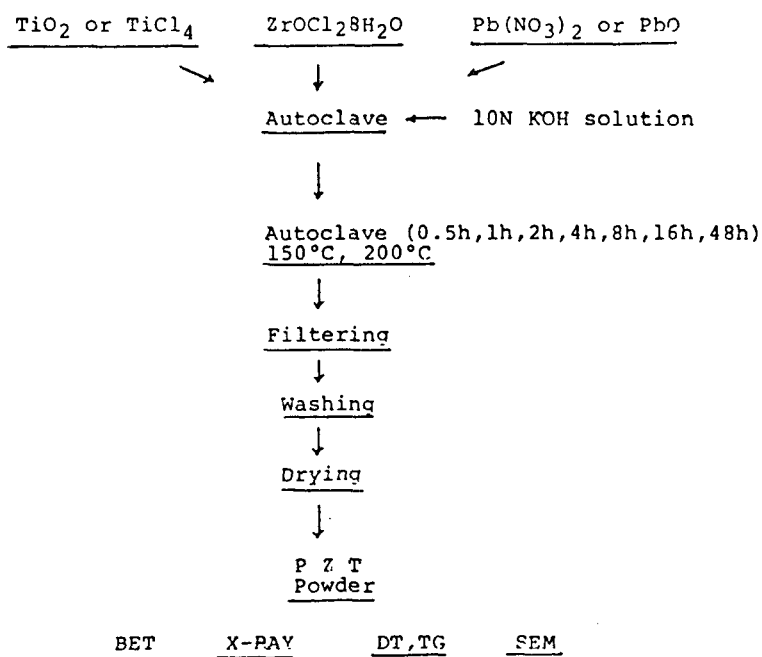


Fig. 10. Flow sheet for pzt powder preparation.

The result showed that activity by alkali was decreased in the sequence of $\text{Pb}(\text{NO}_3)_2$, TiCl_4 , $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$, PbO , TiO_2 and ZrO_2 . Using the first three soluble salts, PZT powder was synthesized at 150°C in 1 hr. (Fig. 11). The SEM photograph of this powder is shown in Fig. 9. In $\text{PbO-TiCl}_4\text{-ZrOCl}_2$ system, PZT powder was synthesized at 150°C in 8 hrs, and SEM photograph is shown in Fig. 12. In $\text{Pb}(\text{NO}_3)_2\text{-TiO}_2\text{-ZrOCl}_2$ system, PZT powder was synthesized at 150°C in 16 hrs (Fig. 12), whereas in $\text{PbO-TiO}_2\text{-ZrOCl}_2$ system, the powder was synthesized at 200°C in 8 hrs. The powders synthesized from 1 and 2 showed typical hexahedral PZT crystals and them from system 3 and 4 showed not clear shape and size but agglomerates of fine particles. It can be said that in system 1 and 2 PZT crystal is formed through intermediate PbO solid solution whereas in system 3 and 4 PZT crystal is formed directly without any intermediate.

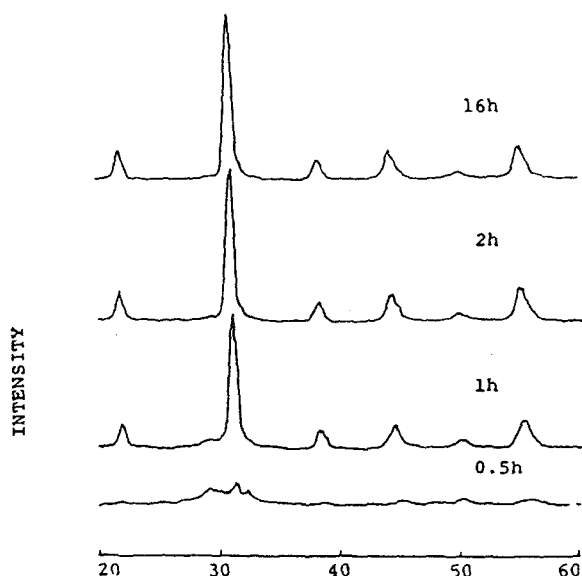
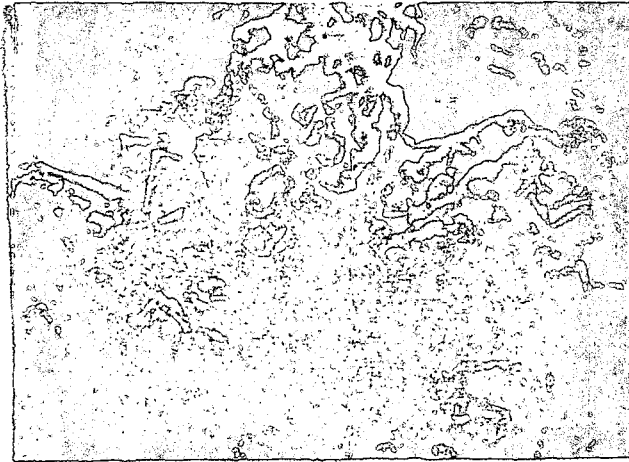


Fig. 11. X-ray diffraction pattern of PZT powder prepared various processing time system $\text{Pb}(\text{NO}_3)_2$, TiCl_4 , $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ and 10N KOH reaction temperature 150°C in autoclave.

It was found that the higher synthesis temperature, the smaller grain size was formed and, at a certain temperature, the longer reaction time, the larger grain size was obtained.

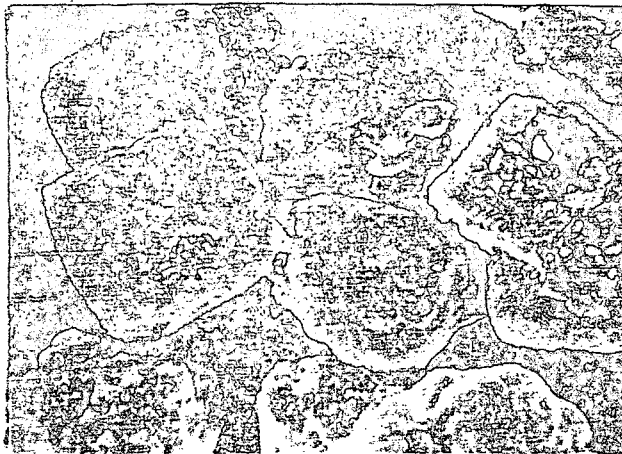
Finally it is concluded that the direct-wet process and hydrothermal synthesis can be effectively applied to prepare high pure and fine powders with controlled particle size distributions at low temperature.

a)



(x10,000)

b)



(x10,000)

Fig. 12. SEM Microphotographs of $\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$ powder prepared at 150 C by hydrothermal process

a) $\text{PbO-TiCl}_4\text{-ZrOCl}_2$ system.

b) $\text{Pb}(\text{NO}_3)_2\text{-TiO}_2\text{-ZrOCl}_2$ system.