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Hydrothermal synthesis of $PbTiO_3$ oxides with perovskite structure

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Abstract The preparation of $PbTiO_3$ powder was carried out using the oxide starting material by hydrothermal method. The powder of a crystalline phase with perovskite structure was synthesized. The optimum conditions for the preparation of powder were as follows; hydrothermal solvent; 8M-KOH or 8M-NaOH, reaction temperature; 250~270°C, run time; 10 h. The shape of synthesized powders were well developed crystalline faces with specific surface area of about 2.3 m^2/g in KOH solution and about 5.0 m^2/g in NaOH solution. The cell parameters of powder were a = 3.90 Å, c = 4.14 Å and cell volume was 57.30 $Å^3$. The cell ratio (c/a) of powder was the same as the theoretical ratio with c/a = 1.06 and the phase transition temperature(T_C) of the powders was about 470°C.

Key words Hydrothermal, $PbTiO_3$, Powder synthesis

1. Introduction

$PbTiO_3$ with perovskite structure has low dielectric constant, high Curie point anisotropy in electro-mechanical coupling constant and high pyroelectric constant [1]. However, $PbTiO_3$ with perovskite structure has bad sinterability and requires high electric field at high temperature for good electro-mechanical coupling constant. In order to solve this problem, effects of additives in $PbTiO_3$ with perovskite structure in solid state reaction has been conducted [2, 3]. As a result, additions of La_2O_3 and MnO_2, and part substitution of Pb with alkali-earth ions have been reported to be effective in improving sintering property and in lowering necessary electric field [4, 5].

The dielectric and piezoelectric properties of $PbTiO_3$ ceramics depends on the composition, particle size distribution, and microstructure. So, new synthesis method of $PbTiO_3$ ceramics has been studied to control the composition, particle size distribution, and microstructure. In general, $PbTiO_3$ has been synthesized using solid state reaction, sol-gel process [6, 7], and co-precipitation process [8, 9]. Among them, sol-gel method is popular due to the easy control of particle size distribution during $PbTiO_3$ synthesis. However, sol-gel method and co-precipitation method needs heat treatment at high temperature over 500°C in order to produce $PbTiO_3$ with perovskite structure.

Recently synthesis of $PbTiO_3$ with perovskite structure by hydrothermal method has been studied a lot because the synthesis of $PbTiO_3$ by this method needs no heat treatment and can control the composition and particle size distribution. Also the morphology of particles during $PbTiO_3$ synthesis depending on the hydrothermal conditions. Kanebo and Imoto has studied the synthesis of $PbTiO_3$ with perovskite structure by hydrothermal method at high temperature and high pressure conditions [10]. Several researchers have studied the synthesis of $PbTiO_3$ with perovskite structure by hydrothermal method at lower temperature [11]. However, they synthesized $PbTiO_3$ powders with perovskite structure by sol-gel method or co-precipitation method at first and treated it hydrothermally in water after that.

The objective of this study is to obtain the stoichiometric $PbTiO_3$ powder with perovskite structure by hydrothermal method using PbO and TiO_2 as starting materials. Optimam solvent and synthesis conditions were studied in order to obtain stoichiometric $PbTiO_3$ powder with perovskite structure.

2. Experimental

Hydrothermal system used in this study is composed of electrical heating system, reaction chamber, pressure controller, and temperature controller as shown in Fig. 1. Reaction chamber is made of stainless steel and designed to withstand hard hydrothermal conditions using test-tube type sealing system. Fig. 2 shows schematic experimental procedure used for the synthesis $PbTiO_3$ with perovskite structure.

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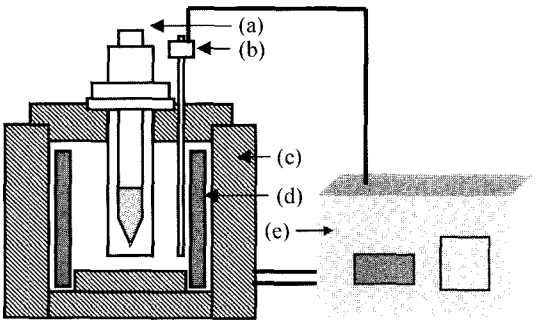

Fig. 1. Schematic diagram of hydrothermal system for the synthesis $PbTiO_3$ with perovskite structure (a) Autoclave, (b) Thermocouple, (c) Furnace, (d) Heater, (e) Controller.

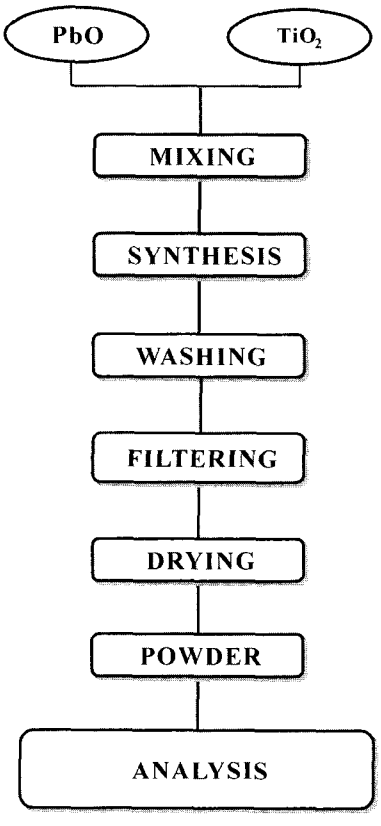

Fig. 2. Flowchart of hydrothermal synthesis of $PbTiO_3$ powder with perovskite structure.

Mixture of PbO and TiO_2 powder with same molar ratio was used as starting materials. Various solutions were used as solvent for hydrothermal synthesis and their concentrations under certain reaction conditions were analyzed quantitatively by weight measurement. Reaction phases were analyzed by X-ray diffractometer(XRD, Enraf Noinus Model FR 590, Netherlands). Particle size distribution and morphology of synthesized $PbTiO_3$ powder with perovskite structure were analyzed by surface area analyzer(BET, Digisob 2600, Micromeritics Instrument Inc., USA), particle size analyzer(Laser Particle Size Analyzer, Malvern Inc., England), and scanning electron microscope(SEM, DS-130S, Akashi Inc., Japan). The ratio of Pb and Ti in the resultant $PbTiO_3$ powder with perovskite structure was analyzed quantitatively by X-ray Fluorspectrometer(XRF, Regaku 3270, Japan). The phase transition temperature(T_C) of the powders was measured by TG-DTA(Seiko SSC 5200, Japan).

3. Results and Discussions

3.1. Solvent selection

In general, solvent for hydrothermal reaction needs to have high solubility and low intermediate products generation. In order to look for optimum solvent against starting material, we are used the PbO and TiO_2 powders as starting materials and the solvents such as 3M-KCl, conc-CH_3COOH, 3M-HCl, 8M-NH_4OH, 8M-NaOH, 8M-KOH, respectively. PbO and TiO_2 powders were inserted

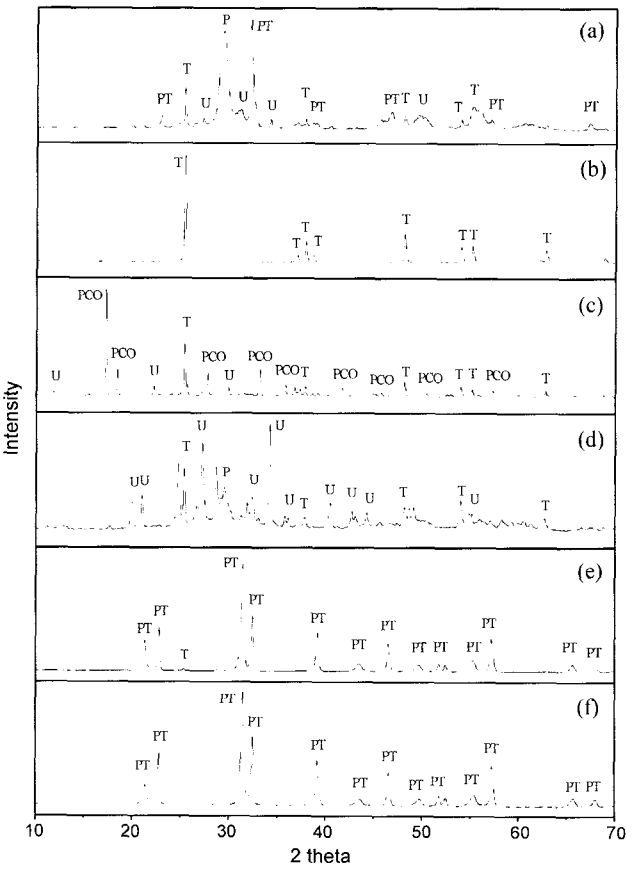

Fig. 3. XRD patterns of powders obtained by using various hydrothermal solution at 250°C for 24h. (a) 3M-KCl, (b) Conc.-CH_3COOH, (c) 3M-HCl, (d) 8M-NH_4OH, (e) 8M-NaOH, (f) 8M-KOH. *PT; $PbTiO_3$, P; PbO, T; TiO_2, PCO; PbCl(OH), U; unknown.

Table 1
Results of hydrothermal treatment of $PbTiO_3$ particles in several solvents

Solvent	Reaction Temp.(°C)	Run time (hrs)	Solubility	Overall result
3M-KCl	200	24	low	unsuitable
3M-KCl	250	24	low	unsuitable
conc.-CH_3COOH	250	24	low	unsuitable
3M-HCl	200	24	other product	unsuitable
3M-HCl	250	24	other product	unsuitable
8M-NH_4OH	250	10	low	middle
8M-NH_4OH	250	24	low	middle
8M-NaOH	200	10	low	middle
8M-NaOH	250	24	high	stable
8M-NaOH	270	10	high	stable
8M-KOH	200	10	low	middle
8M-KOH	250	10	high	suitable
8M-KOH	250	24	high	suitable
8M-KOH	270	10	high	suitable
11M-KOH	170	10	low	middle
11M-KOH	250	24	high	suitable

in the chamber, and then filled with each solvents up to 40% of chamber volume. Mixtures of PbO and TiO_2 powders in solvents were hydrothermally treated at various conditions(temperature: 170~270°C, concentration: 1~11 mol, and time: 10~24 h.). Solubility of PbO-TiO_2 mixture was tested for the selection of optimum solvents in the preparatory experiments. $PbTiO_3$ phase showed good stability in alkaline solvents such as 8M-NH_4OH, 8M-NaOH, and 8M-KOH but decomposed in acidic solvents such as 3M-KCl, conc-CH_3COOH, and 3M-HCl. As a result, acidic solvents are inappropriate and alkaline solvents showed good stability for the synthesis of $PbTiO_3$ powders even though 8M-NH_4OH showed lower stability with unreacted PbO than 8M-NaOH, and 8M-KOH did.

Fig. 3 shows XRD patterns of synthesized $PbTiO_3$ powders as a function of various hydrothermal solvents at 250°C for 24 h. Table 1. shows the results of hydrothermal treatment of $PbTiO_3$ particles in several solvents. KOH and NaOH solvents showed very good solvent properties for the hydrothermal treatment of $PbTiO_3$ particles compared to other solvents. Consequently, KOH and NaOH were selected as appropriate hydrothermal solvents for this study.

3.2. Synthesis condition

PbO and TiO_2 powders were mixed in distilled water with same molar ratio as a starting materials. Solvents such as 8M-NaOH, 8M-KOH were added in the chamber together with the mixture of PbO and TiO_2 and hydrothermally treated at various conditions. Various solvents were used for the hydrothermal synthesis. Their concentrations under certain reaction conditions were analyzed quantitatively by weight measurement. Reaction phases were analyzed by X-ray diffractometer. Fig. 4 and 5 shows XRD patterns of powders obtained by using 8M-NaOH and 8M-KOH solution at various conditions, respectively. As shown in Fig. 4 and 5, unreacted PbO appeared at the temperature below 200°C and hydrated products in KOH solution showed lower crystallinity than those in NaOH solution at 10 h. duration.

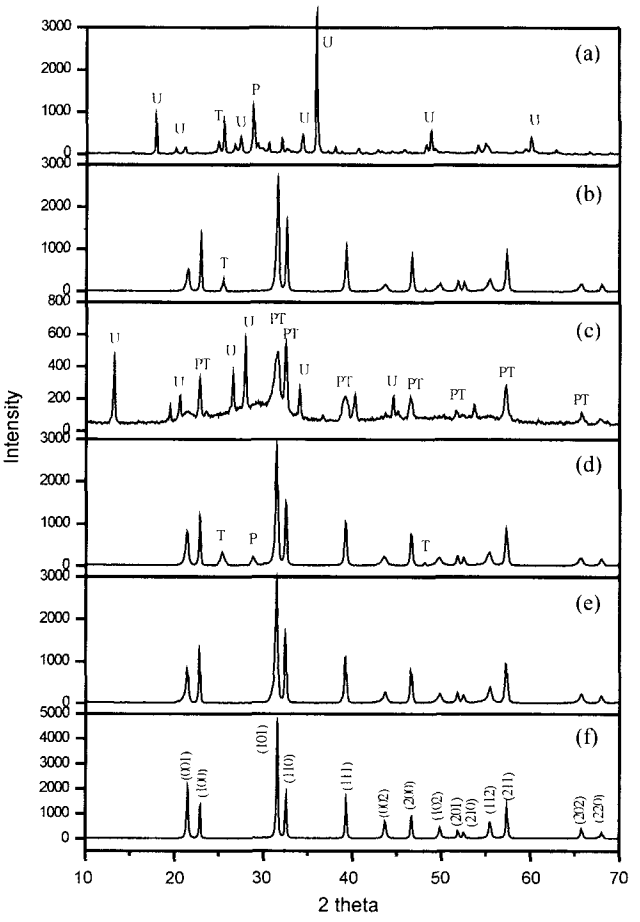

Fig. 4. XRD patterns of powders obtained by using NaOH hydrothermal solution at various conditions. (a) 1M, 170°C, 24h, (b) 3M, 250°C, 24h, (c) 8M, 170°C, 24h, (d) 8M, 250°C, 24h, (e) 8M, 270°C, 10h, (f) 11M, 250°C, 24h. PT; $PbTiO_3$, P; PbO, T; TiO_2, U; unknown.

Table 2. shows summarized results of hydrothermal treatment of $PbTiO_3$ particles in 8M-NaOH and 8M-KOH. As shown in Table 2, optimum conditions for the hydrothermal synthesis of $PbTiO_3$ particles are solvent concentration over 8-mol., synthesis temperature over 250°C, and duration over 10 h. As a conclusion, for the hydrothermal synthesis of $PbTiO_3$ particles with perovs-

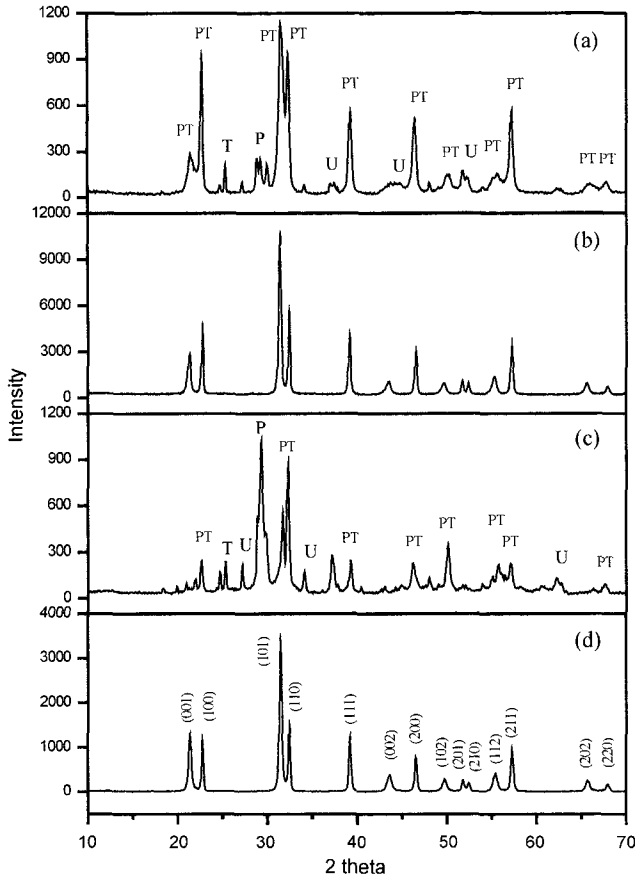

Fig. 5. XRD patterns of powders obtained by using KOH hydrothermal solution at various conditions. (a) 3M, 200°C, 10h, (b) 8M, 250°C, 10h, (c) 11M, 170°C, 24h, (d) 11M, 250°C, 24h. PT; $PbTiO_3$, P; PbO, T; TiO_2, U; unknown.

kite structure, optimum synthesis temperature are 250°C for 8M-KOH solution and 270°C for 8M-NaOH solution. Respectively, where mixture of PbO and TiO_2 powder showed good solubility at the concentration of 8-mol at 10 h. duration for the synthesis of fine $PbTiO_3$ particles.

3.3. Powder properties

Powder properties of $PbTiO_3$ synthesized in 8M-NaOH and 8M-KOH were characterized using SEM, XRD, BET, and TG-DTA. Fig. 6 shows SEM photographs of synthesized powders by using NaOH solvents at various conditions. Fig. 7 shows SEM photographs of synthesized powders by using KOH solvents at the same conditions.

As shown in Fig. 6 and Fig. 7, $PbTiO_3$ powder in KOH and NaOH solutions showed plate-like shape and rod-like shape, respectively. This is due to the difference in the solubility of PbO-TiO_2 mixture in the solvents. Particle size distribution of $PbTiO_3$ particle was measured in order to study the effect of reaction condition on the

Table 2
XRD patterns of the products obtained under various experiment conditions

Solvent Type	Concentration of solvent (M)	Reaction Temp (°C)	Reaction Time (h)	Phase	Crystallity
NaOH	1M	170	24	Other product	×
	1M	200	24	Multi-phase	▲
	3M	200	10	Multi-phase	▲
	3M	250	48	Multi-phase	○
	3M	170	10	Multi-phase	▲
	8M	170	24	Multi-phase	▲
	8M	200	10	Multi-phase	▲
	8M	250	10	Multi-phase	○
	8M	250	24	Multi-phase	○
	8M	270	10	Single-phase	◎
	11M	170	24	Multi-phase	▲
	11M	250	24	Single-phase	◎
KOH	1M	170	24	Other Product	×
	3M	200	10	Multi-phase	▲
	3M	250	24	Multi-phase	▲
	8M	170	24	Multi-phase	▲
	8M	200	10	Multi-phase	▲
	8M	250	2	Multi-phase	▲
	8M	250	5	Multi-phase	○
	8M	250	10	Single-phase	◎
	8M	250	24	Single-phase	◎
	8M	250	48	Single-phase	◎
	11M	170	24	Multi-phase	▲
	11M	250	24	Single-phase	◎

※ Remark : Single phase : $PbTiO_3$, Multi-phase : $PbTiO_3$ + other materials Crystallity : ◎ > ○ > ▲

$PbTiO_3$ particle size. Table 6. shows specific surface area of $PbTiO_3$ measured by BET and mean particles size of $PbTiO_3$ powders obtained under various conditions.

As shown in Table 3, mean particle size and specific surface area are related to the processing temperature and the kind of solvents used. Specific surface area of $PbTiO_3$ increased at higher temperature and mean particle size of $PbTiO_3$ decreased at higher temperature whereas reaction duration did not contribute much in the change of mean particle size and specific surface area. $PbTiO_3$ powders obtained in NaOH solvent are finer than $PbTiO_3$ powders obtained in KOH solvent. This is due to the difference in solubility between two solvents.

Table 4 shows Pb/Ti mole ratio of $PbTiO_3$ powders

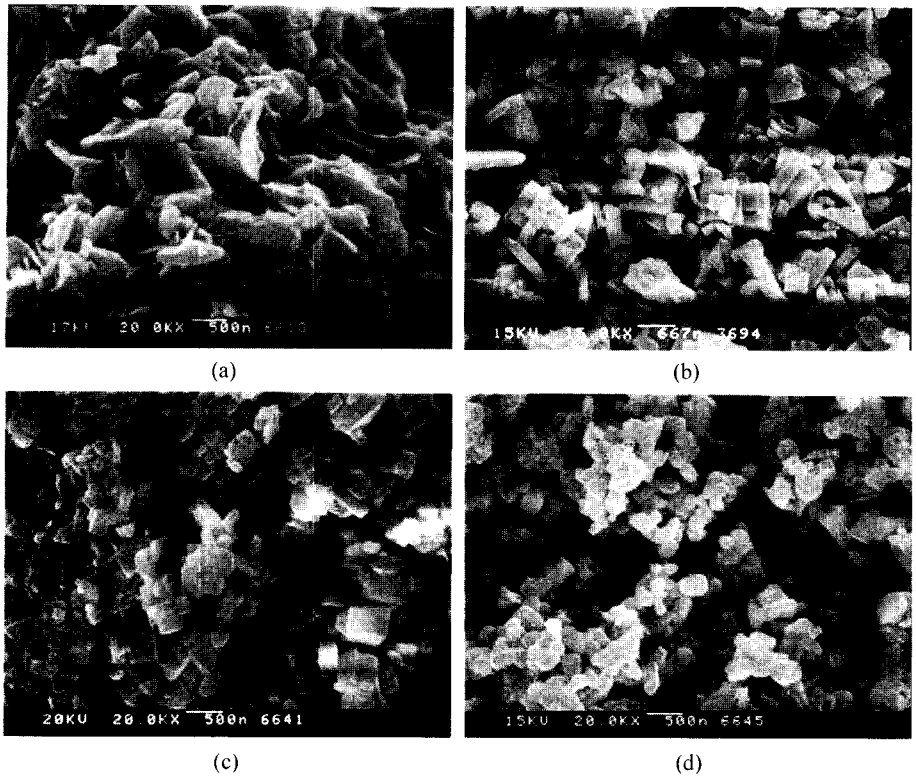

Fig. 6. SEM photographs of powders obtained by using NaOH hydrothermal solution at various conditions. (a) 8 M, 170°C, 24 h, (b) 8 M, 250°C, 10 h, (c) 8 M, 270°C, 10 h, (d) 11 M, 250°C, 24 h.

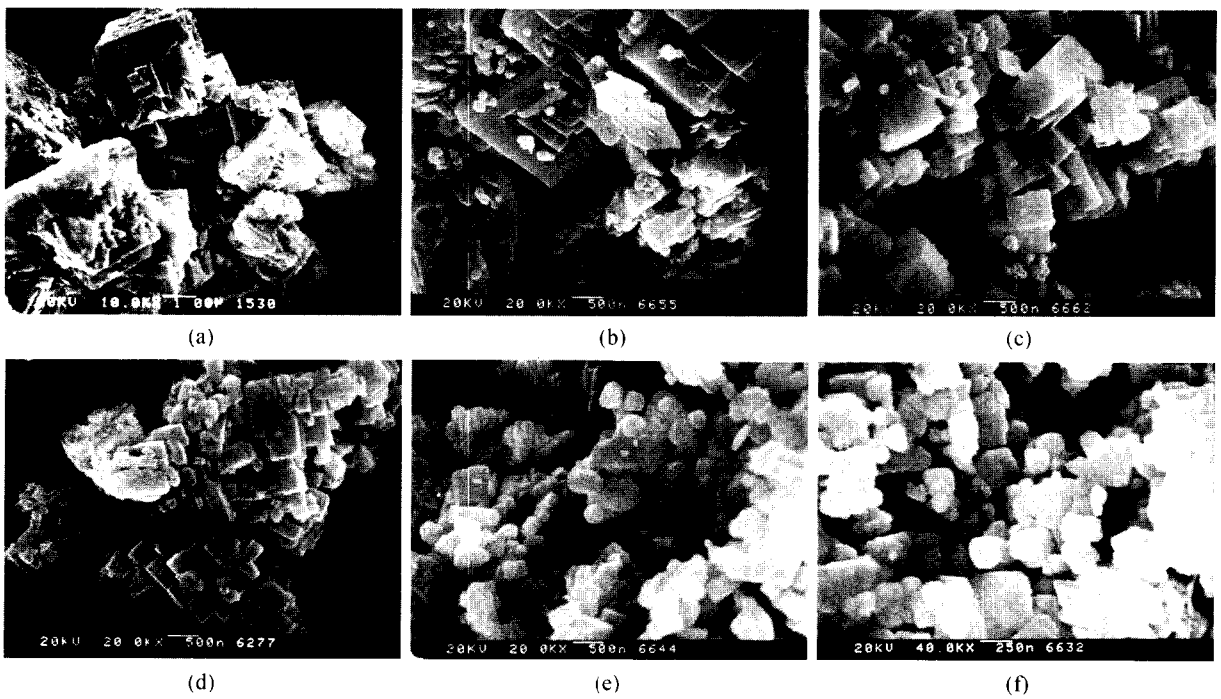

Fig. 7. SEM photographs of powders obtained by using KOH hydrothermal solution at various conditions. (a) 3 M-KOH; 200°C; 10 h, (b) 8 M-KOH; 250°C; 2 h, (c) 8 M-KOH; 250°C; 10 h, (d) 8 M-KOH; 250°C; 24 h, (e) 8 M-KOH; 270°C; 10 h, (f) 11 M-KOH; 250°C; 24 h.

obtained under various processing conditions. Ionic diffusion of Pb^{2+} depends on reaction time and Pb/Ti mole ratio of $PbTiO_3$ powders increased a little at longer duration whereas faster ionic diffusion of Pb^{2+} at higher

Table 3
BET value and mean particles size of $PbTiO_3$ powders obtained under various experiment conditions

	Specific surface area(m^2/g)	Mean particle size(μm)
A	2.2700 ± 0.0613	4.87
B	2.4346 ± 0.0685	2.82
C	4.7420 ± 0.0633	0.55
D	5.5885 ± 0.1429	0.36

Remark : A; 8 M KOH, 250°C, 10 h, B; 8 M KOH, 270°C, 10 h
C; 8 M NaOH, 250°C, 20 h, D; 8 M NaOH, 270°C, 10 h

Table 4
Pb/Ti mole ratio of $PbTiO_3$ powders obtained under various experiment conditions

	PbO(%)	TiO_2(%)	Mole ratio(Pb/Ti)
A	73.66	25.80	1.022 : 1
B	73.59	25.88	1.018 : 1
C	71.98	27.00	0.954 : 1
D	73.61	26.42	0.997 : 1

Remark: A; 8 M KOH, 250°C, 10 h, B; 8 M KOH, 250°C, 20 h
C; 8 M NaOH, 270°C, 10 h, D; 8 M NaOH, 270°C, 20 h

Table 5
Lattice constants of $PbTiO_3$ powders obtained under various experiment conditions

Solvent Type	Reaction Temp(°C)	Run Time (h)	a(Å)	c(Å)	c/a
8M-NaOH	250	10	3.9043	4.1429	1.0611
	250	20	3.8995	4.1537	1.0652
	270	10	3.8995	4.1514	1.0646
	270	20	3.8925	4.1483	1.0657
11M-NaOH	250	10	3.8975	4.1442	1.0633
	270	10	3.8925	4.1429	1.0643
8M-KOH	250	10	3.8995	4.1531	1.0650
	250	20	3.8995	4.1514	1.0646
	250	24	3.8947	4.1483	1.0651
	270	10	3.8975	4.1457	1.0637
	270	20	3.8932	4.1442	1.0645
11M-KOH	250	10	3.8956	4.1486	1.0649
	270	24	3.8912	4.1432	1.0648

reaction temperature lowered Pb/Ti mole ratio of $PbTiO_3$ powders. In general, Pb/Ti mole ratios of $PbTiO_3$ powders are close to the stoichiometric ratio, that is, 1. On the other hand, lattice constants of $PbTiO_3$ powders obtained under various experiment conditions were measured. Table 5 shows lattice constants of $PbTiO_3$ powders obtained under various experiment conditions using slicon powder as standard materials. These results are close to the theoretical c/a raio 1.06, which means that powders obtained are $PbTiO_3$ powders with perovskite structure.

Fig. 8 shows TG-DTA curves of $PbTiO_3$ powders obtained by using 8M-KOH at 250°C for 24 hrs. (heating and cooling rate: 10°C/min.) in order to measure curie temperature. As shown in Fig. 8, exothermic and endothemic peaks appeared on the cooling and heating curves at the temperature of about 470°C, respectively. These peaks are due to the reversible transition of tetragonal and cubic structures. Thus, the phase transition temperature(T_C) of the $PbTiO_3$ powders is about 470°C. No other peaks up to 1000°C were detected, which means that there is little unreacted PbO or decomposed PbO. Strong endothermic peak over 1100°C seems to be due to the melting of $PbTiO_3$ powders.

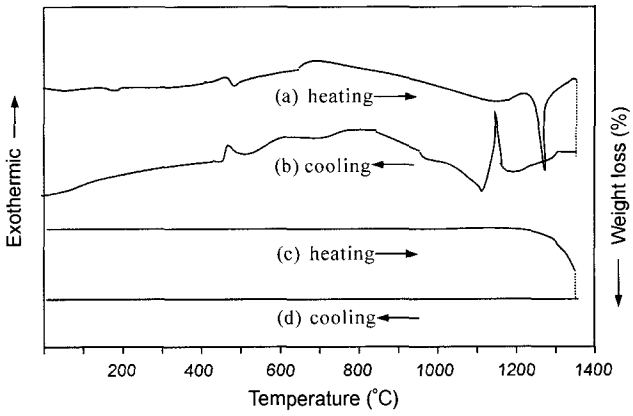

Fig. 8. TG-DTA curves of $PbTiO_3$ powders obtained by using 8 M-KOH at 250°C for 24 h. (heating and cooling rate: 10°C/min).

4. Conclusion

The preparation of $PbTiO_3$ powder was carried out using PbO and TiO_2 starting material by hydrothermal method. The $PbTiO_3$ powder of a crystalline phase with perovskite structure was successfully synthesized. The optimum conditions for preparation of powder were as follows; hydrothermal solvent; 8M-KOH or 8M-NaOH reaction temperature; 250°C~270°C run time; 10 hrs.

Synthesized $PbTiO_3$ powders were non-spherical particles with specific surface area ranging from 2.3 to 5.6 m^2/g. The cell parameters of powder were a = 3.90 Å, c = 4.14Å and cell volume were 57.30 $Å^3$. Lattice axial ratio (c/a) of powder was the same as the theoretical ratio with c/a = 1.06. The phase transition temperature (T_C) of the powders was detected at 470°C.

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