Journal of the Korean Crystal Growth and Crystal Technology
Vol. 13, No. 2 (2003) 63-67

Synthesis of $PbLaTiO_3$: Mn powders by hydrothermal method

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(Received November 28, 2002)
(Accepted January 10, 2003)

Abstract Synthesis of $PbLaTiO_3$: Mn powders containing La and Mn was carried out using PbO, TiO_2, La_2O_3 and MnO_2 as starting materials by hydrothermal method. In the synthesis of single phase $PbLaTiO_3$: Mn powder containing La and Mn, the optimal x value corresponding to La substitution was 0.01 which corresponds to $0.99(Pb_{1-x}La_{2x/3}TiO_3)+0.01MnO_2$. The optimal conditions for the preparation of the powder synthesis were 8 M-KOH solvent of hydrothermal solvent, 270°C of reaction temperature and 24 hrs of run time. It was found that the synthesized powders had spherical morphology with average particle size of 70 nm and specific surface area of 5.5 m^2/g.

Key words Hydrothermal, $PbLaTiO_3$: Mn, Powder synthesis

1. Introduction

$PbTiO_3$ with perovskite structure is hard to sinter. And then high electric field at high temperature is necessary for good electro-mechanical coupling constant. This shows low dielectric constant, high Curie point anisotropy in electro-mechanical coupling constant and high pyroelectric constant[1]. Many additives have been tried in $PbTiO_3$ to optimize these properties [2, 3]. In improving sintering property and in lowering necessary electric field, La_2O_3 and MnO_2 have been known as effective additives [4, 5]. Many factors such as composition, particle size distribution, and microstructure affected the dielectric and piezoelectric properties of $PbTiO_3$.

Recently, sol-gel method and co-precipitation method have been studied widely for their homogeneous particle size distribution. Sol-gel method and co-precipitation method still require heat treatment at high temperature over 500°C in order to calcine the product. After solid state reaction, sol-gel method [6, 7], and co-precipitation method [8, 9] have been applied, new hydrothermal synthesis method of $PbTiO_3$ powder has been proposed for better composition control and homogeneous particle size distribution.

$PbTiO_3$ synthesis by hydrothermal method at high temperature and high pressure conditions was studied at first by Kanebo and Imoto [10]. Consequently, $PbTiO_3$ with perovskite structure synthesized by hydrothermal method at lower temperature later [11]. Synthesis of $PbTiO_3$ with perovskite structure by hydrothermal method has been studied widely because heat treatment is not necessary. Composition, particle size distribution, and the morphology of particles can be easily controlled during the synthesis by changing hydrothermal conditions at the same time.

Optimum solvent, reaction temp. and run time were studied in order to obtain single phase $PbLaTiO_3$: Mn powders containing La and Mn in this study.

Consequently the objective of this study is to obtain single phase $PbLaTiO_3$: Mn powders containing La and Mn by hydrothermal method.

2. Experimental

In General, hydrothermal system is composed of electrical heating system, reaction chamber, pressure controller, and temperature controller. So, hydrothermal system used in this study is self-designed as shown in Fig. 1. Reaction chamber in Fig. 1 is made of stainless steel and is designed to withstand harsh hydrothermal conditions using test-tube type sealing system. The reaction chamber has capacity of 185 m*l* with diameter 36 mm and height 185mm. Sixty percent of reaction chamber capacity is filled with solvent and raw materials for the safety of hydrothermal synthesis. Therefore autoclave pressure is about 60 atm by PVT diagram of water.

In $PbLaTiO_3$ powder containing La, the optimal 'x' value corresponding to La substitution in the formular $Pb_{1-x}La_{2x/3}TiO_3$ was studied, where 'x' increased from

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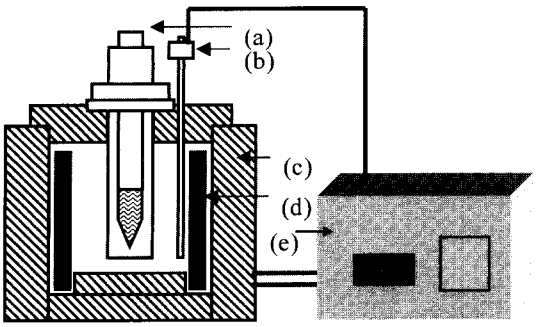


Fig. 1 chematic diagram of hydrothermal system for the synthesis of $PbLaTiO_3$: Mn powder with perovskite structure. (a) Autoclave, (b) Thermocouple, (c) Furnace, (d) Heater, (e) Controller.

0.01 to 0.05, 0.10, and 0.15. At the same time, synthesizing single phase $PbLaTiO_3$: Mn powder containing La and Mn, the optimal y value corresponding to Mn substitution was set to 0.01, which corresponds to the formular $0.99(Pb_{1-x}La_{2x/3}TiO_3)+0.01MnO_2$. Each sample was made by mixing PbO, TiO_2, La_2O_3 and MnO_2 (Aldrich, GR) after batch calculation.

Mixture of PbO, TiO_2, La_2O_3 and MnO_2 was used as starting materials. KOH and NaOH solutions were used as solvent for hydrothermal synthesis in the temperature range from 170°C to 270°C and in running time from 6 hrs to 48 hrs. Then, samples were washed with distilled water and dried in the oven for the further characterization.

Figure 2 shows schematic experimental procedure

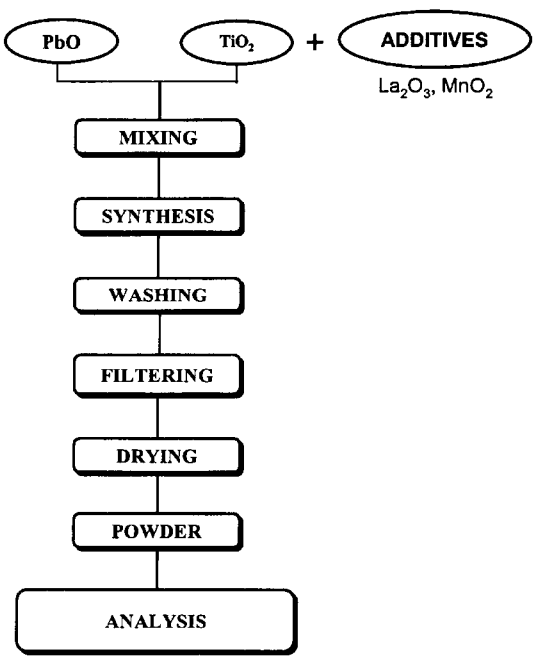


Fig. 2. Flowchart of hydrothermal synthesis of $PbTiO_3$ and 0.99 $(Pb_{1-x}La_{2x/3}TiO_3)+0.01MnO_2$ powders with perovskite structure.

used in this study for the synthesis of $PbTiO_3$ and 0.99 $(Pb_{1-x}La_{2x/3}TiO_3)+0.01MnO_2$ powder with perovskite structure. Their concentrations under certain reaction conditions were analyzed quantitatively by ICP (ICP-OES, Perkin-Elmer Optima 3300DV, USA). Reaction phases and lattice contants were analyzed by X-ray diffractometer (XRD, Enraf Noinus Model FR 590, Netherlands). Particle size distribution and morphology of hydrothermally synthesized powder 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).

3. Results and Discussions

3.1. Synthesis condition

In General, solvent for hydrothermal reaction needs to have high solubility and low intermediate products gen-

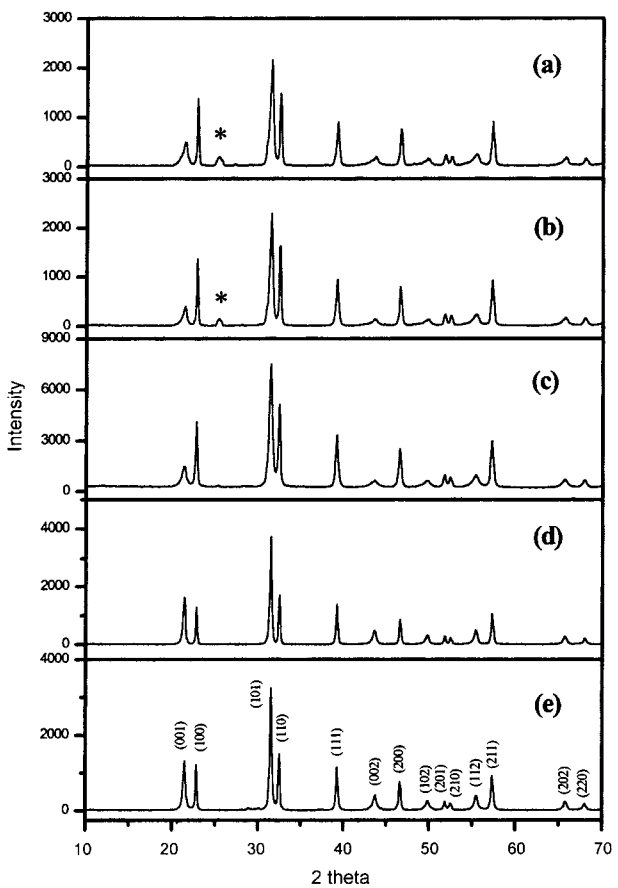


Fig. 3. XRD patterns of the $PbLaTiO_3$: Mn (x = 0.01) powders obtained by various hydrothermal conditions: a) 8M-KOH; 200°C; 24 h, b) 8M-KOH; 270°C; 12 h, c) 8M-KOH; 270°C; 24 h, d) 8M-NaOH; 270°C; 24 h, e) 11M-NaOH; 250°C; 24 h. *: TiO_2.

eration. Solubility of PbO-TiO_2 mixture was tested for the selection of optimum solvents in the preparatory experiments [12], where $PbTiO_3$ phase showed good stability in alkaline solvents like NaOH, and KOH. As a result, alkaline solvents were assumed to show good stability for the synthesis of $PbLaTiO_3$: Mn powders. Thus, alkaline solvents such as NaOH and KOH were, as hydrothermal solvents, used in this study.

Figure 3 shows several XRD patterns of the $PbLaTiO_3$: Mn (x = 0.01) powders obtained at this study. Figure 3a) and b) show some unreacted TiO_2 phase, however Fig. 3c), d), and e) show no unreacted phase.

Table 1 shows the summarized results of hydrothermal treatment of $PbLaTiO_3$: Mn particles in the above conditions. As shown in Table 1, both KOH and NaOH showed good solvent properties for the hydrothermal treatment of $PbLaTiO_3$: Mn particles at 270°C, even though KOH showed good solvent properties for the hydrothermal treatment of $PbLaTiO_3$: Mn particles even at 250°C also.

Figure 4. shows XRD patterns of $PbTiO_3$ and $PbLaTiO_3$: Mn powders synthesized at 270°C for 24 hrs changing the amount of La ions substitution 'x' from 0.01 to 0.15. In the XRD patterns of $PbLaTiO_3$: Mn powders synthesized at 270°C for 24 h at the conditions a) show pure $PbTiO_3$ peaks, however XRD patterns of $PbLaTiO_3$: Mn powders at the conditions b), c) and d) show La_2PbO_x peaks. La_2PbO_x peaks in the XRD analysis imply there were excess La ions for the Pb ions substitution.

On the other hand, Table 2 shows lattice constants of

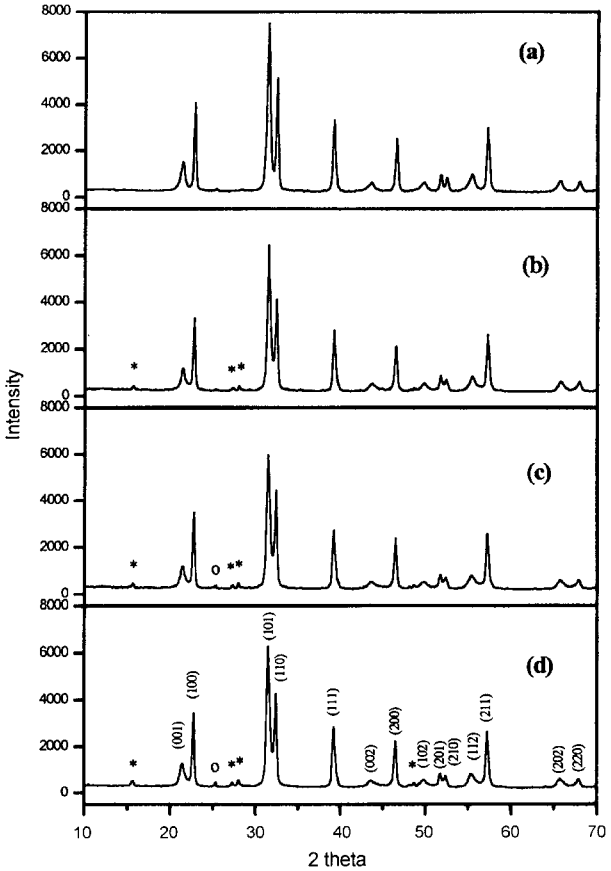


Fig. 4. XRD patterns of $PbLaTiO_3$: Mn powders synthesized at 270°C for 24 h. a) x = 0.01, b) x = 0.05, c) x = 0.1, d) x = 0.15. *; La_2PbO_x, o; TiO_2.

$PbLaTiO_3$: Mn powders obtained by using 8M-KOH hydrothermal solution at various conditions. As shown

Table 1
Results of the $PbLaTiO_3$: Mn (x = 0.01) powders obtained by various conditions

HT solvents	Temperature (°C)	Concentration (M, mole/l)	Duration (hours)	Phase ($PbLaTiO_3$: Mn)	Crystallity
KOH	170	8	10	Multi-phase	▲
	200	8	10	Multi-phase	▲
	250	8	5	Multi-phase	▲
		7	10	Multi-phase	▲
		8	20	Single-phase	○
		10	12	Single-phase	○
	270	8	6	Multi-phase	▲
		8	20	Single-phase	○
		8	24	Single-phase	◎
		8	48	Single-phase	◎
NaOH	170	8	10	Multi-phase	▲
	200	8	10	Multi-phase	▲
	250	7	10	Multi-phase	▲
		8	10	Multi-phase	▲
		10	10	Multi-phase	▲
	270	8	8	Single-phase	○
		8	10	Single-phase	○

※ Remark : Crystallity : ◎ > ○ >▲ .
$PbLaTiO_3$: Mn (x = 0.01) = $0.99(Pb_{1-x}La_{2x/3}TiO_3)$+$0.01MnO_2$(x = 0.01).

Table 2
Lattice constants of $PbLaTiO_3$: Mn powders obtained by using 8M-KOH hydrothermal solution at various conditions.

	Reaction conditions	Lattice constants a (Å)	c (Å)	c/a
$PbLaTiO_3$: Mn (x = 0.01)	250°C, 12 h	3.8948	4.1321	1.0609
	270°C, 6 h	3.8995	4.1429	1.0624
	270°C, 12 h	3.8995	4.1483	1.0638
	270°C, 24 h	3.8995	4.1538	1.0652
$PbLaTiO_3$: Mn (x = 0.05)	270°C, 24 h	3.9043	4.1375	1.0597
$PbLaTiO_3$: Mn (x = 0.10)	270°C, 24 h	3.9043	4.1321	1.0584
$PbLaTiO_3$: Mn (x = 0.15)	270°C, 24 h	3.9043	4.1302	1.0578

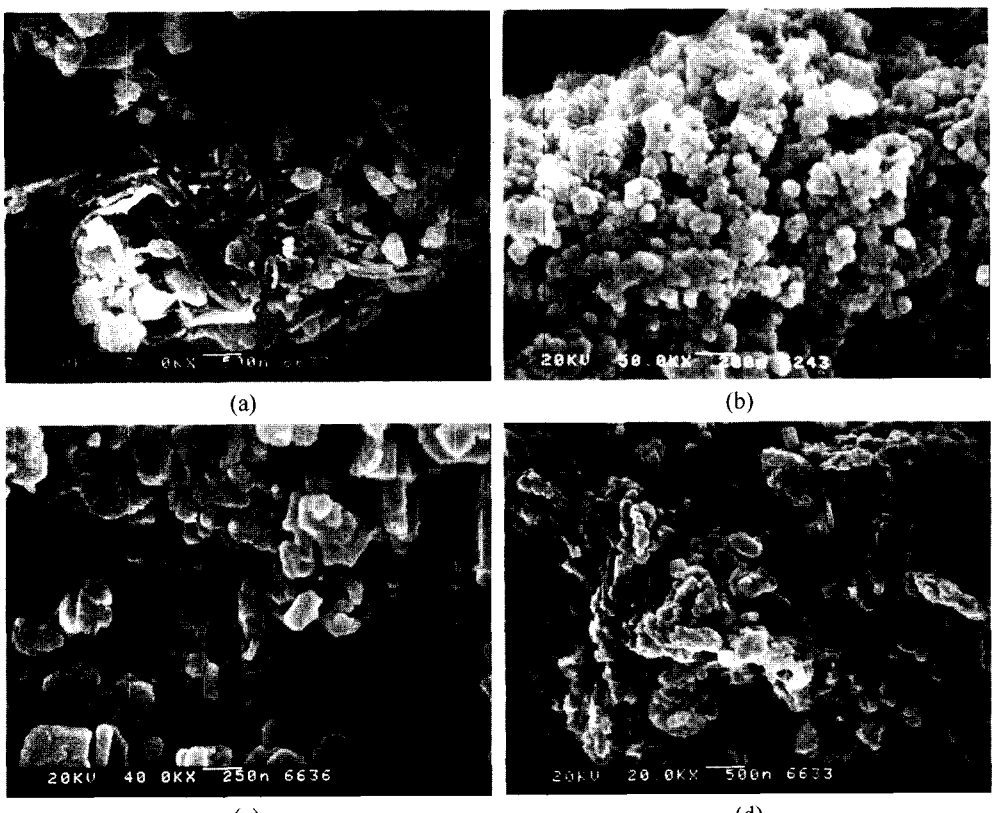
Table 3
Chemical analysis of the powders synthesized and solutions remained after reaction (unit : ppm)

	PbO		La_2O_3		TiO_2		MnO_2	
	pd.	soln.	pd.	soln.	pd.	soln.	pd.	soln.
$PbTiO_3$	68100	18.45	N.D	N.D	29700	2.23	N.D	N.D
$PbLaTiO_3$: Mn (x = 0.01)	65300	8.95	331	N.D	28500	1.33	280	N.D
$PbLaTiO_3$: Mn (x = 0.05)	59400	6.81	1610	N.D	26300	3.66	271	N.D
$PbLaTiO_3$: Mn (x = 0.10)	58700	12.25	3550	N.D	27800	12.09	280	N.D
$PbLaTiO_3$: Mn (x = 0.15)	56500	20.52	5820	N.D	28400	4.44	300	N.D

※ Remark : Pd. = powder, Soln. = solution.
$PbLaTiO_3$: Mn = $0.99(Pb_{1-x}La_{2x/3}TiO_3)+0.01MnO_2$.
N.D = No Detection.

in Table 2, lattice constants of $PbLaTiO_3$: Mn powders decreased with changing 'x' from 0.01 to 0.15, while lattice constant is approaching the theoretical value 1.06 when 'x' is 0.05.

Table 3 shows the chemical analysis of the synthesized powders and the solutions left after hydrothermal reaction. As shown in Table 3, Pb ion content in reaction liquid decreased at 'x' = 0.05, however Pb ion content in reaction liquid increased at 'x' = 0.10 and 'x' = 0.15. This trend is related to Fig. 4, where XRD patterns of $PbLaTiO_3$: Mn powders synthesized at 270°C for 24 hrs are different 'x' from 0.01 to 0.15. As shown in Fig. 4. XRD patterns of $PbLaTiO_3$: Mn powders at the conditions 'x' = 0.01 show pure $PbTiO_3$ peaks, however XRD patterns of $PbLaTiO_3$: Mn powders at the conditions 'x' = 0.05 and above show La_2PbO_x peaks, which means there was little Pb ions left for in the liquid phase at 'x' = 0.05. Concentration changes of La, Ti, and Mn by changing 'x' from 0.01 to 0.15 confirms this trend.



(a) (b) (c) (d)

Fig. 5. SEM photographs of the $PbLaTiO_3$: Mn (x = 0.01) powders obtained at 270°C; 24 h. a) $PbTiO_3$, b) x = 0.01, c) x = 0.05, d) x = 0.10.

Table 4
Specific surface area of the $PbTiO_3$ and $PbLaTiO_3$: Mn powders synthesized at 270°C for 24 h

	Specific surface area (m^2/g)
$PbTiO_3$	1.4006±0.0193
$PbLaTiO_3$: Mn (x = 0.01)	5.4755±0.0552
$PbLaTiO_3$: Mn (x = 0.05)	4.5426±0.0274
$PbLaTiO_3$: Mn (x = 0.10)	3.2767±0.0753
$PbLaTiO_3$: Mn (x = 0.15)	2.6055±0.0815

Remark : $PbLaTiO_3$: Mn = $0.99(Pb_{1-x}La_{2x/3}TiO_3)+0.01MnO_2$.

3.2. *Powder properties*

Powder properties of $PbLaTiO_3$: Mn synthesized in 8M-KOH were characterized using SEM, XRD, BET, and TG-DTA. Figure 7 shows SEM photographs of the $PbLaTiO_3$: Mn (x = 0.01) powders obtained at 270°C for 24 hrs. As shown in Fig. 5a), $PbTiO_3$ powder synthesized in 8M-KOH at 270°C for 24 hrs. showed plate-like shape with the size range from 3 to 300 nm, $PbLaTiO_3$: Mn (x = 0.01) in Fig. 5b) powder synthesized at the same condition showed homogeneous sphere shape agglomerates with the size range around 70 nm, $PbLaTiO_3$: Mn (x = 0.05) powder in Fig. 5c) showed cubic shape with the size about 300 nm, and $PbLaTiO_3$: Mn (x = 0.10) powder in Fig. 5d) showed homogeneous cube shape agglomerates with the size range around 70 nm.

Specific surface area was measured in order to study the effect of reaction condition on the particle size. Table 4. shows the results of the specific surface area measured by BET method and mean particles size of $PbTiO_3$ powders obtained under various conditions.

As shown in Table 4, specific surface area increased at x' = 0.01, however decreased at 'x' = 0.05, 0.10 and 0.15. As explained in Fig. 5a), $PbTiO_3$ powder has the size range from 3 μ to 300 nm, whereas $PbLaTiO_3$: Mn (x = 0.01) powder in Fig. 5b) showed homogeneous sphere morphology with the size range around 70 nm. At the same time, $PbLaTiO_3$: Mn (x = 0.05) powder showed the size range about 300 nm and $PbLaTiO_3$: Mn (x = 0.10) powder showed the size range around 400 nm. These trends in Fig. 5 quite agree well with the results in Table 4.

4. Conclusion

$PbLaTiO_3$: Mn powders were successfully synthesized using PbO, TiO_2, La_2O_3 and MnO_2 as the starting material by hydrothermal method. The optimal x value corresponding to La substitution in single phase $PbLaTiO_3$: Mn powder containing La and Mn was 0.01 which corresponds to $0.99(Pb_{1-x}La_{2x/3}TiO_3)+0.01MnO_2$. The optimal conditions were 8M-KOH solvent of hydrothermal solvent, 270°C of reaction temperature and 24 hrs of run time. It was found that the synthesized powders were spherical particles with average diameter of 70 nm and specific surface area of 5.5 m^2/g.

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