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Hydrothermal Synthesis and Characterization of Lead Titanate Powder

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Lead titanate fine powders were synthesized by the hydrothermal method without using alkali mineralizers such as KOH. Preparation conditions influenced strongly the resultant phases, morphologies, and compositions of the lead titanate powders. Some observations on the prepared lead titanate were also carried out by the transmission electron microscopy and ζ -potential measurement.

Perovskite type lead titanate ($PbTiO_3$) has been known because of its high anisotropic structure effecting on the dielectric properties. Recently preparations of fine lead titanate powders and thin films were investigated by a sol-gel method and a low temperature hydrothermal process.(1,2) Hydrothermal crystallization of lead based perovskite powders have been carried out using alkali metal mineralizers based on a report by Beal et al.(3) Kikuta et al., however, confirmed that alkali metal ions such as potassium ion K^+ were easily incorporated into Pb^{2+} site in the perovskite matrix, causing the hardening of PZT.(4)

In addition to utilizing fine powders for electronic components, the synthesis of fine powders in the range of 50 to 100 nm is urgently demanded for elucidating the size effect on the dielectric properties. Usually the critical size of barium titanate is considered to be around 100 nm. For lead titanate system, the critical size is smaller than 20 nm.(5) Kaneko et al. and Lencka et al. reported a hydrothermal synthesis of lead titanate under low temperature conditions without mineralizers.(6,7) The key factor of the crystallization is a pH control , i.e. , control of coexisting ions. Strong conjugated anion such as a NO_3^- ion from starting compound changes the pH value of the suspension, which affects the resultant phase and composition of the powder. In order to prepare a stoichiometric lead titanate, experimental conditions should be controlled very carefully based on the chemical equilibrium. The present work was carried out to synthesize the fine lead titanate powders without any contamination by K^+ and to characterize the surface charge, which has been required for fabricating electronic components and for elucidating the occurrence of the dielectric behavior in fine particle system.

Lead oxide (PbO) and titanium iso-propoxide were mixed in a water for 2 h beforehand hydrothermal treatment. Since coexisting ions such as an acetate ion increase the solubility of lead species, titanium isopropoxide with very weak acidity is preferred for these experiments. Starting mixture is a white suspension including amorphous titanium hydroxide. The concentration of the suspension was fixed to 0.2 mol/l as $PbTiO_3$. Then 100 ml of the suspension was heat-treated in a hydrothermal reaction vessel with a stirring rate of 100 rpm at 170°C for 24h. After a hydrothermal treatment prepared powders were washed with pure water and filtrated. (In this experiment, acetic acid was not utilized for washing to examine the chemical composition of as-prepared lead titanate powder.)

Prepared powders were characterized by XRD(Rigaku RAD-B), SEM(JEOL JSM-6100), and TEM (HITACHI H-800). A ζ-potential curve of the lead titanate fine powder was measured as a function of pH by the addition of ammonia. Compositions of the lead titanate powders were also analyzed by ICP analysis.

The crystallization of starting compounds can be controlled by the pH of the starting solutions and experimental temperatures. It is easily estimated that the composition of the prepared lead titanate closely related to the solubility of lead in the solution. From the view point of solubility products, the mass of suspension in solution was also one of the important factors. Table 1 summarizes the analytical results of the lead to titanium ratios. All of these prepared powders were confirmed to be a perovskite phase by XRD. It turns out from this table that 4 mol% excess lead dissolved into the solution, which is corresponding to a concentration of 0.01 mol/l. Ichihara et al. already reported about the lead loss in 10N KOH solution for PZT system during crystallization.8)

Table 1. Composition(Pb/Ti ratio) of Lead Titanate by ICP Analysis

Solvent	Nutrient Composition	Powder Composition
Water	1.00	0.96±0.01
Water	1.05	1.01±0.01
Water/i-PrOH =1/1	1.05	1.04±0.01

In their case, lead loss was about 20 wt% of the starting nutrient, which is much higher than that of this experimental results. The higher loss of lead may be caused by the selectively high dissolution of lead into KOH solution to form an intermediate ion. Kaneko and Lencka et al. discussed about the formation mechanism of lead titanate.[6,7] As a result, a few μm size lead titanate particles were prepared in KOH solution, which is significantly larger than that prepared in alkali free solution(<0.1 μm) prepared in this work. These fine particles prepared in alkali free condition shows a round shape indicating dissolution- recrystallization process was not significant. It is considered that lead titanate fine powders can be prepared under low lead concentration conditions.

Further improvement to suppress the selective dissolution of lead was achieved by the employment of mixed solvent(water/alcohol) as given in Table 1.

ζ-potential of the prepared perovskite powders was investigated as a function of pH value. As shown in Fig. 1, ζ-potential of the particle gradually decreased as increasing pH value, and the iso-electric point of the prepared powders is around pH10.

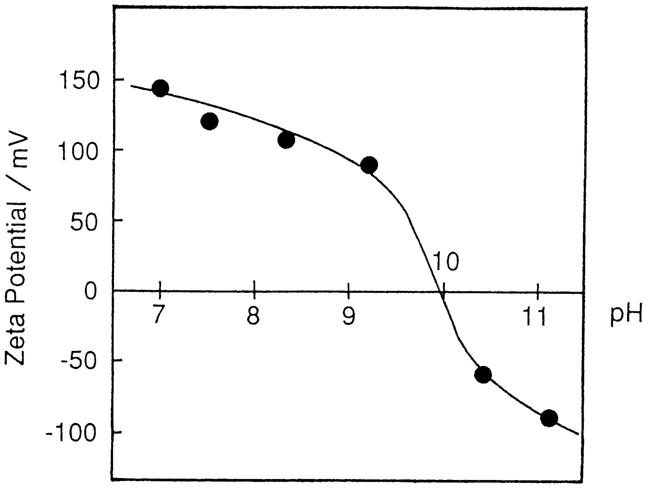

Fig. 1. ζ-Potential Curve of Perovskite Lead Titanate Powder.

It is very close to the boundary, at which the stable lead ion structure changes from PbO to $HPbO_2^-$.7) The difference in pH value between KOH solution and alkali free solution was clearly observed in this experiment. The pH values of the suspension before and after hydrothermal treatment were 10 and 7 respectively, revealing pH of the suspension gradually decreased during crystallization. It is observed that lead titanate particle has large surface charge above 140 mV at pH7. It is considered that the agglomeration of the PT particles was mainly caused by its high spontaneous polarization($Ps \sim 120 \times 10^{-2}$ C/m^2, Tc=490 °C). Such an electric interaction between particles might be also responsible for linear chain morphology in agglomerates. In order to prepare well dispersed powders investigation has to be done to overcome the electrostatic interaction among particles in connection with the formation mechanism of the lead titanate powders in hydrothermal solution.

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