STRUCTURE OF NANOCRYSTALLINE POWDER AND THIN FILMS OF LEAD LANTHANUM TITANATE PREPARED BY THE SOL-GEL PROCESS

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Abstract

Ultrafine powder and thin films of lead lanthanum titanate (PLT) were prepared by the sol-gel process. The structural variation of the powder with increasing annealing temperature was monitored by differential thermal analysis, thermogravimetric analysis and x-ray diffraction. The lowest temperature for the formation of nanocrystals in the powder was found to be about 500°C. Crystallites of various sizes were obtained by controlling the annealing temperature and time. Thin films of PLT were fabricated by spin casting the sol-gel solution onto Si(111) substrates and the microstructure was analyzed using a scanning electron microscope. By controlling the concentration of the precursor and the processing temperature, PLT thin films with uniform crystallite size could be prepared.

1. Introduction

Lead titanate (PbTiO$_3$ or PT) is a perovskite-type ferroelectric ceramic with a Curie temperature (T$_c$) of 490°C. It is a good candidate for pyroelectric infrared detector applications as it has large pyroelectric coefficient and relatively low dielectric permittivity. However, poling of bulk PbTiO$_3$ requires a high electric field because of its high T$_c$ and the large tetragonal distortion [1]. After doping with lanthanum (La), the permittivity of the resulting lead lanthanum titanate (PLT) increases while T$_c$ and the tetragonality decrease with increasing La content. [2] The coercive field required to polarize the ceramic also drops and a pyroelectric coefficient larger than that of PT is observed. [3] In particular, (Pb$_{0.90}$La$_{0.10}$)TiO$_3$ (PLT10) was reported to have good pyroelectric property. [4] Preparation of PLT thin films by sputtering, pulsed laser deposition and the sol-gel process have attracted considerable interest.[5] The present authors are interested in producing nanocrystalline PLT powder since it is planned to incorporate them into a pyroelectric vinylidene fluoride/trifluoroethylene copolymer (P(VDF-TrFE)) matrix to form nano-composites.

In this study, PLT10 powder and thin films were prepared by the sol-gel process. The structural variation of the powder with annealing temperature was studied by differential thermal analysis (DTA), thermogravimetric analysis (TGA) and x-ray diffraction (XRD). From the XRD data, the lowest temperature for the formation of PLT10 nanocrystallites was found and the crystallite size was evaluated using the Scherrer's equation. The activation energy required for the conversion of amorphous phase into nanocrystalline phase was calculated from the DTA results. By controlling the concentration of the precursor, the spinning speed and spinning time, homogeneous PLT10 thin films were produced.

2. Experimental procedure

The procedures for the preparation of PLT10 ultrafine powder and thin films are outlined in Fig. 1. Lead acetate trihydrate was first dissolved in 2-methoxyethanol ($C_3H_8O_2$) in a reaction flask at 80°C, and then the solution was heated to 118°C to remove the residual water. When the temperature of vapour reaching the top of the reflux condenser rose from 100°C to 124°C, the residual water had been completely removed. [6] After cooling to 80°C, a stoichiometric amount of tetrabutyl titanate was added to the lead acetate solution and the solution was refluxed at 124°C for 3h. After cooling the Pb-Ti complex alkoxide solution to room te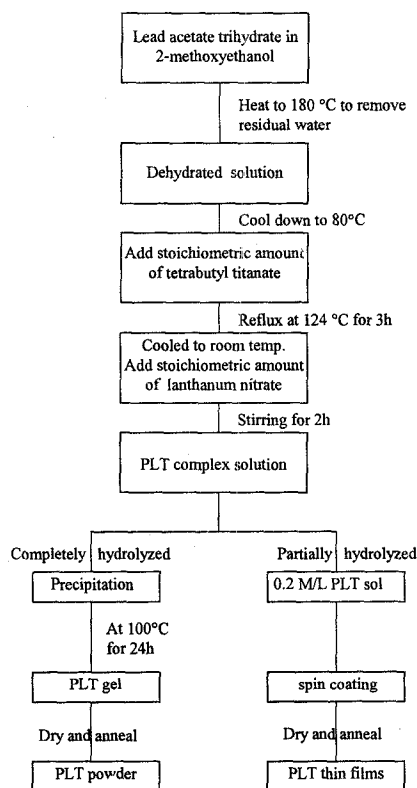mperature, a stoichiometric amount of lanthanum nitrate dissolved in $C_3H_8O_2$ was added and the solution was stirred at room temperature for 2h, thereby forming a Pb-La-Ti complex. By controlling the hydrolysis condition of the complex solution and heating the dry gel at designated temperature, PLT10 powder with various crystallite sizes was obtained [7].

For the deposition of thin films, p-type (111) silicon wafers were used as substrates. The silicon wafers were first cleaned by rinsing in acetone and deionized water and then etched in a 2% HF solution for 1 min. in order to remove the surface oxide layer. Using a 0.2 M/L precursor solution, 240 nm thick films were prepared by spinning the solution at 3000 rpm for 15 seconds. The films were then pre-fired in a furnace at 400°C for 30 minutes. To prepare a thicker (~ 1 μm) films, several layers were deposited by repeating the spinning and pre-firing processes for each layer. Finally the films were annealed at 600°C for 1h in air. With this procedure uniform and crack-free PLT10 films were produced.

The crystallization process of the PLT10 powder was studied by differential thermal analysis (DTA Perkin-Elmer 1700), thermogravimetric analysis (TGA, Perkin-Elmer TGS-2) and x-ray diffraction (Philips x'pert XRD system) with Ni filtered CuKα radiation. The microstructures of the PLT10 films were observed in a scanning electron microscope (SEM, Hitachi S-520).

Fig. 1 A flowchart showing the procedure for preparing PLT nanocrystalline powder and films by the sol-gel process.

3. Results and discussions

Fig. 2 shows the DTA and TGA curves of PLT10 powder at a heating rate of 10°C/min. The DTA curve shows an endothermic peak at 111°C (Fig. 2a) which is accompanied by a small weight loss (Fig. 2b), primarily due to the removal of water and alcohol trapped in the powder.

The two exothermic peaks between 250°C and 400°C, together with the corresponding weight loss, can probably be attributed to the oxidation of acetate groups and nitrate groups and the decomposition of the unhydrolyzed alkoxy groups. The small exothermic peak at about 500°C, not accompanied by a significant weight loss, is assumed to be associated with the crystallization of the powder. According to the Kissinger equation [8]

$$\ell n(h/T_m^2) = - E/(RT_m) + C \quad (1)$$

where h is the heating rate, T_m is the temperature at the exothermic peak near 500°C, E is the activation energy, R is the gas constant and C is a constant. The DTA results of PLT10 powder at different heating rates are shown in Table 1. From the slope of the $\ln(h/T_m^2)$ vs $1/T_m$ curve, the activation energy E was found to be 39.6 Kcal/mol.
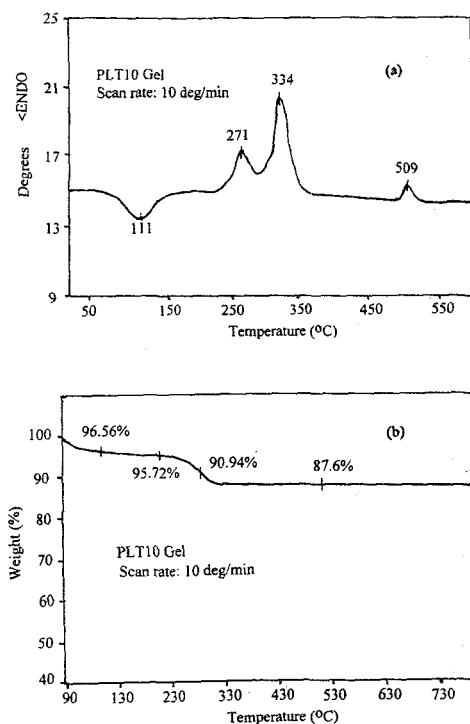
Fig. 2   Presenting (a) a DTA curve of PLT powder and (b) a TGA curve of PLT powder.

Table 1   DTA data for PLT10 powder at various heating rates.

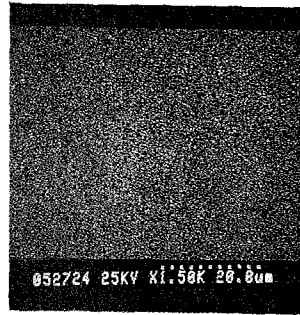| h (°C/min.)	T_m (°C)	h (°C/min.)	T_m (°C)
20	517.7	10	509.2
15	514.7	5	500.7

Fig. 3 shows the XRD patterns of PLT10 powder annealed at various temperatures for 1h. The samples annealed below 450°C exhibits the typical amorphous pattern. When the annealing temperature reaches 500°C, crystalline peaks of PLT10 powder appear, in agreement with the DTA result.

The average crystallite size of the powder at various annealing temperatures were calculated from the full width at half maximum (FWHM) of the (101), (111) and (200) x-ray diffraction peaks using the Scherrer's equation [9]
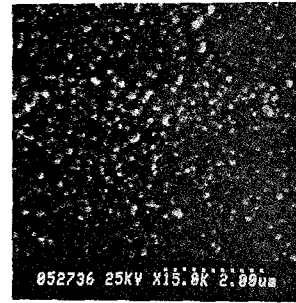
$$D = (K\lambda)/(Bcos\theta) \qquad (2)$$

where D is the crystallite diameter, λ is the wavelength, θ is the diffraction angle, B is the FWHM of a diffraction peak and K is Scherrer's constant (= 0.89). By comparison with the diffraction peaks of a standard material, Si, the width due to the instrument can be evaluated and the true width arising from finite crystallite size can be obtained. The crystallite size is given as a function of annealing temperature in Table 2.

Fig. 3 XRD patterns of PLT powder annealed at various
temperatures for 1 hour.

Table 2 Relationship between the average crystallite diameter and the annealing
temperature of PLT10 nanocrystalline powder

Annealing temperature (°C)	500	600	700	850	900
Average crystallite diameter (nm)	21.6	25.4	28.2	57.6	61.5

The SEM micrographs of PLT10 thin films (Fig. 4) show that the film is homogeneous and crack-free. It contains nanocrystalline particles of diameter 50 to 80 nm. Fig. 5 shows the cross section of a five-layer film deposited on silicon, it can be seen that the film thickness is about 1.2 μm. Research on the growth of orientated thin films and pyroelectric property measurements are in progress.

4(a)

4(b)

Fig. 4 (a) and (b) SEM micrographs with different scales, showing homogeneous PLT film prepared by the sol-gel process.
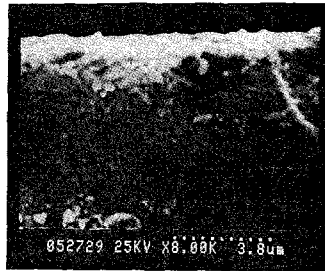

Fig. 5 SEM micrograph of the cross section of a PLT film on Si

4. Conclusion

PLT10 ultrafine powder and thin films have been prepared by the sol-gel process. The lowest annealing temperature for the formation of nanocrystals in the powder is 500°C. The average crystallite size is below 25 nm when the annealing temperature is below 600°C. The activation energy of crystallization determined from DTA is 39.6 Kcal/mol. SEM results show that PLT10 thin films annealed at 600°C for 1h are homogeneous and crack-free.

REFERENCES

[1] Y. Xu, "Ferroelectric Materials and Their Applications", (Elsevier Science Publishers, Amsterdam, 1991)

[2] G.H. Haertling, "Improved hot-pressed electrooptical ceramics in the (Pb, La)(Zr, Ti)$_3$ system", J. Am. Ceram. Soc., Vol. 54, pp. 303-309 , 1971.

[3] R. Takayama, Y. Tomita, K. Lijima and I. Ueda, "Pyroelectric linear array infrared sensors made of c-axis-oriented La-modified PbTiO$_3$ thin films", J. Appl. Phys., Vol. 63, pp. 5868-5872 ,1988.

[4] T. Futakuchi and K. Tanino, "Pyroelectric Properties of La-modified PbTiO$_3$ Thin Films Prepared by Screen Printing", Jpn. J. Appl. Phys., Vol. 33, pp. 5294-5296, 1994.

[5] Y.M. Kang, J.K. Ku and S. Baik, "Crystallographic characterization of tetragonal (Pb, La)TiO$_3$ epitaxial thin films grown by pulsed laser deposition", J. Appl. Phys., Vol. 78, pp. 2601-2606, 1995.

[6] Q.F. Zhou, A.X. Kuang and T.S. Zhou, "Study of preparation and properties of PZT ceramic by sol-gel method", Ferroelectric Letter, Vol. 14, pp.73-78 , 1992.

[7] Q.F. Zhou, H.L.W. Chan and C.L. Choy, "Nanocrystalline powder and fibres of lead zirconate titanate prepared by the sol-gel process", J. Mater. Pro. Tech., in press.

[8] H.E. Kissinger, "Reaction kinetics in differential thermal analysis" Anal. Chem., Vol. 29, pp. 1502-1506, 1951.

[9] L.S. Birks and H. Friedman, "Particle Size Determination from X-ray Line Broadening", J. Appl. Phys., Vol. 17, pp.687-692, 1946.