Properties of Nanocrystalline PT Powder and PT/P(VDF-TrFE) 0-3 Nanocomposites

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Abstract - Nanometer-size powder of lead titanate (PT) was prepared using the sol-gel process. The PT gel was annealed at various temperatures to produce powder with different particle sizes. The structural variation of the PT powder with annealing temperatures was studied by X-ray diffraction (XRD), thermogravimetric analysis (TGA), differential thermal analysis (DTA) and differential scanning calorimetry (DSC). The crystallite size and particle size of the PT powder were measured by XRD and a particle size analyzer, respectively. PT/P(VDF-TrFE) 0-3 composites with a PT volume fraction of 0.4 were prepared by using PT powder of size 30 nm to 270 nm. The permittivities of the composites were measured using an impedance analyzer. After poling, the piezoelectric and pyroelectric coefficients of the composites were also determined.

I. INTRODUCTION

Lead titanate (PT) is an important ferroelectric material possessing good piezoelectric and pyroelectric properties. In the conventional approach, PT is prepared by ball milling followed by calcination above 850°C. Because of the high synthesis temperature, the PT particle produced are too large to be used in integrated sensor applications. In recent years, there has been considerable interest in using the sol-gel process to prepare ceramics from metal alkoxides [1-3] because high-purity ultrafine particles and large-area thin films can be produced at relatively low temperature. The present authors are interested in preparing nanocrystalline powder and incorporating them into a piezoelectric vinylidene/ trifluoroethylene copolymer (P(VDF—TrFE)) matrix to form 0-3 nanocomposites for integrated pyroelectric sensor applications.

II. EXPERIMENTAL PROCEDURES

The procedure for the preparation of PT nanocrystalline powder is outlined in Fig.1.

First, lead acetate trihydrate was dissolved in 2-methoxyethanol ($C_3H_8O_2$) at 80°C in a three-neck reaction flask. After the lead acetate trihydrate had dissolved, the reaction flask was fitted with a reflux condenser and the solution was heated to approximately 118°C to remove adsorbed water. The rise of the temperature of the vapour reaching the top of the reflux condenser from 100°C to 124°C (the boiling point of methoxyethanol) indicated the complete removal of residual water. Then the solution was cooled to 100°C and titanium isopropoxide was added to give a 1:1 molar ratio of lead to titanium. Volatile isopropyl acetate was produced and when it was completely removed, the temperature of the vapour reaching the top of the reflux condenser would increase from 85°C (b.p. of isopropyl acetate) to about 124°C. PT gel was obtained by controlling the hydrolysis condition of the PT solution in which the PH was adjusted to about 11 by adding water, ammonia and alcohol. The gel was dried at 100°C for 24h and then heated to various temperatures (500°C to 900°C) to give particle of various sizes. The crystallization process of the PT gel 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 particle size distributions were measured using a particle size analyser (Horiba CAPA-700). The Curie temperature T_C of the annealed powder was determined by differential scanning calorimetry (DSC, Perkin-Elmer DSC-2).

To prepare 0-3 composites, P(VDF-TrFE) (65/35) copolymer powder supplied by Piezotech in France was first dissolved in methyl-ethyl-ketone (MEK) and then a suitable amount of PT powder was blended into the solution. The mixture was then poured onto a petri-dish and, after evaporation of the solvent, the mixture was moulded into a 0.2 mm thick sheet by hot pressing at 170°C and at a pressure of 0.83 kg/m^2. Composites with a PT volume fraction of 0.4 were fabricated using PT powder annealed at various temperatures. Dics samples of 12.5 mm diameter were prepared.

In order to elicit piezoelectric activity, the composites must be poled by subjecting it to an electric field for a period of time at a suitable temperature to align the dipoles in both phases. The 0-3 composite was poled at 105°C with a field of 26 kV/mm for 2h. The electric field was switched off at 105°C (Curie temperature of the copolymer =102°C) before cooling the sample to room temperature. By this procedure, only the ceramic phase was poled. In order to pole the copolymer, the sample was heated from room temperature to 90°C and a field of 27 kV/mm was applied for 1h, then the sample was cooled to room temperature with the field kept on. The above procedure was repeated in order to better polarize the copolymer. The sample was short-circuited and annealed for 17 hours at 60°C before measurements.
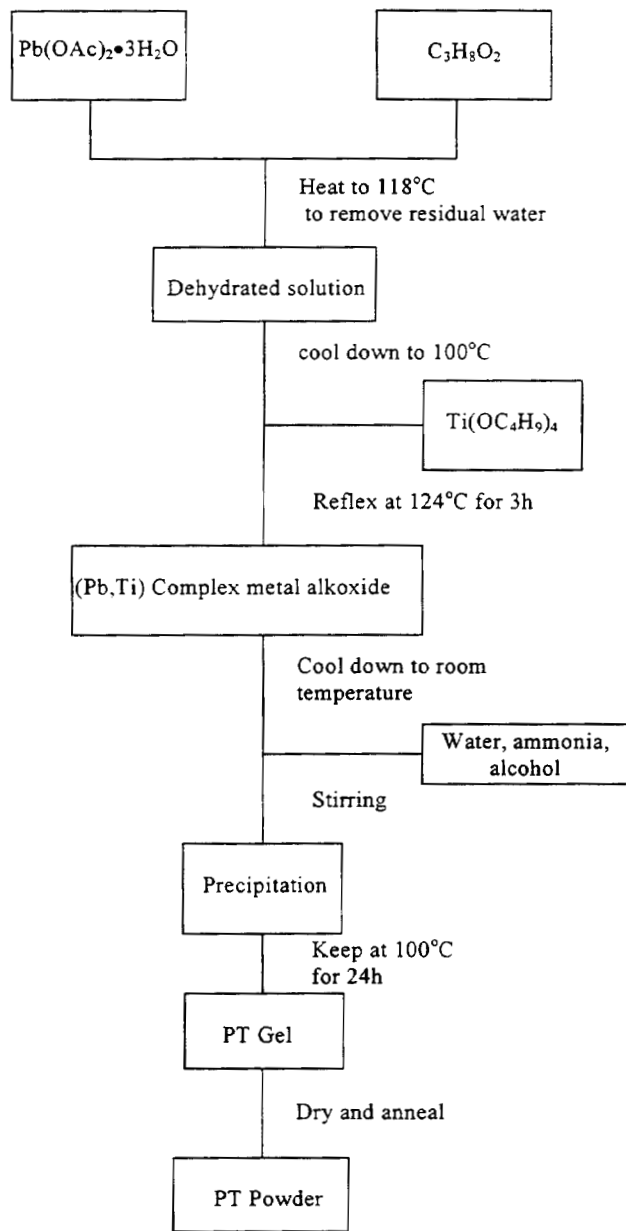
The capacitance of the samples was measured at 1 kHz using an HP4194A impedance analyzer and the permittivity was calculated. The pyroelectric coefficient p was measured using the digital integration method, [4] and the d_{33} coefficient of the samples was measured using a Pennebaker model 8000 piezo d_{33} tester from American Piezo-Ceramics Inc..

The piezo- and pyro-electric coefficients of the polarized samples were measured and results given in Table 1.

III. RESULTS AND DISCUSSION

DTA and TGA were performed on the PT powder at a heating rate of 10°C/min. The DTA curve shows an endothermic peak at 80°C (Fig. 2a) which is accompanied by a small weight loss (Fig. 2b), primarily due to the removal of
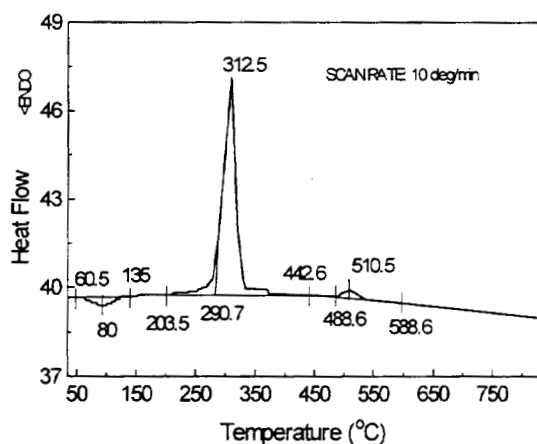

Fig 2a DTA curve of PT gel.

Fig.2b. TGA curve of PT gel.

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

The ceramic poling ratio α was caculated from the peak heights $I_{(200)}$ and $I_{(002)}$ of the (200) and (002) x-ray reflections associated with PT using the relation:

$$\alpha = I_{(002)} / [I_{(002)} + I_{(200)}] \qquad (1)$$

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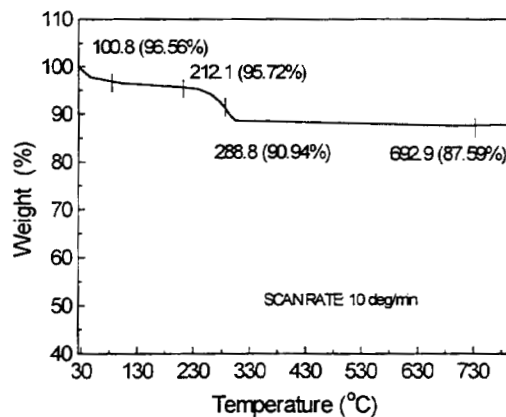
TABLE 1

The Relationship Between The Annealing Temperature, The Average Crystallite Size, Particle Size And T_C Of PT Nanocrystalline Powder α, ε, d_{33} And p Are Properties Of 0-3 PT/P(VDF-TRFE) Composites With A Ceramic Volume Fraction Of 0.4 Using PT Annealed At Various Temperatures.

Annealing Temp. (°C)	crystallite dia. (nm)	particle dia. (nm)	T_c (°C) of PT	ε	ε_1	α_1	$(d_{33})_1$ (pC/N)	p_1 (μC/m²K) (25°C)	p_1/ε_1 (μC/m²K) (25°C)
500	26.8	30	434.5	39.2	32.6	0.73	11.2	44.1	1.35
600	35.0	40	472.5	43.0	32.5	0.73	14.7	49.4	1.52
650	36.5	50	------	44.0	33.6	0.48	6.9	54.1	1.61
700	40.3	70	479.5	40.0	30.9	0.68	14.0	47.2	1.53
800	44.8	120	475.4	40.3	31.4	0.73	14.0	46.0	1.46
900	54.1	270	481.4	44.0	31.9	0.72	13.6	42.6	1.34

Subscript 1 indicates both phases are polarized.

water and alcohol trapped in micropores. The exothermic peak at 312°C, together with the corresponding weight loss, can probably be attributed to the oxidation of acetate groups or the decomposition of unhydrolyzed alkoxy groups. The exothermic peak at 510°C, not accompanied by a significant decrease in weight, probably reflects the crystallization of the PT powder.

Fig. 3 shows the XRD patterns of PT powder after annealing at various temperatures for 1h. Samples annealed at temperatures lower than 500°C exhibit the typical amorphous pattern. When the annealing temperature reaches 500°C, crystalline peaks appear, in agreement with the DTA result. The crystallite sizes of PT powder annealed at various 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 [5]

$$D = (K\lambda)/(B\cos\theta) \qquad (2)$$

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 diameter, obtained by averaging the results for the (100), (111) and (200) peaks, is given as a function of the annealing temperature in Table 1. The average crystallite diameter increases from 27 nm to 54 nm as the annealing temperature increases from 500°C to 900°C.

The particle size distributions of the PT nanocrystalline powder annealed at various temperatures were measured using a particle size analyzer. The size of the PT powder (dispersed by ultrasonic agitation in ethanol) falls in the range of 30 to 270 nm indicating that each PT particle consists of a number of crystallites. The measured Curie transition temperature T_c of the annealed powder (Table 1) was 435°C for powder annealed at 500°C and increased to 475°C- 481°C for annealing temperatures higher than 700°C.
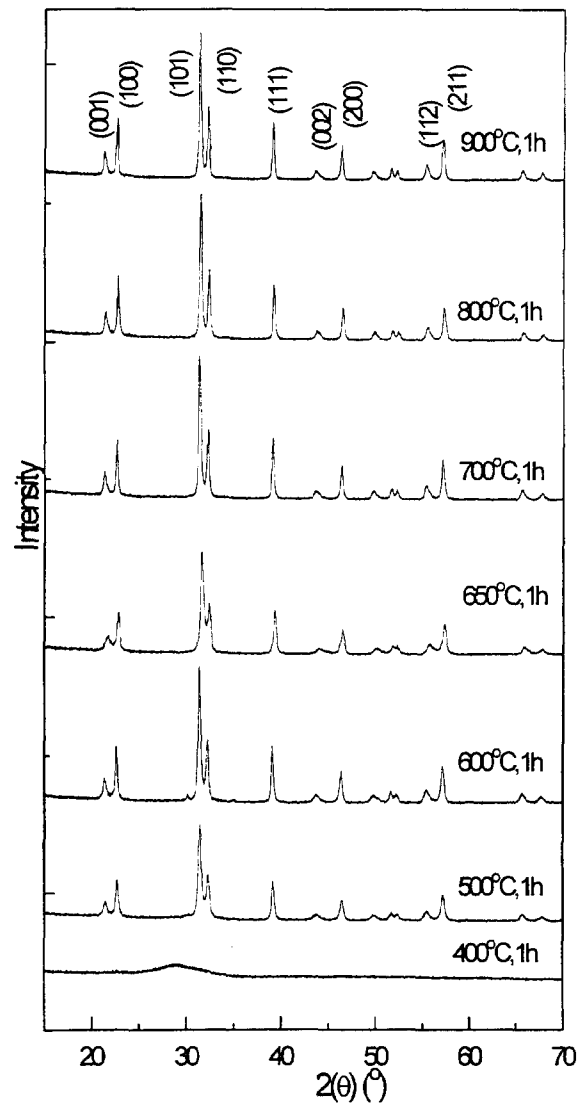

Fig. 3 XRD patterns of PT powder annealed at various temperatures for 1h.

The permittivity ε of the unpoled composites varied slightly with annealing temperature. After poling, the permittivity ε_1 of the samples decreased by about 23%. The polarized composite with PT powder previously annealed at 650°C has the lowest poling ratio α_1 and hence the lowest piezoelectric coefficient $(d_{33})_1$. We had tried to improve α_1 by poling this sample several times but α_1 showed little improvement. However, maximum values of the pyroelectric coefficient p_1 and p_1/ε were achieved in composites with the PT phase annealed at about 650°C.

IV. CONCLUSION

PT nanocrystalline powder has been prepared by the sol-gel process using metal alkoxides. The sizes of both the PT particles and the crystallites within each particle increase with annealing temperature. The PT powder annealed at 650°C has average particle and crystallite diameters of 50nm and 37nm, respectively. The ultrafine PT powder has been incorporated into a P(VDF-TrFE) matrix to form 0-3 composites, and the nanocomposite with PT powder annealed at 650°C has the highest pyroelectric coefficient p and the highest gure of

merit p/ε. Work is in progress to produce 1μm thick 0-3 composite films for integrated pyroelectric sensor and array applications.

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