

# The fabrication of lead titanate ceramics by a two-stage sintering technique

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**Abstract** In this work, a two-stage sintering technique, which began with an initial heating at lower temperature and followed by higher temperature sintering, was employed in the production of  $\text{PbTiO}_3$  ceramics. Effects of designed sintering conditions on phase formation, densification, microstructure and dielectric properties of the ceramics were characterized via X-ray diffraction (XRD), Archimedes method, scanning electron microscopy (SEM) and dielectric measurement, respectively. The potentiality of a two-stage sintering technique as a low-cost and simple ceramic fabrication to obtain highly dense and pure lead titanate ceramics was demonstrated. It has been found that, under suitable conditions, the perovskite phase of densified PT ceramics with reasonable dielectric properties may be achieved with equivalent to those obtained from a single-stage sintering technique.

**Keyword** Lead titanate ·  $\text{PbTiO}_3$  · Two-stage sintering · Perovskite · Microstructure

## 1 Introduction

Lead titanate ( $\text{PbTiO}_3$  or PT) when combined with other oxides can form a series of ferroelectric materials that exhibit many of the most desirable dielectric, piezoelectric and pyroelectric properties for high frequency and temperature applications [1–3]. However, pure and dense PT ceramics are regarded to be one of the most difficult lead-

based perovskite ferroelectric ceramics to produce due to large distortion of the tetragonal phase at room temperature ( $c/a$ , hereafter called tetragonality,  $\sim 1.06$ ) [4]. Apart from general problems of PbO volatilization and associated high porosity, the stress induced by cooling through the phase transition can create cracking in bulk ceramics.

To overcome these problems, several techniques have been introduced, such as utilizing ultrafine powders, using additives, and carrying out appropriated milling and sintering conditions [5–7]. Amongst all the issues reported so far, most attention has been concentrated on the use of additives and powder processing, whereas investigations on modified sintering techniques have not been widely carried out [8]. Therefore, in the present study, a two-stage sintering method has been developed to resolve these problems. The overall aim of the work described here is to design the sintering scheme for fabrication of PT ceramics. The effect of the sintering conditions on phase formation, densification, microstructure and dielectric properties of materials is then investigated.

## 2 Experimental procedure

Commercially available powders of PbO and  $\text{TiO}_2$  (anatase form) (Fluka, >99% purity) were used as starting materials. A simple mixed oxide synthetic route reported earlier [7] was employed to synthesize  $\text{PbTiO}_3$  powders. Ceramic fabrication was carried out by adding 3 wt.% polyvinyl alcohol (PVA) binder, prior to pressing as pellets in a uniaxial die press at 100 MPa. Sintering was carried out with a dwell time of 2 h for each step, with constant heating/cooling rates of  $1^\circ\text{C}/\text{min}$ . Variation of the single sintering temperature between 1150 and  $1250^\circ\text{C}$  was carried out for the first batch of the samples. For the

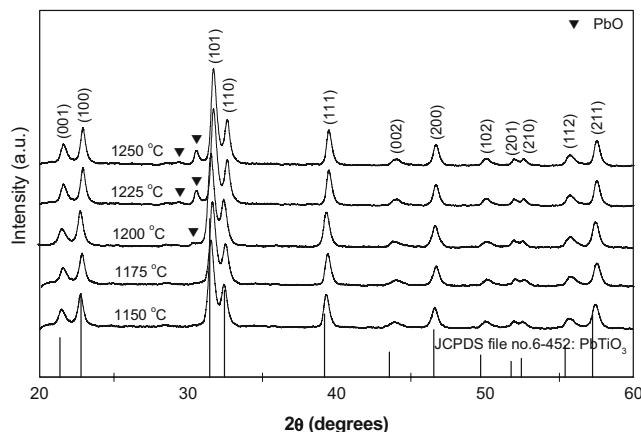
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second batch, the first sintering temperature ( $T_1$ ) was assigned at 900°C for all cases. Variation of the second sintering temperature ( $T_2$ ) from 1000°C to 1250°C was carried out.

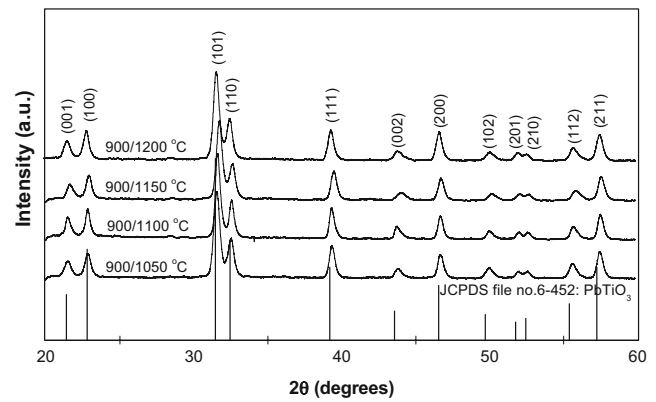
Densities of the sintered products were determined by using the Archimedes principle. Sintered ceramics were examined by room temperature X-ray diffraction (XRD; Siemens-D500 diffractometer) to identify the phase formed. The lattice parameters were calculated from the XRD patterns. The microstructural development was characterized using a JEOL JSM-840A scanning electron microscopy (SEM) equipped with an energy dispersive X-ray (EDX) analyzer. Mean grain sizes of the sintered ceramics were estimated by employing the linear intercept method. The dielectric properties were measured using a HIOKI 3532-50 LCR meter.

### 3 Results and discussion

X-ray diffraction patterns from the singly and doubly sintered PT ceramics are displayed in Figs. 1 and 2, respectively, indicating the formation of both perovskite and impurity phases in each case. The strongest reflections in the majority of the XRD traces indicate the formation of the perovskite phase of lead titanate,  $PbTiO_3$ , which could be matched with JCPDS file no. 6-452, in agreement with other works [5, 7, 9]. For the singly sintered PT ceramics, additional weak reflections are found in the samples sintered above 1175°C (marked by inverted shaded triangle in Fig. 1), which correlate to the starting precursor  $PbO$  (JCPDS file no. 77-1971). This observation could be attributed mainly to the poor mixing of the employed powders derived from the ball-milling technique. More interestingly, a single phase of perovskite is found in most of the doubly sintered PT samples (Fig. 2), in contrast to the observations for the singly sintered samples. This could be due to the lower firing



**Fig. 1** XRD patterns of PT ceramics singly sintered at various temperatures for 2 h with heating/cooling rates of 1°C/min



**Fig. 2** XRD patterns of PT ceramics doubly sintered at various second sintering temperatures

temperature of the doubly sintered samples as compared to the singly sintered ceramics, leading to a smaller degree of lead losses and consequently avoiding the pyrochlore formation. However, many other factors come into play, e.g. homogeneity of materials, reactivity of starting powders, and processing variables.

From Table 1, it is evident that as the sintering temperature increases, the density of almost all the samples increases. The ceramic doubly sintered at 900/1150°C having the highest relative density of about 98% with a smallest average grain size of about 0.8 μm, was of the best interest for further investigations. Nevertheless, most of the samples suffered from severe stresses as a result of the high  $c/a$  ratio so they have broken into pieces once subjected to a cycle of high temperature measurement of dielectric properties.

Microstructural features of PT samples singly sintered at different temperatures are shown in Fig. 3. It was found that the samples subjected to low sintering temperature e.g. 1150°C eventually burst into pieces because of the internal

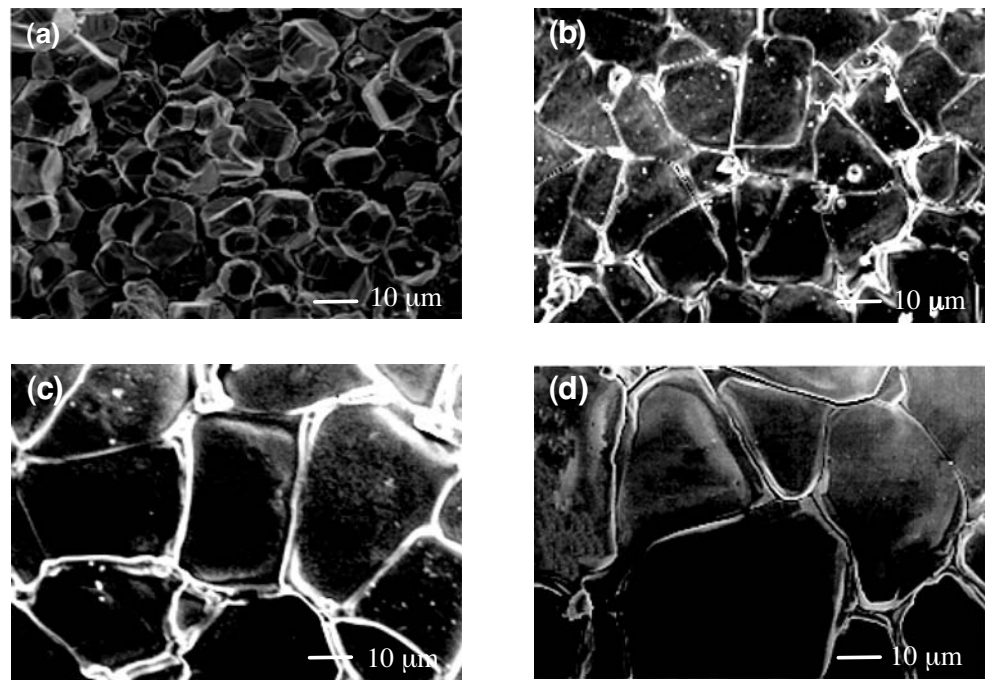
**Table 1** Sintering behaviour of PT ceramics.

$T_1$ (°C)	$T_2$ (°C)	Tetragonality ( $c/a$ )	Relative density (%)	Mean grain size <sup>a</sup> (μm)
1150	–	1.064	87	10
1175	–	1.064	89	21
1200	–	1.063	92	29
1225	–	1.063	94	36
1250	–	1.063	93	41
900	1000	–	–	–
900	1050	1.060	96	1.2
900	1100	1.060	96	1.1
900	1150	1.056	97	0.8
900	1200	1.061	97	1.5
900	1250	–	–	–

*En dash* (–) Data are not available because the samples were too fragile for the measurements.

<sup>a</sup> The estimated precision of the grain size is ±1%.

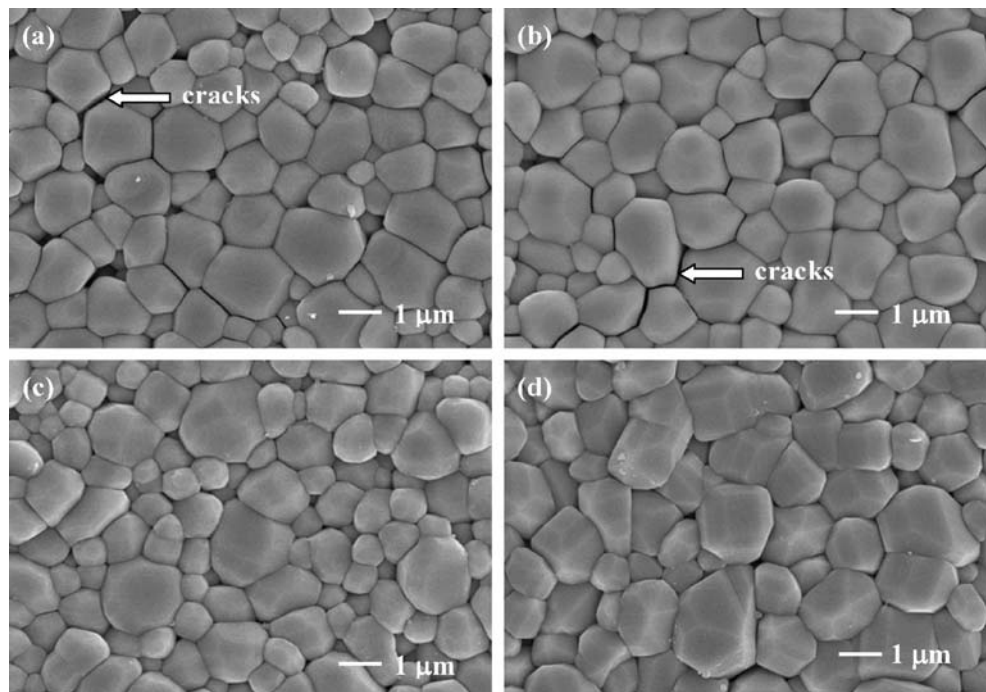
**Fig. 3** SEM micrographs of PT ceramics singly sintered at (a) 1150°C, (b) 1200°C, (c) 1225°C, and (d) 1250°C, for 2 h with heating/cooling rates of 1°C/min



anisotropic stress caused by the phase transition in the ceramics as can be confirmed by the SEM images showing a loose formation of large grains (Fig. 3(a) and (b)), in consistent with high values of  $c/a$  given in Table 1. Additionally, average grain sizes were found to increase with the sintering temperature. For higher temperature treatments, a pronounced second phase is segregated at the grain boundaries. The EDX spectra indicated that there was more Pb and less Ti in the bright region than in the dark region.

The observation of these second phase layers could be attributed to a liquid phase formation during the sintering process as proposed by Wang et al. and Gupta et al. [10, 11]. It should also be noted here that the second phase could also be a result of the purity of the commercial grade starting materials and firing history used in this study. In addition, a combination of SEM and EDX techniques has demonstrated that small amounts of nano-sized ( $\phi \sim 1.7\text{--}2.5\ \mu\text{m}$ ) spherical of  $\text{TiO}_2$  inclusions (brighter phase) exists

**Fig. 4** SEM micrographs of PT ceramics doubly sintered at (a) 900°C/1050°C, (b) 900°C/1100°C, (c) 900°C/1150°C, and (d) 900°C/1200°C, for 2 h with heating/cooling rates of 1°C/min



**Table 2** Dielectric properties of PT ceramics.

Dielectric properties (1 kHz)	Sintering temperature (°C)	
	1225	900/1200
$\epsilon_r$ , room temperature	525	318
$T_C$	486	487
$\epsilon_r$ , max	20423	416997
$\tan \delta_{\max}$	2.35	0.08

on the surface of perovskite PT grains in some samples, as shown in Fig. 3(b) and (c). The existence of a discrete  $\text{TiO}_2$  phase points to the expected problem of poor homogeneity of the samples arising from  $\text{PbO}$  volatilization after subjected to prolong heating scheme, although the concentration is too low for XRD detection.

Representative microstructures for doubly sintered PT ceramics are given in Fig. 4. It is seen that a uniform grain shape of typical perovskite ceramics [12] is observed, with sizes in the range of 0.4–2.0  $\mu\text{m}$ . It should be noted that the average grain size of the doubly sintered PT ceramics is <1.5  $\mu\text{m}$ , which is less than the critical value of 3  $\mu\text{m}$  [13] and gives rise to a volumetric percentage enough to buffer the anisotropic stress caused by the phase transition [5]. Here, it is believed that smaller grains with random orientations result in lower internal stress in sintered samples because they compensate the anisotropy of thermal expansion coefficients.

By comparison with singly sintered PT ceramics, almost clean microstructures with highly uniform, denser angular grain-packing are generally found in doubly sintered PT samples. These microstructures are typical of a solid-state sintering mechanism. However, it should be noted that higher angular grains were evidenced for higher second sintering temperature. The observation that the sintering temperature effect may also play an important role in obtaining a high angularity grains of perovskite ceramics is also consistent with other similar systems [14]. It is also of interest to point out that evidence has been found for the existence of microcracks (arrowed) along the grain boundaries of the samples sintered at lower second sintering temperatures (Fig. 4(a) and (b)), in consistent with other works [8, 15].

Interestingly, only the samples sintered at 900°C/1150°C with the highest relative density and smallest average grain size of about 98% and 0.8  $\mu\text{m}$ , respectively, remained unbroken. It may be assumed that the ceramics consisting of very fine grains suffer less deformation, caused by the high value of  $c/a$  ratio, than the ceramics with significantly large grains (Table 1). Consequently, the experimental work carried out here suggests that the optimum conditions for forming the highly dense PT ceramics in this work are double-sintering temperatures at 900°C/1150°C, 2 h dwell

time, and 1°C/min heating/cooling rates. The dielectric properties of PT samples sintered with different techniques are also compared in Table 2. In general, they all behave as normal ferroelectric. The Curie temperatures are about the same for all samples measured whilst the variation of dielectric constant and dielectric loss of both sets of the sintered PT ceramics seems to be somewhat related to the sintering temperatures. This observation indicates that the presence of the second phases accompanied with porosities is the key factor responsible for the dielectric response of the products. Moreover, this study demonstrated that the dielectric properties of PT ceramics are also influenced by microstructural features especially the grain boundary phase, microcracks and densification mechanism rather than by only pyrochlore phase or by grain size itself.

## 4 Conclusion

This work demonstrated that it was possible to obtain rather dense PT ceramics with homogeneous microstructure by the two-stage sintering technique. It has been shown that, under suitable conditions, the phase formation and densification of the ceramics are better than those obtained from the single-stage sintering. More importantly, with the two-stage sintering technique, small reductions in the maximum required sintering temperature are possible as compared to the single-stage sintering.

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## References

1. A.J. Moulson, J.M. Herbert, *Electroceramics*. (Wiley, Chichester, 2003)
2. G.H. Haertling, *J. Am. Ceram. Soc.* **82**, 797–818 (1999)
3. S. Jiang, D. Zhou, S. Gong, W. Lu, *Sens. Actuators A* **69**, 1–4 (1998)
4. G. Shirane, R. Pepinsky, B.C. Frazer, *Acta Crystallogr.* **9**, 131–140 (1956)
5. T. Suwannasiri, A. Safari, *J. Am. Ceram. Soc.* **76**, 3155–3158 (1993)
6. J. Tartaj, C. Moure, L. Lascano, P. Duran, *Mater. Res. Bull.* **36**, 2301–2310 (2001)
7. A. Udornporn, K. Pengpat, S. Ananta, *J. Eur. Ceram. Soc.* **24**, 185–188 (2004)
8. S. Ananta, N.W. Thomas, *J. Eur. Ceram. Soc.* **19**, 2917–2930 (1999)
9. JCPDS–ICDD Card no. 6-452. International Centre for Diffraction Data. Newtown Square, PA, 2000.
10. H.C. Wang, W.A. Schulze, *J. Am. Ceram. Soc.* **73**, 825–832 (1990)
11. S.M. Gupta, A.R. Kulkarni, *J. Mater. Res.* **10**, 953–961 (1995).
12. Y.-C. Liou, *Mater. Sci. Eng.* **B103**, 281–284 (2003)
13. R.W. Rice, R.C. Pohanka, *J. Am. Ceram. Soc.* **62**, 559–563 (1979)
14. S. Ananta, N.W. Thomas, *J. Eur. Ceram. Soc.* **19**, 1873–1881 (1999)
15. S.R. Dhage, Y.B. Kholam, H.S. Potdar, S.B. Deshpande, B.D. Sarwade, D.K. Date, *Mater. Lett.* **56**, 564–570 (2002)