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Highly dense lead titanate ceramics from refined processing

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Abstract

Lead titanate ($PbTiO_3$, PT) ceramic is a useful pyroelectric and piezoelectric material for high-temperature applications. However, it is very difficult to prepare a pure-phase and dense PT as a result of a high c/a ratio. In this study, conformable PT ceramics with 97% of the theoretical density were successfully synthesized by means of carefully controlled processing parameters that include sintering temperature, soaking time and heating/cooling rates. It can be found that these ceramics exhibit highly densified and uniform microstructure with the optimum conditions of 1225 °C sintering temperature, 2 h soaking time and 1 °C min^{-1} heating/cooling rates. Moreover, relatively inexpensive laboratory grade lead oxide (PbO) and titanium oxide (TiO_2) can be used as starting materials.

Keywords: Grain size; Microstructures; $PbTiO_3$; Powders-solid state reaction

1. Introduction

Lead titanate ($PbTiO_3$) is a ferroelectric, having a highly symmetric perovskite-type structure with a high curie temperature (T_c) of about 490 °C at which the phase transition of tetragonal ferroelectric phase ($< T_c$) to cubic paraelectric phase ($> T_c$) occurs.[1] The PT ceramic is a useful pyroelectric and piezoelectric material for high-temperature or high-frequency applications, such as non-volatile memories, infrared sensors and capacitors.[2] It is difficult to prepare a pure-phase PT ceramics with high density, as a result of a high c/a ratio of about 1.06 which gives rise to stresses in these ceramics, hence they can be easily broken and difficult to prepare in shape and size suitable for device applications.[3,4] The most widely used approach is the formation of solid-solution by adding additives, such as rare earth elements and alkaline earth elements and this is the promising technique for producing crack-free high-density materials.[5] However, the properties of PT itself are subsequently altered by the additives and as it has been known that PT has a good electrothermal property so the stoichiometric $PbTiO_3$ is still needed.[6] A lot of processing techniques for preparing the high purity and ultrafine $PbTiO_3$ powders have been extensively investigated because it is believed that these type of powders aid the formation of high density ceramics.[7] Most of the techniques were based on the chemical routes such as, sol-gel synthesis, hydrothermal reactions, coprecipitation, molten salt preparation and emulsion technique.[8–12] These chemical routes are normally complicated and expensive so they are not suitable for mass production. Therefore, the systematic study of the solid-state reaction between lead oxide and titanium oxide has been studied by Pillai and Ravindran.[13] They successfully found that the optimum sintering temperature was as low as 875 K for the formation of the single phase PT ceramic using DTA and XRD techniques. Even though the sintering temperature reported in their work was considerably low, the long period of up to 16 h dwell time was used.

In this work, the effects of thorough sintering parameters, including sintering temperatures, heating/cooling rates and soaking time on phase formation, density, microstructural development of PT ceramics have been carefully studied in order to find an optimum processing condition for forming the dense PT ceramic using conventional ceramic method.

2. Method

The PT ceramics of stoichiometric composition ($PbO:TiO_2$) were prepared using laboratory grade powders of 99.6% pure lead oxide (PbO) and 99.6% pure titanium oxide (TiO_2) as starting materials. After ball-milling for 24 h, drying in electric furnaces and sieving

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with the 120 mesh, the resulting powders were calcined for 2 h at 400–1000 °C with 5 °C min^{-1} heating/cooling rate. Then various sintering conditions were employed by varying the sintering temperatures from 1185 to 1230 °C and sintering rates from 1 to 10 °C min^{-1} but dwell time was kept constant for 2 h. The bulk densities of the sintered samples were calculated using Archimedes's method. X-ray diffraction (XRD) patterns were recorded using X-ray diffractometer with CuK_α radiation. The as-received and fractured surfaces of selected ceramics were prepared for the scanning electron microscopy (SEM) analysis. The average grain sizes of the ceramics were determined using the mean linear method.

3. Results and discussions

3.1. Phase formation behaviour

Lead titanate (PT) powders were formed easily by solid-state reaction between laboratory grade powders of PbO and TiO_2. In this study, the formation of PT phase was initiated at the calcining temperature of 600 °C with dwell time of 2 h and heating/cooling rates of 3 °C/min, while the value reported by Pillai and Pavindran[12] was 527 °C (800 K). Additionally, the impurities of PbO phase were detected in the calcined powders of 900 and 1000 °C that may cause from the loss of vaporised PbO at high temperature. In order to confirm the complete reaction of $PbO(s)+TiO_2(s)\rightarrow PbTiO_3(s)-H$, the optimum condition of calcination used in this work was 750 °C for 2 h with heating/cooling rate of 3 °C min^{-1}.

The phase formation in the sintered ceramics of sintering temperatures ranging from 1185 to 1230 °C are presented via the X-ray diffraction as shown in Fig. 1. Table 1 presents percent shrinkage, relative density and average grain size of each ceramic sample. From Fig. 1, it can be seen that the tetragonal PT phase was formed in all PT ceramics but impurities of PbO phase were observed in the ceramics sintered at 1200 and 1220 °C while others have a high purity of PT phase. Nevertheless most of the samples suffered from severe stresses as a result of the high c/a ratio so they have broken into pieces after they were once subjected to a measurement of dielectric constant at high temperature. From Table 1,

Table 1
Percent shrinkage, relative density and grain size of PT ceramics from various sintering temperatures

Sintering temperature (°C)	Shrinkage (%)	Relative density (%)	Grain size[a] (μm)
1185	11.15	86.7	49
1190	11.03	88.9	34
1200	12.18	89.5	35
1210	12.63	92.7	27
1220	13.14	92.8	30
1225	14.06	95.4	23
1230	14.01	93.5	52

[a] The estimated precision of the grain size is ±1%.

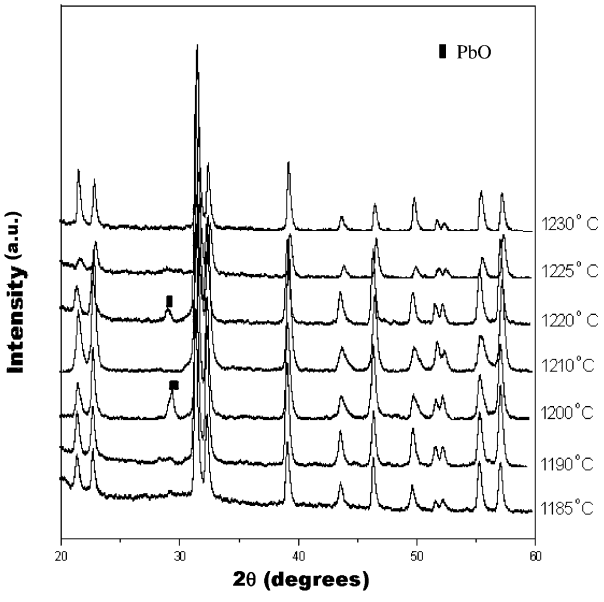

Fig. 1. The X-ray powder diffraction patterns of ceramic samples heated at different sintering temperatures with the constant dwell time of 2 h and heating/cooling rate of 3 °C min^{-1}.

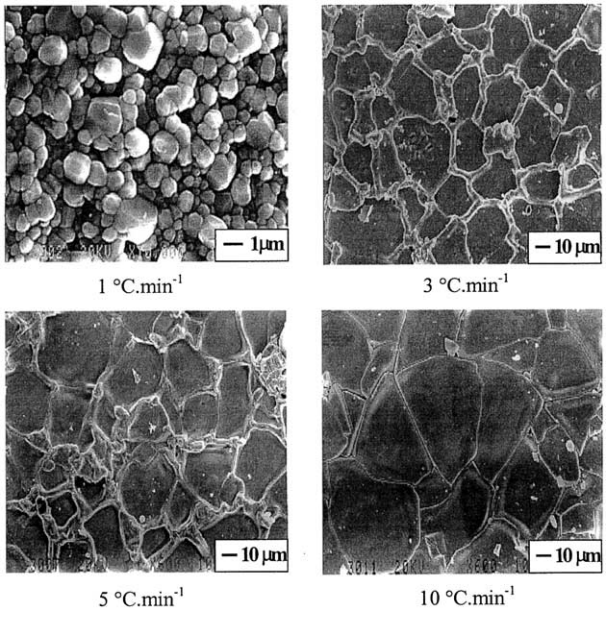

Fig. 2. The SEM images of the as-received surfaces of $PbTiO_3$ ceramics sintered at 1225 °C for 120 min with heating/cooling rate of 1 °C min^{-1} to 10 °C min^{-1}.

the ceramic sintered at 1225 °C having the highest relative density of about 95% with a smallest average grain size of about 23 μm, was of the best interest for further investigation. Therefore, another group of samples were sintered at the chosen sintering temperature of 1225 °C for 2 h with the heating/cooling rates ranging from 1 to 10 °C min^{-1}.

3.2. Densification and microstructures

Figs. 2 and 3 show the SEM images of as-received and fractured surfaces of $PbTiO_3$ ceramics, respectively. The constant sintering temperature was used for all samples at 1225 °C for 2 h while heating/cooling rates were varied from 1 °C min^{-1} to 10 °C min^{-1}. It should be noted that a pronounced second phase is segregated at the grain boundaries in the samples sintered with heating/cooling rates of 3, 5 and 10 °C min^{-1}. This second phase layer is believed to be a PbO-rich composition resulting from a liquid phase formation during the sintering process.[14,15] Table 2 contains the information of relative densities and grain sizes of the ceramics with different heating/cooling rates. It is obviously seen that heating/cooling rates are the important parameters for the development of ceramic microstructures. In that the average grain size increases with increasing heating/cooling rates as shown in Table 2. It was also found that the samples with heating/cooling rates of 3, 5 and 10 °C min^{-1} eventually burst into pieces because of the internal stresses in the ceramics as can be confirmed by the SEM images showing a loose formation of large grains in Fig. 3. Interestingly, only the samples of 1 °C min^{-1} heating/cooling rates remained with the highest relative density and smallest average grain size of about 97% and 0.6 μm, respectively. 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 that of the ceramics with significantly large grains. Consequently, the optimum conditions for forming the highly dense PT ceramics in this work are 1225 °C sintering temperature, 2 h dwell time and 1 °C min^{-1} heating/cooling rates. In addition, the results from Pillai and Ravindran[12] showed that single phase with average grain size of 3 μm could be formed at 602 °C (875 K) for 16 h. Even though the long period of 16 h dwell time was used, the sintering temperature was relatively low therefore the small grains could be formed in their ceramics. Conversely, high sintering temperature of 1225 °C was used in this work but the ceramics with small average grain size of 0.6 μm were still achieved. Therefore, the key parameter that controlled the grain growth here would be attributed to the slow heating rate of 1 °C min^{-1}. Conclusively, the further investigation should be carried out in order to find out exactly what inhibits grain growth in these PT ceramics while they are subjected to a long heating schedule of slow heating/cooling rates.

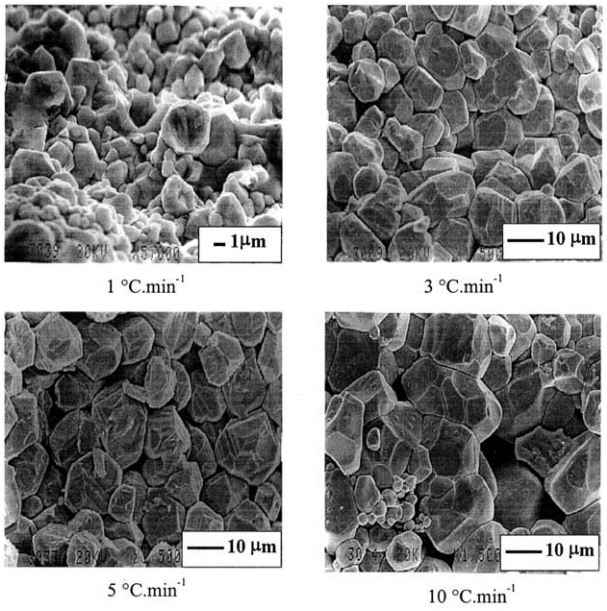

Fig. 3. The SEM images of the fractured surface of $PbTiO_3$ ceramics sintered at 1225 °C for 120 min with heating/cooling rate of 1 °C/min to 10 °C/min.

Table 2
Relative densities and grain sizes of PT ceramics sintered at 1225 °C with different heating/cooling rates

Heating/cooling rate (°C min^{-1})	Relative density (%)	Grain size (μm)[a]
1	96.8	0.6
3	94.6	23.4
5	92.1	25.9
10	92.5	30.3

[a] The estimated precision of the grain size is ±1%.

4. Conclusion

Even though the simple mixed-oxide method was used, the highly dense and stable PT ceramics were successfully formed by the careful control of processing parameters. After the thorough investigation had been performed, the optimum conditions were determined. It is found that the slow heating/cooling rates are important parameters in preparing these dense ceramics. The well defined-grain ceramics with the average grain size of about 0.6 μm could be prepared by heating them to 1225 °C using the considerably slow heating/cooling rates of 1 °C min^{-1} and dwell time of 2 h. Moreover, it was also found that the relative densities of these ceramics would be as high as 97%.

Acknowledgements

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