The effect of TiO$_2$ nanotubes on the sintering behavior and properties of PZT ceramics

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Abstract
In this study, the effect of as-prepared anatase TiO$_2$ nanotubes on the sintering behavior and the piezoelectric properties of lead zirconate titanate (PZT) ceramics was investigated. Two types of PZT (with the use of TiO$_2$ nanotubes and commercial TiO$_2$) were prepared by a conventional oxide-mixing method. The density of samples using TiO$_2$ nanotubes tended to increase and the sintering temperature of these ceramics decreased. The electromechanical coupling factor ($k_p$) of PZT ceramics was improved significantly by the use of TiO$_2$ nanotubes.

Keywords: lead zirconate titanate, TiO$_2$ nanotubes, sintering temperature, piezoelectric

Classification number: 5.11

1. Introduction
Lead titanate zirconate (Pb(Zr$_x$Ti$_{1-x}$)$_2$O$_3$) ceramics are one of the most common piezoelectric materials in industry; they are used as transducers between electrical and mechanical energy, such as phonograph pickups, air transducers, underwater sound and ultrasonic generators, delay-line transducers, wave filters, piezoelectric micromotors, microrobots and actuators [1–4]. Their properties are strongly influenced by the density and microstructure, which depend on the synthesis procedure [5]. Conventionally, PZT ceramics require a sintering temperature of 1200 °C or higher [6]. Such high temperature sintering is undesirable because of the higher energy consumption and, above all, volatilization of lead with the change in composition and deterioration of piezoelectric properties. Therefore, lowering the sintering temperature is an important technique for suppressing compositional fluctuation and improving the piezoelectric properties, reliability and reproducibility of the PZT ceramics. So far, a lot of studies, such as the fast firing technique [7] and sintering aids [5], have been tried with varying success.

It is well known that the large specific surface area of nanostructured materials is very important in enhancing the reaction rate and decreasing the processing temperature in solid state reactions [8]. In the present study, we investigated the effect of TiO$_2$ nanotubes on the densification and microstructural evolution of PZT ceramics. In accordance with this, variations of the piezoelectric properties were also observed and correlated with the microstructures of the specimens.

2. Experimental
2.1. Synthesis of TiO$_2$ nanotubes
There are many methods for the fabrication of TiO$_2$ nanotubes and nanowires: treating TiO$_2$ powders (Merks 99%, Germany) were added to a 10 mol l$^{-1}$ NaOH solution in a pyrex beaker, which was sonicated by ultrasonic transducer (32 kHz, 100 W), as described in our previous work [13]. The sonicated solution was then moved to a teflon vessel and put in a stainless steel autoclave to carry out the hydrothermal treatment at 130 °C for 10 h. After cooling down at room temperature, the precipitates were separated and washed repeatedly with deionized water and 0.1 mol l$^{-1}$ HCl aqueous solution. The final as-prepared products were dried under vacuum at 80 °C for 2 h. The as-prepared products were calcined at different temperatures of 450 °C for 1 h in air. The morphologies were investigated using a...
Figure 1. X-ray diffraction patterns of (a) commercial TiO$_2$ and (b) as-prepared TiO$_2$ nanotubes after calcination at 450°C.

Figure 2. SEM (a) and TEM (b, c) images of TiO$_2$ nanotubes after calcinations at 450°C for 1 h.

Hitachi S-4800 field emission scanning electron microscope (FE-SEM) and transmission electron microscopy (TEM). The crystalline phases of the samples were characterized by using a D8 Advance-Brucker diffractometer (XRD) with monochromatized Cu-Kα irradiation (λ = 1.54056 Å). The specific surface area of titania nanotubes calcined at 450°C was calculated using the Brunauer–Emmett–Teller (BET) method.

2.2. Synthesis of PZT ceramics

The general formula of the materials studied was Pb(Zr$_{0.51}$Ti$_{0.49}$)O$_3$ + 0.4 wt% MnO$_2$. The samples were prepared by a conventional oxide mixing technique, but this study examined the effect of TiO$_2$ nanotubes on the sintering behavior and properties of the PZT ceramics. For comparison, sample A (starting powders included PbO, ZrO$_2$ and TiO$_2$ (Merk)) and sample B (powders of PbO and ZrO$_2$ (Merk) and as-prepared TiO$_2$ nanotubes calcined at 450°C for 1 h) were prepared under the same experimental conditions.

Figure 3. XRD patterns of sample A and sample B sintered at different temperatures.
Using commercial TiO$_2$

Using TiO$_2$ nanotubes

Figure 4. SEM photographs of the PZT(51/49) + 0.4 wt%MnO$_2$ ceramics (sample A and sample B) prepared with the same experimental conditions. The sintering temperature is indicated on the figure.

In this study, 5 wt% excess PbO was added to compensate for the lead loss during sintering. The powders were mixed by ball milling for 20 h using zirconia balls and ethanol as the medium. After drying, the mixture was calcined at 850 °C for 2 h. The calcined powders were again ball milled for 20 h. The resulting powders were uniaxially compacted into pellets of 12 mm in diameter. To investigate their sintering behavior, the specimens were sintered in a sealed alumina crucible at temperatures ranging from 900 to 1150 °C for 2 h.

The density of the sintered bodies was determined by the Archimedes method. To investigate the electrical properties, the sintered disks were lapped on their major faces, then silver electrodes were deposited with a low temperature paste at 500 °C for 15 min. The piezoelectric samples were poled in a silicone oil bath at 120 °C by applying 30 kV cm$^{-1}$ for 20 min then cooling them under the same electric field. They were aged for 24 h prior to testing. The electromechanical coupling factor, $k_p$, was determined by the
shows the SEM and TEM images of the shows SEM micrographs of as-sintered surfaces

3. Results and discussion

3.1. Structure and microstructure of as-prepared TiO$_2$ nanotubes

Figure 1 shows x-ray diffraction (XRD) patterns of TiO$_2$ nanotubes after calcinations at 450°C. Examination of the XRD patterns shows that there is no phase transformation from the starting material.

Figure 2 shows the SEM and TEM images of the as-prepared products of nanotubes after calcination for 1 h at 450°C. The samples have a tubular morphology with an average outer (inner) diameter of 10 nm (5 nm) and a length of hundreds of nm. The specific surface area calculated using the Brunauer–Emmett–Teller model was found to be 330 m$^2$ g$^{-1}$.

3.2. The effect of TiO$_2$ nanotubes on the sintering behavior and the piezoelectric properties of lead zirconate titanate (PZT) ceramics

Figure 3 shows XRD patterns of specimen A (sintered at temperature ranging from 1000 to 1100 °C) and specimen B (sintered at temperature ranging from 900 to 1100 °C) for 2 h. All peaks are well matched with the Perovskite structure. The secondary phase was not observed at all.

Figure 4 shows SEM micrographs of as-sintered surfaces of specimens A and B sintered at temperatures ranging from 950 to 1100°C for 2 h. As shown in figure 6, the grain sizes of the sample B are larger in comparison with sample A. Comparatively, the microstructures of the specimens with the use of TiO$_2$ nanotubes, which were sintered at the same temperature, are more uniform and compact.

The density of the specimens of sample A and sample B as a function of the sintering temperature is shown in figure 5. This shows that the effect of the TiO$_2$ nanotubes on the density of the specimens B were observed, and the density of sample B increased markedly in comparison with sample A. On the other hand, the density of sample B was not influenced strongly by the sintering temperature from 950 to 1150 °C. At 1050 °C, the specimen was almost fully dense and reached the highest density. In that case, the sinterability at lower sintering temperature of the ceramics was as expected. The density of the ceramics was markedly enhanced by using TiO$_2$ nanotubes.

The electromechanical coupling coefficient ($k_p$) of sample B increased remarkably in comparison with sample A, as shown in figure 6. This property was also strongly influenced by the use of TiO$_2$ nanotubes in the synthesis of ceramics. The highest electromechanical coupling coefficient $k_p$ of 0.59 was observed from sample B at a sintering temperature of 1050 °C while the highest $k_p$ of sample A was 0.56 at a sintering temperature of 1150 °C. This means that the large specific surface area of nanostructured materials is very important for enhancing the reaction rate and decreasing the processing temperature.

4. Conclusions

By ultrasonic assistance and a hydrothermal process, we synthesized TiO$_2$ nanotubes successfully. The phase of nanotubes calcined at 450°C is pure anatase and the BET surface area was found to be 330 m$^2$ g$^{-1}$. The effect of as-prepared TiO$_2$ nanotubes on the sintering behavior and the piezoelectric properties of PZT(51/49)+0.4 wt% MnO$_2$ ceramics was observed. The density and piezoelectric property of the ceramics were improved markedly by the use of TiO$_2$ nanotubes. The highest electromechanical coupling coefficient $k_p$ of 0.59 was observed from samples with the use of TiO$_2$ nanotubes at a sintering temperature of 1050 °C.

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