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Sintering at near theoretical density and properties of PZT ceramics chemically prepared

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PZT powder of composition $Pb(Zr_{0.65}Ti_{0.35})O_3$ was prepared by mixing PbO with an adequate mixture of titanium and zirconium tetrabutoxides by blending. Dewatering of the coprecipitated powder in a controlled humidity atmosphere, and a precalcination treatment produced a highly sinterable PZT powder. When sintering of such a powder was performed at 1200° C in an air environment, highly densified bodies (99.5% theoretical density) were obtained. The use of very fine PZT powder, and a rigorous control of PbO losses seem to be the two main factors which enhance the densification process. The microstructure, grain size and electrophysical properties for the more dense PZT ceramic material are reported.

1. Introduction

It is well known that different sintering atmospheres can have a strong influence on increasing the final sintered density. Murray and Dungan [1] reported that niobia-doped $Pb(Zr_{0.65}Ti_{0.35})O_3$ bodies fired in oxygen showed higher densities than those fired in air, nitrogen or helium. On the other hand, the oxygen sintering atmosphere also enhanced the properties of PZT ceramics. In view of their importance in piezoelectric applications, many studies have contributed to a better knowledge of the different variables that influence both their ceramic and electrical properties. Nevertheless, almost all studies used both oxygen-atmosphere sintering [2, 3] or oxygen-hot pressing [4–6] which are rather expensive. The effect of other processing variables, such as a precursor morphology, the agglomerate state of the starting materials and calcined powders, upon the sintering behaviour and properties of PZT ceramic materials is still poorly understood.

The purpose of the present work was to study the effect of variations in the processing method upon powder morphology, sintering behaviour and some electrical properties of $Pb(Zr_{0.65}Ti_{0.35})O_3$ composition.

2. Experimental procedure

2.1. Powder fabrication

The starting materials used were zirconium and titanium tetrabutoxides containing some excess butanol, and lead oxide powder. The required amount of lead oxide was added to the mixture of the organometallic liquid $Zr-Ti(OC_4H_9)_4OHC_4H_9$ and blended rapidly for a few minutes. The blended slurry was slowly transferred to a Pyrex glass containing a water–isopropyl alcohol mixture. As the slurry was added and stirred the zirconium and titanium butoxides hydrolysed. A homogeneous mixture of the hydroxides was obtained at the end of this process. The slurry was poured into a flat porcelain tray and dried at 90° C in an oven with a high-humidity atmosphere. This dewatering could strongly influence the calcining behaviour of the fabricated PZT powder. The dried powder was crushed and calcined at 500° C for 16 h in a high-alumina crucible. After calcining, the powder was ball milled with alumina balls for 2 h in isopropyl alcohol, dried and finally calcined at 750° C for a short time. To the "active pre-reacted" (APR) PZT powder, no PbO excess before sintering was added.

Standard transmission electron microscopy

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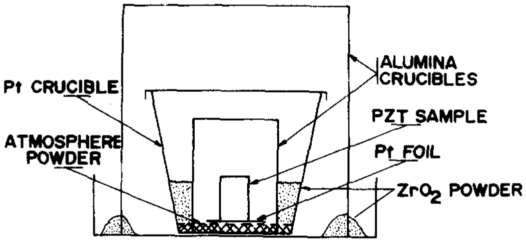


Figure 1 Crucibles arrangement for atmospheric sintering of PZT ceramic materials.

techniques were used to observe the ultimate crystallite size and the state of aggregation. Specific surface areas were determined at low temperature by nitrogen absorption. Coulter particle size analysis, room-temperature X-ray diffraction, and DTA/TGA were also used in the characterization of precipitated and calcined powders.

2.2. Sample preparation

From the APR powder, samples were prepared by isostatic pressing without binder at ~ 150 MPa (green density = 50% theoretical density). The samples were sintered in a special arrangement of alumina and platinum crucibles (see Fig. 1) at temperatures ranging from 1150 to 1300° C in air. The sintering times ranged from 1 to 12 h for each temperature. To maintain a partial pressure of PbO during the sintering experiments a $PbZrO_3$ + 5% ZrO_2 mixture in adequate quantities was used.

2.3. Property measurements

Bulk densities were determined by the liquid displacement method, and water or tetrachlorethylene was used as the liquid medium. Grain-size measurements were taken from electron micrographs of polished and chemically etched surfaces in dilute HCl containing a few drops of concentrated HF. The average grain diameter was determined by the line intercept method [7] counting a minimum of 300 grains for each sample.

Electrical measurements were conducted on 12 mm diameter by 0.5 mm thick discs which were sliced from the sintered samples. After being lapped and ultrasonically cleaned, the discs were electroded with silver paste, fired at 580° C for 30 min and poled at 100° C in a silicone oil bath using an electric field of 25 kV cm^{-1} for 1 min. The dielectric constant and dissipation factor, tan δ, of the samples were measured at a frequency of 1 kHz using a capacitance bridge. Planar coupling determinations were made by the resonance–antiresonance method [8].

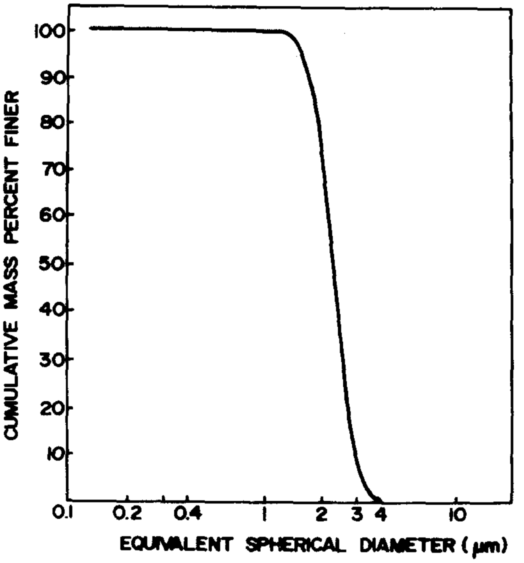


Figure 2 Particle size and distribution of "APR" PZT powder.

3. Results

3.1. Powder characterization

The X-ray diffraction study showed that the precipitated powder was an amorphous material between room temperature and 400° C. After calcining at 500° C for 16 h a well-developed PZT phase was present. The DTA/TGA studies show only a single exothermic peak at 400° C corresponding to a nucleation and growth of crystallites from the amorphous particles. The BET surface-area study showed that the precipitated powder has a specific surface area of ~ 40 m^2 g^{-1}. By heating this powder at 750° C the specific surface area falls to 3 m^2 g^{-1}. By TEM examination it has been shown that both, precipitated and calcined powders had an essentially similar morphology with the appearance of disperse agglomerates of small particles. X-ray diffraction patterns taken of this calcined powder were indexed as the rhombohedral phase and a lattice parameter value of 0.4105 ± 0.0005 nm was calculated, and a value of 7.97 g cm^{-3} was obtained for the theoretical density.

It is well known that powder preparation prior to sample fabrication is one of the most critical steps in the process, and in this sense an adequate knowledge of particle size and size distribution, as well as agglomerate and aggregate size is extremely important. Fig. 2 shows a typical particle size distribution for the "active pre-reacted"

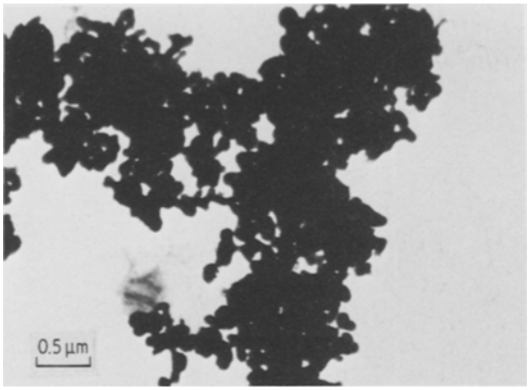


Figure 3 Transmission electron micrograph of "APR" PZT powder.

(APR) PZT powder, and an average particle size of ~2 μm was measured. Fig. 3 shows a transmission electron micrograph of the powder, and this offers direct evidence of the aggregate–agglomerate type microstructure of the powder APR under investigation. The agglomerated microstructure of the powder formed by weakly bonded aggregates, noticeably influence the ability of the powder to flow during compaction, so the green density of the compacts was 4 g cm^{-3}. This result indicates that during compaction the particles accommodate well and, as a consequence, the size and distribution of the resulting pores will be more uniform. From this fact, it is to be emphasized that the presence of weak aggregates or agglomerates is a very important factor for the processing behaviour of the APR powder and, therefore, a rigorous control of these is desirable in fabricating dense ceramics with enhanced final microstructures and properties.

3.2. Sintering studies

From the results it can be seen that a heat-treatment at 750° C for a short time produced a homogeneous powder which retained a high degree of surface activity. This high surface made it possible to sinter the powder compacts to near theoretical density at moderate temperatures. A series of samples was sintered under various conditions in an attempt to find the optimum temperature and time. As can be seen from Fig. 4 the densification was so rapid that at 1200° C the density was as high as 7.90 g cm^{-3} after 2 h and higher than 7.95 g cm^{-3} after 8 h sintering time. These values are higher than that reported by Murray and Dungan [1] for a doped PZT 65/35 sintered in an oxygen atmosphere at 1300° C for 1 h, and are also higher than that reported by Northrop [9] for a similar composition doped with Bi_2O_3 and hot-pressed at 1300° C. It is well known that an oxygen atmosphere is necessary to achieve completely dense bodies [1, 10], and an explanation was done to justify this enhancement [11]. Therefore it is believed that the present work is the first report of a PZT sample which has been sintered at near theoretical density value without using either an oxygen atmosphere or an oxygen hot-pressing technique. From Fig. 4 it can also be seen that the grain size follows a power function of the sintering time.

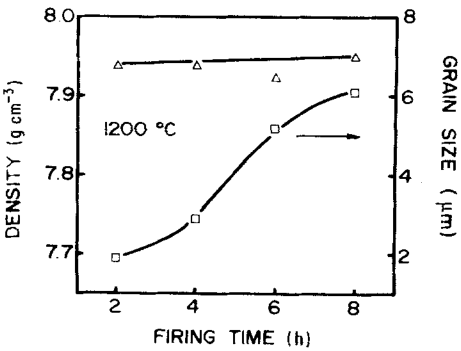


Figure 4 Effect of sintering time on densification and grain growth for PZT sintered at 1200° C.

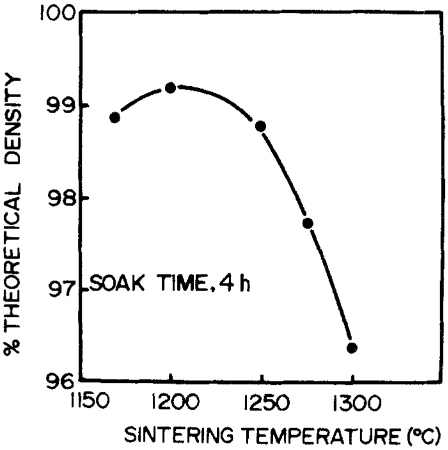


Figure 5 Density of PZT as a function of sintering temperature.

Fig. 5 shows the bulk density as a function of sintering temperature. It can be seen that the density reaches a maximum value at 1200° C, and then falls rapidly with increasing temperature. A similar response was found by Palkar and Multani [12] for a PZT-52/48 material chemically prepared and sintered in an oxygen atmosphere.

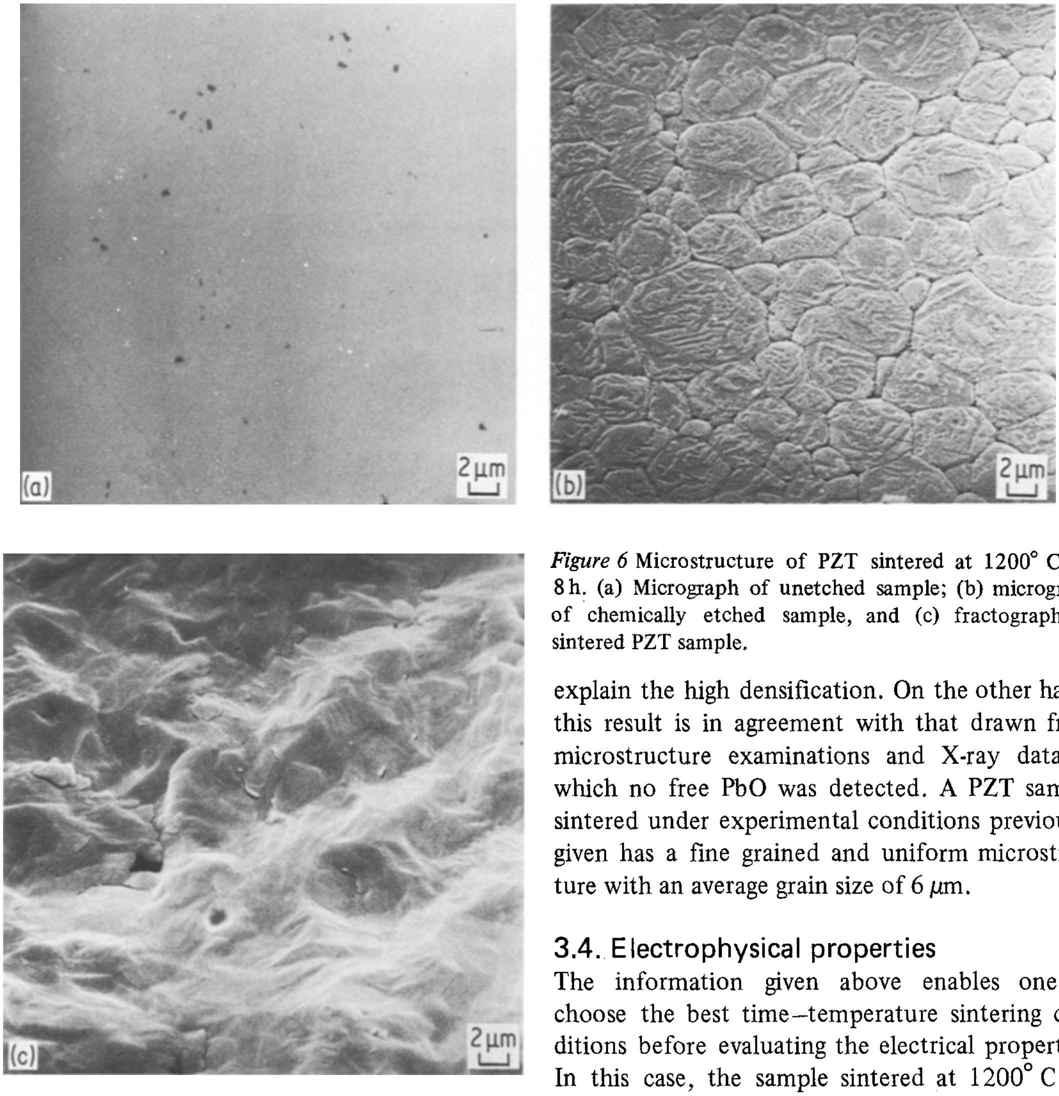


Figure 6 Microstructure of PZT sintered at 1200° C for 8 h. (a) Micrograph of unetched sample; (b) micrograph of chemically etched sample, and (c) fractograph of sintered PZT sample.

3.3. Microstructure

Examination of the microstructure of several PZT samples showed that all were highly dense and no internal porosity in the grain was present. On the other hand, apparently no segregation of a second phase was visible along the grain boundaries. Fig. 6 shows typical electron micrographs of the more highly dense PZT polished unetched (Fig. 6a), and chemically etched (Fig. 6b). The microstructure revealed a dense structure with a very uniform grain size. Fig. 6c shows an SEM fractograph for this PZT ceramic material in which transgranular fracture was present. This fact may be part of the evidence that PZT compacts, in the higher densified PZT sample, had sintered without any formation of liquid phase and, therefore, that a vacancy diffusion mechanism probably could explain the high densification. On the other hand, this result is in agreement with that drawn from microstructure examinations and X-ray data in which no free PbO was detected. A PZT sample sintered under experimental conditions previously given has a fine grained and uniform microstructure with an average grain size of 6 μm.

3.4. Electrophysical properties

The information given above enables one to choose the best time–temperature sintering conditions before evaluating the electrical properties. In this case, the sample sintered at 1200° C for 8 h was selected. Table I shows the electrophysical properties of that PZT ceramic material exhibiting the best overall characteristics. These properties are compared with those of other PZT obtained by oxygen atmosphere sintering [1]. Fig. 7 shows the ferroelectric hysteresis loop for highly densified PZT ceramic materials, and it can be seen that no saturation was reached not even in the case of the more densified sample. This could be related to the small grain size and, probably, to the presence of high internal stresses.

4. Discussion

From the results obtained in the present work the following points may be considered. Dewatering of the precipitated powder in a high-humidity atmosphere can be an effective step in the PZT processing to achieve a highly sinterable PZT

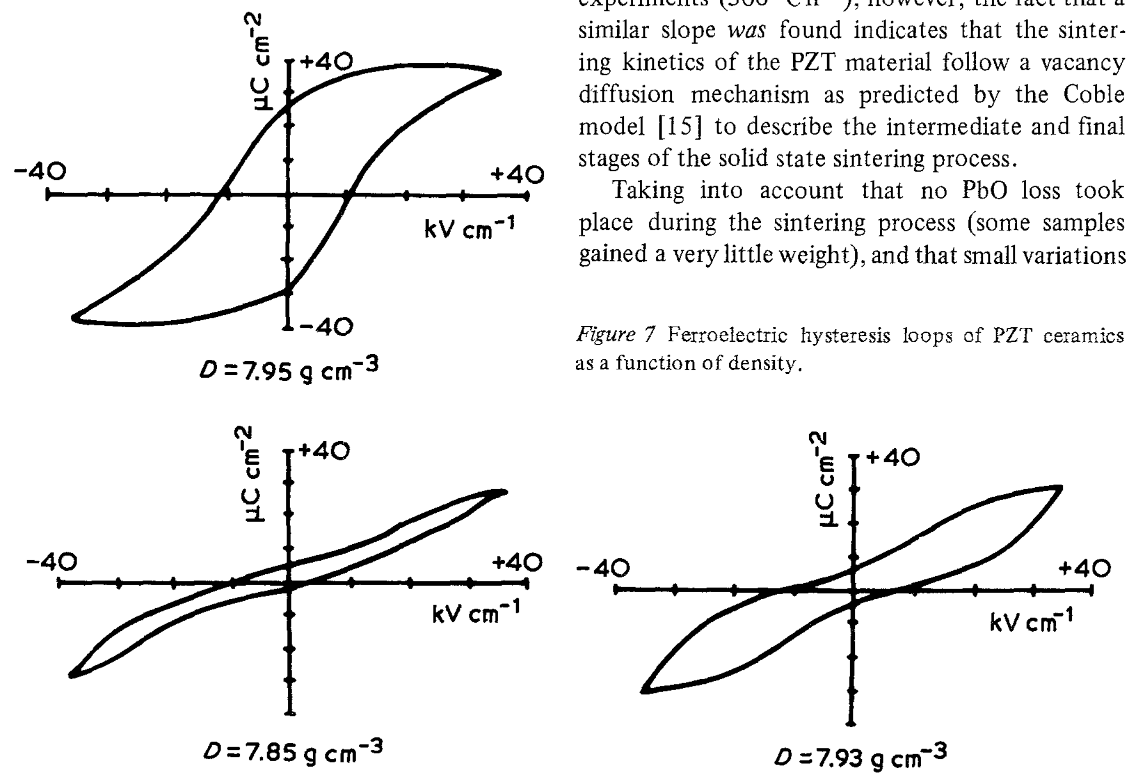
TABLE I The electrophysical properties of PZT ceramics

	Present work	Murray and Dungan [1]
Density (g cm^{-3})	7.95	7.96
Dielectric Constant	700	600
Tan δ	0.02	0.01
Curie temperature (° C)	359	350
K_p	0.30	0.40
Remanent polarization (μC cm^{-2})	30	36
Coercive field (kV cm^{-1})	7.4	22

powder. A similar procedure has been used to obtain highly sinterable rare-earth oxide powders [13]. Nevertheless, this is the first time in which such an experimental procedure has been used to obtain highly sinterable PZT powder. Furthermore, an adequate precalcination of the high-humidity dewatered PZT powder, a short time at 750° C, allows the production of PZT particles with a relatively high degree of surface activity which strongly influences the sintering behaviour, although this is not the only parameter to take into account. Other aspects of the process are necessary to completely define the sintering behaviour of the powder, and in this sense a good control of the aggregate–agglomerate microstructure of the powder is an important factor. Normally dense aggregates consistently survived during compaction and, as a consequence, both the size and distribution of the resulting pores are greater and less uniform. The weak agglomerates normally break down during compaction and a more uniform porosity is obtained. Therefore, the presence of weak agglomerates is better to achieve highly densified ceramic bodies.

It should be stressed that during PZT sintering process, no excess PbO was added to the PZT powder. Comparative analysis of the experimental data, as shown in Fig. 8, with the results obtained by Atkin and Fulrath [14] for the 1215° C isotherm, shows that the slope of the plots is approximately the same although the density values were higher in the present work. This finding could be related to the lower heating rate used in our experiments (300° C h^{-1}); however, the fact that a similar slope *was* found indicates that the sintering kinetics of the PZT material follow a vacancy diffusion mechanism as predicted by the Coble model [15] to describe the intermediate and final stages of the solid state sintering process.

Taking into account that no PbO loss took place during the sintering process (some samples gained a very little weight), and that small variations



D = 7.95 g cm^{-3}

D = 7.85 g cm^{-3}

D = 7.93 g cm^{-3}

Figure 7 Ferroelectric hysteresis loops of PZT ceramics as a function of density.

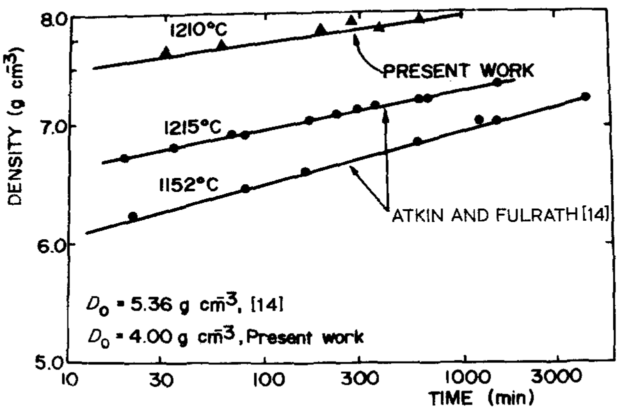


Figure 8 Densification of PZT ceramic materials.

in stoichiometry do not affect the densification [14], it must be assumed that the PZT sintering process is enhanced by the use of very fine powder which plays an important role in the driving force for densification. On the other hand, the agglomerate size interferes with the initial stage of powder sintering and, in this way, responsible for the final density obtained in the sintered bodies.

The influence of different sintering atmospheres on the final density of several PZT ceramics was studied by Murray and Dungan [1], and it was reported that the use of an oxygen atmosphere increased the density of sintered bodies from 97 to 99.5% theoretical density. This enhancement was explained by assuming that the sintering atmosphere had a strong effect on the relative diffusion rates of several gaseous species through the ceramic material. On the other hand, Atkin and Fulrath [14] showed that the densification was independent of the concentration of B- and A-site vacancies, and by reducing the partial pressure of oxygen in the surrounding atmosphere, the sintering process was accelerated. In the present work it is believed that the sintering process was carried out in a closed system in which the lead activity maintained constant between the sample and the packing powder. Therefore, the only moving species that could control the sintering process was the oxygen vacancies in agreement to the reaction $O_{sol} \leftrightarrow 1/2\, O_{2gas} + V_O$. If this is so, it seems reasonable to assume that the two factors which strongly enhance the rapid densification of PZT ceramics, at least for short sintering periods, are:

1. the small particle size of the powder, and
2. The relatively low oxygen partial pressure (compared with that present for oxygen-atmosphere sintering) which increases the oxygen vacancy concentration, and its diffusion towards the grain boundaries which acts as a vacancy sink.

In this way, the elimination of porosity was so rapid that after some hours at 1200° C a ceramic material homogeneously saturated with PbO, but without excess PbO, was obtained. This assumption was corroborated by the absence of any PbO phase in the sintered samples.

An attempt to correlate the dielectric–piezoelectric properties with the microstructure was made on the samples under study. It was found that while K_p was independent of the density, dielectric constant, remanent polarization and Curie temperature were augmented as the density increased. The coercive field diminished as density increased, and dielectric loss, tan δ, remained practically constant.

5. Conclusions

From our results, we may conclude that a dewatering of the precipitated powder in a high-humidity atmosphere, as well as an adequate precalcination treatment, allows one to achieve a highly sinterable PZT powder. When such a powder was sintered at 1200° C in an air environment, the density of the sintered ceramic material was as high as 99.5% theoretical density, which is equivalent to those results obtained when using oxygen-atmosphere sintering or oxygen-hot pressing. This unusual result could only be explained by the use of a very fine powder which rapidly shrinks in the first stages of the sintering process, enhancing the densification of the sintered bodies. On the other hand, the use of an air environment, assuming a closed system and no losses of PbO, seems to favour the vacancy diffusion which is the mechanism controlling the sintering rate.

In conclusion, it should be emphasized that by using a micronized PZT powder, carefully processed before sintering as well as a rigorous control of PbO loss, it is possible to achieve similar results to those obtained by using other more expensive and sophisticated methods such as oxygen-atmosphere sintering or hot-pressing. In this way, it is believed that a deeper study on some processing parameters is desirable in order to render normal use of the conventional sintering process in the obtention of high performance PZT ceramic materials possible.

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