Dielectric and piezoelectric properties of microwave sintered PZT

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Abstract

In this paper, the dielectric and piezoelectric properties of sol–gel derived
and microwave sintered PZT are presented. It has been observed that the
microwave sintering results in a material with a higher dielectric constant
($\approx$1600) than that sintered by conventional methods ($\approx$1480). It also offers
a low dielectric loss tangent and improved d_{33}. Pellets sintered by the
microwave method at $1100\,^\circ$C are found to have high hardness
($\approx$1460 MPa) on the Vickers hardness scale with a theoretical density of
$\approx$94% in comparison with that sintered by the conventional method (i.e.
$\approx$980 MPa and $\approx$84%). From a hysteresis study, the remanent polarization
(P_r) and coercive field (E_c) of the microwave sintered PZT are observed to
be 340 mC m^{-2} and 10 kV cm^{-1}, respectively. The value of E_c in the
microwave sintered sample is low and this property is desirable for device
fabrication of PZT-based smart structures.

1. Introduction

The piezoelectric qualities of the polarized lead-zirconate-titanate (PZT) ceramics were discovered in the 1950s. Since then this smart ceramic has been widely used for commercial applications for piezoelectric materials. The use of PZT ceramics has increased rapidly in naval sonar transducers, ferroelectric memories, optical filters, shutters, actuators, and modulators [1–3]. The reasons for using PZT smart materials for these applications include a large piezoelectric coefficient, large coupling factor, high Curie temperature and a higher use temperature [4]. Since the final properties of PZT ceramics are extremely sensitive to the Zr/Ti ratio, and the PbO stoichiometry, precise control of the composition in the powder preparation of PZT must be ensured.

Conventionally, smart materials are prepared by mixing the respective metal oxides. The disadvantages of the traditional routes are compositional inhomogeneity resulting from the incomplete reaction of the starting materials, volatilization of lead oxide due to the high processing temperatures, and impurities from the grinding media [5]. Furthermore, using higher temperatures in traditional processing is a crucial factor that is directly reflected in the quality factor, as well as the cost effectiveness in the industrial production of smart materials.

In contrast to the traditional mixed-oxide method, wet chemical preparation allows the mixing of the components at a molecular level and results in materials with high compositional homogeneity and lower sintering temperatures. Various chemical routes have been proposed, for example hydrothermal, oxalates, acetic acid, and Pichini methods [6–9]. In addition, it has also been recognized that the sol–gel process, using metal–organic precursors, can lead to fine and homogeneous powders with controlled stoichiometry.

The sintering temperature of PZT bulk ceramics is about $1200\,^\circ$C. A low sintering temperature is required for various technological applications of PZT, for example thin-film capacitors, multilayer bulk stack devices or integrated-memory, to avoid inter-diffusion between layers. It is also well documented in the literature that the various properties, such as, dielectric constant, dielectric loss tangent, d_{33}, of PZT ceramics, are dependent on microstructure, density, and grain size. Ceramics with high density and small grain size can be achieved by: (a) the addition of a solid solution forming additives, which inhibit grain growth, and (b) the application of suitable process control, such as hot pressing or fast firing. Fast firing is a relatively new technique which offers many advantages, such as enhanced densification and reduced grain growth, since the time available for grain growth is severely shortened in this process.
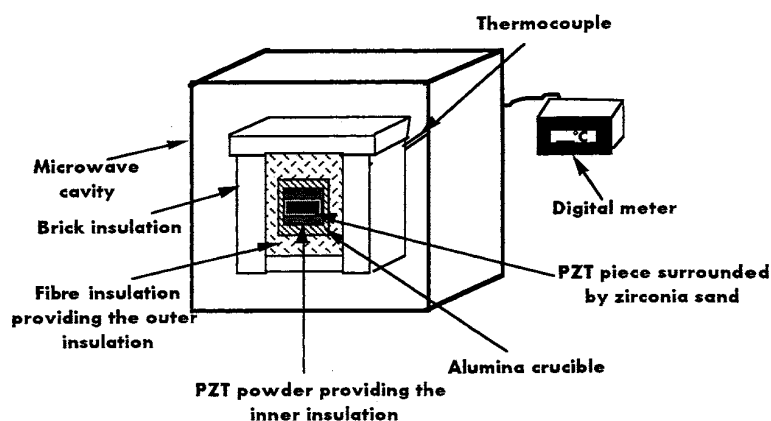
Figure 1. Schematic diagram of the set-up for microwave sintering.

Recently, there has been a growing interest in the heating and sintering of ceramics by microwave energy [10–14]. The interest in the use of microwave processing spans a number of fields from food processing to medical applications to chemical applications. Major areas of research in microwave processing of ceramics include: microwave material interaction, dielectric measurement, microwave equipment design, new material development, sintering, joining, and modelling. Therefore, the microwave processing of ceramics has emerged as a successful alternative to conventional processing. Nevertheless, the microwave method not only offers the advantages of uniform heating at lower temperatures and for shorter times than the conventional method, but it also provides an economic method of processing.

In the present work, a perovskite PZT powder was prepared by the sol–gel method, using methoxyethanol, lead acetate, zirconium n-propoxide, titanium-tetra-isopropoxide, and water. The main purpose of the present study is to investigate the effect of microwave sintering on the structural and physical properties of the PZT smart material. This work also presents an in-depth understanding of the dielectric variation of PZT sintered by the microwave method, for which there have been few reports to date. Furthermore, this paper also compares the piezoelectric properties of PZT sintered by different methods on the basis of density and hardness at room temperature with a 1 kHz sine wave.

2. Experiment

2.1. Processing of PZT

Lead acetate trihydrate, zirconium n-propoxide, titanium isopropoxide, and butanol were used as precursor materials, and 2-methoxyethanol was used as a solvent. Lead acetate trihydrate was dissolved in 2-methoxyethanol and dehydrated repeatedly at $120\,°C$. After cooling to $70\,°C$, zirconium n-propoxide and titanium-isopropoxide were added. The resulting solution was refluxed at $70\,°C$ for 12 h. The PZT sol was then hydrolyzed with a mixture of distilled water and ethanol. The precursor solution was then placed in a ventilated oven at $70\,°C$ to form a viscous gel. The dried PZT gel was crushed into powder and then calcined at $750\,°C$ for 30 min. The volatility of the PbO content of PZT during the sintering has contributed to the difficulty of having

reproducible production of high-quality PZT ceramics. It has been noticed that the loss of PbO and the resultant variation in the composition affect the density, dielectric, and piezoelectric properties of the sintered product [15]. Therefore, a lead zirconate powder was used as the atmosphere powder during sintering in the present work, since such a powder has been shown to produce a constant and reproducible amount of PbO deficiency in the sintered ceramic. Therefore, no excess lead was used in the precursor.

For pellet preparation, the calcined powder was mixed with 2 wt% organic binder (10 wt% polyvinyl alcohol in water solution). The mixture was ball milled for 6 h, and then dried in a ventilated oven at $100\,°C$; after drying the powder was crushed to fine powder, sieved, and pelletized. A pellet (0.5 inch in diameter) from the powder was pressed at 15 000 lbs in a stainless-steel die under uniaxial pressure. The organic binder was burned out of the pressed samples by heat treatment at $500\,°C$ for 2 h. A series of samples were prepared from the powder obtained by heat treatment. Samples were then divided into two series. One series of PZT samples was sintered by the microwave method, and another series was sintered by the conventional method.

2.2. Conventional sintering

The PZT pieces were placed in an alumina crucible on a thin layer of zirconia sand (to prevent the reaction of PZT with alumina). The atmosphere powder was also put in the same crucible, which was then covered to further minimize PbO volatilization. The PZT pieces were covered with platinum to isolate them from the surrounding powders. Lead zirconate was used to provide a PbO atmosphere during conventional sintering.

2.3. Microwave sintering

The microwave sintering of pressed pellets was carried out in a multimode microwave cavity. The PZT pellets were placed in the cavity, as shown in figure 1. The heating rate was controlled, and the temperature was increased up to $500\,°C$. The temperature measurement system used in this study is similar to that used by Roy *et al* [11]. At this point, the heating allowed the reaction of the carbon powder with oxygen. The power was then increased to the maximum (600 W), and the
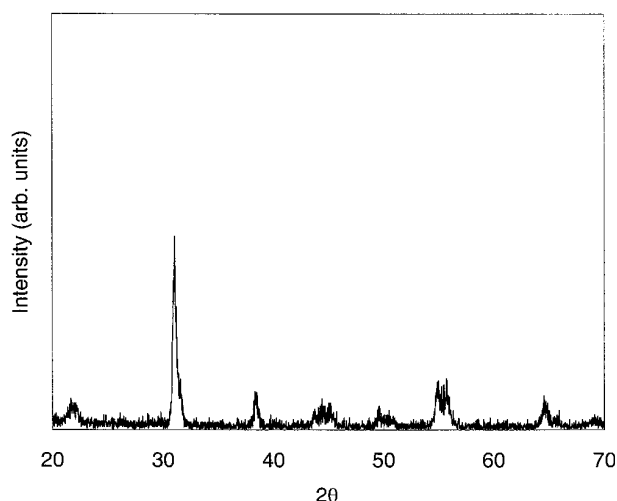
Figure 2. XRD pattern of PZT derived from the sol–gel method after being calcined at 750 °C.

Table 1. Phase analysis of PZT synthesized by sol–gel method.

Calcination temperature (°C)	Phase analysis
300	Amorphous
400	Crystalline with PZT, $Pb(OH)_2$, and TiO_2 phases
750	Single-phase PZT

Figure 3. Thermal runaway behaviour of (a) carbon powder, (b) PZT and (c) PZT with 1 g of carbon powder.

temperature was allowed to reach the sintering temperature of about 900–1220 °C for sol–gel PZT pellets. The thermocouple was kept close to the sample so that an accurate temperature measurement could be made.

2.4. Characterization and property measurements

X-ray diffraction (XRD) analysis of the sample was conducted to assess the degree of crystallization and phase identification of the powder. The x-ray slides were prepared by mixing a small amount of the sieved powder with ethanol. XRD patterns of PZT were recorded on a Phillips x-ray diffractometer using radiation with $k\alpha = 1.5415$ Å. The apparent densities of the sintered pellets were measured by the Archimedes method with water.

Hardness is defined as the resistance of the material to deformation. The Vickers hardness is obtained by dividing the applied load by the surface area of the indentation, according to the equation $HV = P/A = 1.8544 P/d^2$, where P is the applied load in Kgf, A is the surface area of the indentation in mm^2, and d is the mean diagonal length in millimetres. This test is an indentation test which forces a square-based pyramidal-shaped diamond indenter, having a face angle of 136°, into the surface of the material to be tested. For the measurement of Vickers hardness, a smooth sample surface is required, therefore the PZT samples were polished using 600 grit SiC paper. The final polishing was carried out by a paste of 0.5 μm alumina powder in acetone on the paper (600 NP5 grit).

The piezoelectric properties were studied on selected discs electroded on both faces with silver paste and polled at 150 °C by an applied electric field of 30 kV cm^{-1} for 5 min. The piezoelectric measurements were carried out by IEEE standards using an impedance analyser. To measure the parameter d_{33}, a Berlincourt piezo-d-meter was employed. Various low-field parameters, such as the relative dielectric constant, dielectric loss tangent, and piezoelectric coefficient were measured 24 h after poling. Hysteresis measurements were made with a modified Sawyer–Tower hysteresis circuit.

3. Results and discussion

3.1. Phase determination

We evaluated the effect of heat treatment on the structure of the PZT xerogel obtained by sol–gel processing by comparing x-ray diffractograms (see table 1). It can clearly be seen that the xerogel at room temperature is amorphous. This amorphous behaviour existed up to the temperature of 300 °C. Crystallization started to appear when the temperature was increased from 300 °C to 400 °C. XRD results in table 1 indicate the presence of metal hydroxides. Trace metal oxides are also observed in the XRD. A pure phase of perovskite PZT appears when the samples are heated to 750 °C, as shown in figure 2. The intensity of the peaks is enhanced on increasing the temperature to 800 °C.

3.2. Microwave sintering

Ceramics differ in their degree of microwave absorption. Highly absorptive ceramics can be heated in a domestic microwave oven to high temperatures. Ceramics with low loss, such as PZT, however, require a different approach when sintered by microwave energy. In figure 3, curve (a) illustrates a temperature–time profile (T–t) of 1 g of carbon powder placed in a microwave oven for 3 min. Curve (b) shows the T–t profile of 1 g of PZT placed in the same oven for the same amount of time. It is clear that the carbon absorbs the microwaves and, consequently, raises its temperature increase; whereas the PZT ceramics did not absorb the microwaves. Curve (c) in figure 3 shows the heating behaviour of PZT when a small amount of carbon powder (1 g) is mixed with it. The temperature of the PZT is increased to 150 °C within 3 min. This implies that there is a better coupling of the microwaves with the mixture of PZT and carbon. The 'thermal runaway'
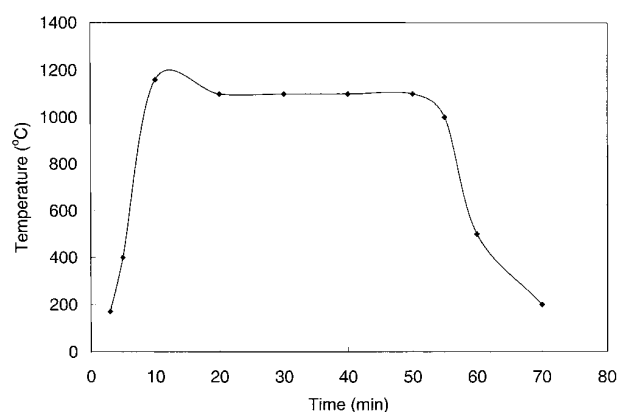
Figure 4. The thermal runaway of PZT at higher temperatures.

Table 2. Effect of sintering method on the dielectric and piezoelectric properties of the sol–gel PZT.

Property	Conventional sintering	Microwave sintering
Density (g cm^{-3})	95%	98%
Vickers hardness (MPa)	980	1460
Grain size (μm)	4	2
Dielectric constant	1500	1600
Loss tangent	0.003	0.003
d_{33} (pC N^{-1})	380	420

profile of PZT is presented in figure 4. As seen from this curve, there is an initial rise in the temperature. When the temperature of the PZT material reaches T_c, there is a sudden increase in temperature, which is the condition referred to as 'thermal runaway'. Thermal runaway is an important aspect of microwave heating that causes undesirable hot spots in the material. When used properly, thermal runaway can be a means of heating the material at rapid rates. It is important to note that without appropriate insulation, parts sintered at 2.45 GHz fail to reach the required sintering temperature. Ounaies *et al* [16] pointed out the possible positive contributions of thermal runaway to the highly efficient microwave sintering of ceramics and the subsequent reduction in the processing time and energy. Therefore, with appropriate layered insulation, the temperature differentials and interactions are minimized.

3.3. Densification and hardness

The rate of densification is generally enhanced over that of coarsening during sintering, such that a finer grain size is obtained in microwave fired pieces, as suggested by Janney *et al* [17]. This allows the sintering of pieces in a microwave either at a lower temperature, or faster sintering at the same temperature. In the microwave case, the density increases much faster with temperature than it does in the conventional case. Recently, Fukushima [18] has also reported the successful sintering of PZT pieces by microwave power, however, the density of the PZT samples could not exceed more than 90%. The hardness of the PZT was measured using Vickers hardness (refer to table 2). It is observed that the sol–gel processed then microwave sintered samples consistently resulted in a PZT that is 1.5 times harder than the PZT derived by the conventional method. The finer, more pure, and more
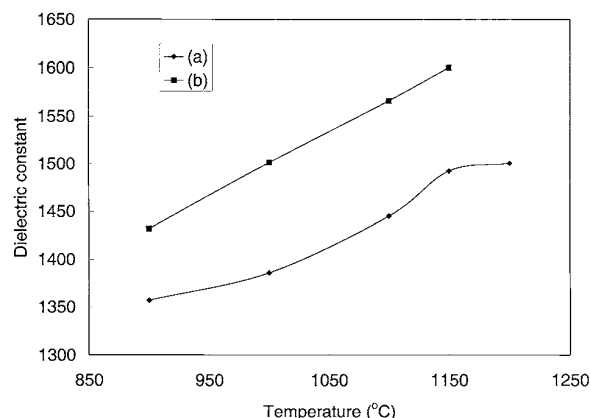

Figure 5. The effect of temperature on the dielectric constant of PZT sintered by (a) conventional and (b) microwave methods at 1 MHz.
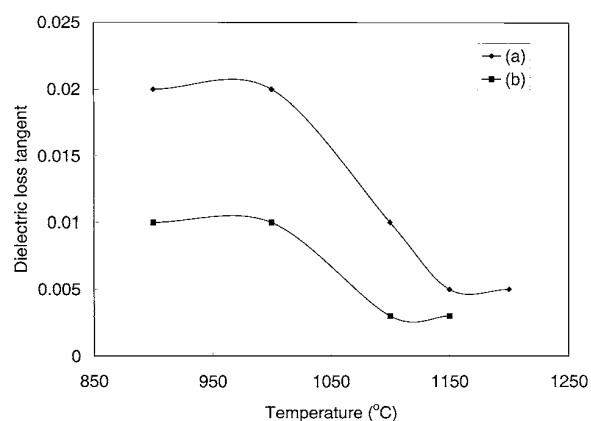

Figure 6. The effect of temperature on the dielectric loss tangent of sol–gel PZT sintered by (a) conventional and (b) microwave methods at 1 MHz.

homogeneous microstructures are the reason for these results. This also indicates that the grains in the microwave assisted sol–gel PZT are much stronger than the grain boundaries, and perhaps this helps deflect the propagation of cracks to the grain boundaries. In the case of conventional sintering of sol–gel PZT, a crack introduced by indentation will travel through the grains more easily. This is also supported by our grain size analysis using scanning electron microscopy (SEM) micrographs (refer to table 2). The conventionally sintered sample exhibits larger grains than the microwave sintered sample. Table 2 clearly indicates the twofold reduction in the grain size of the pellets sintered by microwaves.

3.4. Dielectric properties

The dielectric properties of the sol–gel PZT sintered by conventional and microwave methods are shown figure 5. The dielectric constant of the sol–gel PZT sintered by the conventional method was increased from about 1350 to 1500 on increasing the sintering temperature from 900 °C to 1250 °C. This behaviour of dielectric constant with temperature was also reported by Sharma *et al* [19]. It is reported in the literature that the dielectric constant is highly dependent on the density of the ceramics. Furthermore, higher temperatures lead to higher densification. Results from density
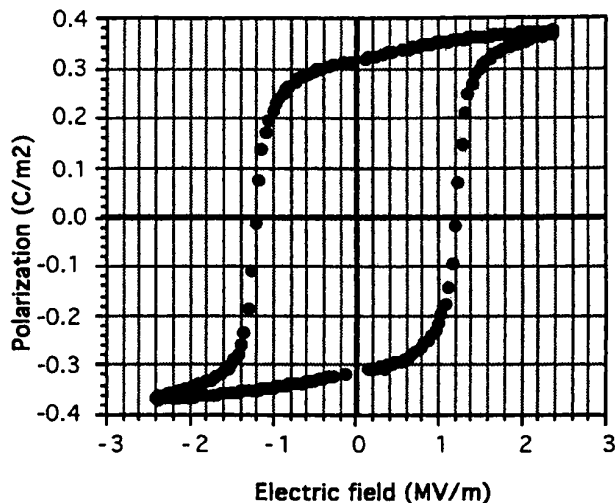
Figure 7. Hysteresis loop measurement of the conventionally sintered sol–gel PZT.
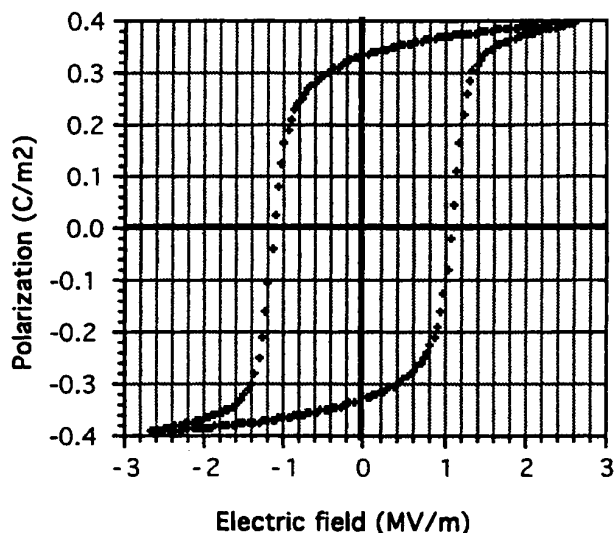
Table 3. The values of E_c, P_r, P_s and S obtained from the hysteresis loops of the PZT sample sintered by the different methods.

Property	Conventional sintering	Microwave sintering
E_c (kV cm^{-1})	12	10
P_r (mC m^{-2})	320	340
P_s (mC m^{-2})	380	400
S	0.84	0.85

measurements also show that the density of PZT increases on increasing the sintering temperature. This also results in a low dielectric loss tangent of the material, as shown in figure 6. A similar trend was also observed when the sol–gel PZT was sintered by the microwave method for different temperatures. When the temperature increases from 900 °C to 1150 °C, a 12% enhancement in the dielectric constant is observed for microwave assisted PZT. The dielectric constant in the PZT samples sintered by the conventional method is increased only by 9% in the temperature range of 900–1150 °C. This implies that the densification occurs in this temperature range. The apparent density of the sol–gel PZTs prepared using microwave and conventional heating, increases from 89% to 96% and 81% to 93%, respectively, when the temperature increases from 900 °C to 1150 °C. The materials obtained by microwave sintering are found to have lower densification than those sintered by the conventional method. This is an indication that the microwave assisted PZT attains rapid densification that occurs at a lower temperature and a shorter time. The microwave assisted PZT shows a higher dielectric constant, possibly related to the dense material, which is caused by the packing of small grains. Wu *et al* [3] have also indicated that the dielectric constant increases on increasing the denseness of the PZT.

3.5. Ferroelectric hysteresis and piezoelectric properties

Figure 7 is a typical hysteresis loop obtained on the specimen sintered by the microwave and conventional methods. The spontaneous polarization (P_s), remanent polarization (P_r),

Figure 8. Hysteresis loop measurement of the microwave assisted sol–gel PZT.

coercive field (E_c), and squareness ratio (S) of the PZT sintered by the different methods are given in table 3. For the conventionally processed samples the remanent polarization value (P_r) is 320 mC m^{-2}, while the coercive field (E_c) and saturation polarization (P_s) are 12 kV cm^{-1} and 380 mC m^{-2}, respectively. The value of P_r increases to about 340 mC m^{-2} and E_c decreases to 10 kV cm^{-1} for the microwave assisted PZT samples. Mohammed and Naik [20] reported that the values of P_s and P_r for the film or bulk are strongly dependent on the grain size of the material. The E_c value reported by Zhang and Zhao [21] is 9 kV cm^{-1}, which is lower than the value reported in this study. It is important to note that the PZT studied by Zhang and Zhao was doped using acceptors and this is presumably a possible reason for it having a lower E_c. The squareness (S), defined by P_r/P_s, is about ≈ 0.85 for the microwave assisted PZT, due to this sample having a higher value of P_s (≈ 400 mC m^{-2}), in comparison with the conventionally heated PZT squareness of $P_r/P_s \approx 0.84$. It is important to note here that the high value of E_c is a disadvantage in most device applications, since it means greater power losses and higher switching voltages. Therefore, to an extent, this can be offset if the specimen can be sintered by the microwave method.

The piezoelectric coefficient (d_{33}) of conventional and microwave assisted PZT is measured and shown in table 2. The PZT sintered by the microwave method gives a d_{33} value of about 420 pC N^{-1}, which is about 11% higher than the value of PZT sintered by the conventional method; this is due to the microwave sintered PZT having better alignment of the domains. Therefore, this implies that microwave assisted sintering leads to higher piezoelectricity with a high value of d_{33}. It is important to note here that values of d_{33} of sol–gel PZT sintered by microwave, as well as conventional methods, are higher than the values reported elsewhere [22]. Nevertheless, the d_{33} value reported in the literature is found to be 296 pC N^{-1} [21].

4. Conclusion

In this study, sol–gel processing is applied for the synthesis of PZT. The results shown here reveal the significant microwave effect on the sintering of the PZT ceramics. Microwave sintering allows significant time and energy saving. The microwave assisted PZT ceramics are highly dense with small grain size in comparison with the conventionally heated sintering of PZT. This sintering method of ceramics by microwaves leads to the development of a material with a dielectric constant higher than that in PZT sintered by the conventional method. Such samples also offer a low dielectric loss tangent and improved piezoelectric properties. From this standpoint, the physical and piezoelectric properties of both the microwave and conventionally sintered PZT are very important. The value of E_c in microwave sintered sample is low and desirable for the device fabrication of PZT-based smart structures.

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