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Microwave enhanced sintering of tape-cast ferroelectric films

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Abstract

Porous $Pb(Zr_xTi_{1-x})O_3$(PZT) thick films that had been prepared by tape casting were densified by microwave energy. The microwave absorption effect is substantially correlated with the film thickness. In microwave-processed PZT thick films, rapid particle necking causes densification with no grain growth nearly in a short treatment time of 20 min at 820 °C. The same porous PZT thick films are difficult to densify in a conventional process. A 30-μm-thick PZT thick film has a pure perovskite structure. Self-supporting PZT thick films with a crack-free and uniform microstructure formed in a microwave process have larger coercive field than conventionally processed bulk PZT. The polarization, 14 $\mu C/cm^2$, of PZT thick films in a microwave process exceeds that, 7 $\mu C/cm^2$, of PZT bulk formed in a conventional process.

Keywords: Microwave sintering; PZT; Ferroelectric properties

1. Introduction

Piezoelectric and ferroelectric $Pb(Zr_xTi_{1-x})O_3$ (PZT) materials have been developed for use in various smart devices with a displacement of several microns and polarization.[1] Films of PZT with various thicknesses (0.5–200 μm) have wide applications.[2] A conventional thick-film process, such as tape casting[3] or screen-printing[4] yields films with a thickness of micron. Thick films thus prepared cannot be easily densified by conventional furnace heating in a short processing time at low processing temperature.

The microwave process is known to promote material densification at low processing temperature with a shorter processing time than the conventional process.[5,6] Microwave/millimeter-waves are also used to enhance crystallization and to sinter bulk PZT materials.[7,8] The use in PZT sintering of 2.45 GHz microwaves that are suitable for industrial applications is also investigated.[9,10] Several parameters must be considered to ensure the success of the microwave process such as the arrangement of the specimen set and the specimen mass, as well as the microwave heating chamber configuration.[10] The porosity of the green specimens is an important parameter in microwave heating because the porosity of the specimen is related to microwave absorption and affects the increase in temperature.[11] The S-curve associated with temperature-microwave absorption is simulated with respect to sample size and the change in material properties such as conductivity, dielectric loss, etc.[12,13] However, data on microwave absorption behavior of most dielectric materials remain few and further experiments must be conducted.

One of the challenges in preparing PZT thick films is to obtain crack-free, dense, uniform microstructures with the desired properties. PZT thick films on various substrates have been studied to solve such problems.[1,2,14,15] However, self-supporting thick films sintered without cracking; do not warp, but have a dense uniform microstructure and favorable ferroelectric properties are difficult to prepare and have not been examined in detail. Microwaves are effective in the volume heating of materials. However, microwaves may have not effect on a small mass or thin piece. Additionally, low-loss material, such as PZT, at room temperature is frequently microwave-sintered with casketing or using a susceptor to promote microwave absorption.[9,16] This work investigated the focusing of microwave energy to treat self-supporting ferroelectric PZT thick films of various thicknesses to study thick highly porous green PZT film and the effects of thickness on microwave absorption. Such microwave processing results were also compared to conventional processing results.

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2. Experimental procedure

Commercially available low temperature sintering PZT powders (mean particle size of 0.7 μm) were used as starting particles. The sintering condition 820 °C/2 h was used as a reference. PZT thick films with thicknesses of 10, 30, 50 and 100 μm were prepared using a tape casting machine (AEM Inc., model 2104, USA) using 66 wt.% solid PZT slurry.

The tape-cast green PZT thick films were punched into pieces with a diameter of 10 mm. Die-pressed bulk samples of PZT with a diameter of 12 mm and a thickness of 1.38 mm were also employed in conventional and microwave heating processes. The prepared green PZT films were either single piece or stacked with a 1-mm-thick top and a bottom alumina sheet to form a sandwiched stacking assembly; Fig. 1 displays the stacked PZT. Sparse ZrO_2 powder was spread on thick PZT films to prevent the adhesion of PZT from the PZT films or the alumina sheet. Such a stacking assembly was subsequently heated to decompose the binder in a furnace for 500 °C/5 h. After the binder had decomposed, the stacking assembly was heated in an electrical furnace or in a microwave cavity at ramp rates of 2 °C/min and 10 °C/min in an electrical furnace and 40 °C/min in a microwave cavity. The soaking was at 820 °C for 20 min, 30 min, 40 min and 2 h. In the microwave process, the sandwich stacking assembly was placed in a microwave susceptor with SiC and refractory materials. Then, the susceptor that contained the sandwich stacking assembly was set in a microwave cavity to facilitate microwave processing, as schematically presented in Fig. 1. The SiC was adopted to promote the pumping microwave absorption of PZT at low temperature. The microwave processing cavity was an elliptical single-mode cavity with a designed energy-focused region with a diameter of about one inch. The design and field distribution have been presented elsewhere.[17]

The microstructure and morphology of the samples were determined using a field emission-scanning electron microscope (FE-SEM, LEO 1530). The crystal structure was characterized by X-ray diffraction (XRD, Rigaku D/MAX-IIB, Cu Kα radiation wavelength λ = 1.5405 Å, scan speed of 4°/min). Gold top electrodes were deposited on the surfaces of heat-treated PZT thick films to enable electrical measurements to be made. A ferroelectric P–E hysteresis loop was obtained using a Sawyer-Tower circuit.

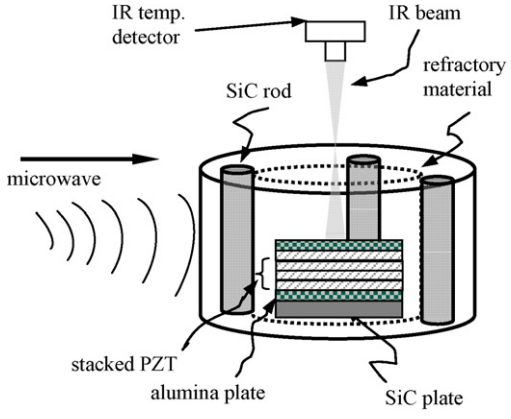

Fig. 1. Schematic diagram of microwave susceptor, including stacked PZT thick film assembly.

3. Results and discussion

The heat-treatment temperature was set at 820 °C for both conventional (*F*) and microwave (MW) processes. The shrinkage in the diameter of a single PZT thick film treated by either conventional or microwave heating depends on the thickness of the film and the ramp rate, as shown in Fig. 2. The shrinkage of specimens by a conventional process increases with the film thickness at a high ramp rate of 10 °C/min but not at a low ramp rate of 2 °C/min. The shrinkage saturation remained at approximately 11% when specimens that were larger than 100 μm were conventionally treated, regardless of whether the soaking time was 20 min or 2 h at 820 °C. However, the shrinkage of the single PZT thick film that was microwave processed at 820 °C/20 min increased with the film thickness. The shrinkage in MW was larger than in F when the thickness of a single thick film exceeded 80 μm, as shown by the line of circular symbols in Fig. 2.

The phase transformation in the microwave process in Fig. 3 is strongly related to the thickness of the film. X-ray diffraction (XRD) analysis of an as-sintered single PZT thick film following 820 °C/20 min microwave heat-treatment reveals a pyrochlore (pyro) phase on the 10 and 30-μm-thick films, as shown in Fig. 3(a) and (b). It indicates that PbO volatilization is serious on thin PZT films during the microwave process. Almost no second phase of prochlore was detected when the film thickness exceeded 30 μm, as displayed in Fig. 3(c) and (d). The ZrO_2 phase in the XRD patterns was resulted from the powder used to prevent adhesion between PZT thick films. The presence of a second phase depended on the film thickness because the ratio of the thickness of the PbO loss layer on the film surface to the total film thickness was higher for thinner films (≤30 μm).

The circular symbols in Fig. 2 reveal the microwave absorption increased with the thickness of the specimen. More surprisingly, the shrinkage increased markedly with the number of stacked 30-μm-thick PZT thick films in the microwave process, as indicated by the curve of square symbols in Fig. 4. Four stacked 30 μm PZT thick films exhibit almost the same

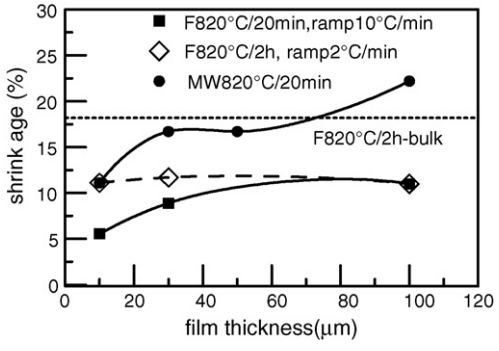

Fig. 2. Variation of shrinkage with thickness of single piece of PZT thick film, treated by both conventional and microwave processes. The shrinkage of the conventionally sintered bulk PZT is used as a reference, plotted as a dotted line.

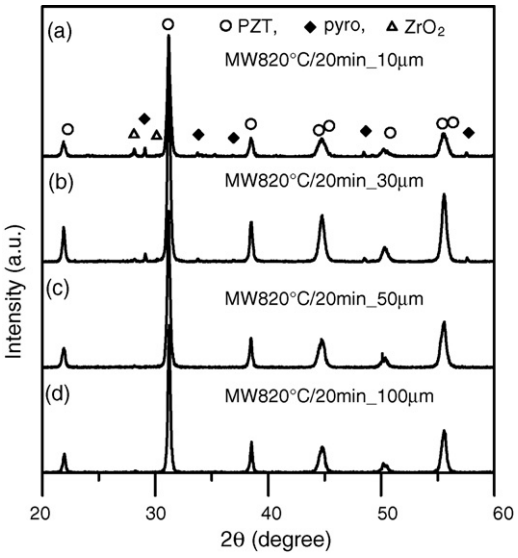

Fig. 3. X-ray diffraction patterns of single piece of PZT thick films following microwave sintering at 820 °C/20 min: (a) 10 μm, (b) 30 μm, (c) 50 μm and (d) 100 μm.

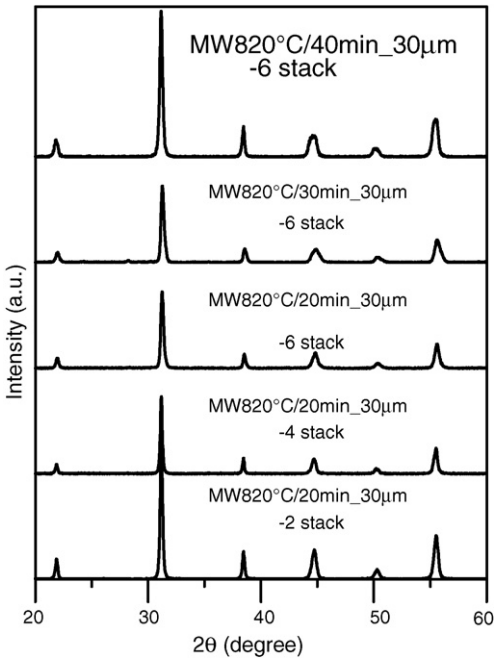

Fig. 5. X-ray diffraction patterns of stacked 30 μm PZT thick films that had been microwave sintered at 820 °C/20 min, 30 min and 40 min.

shrinkage as a single 100 μm PZT thick film in the microwave process, as revealed by a comparison of Figs. 2 and 4. This result further demonstrates that the absorption of microwaves by thick PZT films significantly increases with thickness above 100 μm. Accordingly, six stacked PZT thick films were examined to elucidate the effect of microwaves on a self-supporting thick PZT film. In Fig. 4, the line of circular symbols shows that the shrinkage slightly increase with the soaking time up to 40 min at 820 °C. It also indicates that shrinkage saturation occurs under 820 °C/40 min microwave treatment.

Various numbers of 30-μm-thick PZT films and six stacked films soaked for various times all exhibit pure phases, according to XRD analysis in Fig. 5. No second phase was present in the stacked PZT thick film due to such large, massive PZT materials providing sufficient PbO atmosphere. There no excess PbO atmosphere compensation was in the microwave process.

The fractured microstructures of microwave-processed specimens exhibited trans-granular fractured surfaces, as shown in Fig. 6(a)–(c). Particle necking is the main feature, and grain growth in microwave-treated specimens of six stacked pieces is slight, as displayed in Fig. 6(a) and (b). The grain size is almost the same as the original particle size, 0.7 μm, for a single 100-μm-thick PZT thick film, as shown in Fig. 6(c), which exhibits particle necking but without grain growth. In contrast, Fig. 6(d) displays no particle necking or grain growth in six stacked 30-μm-thick specimens that were conventionally treated at 820 °C/20 min with a high ramping rate of 10 °C/min. However, the die-pressed bulk PZT sintered by conventionally at 820 °C/2 h with a ramping rate of 2 °C/min exhibits an inter-granular fracture with abnormal grain growth, as shown in Fig. 6(e). The full densification of PZT proceeded with a sufficiently long soaking time at the sintering temperature, and the grain growth was more extensive in the conventional process. Rapid necking of particles, resulting in the densification of PZT, and grain growth depression in a short soaking period, are features of selective microwave heating.

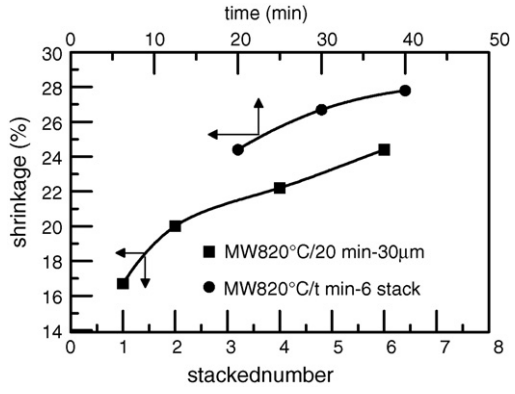

Fig. 4. Variation of shrinkage with number of stacked 30-μm-thick PZT thick films treated by a microwave process, and six stacked 30-μm-thick PZT thick films under microwave treatment with various soaking times at 820 °C.

The polarization–electric field (P–E) hysteresis loops in Fig. 7 show that the 820 °C/2 h conventionally treated bulk specimen had the smallest coercive field and the smallest remanent polarization, 7 μC/cm^2. Microwave 820 °C/20 min treatment thick film specimens have a larger coercive field and larger remanent polarization of 14 μC/cm^2. The microwave-treated single 50-μm-thick PZT film has a larger coercive field than the single 100 μm or the stacked 30-μm-thick PZT thick film, but they all have the same remanent polarization. The larger coercive field may be ascribed to the porous microstructure and the large surface areas and long boundaries of particles. When full densification was achieved, the coercive field reached a constant value, as for the conventionally sintered die-pressed bulk PZT, shown in Fig. 7. The same result was obtained for die-pressed bulk PZT microwaves sintered at 820 °C/20 min (not

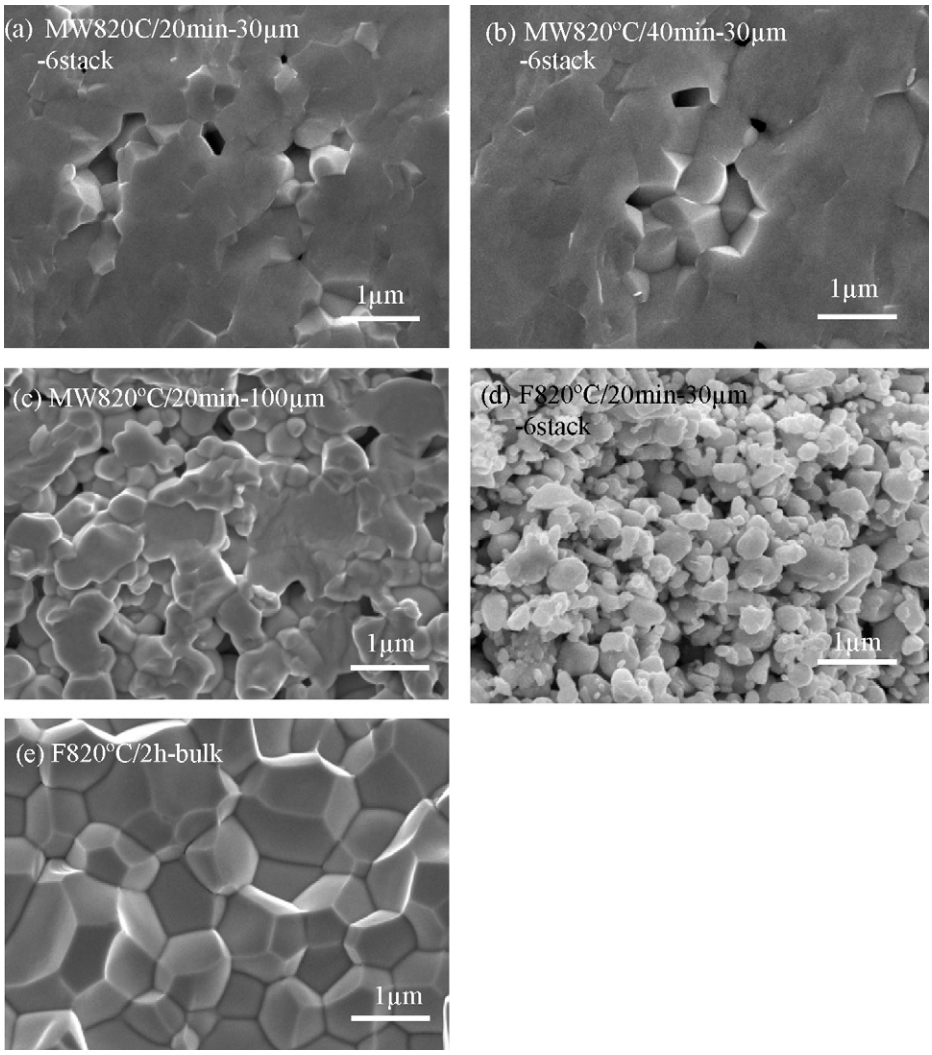

Fig. 6. Micrographs of 30-μm-thick PZT thick film produced from six stacked pieces following microwave sintering at: (a) 820 °C/20 min, (b) 820 °C/40 min; micrograph of (c) a single 100-μm-thick PZT thick film that had been microwave sintered at 820 °C/20 min; micrographs of (d) 30-μm-thick PZT thick film formed from six stacked pieces that had been conventionally sintered at 820 °C/20 min, and (e) bulk PZT conventionally sintered at 820 °C/2 h.

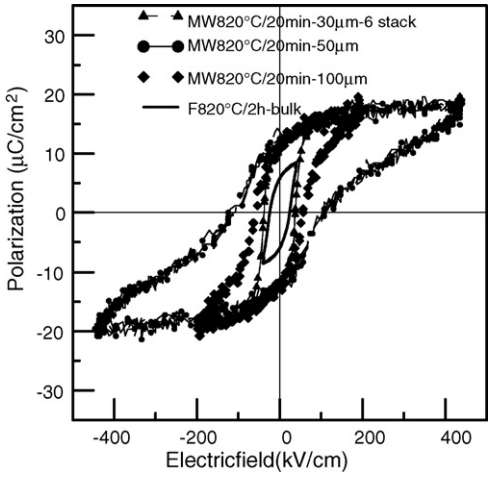

Fig. 7. Polarization-electric field hysteresis loops of 30-μm-thick PZT thick film formed from six stacked pieces (triangular symbols), a single 50-μm-thick film (circular symbols), single 100-μm-thick (diamonds) PZT thick film, all microwave-sintered at 820 °C/20 min; also bulk PZT (solid line) conventionally sintered at 820 °C/2 h.

shown here). Almost the same remanent polarization for MW PZT thick films indicates that same grain size is associated with the same amount of dipole polarization, which exceeds that of the conventionally 820 °C/2 h heat-treated bulk specimen. This difference may be associated with the fact that more dipoles are aligned when a large number of small grains undergo the microwave process than when a small number of large grains undergo the conventional process.

A short microwave processing treatment time was applied to PZT thick films, causing rapid particle necking and very little grain growth. The thickness of the PZT thick films significantly affected the microwave absorption efficiency, which effect was for the first time quantified as a mass effect in microwave heating. The grain size remained the original PZT particle size but fast particle necking densified the specimen in MW because of the presence of numerous amount of vacancies, space charges and charged point defects in porous tape-cast PZT thick films. Microwaves selectively interact with the defects and vacancies to cause the diffusion flow of defects, driving fast particle necking. Hence, porous green PZT thick films can be shrunk and

densified rapidly by the MW but not by the conventional process under the same heat treatment conditions of temperature and soaking time, such as 820 °C/20 min.

4. Conclusion

The porous tape-cast PZT thick films were treated in a focused microwave cavity and a conventional furnace. The second phase appeared on the PZT thick film with a thickness of less than 30 μm because of PbO loss, which is avoided by stacking PZT thick films in the microwave process. A highly dense self-supporting 30 μm PZT thick film is obtained by stacking six pieces of PZT thick film and treating them with microwaves at 820 °C/20 min. Microwave energy efficiently promoted particle necking, rapidly densifying the PZT thick film in a short soaking time. The dense microstructure with a microwave energy exhibits a clear crystal surface and edges, with slight grain growth. The microwave process densified the PZT thick film more than the conventional process, with a smaller coercive field observed in the P–E hysteresis loops. The same large polarization, 14 $\mu C/cm^2$, of the microwave-treated PZT thick films of various thicknesses, exceeds that, 7 $\mu C/cm^2$, of the conventionally treated bulk PZT.

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