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Sintering of PZT Powders in MW Furnace at 2·45 GHz

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Abstract

The feasibility of sintering PZT powder compacts—by direct MW heating, in multimode applicators at 2·45 GHz—was examined. Continuous heating from 20°C to sintering temperatures proved possible. Full sintering was achieved after heating cycles of about 1 h. PbO loss and electromagnetic fields intensity non-uniform spatial distribution are the main factors with negative influence on sintering. Cracking-warpage propensity is a strong function of specimens shape, size and the heating chamber set up. Dielectric and piezoelectric properties of MW and conventionally sintered specimens are similar. © 1999 Elsevier Science Limited. All rights reserved

Keywords: microwave processing, firing, sintering, PZT.

1 Introduction

Due to potential benefits—like sintering rate enhancement and microstructural refinement—sintering based on the material's interaction with microwaves (MW) is currently examined for a wide variety of ceramics, (Refs 1–4). For the case of PZT, MW sintering was studied only in 'high' frequency, $\nu > 25$ GHz, gyrotron powered furnaces, not practically usable.[5,6] The only previous study performed in systems operating at 2·45 GHz—suitable for industrial applications—used sintered PZT containers for the specimens so that a hybrid heating (thermal radiation from the container and autoheating of the specimens) took place Ref. 7. The shielding effect of such containers markedly reduces the direct MW/specimen interaction.

In this work the sintering of PZT—based on the heat developed by its interaction with 2·45 GHz electromagnetic waves, in *multimode applicators*—is examined. Aspects investigated include optimization of heating system set up and forward power profiles, determination of maximal densification levels, influence of SiC susceptor on temperature distribution, comparison of MW and conventionally sintered specimens regarding their density and piezoelectric characteristics.

2 Experimental

In most of the experiments a commercial soft PZT (PZT-S), fine powder [mean particle size (d_p)~1·1 μm; doped with Sb, Sn; $T_c = 190$°C] was used. A hard PZT (PZT-H) material ($d_p = 3{\cdot}2\ \mu$m; doped with Sr, Fe; $T_c = 325$°C), was also examined. Specimens of various shape and size (maximal plate length = 50 mm) were formed by cold isostatic pressing at 200 MPa.

MW sintering was performed in a custom made 2·45 GHz furnace (model 101 of MMT, USA), powered by two magnetrons, having a large size applicator and mode stirrer (field uniformity enhancement). Computer programming of forward power or temperature-time profile is possible. An S-type, Pt/6% Rh sheathed, thermocouple was used for temperature measurements. The thermocouple, inserted in a sintered alumina tube, was put in contact with the specimens.

Poling of silver electroded specimens was done under a 2 kV mm^{-1} field at 120°C, in silicon oil for 20 min. Small signal properties were measured in conformity with the IEEE standard on piezoelectricity.

3 Results and Discussion

3.1 MW/PZT interaction

Low loss materials like alumina could be *directly* MW heated only at $\nu > 25$ GHz.[2] The high dielectric loss of PZTs (for PZT-S $\varepsilon_r'' \sim 40$) allows better coupling to the MW fields so that fast *direct heating* (without susceptors) from room temperature

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*To whom correspondence should be addressed. Fax: +972-4-8325-339; e-mail: adgold@netvision.net.et.il should be possible also at 2·45 GHz. Preliminary tests showed that, indeed, such a sintering approach may be applied to PZT. The drop of ε'_r at the transition from ferro to paraelectric state (the Curie temperature for PZT-S was $T_c = 195°C$) did not influence the heating process. Temperatures in the 1300–1400°C domain were easily attained. Not even the heating rate was modified around T_c. Probably the reduction of loss due to polarization processes—stronger in the ferroelectric state—is compensated by the increase in electrical conductivity with temperature (at 300°C pure PZT exhibits an electrical conductivity $(\sigma_e) \sim 10^{-4}\,Sm^{-1}$ compared to $\sigma_e \sim 10^{-10}\,Sm^{-1}$ at 20°C).[8]

The temperature profiles recorded during the MW sintering of both a soft and a hard PZT are presented in Fig. 1.

For a given forward power profile the hard PZT heats quicker than the soft one despite the lower ferroelectric-state-polarization related loss in the former. The higher electric conductivity of the hard materials may explain this behaviour.[8]

The penetration depth of the 2·45 GHz wave in PZT-S, at room temperature, is $D_p \sim 16$ mm. Calculation of D_p was made according to Ref. 9, assuming energy transfer from field to specimens due only to polarization processes. The obtained value means that one may expect, at least for cm size specimens, relatively uniform field distribution within the specimen in the first stage of sintering, until significant open porosity is present (if porosity is uniformly distributed). Further heat distribution enhancement, during this stage, comes from the Meek effect.[10] On the other hand, in the last stage of sintering only the external region of the specimen is directly heated. As a result, temperature gradients—over the specimen—increase.

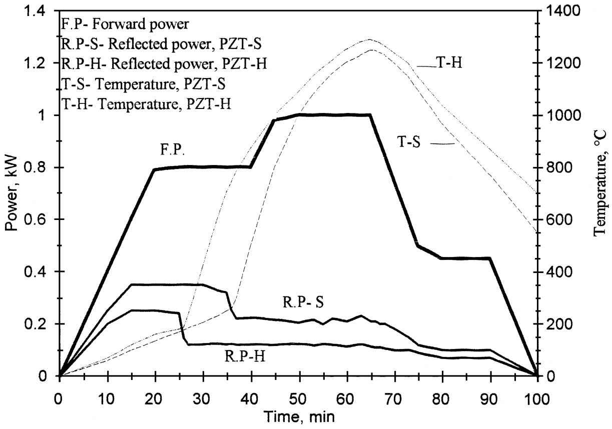

Fig. 1. Forward (and reflected) MW power and resulting temperature–time profiles recorded during the sintering of PZT-S,H.

3.2 PZT MW-sintering process

In order to obtain *fast* heating to sintering temperatures—without thermal runaway—target PZT load's mass *and* architecture had to be correlated with forward power time profile. In the set up used here the minimal sinterable mass was ~20 g. Further reduction of specimen mass could not be achieved by increasing forward power level. Arrangement of specimens set and 'heating chamber' configuration had also to prevent massive PbO loss. The evolvement of PbO from the PZT lattice, during heating, is more intense in the MW than in resistive furnaces. After a one hour sintering cycle PbO deposits were present in various regions of the heating chamber when an unsuitable set up was used; 4%PbO was detected in the m-ZrO_2 setter. In the optimal configuration this value decreased to ~1%. In Fig. 2 the X-ray diffraction pattern (XRD) of specimens sintered in optimal and unsuitable configurations are compared. Only in the former case the densified components are single phase PZT. Otherwise various degrees of PZT's decomposition occurred. An extreme case is shown in Fig. 2(B). In that case only $PbTiO_3$ and m-ZrO_2 remained in the fired pieces.

The optimal heating chamber set up included multicolumnar specimen stacks, seated on pure zirconia coarse powder, placed inside a sintered alumina crucible (bottom up). Two other larger crucibles were placed over the first one, with Pb zirconate grog put in-between the crucibles walls. Further thermal insulation was provided by bubble alumina and porous alumina tiles. The presence of the thermocouple contributed in many cases to the lowering of electromagnetic field distribution *uniformity* (as judged from the spatial distribution of cracks in the specimens set).

3.3 Sintered specimens characteristics

The densification level and the value of the dielectric and piezoelectric coefficients of MW and conventionally sintered specimens are given in Table 1.

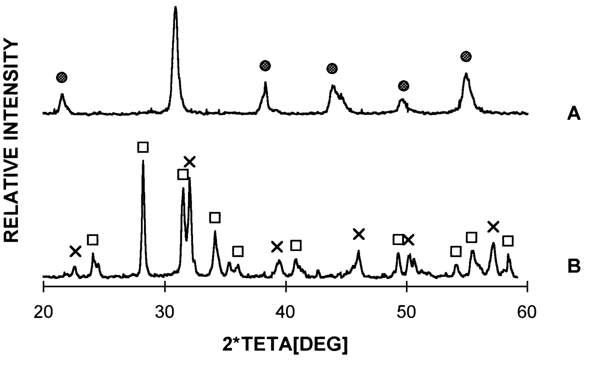

Fig. 2. XRD pattern of MW sintered PZT-S specimens: (A) optimal heating chamber set up; (B) unsuitable architecture of specimens set. ● PZT, □ ZrO_2, x $PbTiO_3$.

Table 1. Characteristics of MW and conventionally sintered PZTs

Properties	*Microwave sintering*		*Conventional sintering*			
	Experimental (ICSI)		*Experimental (ICSI)*		*Catalog data*	
	PZT-S	*PZT-H*	*PZT-S*	*PZT-H*	*PZT-S*	*PZT-H*
Sintering temperature/time (°C/h)	1250/0	1290/0	1270/1·5	1320/4	—	—
Bulk density ($\mathrm{g\,cm^{-3}}$)	7·54–7·60	7·17–7·26	7·50	7·56	7·50	7·60
Water absorption (%)	0.02-0·01	0·2-0·7	0·04	0·002	—	—
ε_r before poling	2400	1050	2300	1000	—	—
$\varepsilon_r{}^{\mathrm{T}}{}_3$	3170	—	3120	780	3400	1000
tan δ	0·021	—	0·021	0·0045	0·020	0·003
K_p	0·595	—	0·600	0·537	0·650	0·500
$d_{31}(\times 10^{-12}\mathrm{m/V})$	230	—	250	—	270	120

Sintered bulk densities, similar to those obtained in industrial furances (see Table 1), were achieved, in the case of PZT-S, by MW sintering. While peak temperatures required were in the same range as in the case of conventional heating, overall firing cycle length was—in the case of MW heating—only one tenth of that needed in the resistive furnace.

The microstructure of the MW fired components (PZT-S) is finer, with a mean grain size equaling $d_\mathrm{g} \approx 2{\cdot}5\,\mu\mathrm{m}$ compared to $d_\mathrm{g} = 4{\cdot}3\,\mu\mathrm{m}$ (abnormal size grains included) in the case of conventionally fired ones. In Fig. 3 electron microscope (SEM) pictures of both MW and conventionally fired specimens are presented.

The cracking-warpage propensity (C-W-P) of MWed specimens showed a strong dependence on their size and shape and specimens set architecture. Isometric shapes and small size increased the yield in uncracked sintered bodies. For instance, in the case of PZT-S, 12·5 mm cubes (fired in sets of 27 pieces) showed a yield of 45%, cylinders [diameter (ϕ) = 10 mm, height (h) = 14 mm] a yield of 30%. In the case of discs (ϕ = 25 mm, h = 6 mm) the yield dropped to 10%, while 40 to 50 mm length plates could not be obtained without cracks. The yields mentioned above were obtained in 'blind' runs without thermocouple inserted in the heating box. A further improvement of heat distribution uniformity—which translated in a 5–10% increase in uncracked specimens yield—was obtained by introducing a suitable mass of coarse α-SiC, *in particulate form*. It was placed between the second and third alumina containers. Such a susceptor form contributes to temperature gradient reduction *without* markedly shielding the specimens from the MW fields. The fired bulk density is, though, somewhat lower when susceptor is used.

The C-W-P of PZT-H was noticeably higher than that of PZT-S.

Unlike in the case of,[7] but in accord with,[6] the dielectric and piezoelectric properties of MW and conventionally sintered specimens were similar (see Table 1).

4 Conclusions

Fast sintering of PZT powder compacts is feasible by direct MW heating, starting from room temperature, in multimode applicators at 2·45 GHz.

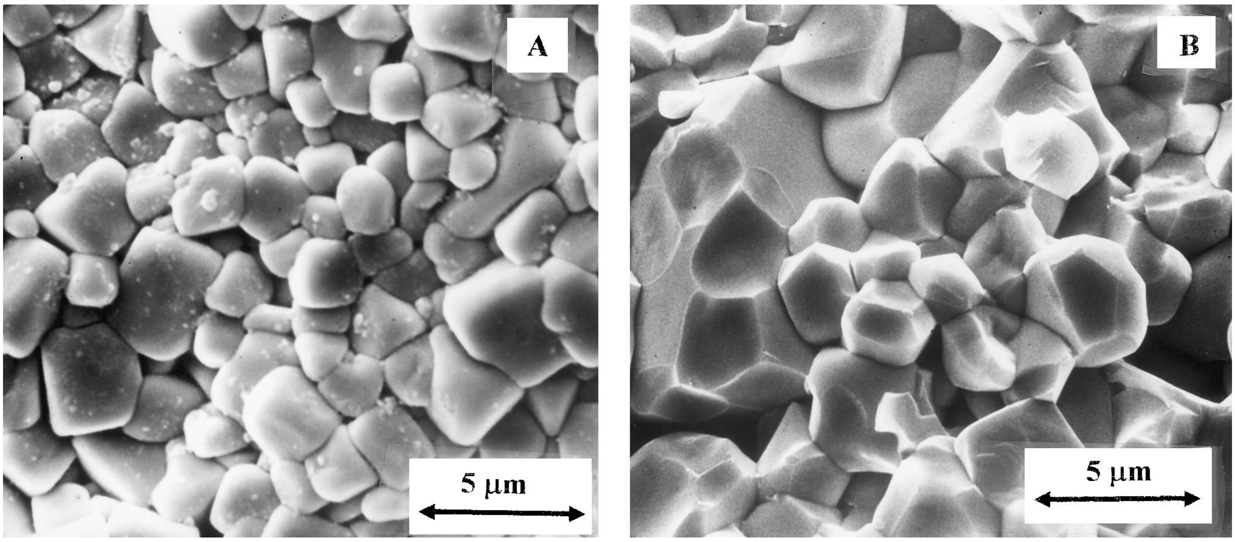

Fig. 3. Microstructure of sintered PZT-S specimens. SEM pictures: (A) MW sintered; (B) sintered in conventional furnace.

Densification levels obtainable are similar to those achieved in conventional furnaces after much longer heating cycles. Suitable heating set ups are essential for successful densification and obtainment of reasonable yields in uncracked components. Dielectric and piezoelectric characteristics of MW and conventionally sintered specimens are similar.

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