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Characterization of lead-based relaxor ferroelectric ceramics sintered in a 2.45 GHz microwave radiation

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Microwave processing of $x\mathrm{Pb(Mg_{1/3}Nb_{2/3})O_3}$-$y\mathrm{Pb(Zn_{1/3}Nb_{2/3})O_3}$-$z\mathrm{PbTiO_3}$ relaxor ferroelectric ceramics was investigated in a 2.45 GHz multimode cavity. The microwave-sintered samples were densified more rapidly and in a shorter time than the conventional sintered sample. A much smaller grain size and more uniform microstructure was developed in microwave heating. Dielectric measurement showed microwave sintered samples could obtain comparable dielectric properties (high pemittivity of 20,000) to the conventional. It was found that a high breakdown strength of 10 kV/mm and mechanical strength of 90 MPa can be achieved by the microwave method. It shows the potential to improve the figure of merit for the materials. The results reveal that microwave processing is a promising method for sintering the high dielectric ceramics. *© 2000 Kluwer Academic Publishers*

1. Introduction

Microwave sintering is a novel electrical processing technique for ceramic materials which differs fundamentally from conventional processes. Over last decade microwave processing of ceramic materials, which range from structural ceramics to functional ceramics, has been widely investigated by various researchers [1–3]. The growing interest in microwave processing over conventional processing methods is due to the fact that the electromagnetic-wave interacts with ceramic materials leading to volumetric heating by dielectric loss, which offers several technical and economic advantages, including more rapid heating rate, improved microstructure properties improved product uniformity and yields, and shorter furnace response time. In addition, this unique heating method has the potential for significant reductions in manufacturing cost due to energy saving and shorter processing time [4–6].

For microwave sintering of electronic ceramics, Harrison [7] showed that PZT and PLZT can be densified in air with fast heating and short hold time of 5 min. Varadan *et al.* [8] rapidly sintered $\mathrm{SrTiO_3}$ to a density of 98% by microwave heating to 1300 °C at 3 °C/s whereas conventional heating (0.08 °C/s) resulted in a sintered density of 80%. Similar results have been reported [9] for $\mathrm{BaTiO_3}$, $\mathrm{PbTiO_3}$ and PMN-PFN where a monomode cavity linked to a 1 kW–2.45 GHz microwave generator was used. Also the barium ferrite magnets can be sintered very rapidly by microwave heating and the physical and magnetic properties of microwave and conventional sintered are comparable [10].

Perovskite ferroelectric relaxors, especially for the lead-based relaxors having the general formula $\mathrm{Pb(B_1, B_2)O_3}$ such as PMN-PT [11], PNN-PZT and PMN-PZN-PT [12–14], are of considerable interest because their high dielectric constants, broad maxima, and relatively low firing temperature have made them promising candidate materials for multilayer ceramic capacitors [15]. In the present work, microwave sintering of the relaxor ferroelectric ceramics with compositions of $x\mathrm{Pb(Mg_{1/3}Nb_{2/3})O_3}$-$y\mathrm{Pb(Zn_{1/3}Nb_{2/3})O_3}$-$z\mathrm{PbTiO_3}$($x = 0.85$–$0.95$, $y = 0.0$–0.1, $z = 0.02$–0.10) (PMN-PZN-PT) and resulting microstructure were investigated. Their dielectric/mechanical properties were also measured and discussed.

2. Experimental procedure

2.1. Materials preparation

In order to prevent the presentation of undesired pyrochlore phase with poor dielectric properties in the final product, the powder of PMN-PZN-PT was prepared by the followings. First, MN and ZN powder were synthesized by Columbite precursor method respectively. Second, the two powders mixed with $\mathrm{Pb_3O_4}$, $\mathrm{TiO_2}$ etc. through wet ball-milling, then dried and calcinated at 700 °C. Finally it was crushed and sieved. The mixed powder of PMN-PZN-PT was consolidated by uniaxial/isostatically pressing into three size samples: (1) disks with 10 mm diameter × 1 mm thickness for measurement of dielectric properties, (2) disks with 15 × 1 mm thickness for dielectric breakdown strength,

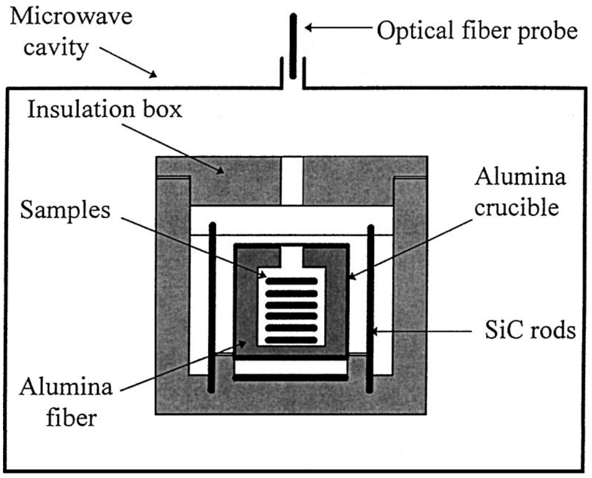

Figure 1 "Picket fence" susceptor/thermal insulation arrangement for microwave hybrid heating.

and (3) bars with 6 × 5 × 40 mm^3 for flexural strength. The resulting compacts had a green density of approximately 60%.

2.2. Microwave sintering

The green samples were sintered in air using 2.45 GHz microwave radiation. The microwave sintering system is consisted of 0.78×10^{-2} m^3 multimode cavity and a continually adjustable power supply of 0.5–5 kW, which has been illustrated in detail elsewhere [16]. SiC rods (picket fence) susceptors, as described in [17, 18], was used to initially hybrid heat shown as in Fig. 1. The microwave method could produce heating rates from several to more than one hundred centigrade per minute by controlling the net power which is equal to the difference between input power and reflected power. The temperature of specimens in microwave oven was measured by using a far inferred fiber optic pyrometer in the range of 550–2000 °C. For comparison, conventional sintering also was done where a heating rate of 5 °C/min and a holding time of 4 h at 960 °C were employed to get best dielectric properties. In addition, various hold time and peak sintering temperature were performed for investigating densification behaviors of the two sintering methods.

2.3. Property measurement

Bulk and relative density of the specimens were obtained by the Archimedes method. The microstructure of the samples was observed by the CSM-950 scanning electron microscope (OPTON, German). Dielectric constant and dielectric loss were measured by Hewlett-Packard precision LCR meter in the temperature ranging from −30 to 85 °C at the rate of 1.5 °C/min. The dielectric breakdown strength was measured with D.C power supply with high stability (GYW-100, China) where samples with thickness of 0.30–0.35 mm were used. Samples for measurement of mechanical property were polished to 3 × 4 × 40 mm^3, and flexural strength was examined by three point bending test with a loading rate of 0.05 mm/min.

3. Results and discussion

3.1. Sintering and densification

A constant power input of 0.5 kW was applied for first several minutes and then was gradually increased to reach the sintering temperature. Typical heating profile and power profile for microwave processing of the materials are shown as in Fig. 2. It can be seen that only about 30 min was needed for the heating stage from room temperature to peak. Also in this heat periods no thermal runaway, which would result in a uncontrolled heating rate, was observed. Consequently no any crack or deformation occurred for rapid sintered samples. This is due to that microwave heating with a susceptor made sample couple electromagnetic energy more uniformly than no susceptor in the multimode cavity with large volume. Microwave absorption of the materials is mainly attributed to its polarization and electronic conductivity because of their perovskite structure and conduction band.

Fig. 3 shows bulk density of the samples sintered by microwave and conventional with various hold time at 960 °C. Clearly density increase with hold time in microwave heating is much faster than in conventional heating. For example, after 15 min holding time in microwave radiation the sample reaches high density of 98.8% theoretical, but less 97%th for conventional in same hold time.

As shown in Fig. 4, plotted a function of the sintering temperature, microwave sintered samples show enhanced densification compared to their conventional equivalents, especially below 920 °C. Microwave

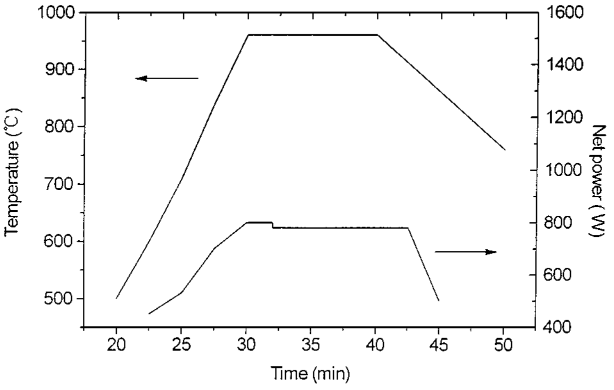

Figure 2 Microwave sintering schedule.

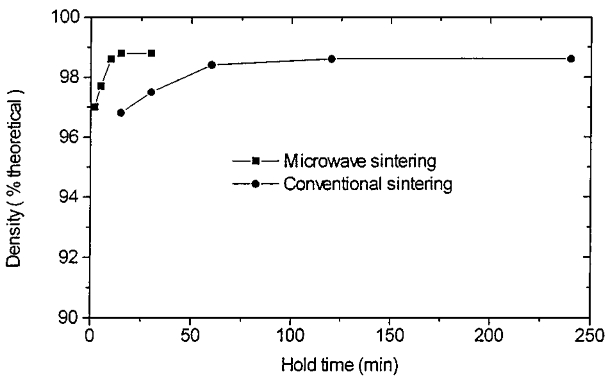

Figure 3 Relative density vs. hold time at 960 °C.

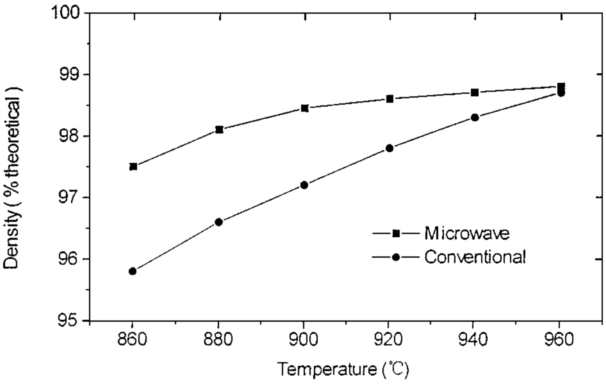

Figure 4 Sintering densification behaviors in microwave and conventional method.

sintered samples, for example, reach a 98% theoretical density at 880 °C, whereas at 940 °C for conventional sintering to the same density. A temperature difference of 60 °C was observed between microwave and conventional processing. The pronounced difference exhibits that sintering densification in microwave radiation can be achieved in much shorter time and low temperature compared to the conventional of the materials. And the shorter processing in microwave is very helpful to reduce PbO volatilization in materials.

3.2. Microstructure and grain size

Scanning electron micrographs on fracture section of sintered samples with high densification of 98%th both in microwave and conventional are shown in Fig. 5. Clearly microwave sintering produces a product with a much smaller and more uniform grain structure, whereas conventional sintered samples, even though they have a short hold time of 30 min, appears in large grain structure. From Table I, which illustrates the variation of grain sizes with a hold time at 960 °C, it can be found that the averaged grain size increased from 2.5 to 3.8 μm in microwave radiation; however the grain size growth considerably increase, ranging from 5.6 to 7.5 μm in conventional method. For a comparison of grain size in same density more than 98%th, the averaged grain size is about 3.5 and 7.2 μm by microwave and conventional firing respectively. Obviously the rapid heating and densification rate should be responsible for the finer grain sizes since grain growth in ceramics is a function of both the peak sintering temperature and its soak time.

TABLE I Grain size difference between microwave and conventional sintering at 960 °C

Hold time	(min)	5	10	15	20	30	60	120	240
Grain size (μm)	Microwave	2.8	3.2	3.4	3.5	3.8			
	Conventional			5.6		6.0	6.4	7.2	7.5

Several researchers [19, 20] have reported that microwave sintering of oxide ceramics lead to a reduction of grain size; however there the grain size reduction was limited in some extent. For example, Patterson *et al.* [21] sintered alumina (>99.8%) to density of 98% theoretical, where mean grain size was 3.19 and 4.38 μm in microwave and conventional processing respectively.

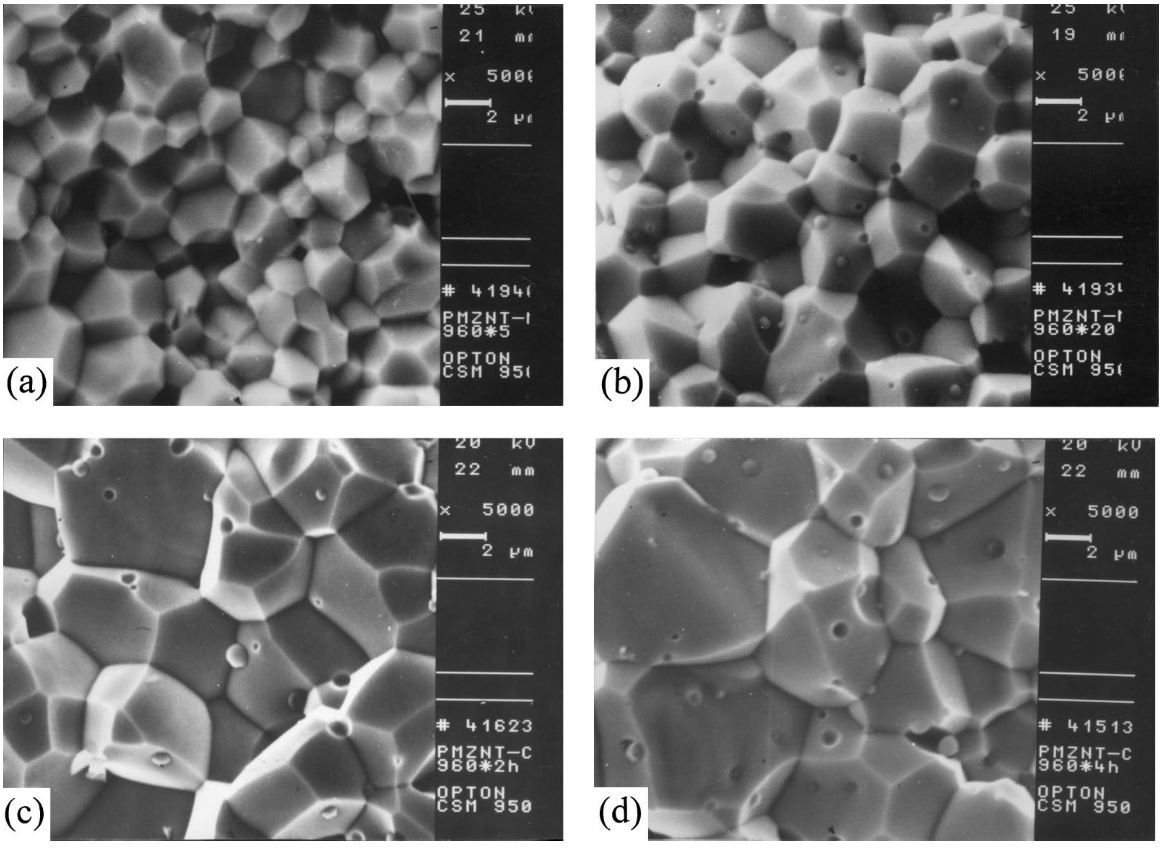

Figure 5 SEM micrographs of (a) microwave sintering at 960 °C/15 min; (b) microwave sintering at 960 °C/20 min; (c) conventional sintering at 960 °C/30 min; (d) conventional sintering at 960 °C/4 h.

Similar results was observed by Janney [22] for the sintering of zirconia. It is concluded that the grain size growth in microwave processing can be prevented more for relaxor ferroelectric ceramics than for some of other oxide ceramics such as alumina and zirconia. Perhaps this is attributed to their different microwave absorption behavior. In general alumina and zirconia, which have low dielectric loss, couple electromagnetic energy by ionic conductivity. Relaxor ferroelectric materials with perovskite structure, however, can more effectively couple microwave energy through polarization and electronic/ionic conductivity loss. Therefore a smaller grain size structure, resulted from the enhanced diffusion and accelerated densification, can be obtained in the latter case.

3.3. Dielectric and mechanical properties

An advantage of the PMN-PZN-PT is its higher dielectric constant than that of other ferroelectric ceramics [12, 23]. Dielectric constant and loss tangent of sintered samples versus temperature from −30 to 85 °C were shown as in Fig. 6. The samples both by microwave and conventional methods have a high dielectric constant of about 20,000 at certain temperature, which reveals rapid sintering in microwave can obtain a comparable dielectric properties in compared with the conventional. Fig. 7 illustrates the effect of hold time on dielectric properties in microwave processing, it can be seen that dielectric constant can reach to 20,000 for the hold time range of 10–30 min. whereas the dielectric constant decreases obviously for 2 min. The variation above is consistent with the densification of sintered samples where relative densities in held of 10–30 min are larger than that of in 2 min held.

Breakdown strength of polycrystalline dielectrics is approximately inversely proportional to the level of dielectric constant. Consequently the breakdown strength of ferroelectric relaxors is lower than that of $BaTiO_3$-based capacitors sintered by conventional process. The breakdown strength was measured for the samples sintered by microwave and conventional methods. Conventional sintered-samples produce a breakdown strength of 60 kV/mm. Microwave sintered-sample, however, can reach high breakdown strength of 100 kV/mm, which is comparable to that of $BaTiO_3$ ceramics. A significant increase by 80% was obtained compared to conventional sintered-sample. This is due to the fact that a more uniform and smaller grain microstructure was developed in microwave processing, since the breakdown strength is strongly related to various defects and overall uniformity of the product [24].

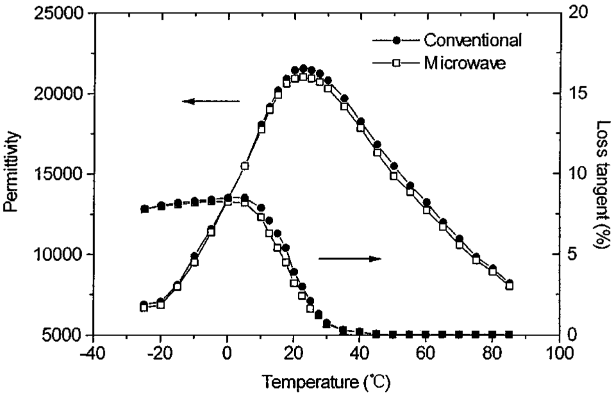

Figure 6 Dielectric properties of the samples sintered by microwave and conventional.

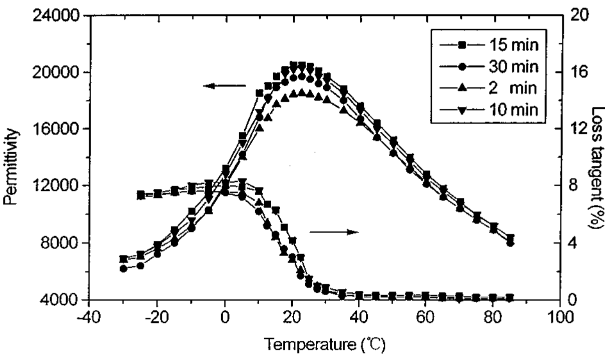

Figure 7 Dielectric properties versus sintering time in microwave method.

A qualitative figure of merit which encompasses many of the important parameters of a MLC and associated fabrication processes was formulated by Yamashita [25] given as:

$$\text{Figure of Merit} = \frac{K \times \text{BDS} \times \text{RC@125}\,^\circ\text{C}}{\text{TCC} \times \text{G.S} \times \text{Sintering Temperature}}$$

Where K: dielectric constant, BDS: breakdown strength (V/mm), $RC_{125\,^\circ C}$: product of resistance and capacitance, G.S: grain size (μm). From this expression, high breakdown strength and small grain size obtained by microwave processing is helpful to improve the figure of merit. It has been reported that there is a good correlation between BDS and mechanical strength [26]. The mechanical strength measurement of samples also revealed that microwave sintering can reach higher flexure strength (∼90 MPa) than conventional sintering (∼65 MPa). And about 40% strength increase was obtained for microwave method. The improved mechanical strength in microwave processing should be attributed to small grain size and uniform microstructure where large pores and defects as cracking origin were reduced. In addition, rapid microwave processing can abstain PbO volatilization and reduce impurity/solute segregation at grain boundaries. Previous work [27] has shown fining and clearing of the grain boundaries was effective to increase mechanical strength.

4. Conclusions

This work showed the relaxor materials with compositions of PMN-PZN-PT prepared by microwave processing can reach high density of more than 98% theoretical in a held of 10–20 min where as 4 h hold time was needed by conventional for the density. At the same time, the grain size can be significantly reduced from 7.2 μm in conventional sintering to 3.5 μm in microwave processing. Also a more uniform microstructure was developed due to volumetric and rapid heating in microwave radiation. Dielectric measurement showed microwave sintered samples could obtain comparable dielectric properties to the conventional. Another benefit for microwave sintering is that a breakdown strength as high as 10 kV/mm and mechanical strength of 90 MPa were achieved, which are comparable to $BaTiO_3$. The excellent breakdown and mechanical strength and associated with small grain size and uniform structure are desirable qualities for the application of relaxors materials used as multilayer capacitors.

Acknowledgements

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