Journal of Optoelectronics and Advanced Materials Vol. 3, No. 1, March 2001, p. 83 - 87

ADVANCED TECHNOLOGY FOR MAKING PZT TYPE CERAMICS BY FAST FIRING

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Densification and piezoelectric performances of some fast fired lead zirconate-titanate ceramics were investigated in comparison with those made by conventionally sintering technique. Micro and nano PZT powders were used as initial powders for the compacts subjected to the fast and conventionally sinterings. Density maxima of about 98 % of the theoretical density, were obtained for nanopowder compacts fast fired at 1350 ^{o}C for 20 minutes. The piezoelectric properties of the fast fired and conventionally sintered compacts were determined. Significant increase for $\boldsymbol{d_{33}}$ piezoelectric charge constant was observed in the case of fast fired samples compared to conventionally sintered ones. The electromechanical planar coupling factor $\boldsymbol{k_p}$ was also increased from 0.62 to 0.65 for fast fired samples. The densification mechanism was discussed in terms of a predominantly transient stresses induced during the initial stage of densification by the rather high temperature gradient of the fast fired samples.

(Received January 21, 2000; accepted February 9, 2001)

Keywords: PZT, Ceramics, Fast firing, Piezoelectric properties

1. Introduction

The fast firing process of compacted powders is known to provide higher or at least equivalent densities compared to the conventional sintering. This process was successfully used for a number of materials, such as alumina [1-5], soft ferrites [6], barium titanate [7,8] and lead zirconate titanate [9]. It involves a rapid insertion of a compacted powder specimen into a preheated furnace at high temperature followed by soaking for a shorter time than used in conventional sintering.

The validity of the fast firing concept has not been yet fully understood though for some ceramics there were confirmations that the superior densification is basically connected to fine particle size were the initial stage sintering predominates so that densification may be attributed to a rapid passage of a specimen through a lower temperature regime followed by the higher temperature region where the densifications mechanism by grain boundary diffusion play the major role in the finer grain conditions.

The temperature gradients are extremely important in mass transport and it was suggested that such gradients as well as dislocation movement are essential in driving densifications during fast firing process [5,10,11].

Rapid sintering is a fenomena uniquely associated to fine particle size where reactive particles are required in order to overrule the tensile stress in the dense region as well as to enhance the relaxation by creep phenomena [11].

In the case of fast firing of PZT type ceramics, different densification mechanisms were discussed [9] but no special reference has been made about the influence of the fast firing process on the piezoelectric properties of such ceramics.

In the present work we investigated the influence of the sintering process on the piezoelectric properties of such materials and compared the performance of rapidly and conventionally sintering of PZT ceramics.

2. Experimental

We used a soft material which shows high piezoelectric characteristics [12]. The powders were prepared both by the usual ceramic technique and by the chemical methods.

2.1. Ceramic technique

The raw materials used were oxides of p.a. purity. The stoichiometric amounts of oxides were mixed for 2 hours in methanol by means of a planetary ball mill, then double calcined at 850 ^{o}C and 880 ^{o}C respectively, with an intermediate milling of 2 hours and a final milling of 6 hours. The fine powder thus obtained, have particles with an average spherical equivalent diameter of about 0.5 μm and designed it as MmP (Micrometric Powder).

2.2. Chemical method

The raw initial materials used were pure reagent grade lead nitrate, titanium tetrachloride and zirconium tetrachloride [13].

The coprecipitated product derived from the mixture of the basic components: lead nitrate peroxytitanil and lead nitrate peroxyzirconil [14] were calcined at 800 ^{o}C for 2 hours.

The average grain size of this powder was situated around 50 nm and, consequentlly, we designed it as NmP (Nanometric Powder).

2.3. Pressing

Disc shaped samples from both types of powders were uniaxially pressed in a steel die giving the green densities of about 4.6-4.8 g/cm^3, representing nearly 58-60 % of the theoretical density (TD).

The pressed powder compacts were slowly dried at 150 ^{o}C for 4 hours in a small oven in order to remove any trace of water, before sintering.

2.4. Sintering

Both types of sintering processes, fast and conventional, were carried out in a chamber type furnace, heated with SUPER KANTHAL elements.

For conventional sintering the saggers containing PZT samples were introduced into the furnace from the beginning and heated up to the sintering temperature, followed by soaking for 6 hours, then naturally cooled with the furnace down to room temperature.

For fast firing, the saggers containing the PZT samples were directly inserted into the preheated furnace at the firing temperature, soaked for a certain time at this temperature, then removed from the furnace, and cooled down to room temperature in a few minutes.

Conventionally sinterings were carried out with both types of powders (MmP and NmP) for temperatures ranging between 1200-1350 ^{o}C and soaking of 6 hours while fast firings were made at two temperatures only, namely 1300 ^{o}C and 1350 ^{o}C and, for soaking times of up to 60 minutes.

Following sintering procedures, the densities of all samples were measured by Archimede's method. The specimens for measurements were prepared by mechanical processing on a special lapping machine in the shape of discs with 10 mm diameter and 1 mm thickness, electroded with a Ni thin film on both surfaces using an electroless process. Then the samples were poled in a silicon oil bath at 220 ^{o}C under an electric field of 3 kV/mm. The piezoelectric properties were measured by means of resonance-antiresonance method using an HP 4194A Impedance Gain Phase Analyzer.

3. Results and discussions

Fast firing of compacted powder samples by rapid insertion and removal, into preheated furnaces implies extremely high heating and cooling rates. This involves extremely high temperature gradients accompanied by rapid solid state reaction processes during the initial stage of sintering that may give rise to a distribution of the density within the sample. Thus, it is formed a dense outer layer which migrates from the surface to the center of the sample with a certain speed, that can by hardly exactly determined, but it was estimated to about $5{\cdot}10^{-6}$ m/s from the densification time.

This result is consistent with the one obtained for fast firing of alumina where the speed of the interface movement was estimated to $4{\cdot}10^{-6}$ m/s [4].

Therefore, it seems plausible to assume that the transient stresses play the main role in the densification mechanism of fast fired samples. This may also be associated with the stress induced diffusion.

According to the scaling laws [16] the grain boundary diffusion is enhanced in small grain size powder compacts and therefore it seems reasonable to assume, that grain boundary diffusion is the rate controlling mechanism for densification in small grain size powder compacts as is the case for our nanopowders.

Fig. 1 shows the densification data as a function of soaking time for the two types of powders,

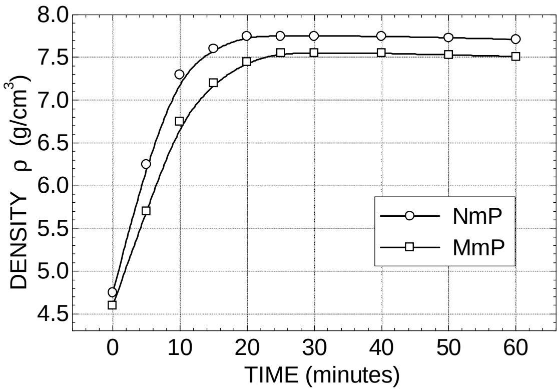

Fig. 1. Density versus soaking time in the fast firing process.

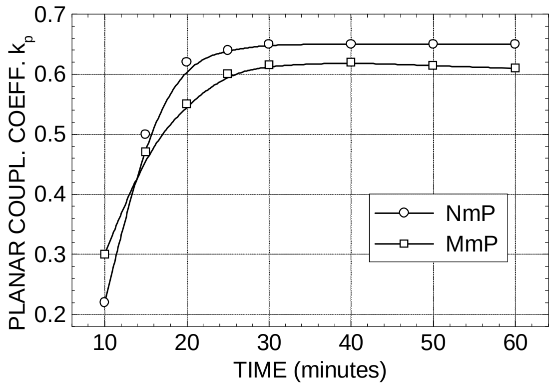

Fig. 2. Planar coupling coefficient versus soaking time in the fast firing process.

fast sintered at 1350 °C. It can be seen that practically after 20 minutes the densification is completed and the densities reach their maxima of 7.52 g/cm^3 for MmP and 7.75 g/cm^3 for NmP respectively. Such a behavior suggests that the predominant mechanisms involved in this process is the *rearrangements* of the particles induced and sustained by the transient stresses, taking place in a very short time followed by stress induced diffusion [4,5,21].

Fig. 2 shows the behaviour of the planar coupling coefficient as a function of firing time for powder compacts fired at 1350 °C. It can be seen that after 30 minutes the coupling coefficient reach their maximum values for both powders. Here too the values of $\boldsymbol{k_p}$ are higher for NmP samples compared to MmP which seems obvious since the NmP is more reactive and consequentlly densifies easier at higher values compared to MmP.

In the case of conventional sintering process both densification and planar coupling coefficient behave in a similar manner as a function of the sintering temperature as can be seen in Fig. 3 and 4. The most densified samples were those made of NmP reaching 7.73 g/cm^3 at 1250 °C compared with 7.62 g/cm^3 for MmP at 1300 °C.

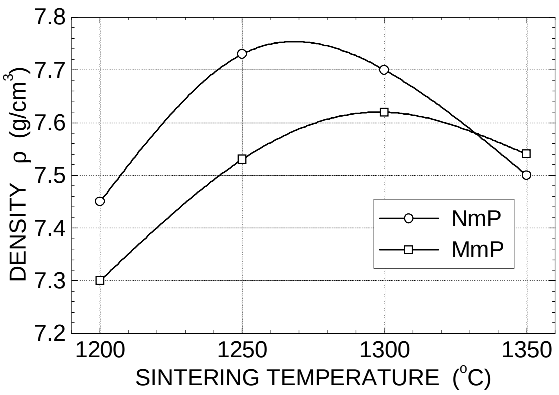

Fig. 3. Density versus sintering temperature for samples conventionally sintered.

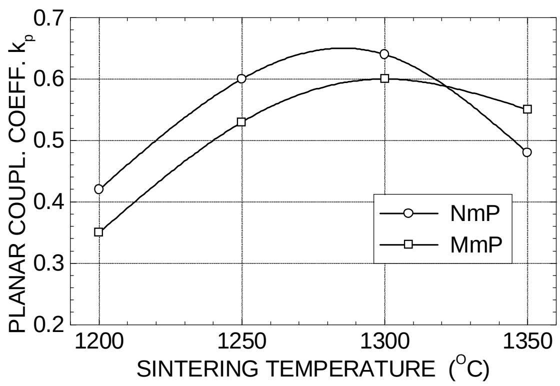

Fig. 4. Planar coupling coefficient versus sintering temperature for samples conventionally sintered.

Some of the main piezoelectric parameters of the fast and conventionally sintered powders are shown in Table 1.

Table 1. Experimental values of the main piezoelectric parameters of samples made by conventional sintering and by fast firing process respectively.

		Powder type	ε_r	k_p	$d_{33}\cdot10^{-12}$ (m/V)	$g_{33}\cdot10^{-3}$ (m•V/N)	$d_{31}\cdot10^{-12}$ (m/V)	$g_{31}\cdot10^{-3}$ (m•V/N)	Q_m
Conv. Sintr.	1300 °C/6h	MmP	1520	0.61	380	26	-173	-15	68
	1275 °C/6h	NmP	1602	0.62	396	25	-170	-14	66
Fast firing	1350 °C/30 min.	MmP	1645	0.62	510	22	-181	-11	58
	1350 °C/30 min.	NmP	1855	0.65	570	20	-190	-9	60

It is interesting to note that for fast fired samples the properties are well improved compared to the conventionally sintered ones.

Thus for example the most spectacular change was recorded for the dielectric constant, which increases with about 40% for MmP and with 80% for NmP respectively. For the charge constant d_{33}, the increases were of 34% for MmP and 44% for NmP respectively. For the planar coupling coefficient k_p, the improvement was not significant: 1% for MmP and 5% for NmP only. The improvement for the other constants was insignificant.

We assumed that the improvement of the piezoelectric properties of fast fired samples is a grain size effect since samples with uniform and low grain size and low porosity showed the highest values for piezoelectric constants [22-25].

4. Conclusions

PZT type powders were prepared both by ceramic technique as well as by chemical method. The average grain sizes of the particles in the case of ceramic technique were 0.5 μm and this powder was consequentlly designed as MmP and 50 nm for chemically prepared powder and it was designed as NmP. Using conventionally sintering and fast firing approaches, dense piezoceramic samples were fabricated and their piezoelectric properties were measured and compared.

The densification process in fast firing approach was completed after 30 minutes, giving a maximum density of 98.5% for more reactive nanopowder and of 96.2% for less reactive micropowder.

The piezoelectric properties of conventionally and fast fired samples were measured and compared. All the properties were improved by fast firing process compared to the conventional sintering. Thus the dielectric constant increases by 40% and 80% for MmP and NmP respectively. The charge constant d_{33} increases by 34 and 44%, respectively, while the planar coupling coefficient k_p does not change significantly (1 to 5% only).

This improvement is assumed to be a grain size effect combined with a low porosity characteristics to fast fired samples.

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