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Effect of sintering parameters on the microstructure and properties of strontium modified PZT ceramics prepared using spray-dried powders

RAMJI LAL, N. M. GOKHALE, R. KRISHNAN
Naval Chemical and Metallurgical Laboratory, Naval Dockyard, Bombay-400023, India
P. RAMAKRISHNAN
Department of Metallurgical Engineering, Indian Institute of Technology, Powai, Bombay-400076, India

PZT powders of the composition $Pb_{0.94}Sr_{0.06}(Zr_{0.53}Ti_{0.47})O_3$, prepared by spray drying and calcining techniques, were processed to sintered ceramics by conventional cold pressing and sintering at various temperatures and periods between 1000 to 1250° C for 0.5 to 12 h. Sintered ceramics were evaluated for their microstructure and electromechanical properties. Highly dense ceramics having bulk density of the order of 97% of the theoretical value could be obtained after sintering at a considerably lower temperature of 1000° C in comparison to the 1300° C generally required for powders prepared by conventional ceramic processing. However, the increase in sintering temperature of reactive spray-dried powders causes the entrapment of closed pores as a result of exaggerated grain growth and subsequent pore coarsening thereby leading to a decrease in the bulk density of the ceramics. It has been observed that minor variations in the sintering parameters influence the porosity, grain size and electromechanical properties. Values of the dielectric constant, piezoelectric strain coefficient and electromechanic coupling factor increase with the increase in grain size and decrease with the increase in porosity of the sintered ceramic whereas the dielectric dissipation factor decreases with the increase in sintering temperature.

1. Introduction

The properties of lead zirconate titanate (PZT) ceramics have been found to be considerably influenced by the variation in their microstructure particularly grain size and porosity which are dependent on the initial powder characteristics and processing parameters [1–6]. However, most of the earlier studies have been carried out using powders prepared by the "dry" mixing technique of ball milling the constituent solid oxides by which it is difficult to provide adequate control on the powder characteristics and consequently on the microstructure and properties of the finished ceramics. Hence, much of the published information concerning such ceramics can not be reproduced [7, 8]. On the other hand, the inhomogeneity in microstructures has been overcome to a large extent by the use of powders prepared by wet chemical methods and the ceramics produced in this way have shown encouraging results [9–13]. However, in this respect, very little effort has been made to correlate the influence of the processing parameters with the microstructural development and properties of the finished ceramics. In the present investigation, strontium modified PZT powders prepared by spray drying the mixed nitrate solution of the constituents have, therefore, been used to study the influence of the sintering parameters on the microstructure particularly grain size and porosity and their consequent effect on the variation in electromechanical properties of the finished ceramics.

2. Experimental procedure

The powders used for fabricating the ceramics were prepared by spray drying the mixed nitrate solution of the constituents. Reagent grade $Pb(NO_3)_2$ (99.5%), $Sr(NO_3)_2$ (99.99%), $Zr\ OCl_2 \cdot 8H_2O$ (98.8%) and $TiCl_4$ (99.99%) were used as the primary raw materials. Prior to the preparation of the composite nitrate solution, $ZrOCl_2 \cdot 8H_2O$ was crystallized in HCl to minimize the deleterious impurities of iron and silicon. $Pb(NO_3)_2$, crystallized $ZrOCl_2 \cdot 8H_2O$ and $TiCl_4$ were precipitated separately as hydroxide and converted into their nitrate solutions by dissolving the precipitates in dilute HNO_3. These nitrate solutions, along with $Sr(NO_3)_2$, were then mixed in the stoichiometric proportions corresponding to the composition $Pb_{0.94}Sr_{0.06}(Zr_{0.53}Ti_{0.47})O_3$ for spray drying. Details of the procedure for the preparation of powders by spray drying have been described elsewhere [14]. Spray dried powders were calcined at 550° C for 4 h followed by 650° C for 2 h and then at 750° C for 2 h in order to

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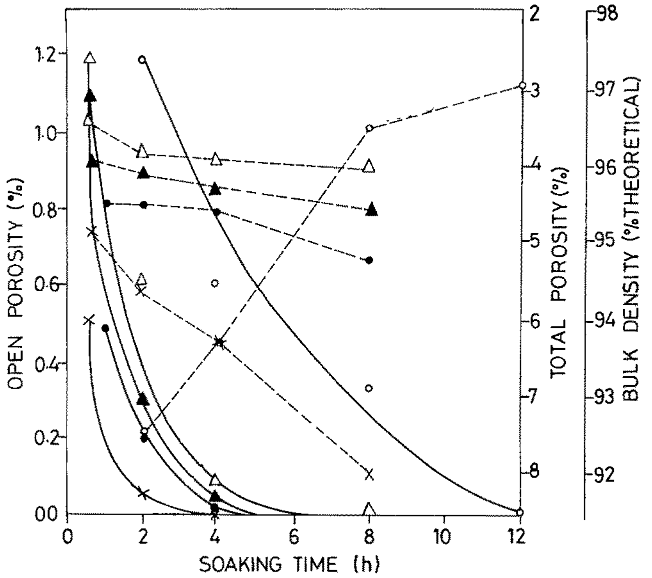

Figure 1 Variation of open porosity (——), total porosity and bulk density (– – –) with sintering temperature and soaking time. (△ 1100° C, ▲ 1150° C, ● 1200° C, ○ 1000° C, × 1250° C).

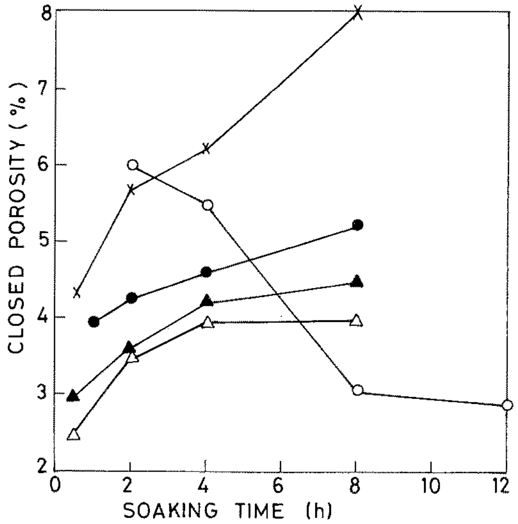

Figure 2 Variation of closed porosity with sintering temperature and soaking time. (○ 1000° C, △ 1100° C, ▲ 1150° C, ● 1200° C, × 1250° C).

obtain well reacted and fine grained crystalline powder of the stoichiometric composition. Calcined powders were then compacted uniaxially at 207 MPa into circular discs of 18 mm diameter and 2.5 mm thickness using 1.5 wt % PVA as binder. These discs were sintered at different temperatures varying from 1000 to 1250° C and soaking time from 0.5 to 12 h. An appropriate PbO atmosphere was maintained during sintering to suppress the volatility of PbO from the specimens. Sintered discs were lapped to make both the surfaces flat and parallel and then polished on a cloth wheel using diamond paste. Lapped and polished discs were electroded by brushing with silver paste and subsequently firing at 600° C for 1 h. Discs were then poled by applying a d.c. electric field of 30 kV cm^{-1} at 100° C in a silicone oil bath for 15 min. Electromechanical properties were measured 24 h after poling as per the IRE standard procedure [15]. Bulk density, ϱ, and open porosity, P_0, of the sintered specimens were determined by water immersion method using the formulae $\varrho = W_1/(W_2 - W_3)$ and $P_0 = (W_2 - W_1)/(W_2 - W_3)$ where W_1, W_2 and W_3 are the weight of the dry specimen, the weight of the same specimen saturated with boiling water, and the suspended weight of the saturated specimen in water, respectively. Total porosity, P_t, of the specimens was calculated using the formula $P_t = 1 - \varrho/\varrho_t$ where ϱ_t is the theoretical density.

The value of closed porosity (P_c) was then calculated from the relation $P_c = P_t - P_0$. Microstructural examinations were carried out from the electron micrographs of the test specimens which were polished and chemically etched in dilute HCl containing a few drops of HF. Average grain size was determined by the lineal intercept method counting nearly 300 grains for each sample. Number and size of the pores in the sintered samples were calculated from the SEM photomicrographs of the fractured surfaces of the specimens.

3. Results and discussion

In order to study the densification characteristics of the reactive spray dried powders, data were generated in respect of open, closed and total porosity of the ceramics sintered at different conditions. Variation in the open and total porosity as well as bulk density of the samples as a function of sintering temperature and soaking time is shown in Fig. 1. It can be seen from the figure that the bulk density of the sample increases with the increase in soaking time at 1000° C and attains a value of ~ 97% theoretical at a considerably

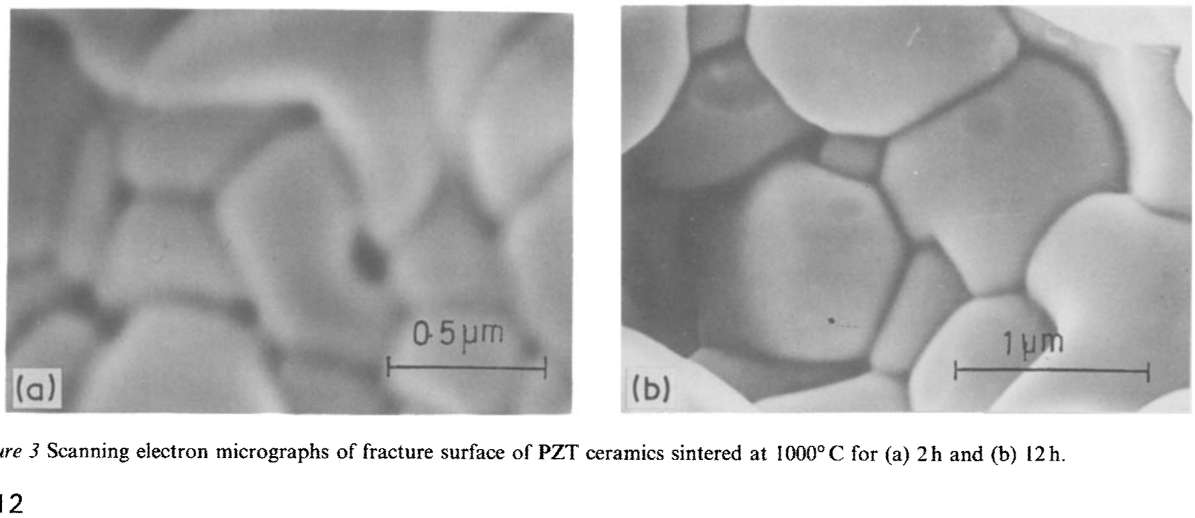

Figure 3 Scanning electron micrographs of fracture surface of PZT ceramics sintered at 1000° C for (a) 2 h and (b) 12 h.

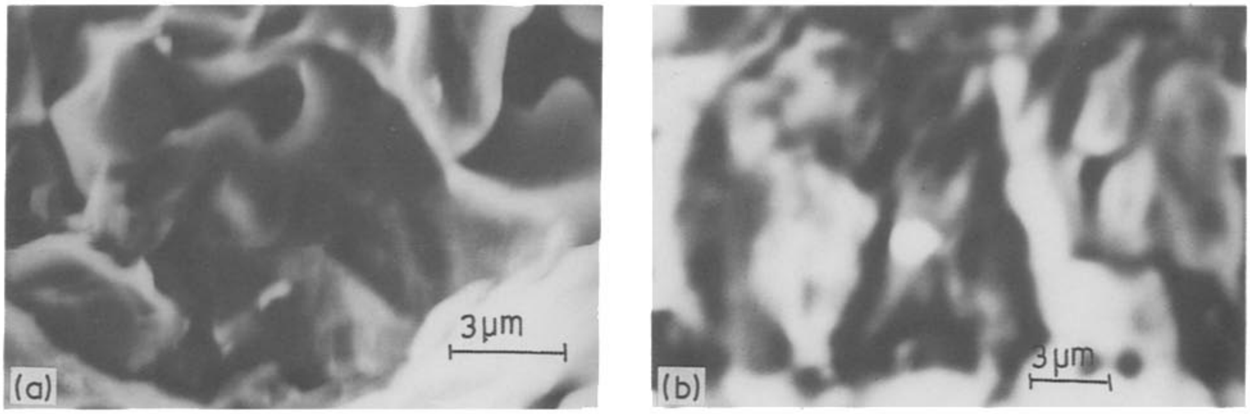

Figure 4 Scanning electron micrographs of fracture surface of PZT ceramics sintered at 1250° C for (a) 0.5 h and (b) 8 h.

lower temperature in comparison to the 1300° C generally required to achieve even 95% theoretical density for powders prepared by conventional ball milling and calcining [16]. However, with the increase in sintering temperature beyond 1000° C, bulk density decreases with the increase in sintering temperature and associated soaking time. In our earlier publication [17], the phenomenon of the decrease in the bulk density (with corresponding increase in total porosity) of ceramics with the increase in sintering temperature beyond 1000° C, (Fig. 1) could be attributed to the rapid material flow due to the high surface activity of spray dried powders thereby leading to entrapment of porosity and subsequent pore coarsening. This phenomenon has been further investigated in the present investigation on the basis of the variations in the closed and open porosity of ceramics during sintering. It can be seen from Fig. 1 that the open porosity decreases and becomes negligible with the increase in sintering temperature and soaking time as a result of pore closure and migration of pores through the grain boundaries. However, variation in closed porosity exhibits a different trend as shown in Fig. 2. Values of closed porosity decreases with the increase in soaking time at 1000° C whereas beyond 1000° C, closed porosity increases with the increase in sintering temperature and associated soaking time which ultimately causes a decrease in the bulk density of ceramics in spite of the open porosity being negligible. Thus the decrease in the bulk density with the increase in sintering temperature (Fig. 1) can be attributed to the increase in closed porosity during sintering. Figs 3 and 4 are the scanning electron micrographs of the fractured surfaces of the specimens sintered at 1000 and 1250° C respectively. It can be seen from the photomicrographs that the specimen sintered at 1000° C for 2 h (Fig. 3a) has pores at the grain boundaries which decrease in number with the increase in soaking time (Fig. 3b). The microstructure shown in Fig. 4 reveals that the increase in sintering temperature causes pores to be trapped inside the grains as a result of grain growth. Such trapped pores are visible in the microstructure of samples sintered at 1250° C as shown in Fig. 4a, whereas Fig. 4b shows the evidence of pore coarsening with the increase in soaking time. This phenomenon of the entrapment of closed porosity followed by pore coarsening has also been demonstrated by the trend of the variation of closed porosity as a function of sintering temperature and time in Fig. 2. As shown in the figure, the increase in the values of closed porosity with the rise in sintering temperature and time takes place due to the entrapment of closed pore and pores coarsening. These observations, indicate that spray dried powders possess greater driving force for sintering and, therefore, exhibit enhanced densification at the lower temperature of 1000° C whereas with the increase in temperature, the greater surface activity of the powders causes entrapment of closed pores followed by pore coarsening thereby leading to the increase in closed porosity (Fig. 2) and consequently to the decrease in the bulk density as shown in Fig. 1.

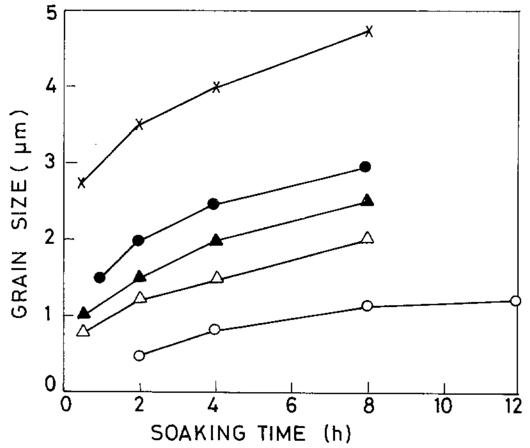

Figure 5 Variation of grain size with sintering temperature and time. (○ 1000° C, △ 1100° C, ▲ 1150° C, ● 1200° C, x 1250° C).

As evident from Fig. 5, the grain size of the ceramics increases with the increase in sintering temperature and soaking time. The rate of the grain growth also increases with the increase in sintering temperature and decrease with the increase in soaking time at each temperature. Microstructures of the finished ceramics were examined from the SEM photomicrographs shown in Figs 6 and 7. Small crystallites of similar size to those of the initial powder have been observed in samples sintered at 1000° C for 2 h as shown in Fig. 6a. These crystallites aggregate with the increase in sintering temperature and time and as a result, the grain size of the ceramics increases (Fig. 6b) maintaining their initial morphology with pores mostly at the grain

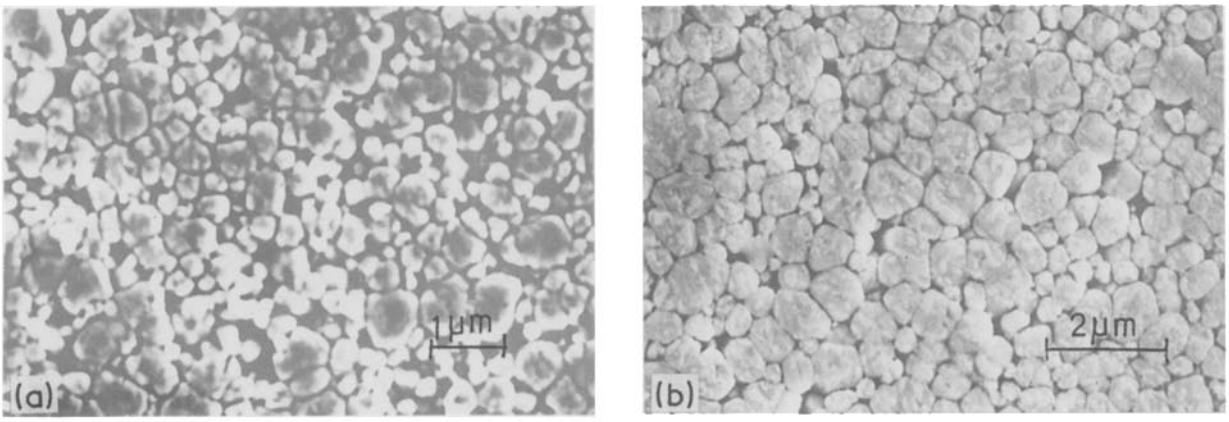

Figure 6 Scanning electron micrographs of PZT ceramics sintered at 1000° C for (a) 2 h and (b) 12 h.

boundaries. Uniformity in grain structures takes place after 4 h of soaking at each temperature between 1100 and 1200° C (Figs 7a, b and c) whereas at 1000° C, the grains become uniform after 12 h (Fig. 6b) and at 1250° C exaggerated grain growth having closed porosity has been observed as shown in Fig. 7d.

The trend of the variation of electromechanical properties such as dielectric constant, ε, piezoelectric strain coefficient, d_{33}, and electromechanical planar coupling coefficient, K_p, of sintered ceramics as shown in Figs 8, 9 and 10 respectively has been found to be similar in nature. At 1000° C of sintering, values of ε, d_{33} and K_p increase with the increase in soaking time which can be attributed to the increase in the grain size and uniformity in their structure as well as the decrease in porosity of the sintered ceramics. At 1100 and 1150° C, values of these properties increase with the increase in soaking time even when porosity remains almost constant. This phenomenon can be attributed to the increase in the grain size. At the sintering temperature of 1200° C, values of ε, d_{33} and K_p increase upto 4 h of soaking due to increase in the grain size (Figs 8, 9 and 10) and then decrease when the soaking time is increased beyond 4 h, whereas at 1250° C there is a fast decrease in the values of the properties with the increase in soaking time. The decrease in the values of the properties can be attributed to the increase in the total porosity of ceramics (Fig. 1). Thus the values of ε, d_{33} and K_p decrease with the increase in porosity and increase with the increase in grain size and uniformity of microstructure.

However, a different trend has been observed in the variation of tan δ with respect to sintering parameters as shown in Fig. 11 which indicates that the value of

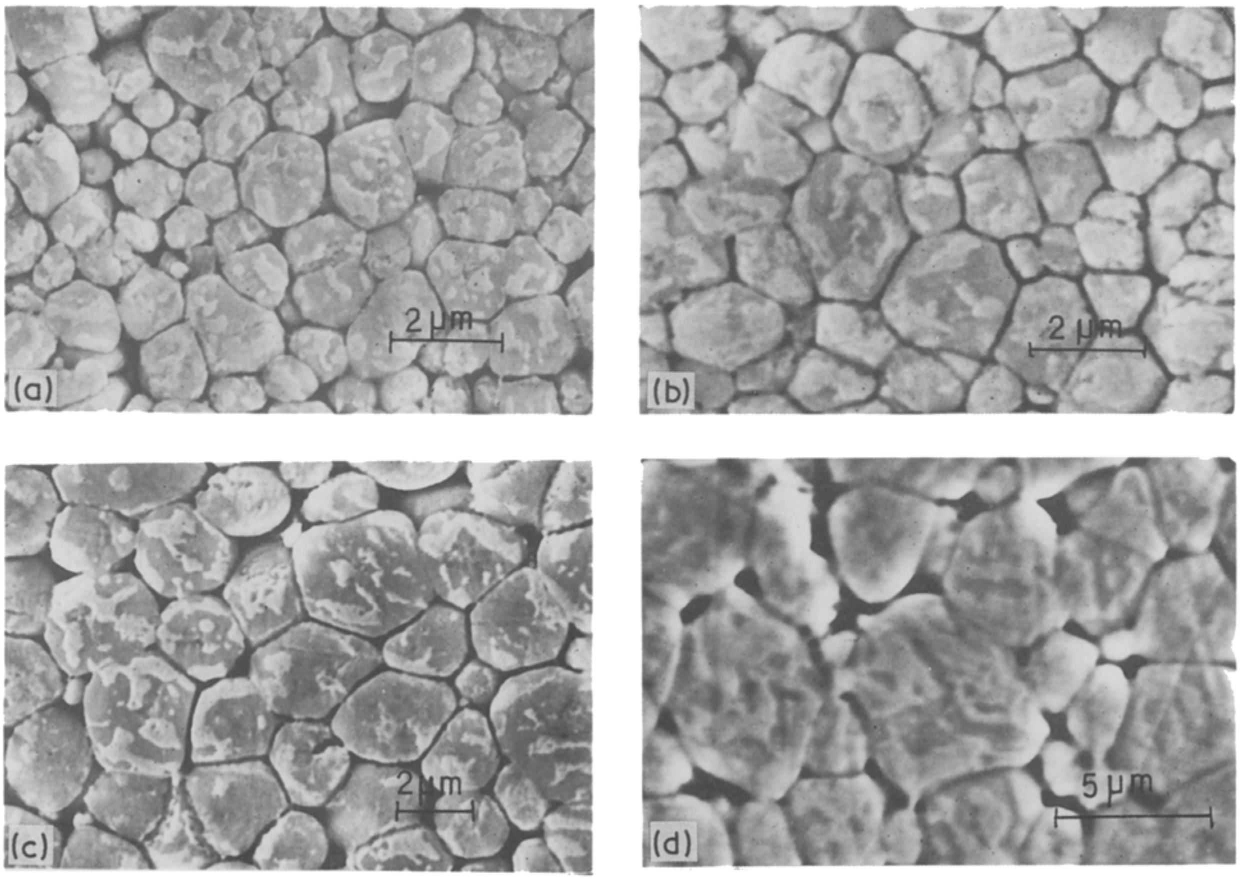

Figure 7 Scanning electron micrographs of PZT ceramics sintered for 4 h at (a) 1100° C (b) 1150° C (c) 1200° C and (d) 1250° C for 8 h.

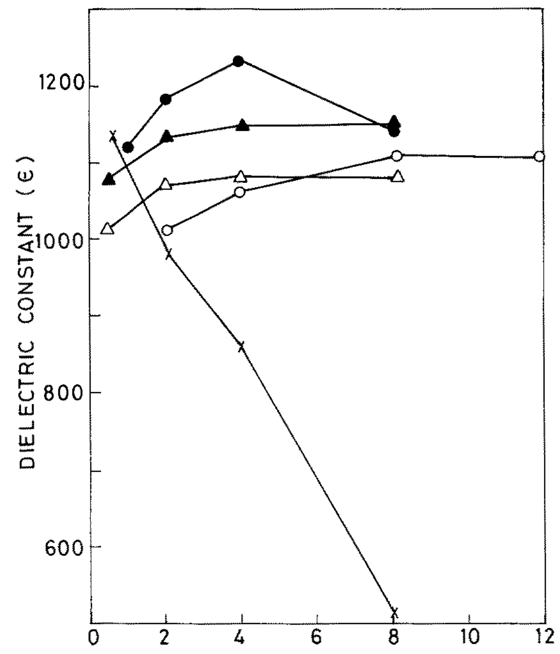

Figure 8 Variation of dielectric constant (ε) with soaking time and sintering temperature (○ 1000° C, △ 1100° C, ▲ 1150° C, ● 1200° C, × 1250° C).

tan δ decreases with the increase in soaking time at lower temperature of 1000° C whereas at higher temperature of 1200 and 1250° C, its value increases initially and then gradually decreases. In contrast, at the intermediate temperature of sintering (1100 and 1150° C), tan δ decreases initially and then gradually increases with the increase in soaking time. On the whole, values of tan δ decrease with the increase in sintering temperature. Thus to develop materials from the application point of view where high values of ε, d_{33} and K_p as well as a lower value of tan δ are required, sintering parameters should be judiciously selected taking into consideration the variation of porosity, grain size and uniformity in microstructure.

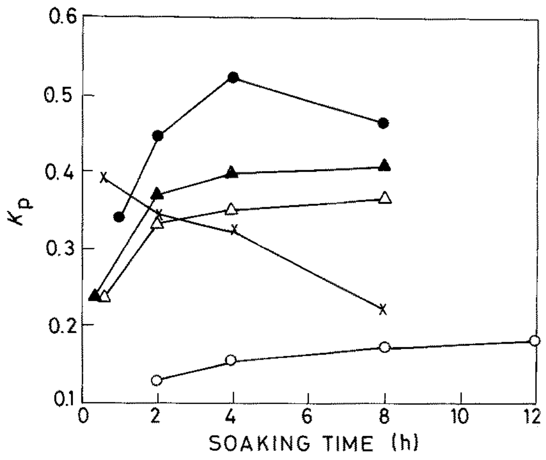

Figure 10 Variation of electromechanical coupling coefficient (K_p) with sintering temperature and soaking time. (○ 1000° C, △ 1100° C, ▲ 1150° C, ● 1200° C, × 1250° C).

4. Conclusions

Microstructural studies of ceramics sintered at different temperatures in the range of 1000 to 1250° C have indicated that an increase in the sintering temperature increases the grain size which also increases with an increase in soaking time at each temperature. Ceramics sintered at 1000° C for 12 h have minimum porosity of 2.9%. Values of ε, d_{33}, and K_p improve with the increase in grain size and deteriorates with the increase in porosity whereas the value of tan δ decreases with the increase in sintering temperature thereby improving the properties of the ceramics. However, the sintering temperature can not be increased beyond 1200° C for the sake of increasing the grain size because of the associated increase in closed porosity leading to deterioration in properties. Thus the sintering conditions have to be optimized for processing spray dried powders in order to develop materials with optimum microstructure and electromechanical properties. In the present investigation, ceramics sintered at 1200° C for 4 h exhibit optimum electromechanical properties with average grain size and porosity approximately 2.5 μm and 4.5 % respectively.

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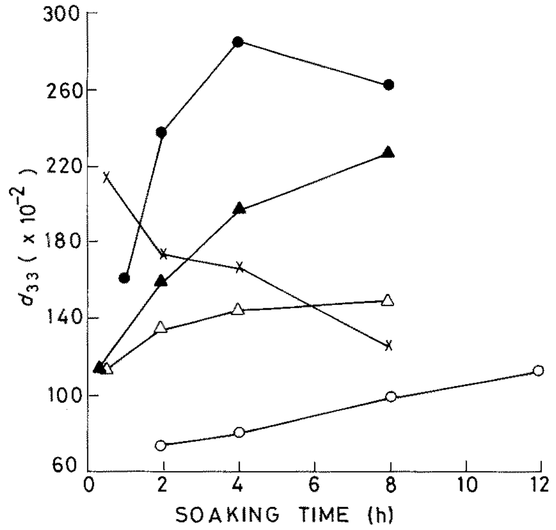

Figure 9 Variation of piezoelectric strain coefficient (d_{33}) with sintering temperature and soaking time. (○ 1000° C, △ 1100° C, ▲ 1150° C, ● 1200° C, × 1250° C).

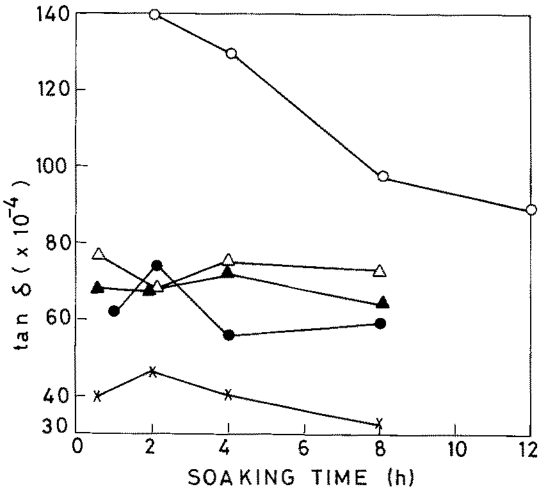

Figure 11 Variation of dissipation factor with sintering temperature and soaking time. (○ 1000° C, △ 1100° C, ▲ 1150° C, ● 1200° C, × 1250° C).

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