ELSEVIER

Ceramics International 27 (2001) 243–246

CERAMICS
INTERNATIONAL

Short communication

Effect of post sinter annealing on the dielectric constants of PMN and PFN

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Received 14 January 2000; received in revised form 26 February 2000; accepted 18 April 2000

Abstract

Lead magnesium niobate (PMN) and lead iron niobate (PFN) are the ferroelectric ceramics having perovskite structure. Both of these compounds have high dielectric constant (10 000–20 000) and the change in their dielectric constant with respect to temperature is gradual, showing diffused phase transition peaks at −12°C (PMN) and 110C (PFN) respectively. The dielectric properties of these compounds depend very much on their microstructural features i.e. grain size, grain boundary thickness etc. In this study, the PMN and PFN powders prepared by semi-wet hydroxide route were sintered in PbO atmosphere at 1000–1150°C. The sintered pellets were heated in air at 1000°C for 1/2 to 1 h. Their dielectric properties with respect to temperature were studied and the effect of post sinter annealing on their dielectric constants was analysed. © 2001 Elsevier Science Ltd and Techna S.r.l. All rights reserved.

Keywords: A. Sintering; B. Grain boundaries; E. Capacitor; PMN; PFN

Lead magnesium niobate (PMN) and lead iron niobate (PFN) belong to a family of complex Pb (B_1B_2) O_3 perovskites, where B_1 is typically a low-valence cation e.g., Mg^{+2}, Zn^{+2}, Fe^{+3}, Ni^{+2}, Sc^{+3} etc. and B_2 a high valence cation e.g. Ti^{+4}, Nb^{+5}, Ta^{+5} and W^{+6} [1]. These materials exhibit broad and anomalously large dielectric maxima, which make them ideal candidates for multilayered ceramic capacitors (MLCs) [2]. PMN also has very large electrostrictive and field induced piezoelectric coefficients, which coupled with its other characteristics such as low hysteresis losses and low thermal strain coefficients, make this material suitable for many optical, biomedical and sonar devices [3]. PMN [Pb (Mg1/3 Nb2/3)O_3], the first lead-based relaxor ceramic, was discovered by Smolenski and Agramoveskaya in the late 1950s [4]. In a relaxor like PMN, the dielectric constant peak shifts to higher temperature at higher measuring frequencies and vice-versa. It is believed that relaxation in PMN is due to the presence of nanoscale ordering of Mg and Nb ions at octahedral B sites. The ordering is 1:1 type making ordered region and its surrounding as P type and N type materials respectively. As the ordering is of non-stoichiometeric nature, creating large charge imbalance between ordered and disordered region, ordering in PMN is restricted to 2–5 nm size. The size of ordered region could not be enhanced by thermal treatment. However the size of ordered region could be manupulated by doping at A site [5,6]. PFN [Pb (Fe1/2 Nb1/2)O_3] on the other hand has a complete disordered structure and behaves as a normal dielectric material.

The dielectric properties of these materials strongly depend on their microstructure and impurity content [7,8]. The dielectric constant in PMN ceramics is reported to depend on grain size and grain boundary thickness following a relation given below:

$$\frac{1}{K} = \frac{1}{K_{\text{crystal}}} + \frac{1}{R.K_{\text{GB}}}$$

K = maximum dielectric constant of ceramic sample.
K_{crystal} = maximum dielectric constant of PMN crystal.
R = ratio of grain size to grain thickness.
K_{GB} = dielectric constant of grain boundry phase.

It is reported that grain boundary phase is made of lead based material [7,9]. The presence of an excess lead oxide phase at grain boundaries adversely affects the

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PII: S0272-8842(00)00066-3

dielectric constant, insulation resistance and mechanical strength of ceramic bodies [2]. In this study the effect of air annealing of sintered pellets at 1000ºC (which is aimed to reduce the lead oxide phase at grain boundaries) on the dielectric constant of PMN and PFN ceramics was carried out.

PMN and PFN powders were synthesised by semi-wet-hydroxide route [10]. The powders were compacted on a hydraulic press at 230 MPa to make pellets of 10 mm diameter and 1 mm thickness. These pellets were sintered in PbO atmosphere in closed alumina containers. The PbO atmosphere was created by placing $PbZrO_3$ powder around the pellets. The sintering of PMN and PFN ceramics was carried out at 1150 and 1000°C respectively. The PFN sample used in this study contained 0.5 wt.% of mangenese oxide (to reduce the tangent losses). After sintering,the flat surfaces of the pellets were ground on a 400 grit emery paper and their geometrical dimensions and densities were measured. The geometrical densities of PMN and PFN samples were 7.12 and 7.32 g/cc respectively. Air fired silver paste was then applied to flat surfaces of the pellets. The pellets were fired at 550°C in air and then lead wires were soldered to their flat surfaces. The capacitance of PMN pellet was measured between −65 and 20°C with the help of a LCR meter (model 715 Stanford Research System,USA). For these measurements, the soldered PMN sample and a chromel- alumel thermocouple were suspended in a closed copper vessel. The copper vessel was dipped in liquid nitrogen and was then allowed to warm up in air naturally and readings of capacitance were noted down at different temperatures. The capacitance values of PFN sample were measured between 25 and 130°C. The soldered sample and a digital thermometer were suspended in a stirred silicone bath. The bath was heated above 130°C and then allowed to cool naturally. The capacitance values were measured at different temperatures. The dielectric constant (K) of a pellet was determined by dividing the capacitance of the pellet by its equivalent air capacitance. The dielectric constant values were corrected for porosities by using a relation $K = K_{\text{measured}} \times$ theoritical density/sintered density. The flat surfaces of PMN and PFN pellets were then ground to remove the silver layer. The PMN and PFN pellets were heated in air at 1000°C for 1/2 h and 1 h respectively. No discernible changes in the densities and average grain sizes of these pellets were noticed after the annealing treatment. The dielectric constants of these samples were then again measured as described earlier. A TEM sample was made out of a pellet of PMN and PFN solid solution to study the grain boundary and its phase structure.

Fig. 1 shows the grain boundary triple junction of a PMN–PFN solid solution sample at a magnification of 50 K. The grain boundary thickness is of the order of 50°A. This value matches with the reported value of grain boundary thickness of PMN sample [7]. Fig. 2 shows the diffraction pattern of grain boundary phase showing a dim continuous ring. It indicates the presence of amorphous phase at grain boundaries and its triple junction.

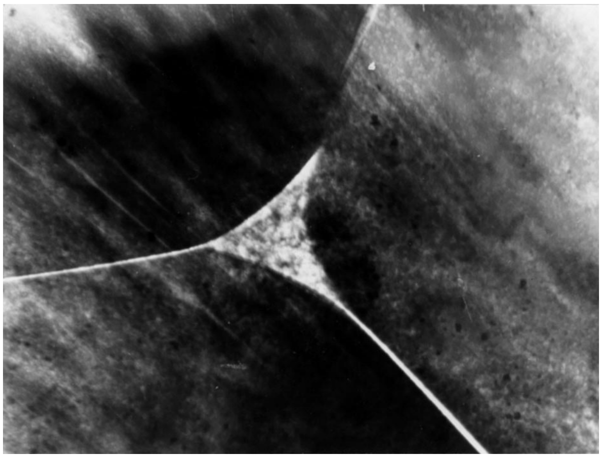

Fig. 1. Grain boundary triple junction of PMN–PFN solid solution sample (magnification 50×).

The dielectric constants of PMN and PFN sintered samples before and after heating in air at 1000°C are given in Figs. 3 and 4 respectively. It is found that there is a substantial gain in the dielectric constants of PMN and PFN samples after post sinter annealing. The increase in the peak dielectric constant values of PMN and PFN samples were 17.5 and 36.1% respectively. Similar trends were noticed after giving annealing treatment to other sintered PMN and PFN pellets. The Curie temperature of both PMN and PFN samples were lowered by 1°C after the annealing treatment.These results substantiate the importance of removing the excess lead bearing phase at the grain boundries for improving the dielectric constants of PMN and PFN ceramics.

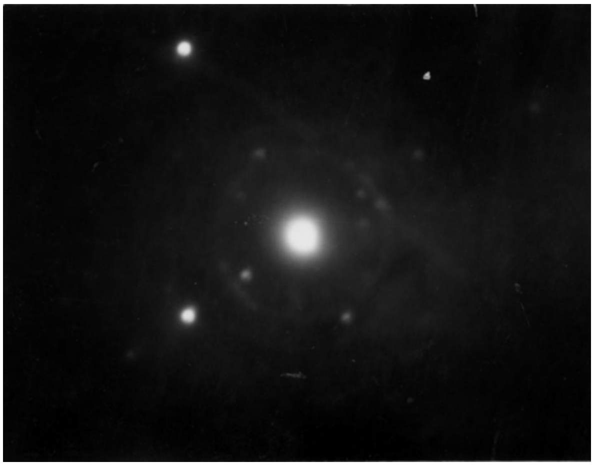

Fig. 2. Electron diffraction pattern of grain boundary phase of PMN–PFN pellet.

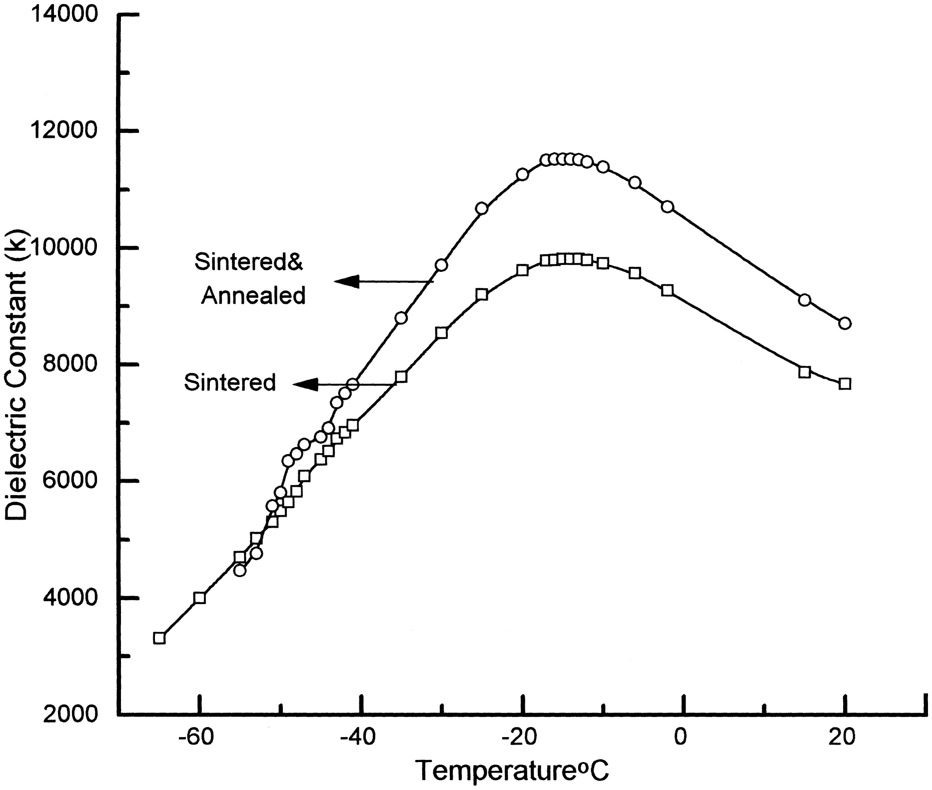

Fig. 3. Dielectric constant vs. temperature of PMN ceramic, sintered at 1150°C. and annealed at 1000°C.

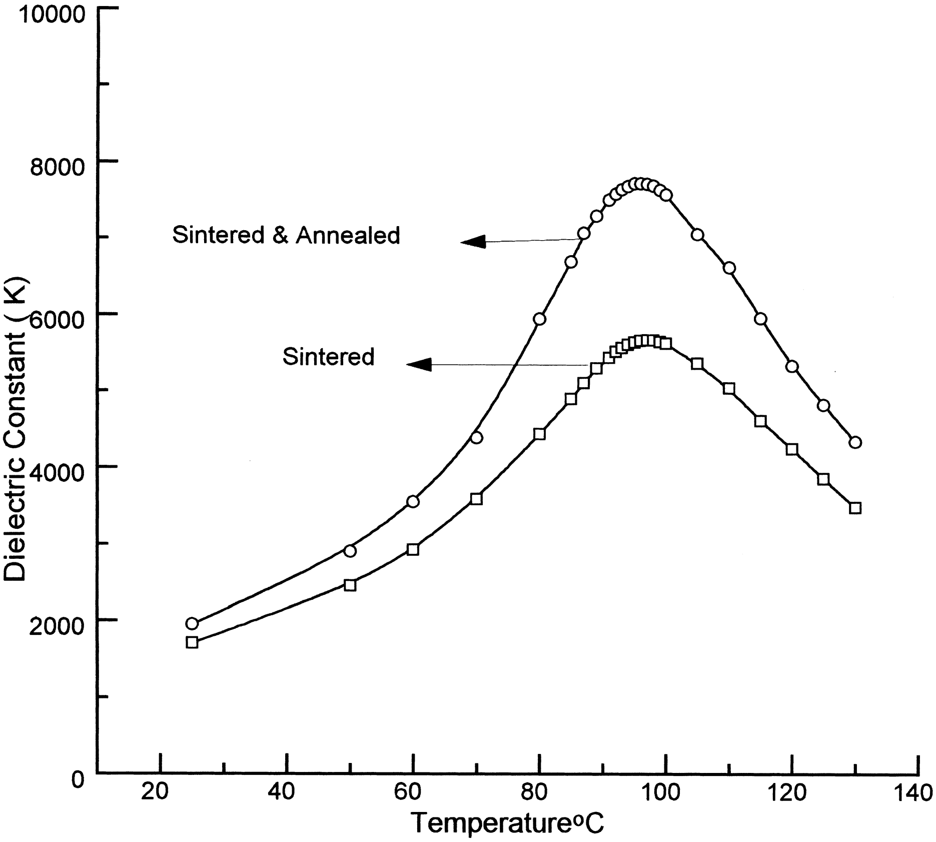

Fig.4. Dielectric constant vs. temperature of PFN ceramic, sintered and annealed at 1000°C.

It is concluded that PMN and PFN ceramics have amorphous phase at grain boundaries. The grain boundary thickness is of the order of 50° Å. The dielectric constants of PMN and PFN ceramics can be increased substantially by post sinter annealing of these ceramics in air at 1000°C.

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