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Pressureless Sintering of PMN–PT Ceramics

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Abstract

PMN–PT ceramics with PMN to PT ratios of 60:40, 65:35, and 70:30 were prepared from PMN–PT powders synthesized by the columbite precursor method, and their sintering and grain growth characteristics at temperatures less than 1000°C were investigated. Results indicate that the PMN–PT ceramics can be pressureless-sintered to a relative density of approximately 96% at 950°C. However, full densification was prevented by the onset of abnormal grain growth. The addition of 0·5 wt% PbO to 65:35 PMN–PT ceramics lowered their sintering temperature to 900°C, but caused abnormal grain growth at lower temperatures. Preliminary TEM analyses indicate the presence of submicron-sized MgO particles at some ceramic microstructure triple points. Further studies will be required to understand abnormal grain growth behavior and to devise means for full densification. © 1999 Elsevier Science Limited. All rights reserved

Keywords: lead magnesium niobate, sintering, powders: solid state reaction, microstructure-final

1 Introduction

Solid solutions of relaxor $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN) and the firstorder ferroelectric $PbTiO_3$(PT) are known to exhibit many properties conducive to dielectric and electrostrictive applications. The high dielectric constants over temperature ranges close to room temperature make systems like $(1-x)$PMN:xPT very attractive for multilayer capacitor and actuator applications.[1] The recent discovery of very large strains induced in PMN–PT and PZN–PT single crystals by electric fields[2] has attracted intense research efforts around the world.

Cerone, Inc. has been involved in the growth of relaxor single crystals by the solid state method. In this method, a single crystal is grown by the solid state method by contacting a dense polycrystalline ceramic which exhibits discontinuous grain growth to a seed single crystal and heating them both to a temperature lower than the critical temperature for the onset of discontinuous grain growth.[3–5] In order to grow high quality single crystals from dense polycrystalline ceramics by the solid state method, polycrystalline ceramics must have a narrow distribution of fine grains with grain sizes less than a few micrometers and near theoretical density (a relative density higher than 99·5%). Since 1996, Cerone, Inc. has been conducting research and development on the synthesis and sintering of high-purity, high-reactivity PMN and PMN–PT powders to meet these objectives. In this paper some preliminary results from our development efforts will be presented.

2 Experimental

PMN–PT powders were synthesized by the columbite precursor method.[6] Columbite ($MgNb_2O_6$) was first synthesized from MgO and Nb_2O_5 powders by the mixed oxide method. Then, PMN–PT powders with PMN to PT ratio of 60:40, 65:35, and 70:30 were synthesized by thoroughly mixing columbite, PbO and TiO_2 powders and firing the mixed powders at 700°C. A small amount of epoxy resin dissolved in acetone along with a few drops of a dispersant, Darvan-C obtained from R. T. Vanderbilt Company, was added to the PMN–PT powders synthesized. The resultant slurries were milled overnight with high-density zirconia grinding media. After milling, the acetone was allowed to evaporate in ambient from the slurries. The dried cakes were ground gently by an agate mortar and pestle prior to uniaxial pressing of discs (2·54 cm in diameter and 0·35 cm in thickness) at 86 MPa (12·5 ksi) using a stainless steel die. The green ceramic discs were subsequently bisqued as follows. The discs were heated to 650°C at a rate of $0{\cdot}2°C\,min^{-1}$, then heated to 800°C at a rate of $1°C\,min^{-1}$, held at the temperature for 2 h, and finally cooled to room temperature at a rate of 2°C $\min^{-1}$. In order to minimize the loss of PbO by evaporation, the bisqued discs were completely covered with high-purity PMN powder and then pressureless-sintered in air. The synthesized powders were examined by SEM and XRD prior to any further processing. The density of the sintered discs with closed porosity was determined by the liquid immersion method. For sintered discs with open porosity the density was determined from their weights and dimensions. Uncertainties in density are estimated to be $\pm 0{\cdot}005\,\mathrm{g\,cc^{-1}}$ for samples with closed porosity and $\pm 0{\cdot}03\,\mathrm{g\,cc^{-1}}$ for samples with open porosity. Microstructures of the sintered discs were examined as follows. The sintered discs were first ground and polished to a $0{\cdot}25\,\mu$m diamond finish. The polished discs were then thermally etched either at 750°C for 1 h or at 800°C for 30 min. Finally, a thin layer of Pd metal was sputter-deposited on the thermally etched ceramic discs prior to SEM examination.

3 Results and Discussion

As-synthesized PMN–PT powders have an average grain size of approximately 300 nm and are heavily agglomerated. XRD indicates that the PMN–PT powders have a tetragonal symmetry [Fig. 1(a)], while PMN–PT discs after sintering have a rhombohedral symmetry [Fig. 1(b)].

Isothermal sintering curves of PMN–PT ceramics sintered at 950°C are shown in Fig. 2. The figure indicates that MN-PT ceramics with a composition between 60:40 and 70:30 have almost identical sintering characteristics. The density of the sintered ceramic discs increased asymptotically to a final density of approximately $7{\cdot}8\,\mathrm{g\,cc^{-1}}$, which

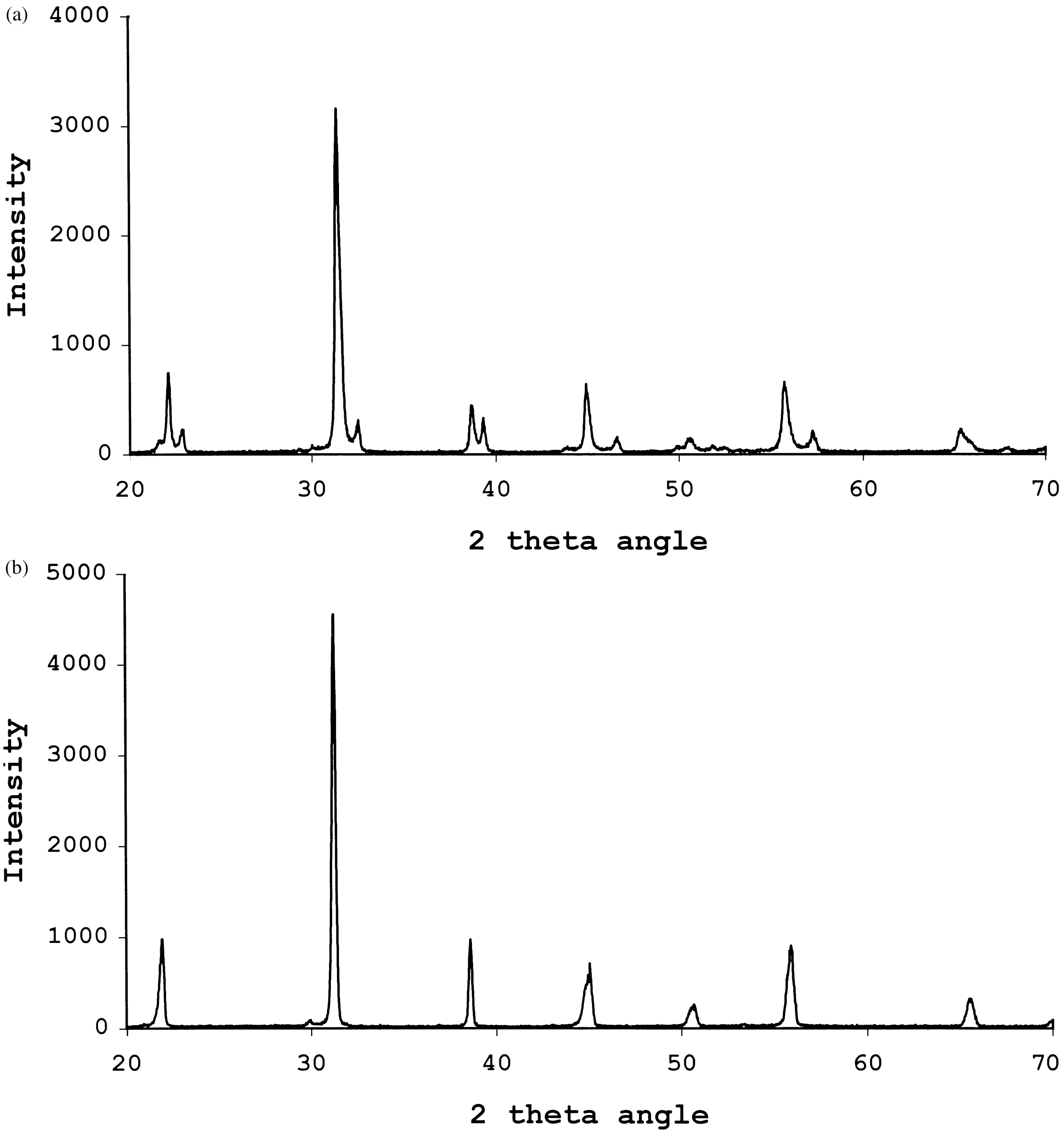

Fig. 1. (a) XRD of as-synthesized 65:35 PMN–PT powder. (b) XRD of a 65:35 PMN–PT ceramic sintered at 930°C.

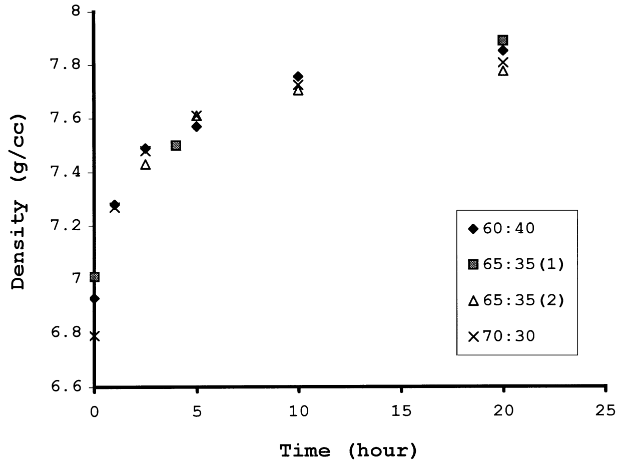

Fig. 2. Isothermal sintering curves for PMN–PT ceramics sintered at 950°C.

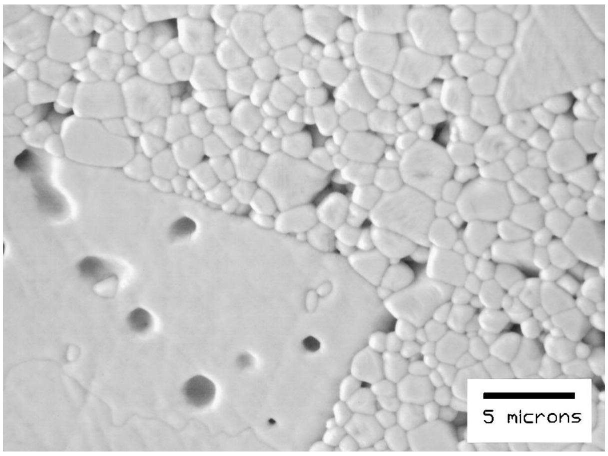

Fig. 4. Abnormal grain growth in the microstructure of a 65:35 PMN–PT ceramic sintered at 950°C for 10 h.

is approximately 96% of the theoretical density of these PMN–PT ceramics. However, no further densification was observed when the ceramic discs were heated for a time period longer than 20 h. SEM examination of the sintered discs indicates that sintering proceeded without appreciable grain growth for a time period less than 5 h (Fig. 3). On the other hand, the onset of abnormal grain growth was observed in the ceramic disc fired for 10 h (Fig. 4). The figure also indicates that the abnormally growing grain contains voids and entrapped secondary grains. Extensive abnormal grain growth can be observed in the ceramic discs fired for a time period longer than 20 h. Therefore, it may be reasonable to conclude that full densification was not possible due to abnormal grain growth during the later stages of sintering.

In order to ascertain the causes of abnormal grain growth, we have been conducting TEM examination of sintered PMN–PT ceramics. Preliminary results indicate the presence of submicronsized particles of MgO at some ceramic microstructure triple points. However, we have not been able to conclusively identify the presence of liquid phases along grain boundaries. We will report our TEM results in detail in the near future.

In order to further understand the sintering characteristics of 65:35 PMN–PT ceramics, an attempt was made to assess the effect of excess Pbo. Figure 5 shows a sintering curve for 65:35 PMN–PT ceramics with 0·5 wt% excess PbO fired at temperatures between 800 and 1050°C for 2 h. A rapid increase in sintered density was observed between 850 and 950°C. The sintered density decreased slightly due to PbO loss at temperatures above 950°C. Microstructural analyses by SEM indicate that abnormally grown grains are present in ceramics fired at temperatures above 900°C. Therefore, it may be fair to conclude that full densification cannot be attained due to the onset of abnormal grain growth. Furthermore, the comparison of Figs 2 and 5 indicates that a small amount of excess Pbo is beneficial in promoting the densification of 65:35 PMN–PT ceramics.

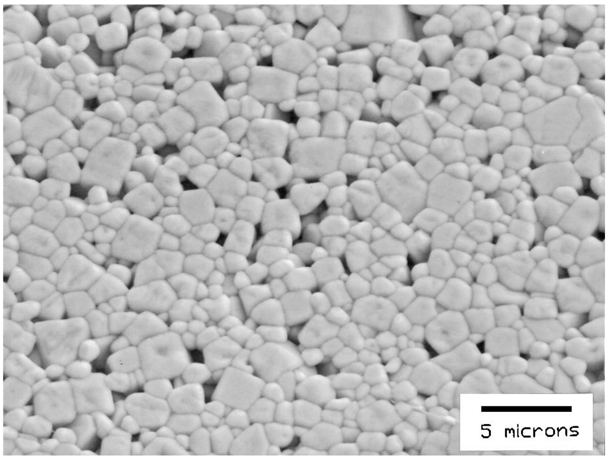

Fig. 3. Normal grain growth in the microstructure of a 65:35 PMN–PT ceramic sintered at 950°C for 5 h.

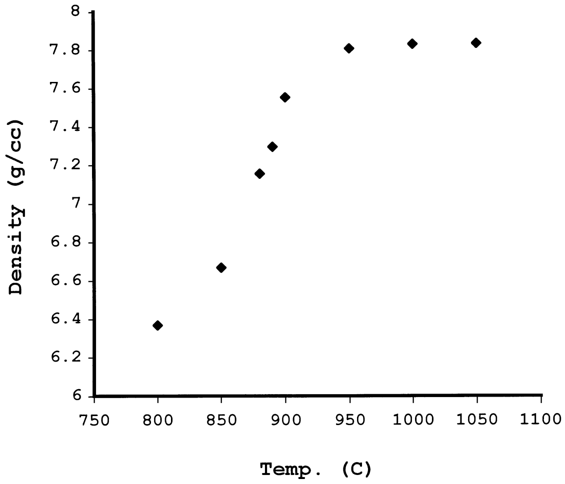

Fig. 5. Sintering curve of a 65:35 PMN–PT ceramic with 0·5 wt% excess PbO sintered at various temperatures for 2 h.

However, excess PbO promotes abnormal grain growth. Thus, the addition of PbO is deleterious for the fabrication of dense PMN–PT ceramics with fine grains (an average grain size less than a few micrometers).

In the following paragraphs our results will be compared with those in the literature. Pressureless sintering of PMN has extensively been investigated. Some pertinent conclusions[7] are as follows. Grain growth during sintering is promoted by excess MgO of up to 5 mol%. Excess MgO was found to exist as micron-sized spherical particles either in the grain boundary as discrete particles or in the grain as an inclusion. The excess PbO can affect the grain growth of pure PMN depending on other chemical and microstructural factors. The addition of a small amount of La_2O_3 to PMN has been known to promote densification, but to inhibit grain growth.[8,9]

Compared to the sintering results discussed above, our PMN–PT powders seems to be more sinterable. Our sintering temperature of 950°C is considerably lower than temperatures reported in the literature for powders synthesized by the columbite method and is comparable to those reported in the sintering of PMN powders synthesized by the alkoxide,[8] sol–gel,[10,11] and oxalate methods.[12] The high sinterability of our PMN–PT powder may be attributed to its weakly agglomerated particles with an average particle size of 0·2 to 0·3 μm, which are ideal for pressureless sintering.

Although extra care was taken during the synthesis of columbite to make it as stoichiometric as possible, a small amount of unreacted MgO may be present in our columbite. This may explain the presence of submicron-sized particles of MgO in our ceramics compared to micron-sized particles in the PMN ceramics with excess MgO. However, it is not certain whether excess MgO has caused the abnormal grain growth or not. Further work will be needed to ascertain the causes of abnormal grain growth.

4 Conclusion

Highly reactive submicron-sized powders of PMN–PT have been synthesized by the columbite precursor method. The powders have been sintered to 96% of their theoretical densities at 950°C. Further densification was prevented by abnormal grain growth. Voids and secondary grains have been observed in abnormally grown grains. Additional work will be required to identify the causes of abnormal grain growth.

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