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INVESTIGATIONS OF THE EFFECT OF THE MORPHOLOGY OF Nb DOPANT ON LEAD ZIRCONATE CERAMIC*

J. D. KECK AND P. D. WILCOX
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The microstructures of ferroelectric ceramics are a result of the dopants and of the many process variables associated with raw materials, powder processing, and ceramic firing. Metal ion substitutions of higher than normal valency are used as sintering aids to promote densification, to increase electrical resistivity, and to develop mature homogeneous microstructures with desirable piezoelectric and ferroelectric properties. Investigations are reported here for the barium modified lead zirconate system which is analogous to the lead zirconate titanate system, in which Nb is used as a sintering aid. The morphology and concentration of the Nb are shown to affect both electrical properties and the microstructure.

INTRODUCTION

This study was initiated as a result of other work[1] which indicates that the barium modified lead zirconate system (PBZ) would be analogous to the titanium modified lead zirconate system (PZT) with advantages in manufacturing due to improved thermal expansion properties and suitability of high pressure phases for depoling applications. Niobium in particular, as an additive, promotes both sintering and stability of the orthorhombic antiferroelectric phase under high pressure. It was found that the properties of interesting compositions was dependent on the type of Nb compound used to dope the compositions. This study shows the major physical and electrical differences which depend on the form of the Nb dopant. Based on extensive use of Nb dopant in the PZT system, it is believed that the type of behavior seen in this system is typical of the family of modified PZ materials.

EXPERIMENTAL PROCEDURE

Compositions were prepared according to the general formula, $Pb_{0.94-x/2}Ba_{0.06}Nb_xZr_{1-x}O_3$. The raw materials were PbO, $BaCO_3$, ZrO_2, Nb_2O_5, and Nb-oxalate as a water solution and were of reagent grade. The zirconia was exceptionally low in Ti content (280 ppm). The niobium-oxide powder had an average particle size of 0.5μm. The starting materials were wet milled with water, dried, and calcined at 900°C for 4 hours in open crucibles. The powder was milled in water for 2 hours, dried, and pressed into pellets of 25 mm diameter by 10 mm high. The pellets were buried in $PbZrO_3$ powder to maintain a PbO rich atmosphere and fired at 1340°C for

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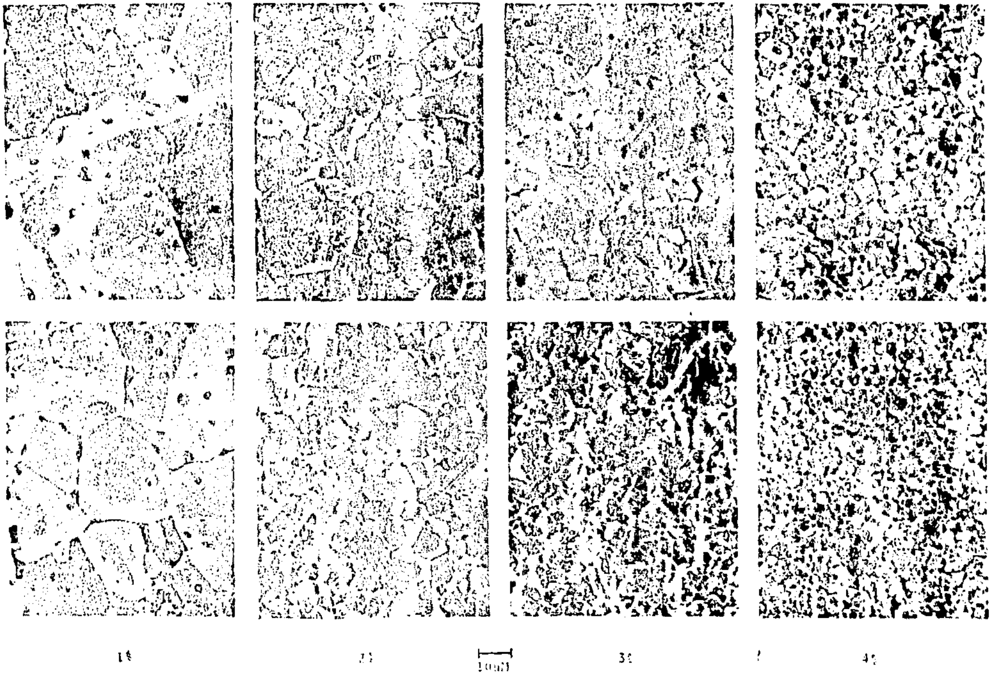

FIGURE 1. SEM Fractographs with Various Mole Percent Additions of Niobium: Top Row - Niobium Added as Niobium Oxalate; Bottom Row - Niobium added as Niobium Oxide. All Pictures are the Same Magnification.

4 hours. Samples were cut from the centers of the pellets and electroded with an air drying silver preparation.

Densities were measured by the Archimedes method using Freon-TF liquid. The temperature of the ferroelectric-paraelectric (FE-PE) transition was measured from the peak of the dielectric constant versus temperature curve measured at 1 KHz. Remanent polarization was measured from 0.05 Hz hysteresis loops to a maximum field of 4MV/m, which is at least three times the coercive field, using a Sawyer-Tower circuit.[2] The microstructures were observed from SEM photographs of freshly fractured surfaces.

RESULTS AND DISCUSSION

The undoped PBZ specimens sintered very poorly with bulk densities only about 7.2 Mg/m^3 and grain sizes of $\leq$ 3 m. These results attest to the relatively high purity of the raw materials. A one mole percent (M/O) addition of Nb makes a remarkable difference in the sintering, bulk density and grain size as shown in Figures 1 and 2. The rapid sintering and unimpeded grain boundary motion due to the Nb substitution enclosed numerous pores and resulted in large 40-60μm grains. At two M/O and larger additive amounts, the rapid growth is impeded. Only a few grains contain enclosed pores at the 2 M/O level. The grain size is decreasing and the range of grain sizes is increasing. As more Nb is added, the grain development is further impeded and smaller grain sizes result. At four M/O, some clusters of very small grains appear with the oxalate additive which are not evident in samples made with the oxide. The more apparent transgranular fracture in the three percent oxalate sample is probably a result of the fracturing technique.

The reduction in density from 1 M/O Nb to 4 M/O (Figure 2) is greater than can be accounted for by the increase in lead vacancies from the Nb additions. However, these differences are not major ones and the two forms of the additive behaved in a similar manner with respect to bulk density and grain size.

The FE-PE transition temperatures are plotted (Figure 3) and show a very uniform, and significant change with each mole percent of niobium. Both the oxide and oxalate produced the same results within 1°C. One mole percent results in a 9°C difference in the transition temperature. The shape of the dielectric constant versus temperature plot was similar for all samples. There were many cracks observed in these sintered pellets. The color and texture were generally uniform within samples and not distinctly different between the oxide and oxalate additive. These results indicate that the Nb was uniformly distributed and the same composition resulted for the two additive forms.

Grain growth inhibition has been observed for Nb doped $BaTiO_3$ when the Nb is concentrated at grain boundaries.[3,4] The nonhomogeneous distribution of Nb is the reason that two peaks in dielectric constant versus temperature curve were observed. In samples with the same average Nb concentrations that had different thermal treatments and which yielded large grain sizes, single peaks were observed indicating a homo-

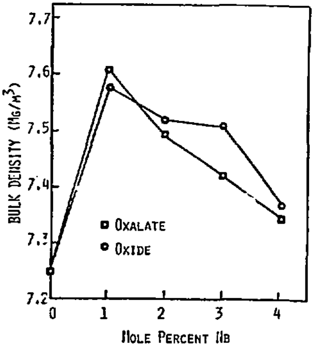

FIGURE 2. BULK DENSITY AS A FUNCTION OF NIOBIUM CONTENT

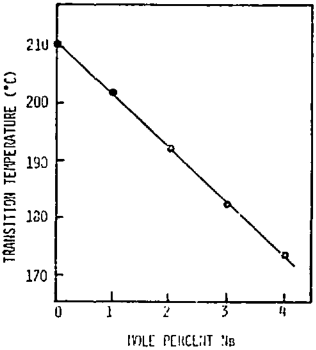

FIGURE 3. TRANSITION TEMPERATURE AS A FUNCTION OF NIOBIUM CONTENT

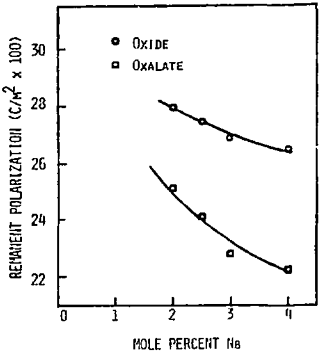

FIGURE 4. REMANENT POLARIZATION AS A FUNCTION OF NIOBIUM CONTENT

At 2 M/O the difference in Pr is $2.8 \times 10^{2} \mathrm{C/m^2}$ and increases to $4.2 \times 10^{2} \mathrm{C/m^2}$ at 4 M/O.

Loops after hot poling at 105°C and 3.3 MV/m are similar for both additive forms at the 2 M/O level of Nb. As more Nb is used, Pr in samples with the oxalate additive decreases more rapidly than with the oxide additive. The reduction in grain size may correspond with the general decrease in Pr as the Nb concentration is increased.[5] The difference is Pr between the oxide and an oxalate addition cannot be satisfactorily explained with the data available at this time.

CONCLUSIONS

Small amounts, $\leq$ 1 M/O Nb, added to PZT compositions greatly enhances the sintering rate and growth. Larger additions impede grain growth and reduce remanent polarization. The morphological form of the additive causes some differences in microstructural features but these are small and equivalent to less than 0.5 M/O of the additive. A real but unexplained difference exists in Pr between the oxide and oxalate additions.

REFERENCES

1. I.J. Fritz and J.D. Keck, J. Phys. Chem. Sol, 39, 1163 (1978).
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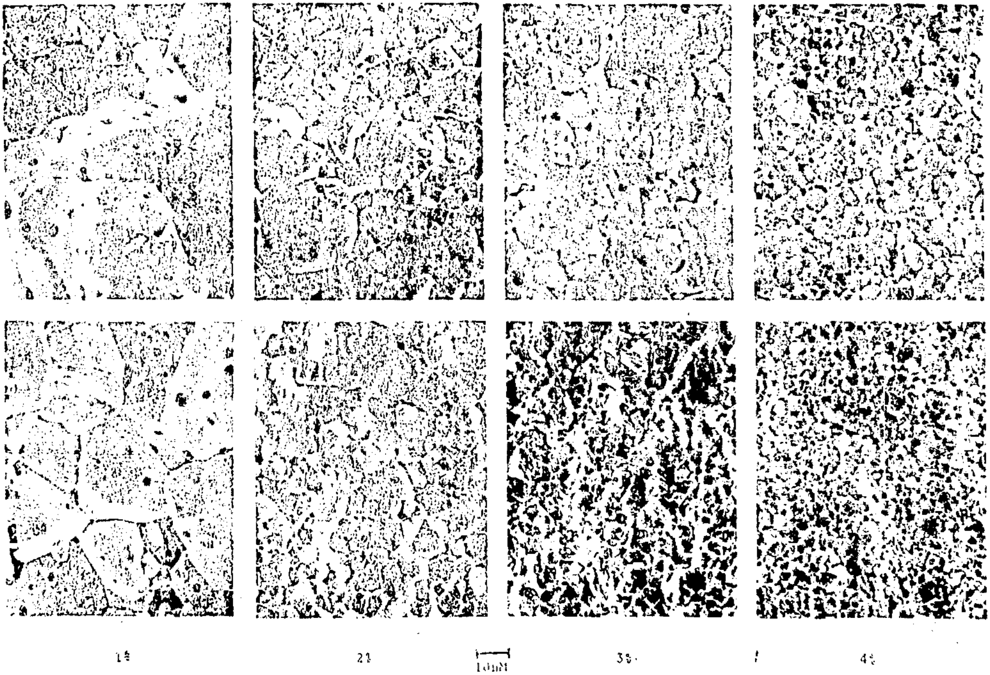

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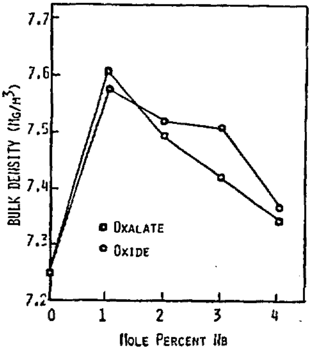

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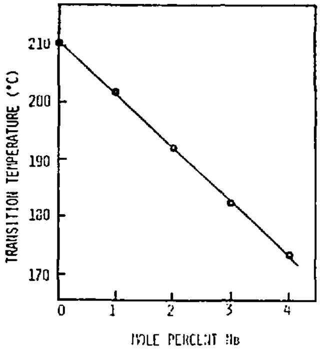

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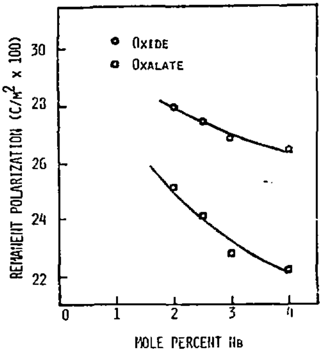

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