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Microstructural Inhomogeneity In Sintered Pb(Mg1/3Nb2/3)O3-PbTiO3 Based Dielectrics

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REFERENCES

[1]J. E. Shelby, "Formation and Properties of Calcium Aluminate Glasses," *J. Am. Ceram. Soc.*, **68**, 155–58 (1985).

[2]H. Rawson, Inorganic Glass-Forming Systems, Academic, London, 1967.

[3]H. Hosono, K. Yamazaki, and Y. Abe, "Dopant-Free Ultraviolet-Sensitive Calcium Aluminate Glasses," *J. Am. Ceram. Soc.*, **68**, C-304–C-305 (1985).

[4]J. E. Stanworth, "XIV.—On the Stucture of Glass," *J. Soc. Glass Technol.*, **32**, 154–72T (1948).

[5]J. A. Duffy, "Coordinating Behavior of Ultra-High Alkali Borate Glass Toward Transition Metal Ions," *Phys. Chem. Glasses*, **16**, 22–29 (1975).

[6]S. Manabe and K. Kitamura, "Effect of Sodium Sulfate and Temperature on the Fining of Float Glass," *J. Non-Cryst. Solids*, **80**, 630–36 (1986).

[7]J. H. Lunsford, "ESR of Adsorbed Oxygen Species," *Catalysis Rev.*, **8**, 135–57 (1973).

[8]E. J. Friebele, D. L. Griscom, M. Stapelbrock, and R. A. Weeks, "Fundamental Defect Centers in Glass: Peroxy Radicals in Irradiated High-Purity Fused Silica," *Phys. Rev. Lett.*, **42**, 1346–49 (1979).

[9]R. Cases and D. L. Griscom, "On the Structure of Defect Centers in γ-Irradiated, Alkali Silicate Glasses," *Nucl. Instrum. Methods Phys. Res.*, **B1**, 503–10 (1984). □

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Microstructural Inhomogeneity in Sintered $Pb(Mg_{1/3}Nb_{2/3})O_3$-$PbTiO_3$ Based Dielectrics

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The sintering behavior and microstructural development of dielectric ceramics based on $Pb(Mg_{1/3}Nb_{2/3})O_3$-$PbTiO_3$ solid solutions are greatly affected by the formation of a liquid phase at ≈1290°C. Prolonged sintering at and above this temperature gives rise to an excessive PbO loss and the resultant variation in composition leads to an inhomogeneous microstructure. The inhomogeneity is characterized by the formation of a dense, localized region containing a PbO-rich liquid near the surface with a porous interior region in the bulk of the sample.

THE sintering characteristics and dielectric properties of ceramics based on the solid solutions of $Pb(Mg_{1/3}Nb_{2/3})O_3$-$PbTiO_3$ have been reported by several workers.[1,2] In these studies, it has been shown that the presence of excess MgO in the stoichiometric composition and increased sintering temperatures resulted in an increase in grain size with a corresponding increase in dielectric constant of the ceramics. It has been further reported[3] that prolonged sintering at 1300°C leads to a compositional variation that affects the dielectric properties.

Although the dielectric properties of the solid solutions have been reported extensively in the literature, very little is known about the sintering characteristics and microstructural development at elevated temperatures. The present communication is intended to show that prolonged sintering of $Pb(Mg_{1/3}Nb_{2/3})O_3$-$PbTiO_3$ solid solutions gives rise to excessive PbO loss, causing a change in the composition. The resultant inhomogeneity of microstructure and the sintering conditions under which such inhomogeneity occurs are discussed.

EXPERIMENTAL PROCEDURE

Solid solutions of the general composition $Pb(Mg_{1/3}Nb_{2/3})_{1-x}Ti_xO_3$ (where $x=0.09$ to 0.04) were prepared from appropriate amounts of prefabricated $MgNb_2O_6$, and reagent-grade PbO and TiO_2 powders. An excess of MgO (5 mol%) was added to all compositions to facilitate the formation of a pyrochlore-free perovskite phase. The mixtures were pressed into pellets and calcined in air for 3 h. The calcined pellets were crushed to powder, mixed with a 4% poly(vinyl alcohol)-water solution, and pressed into disks 14 mm in diameter and 2 mm thick. The disks were supported on presintered $Pb(Mg_{1/3}Nb_{2/3})O_3$ setters and stacked inside a covered alumina crucible to minimize PbO loss during sintering. The disks were then sintered in air at temperatures between 1250° and 1300°C for periods ranging from 2 to 10 h at a heating rate of 300°C/h. At the end of the firing period, the crucible was cooled inside the furnace and the phases present in the samples were identified by powder X-ray diffraction (XRD) using Cu$K\alpha$ radiation. The weight losses at various sintering temperatures were ascertained by the change in weight of the samples before and after the firing. The fracture surfaces were examined by scanning electron microscopy (SEM), and elemental analysis of the phases present in the sintered samples was conducted by an X-ray energy dispersive spectrometer (EDS) attached to the SEM.

RESULTS AND DISCUSSION

The XRD analysis of the sintered samples revealed a single-phase cubic perovskite pattern that essentially corresponded to the $Pb(Mg_{1/3}Nb_{2/3})O_3$-$PbTiO_3$ solid solution. It was observed that increasing additions of $PbTiO_3$ in the solid solutions did not cause any appreciable shift in the characteristic reflections of the perovskite pattern. This result was probably due to the similarity of the radii of Nb^{5+} (0.69) and Ti^{4+} (0.68) ions.

The sintering characteristics of various compositions indicated similar trends in density variations and weight losses at different firing temperatures irrespective of the $PbTiO_3$ content in the solid solutions. In general, the densities increased with increasing sintering temperature. However, a rapid increase of density values was observed for the sintered samples at 1290°C followed by a small decrease at 1300°C for the same sintering time. A maximum density of 96% of the theoretical was achieved by sintering at 1290°C for 3 h. Further increase in the sintering time at this temperature did not show any significant increase in the density values. The corresponding weight loss data indicated that the rate of loss was considerably higher at temperatures at and above 1290°C. Most of the losses occurring at this temperature appeared to take place during the initial

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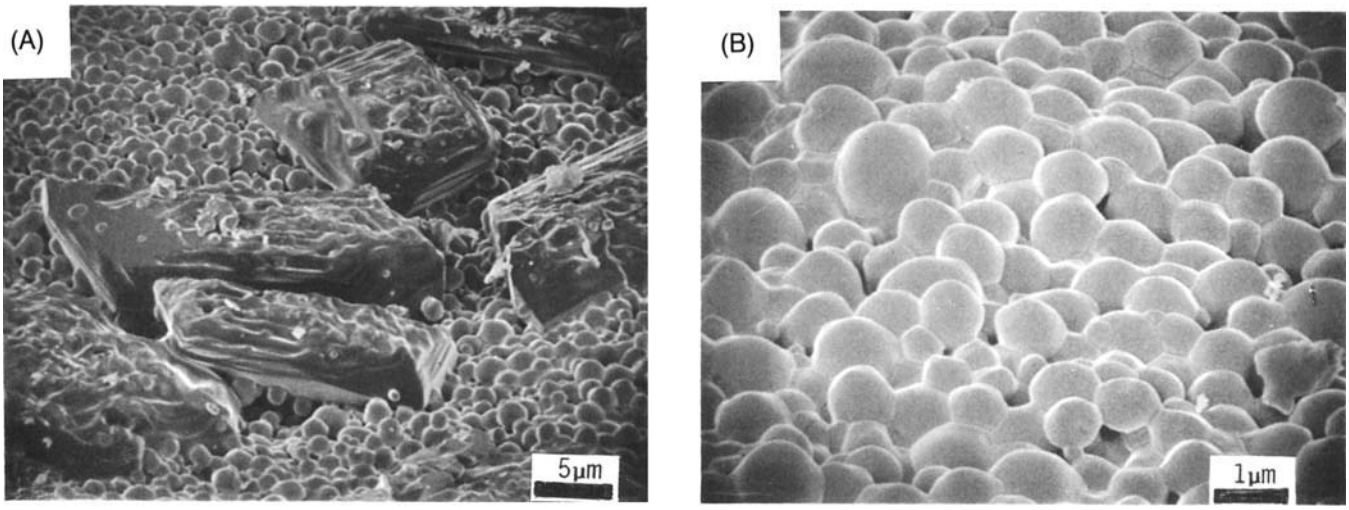

Fig. 1. SEM showing inhomogeneity in composition 0.92 $Pb(Mg_{1/3}Nb_{2/3})O_3$-0.08 $PbTiO_3$ after sintering at 1290°C for 8 h: (*A*) distribution of $MgNb_2O_6$ in a liquid matrix and (*B*) morphology of the PbO-rich liquid phase.

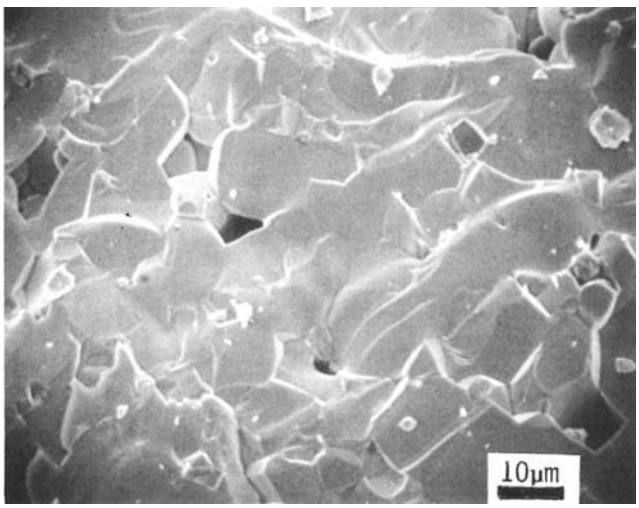

Fig. 2. SEM of the fracture surface showing large and coarsened grains of the solid solution with residual porosity at the interior of the sintered sample.

period of the sintering; thereafter, the rate became linear with time.

The sequence of microstructural changes observed during the sintering of the solid-solution compositions clearly demonstrated that a liquid phase was formed at ≈1290°C. With increasing sintering time and temperature, the rapid increase in the densification rate appeared to be consistent with sintering in the presence of a liquid phase. The microstructures of the sintered samples showed a significant increase in the grain size with a corresponding decrease in porosity. However, the slight decrease in density at 1300°C can be accounted for by the loss of PbO from the samples as observed by the weight-loss experiments. Seemingly, the PbO loss, which increases rapidly at the onset of the liquid formation at 1290°C, appeared to have caused some variations in the composition and led to an inhomogeneous microstructure. This behavior was evident from the morphology of the fracture surfaces which revealed the presence of a highly dense localized region near the surface with a porous yet rigid interior forming the bulk of the sample. The SEM micrograph of the localized region showing the distribution of various phases is exhibited in Fig. 1(*A*). This distribution is typical of the microstructures resulting from prolonged sintering at elevated temperatures which revealed the presence of many rectangular solid particles evenly distributed in a liquid matrix. The EDS analysis indicated that the solid phase contained Mg^{2+} and Nb^{5+} with very little Ti^{4+}, and no Pb^{2+} was present. The surrounding liquid layer, the morphology of which is shown in Fig. 1(*B*), was found to be mostly homogeneous and contained, predominantly, Pb^{2+}. By contrast, the less-dense interior region, as shown in Fig. 2, was found to be essentially unchanged and consisted of coarsened grains of the solid solution with some residual porosity evenly distributed in the bulk.

The concentration of a PbO-rich liquid phase near the surface during sintering is believed to be the result of the simultaneous volatilization of PbO from the surface and liquid migration within the samples. As is evident from this study, a significant weight loss occurs mainly because of the volatilization of PbO at the liquid formation temperature (1290°C). Seemingly, prolonged sintering at and above this temperature gives rise to extensive PbO loss from the surface and leads to a compositional variation. With the progressive loss of PbO from the surface, the PbO content of the liquid phase must have decreased to a sufficient extent to allow the formation of $MgNb_2O_6$ solid particles in the PbO-rich liquid matrix. It seems likely that liquid migration within the bulk of the sample during sintering is a necessary condition for allowing the change in the composition near the surface, leaving a rigid yet porous structure in the interior. It is apparent that further study is required to understand the nature of the liquid phase and its behavior inside the samples throughout the sintering process.

References

[1]K. Furukawa, S. Fujiwara, and T. Ogasawara, "Dielectric Properties of $Pb(Mg_{1/3}Nb_{2/3})O_3$-$PbTiO_3$ Ceramics for Capacitor Materials"; p. T-4 in Proceedings of the Japan-US Study Seminar on Dielectric and Piezoelectric Ceramics, 1982.

[2]S. L. Swartz, T. R. Shrout, W. A. Schultz, and L. E. Cross, "Dielectric Properties of Lead Magnesium Niobate Ceramics," *J. Am. Ceram. Soc.*, **67** [5] 311–15 (1984).

[3]J. P. Guha, "Comment on Dielectric Properties of Lead Magnesium Niobate Ceramics," *J. Am. Ceram. Soc.*, **68** [3] C-86–C-87 (1985). □