Grain Growth in Relaxor Ferroelectrics

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Introduction

The relaxor ferroelectric lead magnesium niobate (PMN) and its solid solutions hold promise as a transducer material for sonar, particularly if large, shaped single crystals can be fabricated economically. Solid state crystal growth (SSCG) with an equilibrium liquid phase is a promising candidate process for producing inexpensive crystals for such applications. During SSCG, a seed crystal grows into a polycrystalline matrix while the matrix is undergoing both normal and exaggerated grain growth. The maximum size of crystals formed by SSGC may be limited by the competition in growth between the seed and the matrix. However, the properties of SSCG-grown PMN crystals are typically inferior to those of flux-grown single crystals due to a range of defects incorporated during the growth process.

From investigation of exaggerated grain growth in a range of ceramic systems, a fundamental understanding of the relationship between grain migration processes and the competition between interface migration and the "pinning" effect of pores, liquid-filled pockets, and crystalline second phases has developed. If one looks at microstructural evolution trajectories in alumina, for example, there are accessible experimental regimes for which interfaces migrate without entrapping pores or second phases. Grain growth in such a regime would yield single crystal grains without second phase inclusions or other defects.

Fundamental grain growth mechanisms in the PMN system can be identified through controlled experiments which are designed to identify the effect of chemistry, initial microstructure, and grain defect level on the rate of SSCG. There are several mechanisms which can be important for controlling the rate of exaggerated grain growth and the achievement of SSCG. Multiple nucleation events of exaggerated growing grains in the matrix will prevent the complete conversion to a single grain due to impingement of the large grains. In order to control the nucleation of exaggerated growing grains, an understanding of the conditions which cause a single grain to grow at the expense of the matrix grains is required.

Another issue to be examined is how to maintain both a high driving force for of the seed crystal and a high mobility for the seed crystal's interfaces with the matrix grains during SSCS. As growth proceeds, the matrix grain size will increase following normal growth kinetics for interface controlled growth. Both fast matrix grain growth and EGG reduce the driving force for SSCG. In addition the mobility of the seed crystal interface with the matrix grains will be determined by the rate-limiting attachment process along the interface, which in turn will be influenced by the presence of defects, such as dislocations

and twins, and the limiting growth shape of a defect-free crystal. As a start in examining how to manipulate matrix grain growth and interface mobility we have looked at grain growth as a function of PMN volume fraction. The purpose of these experiments is three-fold: (1) to demonstrate whether grain growth is interface or diffusion controlled in the powder system we are using; (2) to measure the limiting growth shape; and (3) to set up the baseline conditions for future studies of the effects of dopants and roughening transitions on growth anisotropy and kinetics during SSCG.

Experimental

Experiments have been performed to determine the mechanism which control the rate of grain growth of PMN in the presence of a PbO-rich liquid phase. The powder was provided by Hisao Yamada of Cerone, Inc.[1] in Cleveland Heights, OH. Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) of the powder showed no phase transformations during heating to 1250°C and a loss of ~4% of its initial weight. Mixtures of PMN and PbO were made which would result in 20%, 40%, 60%, 80% and 96% solid fraction by volume at temperature. The PbO – PMN phase diagram was used to estimate the amount of PMN which would be dissolved in the PbO during equilibration. The powders were pressed into pellets at 6MPa. Heating was done in a covered MgO crucible which had be pre-equilibrated with PbO at 950°C. The samples were placed on single crystal MgO to minimize reaction and there was excess PbO in the crucible to minimize PbO loss during heating. The samples were heated at 950°C in a static O_2 atmosphere in a closed end Al_2O_3 tube. Heating times were 0.5, 1 or 2 hours with a heating and cooling rate of 600°C/hr. Samples were polished using diamond and etched for 30 sec in a H_2O:HF:HCl (600:11:1) mixture. After etching the samples were coated with 15nm of Au/Pd alloy and examined by SEM. The grain size was determined by measuring the average linear intercept length of the grains.

Results and Discussion

Figure 1 shows representative microstructures for the samples after 0.5 hours at 950°C. The faceting of the grains in the PbO liquid is clearly seen. As the fraction of PMN increases, impingement occurs as shown by the shape changes in the grains. At 96% PMN the grains have curved grain boundaries which are probably wetted by a thin layer of PbO and exhibit shapes typical of normal grain growth. The shape of the grains for $\leq$ 40% PMN sample are cuboidal, with slightly curved surfaces apparent for some grains. It is not known if the cuboids have aligned in the liquid. In order to determine this, the size of the individual grains will have to be measured in the directions normal to the grain faces and the statistics of the lengths examined. For longer times the grain shape did not change as the average size increased. Figure 2 shows grain evolution in the 20% PMN sample at 950°C as a function of time. Figure 3 shows the grain size as a function of the fraction of PMN and time at 950°C. It is seen that for 0.5 hrs and 1 hr anneals, the grain size for samples containing $\leq$60% PMN is independent of the amount of liquid. At 80%

[1] The use of commercial designations is for identification purposes only, and does not imply endorsement by the National Institute of Standards and Technology.

and 96% PMN, the average grain size is smaller due to the impingement of the growing grains. The observation of constant grain size independent of fraction solid indicates that growth is interface controlled. If diffusion through the liquid were rate controlling, the increased amount of liquid at low PMN fractions would lead to longer diffusion distances between grains and to lower growth rates. For the 2 hr anneals, the PbO loss during annealing was significant and the fraction PMN in the samples is higher than the initial fraction. Thus the PMN volume fractions for the 2 hr samples need to be corrected for the PbO loss. Qualitatively, this would shift the points to the right (towards higher PMN fractions) and as a result the data for the 2 hr anneal would be in agreement with the shorter time data for the higher fractions PMN.

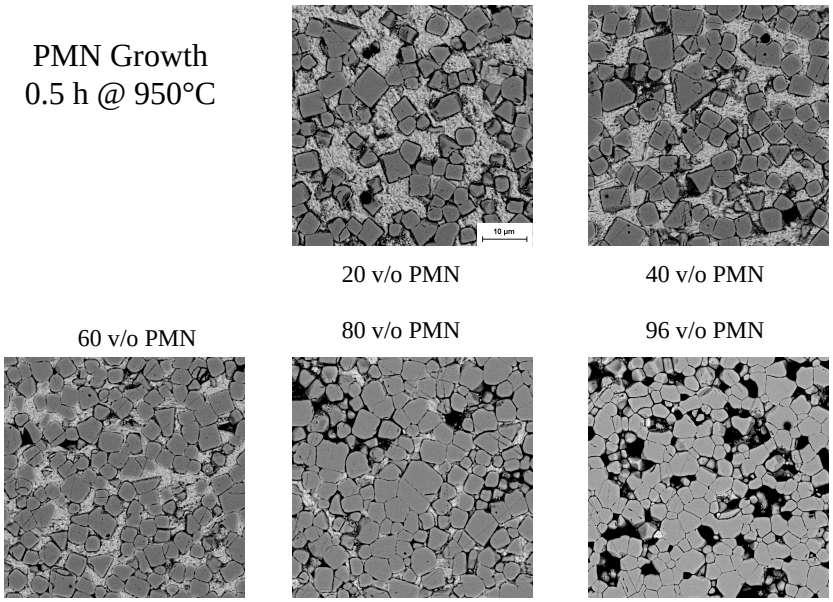
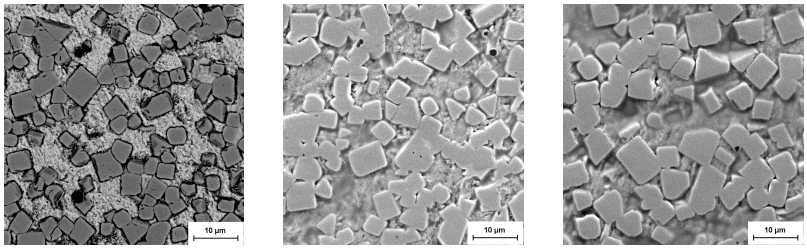


Figure 1

Growth of 20 v/o PMN



0.5h @ 950°C 1h @ 950°C 2h @ 950°C

Figure 2

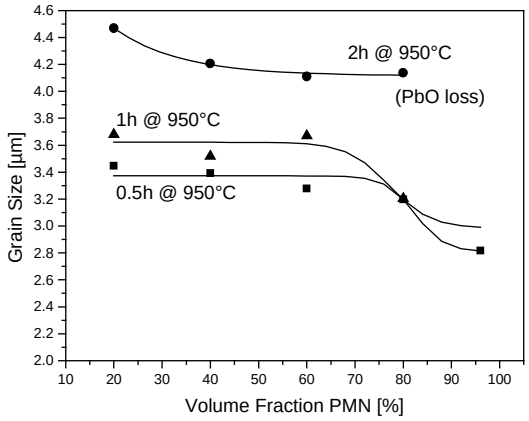


Figure 3

Summary
The shape of PMN grains growing without impingement in a PbO rich liquid is cuboidal. As the fraction of PMN increases, impingement leads to the grains changing shape to accommodate constraints of the surrounding grains. The grain size is not dependent on the fraction solid for low (≤60%) fractions, but decreases at higher fractions. This indicates that the growth is controlled by interfacial attachment rather than diffusion through the liquid. PbO loss occurs for long annealing times and can significantly change the grain growth.

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