Changes in the Distribution of Interfaces in PMN- 35 mol% PT as a Function of Time

Edward P. Gorzkowski, Helen M. Chan, and Martin P. Harmer

Center for Advanced Materials and Nanotechnology, Lehigh University, Bethlehem, PA 18015

Tomoko Sano,* Chang-Soo Kim,* and Gregory S. Rohrer*

Department of Materials Science and Engineering, Carnegie Mellon University, Pittsburgh, PA 15213-3890

Abstract

The crystallographic distribution of surfaces surrounding grains in PMN- 35 mol% PT has been measured in samples annealed for 0, 2, and 4 hours at 1150 °C. At all stages of the growth, grains are bounded predominately by {100} planes while surfaces with the {111} orientation represent a minimum in the distribution. During annealing, the fraction of the total area bounded by surfaces with the {100} orientation increases by 50%. As the relative areas of the {100} surfaces increase, the rate constant for growth decreases. Both the evolution of the external shape and the overall reduction in the growth rate suggest that interfaces with the {100} orientation have a low relative mobility.

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I. Introduction

Many studies have shown that single crystals of the relaxors $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN) or $Pb(Zn_{1/3}Nb_{2/3})O_3$ (PZN) with $PbTiO_3$ (PT) have superior electromechanical properties compared to their polycrystalline counterparts.[1,2] The military and the medical industry are actively pursuing these materials because the properties of these crystals are expected to translate into exceptional device performance. Moreover, the single crystal properties can be exploited for more precise actuators[3], more powerful undersea transmitters for sonar applications [4] (i.e. surveillance, tactical, navigation), and more sensitive ultrasonic transducers for medical imaging applications.[5,6] As a result, there is a drive to find a viable method for producing high quality single crystals in a cost-effective and time-efficient manner.

Traditionally, these single-crystals are formed by melt techniques such as high temperature solution growth from PbO-based fluxes[7] and modified Bridgman [8] growth. These methods are suitable for growing bulk single crystals, but have relatively slow growth rates and are not readily transferable to large-scale manufacturing. The seeded polycrystal conversion (SPC) process is an alternative single-crystal growth method that offers advantages over the melt methods and is fully described elsewhere. [9,10] This method is potentially more cost-effective, able to provide for niche applications (such as 1-3 composites), and directly compatible with current manufacturing of polycrystalline components. Also, the SPC process is similar to solid-state growth methods demonstrated in Al_2O_3[11] and $BaTiO_3$.[12]

Growth of PMN-35PT single crystals has been shown to be critically dependent on a PbO-based grain boundary-wetting phase within the polycrystalline PMN-35PT precursor.[13] In fact recent studies by Gorzkowski et al.[14] have shown that a critical amount of excess PbO of 1.5

vol% is required to coat all boundaries, thus achieving maximum growth potential. The growth mechanism of single crystals grown into dense matrices was also shown to be interface reaction controlled. This was concluded because the kinetic data best fits parabolic growth ($t^{1/2}$), the matrix grains were faceted, and the growth rate was invariant with liquid content. However, the growth process still slowed down after initially being very rapid. This was also observed in previous studies[15,16] suggesting that other factors besides porosity aid in slowing the single crystal interface.[14] It was also shown that the chemistry of the liquid phase (excess PbO) was dynamic throughout the annealing process. In fact, MgO was found to precipitate out of the system due the saturation of MgO in the liquid, which in turn altered the liquid/solid surface energy.[17]

Recent quantitative studies of the distributions of internal interfaces in polycrystals have shown that the tendency for crystals in dense compacts to adopt low index orientations is not only widespread, but that it occurs even in materials where the grains do not macroscopically develop facets. In polycrystalline MgO[18], $SrTiO_3$[19], TiO_2, Mg_2AlO_4 and Al[20], the planes preferred by the grain boundaries correspond to the low index planes that dominate the external growth forms and equilibrium shapes of isolated crystals of the same phase. This observation suggests that grains in polycrystals might grow by mechanisms analogous to those of single crystals growing in the vapor or liquid phase.

Here, we apply the same methods to PMN-PT to quantify the distribution of grain boundary surface planes. This situation differs somewhat from those mentioned above, because of the presence of a deliberately added intergranular liquid phase. It has previously been noted that these grains grow in an approximately cubic morphology.[14,21] However, at the junctions where the three grains meet, there is obvious curvature, which suggests that nonsingular

orientations occur on the growth form. The goal of the present paper is to quantitatively measure the relative area of different grain surfaces and to determine if this changes during the coarsening process. In addition, this data may add insight into why the single crystal growth process slows as annealing time is increased.

II. Experimental Procedure

PMN- *35* PT powder (TRS Ceramics, State College, PA) was mechanically admixed with 1.5 and 5 vol% PbO.[§] The PMN-PT-PbO powder was then jar-milled for 24 hours in ethanol. After milling, the powders were dried and subsequently calcined at 450°C for 4 hours in air, ground using an agate mortar and pestle, and sieved with a 100-mesh sieve. Oriented {001} PMN-PT single crystal seeds (Crystal Associates, East Hanover, NJ) were embedded in the PMN-35PT powder and uniaxially pressed at 10 MPa in an Al_2O_3 die to make pellets nominally 13 mm in diameter. These pellets were then cold isostatically pressed at 340 MPa. Subsequently the pellets were hot-pressed into fully dense disks at 880°C for 30 min and 20 MPa of pressure in vacuum. After hot-pressing, each disk was sectioned into six equivalent specimens for annealing treatments at 1150ºC for times of 0–10h utilizing heating and cooling rates of 5 ºC/min.

The specimens were wrapped in Pt-foil pouches to prevent the packing powder from sintering to them. The pouches were embedded in PMN-35PT powder with an excess PbO level that was predetermined experimentally so as to result in negligible net specimen weight change during annealing. The sacrificial packing powder, in conjunction with the double-crucible method, helped reduce PbO volatilization.[13] Specimen weight, before and after annealing, was measured to ensure that weight loss, and hence PbO loss, was minimal during annealing. In fact, samples with a weight change greater than ±0.2 wt.% were excluded from further study.

Specimens were mounted in epoxy resin, polished to 0.05 μm SiO_2, and chemically etched with Kroll's reagent (1% HF, 4 % HNO_3, 95% H_2O, % by volume). The average linear single crystal growth in each annealed specimen was measured using an automated image analysis system. The measurements were calibrated using a stage micrometer (Olympus), and normalized to the <001> direction by finding the ratio of the cross-sectional thickness of the seed to the original seed thickness of 500 μm. Approximately twenty measurements were made along the single crystal layer. Orientation image microscopy (OIM) maps (TexSEM Laboratories, Provo, UT) were obtained from electron backscattered diffraction (EBSD) patterns in a scanning electron microscope (Model XL40 FEG, Phillips, the Netherlands) to determine the crystal orientations. In each case, a thin carbon coating was applied to reduce the effects of charging and the samples were inclined by 60° with respect to the 20 kV electron beam. EBSD patterns were recorded every 0.75 microns in areas less than 500 microns x 500 microns. In each case, multiple maps were recorded until data from approximately 5000 grains was accumulated.

The orientation data was "cleaned-up" using a procedure that replaces orientation measurements of low quality with the average orientations of more reliable adjacent points. Clusters of low quality orientation measurements, which occur at pores and pools of PbO, are not affected by this process. An automated procedure, described by Wright and Larsen,[22] was used to identify line segments that represent boundaries between adjacent grains. Portions of the data are shown as image quality maps in Fig. 1. The black lines are the segments that represent the boundaries. Note that boundary segments are not assigned if the orientation is not well-defined on one side of the interfaces. Thus, the boundaries with pores, pulled out grains, or PbO pools are not included in the analysis. From each sample, the number of line segments was greater

[§] Alfa Aesar, purity > 99.999% (metals basis)

then 1.4×10^4. Each segment has a length and a direction (in the sample reference frame) and is associated with the two adjacent orientations, each represented by three Euler angles. These data are the basis for the stereological analysis.

The line segments are used to compute the relative areas of different grain surface orientations using a stereological procedure. The basic principle of the method is that although the orientation of the plane within the specimen is not known, the plane must belong to the zone of the line segment. This then defines a list of possible planes. The probability that the correct plane is in this list is one, while the probability that any other possible plane is sampled is less than one. Therefore, after repeating this process on many line segments, the correct plane or planes are observed more frequently than the incorrect planes. This procedure was implemented as described in an earlier paper by Saylor and Rohrer,[23] with two differences. First, the original procedure considered crystals isolated in a second phase and the line segments were analyzed in the reference frame of the crystal on whose periphery they were found. Here, each line segment is considered twice: once in each of the reference frames of the adjoining crystals. The second difference is that in the original procedure, the relative areas of different habit planes were calculated under the assumption that there is a small and finite number of habit planes. In the current situation, it is obvious from the microstructure that there is a more continuous distribution of bounding planes and the calculation of the relative areas was carried out as described in reference 24. The result is the function $\Omega(\mathbf{n})$, the relative population of surfaces with orientation $\mathbf{n}$, measured in multiples of a random distribution.

III. Results and Discussion

OIM image quality maps of the PMN-35PT matrix grains after various annealing treatments at 1150°C are shown in Fig. 1. Inspection of the maps does not clearly show any trends. For the most part the grains are faceted with some equiaxed to rounded grains. This is in accordance to previous studies, which show that at 1.5 vol% PbO and greater faceted grains dominate the microstructure.[14] Figure 2 shows the corresponding single crystal growth data obtained from these samples as well as a calculated ideal amount of crystal growth for a PMN-35PT sample with a constant growth rate rather than the observed reducing rate. The data for this ideal plot was based on a growth constant of 2.5×10^{-09} m^2/hr remaining constant throughout. This value was obtained from the kinetic data from a previous study and is the growth constant for the "early" part of growth, i.e. the first 2 hours of growth.[14] The overall growth constant was measured to be 1.05×10^{-09} m^2/hr including all annealing times. At the late stages, the growth constant was consistently measured to be 5×10^{-10} m^2/h, showing that the growth rate indeed does decrease with time. It can be seen that the measured growth does not reach the ideal values calculated using the rate constant measured in the early stages of growth.

A previous study observed the effect that PT content has on single crystal growth in the PMN-PT.[17] The results showed that as PT content was increased from 0 to 50 %, the single crystal growth decreased. This was accompanied by a clear faceting of the matrix grains that occurred in the 35 and 50 PT samples. In contrast, the 7 and 0 PT samples were rounded. Therefore, a link exists between faceting and single crystal growth rate, and quantification of this relationship may be possible by observing the distribution of specific planes in PbO rich PMN-35PT samples.

The stereograms in Fig. 3 show how the relative areas of different surfaces change during growth. During the course of annealing, the relative areas of the {100} surfaces and surfaces vicinal to this orientation increase. At the last stage, the relative areas of the {100} surfaces are four times greater than that of the {111} surfaces.

Under the conditions studied here, the growth of PMN/PT has been shown to be interface controlled. In other words, the interfaces move slowly in comparison to the rate of diffusion so that their motion depends on crystallographic orientation, structure, and curvature. Inspection of the OIM micrographs in Fig. 1 reveals that even though the grains have boundaries that are approximately flat, there is noticeable curvature. While the current data do not rule out the possibility of faceting on a microscopic level, we assume that the interfaces are non-singular and that nucleation will not limit their motion. In this case, the change in shape is most easily explained in terms of an orientation dependent interface mobility.

In the initial state, we assume the milled and compacted particles are equiaxed and have a random distribution of interfaces. As the crystals grow, the slowest moving surfaces are enlarged as the higher mobility surfaces move away from the center of the crystal at a greater velocity. If it is the anisotropic mobility that creates the observed distributions, then we must conclude that the {100} surfaces have the smallest mobility and the {111} surfaces have the largest. This is consistent with the report that {001} oriented single crystals grow more slowly than {111} oriented crystals[16] and that the rate constant for grain growth decreases as a function of time. As a larger fraction of the interfacial network is made up of slow moving interfaces, the rate of growth decreases.

It should also be noted that the mean surface energy is also likely to decrease during growth. While the surface energies for PMN/PT are not known, most data on the surface energy

anisotropy of the $SrTiO_3$, which also has the perovskite structure, leads to the conclusion that the (100) orientation represents a minimum in the surface energy.[25] If it this is the same in PMN/PT, then the average energy per unit area of the surfaces bounding each crystal also decreases. This factor will reduce the driving force for growth beyond that which would be predicted only on the basis of grain size. Therefore, this factor may also contribute to the decrease in the rate constant for grain growth. The relative contributions of the decreasing energy and the increasing area of reduced mobility interfaces to the reduction of the growth constants are currently being evaluated.

The fact that the {001} facets become more prevalent with time in the PMN-35 PT samples suggests that kinetics is not the only factor. This is due to the fact that once the grains facet, which occurs early on,[15] {001} interfaces should stay constant unless other external factors exist. As mentioned previously, the chemistry of the liquid phase (excess PbO) is also changing throughout the annealing process.[17] In fact, the chemistry starts changing at the same annealing time that the {001} interfaces increase, suggesting a connection. Furthermore, MgO was shown to precipitate out of the system effectively changing the PT content of the liquid phase. This change in PT content will also change the solid\liquid interfacial energy contributing to the observed change in distribution of surfaces. Therefore a direct link to morphology and interfacial distribution can be made. The more grains are faceted, the more {001} interfaces that exist. This statement may seem trivial, but in the case of PMN-35PT samples where the degree of matrix faceting was not obvious without OIM data, this verification is valuable. Additional work needs to be completed on the PMN-*x*PT to quantitatively show that indeed the distribution of {001} surfaces is higher in the lower growth rate samples, i.e. the higher the PT the slower the single crystal growth rate.

IV. Conclusions

During the growth of PMN/PT, there is a change in the distribution of interfaces. As the average grain size increases, so does the fractional area of the surfaces with {100} orientations. This indicates that interfaces with the {100} orientation move more slowly than others and suggests an explanation for the simultaneous decrease in the rate constant for grain growth.

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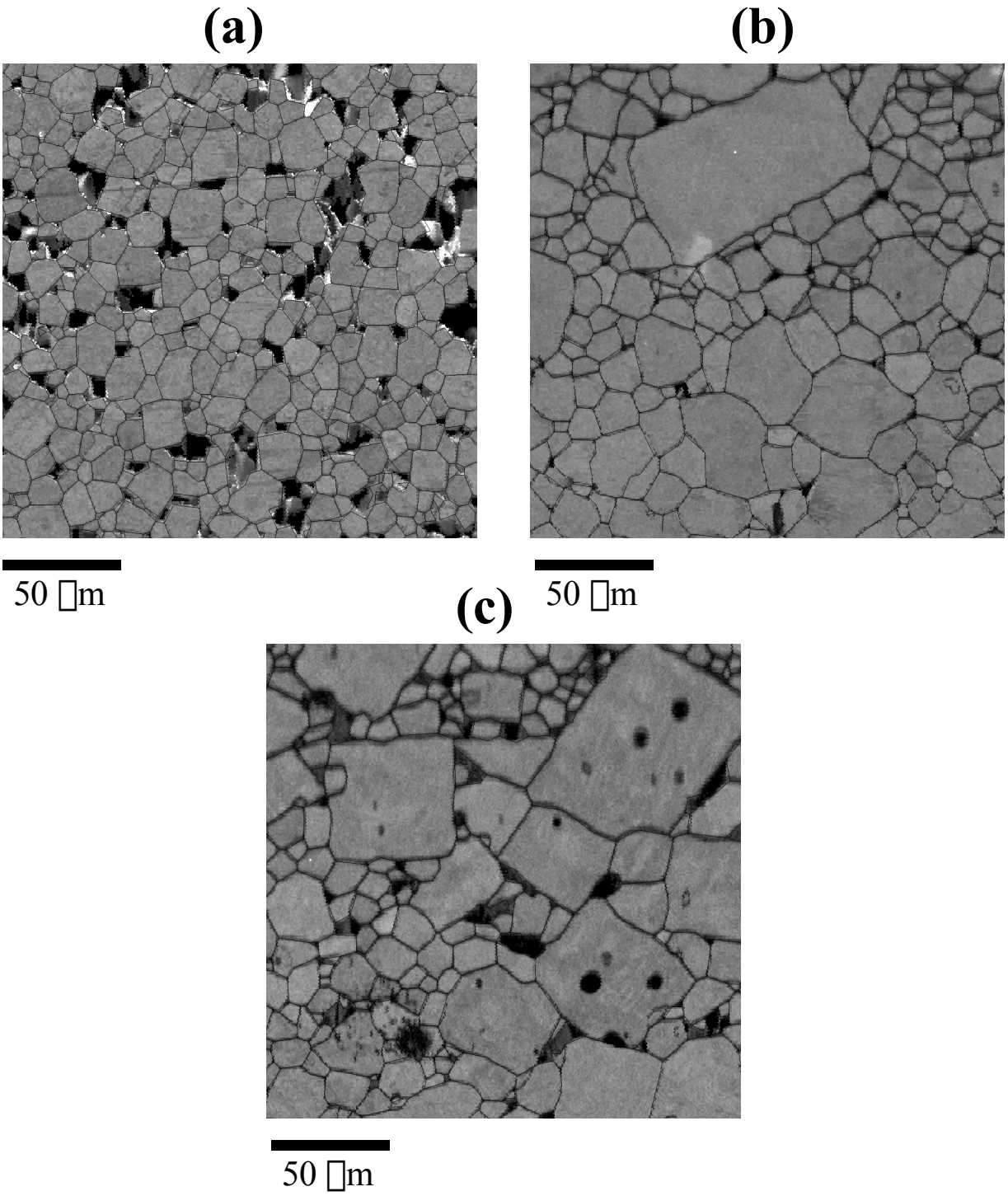

Figure 1. OIM image quality maps of matrix grains in PMN-35PT + 1.5 vol% PbO annealed for (a) 0 hrs, (b) 2 hrs, and (c) 4 hrs showing that the morphology is mostly faceted.

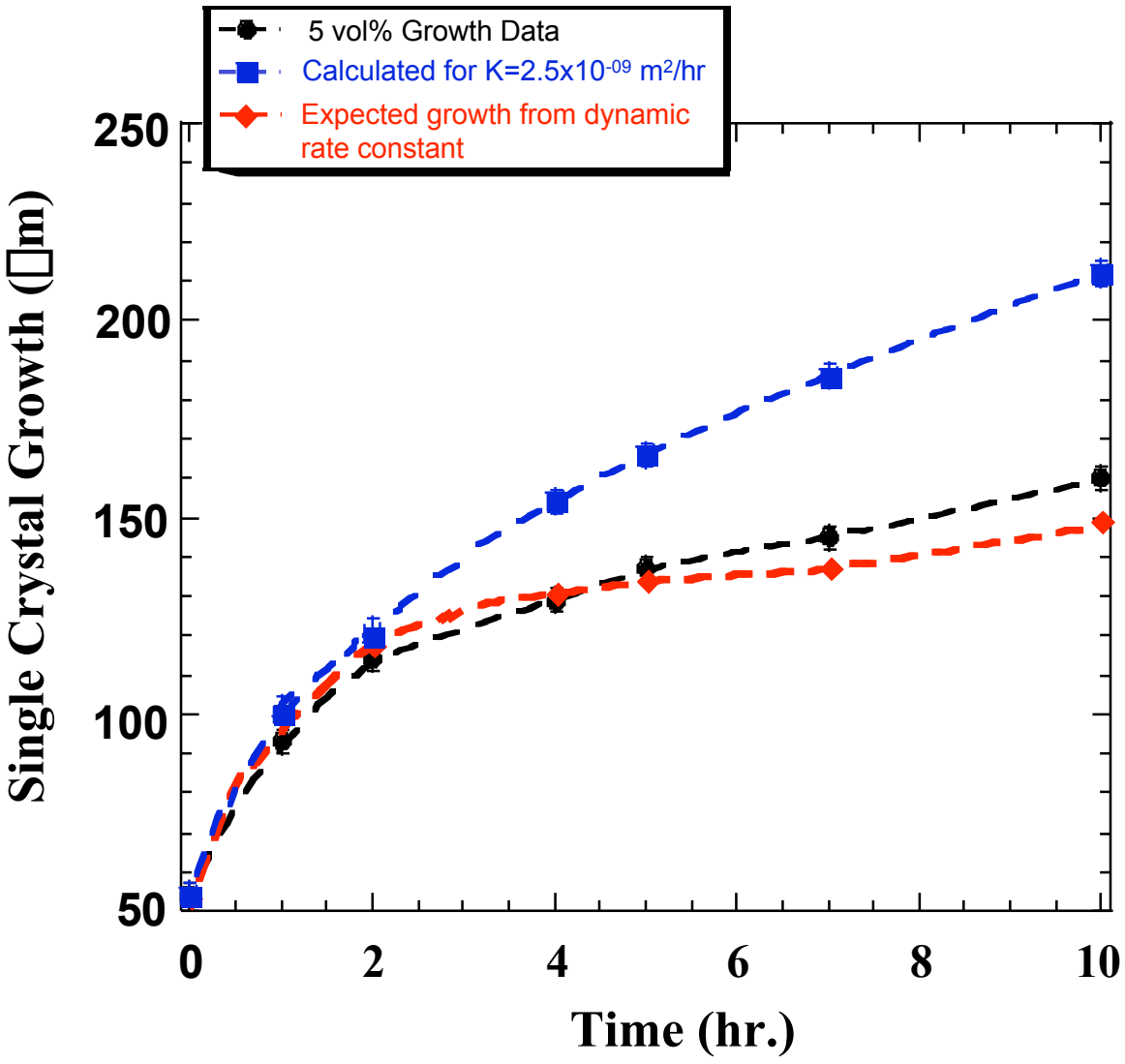

Figure 2. Plot of single crystal growth versus time for PMN-35PT + 1.5 vol% PbO including the calculated ideal crystal growth.

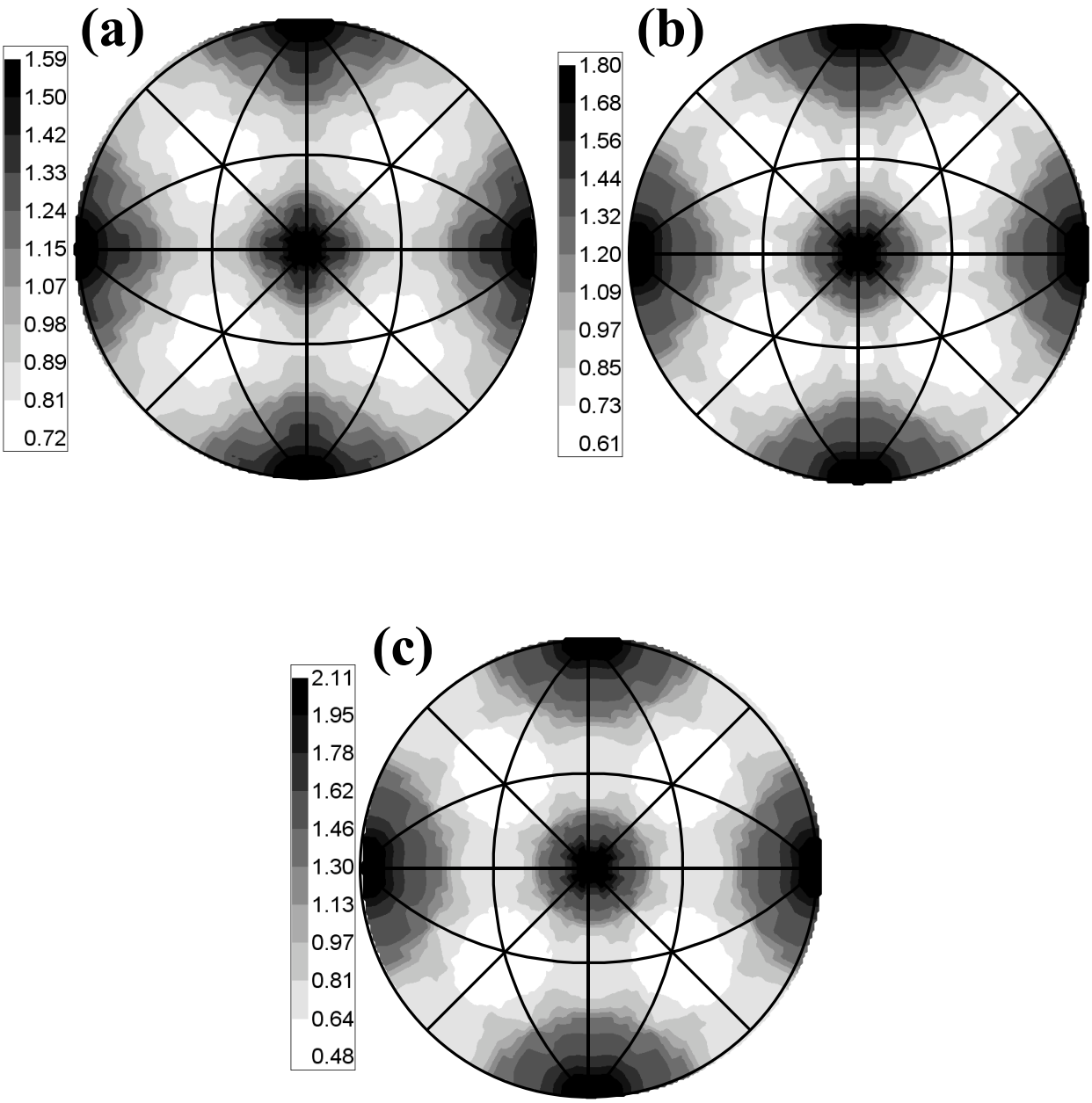

Figure 3. Stereograms of PMN-35PT + 1.5 vol% PbO annealed for (a) 0 hrs, (b) 2 hrs, and (c) 4 hrs showing the distribution of interfaces in each sample.