

Neutron Scattering Studies of Compositional Heterogeneity in Sol–Gel Processed Lead Zirconate Titanates

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Rietveld analyses of neutron diffraction data collected on a series of $\text{Pb}(\text{Zr}_{0.5}\text{Ti}_{0.5})\text{O}_3$ samples, which had been prepared by sol–gel and conventional mixed oxide methods, showed that each sample contained both rhombohedral and tetragonal PZT ($\text{Pb}[\text{Zr}_{1-x}\text{Ti}_x]\text{O}_3$). The zirconium-to-titanium ratio in the two phases was found to be markedly different. Pair distribution functions were also calculated for some of the samples. The inability of a commonly used alkoxide-based sol–gel processing method to produce compositionally homogeneous samples is attributed to a compositional segregation that occurs early on during sol–gel processing and is not fully eliminated on high temperature heat treatment of the samples. A deliberate attempt to produce compositionally inhomogeneous materials, via the separate prehydrolysis of lead titanate and lead zirconate precursors, followed by mixing the resulting sols, was found to induce no more inhomogeneity than is present in materials prepared via the hydrolysis of precursors that were completely mixed.

Introduction

Compositional Homogeneity in Sol–Gel Processed Samples: General Considerations. Sol–gel methods^{1–3} are very widely used for the preparation of complex mixed-metal oxides.^{4–6} It is often stated that this approach allows the low cost preparation of ceramic films and fibers, sometimes gives the synthetic chemist access to metastable materials, and provides precursor mixing at a molecular level, leading to compositionally homogeneous products.^{4,5} However, the preparation of compositionally homogeneous products is not guaranteed by molecular scale mixing. A simple consideration of how sols and gels are formed indicates that their compositional homogeneity may be heavily dependent upon kinetic factors. Consider a synthesis starting with an alcoholic solution of two metal alkoxide precursor species containing metals A and B. In the absence of a mechanism for the breaking and remaking of M–O–M links, the hydrolysis of this solution will only lead to a compositionally homogeneous gel if the kinetics for the formation of A–O–A, A–O–B and B–O–B links are similar. However, if there is a facile mechanism for the breaking and reformation of all the M–O–M links, then

the compositional homogeneity of the system will be dictated by thermodynamic considerations rather than by the kinetics of M–O–M link formation or the homogeneity of the precursor solution prior to hydrolysis. Dramatic differences in the hydrolysis kinetics for the various precursor species used in sol–gel syntheses are very common. For example, a considerable amount of work has been done on the sol–gel synthesis of PZT ($\text{Pb}[\text{Zr}_{1-x}\text{Ti}_x]\text{O}_3$) using alcoholic solutions containing titanium and zirconium alkoxides;^{7–13} titanium alkoxides typically hydrolyze and form M–O–M bridges much faster than the corresponding zirconium compounds.

Compositional Homogeneity in Sol–Gel Processed PZTs. While for most systems very little is known about the compositional homogeneity of precursor solutions, gels, xerogels, glasses, and ceramics, some of these issues have been examined for the PZT system. Several experiments involving the isolation of molecular species from solution strongly suggest that there is compositional heterogeneity on a very short length scale in unhydrolyzed precursor solutions. For example, Chae et al.¹⁴ isolated $[\text{PbTi}_2(\mu_4\text{-O})(\text{OOCCH}_3)(\text{OCH}_2\text{-}$

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CH₃)₇]₂ from a solution with a 1:1 Pb:Ti ratio, Ma and Payne¹⁵ isolated both the previously mentioned compound and [PbZr₂(O)(OOCCH₃)₂(OCH₂CH₃)₆]₂ from a solution with Pb:Ti:Zr 1:1:1, and Hubert-Pfalzgraf and co-workers¹⁶ have reported the isolation of both mixed lead and zirconium molecular species and mixed lead and titanium molecular species with stoichiometries that differed from the bulk compositions of the solutions they were prepared from.

The EXAFS study by Payne and co-workers¹⁷ of heat-treated xerogels at the Pb L_{III}, Zr K- and Ti K-edges shed considerable light on the nature of these materials. They found that PZT gels prepared by the hydrolysis of precursor solutions synthesized from lead acetate, titanium isopropoxide, and zirconium *n*-propoxide in 2-methoxyethanol under neutral conditions⁷ displayed considerable compositional heterogeneity; their PZT gels contained large numbers of Ti–O–Ti and Zr–O–Zr links but very few Zr–O–Ti links and Pb did not appear in the second coordination shell of either the Zr or Ti. Earlier, Ahlfänger et al.¹⁸ studied PZT sols and gels using only Zr K-edge EXAFS. Their samples were made by hydrolyzing a solution prepared by mixing Zr and Ti isopropoxides in 2-propanol with acetic acid and lead acetate in methanol. They concluded that their samples contained many Zr–O–Ti links. The differences between the results of Ahlfänger and Payne may reflect real differences in the samples studied as both the chemistry used to prepare the gels and the heat treatments of the samples differed markedly. A later EXAFS study on dry PZT gels, prepared by the same method as Ahlfänger et al., at the Zr K- and Pb L_{III}-edges was interpreted as indicating that there were probably no Zr–O–Pb links in the samples examined,¹⁹ in apparent contradiction with earlier Raman studies.²⁰ Recent EXAFS studies of lead titanate gels by Antonioli, et al.²¹ suggest that Pb–O–Ti links do not occur in these materials. Very recently a differential anomalous scattering study,²² at the Pb L_{III}-edge, of PZT glasses and partially crystallized materials indicated that, in calcined gels prepared by the same method as that used by Ahlfänger et al., the lead local environment was the same in materials heated at 200, 300, and 450 °C although the overall structure of the gel was different for each of the three samples. Barboux et al. examined the synthesis of PZ from zirconium and lead alkoxides and found that the poorly crystallized fluorite related phase that appeared at very low temperatures was not due to gross phase separation; each crystallite contained

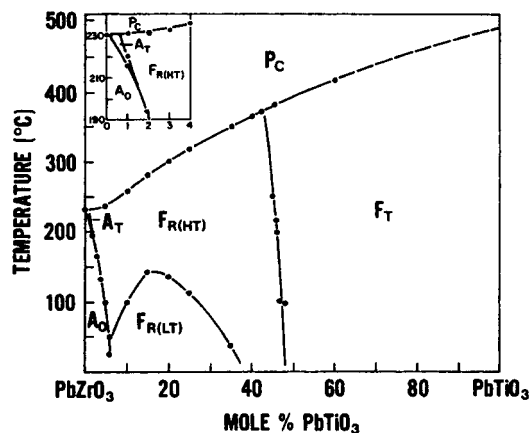


Figure 1. The Pb(Zr_{1-x}Ti_x)O₃ phase diagram (reproduced with permission from Amin, A.; Newham, R. E.; Cross, L. E. *Phys. Rev. B* **1986**, *34*, 1595. Copyright 1986 by the American Physical Society).

both lead and zirconium.²³ They also concluded that Zr K-edge EXAFS was not a reliable guide to the presence of lead along with the zirconium in the fluorite phase. Studies of microstructure evolution on heating sol-gel-derived PZT films have also revealed strong evidence for the presence of nanoscale compositional heterogeneity at temperatures lower than that needed for the complete crystallization of perovskite PZT. Lakeman et al.¹³ reported the presence of both zirconium-rich, lead-deficient regions and basic lead carbonate in films subjected to low-temperature treatments. Tuttle et al.²⁴ also found evidence for zirconium-rich, lead-deficient regions in films that had partly crystallized to "pyrochlore" and perovskite phases. They proposed that these regions were remnants of a compositional segregation that occurred as the gel formed by hydrolysis and condensation of alkoxides.

While some of the experimental evidence relating to the compositional homogeneity of PZT gels is contradictory, the overall picture is reasonably clear. Lead is not uniformly distributed throughout a typical gel, and the titanium and zirconium are not randomly distributed in the gel polymeric backbone.

Compositional Homogeneity and the Morphotropic Phase Boundary in the PZT System. While compositional inhomogeneity in PZT sols and gels has received moderate attention, the issue of compositional inhomogeneity in PZT ceramics and its relationship to the phases present in samples with bulk compositions close to the morphotropic phase boundary (MPB) (see Figure 1) has received considerable attention. The MPB is often stated to lie at Pb(Zr_{0.535}Ti_{0.465})O₃, although its reported position will depend on the working definition that the experimenters used; it is usually, but not always, defined as the composition at which there is a 50:50 mix of tetragonal and rhombohedral PZT in the sample. Additionally, some workers have speculated that the MPB location is dependent upon the sample's preparation temperature.²⁵ The large amount of ex-

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perimental and theoretical work done on PZT compositions close to the MPB^{26,27} is a consequence of the excellent piezoelectric properties associated with this region of the phase diagram.²⁸ There are many reports of samples with bulk compositions close to that of the MPB containing both tetragonal and rhombohedral PZT. It was initially suggested that there was a two-phase coexistence region for either thermodynamic^{29,30} or kinetic reasons,³¹ but experiments with different preparation techniques indicated that compositional inhomogeneity was responsible for the presence of the two phases.^{25,32–34} Relatively recently, Cao and Cross have proposed that the coexistence of both phases is due to quenched thermal fluctuations³⁵ and that at the morphotropic phase boundary there should be a 3:2 ratio of rhombohedral:tetragonal PZT.^{27,35} This ratio was arrived at by using the true thermodynamic definition of a phase boundary: the MPB occurs at the composition where the tetragonal and rhombohedral phases have equal free energies. The later workers predicted that there will be a well-defined phase coexistence region in the absence of any compositional inhomogeneity and that the width of the phase coexistence region is dependent upon the particle/grain size of the samples under consideration. They proposed that the relationship between the width of the phase coexistence region and the processing route used may be a consequence of the different particle sizes produced by the various synthetic approaches.

Compositional inhomogeneity in PZT samples has been reported to arise from a number of factors, including poor mixing of the starting materials,³² the reaction pathway followed,³⁶ and the presence of excess PbO in the reaction mixture.^{25,37} It is interesting to note that Kakegawa and co-workers³⁷ reported that the presence of excess PbO during high-temperature heat treatments can lead to enhanced inhomogeneity, while Fernandes et al.²⁵ reported that the presence of excess PbO improved the homogeneity of their samples.

Several different experimental approaches have been used to evaluate the homogeneity of PZT samples with compositions close to that of the morphotropic phase boundary. Many workers have employed measurements of lattice parameters to estimate the average composition of a phase,^{25,32,33,36,37} the relative intensities of a small number of Bragg peaks have been used to estimate phase fractions,^{25,30,33,36,37} peak widths have been used to estimate the compositional range of a given

phase,^{32,33,37} and dielectric constant measurements have been employed to analyze the phase mixture.³⁸

Neutron Scattering Studies of Compositional Heterogeneity in Sol–Gel Processed PZT. In the present paper we report the results from a neutron scattering study of compositional heterogeneity in $(\text{PbZr}_{0.5}\text{Ti}_{0.5})\text{O}_3$ samples prepared by sol–gel procedures closely related to those of Payne and co-workers.⁷ We set out to examine the possibility that compositional inhomogeneity could be deliberately introduced into the final perovskite by modifying the sol–gel processing procedure. In particular, we hoped that prehydrolyzing PbTiO_3 and PbZrO_3 precursor solutions, mixing the resulting sols, drying the mixture, and then calcining the resulting xerogel would allow us to introduce compositional inhomogeneity into perovskite PZT in a controllable fashion. We subsequently refer to this approach as an “inhomogeneous” sol–gel method. We also examined materials prepared by conventional mixed oxide and “homogeneous” (conventional) sol–gel procedures. In the context of our sol–gel preparation procedures, the terms “homogeneous” and “inhomogeneous” are used to describe the way in which the hydrolysis of the metal alkoxides was performed. In particular, “homogeneous” does not imply that there is only one species present in solution. Our examination of the PZT samples suggested that there was considerable compositional inhomogeneity present in the final perovskite PZT, even when the conventional “homogeneous” sol–gel process was used.

Time-of-flight neutron scattering data were obtained for each PZT sample and used for Rietveld analyses. Additionally, pair distribution functions were calculated for some of the materials. The pair distribution functions provide structural information on short and medium length scales, and the Rietveld analyses probe longer length scale effects. The Rietveld method allowed us to directly estimate phase fractions and compositions for each phase present in the samples. PZT is very well-suited to examination by neutron diffraction, as the scattering contrast between titanium and zirconium is very large; the neutron scattering lengths for natural abundance Ti and Zr are -0.344 and 0.716×10^{-14} m, respectively.

Experimental Section

Sample Preparation. Five PZT 50:50 samples were prepared; one of them by the direct reaction of mixed oxides (subsequently referred to as PZT-MO) and the others by sol–gel procedures closely related to those used by Payne's group.^{7,11} Although excess lead is usually employed in the preparation of PZT, both via sol–gel methods and the direct reaction of oxide powders, it was not used in any of the reported preparations. Avoiding excess lead minimizes the possible effect of low-melting lead oxide-rich phases on the samples compositional homogeneity. As excess lead was not employed in any of the preparations, the maximum temperature used for the sample prepared by direct reaction of oxides was somewhat lower than that typically employed by other workers, so that lead loss by evaporation would not be a major problem.

Sample PZT-MO was prepared by mixing, grinding, and firing 0.12 mol PbO along with 0.06 mol each of TiO_2 and ZrO_2 . The mixture was initially slowly heated to 700 °C (~40 h at

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700 °C). It was ground, reheated to 750 °C, and held at that temperature for ~82 h. Part of the sample was then pressed into pellets. The pellets were covered with the remaining PZT powder and heated to 1000 °C using a tube furnace that had been deliberately heavily contaminated with PbO prior to use. After 13 h the sample was cooled, and the pellets were ground, repressed, and heated to 1000 °C under PZT powder for a further 13 h.

Sol-gel samples PZT-SGLH and PZT-SGLI (sol-gel low-temperature "homogeneous" and sol-gel low-temperature "inhomogeneous", respectively) were both prepared from stock solutions of titanium isopropoxide and zirconium butoxide in anhydrous 2-methoxyethanol (1.24 and 1.35 M, respectively). Sample PZT-SGLH was prepared by refluxing 0.1 mol of hydrated lead acetate in ~140 mL of anhydrous 2-methoxyethanol for ~1 h, removing ~90 mL of the solvent by distillation, and adding 0.05 mol each of the titanium and zirconium alkoxides along with an additional 20 mL of anhydrous 2-methoxyethanol. After standing overnight, the solution was briefly refluxed and ~90 mL of solvent was removed by distillation. Rapid gelation was achieved by the addition of 7.2 mL of water diluted to 20 mL with 2-methoxyethanol. The resulting gel was then dried in a vacuum oven. The xerogel was heated in stages to 750 °C. It was held at this temperature for ~28 h.

Sample PZT-SGLI was prepared by an inhomogeneous hydrolysis procedure. A lead titanate (PT) precursor solution was prepared by dissolving 0.07 mol of hydrated lead acetate in 95 mL of anhydrous 2-methoxyethanol, briefly refluxing the solution and distilling off ~70 mL of solvent, adding titanium alkoxide stock solution containing 0.07 mol of Ti, refluxing the mixture, and distilling off a further 65 mL of liquid. A lead zirconate (PZ) precursor solution was prepared by dissolving 0.07 mol of hydrated lead acetate in ~100 mL of anhydrous 2-methoxyethanol, briefly refluxing the solution, removing excess solvent by distillation, adding alkoxide stock solution containing 0.07 mol of zirconium, briefly refluxing, and then removing excess solvent by distillation. The concentrations of the PT and PZ precursor solutions were determined gravimetrically to be 1.64 and 1.79 M, respectively. A solution containing 0.4 mol of water diluted to 320 mL with 2-methoxyethanol was used to hydrolyze the PT and PZ precursors. Approximately 130 mL portions of this solution were added to 0.041 mol portions of PT and PZ precursor (4:1 H₂O:metal). After 20 min at room temperature the PT precursor started to gel. At this point the partially hydrolyzed PT and PZ precursors were thoroughly mixed. After 3 days at room temperature the resulting gel was dried in a vacuum oven (50 °C over a 2 day period). The dry gel was heated to 600 °C in stages. The resulting material was then heated to 750 °C for a total of ~42 h.

Samples PZT-SGH1 and SGH2 (sol-gel high-temperature sample 1 and 2, respectively) were prepared from a PZT gel that was synthesized as follows. Approximately 0.186 mol of lead acetate hydrate was dissolved in 140 mL of 2-methoxyethanol, the solution was briefly refluxed, and then 60 mL of liquid was removed by distillation. After cooling the flask, stoichiometric amounts of zirconium *n*-butoxide (0.643 M in 2-methoxyethanol) and titanium isopropoxide (1.250 M in 2-methoxyethanol) stock solutions were added. The mixture was briefly refluxed, and 120 mL of liquid was removed by distillation. A 13.4 mL portion of water diluted to 25 mL with 2-methoxyethanol was used to hydrolyze the PZT stock solution (4:1 water to metal alkoxide ratio). After 2 days at room temperature, the gel was dried overnight in a 110 °C vacuum oven. PZT-SGH1 and SGH2 were prepared by rapidly heating portions of the dry gel to 1000 and 1100 °C, respectively, and holding the samples at the final temperature for 1 h.

Diffraction Data Collection. Neutron diffraction data were collected for all five samples using the SEPD instrument at the Intense Pulsed Neutron Source, Argonne National

Laboratory.³⁹ Data sets for samples PZT-SGLH, MO, SGLI, an empty vanadium can, a nickel rod, a vanadium rod, and the instrument background were obtained by grouping (time focusing) the data from each counter tube into banks with effective scattering angles (2θ) of 139.69°, 150.00°, 90.00°, and 60.00°. The later grouping of detectors is not typically used to obtain data for Rietveld analysis on SEPD, but it is often used when acquiring data for the calculation of pair distribution functions. It allows a comparison of the 139.69° and 150.00° banks (which have similar resolution) so that the quality of the data can be assessed. The time-of-flight (TOF) range 1000–30 000 μ s was recorded for each detector bank. Data sets for samples PZT-SGH1 and SGH2 were recorded with the counter tube's time focused into banks with effective scattering angles (2θ) 144.85°, 90.00°, and 60.00° (typical for SEPD). The time-of-flight range recorded was 2000–30 000 μ s.

Powder X-ray diffraction patterns were collected for all of the samples using a Scintag instrument equipped with a Cu K α radiation source and a Peltier cooled solid-state detector.

Diffraction Data Analyses. Rietveld analyses of the neutron diffraction data were performed for all five samples using the program package GSAS.⁴⁰ Additionally, pair distribution functions were calculated for samples PZT-SGLH, MO, and SGLI using the TOF neutron scattering data. As an instrument parameter file for SEPD under the conditions used for the acquisition of data on samples PZT-SGLH, MO, and SGLI was not available, the unknown incident spectrum parameters for the 139.69° and 150.00° banks were obtained by fitting to the vanadium rod data that had been collected using the same instrument configuration. Starting values of the diffractometer constants for the 139.69°, 150.00° banks of detectors were then determined by fitting the data obtained on a standard nickel sample under the same instrument conditions.

Pair distribution functions^{41–44} were calculated for samples PZT-SGLH, MO, and SGLI using a program suite based upon the GLASS package.⁴⁵ The raw data were processed to take into account absorption, multiple scattering, the Placzek correction, the incident intensity distribution, the scattering contribution from the can, and the instrument background. The data from the different detector banks were normalized and merged. A pair distribution function was then calculated by Fourier transformation over the range 0.9–25 Å^{-1} . The resulting pair distribution functions for samples PZT-SGLH and SGLI are compared in Figure 2.

The diffraction data for each of the five samples were modeled by the Rietveld method as arising from a two-phase mixture of rhombohedral and tetragonal PZT. In each case three banks of data were analyzed in a combined refinement (145°, 90°, and 60° for samples PZT-SGH1 and SGH2, and 150°, 140°, and 90° for samples PZT-SGLH, MO, and SGLI). Only reflections with *d* spacing greater than 0.5 Å were included in the analyses. During the refinements the diffractometer constant DIFC was fixed for the 90° bank and all of the other diffractometer constants were allowed to vary (the 90° bank was the only one that was available for every sample). This procedure was adopted to ensure that the lattice constants obtained for each of the five samples could be compared to one another. Starting models for tetragonal and rhombohedral PZT (*R3m* phase) were obtained from Glazer and Mabud,⁴⁶ and Glazer et al.,⁴⁷ respectively. With the

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Table 1. Summary of the Results from the Compositionally Restrained Rietveld Refinements

sample	PZT-SGH1	PZT-SGH2	PZT-MO	PZT-SGLH	PZT-SGLI
phase fraction tetragonal	0.793(3)	0.837(3)	0.853(2)	0.708(4)	0.704(4)
phase fraction rhombohedral	0.207(3)	0.163(3)	0.147(2)	0.292(4)	0.296(4)
tetragonal Zr+Ti	0.441(2)+0.559(1)	0.449(3)+0.551(3)	0.444(2)+0.556(2)	0.408(3)+0.592(3)	0.404(3)+0.596(3)
rhombohedral Zr+Ti	0.685(5)+0.315(5)	0.739(5)+0.261(5)	0.778(6)+0.220(6)	0.683(5)+0.317(5)	0.691(6)+0.309(6)
tetragonal a , Å	4.036(1)	4.034(1)	4.0443(8)	4.052(1)	4.058(1)
tetragonal c , Å	4.146(1)	4.149(1)	4.1552(8)	4.132(1)	4.134(1)
c/a	1.0273	1.0285	1.0274	1.0197	1.0187
rhom a , Å	4.085(1)	4.087(1)	4.0896(8)	4.092(1)	4.098(1)
rhom α , deg	89.71(1)	89.72(1)	89.74(1)	89.705(1)	89.661(3)
tetragonal Pb U_{iso} , Å ²	1.95(7)	1.80(7)	2.10(4)	2.25(5)	2.19(5)
Zr/Ti U_{iso} , Å ²	0.33(9)	0.8(1)	0.18(7)	.27(6)	0.06(6)
tetragonal O1 U_{iso} , Å ²	1.65(8)	1.63(8)	1.82(5)	1.09(8)	0.98(9)
tetragonal O2 U_{iso} , Å ²	1.68(6)	1.72(7)	1.78(4)	2.20(7)	2.27(8)
tetragonal Zr/Ti z	0.555(2)	0.557(2)	0.559(1)	0.565(4)	0.573(4)
tetragonal O1 z	0.0882(7)	0.0879(7)	0.0889(5)	0.0791(7)	0.0771(7)
tetragonal O2 z	0.6075(6)	0.6084(6)	0.6086(4)	0.6038(6)	0.6035(7)
rhombohedral Pb1 x	0.570(1)	0.572(1)	0.5715(9)	0.5622(6)	0.5639(6)
rhombohedral Zr/Ti x	0.020(2)	0.019(2)	0.027(1)	0.018(1)	0.0222(9)
rhombohedral O1 x	0.520(1)	0.520(2)	0.526(1)	0.5177(8)	0.5172(8)
rhombohedral Pb U_{iso} , Å ²	1.7(2)	1.5(2)	2.10(4)	2.25(5)	2.19(5)
rhombohedral O1 U_{iso} , Å ²	1.1(1)	0.8(1)	0.68(8)	2.05(8)	1.90(8)
χ^2	3.74	4.61	8.17	7.00	7.22
R_{pw} 150° data bank, %			5.82	6.03	5.79
R_{pw} 145° data bank, %	6.36	6.90			
R_{pw} 140° data bank, %			6.46	6.26	6.17
R_{pw} 90° data bank, %	5.55	6.79	4.83	5.64	5.70
R_{pw} 60° data bank, %	4.80	6.23			
R_F^2 150° data bank, %			11.02	10.44	9.78
R_F^2 145° data bank, %	11.67	10.65			
R_F^2 140° data bank, %			10.72	11.36	10.44
R_F^2 90° data bank, %	8.92	11.01	11.54	8.01	7.48
R_F^2 60° data bank, %	9.40	10.77			

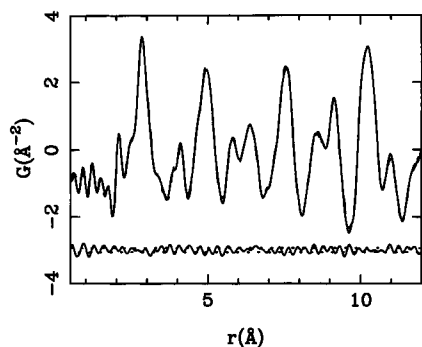


Figure 2. The experimental pair distribution functions (PDFs) for samples PZT-SGLH and SGLI are compared. The PDFs for the two samples are essentially identical, as indicated by the almost flat difference curve even though the synthesis procedures were markedly different.

exception of the Pb z parameter in the tetragonal phase and the oxygen y and z parameters for the rhombohedral phase, all the positional parameters were varied during the refinement (These parameters were fixed to define the origins in the polar space groups $P4mm$ and $R3m$). Isotropic thermal parameters were refined for all atoms in both phases. For the data sets on samples PZT-SGLH, MO, and SGLI the thermal parameters for the lead atoms in both the tetragonal and rhombohedral phases were constrained to be the same. The zirconium and titanium atoms were constrained to have identical positional and thermal parameters. Although these two elements will not be located at exactly the same position (see later for further discussion), the later assumption was needed, as refinement of independent positional and thermal parameters led to problems with the stability of the refinements because the positional parameters for these sites are highly correlated with one another and other parameters in the refinement. The occupancies of the zirconium and titanium sites were refined

subject to the constraint that the total occupancy was unity. The phase fractions for the tetragonal and rhombohedral phases were refined subject to the constraint that they summed to unity. Initial refinements were performed without any constraint or restraint on the overall sample composition. However, the final refinements were performed with a restraint on the sample composition. This was done by taking the refined phase fractions, putting them into the restraint, further refining the phase fractions and site occupancies, putting the new phase fractions into the restraint, and repeating the process until convergence was achieved. This is the only approach that can presently be used for multiphase samples with GSAS; however, it leads to an underestimation of the errors on the phase fractions and site occupancies, as the correlation between these variables is not properly taken into account. A Gaussian function convoluted with two back-to-back exponentials was adopted as a peak shape model for the analysis of the data obtained for samples PZT-SGLH and SGLI. The background was fitted using a cosine Fourier series in each case. The results from the compositionally restrained refinements are presented in Table 1 and some of the fitted profiles are shown in Figure 3.

Results

The laboratory powder X-ray diffraction patterns for samples PZT-SGH1 and SGH2 clearly indicated that they contained both rhombohedral and tetragonal PZT (see Figure 4). The neutron diffraction data sets for these samples show an additional very weak peak at $d \sim 2.3$ Å. This peak is either extremely weak or absent in the X-ray data and it is not consistent with the presence of a pyrochlore phase, ZrO_2 , or the known superlattice for rhombohedral PZT in space group $R3c$.⁴⁷ However, it may be due to scattering from the sample mount in the neutron diffraction experiment. A close

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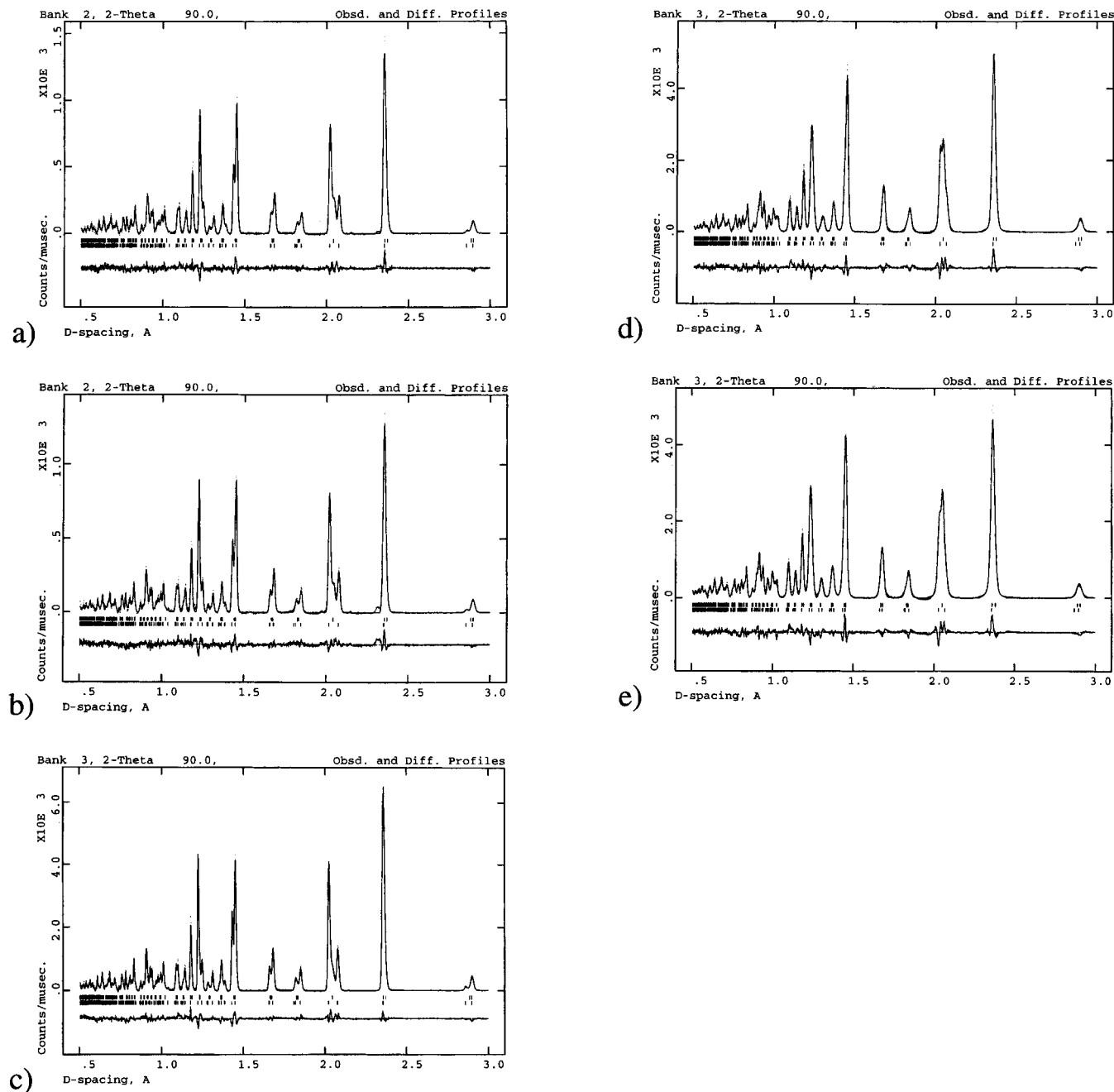


Figure 3. The observed, calculated, and difference profiles are shown for the Rietveld analysis of the 90° neutron scattering data for samples (a) PZT-SGH1, (b) PZT-SGH2, (c) PZT-MO, (d) PZT-SGLH, and (e) PZT-SGLI. The tick marks on the plots indicate the calculated peak positions for each phase. The bottom set of ticks on each plot is for the tetragonal phase. The 90° data was the only detector bank that was analyzed for all of the samples.

inspection of the powder X-ray diffraction data for samples PZT-SGLH, MO, and SGLI indicated that all of the samples were two-phase mixtures (see Figure 4). This was confirmed by the Rietveld analysis of the time-of-flight neutron diffraction data; a satisfactory profile fit could not be obtained for any of the five PZT samples using a single phase model. It should be noted that the powder X-ray diffraction data indicated that all of the samples were of good purity.

Preliminary two-phase Rietveld refinements using the neutron data for PZT-SGH1 and PZT-MO were attempted without any restraint on the overall chemical composition of the samples. These refinements indicated that the rhombohedral and tetragonal phases had distinct Zr:Ti ratios; the rhombohedral phase was

zirconium-rich and the tetragonal phase titanium-rich when compared to the known bulk composition of the sample. However, the overall compositions for the samples, as calculated from the site occupancy and phase fraction refinements, were not in close agreement with the known bulk compositions, and the isotropic thermal parameters for the Zr/Ti sites were significantly negative. The application of a restraint on the overall sample composition (Zr:Ti ~ 1:1) improved the agreement between the known and calculated compositions and led to positive definite thermal parameters for the Zr/Ti sites. All further refinements were performed using a compositional restraint.

The results of the compositionally restrained refinements (Table 1) clearly show that in each sample the

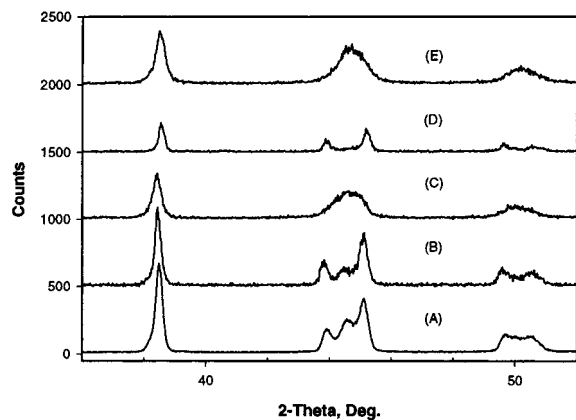


Figure 4. Selected sections of the powder X-ray diffraction patterns for (A) PZT-SGH1, (B) PZT-SGH2, (C) PZT-SGLH, (D) PZT-MO, (E) PZT-SGLI. For each of the samples the group of peaks at around 43° – 46° has at least three components (note that for sample PZT-MO the trace does not return to background between the two maxima), indicating that all of the samples contains both tetragonal and rhombohedral PZT. Although there are no resolved features in the peak grouping at around $\sim 44^{\circ}$ in (C) and (E), the width of this grouping compared to the peak at $\sim 38.5^{\circ}$ provides strong evidence for the presence of tetragonal and rhombohedral PZT.

two PZT phases have markedly different compositions; the rhombohedral phase is always zirconium-rich and the tetragonal phase is always titanium-rich. This difference is very large relative to the likely errors on the refined composition, even after taking into consideration the underestimation of the standard deviations on the site occupancies (see the Experimental Section).

Discussion

Data Analysis. The Rietveld method offers significant advantages over other approaches to quantitative phase analysis using diffraction data. It is very sensitive to the presence of additional phases, as it is a whole pattern fitting procedure. The method can directly provide information about the composition of each phase through site occupancy refinement, and it accounts for the average composition of each phase when determining the phase fractions present in the sample. The use of neutron diffraction along with the Rietveld method provides improved sensitivity to the Zr/Ti ratio in each PZT phase as the scattering contrast between these elements is large. The ability to directly determine phase compositions without reliance on lattice parameter values is very important in cases where the lattice parameters may depend on sample characteristics other than composition, for example, particle size.

The refined compositions for the rhombohedral phases in all of the samples examined (see Table 1) lie close to or within the region (see Figure 1) where the low-temperature rhombohedral phase ($R3c$ structure with a supercell due to octahedral tilts) might be expected to form. As there was no clear evidence in the diffraction patterns for the superlattice peaks associated with this phase, the simpler high-temperature structural model ($R3m$) was used for all of the refinements.

In our initial refinements with no overall compositional constraint, the thermal parameters for the Zr/Ti sites in the rhombohedral and tetragonal phases refined to negative values. The application of an overall

compositional restraint led to more realistic values for these parameters. The use of this restraint to reduce the correlation between site occupancies, thermal parameters, and phase fractions is reasonable in the absence of significant amounts of zirconium- and titanium-containing impurities. In general, thermal parameter refinements for the Zr/Ti sites in PZT samples using neutron diffraction data are plagued by two problems: the difference in sign between the scattering lengths of Zr and Ti leads to a low mean scattering length for the Ti/Zr site when the sample composition is close to $0.32 \text{ Zr} + 0.68 \text{ Ti}$, and the assumption that the Zr and Ti ions lie at exactly the same position is not strictly valid. The first problem can be readily illustrated for the samples used in this study, as their bulk composition is $\text{Zr}:\text{Ti} \sim 1:1$ the average neutron scattering length of the Zr/Ti sites is $0.186 \times 10^{-14} \text{ m}$. This should be compared to the neutron scattering lengths for Pb and O which are 0.940 and $0.665 \times 10^{-14} \text{ m}$, respectively. The situation is even worse when the tetragonal phase is considered as we typically found a $\text{Zr}:\text{Ti}$ ratio of $\sim 0.45:0.55$ giving an average site scattering length of $\sim 0.13 \times 10^{-14} \text{ m}$. The average positions of the Zr and Ti in the unit cell are clearly not going to be exactly the same even though this assumption usually, but not always,⁴⁸ must be made in order to get a stable Rietveld refinement; it is expected that the average Ti–O distance will be slightly shorter than the average Zr–O distance due to differences in ionic radii. The slightly different average positions of the Zr and Ti, which are not explicitly accounted for in our Rietveld model, may be partly responsible for the negative thermal parameters in the unrestrained refinements; see Corker et al.⁴⁸ The pair distribution function shown in Figure 2 provides strong experimental evidence for the different mean lengths of the Ti–O and Zr–O bonds in our PZT samples. The first-derivative-like feature centered at $\sim 2.0 \text{ \AA}$ is a result of the negative contribution (due to the negative scattering length of Ti) from Ti–O vectors to the PDF at a slightly shorter distance than the positive contribution from Zr–O vectors.

The final fit for each of the refinements is shown in Figure 3 for the 90° data bank (the only bank that was analyzed for all of the samples). The general quality of the fit, while satisfactory, is not as good as we expected given the outwardly simple nature of the materials being examined. It is clear that the fits for samples PZT-SGH1, SGH2, and MO are superior to those for samples PZT-SGLH and SGLI. An entirely satisfactory peak shape model was never found for samples PZT-SGLH and SGLI. For all of the refinements, the fits to the backscattering data appear to be worse than those to the lower angle banks due to peak shape modeling difficulties, and for the 60° data banks that were only analyzed for samples PZT-SGH1 and SGH2, the fit quality was very good. Some of the discrepancies between the calculated and observed profiles are probably a consequence of deficiencies in our structural model such as significant local deviations from the average structure that are not accounted for.^{48,49}

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Comparison with Prior Perovskite PZT Literature. Prior to our work, there have been several structural studies of rhombohedral PZT: $\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$ ($x = 0.08, 0.13, 0.18, 0.23, 0.28, 0.33, 0.38$),⁴⁸ $\text{Pb}(\text{Zr}_{0.94}\text{Ti}_{0.06})\text{O}_3$,⁴⁹ $\text{Pb}(\text{Zr}_{0.9}\text{Ti}_{0.10})\text{O}_3$,^{47,50} $\text{Pb}(\text{Zr}_{0.75}\text{Ti}_{0.25})\text{O}_3$,⁵¹ and $\text{Pb}(\text{Zr}_{0.58}\text{Ti}_{0.42})\text{O}_3$.⁵⁰ Our refined parameters for the rhombohedral PZT are close to those reported for $\text{Pb}(\text{Zr}_{0.75}\text{Ti}_{0.25})\text{O}_3$ in space group $R3m$ ⁵¹ and in reasonable agreement with those reported for $\text{Pb}(\text{Zr}_{0.58}\text{Ti}_{0.42})\text{O}_3$.⁵⁰ An adequate comparison of our parameters for the tetragonal phase with literature values is not possible as only data for the end member PbTiO_3 is available.^{46,52}

An examination of the lattice parameter ratios (c/a) for the tetragonal phase in the five samples studied shows that they fall into two groups. Samples PZT-SGH1, SGH2, and MO have similar c/a ratios and compositions ($\sim 0.45:0.55$ Zr:Ti), and samples PZT-SGLH and SGLI have similar c/a ratios and compositions ($\sim 0.4:0.6$ Zr:Ti). A comparison of our lattice parameters with those in the literature reveals some of the problems associated with using them as an indicator of phase composition. Recently Kakegawa et al.³⁷ reported data for the variation of the lattice constants a and c with composition in tetragonal PZT and the variation of the lattice constant a with composition for rhombohedral PZT. Our refined lattice parameters and compositions for the rhombohedral PZT are consistent with their data. However, using Kakegawa's data, the lattice constants for the tetragonal component of our samples suggest a composition that is significantly different from that determined by our refinement of site occupancies. While the absolute values of our lattice constants may be in error due to calibration with an external standard rather than the internal silicon standard used by Kakegawa et al., the c/a ratios should be reliable. Using our c/a ratios and the data of Kakegawa et al., we would predict that the tetragonal components of our samples would all have $>50\%$ Zr; this is clearly not possible as the bulk sample compositions were 50% Zr and both our refined occupancies and the lattice constants for the rhombohedral phase indicate that it contains $>50\%$ Zr. Klee and co-workers⁵³ have previously reported that the absolute lattice constants and c/a ratios of tetragonal PZT vary with preparation procedure as well as composition. They ascribed this to the influence of grain size on the lattice constants of the tetragonal phase. It is well-known that particle and grain size can play an important role in determining lattice strain for ferroelectrics such as BaTiO_3 ⁵⁴ and PbTiO_3 .⁵⁵ Unfortunately, we are not aware of any work examining in detail the effect of particle size on c/a for tetragonal PZT near to the MPB. However, studies of PbTiO_3 indicate that the reduction of particle size (in this case coherent diffracting domain size) to less than

~ 100 nm leads to a significant decrease in c/a .⁵⁵ The line widths in our X-ray diffraction data for the tetragonal PZT are generally consistent with coherent diffracting domain sizes of less than 100 nm. For example, a rudimentary analysis of the data for samples PZT-MO and PZT-SGH2 (expected to have the largest grain size based on heat treatments) indicated that the materials display some strain broadening, presumably due to compositional fluctuations within the tetragonal PZT, and size broadening consistent with a domain size of ~ 75 nm. It seems likely that the apparent discrepancies between the results from our Rietveld analyses and the measurements of Kakegawa may arise because the lattice constants for the tetragonal phase are dependent upon factors other than composition.

Compositional Inhomogeneity of the Perovskite PZT Samples. The presence of two phases with differing composition in sample PZT-MO is not surprising given the extensive literature reporting the presence of both rhombohedral and tetragonal PZT in samples spanning a wide range of average compositions that were prepared by cofiring binary oxides.^{25,30} However, the refinements for samples PZT-SGH1 and SGH2 clearly demonstrate that our adaptation of a widely used sol-gel route to PZT also produces two-phase samples even after a high-temperature heat treatment. The presence of the two phases is associated with compositional inhomogeneity in the sample and does not require an explanation based on the "quenched in thermal fluctuations" hypothesized by Cao et al.³⁵

While there is strong evidence in the literature that PZT *gels and glasses* prepared by alkoxide sol-gel chemistry are compositionally inhomogeneous (see the Introduction),^{13,17,19,21} reports on the use of solution preparation methods for compositions close to the morphotropic phase boundary usually claim a relatively narrow region for phase coexistence^{32,34} and we are not aware of any other work indicating that the rhombohedral component differs so greatly in composition from that of the bulk sample. The large difference between the compositions of the two phases could arise for a number of reasons: (i) the zirconium-rich rhombohedral phase could be a remnant of the compositional inhomogeneity that other workers^{7,13,24} have observed in PZT glasses prior to complete crystallization, (ii) the rapid heating used for samples PZT-SGH1 and SGH2 could have led to compositional segregation during the firing process, or (iii) there may be a miscibility gap in the phase diagram. We favor the first explanation as we are not aware of any other evidence for a miscibility gap, and the presence of a large composition difference between the rhombohedral and tetragonal PZT phases in samples PZT-SGLH and PZT-SGLI, which were prepared by slowly heating the gels, suggests that the rapid heating of samples PZT-SGH1 and SGH2 was not responsible for the compositional inhomogeneity of these materials. The presence of two phases with differing compositions in all of our samples suggests that none of them had equilibrated on heat treatment. This is significant as the heat treatment used for our sol-gel samples PZT-SGH1 and SGH2 is "severe" when compared to those typically used for sol-gel PZT.

The paucity of reports indicating phase coexistence in alkoxide sol-gel-prepared samples with compositions different from that of the MPB is probably a conse-

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quence of two factors: (i) the excess lead that is commonly used in sol-gel PZT preparations may lead to homogenization of the sample at temperatures close to the melting point of PbO , and (ii) for samples that have been crystallized at low temperatures, such as our materials PZT-SGLH and SGLI, or for samples that contain very little of a poorly crystallized second phase, such as our sample PZT-MO, a close inspection of the diffraction data is needed to detect the presence of two phases, even when quite large amounts of both phases are present.

While the refinement results for samples PZT-SGLH and SGLI are likely to be less reliable than those for the other specimens, as there were no resolved splittings in the diffraction data, the great similarity between the results for the two different samples is of note. Sample PZT-SGLH was prepared from a gel that had been made by the hydrolysis of a supposedly homogeneous solution of molecular precursors, whereas sample PZT-SGLI was prepared from a gel that was produced by mixing prehydrolyzed PT and PZ precursor solutions. The Rietveld refinement results for samples PZT-SGLH and SGLI are similar and the pair distribution functions (PDFs) for these samples are indistinguishable (see Figure 2), suggesting that the local structure in these materials is identical. There are two factors that could be important in explaining the similarity of both the refinement results and the PDFs and, by implication, the similarity of the compositional inhomogeneity in the two samples. Some of the compositional inhomogeneity introduced by prehydrolyzing the PT and PZ precursor solutions and then mixing them could have been lost during the subsequent sample processing steps. This could occur if M-O-M link breaking and reforming took place in the alcogel while it was aging prior to drying. It also seems possible that the hydrolysis of a "homogeneous" solution of precursors leads to a gel with levels of inhomogeneity comparable to that introduced by separately hydrolyzing the PT and PZ precursors due to the markedly different hydrolysis kinetics of the titanium and zirconium alkoxides. The possible role of an M-O-M link breaking and reforming process will be the subject of future work.

As this work is a first attempt at deliberately introducing inhomogeneity into PZT samples, the prehydrolysis procedure that was adopted as part of the "inhomogeneous" sol-gel preparation was not optimized to produce the maximum compositional inhomogeneity in the sample. It is possible that other hydrolysis procedures would have led to more compositional inhomogeneity in the "inhomogeneous" sample.

Conclusions

Our Rietveld refinement results clearly indicate that the use of a common sol-gel processing method for PZT does not guarantee the production of compositionally homogeneous materials. This observation suggests that careful consideration needs to be given to the issue of compositional homogeneity when selecting a synthetic approach to a particular material. Our initial attempt to manipulate the compositional homogeneity of a PZT solid solution, via control of the hydrolysis procedure used during a sol-gel preparation, demonstrates that the hydrolysis of PZ and PT precursors prior to mixing them does not necessarily introduce more compositional inhomogeneity into the final ceramic product than would be obtained if a single solution containing all of the precursor species were hydrolyzed.

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