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Sinterability and Decomposition of $Pb_{0.9175}La_{0.055}Zr_{0.975}Ti_{0.025}O_3$: Influence of Calcination and Sintering Temperature

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The sinterability and decomposition of PLZT, (Pb,La)(Zr,Ti)O₃, depend on the temperature and soaking time of both the calcination and sintering temperature. They were determined from the density, linear shrinkage, weight loss, and appearance of extra phases. At moderate calcination temperatures and times, there is no escape of PbO from the PLZT. At calcination temperatures higher than 1050°C and soaking times above 3 h, PbO escapes, and ZrO_2 and $La_2Zr_2O_7$ can be detected. Even when sintered in a PbO-rich atmosphere, some PbO evaporates during sintering either from free PbO or from the PbO bound in the PLZT in regions in the outer surfaces of the sintered body. An aggressive depletion of PbO during sintering can result in a complete disappearance of the grain boundary phase, giving an intragranular fracture.

I. Introduction

(1) Composition and Structure

THE PLZT, (Pb,La)(Zr,Ti)O₃, is a useful material for pulse discharge multilayer capacitors due to the capability of storing and releasing large amounts of energy,[1] especially for the antiferroelectric orthorhombic PLZT phase for L< ∼0.08 and T< ∼0.075. In our notation, a PLZT composition is designated L/Z/T, indicating the amount of lanthanum, zirconium, and titanium in the structure. For example, the composition $Pb_{1-3x/2}La_xZr_yTi_{1-y}O_3$ is written as $100x/100y/100(1-y)$.

PLZT has a perovskite ABO₃ structure and is a crystalline solution system with La substitution for Pb and Ti substitution for Zr in the PbZrO₃. On substituting La for Pb, vacancies are introduced into the lattice,[1] and when sintered in excess of PbO, only B-site vacancies occur in the so-called B-site formula: $Pb_{1-x}La_x(Zr_yTi_{1-y})_{1-x/4}O_3$, and only A-site vacancies can occur in the A-site formula: $Pb_{1-3x/2}La_xZr_yTi_{1-y}O_3$. It has been stated[2] that PLZT materials often have compositions between the A and B formulas. However, the A site predominates because the PbO partial pressure, necessary to produce a B formulation, is limited by the condensation of liquid PbO at the grain boundaries.[3] Land *et al.*[4] stated that for L≤5%, only A compositions could exist. In the present study, the La concentration of 5.5% is not far from this limit, and in the present study of 5.5/97.5/2.5, the raw materials were prepared using the A formulation and, after sintering, were considered to be the A composition (the A-site vacancy formulation).

(2) Sinterability

Sinterability can be described as the ability to obtain a density near the theoretical density, which is often related to the linear shrinkage. To ensure a high density, extra PbO is added to the formula to avoid PbO depletion during sintering.[1–4] PbO has a melting point at 888°C and therefore a high vapor pressure at sintering temperatures. For these reasons, there is a relatively large amount of liquid PbO grain boundary phase. The sintering process can therefore be categorized as sintering with a reactive liquid.[5] This type of sintering generally results in a rapid densification if (i) there is an appreciable amount of the liquid phase, if (ii) there is an appreciable solubility of the solid in the liquid, and if (iii) the solid is wetted by the liquid. The first criterion is fulfilled as an excess of PbO is added to the formula. The second criterion is also met. See Phase diagrams by Fushimi and Ikeda[6] and by Warzee *et al.*,[7] which show that the solubility of PbZrO₃ in PbO varies from 3 to 6 wt% when going from 1100° to 1300°C. The corresponding numbers for PbTiO₃ in PbO are 50–100 wt%. When La₂O₃ is also present, the solubility of PbZrO₃ and PbTiO₃ becomes even higher.[7–9] Finally, ceramic grain boundary phases, in this case PbO, generally wet well,[5] resulting in a high capillary pressure. These three criteria are responsible for the rearrangement of particles, dissolution, and recrystallization of solid PLZT at contact points toward a more effective packing, before a solid skeleton is formed at which time the densification process stops. When pressing powder into a pellet, the green density generally becomes denser in the exterior. Therefore, pressed bodies have a tendency to have a larger firing shrinkage in the interior than in the outer parts near the surface.[5] Shrinkage also occurs via diffusion of oxygen vacancies from the pores to the outer part of the sample,[3] but this process is comparatively very slow. One of the purposes of this work was to study the densification and linear shrinkage of the 5.5/97.5/2.5 PLZT during sintering.

(3) Thermal Decomposition

The decomposition of PLZT is a measure of how much PbO evaporates from the PLZT during heating. As explained above, the evaporation of PbO into the surroundings was controlled by adding extra PbO to the formula. Extensive efforts have been made to establish an appropriate atmosphere to allow the excess PbO to flow out without PbO disappearing from the PLZT phase.[3,4] A fundamental work was carried out by Härdtl and Rau,[10] who determined the vapor pressure of PbO for pure PbO and of various PZT compositions, for different temperatures. Atkin and Fulrath[3] determined which powder mixtures of PZ, PZT, PT, ZrO₂, and PbO should be used to allow the PZT specimen to equilibrate with the powder to prevent PbO loss from the PZT structure. If, after sintering, there is still some PbO left in the grain boundary phase, it is possible to anneal to a temperature just high enough to allow the PbO to evaporate without losing PbO from the PZT phase.[11,12] Xia and Yao[11] and

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Kingon and Clark[13,14] pointed out that it was also possible to establish an excess PbO vapor pressure in the surrounding atmosphere during sintering. This excess produced lower densities when using a high PbO pressure in the sintering atmosphere. It is important that the powder for maintaining the PbO atmosphere is not in contact with the sintering sample[13,14] unless it has exactly the same composition as the sample, as Ti can diffuse either way depending on the concentrations of Ti in the powder and the sintering body.

The migration of PbO from a PZ structure during sintering was investigated by Northrob.[15,16] By creating a low-PbO environment during sintering, a PbO depletion of the surface occurred. The depletion of PbO took place in two stages: (1) a quick evaporation of free PbO, (2) followed by a slow diffuse-controlled migration of Pb from the PZ lattice. A similar experiment carried out by Xia and Yao[11] showed that $Pb(Zn_{1/3}Nb_{2/3})O_3$ sintered in an atmosphere containing sufficient PbO experienced an intergranular fracture, presumably because of the PbO in the grain boundary, whereas the PbO-depleted structure was porous and had an intragranular fracture. When La was substituted for Pb in the PZT structure, it was found[17] that ZrO_2 and/or $La_2Zr_2O_7$ could be formed. However, the presence of $La_2Zr_2O_7$ may not necessarily be a sign of PbO depletion; it could also be caused by a low temperature during sintering.[17] Further heating would then make $La_2Zr_2O_7$ disappear. The second purpose of the present study was to explore the decomposition of an antiferroelectric PLZT phase (5.5/97.5/2.5) at different calcination and sintering temperatures.

II. Experimental Procedure

(1) Materials: Synthesis and Heating

Raw materials for PLZT powder with the composition 5.5/97.5/2.5 were weighed off as the A composition with 2.5 wt% extra PbO as described earlier.[18,19] Small batches (5 g) were calcined up to the calcination temperature ranging from 400° to 1050°C with a heating ramp of 7° to 8°C/min and a soaking time from 3 to 24 h. Large batches (6 kg) were calcined with a heating ramp of ~1°C/min up to 875–1050°C with a soaking time from 2 to 4 h. A total acceptable weight loss during calcination would be 0.5 wt% from adsorbed water in the raw La_2O_3 material. If some of the extra PbO was lost too, an additional 2.5 wt% loss could stem from the extra PbO.

For sintering, the calcined powder was crushed in a mortar, sieved through a 100-mesh sieve, 4 ± 1 wt% binder was added, and the powder was again sieved through a 100-mesh sieve. Pellets of 12.5-and 25-mm diameter and 2-mm thickness were pressed at a pressure of 20 N/m². Binder burn-out was carried out in air with a ramp rate of RT to 350°C in 150 min, held at 350°C for 120 min, ramped up from 350° to 550°C in 120 min, and held at 550°C for 60 min. The sintering was carried out in covered crucibles in air at 1270° or 1300°C for 2 h at a ramp-up of 10°C/min. The maximum firing temperature was frequently monitored by placing a so-called Tempring (Bickley, Bensalem, PA) on top of the covering crucible. A protective atmosphere was established by placing a boat with fresh PbO source powder inside the crucible during the sintering. The covers did not fit airtight; therefore, PbO can disappear out of the crucible through the gap between crucible and cover. In no case did a significant amount of PbO source powder disappear during the sintering. An acceptable weight loss during binder burn-out and sintering would then stem from: (i) extra PbO if still remaining (2.5 wt%), and (ii) binder burn-out (4 ± 1 wt%).

That would give a total of max 6.5 ± 1 wt% sinter weight loss. In one experiment, a sintering atmosphere of insufficient PbO was produced by placing a Tempring inside the crucible instead of the PbO source powder. The Tempring is very porous and able to absorb large amounts of PbO and thereby produce a PbO-deficient-sintered pellet. In another experiment, an attempt was made to create a dense PbO grain boundary phase by impregnating a pellet with $Pb(NO_3)_2$ before sintering in air.

(2) Characterization Methods

X-ray diffractometry (XRD) of powder was carried out on an automated X-ray powder diffractometer PAD V, Scintag (Santa Clara, CA), using Cu$K\alpha$ radiation and $\lambda = 1.540598$ Å. Powders from crushed pellets were used to ensure average results from the entire pellet. The intensity of each X-ray phase is calculated as the intensity of the strongest peak of this phase normalized to the strongest peak in the entire spectrum. For small batches (5 g), the entire sample was used for X-ray diffraction. For a large sample (6 kg), the sample is powder from the top, middle, and bottom of the crucible.

SEM/EDS (Hitachi S-3500N/EDS PGT, Tokyo, Japan) techniques were used to study morphology and element determination and distribution to visualize phases, including those that were in too small amounts to be detected by XRD.

The loss on ignition at 1000°C for 30 h of raw materials except PbO was determined. For PbO, the test temperature was 700°C. Weight loss during calcination was established by weighing the powder before and after calcination.

Weight loss was also determined for the sintering of the pellets. The density and linear shrinkage during sintering were determined by weighing the pellets and measuring the dimensions.

III. Results and Discussions

(1) Calcination: Temperature, Time, and Batch Size as Parameters

Table I and Fig. 1 describe the calcination of 5 g of powder when calcined for 3 h at temperatures from 400° to 1050°C. The weight loss and phase changes were followed by 50°–100°C intervals. A major part of the weight loss occurred between 550° and 700°C; PLZT was formed between 650° and 700°C. At higher temperatures, small amounts of free PbO appeared, but disappeared again at 900°C. The XRD reflections of the free PbO showed that this phase was $PbO_{1.55}$ (ICDD 27-1200), indicating a Pb_2O_3 structure with Pb vacancies. $La_2Zr_2O_7$ appeared only for high calcination temperatures (1050°C) and long soaking times (≥ 12 h). At that time, all the free PbO had evaporated, together with some of the PbO from the PLZT phase. Figure 1 depicts the weight loss as a function of temperature and time. The reason for the limited weight losses is that PLZT was formed between 650° and 700°C, binding most of the free PbO into the PLZT structure. Figure 1 shows that only very little free PbO, and no PbO from the PLZT phase can evaporate within 24 h at temperatures below 1000°C in the small batches tested. At 1050°C, PbO in PLZT can only evaporate after about 7.5 h, at which time 3% (0.5% from OH groups from the La_2O_3 and 2.5% from the extra PbO) would have evaporated. Most industrial calcination times would be 2–3 h, ensuring no evaporation of PbO from the PLZT.

Table II shows the calcination of 6 kg of powder when calcined at different calcination schedules. The weight loss was only determined for a few of the experiments. It can be seen that the weight loss, as expected, is slightly less than when using 5-g batches, as shown in Table I. The phase distribution varies somewhat between the experiments. The reason may be due to difficulties with taking average powder samples from the 6-kg batch. Second phases can appear in the batches, small amounts of ZrO_2, and larger amounts of $PbO_{1.55}$ and $La_2Zr_2O_7$. These phases did not show up in the small batches when using the same calcination schedules. Table III shows a comparison between small (5 g) and large (6 kg) batches. The second phases for the large batches are calculated as averages from Table II. The reason for the differences between small and large batches of same calcination schedule is not clear.

(2) Sintering: Calcination, and Sintering Conditions as Parameters

In one sintering experiment, two of the large-batch powders were used: one calcined at 950°C/2 h, and the other at 1050°C/3 h.

Table I. Weight Loss and XRD Phases from 5-g Batches of Raw PLZT 5.5/97.5/2.5 after Different Calcination Temperatures and Times

Calcined temperature/ time (°C/h)	Weight loss (wt%)	X-ray phases								
		ZrO_2 (i%)	PbO_L (i%)	PbO_M (i%)	La_2O_3 (i%)	$La(OH)_3$ (i%)	TiO_2 (i%)	PLZT (i%)	$PbO_{1.55}$ (i%)	$La_2Zr_2O_7$ (i%)
Uncalcined	0	23.01	16.48	100	3.80	1.09	Trace	0	0	0
400/3	1.06	20.65	20.11	100	3.80	0	Trace	0	0	0
500/3	1.08	16.13	18	100	3.80	0	Trace	0	0	0
600/3	1.34	12.77	3.2	100	3.26	0	Trace	0	0	0
650/3	1.38	12.23	0	100	3.26	0	0	0	1.06	0
700/3	1.64	0	0	0	0	0	0	100	4.79	0
750/3	1.65	0	0	0	0	0	0	100	3.61	0
800/3	1.71	0	0	0	0	0	0	100	3.11	0
850/3	1.71	0	0	0	0	0	0	100	1.79	0
900/3	1.73	0	0	0	0	0	0	100	0.62	0
950/3	1.72	0	0	0	0	0	0	100	0	0
1000/3	1.81	0	0	0	0	0	0	100	0	0
1050/3	1.93	0	0	0	0	0	0	100	0	0
Uncalcined	0	23.01	16.48	100	3.80	1.09	Trace	0	0	0
900/3	1.73	0	0	0	0	0	0	100	0.62	0
900/6	1.76	0	0	0	0	0	0	100	0.10	0
900/12	1.77	0	0	0	0	0	0	100	0	0
900/24	1.85	0	0	0	0	0	0	100	0	0
Uncalcined	0	23.01	16.48	100	3.80	1.09	Trace	0	0	0
950/3	1.72	0	0	0	0	0	0	100	0	0
950/6	1.76	0	0	0	0	0	0	100	0	0
950/12	1.86	0	0	0	0	0	0	100	0	0
950/24	1.87	0	0	0	0	0	0	100	0	0
Uncalcined	0	23.01	16.48	100	3.80	1.09	Trace	0	0	0
1000/3	1.81	0	0	0	0	0	0	100	0	0
1000/6	1.87	0	0	0	0	0	0	100	0	0
1000/12	2.05	0	0	0	0	0	0	100	0	0
1000/24	2.56	1.78	0	0	0	0	0	100	0	0
Uncalcined	0	23.01	16.48	100	3.80	1.09	Trace	0	0	0
1050/3	1.93	0	0	0	0	0	0	100	0	0
1050/6	2.46	2.14	0	0	0	0	0	100	0	0
1050/12	4.23	0	0	0	0	0	0	100	0	3.61

The intensity of each X-ray phase is given as the intensity of the strongest peak of this phase normalized to the strongest peak in the entire spectrum (i%). PbO_L (litharge). PbO_M (massicot). $PbO_{1.55}$ (near Pb_2O_3 structure). PLZT, $(Pb,La)(Zr,Ti)O_3$.

The sintering took place side by side in the same sintering experiment. See Table IV and Figs. 2 and 3 for details.

The powder calcined at 950°C for 2 h did not contain a second phase. However, $La_2Zr_2O_7$ appeared on sintering at 900–1200°C, and above 1200°C, it disappeared; it probably dissolved in the PLZT as predicted by Schulze *et al.*[17] However, above 1300°C, some of the PLZT disintegrated, and ZrO_2 was formed.
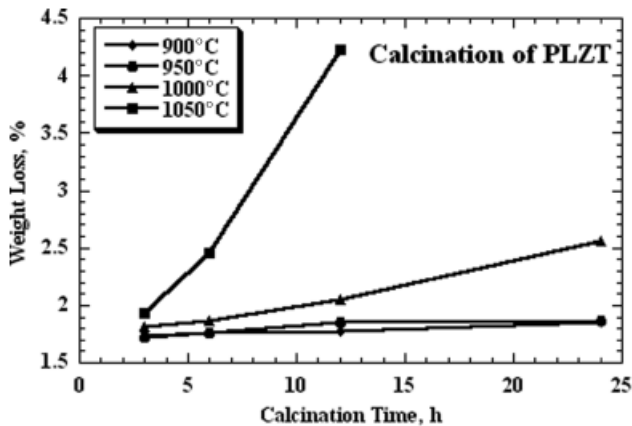
Fig. 1. Weight loss after calcination (5-g batch) at 950°, 1000°, and 1050°C.

Table II. Effect of Different Calcination Schedules in Air

Temperature/ time (°C/h)	Weight loss (wt%)	X-ray data		
		ZrO_2 (i%)	$PbO_{1.55}$ (i%)	$La_2Zr_2O_7$ (i%)
875/4	1.56	0.94	1.93	1.33
950/2	1.51	0.5	2.76	3.84
950/2	1.50	0.2	0.4	0.05
950/2	N/A	0	0.76	0
950/2	N/A	0	2.27	2.27
950/2	N/A	0	2.38	0
950/2	N/A	0	5.29	2.87
950/2	N/A	0	0	0
950/2	N/A	0	1.15	3.33
950/2	N/A	0	1.69	0
950/2[†]	N/A	0	0	0
950/2	N/A	0	0	0
950/2	N/A	1.44	0	0
950/3	N/A	0	1.0	4.39
950/3	N/A	1.15	3.68	0
950/3	N/A	1.0	3.37	0
1050/3	1.75	0	1.82	4.89
1050/3[†]	N/A	0	0	5.88

Phase distribution of PLZT 5.5/97.5/2.5 with 6 kg batches. The intensity of each X-ray phase is given as the intensity of the strongest peak (PLZT) in the entire spectrum (i%). [†]The batches were used for the experiments shown in Table IV. PLZT, $(Pb,La)(Zr,Ti)O_3$.
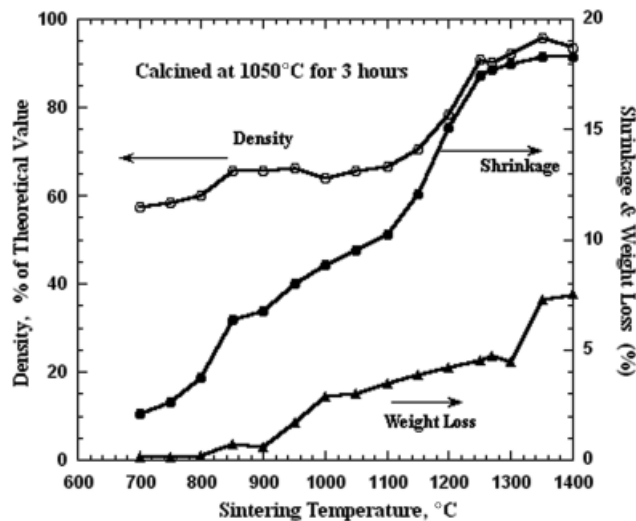
Table III. Effect of Batch Size

Calcined temperature/ time (°C/h)	Batch amount (g)	X-ray data		
		ZrO_2 (i%)	$PbO_{1.55}$ (i%)	$La_2Zr_2O_7$ (i%)
875/4	5	0	1.2	0
875/4	6000	0.9	1.9	1.3
950/2	5	0	0	0
950/2	6000	0.2	1.3	1.0
950/3	5	0	0	0
950/3	6000	0.7	2.7	1.5
1050/3	5	0	0	0
1050/3	6000	0	0.9	5.4

Phase distribution of PLZT 5.5/97.5/2.5 when calcined with different calcination schedules in air. The 6-kg batches are calculated as an average from Table II. The intensity of each X-ray phase is given as the intensity of the strongest peak (PLZT) of this phase normalized to the strongest peak in the entire spectrum (i%). PLZT, $(Pb,La)(Zr,Ti)O_3$.

At 1400°C, further PbO weight loss from the PLZT phase gave a high total weight loss of 17.92 wt%, a low density, and a linear shrinkage slightly higher than that at 1300°C. The powder calcined at 1050°C for 3 h contained $La_2Zr_2O_7$, but this also dissolved in the PLZT when sintered above 1200°C as predicted by Schulze *et al.*[17] No foreign X-ray-detected phases appeared even when sintered at 1400°C, which gave a linear shrinkage that was nearly the same as found when sintered at 1300°C. The density (when sintered at 1400°C) was high and the weight loss was only 7.56 wt%. This is only a fraction larger than the threshold value of $\sim 6.5 \pm 1$ wt% stemming from loss of binder phase and extra PbO, indicating that only a relatively small amount of PbO from the PLZT evaporated. Figures 2 and 3 show that there is a close relationship between density, shrinkage, and weight loss, except at a sintering temperature of 1400°C for the powder calcined at 950°C. At this high temperature, an exceptionally large weight loss occurred.

The only difference between the two powders is that the powder calcined at 1050°C contains $La_2Zr_2O_7$, whereas the powder calcined at 950°C does not. To compare the two calcined powders, the samples sintered at 1300°/2 h were further investigated in the SEM. To avoid artifacts from any polishing agent, the samples were fractured, and both the interior and the exterior parts were studied. According to Table IV, both samples had no foreign phases detected by the XRD, and the same shrinkage.
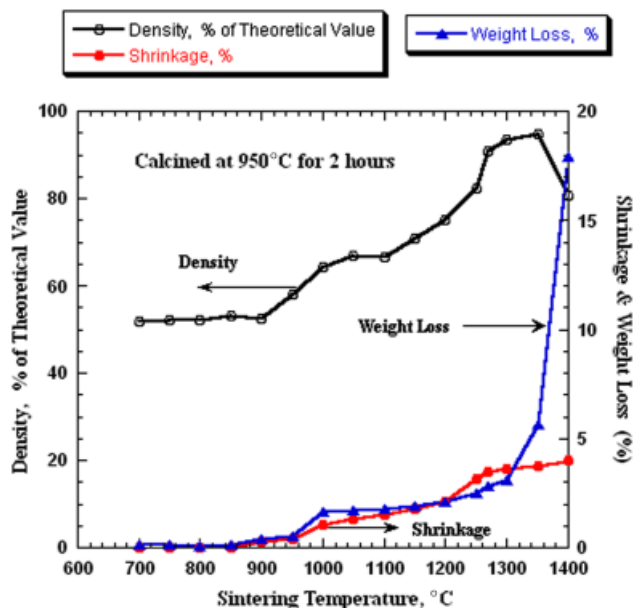
Fig. 2. Density, shrinkage, and weight loss as a function of weight loss for PLZT 5.5/97.5/2.5 calcined at 950°C/2 h (6 kg, large batch).

Fig. 3. Density, shrinkage, and weight loss as a function of weight loss for PLZT 5.5/97.5/2.5 calcined at 1050°C/3 h (6 kg, large batch).

Table IV. Effect of Sintering Temperature

| Calcined temperature/ time (°C/h)	Sintered temperature/ time (°C/h)	Sintering data			Extra X-ray phases	
		Density (% of theor.)	Shrinkage (%)	Weight loss (wt%)	$La_2Zr_2O_7$ (i%)	ZrO_2 (i%)
950/2	Unsintered	—	—	—	0	0
950/2	700/2	51.7	0	0.11	0	0
950/2	750/2	52.2	0	0.11	0	0
950/2	800/2	52.2	0	0.09	0	0
950/2	850/2	53.2	0.17	0.16	0	0
950/2	900/2	52.4	1.24	0.38	1.19	0
950/2	950/2	58.2	2.07	0.50	1.09	0
950/2	1000/2	64.2	5.14	1.62	3.98	0
950/2	1050/2	67.0	6.61	1.71	3.53	0
950/2	1100/2	66.5	7.54	1.77	4.60	0
950/2	1150/2	70.7	8.84	1.93	2.50	0
950/2	1200/2	75.2	10.57	2.10	1.14	0
950/2	1250/2	82.3	15.78	2.47	0	0
950/2	1270/2	90.8	17.53	2.84	0	0
950/2	1300/2	93.4	17.91	3.06	0	0
950/2	1350/2	94.7	18.75	5.67	0	1.35
950/2	1400/2	80.8	19.98	17.92	0	11.63
1050/3	Unsintered	—	—	—	5.88	0
1050/3	700/2	57.4	2.13	0.11	5.29	0
1050/3	750/2	58.5	2.61	0.16	5.88	0
1050/3	800/2	60.0	3.72	0.19	5.61	0
1050/3	850/2	65.5	6.35	0.70	4.48	0
1050/3	900/2	65.6	6.73	0.60	5.60	0
1050/3	950/2	66.2	8.02	1.72	5.37	0
1050/3	1000/2	63.9	8.84	2.90	5.37	0
1050/3	1050/2	65.7	9.49	3.03	5.24	0
1050/3	1100/2	66.5	10.21	3.46	4.06	0
1050/3	1150/2	70.5	12.04	3.84	3.93	0
1050/3	1200/2	78.3	15.09	4.22	1.33	0
1050/3	1250/2	90.9	17.44	4.53	0	0
1050/3	1270/2	90.1	17.74	4.74	0	0
1050/3	1300/2	92.1	17.98	4.43	0	0
1050/3	1350/2	95.8	18.28	7.25	0	0
1050/3	1400/2	93.5	18.31	7.56	0	0

Sintering using large batches of PLZT 5.5/97.5/2.5 powder calcined at 950°C/2h, 1050°C/3 h, respectively. The density (in % of theoretical density) and shrinkage (linear reduction of the sintered pellet, i.e. sintered diameter in % of the green diameter) are a measure of the sinterability. The intensity of each X-ray phase is given as the intensity of the strongest peak of this phase normalized to the strongest peak in the entire spectrum (i%). No $PbO_{1.55}$ was found in any of the samples. PLZT, $(Pb,La)(Zr,Ti)O_3$.
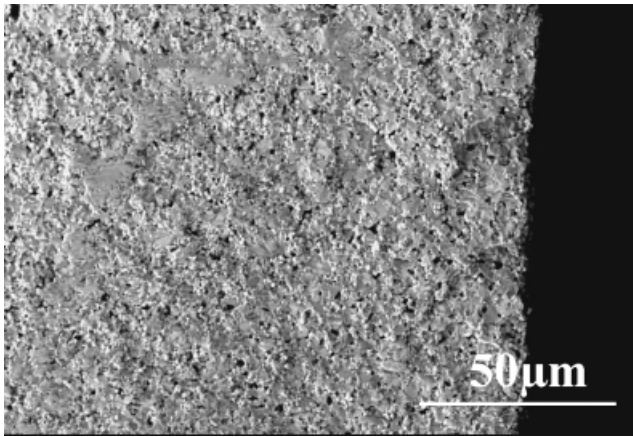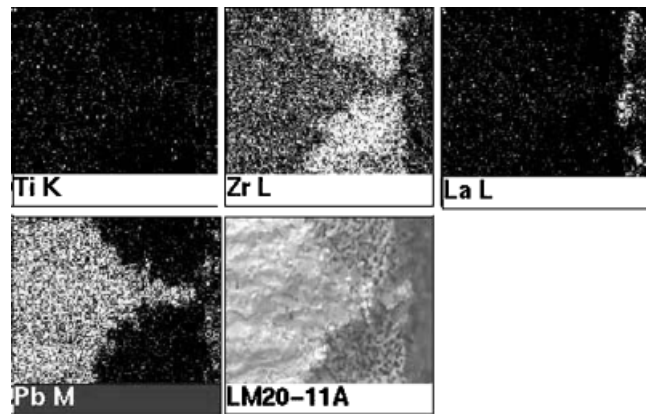
Fig. 4. PLZT 5.5/97.5/2.5 calcined at 950°/2 h (6 kg, large batch) and sintered at 1300°C/2h. SEM image: fractured cross section with top surface to the right.
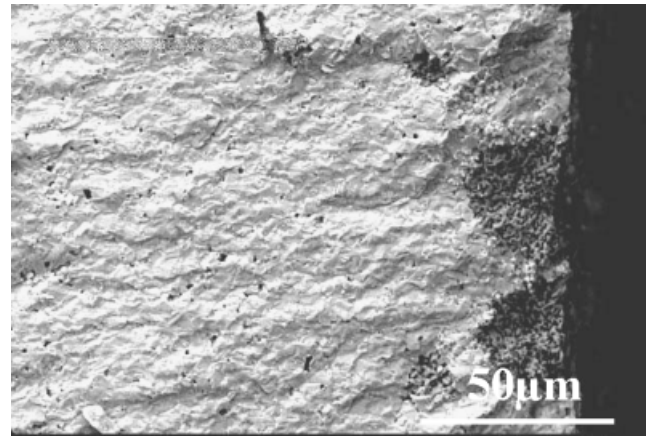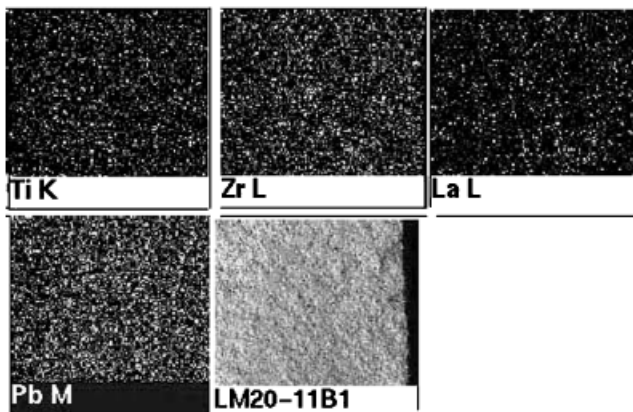

Fig. 6. PLZT 5.5/97.5/2.5 calcined at 1050°C/3 h (6 kg, large batch) and sintered at 1300°C/2 h with a loss of 4.4 wt%. SEM image: fractured cross section with top surface to the right.

The weight loss was slightly smaller and the density slightly larger for the sample made from the powder calcined at 950°C. This sample (Figs. 4 and 5) was homogeneous almost to the edge, but had more porosity in the interior than the sample sintered from the powder calcined at 1050°C (Figs. 6 and 7), which showed different-looking regions in the upper ∼50 µm of the surface. These regions were Pb-deficient and Zr-rich. The very upper ∼10 µm contained large amounts of La. This indicates evaporation of PbO from PLZT near the edge. For this sample, the larger weight loss indicates that more PbO must have evaporated, some of which may be free PbO from the grain boundaries and some may be PbO from the PLZT near the edge. The difference in sintering behavior between the two powders can be seen in Figs. 2 and 3. At sintering temperatures below ∼1200°C, when $La_2Zr_2O_7$ is present (in the sample from powder calcined at 1050°C), it can dissolve in free PbO.[7–9] This leads to a lower temperature for the formation of a liquid grain boundary phase, together with a larger volume of grain boundary phase. Thereby, the formation of the skeleton[5] is delayed, resulting in a higher densification and shrinkage at low sintering temperatures. There may be a connection to the PbO effect as explained by Kingon and Clark.[13,14] They found that a large amount of a PbO-rich liquid phase increases the rate of densification in the initial and intermediate stages, but lowers the final density. The skeleton of PLZT[5] may be formed at a lower temperature in the powder calcined at 950°C (without $La_2Zr_2O_7$). This is in agreement with the higher porosity in this sample. Therefore, the free PbO in the grain boundaries may more easily evaporate from the interior during the sintering rather than PbO from the PLZT.
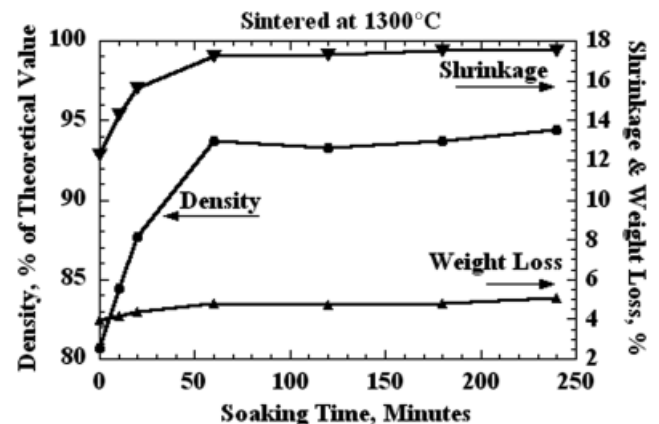

Fig. 7. PLZT 5.5/97.5/2.5 calcined at 1050°C/3 h (6 kg, large batch) and sintered at 1300°C/2 h. X-ray dot map from the area seen in Fig. 6. Zr-rich, Pb-deficient regions are visible. The top surface contains a La-rich phase.

The effect of soaking time for sintering at 1300°C is shown in Fig. 8. As expected, a short soaking time results in poor densities, a low linear shrinkage, and low weight losses. Different soaking times show that optimum sintering in terms of density, linear shrinkage, and weight loss is already obtained at a soaking time of about 50 min, after which there are no major changes. However, an extended soaking time of 200–240 min can lead to further weight loss (see Fig. 8).

Fig. 5. PLZT 5.5/97.5/2.5 calcined at 950°/2 h (6 kg, large batch) and sintered at 1300°C/2 h. Element X-ray dot map from the area seen in Fig. 4.

Fig. 8. Density, shrinkage, and weight loss after sintering of PLZT 5.5/97.5/2.5 (calcined 950°C/3h, 6 kg, large batch) sintered at 1300°C up to 240 min.

Table V. Effect of Pellet Diameter

| Sintering temperature/ time (°C/h)	Radius (mm)	Height (mm)	Volume/ surface (mm⁻¹)	Density (% of theor.)	Shrinkage (%)	Weight loss (wt%)
1300/2	12.2	2	0.75	93.3	17.30	4.58
1300/2	6.1	2	0.60	94.9	13.19	4.31

Sintering using large batches of PLZT 5.5/97.5/2.5 powder calcined at.950°C/3 h. Effect of pellet diameter. The density (in % of theoretical density) and shrinkage (linear reduction of the sintered pellet, i.e. sintered diameter in % of the green diameter) are here used to describe the sinterability. PLZT, (Pb,La)(Zr,Ti)O₃.

(3) Sintering: Pellet Size as a Parameter

The effect of pellet size is shown in Table V. Two pellets, both 2-mm thick, with 12.2- and 6.1-mm diameter, have nearly the same density and weight loss. The green density of the smaller pellet was 56.2% of the theoretical value, and the larger pellet 53.4%. Only slightly higher density and slightly smaller weight loss indicate slightly better sinterability in the smaller diameter pellet. However, there is a significantly larger linear shrinkage in the 12.2-mm pellet. The reason can be explained by the smaller compression of interior material during pressing[5] leading to larger shrinkage in the pellet with more interior material relative to the exterior material (see Table V). The linear shrinkage is therefore an ambiguous measure of the sinterability when using pellets of the same size, pressed, and sintered in the same way.

(4) Sintering: PbO Environment as a Parameter

The effect of PbO environment in the sintering atmosphere was studied. A PbO-deficient atmosphere was created by placing a Tempring inside the crucible instead of the PbO source powder. The Tempring is very porous and able to absorb large amounts of PbO and thereby produce a PbO-insufficient sintered pellet. Also, an experiment with Pb salt impregnation was performed by impregnating the pellet with a Pb(NO₃)₂ solution before the regular sintering. The idea was to introduce PbO evenly around the particles to use PbO as a sintering aid. These two samples were compared with a regularly sintered sample. Table VI shows that there is nearly the same linear shrinkage for all three samples. There was only small difference between the normal PbO pressure samples and the Pb(NO₃)₂-impregnated sample in terms of density and weight loss, and both samples were phase pure. However, for the low PbO pressure sample, the density was significantly lower and the weight loss was significantly higher, and was linked to the appearance of ZrO₂ as an indicator of escape of PbO. A more detailed study was performed on the samples sintered in a normal and PbO-deficient atmosphere. Figure 9 shows SEM images of fractured surfaces of the two pellets. The pellet in the normal PbO atmosphere (Fig. 9(a)) showed an intergranular fracture, indicating that the grain boundary phase is weaker than the PLZT grains. The pellet in the PbO-deficient atmosphere (Fig. 9(b)) showed an intragranular fracture. This is in agreement with the results of Xia and Yao,[11] who found a tendency toward intergranular fracture in
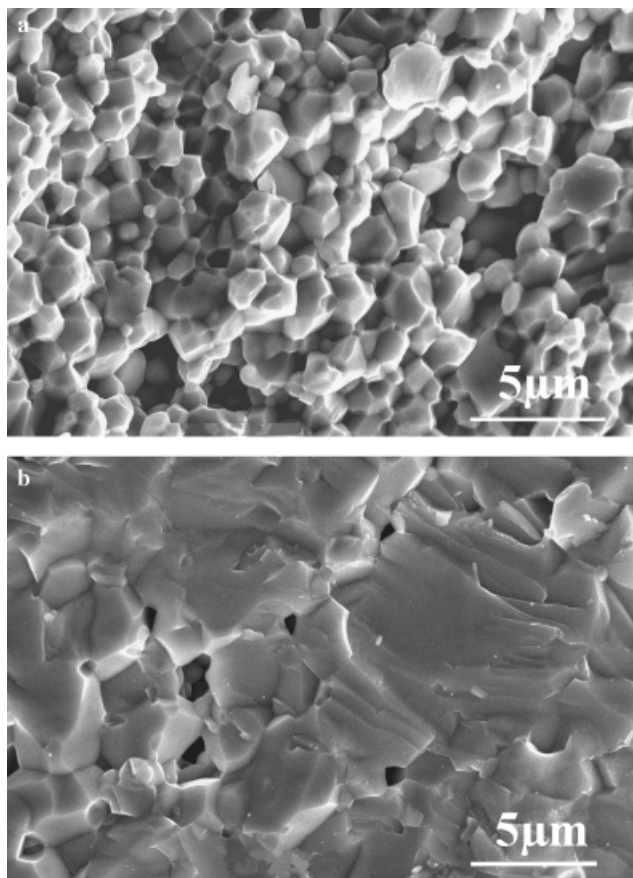
Fig. 9. SEM image of the fractured surface of PLZT 5.5/97.5/2.5. (a) Regular sintering in a covered crucible containing PbO source powder. (b) PbO-deficient sintering atmosphere.

PNZ samples sintered in surplus of PbO and intragranular fracture in samples sintered with a deficiency of PbO. Table VII shows EDS results of fractured surfaces in the interior of the samples sintered in a normal and in a deficient PbO atmosphere as can be seen in Fig. 9. In the latter, some PbO had escaped, leading to a larger ZrO₂ content.

Table VII. EDS Quantitative Analyses of the Fractured Surface Areas Representing the Composition of the Interiors of a Regular and a PbO-Deficient Pellet Described in Table VI

Sintering (wt%)	Normal PbO pressure	Low PbO pressure
PbO	68.0	61.3
La₂O₃	4.4	4.4
ZrO₂	26.9	33.4
TiO₂	0.7	0.9

Table VI. Effect of PbO Environment During Sintering Using Large Batches of PLZT 5.5/97.5/2.5 Powder Calcined at 950°C/3 h

PbO environment	Sinter data			Extra phases		
	Density (% of theor.)	Shrinkage (%)	Weight loss (wt%)	La₂Zr₂O₇ (i%)	ZrO₂ (i%)	PbO₁.₅₅ (i%)
Low PbO pressure	89.0	17.74	11.83	0	2.25	0
Normal PbO pressure	93.4	17.53	4.49	0	0	0
Pb(NO₃)₂ impregnated	95.0	17.20	4.64	0	0	0

Sintered at 1300°C/2 h at three different PbO environments: below normal PbO pressure (Tempring inside the crucible), normal PbO level (regular sintering), and with PbO sintering aid (pellet impregnated with Pb(NO₃)₂). The density (in % of theoretical density) and shrinkage (linear reduction of the sintered pellet, i.e. sintered diameter in % of the green diameter) are used to describe the sinterability. Decomposition is described by weight loss above 6.5 wt% and the formation of new phases from the PLZT. The intensity of each X-ray phase is given as the intensity of the strongest peak of this phase normalized to the strongest peak in the entire spectrum (i%). PLZT, (Pb,La)(Zr,Ti)O₃.

IV. Conclusions

On calcining raw materials for 2 h at temperatures up to 1050°C for 5.5/97.5/2.5, the PLZT structure appears from 650° to 700°C. The weight loss remains well within the margin of extra PbO added to the formula.

Minor phases may appear after the calcination. The presence of PbO indicates that extra PbO is still available. ZrO_2 and $La_2Zr_2O_7$ in amounts of more than 2% and 5%, respectively, may indicate overcalcination.

Sintering of PLZT needs an effective PbO-protective atmosphere. This gives a body with an intergranular fracture.

The presence of $La_2Zr_2O_7$ in the calcined powder can prevent the formation of porosity.

An ineffective PbO-protecting atmosphere results in a large weight loss and results in an intragranular fracture.

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