Low Temperature Sintering of PZT

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Abstract. This paper describes the fabrication and characterization of lead zirconate titanate (PZT) films fired in a liquid-phase sintering process at 900 °C in air. In detail the manufacturing of piezoelectric multilayers with internal pure silver (T_m = 961 °C) electrodes are reported. The feasibility of ten sintering aids in two different volume fractions was investigated for a commercial hard PZT powder (PIC 181, PI Ceramics) with respect to density, microstructure, mechanical behaviour, and piezoelectric properties. Li_2O, Li_2CO_3, PbO, MnO_2, V_2O_5, CuO, Bi_2O_3, the eutectic mixtures $Cu_2O \cdot PbO$ and $PbO \cdot WO_3$ and the ternary system $Li_2CO_3 \cdot Bi_2O_3 \cdot CuO$ (LBCu) have been tested as liquid phase sintering aids. The combination of PZT with LBCu showed the best results. With 5 vol.% LBCu an average relative density of 97% and a characteristic breaking strength of 77 MPa was achieved. Composition of PZT with 2 vol.% LBCu exhibits the highest averaged piezoelectrical charge constant (d_{33}) of 181 pC/N.

1. Introduction

Piezoelectric devices based on PZT ceramic components have a current worldwide market of several billion dollars [1]. Despite lead-containing, PZT is still the most commonly used piezoelectric material, due to the unreached high electromechanical coupling constant. Especially the applications of piezoelectric materials as transducers are continuously growing. Transducers are devices that convert electrical energy into mechanical energy and vice versa. A special kind of transducers are energy harvesters, which use the energy of ambient vibrations to generate electrical energy. A high electrical output is expected for multi-layer bending transducers from hard PZT. For multilayered stacks the inner electrodes have to be co-fired with the ceramic. The electrical connection of PZT in multilayer devices is mostly realized by expensive high-temperature resistant metals, as Pt [2] or Ag/Pd [3]. The usage of cost-effective Ag-electrodes is hampered by the high sintering temperature of PZT, which is about 1200 °C. For sintering temperatures ≤ 900 °C pure Ag-electrodes can be used. Besides cost reduction for electrode material and energy consumption of the firing process, the volatility of PbO is reduced significantly. Due to that the stoichiometric composition of the PZT is more constant, which is necessary to realize stable electromechanical properties and reliable electrical components. Therefore a lot of effort was done and a variety of approaches, like sol-gel method [4], hot-pressing in oxygen [5], the vacuumed-air-venting process [6], or using fine ball-milled powders [7], has already been attempted. Nevertheless the liquid-phase sintering technique remains one of the most successful in lowering the sintering temperature of PZT by several hundred degrees.

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This technique is based on the acceleration of the densification progress by forming a liquid phase out of a lower melting sintering aid, which facilitates rearrangement of the PZT particles and hence lowers the required sintering temperature.

2. Fabrication Process

Piezoceramic green tapes based on a commercial hard PZT powder (PIC 181, PI Ceramics) were manufactured by tape casting. Slurries with a specially developed formulation were prepared with azeotropic mixture of ethanol and toluene as solvent and other organic additives. 3,6,9-trioxadecanoic acid (Clariant) was added as dispersant, polyvinyl butyral (Mowital-B45H, Kuraray) as temporary binder, and polyethylene glycol (Roth) as plasticizer. All slurries were ball-mixed in a planetary mill for 24 h and degased for 15 min directly before tape casting. The tape casted films were dried at ambient conditions. For each sintering aid two slurries with the same composition of PZT powder and organic additives were prepared containing 2 or 5 vol.% of the corresponding sintering aid in relation to the volume of PZT powder. The complex sintering aids were added in their eutectic mixtures. $PbO \cdot WO_3$ containing 16.5 mol% of WO_3 has a melting point of 730 °C [8], while $Cu_2O \cdot PbO$ (1:4) has a melting point of about 680 °C [9]. The ratio of Li_2CO_3, Bi_2O_3, and CuO (1:1:3.7) in the ternary system LBCu was chosen according to Wang *et al.*[10].

2.1. Single-Layer (SL)

Square-shaped green bodies (18 x 18 mm^2 and 12 x 12 mm^2) were punched out of dried green tapes and sintered in ambient air at 900 °C for 3 h. The samples were heated up to 400 °C with a slow heating rate of 1 K/min to ensure a complete removal of the organic additives (debinding). The sintered bodies (≈ 100 µm thick) have been metallized with a silver-conductive varnish (L100, Kemo-Electronic) to realize electrodes on both sides. Poling of each sample was performed in a silicon oil bath at 120 °C for 15 min in an electrical field of 3 kV/mm. Fig. 1 shows the intermediate steps of this fabrication process. Additional to the squared samples, beam-shaped specimens with respect to DIN EN 843-1 were sintered at the same temperature program for bending tests.


Figure 1. Fabrication process of investigated samples: 1. Preparation of a pourable slurry from PZT, organic and sintering additives, 2. Tape casting of films, 3. Punching out green bodies, 4. Debinding and sintering, 5. Metallizing with Ag varnish and poling with 3 kV/mm.

2.2. Multi-Layer (ML)

Beam-shaped pieces were punched out from green tapes. Metallization was performed by coating them with a conductive paste containing Ag-microparticles (Sigma-Aldrich). The metallized layers were stacked in a stepped manner to provide easy access to inner electrodes. The whole stack of alternating ceramic and metallic layers has been sintered in a co-firing process at 900 °C for 3 h. External electrodes (top and bottom) were applied after the co-firing process with a silver-conductive varnish (L100, Kemo-Electronic GmbH). Fig. 2 shows the sintered multi-layered stack including a magnified side view. In a new co-casting process the highly viscous Ag-paste (Sigma-Aldrich) was directly tape casted on a dried ceramic green tape. Subsequently, a second ceramic layer was tape casted on top of the dried Ag-film. This step is depicted in Fig. 3. Beam-shaped bimorphs were cut by laser (DPL *Smart* Marker, ACI Laser) from this co-casted three-layered stack and co-fired at 900 °C for 3 h. Access to the inner electrode was realized after the sintering process by removal of a squared area of the upper ceramic layer by laser treatment. This laser structured entry to the internal Ag-electrode is shown in a SEM micrograph in Fig. 4 (upper right corner).
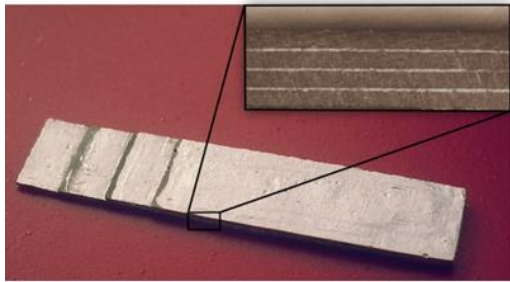
Figure 2. Co-fired multilayer with Ag-electrodes fabricated by stacking. No degradation of Ag or de-lamination of the layers was observed by SEM.
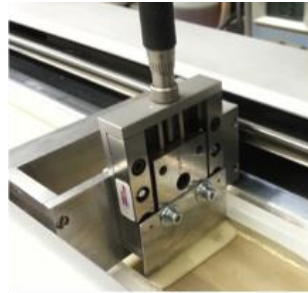
Figure 3. Co-casting plant (on lab scale) for manufacturing ML without stacking of SLs.
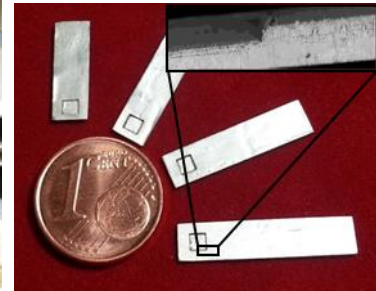
Figure 4. Co-casted bimorphs. Tailoring and access to the inner Ag-electrode was made by laser treatment.

3. Characterization

Densities of sintered bodies (single-layers), as depicted in Fig. 5, have been determined from their geometrical dimensions for assaying the potency of the sintering aids on densification progress of the PZT particles. Layer thicknesses have been measured with a digital measuring sensor system (MT 25, Heidenhain). Theoretical densities for each composition were calculated as mean values with respect to the volume fractions of the powder components. Relative densities were related to the theoretical densities of each composition. Microstructure was analyzed by SEM (Phenom G2 pro). For meeting a reliable statement concerning the mechanical stability of the sintered bodies from all PZT-based compositions 3-point-bending tests have been performed on specially prepared specimens from the same green tapes with dimensions referring to DIN EN 843-1. The characteristic breaking strengths were evaluated with Weibull statistic using the Maximum-Likelihood-Method. Longitudinal piezoelectric charge constants d_{33} have been determined by means of the piezoelectric d_{33} testing system PM300 (Piezotest).

4. Results and Discussion

Due to different efficiencies of added liquid sintering aids the sintered bodies show different thicknesses and sizes. A sample of each composition is pictured in Fig. 5. It must be taken into consideration that the investigated amounts of sintering aids are differently well suited for each PZT-aid combination. While PZT with PbO, Bi_2O_3 or $PbO\cdot WO_3$ shows improved mechanical and piezoelectric properties with increased amount of sintering aid, the Li-compounds suffer from significantly deteriorated piezoelectric properties (see Tab. 1). For usage of Li_2O or Li_2CO_3 as a sintering aid for PZT significantly lower amounts than 2 vol.% are recommended [11]. In this study we used these amounts to give a direct comparison for equal volume fractions of all sintering aids.


| MnO_2 | V_2O_5 | Bi_2O_3 | Li_2O | Li_2CO_3 | LBCu | CuO | $Cu_2O\cdot PbO$ | PbO | $PbO\cdot WO_3$ |
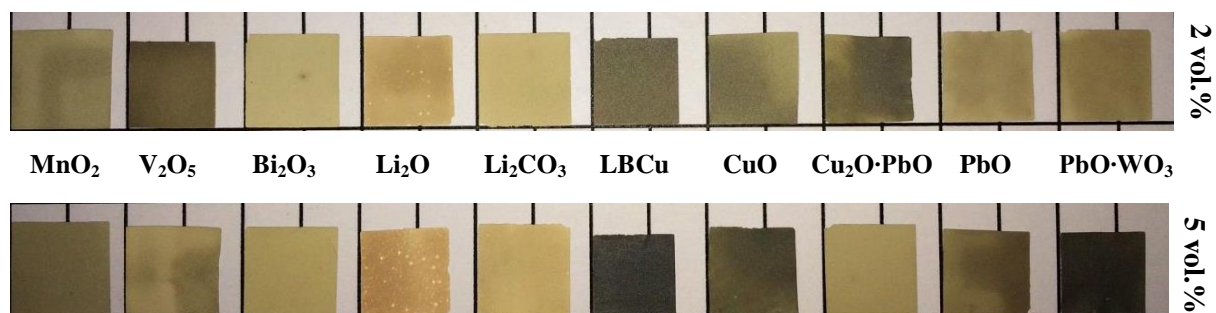
Figure 5. Sintered bodies from compositions of PZT with 2 and 5 vol.% of sintering aids.

4.1. Dimensional Reproducibility

A balanced and reliable shrinking behavior is crucial to dimensional reproducibility of future piezoelectric devices. Quite obvious is the imbalanced shrinkage of samples with $Cu_2O \cdot PbO$ or PbO as sintering aid (see Fig. 5). Samples with V_2O_5, Li_2O and CuO show also an imbalanced shrinkage, which causes distortion of the originally squared sample shape. The unequal discoloration of these samples is another hint for the inhomogeneous microstructure of these material composites. Shrinkage of the sintered bodies of PZT with MnO_2 after sintering at 900 °C is so low that it seems to be regular. A balanced shrinkage behavior was obtained for PZT with the sintering aids Li_2CO_3, Bi_2O_3 or the complex sintering aid LBCu, which is a combination of these aids and CuO.

4.2. Mechanical stability

Extremely brittle are samples with MnO_2 as sintering aid. Samples of PZT with Li_2O, Li_2CO_3 or Bi_2O_3 exhibit hardly any higher breaking strengths (see Tab. 1). Due to insufficient densification of the PZT particles in these composites the microstructure remains porous during sintering at 900 °C (see Fig. 6). PbO is also not able to effect an adequate densification of the PZT particles. Nevertheless, the samples with PbO revealed average breaking strengths above 40 MPa. Combination of PZT with V_2O_5 shows also low densification. However, V_2O_5 stabilizes the porous PZT matrix through a formation of V_2O_5-ligaments on the surface (see Fig. 6). For that reason breaking strengths above 50 MPa were measured for PZT with V_2O_5. The sintering aids CuO and Li_2O accumulate also on the surface of the sintered bodies. Unlike in the case of the Li-compounds, the compositions with CuO delivers mechanical very stable films with a high average breaking strength of 66 MPa for the addition of 2 vol.% (see Tab. 1). Significant densification of the PZT particles and formation of sintering necks during the sintering process at 900 °C were observed for samples with 5 vol.% of $Cu_2O \cdot PbO$ or $PbO \cdot WO_3$ (see Fig. 6). However, cracks within these materials obviously reduce their mechanical stability. Actually dense sintered and stable films with significant grain growth of the PZT particles are provided by the addition of 5 vol.% LBCu. Samples with this composition showed the highest average relative density of 97 ± 3 % and a characteristic breaking strength of 77 MPa.
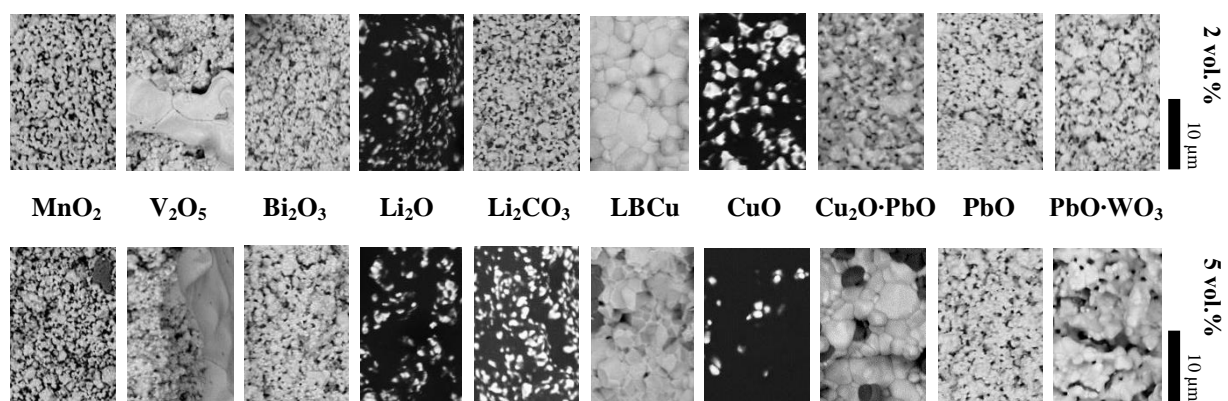
Figure 6. SEM micrographs of the surfaces of sintered films from compositions of PZT with 2 and 5 vol.% of sintering aids.

4.3. Piezoelectric charge constant

In principle, all sintering additives have to be considered as impurities which remain in the PZT matrix and cause a deterioration of the piezoelectric properties. Concurrently, sintering aids support the densification progress of the PZT particles. For most of the samples with 5 vol.% of sintering additive we measured lower d_{33} values compared to the corresponding samples with 2 vol.%. Strongly enhanced d_{33} values were obtained for samples with an increased amount of $PbO \cdot WO_3$ or V_2O_5 (see Tab. 1). The highest average d_{33} value of 181 pC/N was measured for films out of PZT and 2 vol.% LBCu.

We assume that the content of CuO in LBCu is responsible for this high piezoelectric constant, since all samples containing CuO (or Cu_2O in low amounts) show extraordinary high d_{33} values (see Tab. 1). Due to the increased d_{33} values of samples with 5 vol.% $PbO \cdot WO_3$ of 143 pC/N in average, we suggest that WO_3 could have a similar effect as CuO. This piezoelectric properties increasing effect could be related to the semiconductive nature of CuO [12] and WO_3 [13].

Table 1. Density, characteristic breaking strength and piezoelectric charge constant of PZT-based, at 900 °C sintered films in relation to sintering aid amount.

Sintering additive	2 vol.%					5 vol.%				
	ρ_{abs} [g/cm^3]	ρ_{rel} [%]	σ_0 [MPa]	$d_{33}(\text{ø})$ [pC/N]	d_{33} (max) [pC/N]	ρ_{abs} [g/cm^3]	ρ_{rel} [%]	σ_0 [MPa]	d_{33} [pC/N]	d_{33} (max) [pC/N]
MnO_2	4.2	55	12	13	14	4.5	59	10	4	5
V_2O_5	5.7	74	61	51	70	5.8	77	51	67	**140**
Li_2O	5.3	69	29	34	74	5.7	76	24	17	37
Li_2CO_3	4.9	63	31	79	**146**	5.7	75	34	53	82
Bi_2O_3	4.8	62	22	29	42	5.6	71	53	34	71
LBCu	6.3	**81**	49	**181**	**246**	7.4	**97**	**77**	98	113
CuO	5.8	70	**66**	136	**196**	6.0	78	58	134	**262**
$Cu_2O \cdot PbO$	5.7	74	45	126	**151**	5.6	72	36	46	52
PbO	5.4	69	40	30	46	6.4	81	48	34	46
$PbO \cdot WO_3$	5.4	69	26	59	67	7.0	89	55	**143**	**185**

5. Conclusion

CuO cannot be considered a liquid phase sintering aid in original sense, since its melting point is about 1326 °C. However, its addition increases significantly both, the piezoelectric properties and the mechanical stability of hard PZT films. LBCu, a combination of Li_2CO_3, Bi_2O_3 and CuO, acts as a great sintering aid for PZT. The highest average piezoelectric constant was measured for PZT with 2 vol.% LBCu. Additionally, LBCu provides the highest densification progress of all investigated PZT-sintering aid composites. With an addition of 5 vol.% LBCu a relative density of PZT-based films (≈100 μm thick) of 100% could be achieved after sintering at 900 °C for 3 h.

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