Comparison of Sintering Aids for Low Temperature Sintering of Hard PZT

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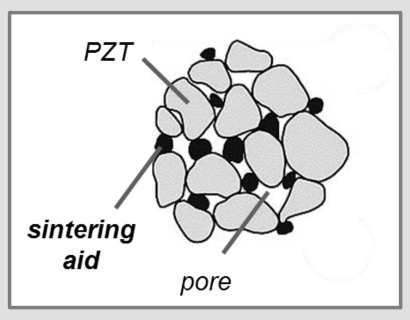
Introduction

- **PZT** ($PbZr_xTi_{1-x}O_3$) is the most commonly used piezo ceramic
- **100 µm thick PZT-films** were fabricated by tape casting methode and **sintered** in air for 3h **@ 900 °C** instead of normally needed 1200 °C
- **Used Technique:**



LIQUID-PHASE SINTERING

Acceleration of densification of the major phase particles (PZT) by adding of lower melting sintering aids which form a liquid phase and facilitate the rearrangement and grain growth of the matrix phase at significantly reduced sintering temperatures.

Advantages of LT-Sintering of PZT

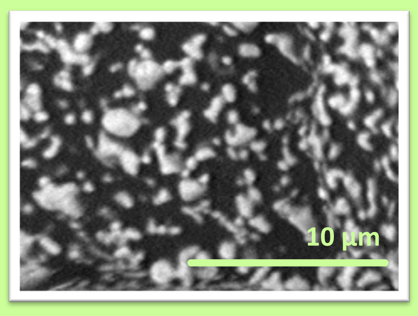
MATERIAL COMPATIBILITY	STABILIZATION OF ELECTROMECH. PROP.	REDUCTION OF PROCESS COSTS
Co-firing of multilayer stacks made from PZT- and **LTCC-layers or internal electrodes from pure Ag**	**Evaporation of volatile PbO** out of PZT during the sintering process is **suppressed**, so that stoichiometric composition of PZT is stabilized and subsequent piezoelectric **components** become **more reliable**	**Less cost-effective electrodes** from Ag instead of Pt or Ag/Pd-alloys **Less environmental pollution** through evaporation of Pb-compounds **Less energy consumption** through lowered sintering temperatures

Results

Sintering aid amount

Contents of Li-compounds above 1 vol-% deteriorate the piezoelectr. prop. of PZT.

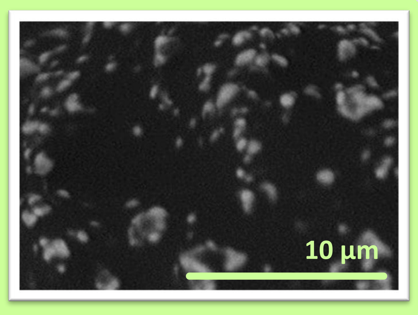
+ Li_2CO_3



T_m = 720 °C

Amount	2 vol-%	5 vol-%
ρ [%]	4.9	5.7
$σ_0$ [MPa]	31	34
Ø-d_{33} [pC/N]	79	53
max. d_{33} [pC/N]	**146**	**82**

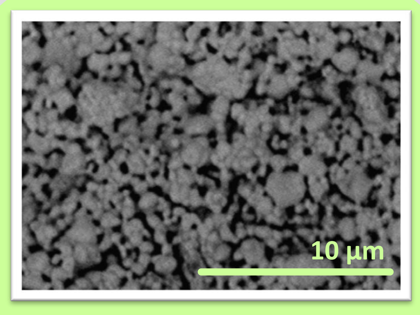
+ Li_2O



T_m = 1427 °C

Amount	2 vol-%	5 vol-%
ρ [%]	5.3	5.7
$σ_0$ [MPa]	29	24
Ø-d_{33} [pC/N]	34	17
max. d_{33} [pC/N]	**74**	**37**

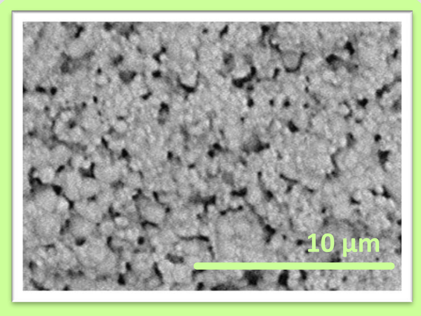
+ MnO_2



T_m = 535 °C

Amount	2 vol-%	5 vol-%
ρ [%]	4.2	4.5
$σ_0$ [MPa]	12	10
Ø-d_{33} [pC/N]	13	4
max. d_{33} [pC/N]	**14**	**5**

+ PbO



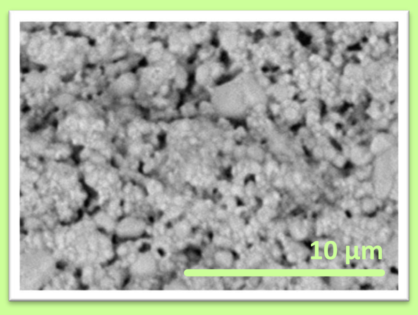
T_m = 888 °C

Amount	2 vol-%	5 vol-%
ρ [%]	5.4	6.4
$σ_0$ [MPa]	40	48
Ø-d_{33} [pC/N]	30	34
max. d_{33} [pC/N]	**46**	**46**

Mechanical stability

*High characteristic breaking strengths $σ_0$ above 50 MPa were obtained for **addition of V_2O_5, LBCu, CuO** and higher amounts of PbO, Bi_2O_3 or PbO·WO_3*

+ Bi_2O_3

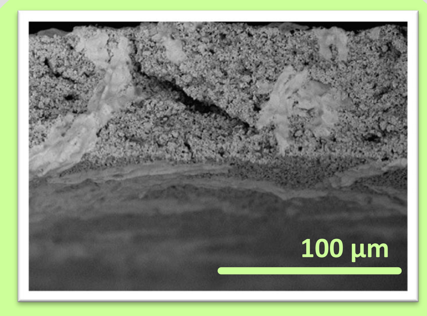


T_m = 817 °C

Amount	2 vol-%	5 vol-%
ρ [%]	4.8	5.6
$σ_0$ [MPa]	22	53
Ø-d_{33} [pC/N]	29	34
max. d_{33} [pC/N]	**42**	**71**

PZT

+ V_2O_5



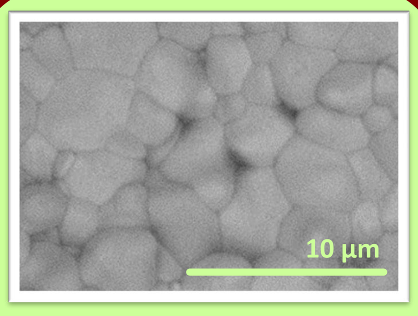
T_m = 690 °C

Amount	2 vol-%	5 vol-%
ρ [%]	5.7	5.8
$σ_0$ [MPa]	61	51
Ø-d_{33} [pC/N]	51	67
max. d_{33} [pC/N]	**70**	**140**

Piezoelectr. Properties

*A sufficiently dense micro-structure and the highest piezoelectric charge constant **d_{33} of 181 pC/N** provide the @ 900 °C for 3h sintered **PZT-films with** sintering aid **LBCu** (2 vol%).*

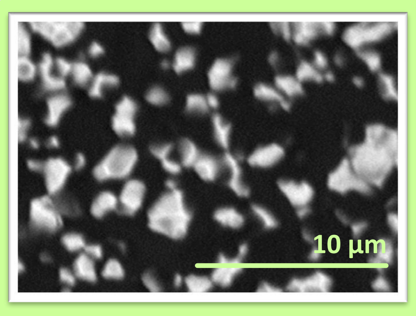
+ LBCu



Li_2CO_3·Bi_2O_3·CuO (1:1:4)

Amount	2 vol-%	5 vol-%
ρ [%]	6.6	7.4
$σ_0$ [MPa]	49	77
Ø-d_{33} [pC/N]	181	98
max. d_{33} [pC/N]	**246**	**113**

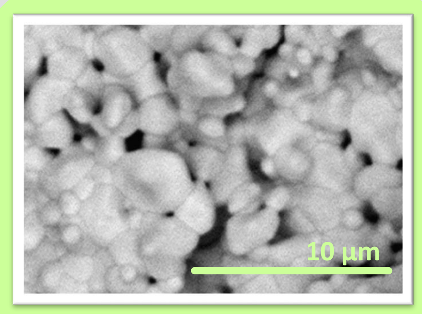
+ CuO



T_m = 1326 °C

Amount	2 vol-%	5 vol-%
ρ [%]	5.8	6.0
$σ_0$ [MPa]	66	58
Ø-d_{33} [pC/N]	136	134
max. d_{33} [pC/N]	**196**	**262**

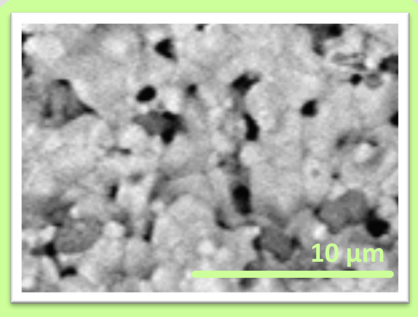
+ Cu_2O·PbO



eutectic mixture, T_m = 680 °C

Amount	2 vol-%	5 vol-%
ρ [%]	5.7	5.6
$σ_0$ [MPa]	45	36
Ø-d_{33} [pC/N]	126	46
max. d_{33} [pC/N]	**151**	**52**

+ PbO·WO_3



eutectic mixture, T_m = 730 °C

Amount	2 vol-%	5 vol-%
ρ [%]	5.4	7.0
$σ_0$ [MPa]	26	55
Ø-d_{33} [pC/N]	59	143
max. d_{33} [pC/N]	**67**	**185**

V_2O_5-Ligaments

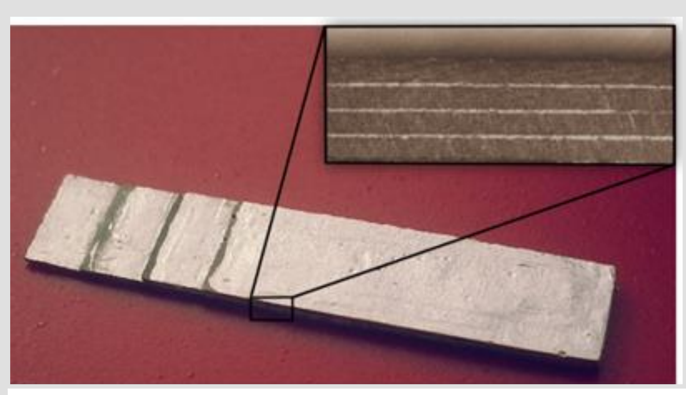
Addition of V_2O_5 increases the mechanical stability by formation of V_2O_5-ligaments through the still porous PZT-matrix. Densification of the PZT particles remains low.

Conclusion

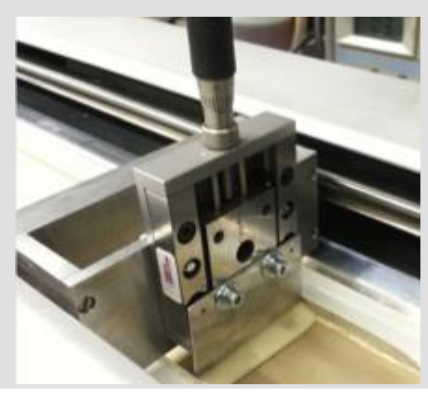
- Most effective sintering aid for hard PZT is the ternary system LBCu (Li_2CO_3:Bi_2O_3:CuO, 1:1:4).
- Highest densification progress of PZT particles with a relative density of 97 ± 3 % and highest characteristic breaking strength of PZT-films sintered @ 900 °C was achieved with 5 vol-% LBCu as sintering aid.
- Highest piezoelectric charge constant in average (181 pC/N) was measured for PZT-films with 2 vol-% LBCu.
- The combination of hard PZT and CuO leads to increased piezo-electric properties, while contents of Li-compounds in the investigated volume range deteriorate the piezoelectric properties of PZT significantly.

Outlook

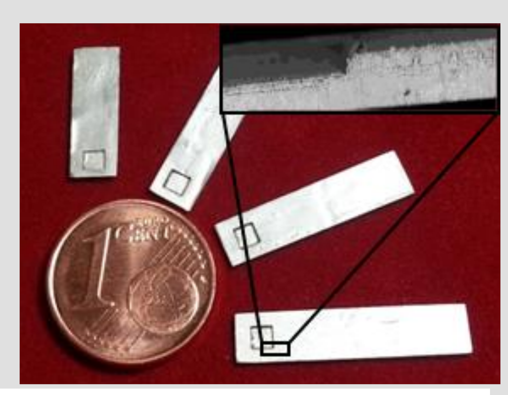
Development of a new fabrication method for piezoelectric bimorphs and multilayer by **Co-Casting** a whole stack of alternating sheets from PZT and Ag **instead of Tape Casting** of single PZT green tapes, which have to be metallized individually, stacked properly and laminated without distortion.



Co-fired multilayer manufactured from metallized single green tapes. Access to internal Ag-electrodes realized by stepped stacking with the problem that the undermost layer is not stable.



Co-casting setup on lab scale for multilayer stacks manufacturing out of alternating cera-mic and metal layers.



First co-casted bimorphs tailored by punching out. Access to the internal Ag-electrode was made by laser treatment.

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