

# Piezoelectric properties and conductivity of $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$ with $\text{SrO}-\text{WO}_3$ additive

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**Abstract** The influence of  $\text{SrO}-\text{WO}_3$  additive on the piezoelectric properties and electric conductivity of lead zirconate–titanate (PZT) near the morphotropic phase boundary was investigated. Starting from the composition  $0.995 \text{ Pb}(\text{Zr}_{0.525}\text{Ti}_{0.475})\text{O}_3 + 0.015 \text{ SrO} + 0.005 \text{ WO}_3$  (corresponding to 0.5 mol% of  $\text{Sr}_3\text{WO}_6$ ) the fraction of  $\text{WO}_3$  was increased until  $\text{Sr}:\text{W} = 1:1$ . These samples were compared to a set of samples of PZT with  $\text{WO}_3$  addition but without SrO.  $\text{Sr}_3\text{WO}_6$  has pseudocubic  $\text{K}_2\text{NaAlF}_6$  structure with part of the strontium being octahedrally coordinated. In a solid solution with PZT this opens the possibility of realizing Sr on a B-site adjacent to a B-site occupied by W. Piezoelectric properties were measured on sintered disc samples under high field conditions. Impedance spectroscopy was used to investigate the conductivity and dielectric properties of the ceramics at various temperatures. The combined addition of SrO and  $\text{WO}_3$  increases the piezoelectric strain compared to samples of PZT with  $\text{WO}_3$  addition only. The results in polarization and conductivity indicate that the donor effect of  $\text{WO}_3$  is counteracted by the addition of SrO.

## Introduction

Especially for actuator applications piezoelectric ceramics based on lead–zirconate–titanate are under development in order to improve strain, efficiency, and life-time of the actuator, because their properties still exceed those of all lead-free systems. Donor- and acceptor doping have shown to be successful concepts in order to adjust the materials properties to a wide range of applications [1]. Recently, interest arose in more complex doping systems involving alkaline earth elements together with tungsten [2, 3]. The role of alkaline earth elements, which are isovalent substituents for lead on the A-site of the perovskite system, should be mostly the lowering of the phase transition temperature (9.5 K/mol% according to [4]). This would lead to a higher permittivity at room temperature, which in turn may cause a slight increase of the strain constant  $d_{33}$ . The electrical doping effect is then left to tungsten, which acts as an effective donor dopant. Further,  $\text{PbO}-\text{WO}_3$  additive with eutectic composition assists the densification process by liquid phase formation [5]. On the other hand in phase diagrams of alkaline earth elements (AE) with  $\text{WO}_3$  [6, 7], a compound according to  $\text{AE}_3\text{WO}_6$  was identified and crystallographically described by Steward and Rooksby [8] as  $\text{K}_2\text{NaAlF}_6$ -type with space group Fm-3m and lattice constants ranging from 8.02 Å for  $\text{Ca}_3\text{WO}_6$  to 8.62 Å for  $\text{Ba}_3\text{WO}_6$ . This structure is very similar to a perovskite with one-third of the alkaline earth ions being on octahedrally coordinated sites (B-site of a perovskite system, respectively). In a solid solution with lead zirconate–titanate (PZT) this would open the possibility to find Sr on B-site adjacent to a B-site occupied by W. Such a doping concept was proven in a solid solution of PZT with strontium niobate by Feltz et al. [9]. This remarkable site occupancy could induce further effects on the piezoelectric properties of this system.

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The objective of this work was to investigate the influence of SrO–WO<sub>3</sub> additive on the piezoelectric properties and electric conductivity of PZT near the morphotropic phase boundary. A series of PZT with WO<sub>3</sub> ranging from 0.5 to 1.5 mol% was compared with a series additionally containing 1.5 mol% SrO. The sample of PZT with 1.5 mol% SrO and 0.5 mol% WO<sub>3</sub> corresponds to a solid solution of 0.5 mol% Sr<sub>3</sub>WO<sub>6</sub> (or 1 mol% Sr[Sr<sub>0.5</sub>W<sub>0.5</sub>]O<sub>3</sub>) in PZT.

## Experimental procedure

Ceramic powders were prepared by mixing the single compounds (Pb<sub>3</sub>O<sub>4</sub> from Penarroya Oxide, ZrO<sub>2</sub> from MEL Chemicals, TiO<sub>2</sub> from Tronox, SrCO<sub>3</sub> from HP Solvay, WO<sub>3</sub> from Merck) in an agate mortar with ethanol. The set of compositions is shown in Table 1. All compositions contained a lead oxide excess of 2 mol%. As reference an undoped PZT with the same excess of lead oxide was taken. After calcination in a box furnace at 925 °C/5 h, the powder was milled in a planetary mill (Fritsch Pulverisette 4) to an average grain size of 0.5 μm. The powder was mixed with binder (3%w PEG 20000) and pressed to pellets of 13 mm diameter at 350 kg/cm<sup>2</sup>. Debinding and sintering was carried out in a box furnace at 1110 °C for 2 h in an alumina crucible covered with PZT-powder. The density of the samples exceeded 96% of theoretical density except that of the reference, which exhibited 93% of theoretical density. The sintered pellets were grinded and gold electrodes were sputtered for polarization measurements. Poling was done with 2.5 kV/mm electric field at room temperature with a FGK 12500 High Voltage Source. The strain constants and relative permittivities were measured under high field conditions ( $E_{\max}$ : 2.0 kV/mm) with a strain measuring sensor Mahr Militron 12021C. For conductivity and relative permittivity measurements, silver paste was deposited on the two sides of each sample; test experiments showed that it played no role whether or not the sputtered Au electrodes were removed prior to silver electrode deposition. The impedance of each specimen was measured by using an impedance analyser PSM1735 (incl. interface IAI) from Newtons4th Ltd in the frequency ranging from 0.01 Hz to 500 kHz at temperatures from ca. 265 °C to 520 °C. X-ray diffraction patterns of sintered pellets were

**Table 1** Set of compositions of sintered samples of PZT with SrO and WO<sub>3</sub>

99.5 mol% Pb(Zr <sub>0.525</sub> Ti <sub>0.475</sub> )O <sub>3</sub> + x mol% WO <sub>3</sub> + y mol% SrO + 0.02 mol% PbO			
Series 1, y = 0	x = 0.5	x = 1.0	x = 1.5
Series 2, y = 1.5	x = 0.5	x = 1.0	x = 1.5

measured on a Siemens D5005 diffractometer and showed single phase perovskite. Micrographs of fractured samples were taken on a JEOL JWF 751-5 scanning electron microscope. The average grain size of the samples was determined from the micrographs by the line section method.

## Results and discussion

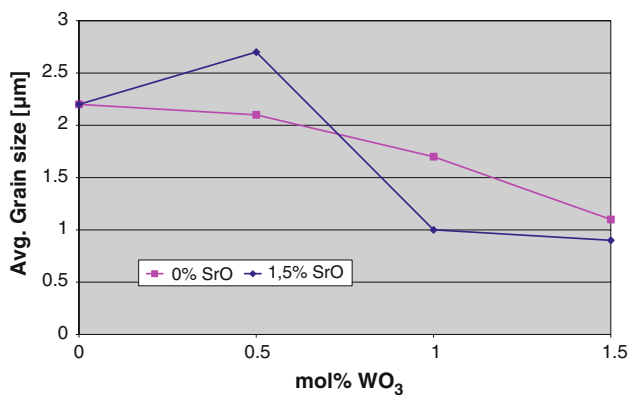
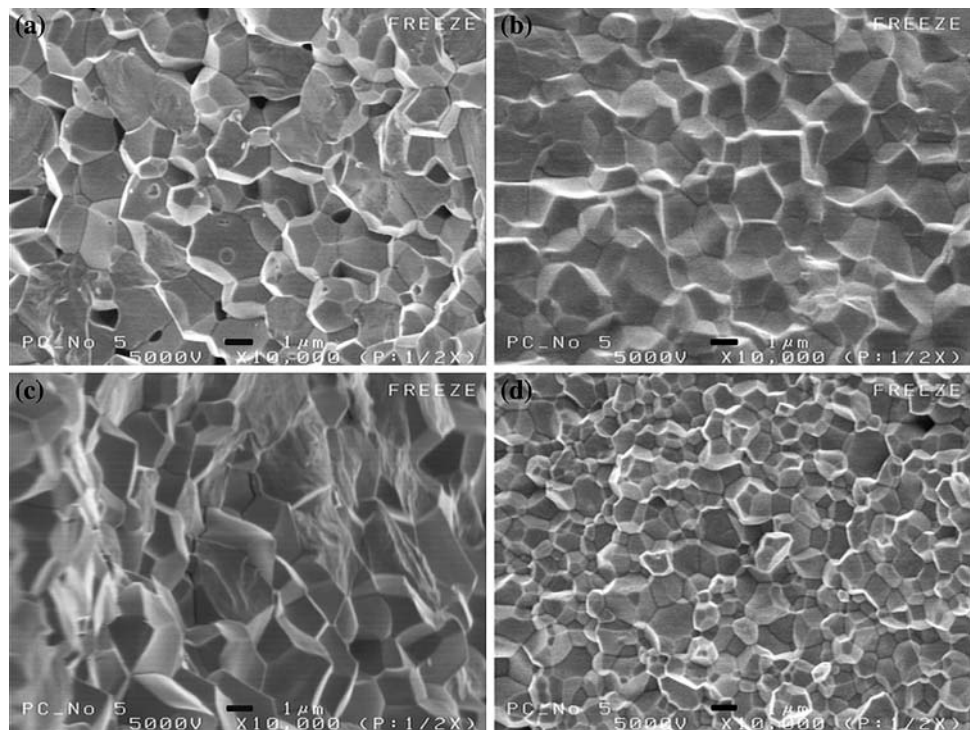
The micrograph of the fractured surface of the undoped PZT reference (Fig. 1a) shows a porous ceramic with an average grain size of about 2.2 μm (±0.1 μm). Addition of 1 mol% of WO<sub>3</sub> decreases porosity while the grain size remains the same (Fig. 1b). Figure 1c shows the fractured surface of PZT with 0.5 mol% WO<sub>3</sub> and 1.5 mol% SrO. The ceramic is well densified with an increased grain size compared to the sample with 1 mol% WO<sub>3</sub> only. Figure 1d shows the fractured surface of PZT with 1 mol% WO<sub>3</sub> and 1.5 mol% SrO. The ceramic is again well densified but the grain size is reduced to approximately 1 μm. The development of the average grain size over composition is shown in Fig. 2. WO<sub>3</sub> addition continuously decreases the grain size. Remarkable is the increase in grain size observed at the sample with 0.5 mol% WO<sub>3</sub> and 1.5 mol% SrO.

The data of the strain constant  $d_{33}$  of the samples are presented in Fig. 3a. The addition of 1.5 mol% of SrO increases the strain constant in all cases. A maximum is reached in PZT with 1 mol% WO<sub>3</sub> and 1.5 mol% SrO. The decrease of the strain of the sample with 1.5 mol% WO<sub>3</sub> and 1.5 mol% SrO possibly indicates a slight shift of the morphotropic phase boundary. Figure 3b shows the relative permittivity of the samples. After a drop compared to the undoped sample the permittivity raises again with increasing WO<sub>3</sub> content. The sample with 1.5 mol% WO<sub>3</sub> and 1.5 mol% SrO shows a decrease of the permittivity, which might be again due to a shift of the morphotropic phase boundary.

The polarization curves (Fig. 4) of the PZT with WO<sub>3</sub> addition (without SrO) showed that 0.5 mol% WO<sub>3</sub> increased the polarization, but decreased the coercive field which is in accordance with the donor effect of WO<sub>3</sub>. For higher WO<sub>3</sub> content, polarization decreased and the coercive field slightly exceeded that of the undoped sample. For 1.5 mol% SrO and 0.5 mol% WO<sub>3</sub> the sample exhibited the highest polarization maintaining the coercive field. By further increase of the WO<sub>3</sub> content the coercive field is significantly increased but polarization decreases.

Impedance spectra showed a single semicircle in the complex impedance plane and the corresponding DC-resistance, obtained from the intercept with the axis of the real impedance part, was used to calculate the

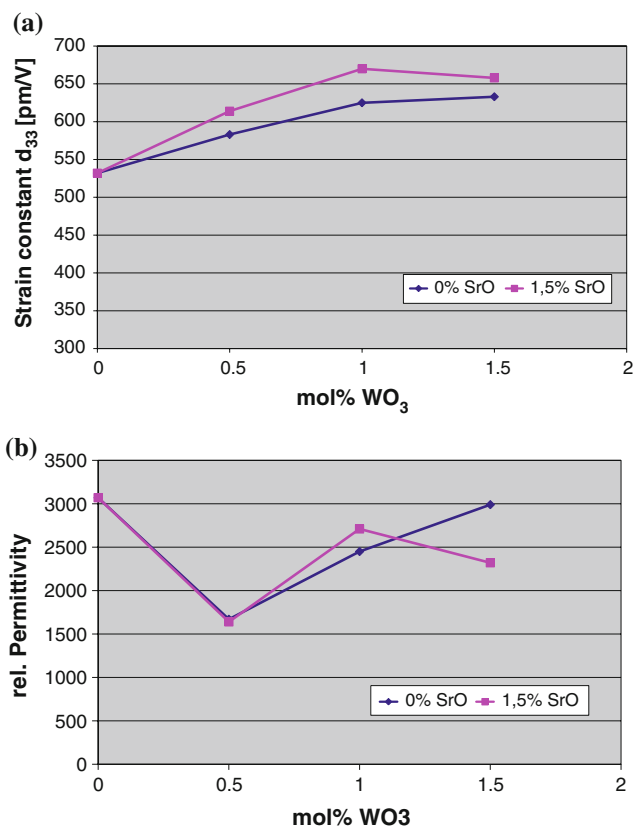
**Fig. 1** Micrographs of fractured surfaces of **a** undoped PZT (reference), **b** PZT + 1 mol% WO<sub>3</sub>, **c** PZT + 0.5 mol% WO<sub>3</sub> + 1.5 mol% SrO, **d** PZT + 1 mol% WO<sub>3</sub> + 1.5 mol% SrO. The scale of the bar is 1 μm



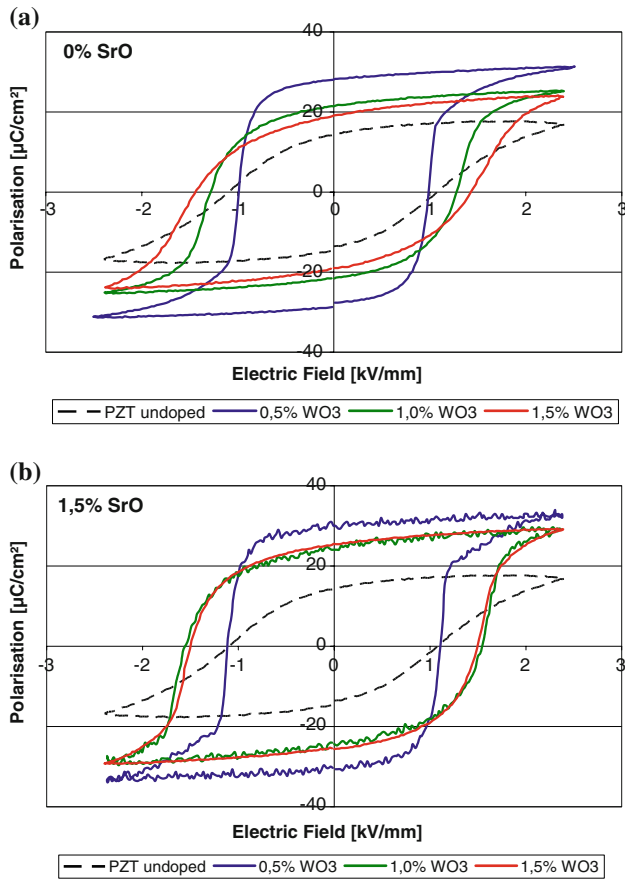
**Fig. 2** Development of the average grain size over composition determined from micrographs by the line section method

conductivity of each sample. Figure 5 shows the conductivity of the samples versus the reciprocal temperature.

The activation energies derived from these plots are listed in Table 2. The addition of WO<sub>3</sub> to the PZT (Fig. 5a) decreases the conductivity by approximately two orders of magnitude, which can be explained by the donor effect of W<sup>6+</sup> substituting Ti<sup>4+</sup> and eliminating defect electrons (holes) in the PZT [4]. Samples containing 1.5 mol% SrO and 0.5 mol% WO<sub>3</sub> exhibit a significantly higher conductivity in the low temperature range (Fig. 5b) compared to samples with higher WO<sub>3</sub> content and the samples without SrO. This difference was reproducibly found for different samples and for sweeping temperatures up as well as down.



**Fig. 3** **a** Strain constants and **b** relative permittivities of samples with increasing WO<sub>3</sub> content, with and without the addition of 1.5 mol% of SrO, both measured under high field conditions ( $E_{max} = 2.0$  kV/mm)



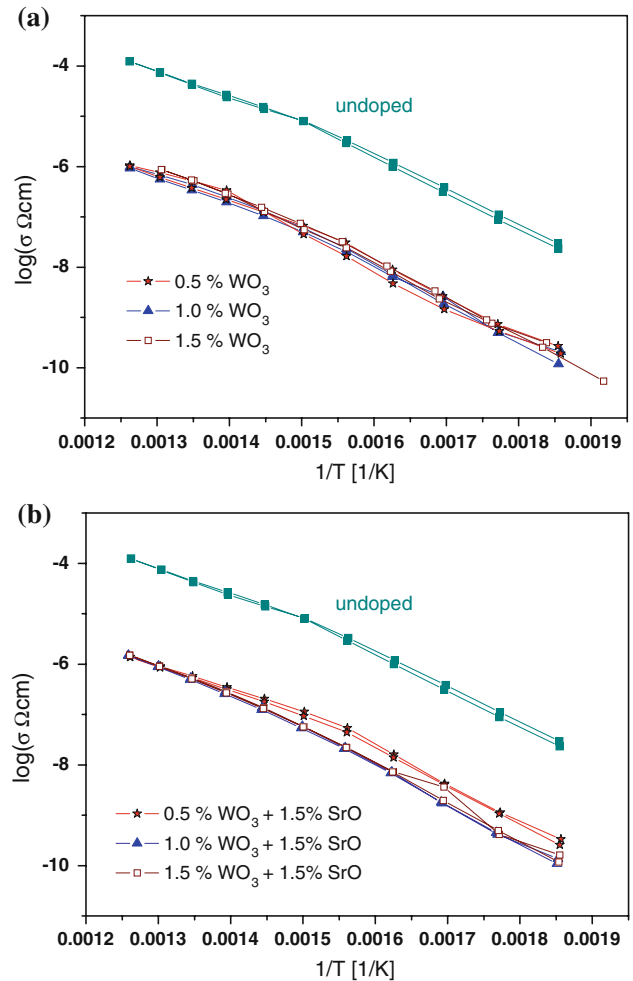
**Fig. 4** Polarization curves of PZT **a** with varying  $\text{WO}_3$  content without SrO, **b** with varying  $\text{WO}_3$  content and 1.5 mol% SrO

Obviously, SrO counteracts the donor effect of  $\text{WO}_3$  in this molar ratio, which suggests that possibly a part of  $\text{Sr}^{2+}$  acts as acceptor on B-sites thus compensating the donor effect of  $\text{W}^{6+}$ .

The impedance data also revealed the dielectric properties and from the temperature dependence of the relative permittivity (obtained from impedance data taken at 1 kHz) the Curie-temperature was determined employing Curie–Weiss-law. The values are listed in Table 3. For the addition of  $\text{WO}_3$  only, the change in Curie-temperature is at most 7 K. In the sample with 1.5 mol% SrO and 0.5 mol%  $\text{WO}_3$ , the decrease in Curie-temperature is 5 K, which does not reach the expected value of about 14 K (9.5 K/mol% according to [4]). This again fits to the assumption of a fraction of Sr acting as acceptor.

## Conclusion

This work shows that the combined addition of SrO and  $\text{WO}_3$  to PZT near the morphotropic phase boundary increases the piezoelectric strain compared to samples of



**Fig. 5** Conductivity of PZT versus reciprocal temperature **a** with varying  $\text{WO}_3$  content without SrO, **b** with varying  $\text{WO}_3$  content and 1.5 mol% SrO

**Table 2** Activation energy  $E_a$  of charge transport of samples ( $\pm 0.02$  eV)

Sample	$E_a$ for $T > T_c$ (eV)	$E_a$ for $T < T_c$ (eV)
$\text{Pb}(\text{Zr}_{0.525}\text{Ti}_{0.475})\text{O}_3$ (PZT)	0.98	1.43
PZT + 0.5% $\text{WO}_3$	1.05	1.45
PZT + 1.0% $\text{WO}_3$	1.08	1.44
PZT + 1.5% $\text{WO}_3$	1.22	1.41
PZT + 1.5% SrO + 0.5% $\text{WO}_3$	1.00	1.50
PZT + 1.5% SrO + 1.0% $\text{WO}_3$	1.21	1.50
PZT + 1.5% SrO + 1.5% $\text{WO}_3$	1.21	1.50

PZT with  $\text{WO}_3$  addition only. Polarization curves show that the addition of SrO counteracts the lowering of the coercive field due to the donor effect of  $\text{WO}_3$ . Furthermore, the donor effect of  $\text{WO}_3$  is clearly demonstrated in the conductivity of the samples, which is lowered by more than

**Table 3** Curie-temperature of samples

Sample	$T_c$ (°C)
Pb(Zr <sub>0.525</sub> Ti <sub>0.475</sub> )O <sub>3</sub> (PZT)	381
PZT + 0.5% WO <sub>3</sub>	379
PZT + 1.0% WO <sub>3</sub>	379
PZT + 1.5% WO <sub>3</sub>	374
PZT + 1.5% SrO + 0.5% WO <sub>3</sub>	376
PZT + 1.5% SrO + 1.0% WO <sub>3</sub>	362
PZT + 1.5% SrO + 1.5% WO <sub>3</sub>	363

two orders of magnitude compared to undoped PZT. The sample with 1.5 mol% SrO and 0.5 mol% WO<sub>3</sub> exhibits a significantly higher conductivity, suggesting that SrO may counteract the donor effect of WO<sub>3</sub>. The Curie-temperature of this sample is also higher than expected for an exclusive A-site occupation of Sr<sup>2+</sup>.

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