Journal of the European Ceramic Society 19 (1999) 1265–1268

PII: S0955-2219(98)00417-8
0955-2219/99/$ - see front matter

Phenomenological and Structural Properties of Piezoelectric Ceramics Based on xPb(Zr,Ti)O_3-(1-x)Sr($K_{0\cdot25}Nb_{0\cdot75}$)$O_3$ (PZT/SKN) Solid Solutions

Günter Helke,[a] Susanne Seifert[b]* and Sang-Jin Cho[b]

[a]CeramTec AG, 91207 Lauf, Germany
[b]Fraunhofer-Institut für Silicatforschung, Neunerplatz 2, 97080 Würzburg, Germany

Abstract

Solid solution ceramics with a stoichiometry xPb(Zr,Ti)O_3-(1-x)Sr($K_{0\cdot25}Nb_{0\cdot75}$)$O_3$ (PZT/SKN) exhibit a piezoelectric modulus temperature coefficient of less than 10^{-3} K over the temperature range from −50 to 150°C. Additionally, PZT/SKN has a Curie temperature in excess of 335°C. These properties, together with the piezoelectric characteristics indicate that PZT/SKN in this stoichiometric range may be an excellent sensor material. The best piezoelectric properties and thermal stability in PZT/SKN solid solutions has been obtained for ceramics with a mean grain size of 3 μm. For a better correlation between physical performance and material properties, the change in temperature coefficients with stoichiometry around the morphotropic phase transition has been studied. The effect of varying the sintering temperature between 1100 and 1250°C was investigated and correlated with the grain size and crystallography. © 1999 Elsevier Science Limited. All rights reserved

Keywords: structural properties, piezoelectric properties, thermal properties, PZT.

1 Introduction

Around the morphotropic phase transition of lead zirconate titanate (PZT) ceramics tetragonal and rhombohedral crystal structures coexist. The maximum dielectric and electromechanical properties observed in this region are related to structural anomalies.[1]

Compositions of the multicomponent system $PbTiO_3$-$PbZrO_3$-$\Sigma_n PbM'_{1-\alpha}M''_{\alpha}O_3$ (where $n = 1$–3, M′ are 5- or 6-valent cations, M″ are 1- or 2-valent cations and $\alpha = 0\cdot25 - 0\cdot5$) show enhanced piezoelectric activity due to the substitution of heterovalent cations within the perovskite structure.[2] Many technologically relevant piezoceramics are based on lead zirconate titanate modified by complex lead compounds.[3–5] In order to develop piezoceramics with properties tailored especially for sensor applications we have investigated PZT ceramics substituted with the lead free complex compound Sr($K_{0\cdot25}Nb_{0\cdot75}$)$O_3$ (SKN).

The physical properties of PZT compositions close to the morphotropic phase transition are very sensitive to preparation conditions within this region. In conventionally prepared PZT rhombohedral and tetragonal phases coexist over a 2–5 mol% range. Multicomponent systems containing complex compounds can exhibit even more latitude.[6]

The PZT composition exhibiting maximum piezoactivity differs by a few mol% from that for minimum temperature coefficients of the dielectric and piezoelectric moduli.[7–9] Usually one must compromise between a loss in piezoelectric performance and temperature stability. However, for the solid solution PZT/SKN, compositions with both excellent thermal stability $< 10^{-3}$/K and very good piezoelectric properties can be prepared.

2 Experimental

PZT/SKN ceramics have been prepared with the theoretical ionic complex Sr($K_{0\cdot25}Nb_{0\cdot75}$)$O_3$ using a conventional mixed oxide route. The Zr/Ti-ratio of the PZT phase was varied around the morphotropic

---

*To whom correspondence should be addressed. Fax: +49-931-4100498; e-mail: seifert@isc.fhg.de

phase transition between 58/42 and 48/52 in 0·5–1 mol% steps. Sintering was carried out in a PbO-atmosphere at temperatures between 1000 and 1250°C. The poling conditions for samples 10 mm in diameter and 1 mm thick were 2·5 kV mm^{-1} at 120°C for 5 min.

The samples were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The dielectric permittivity was measured for temperatures between −50 and +150°C by a capacitance bridge, whereas the piezoelectric modulus d_{33} was determined from measurements of the submicron deformation under low voltage operation conditions.

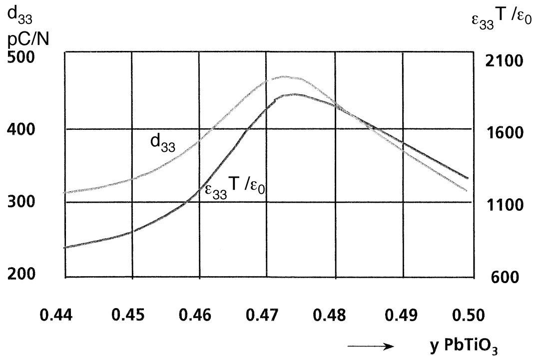

Fig. 2. Piezoelectric modulus d_{33} and dielectric permittivity $\epsilon_{33}{}^T/\epsilon_0$ in the solid solution system PZT/SKN as a function of the Zr/Ti ratio. The maximum of $\epsilon_{33}{}^T/\epsilon_0$ is slightly shifted towards higher Ti-contents compared with the maximum of d_{33}.

3 Results

3.1 Variation in the Zr/Ti-ratio

The lattice parameters of PZT/SKN samples with different Zr/Ti ratios sintered at 1180°C were calculated from XRD measurements. The expected phase transition from the rhombohedral to the tetragonal phase could clearly be observed in a region about 3 mol% wide around the morphotropic phase transition (Fig. 1). For Ti-contents greater than 47 mol% the PZT was tetragonal.

The dielectric and piezoelectric properties of the solid solution PZT/SKN were investigated as a function of the Zr/Ti-content. The maximum in piezoelectric modulus d_{33} and relative dielectric permittivity $\varepsilon_{33}{}^T/\epsilon_0$ were found at slightly different stoichiometries, with Ti-contents of 47·2 mol% and 47·5 mol%, respectively (Fig. 2).

The very small differences in the stoichiometries for both maxima seems to indicate enhanced homogeneity at the low sintering temperature of PZT/SKN compared to conventional PZT.

Thermal stability was investigated with respect to the Zr/Ti ratio and correlated with dielectric and piezoelectric properties. The temperature coefficients drastically decrease and stabilize with increasing Ti-content (Fig. 3).

Both minima of temperature coefficients TC_d and TC_ε, were slightly shifted towards higher Ti-contents compared with the maxima in the piezoelectric and dielectric properties. The lowest TC values for piezoelectric modulus and dielectric permittivity were $\sim 1\times10^{-3}$/K at a Ti-content of 48 mol% and $\sim 2\times10^{-3}$/K at a Ti-content of 48·5 mol%, respectively.

In comparison with the XRD results, thermal stability was greatest for a stoichiometry shifted slightly towards the tetragonal region.

3.2 Variations in sintering temperature

Samples with a Zr/Ti ratio of 52/48 were prepared under different sintering conditions and examined by SEM. The average grain sizes of the ceramics were determined on polished surfaces for each sintering temperature. The average grain size of the ceramics increases with sintering temperature (Fig. 4); especially above 1100°C a marked increase takes place.

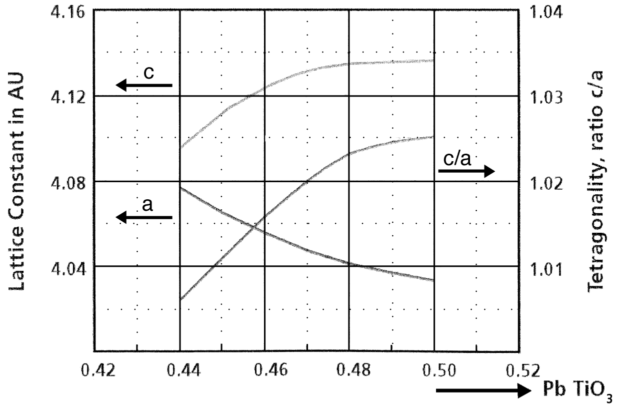

Fig. 1. Lattice parameters and tetragonality of the PZT/SKN solid solution system as a function of the Zr/Ti ratio around the morphotropic phase transition. All samples sintered at 1180°C.

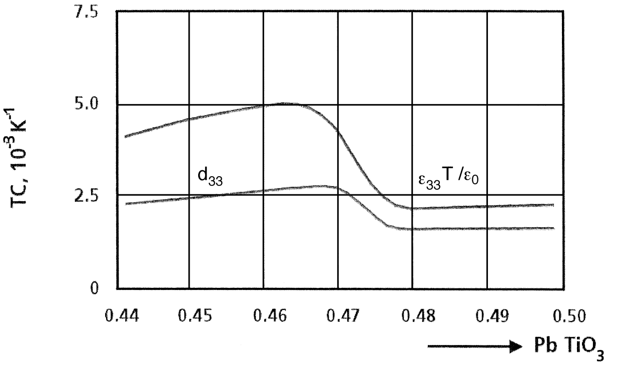

Fig. 3. Temperature coefficients of the dielectric permittivity and the piezoelectric modulus as a function of the Zr/Ti ratio. The minima of both temperature coefficients are slightly shifted towards higher Ti-contents compared to the maxima of d_{33} and $\epsilon_{33}{}^T/\epsilon_0$.

The lattice parameters of these materials were calculated as a function of the Zr/Ti content from X-ray diffractograms. All samples were tetragonal due to the stoichiometry of PZT(52/48).

Tetragonality strongly increased with increasing sintering temperature, especially between 1100 and 1150°C, where the strong increase in average grain size was observed. The tetragonality of the samples prepared at 1180°C is in good agreement with the measurements described in Fig. 1.

The dielectric and piezoelectric properties of the PZT/SKN ceramics with a Zr/Ti ratio of 48/52 prepared under different sintering temperatures were measured and correlated with the average grain size shown in Fig. 4. The correlation between physical properties and average grain size is shown in Fig. 6.

The $\epsilon_{33}{}^T/\epsilon_0$ values increased strongly with increasing grain size and had a maximum at ~3·5 μm. For further increases in grain size, $\epsilon_{33}{}^T/\epsilon_0$ decreased slightly. A similar behavior was found for the piezoelectric modulus d_{33}. The maximum value of d_{33} was found for a grain size of ~2·5 μm. The d_{33} values are much more sensitive to the grain size than is dielectric permittivity, and there is a significantly stronger decrease with further increased grain size.

The best thermal stability in dielectric properties was obtained for ceramics with large grain sizes (Fig. 7). The temperature coefficient of the dielectric permittivity for ceramics with a mean grain size of 6·2 μm was of $1{\cdot}4\times10^{-3}$/K; this is less than half the coefficient of $3{\cdot}8\times10^{-3}$/K obtained for ceramics with an average grain size of only 1·95 μm. Because of this, temperature variation in d_{33} and g_{33} is very small (Fig. 8). This observation is in good agreement with the correlation $TC_d=-TC_g\approx 1/2\ TC_\varepsilon$.[10]

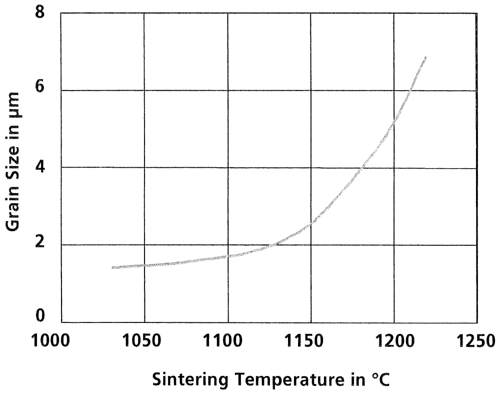

Fig. 4. Average grain size of PZT/SKN ceramics with a Zr/Ti ratio of 52/48 as a function of the sintering temperature. The grain size increases markedly above 1100°C.

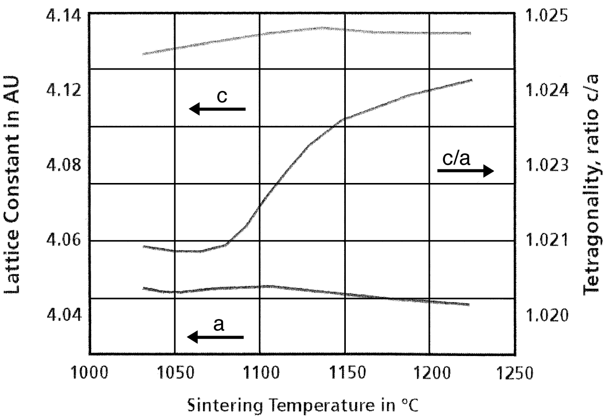

Fig. 5. Lattice parameters and tetragonality of the PZT/SKN solid solution system as a function of the sintering temperature. Zr/Ti ratio: 52/48.

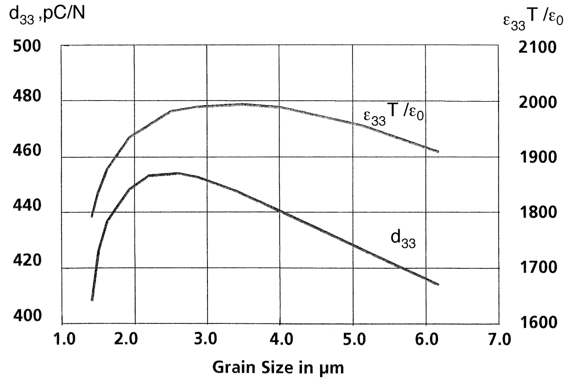

Fig. 6. Dielectric permittivity and piezoelectric modulus of the PZT/SKN system as a function of average grain size. Zr/Ti ratio: 52/48; the variations of the average grain size are due to the sintering temperatures (see also Fig. 4).

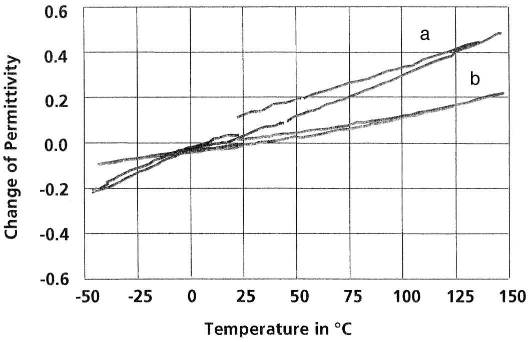

Fig. 7. Changes in dielectric permittivity with temperature between −50 and +150°C for PZT/SKN (Zr/Ti ratio: 52/48). Average grain sizes: a: 1·93 μm, b: 6·17 μm.

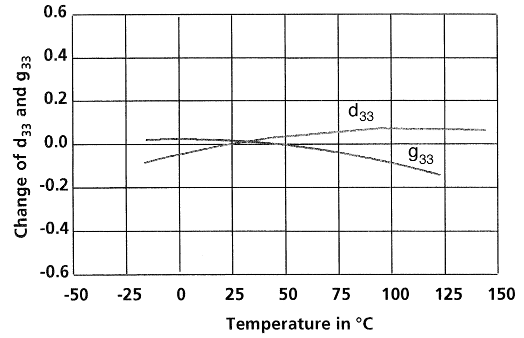

Fig. 8. Changes in d_{33} and g_{33} with temperature for PZT/SKN sample corresponding to the sample from Fig. 7(b).

4 Conclusion

PZT ceramics of the solid solution system PZT/SKN with Zr/Ti contents around the morphotropic phase transition and different sintering temperatures have been investigated. Maximum dielectric and piezoelectric properties were measured for Zr/Ti ratios between 53/47 and 52/48, respectively. The lowest temperature coefficients were found for stoichiometries shifted slightly towards the tetragonal region.

By varying sintering temperature, a strong increase in grain size, as well as in tetragonality was found for ceramics with a Zr/Ti ratio of 52/48.

The piezoelectric and dielectric properties of these samples vary significantly with the average grain size; the best performance was found for grain sizes of $\sim 3\,\mu$m. For larger grain sizes there was a decrease in the electrical properties. In contrast to the piezoelectric and dielectric properties, the best thermal stability was found for samples with grain sizes of $\sim 6\,\mu$m and distinctly enhanced tetragonality. For thermal stability the tetragonality of the sample seems to be the overriding factor.

As a summary, solid solutions with a thermal coefficient less than 10^{-3}/K between -50 and $+150$°C have been prepared by adapting the sintering temperatures to the target microstructure and tetragonality of the sensor material.

References

1. Jaffe, B., Cook, W. R. and Jaffe, H., *Piezoelectric Ceramics*. Academic Press, London, 1971.
2. Xu, Y., *Ferroelectric Materials and Their Applications*. North-Holland, Tokio, 1991.
3. US Pat. 4,313,839 Piezoceramic Material, 2·2. 1982.
4. Fesenko, E. G., Dantsiger, A. J., Reznichenko, L. A. and and Kuprijanov, M. F., Composition-structure-properties dependences in solid solutions on the basis of lead-zirconate-titanate and sodium niobate. *Ferroelectrics*, 1982, **41**, 137–142.
5. Don Berlincourt, H., Piezoelectric ceramic compositional development. *J. Acoust. Soc. Am.*, 1992, **91**, 3034–3040.
6. Panich, A. E., and Kuprijanov, M. F., *Fizika i Technologija Segnetokeramiki* (in Russian: Physics and Technology of Ferroelectrics), publ. University Rostov-on-Don, 1989.
7. Wersing, W., Temperature coefficient of resonance frequencies and permittivity in PZT ceramics near the morphotropic phase boundary. *Ferroelectrics*, 1991, **37**, 611–614.
8. Boudys, M., Relations between temperature coefficients of permittivity and elastic compliances in PZT ceramics near the morphotropic phase boundary. *IEEE Trans. UFFC.*, 1991, **38**, 569–571.
9. Helke, G., Workshop perspectives on Piezoelectric Material Research: The Morphotropic Phase Transition in Lead Zirconate Titanate Based Polycrystalline Solid Solutions. Hartley Wintney, Great Britain, 21–24 February, 1993.
10. Draft Standard Piezoelectric Ceramics CENELEC BTTF 63-2, 1997. Part 2 Guide on Methods of Measurement.