Journal of the European Ceramic Society 21 (2001) 1459–1462

www.elsevier.com/locate/jeurceramsoc

Properties of fine scale piezoelectric PZT fibers with different Zr content

R. Steinhausen [a,*], T. Hauke [a], H. Beige [a], W. Watzka [b], U. Lange [b], D. Sporn [b], S. Gebhardt [c], A. Schönecker [c]

[a] *Martin-Luther-Universität, Halle-Wittenberg, Germany*
[b] *Fraunhofer-Institut für Silicatforschung, Würzburg, Germany*
[c] *Fraunhofer-Institut für Keramische Technologien und Sinterwerkstoffe, Dresden, Germany*

Received 4 September 2000; accepted 30 October 2000

Abstract

Smart materials containing piezoelectric fibers have a large potential in sensoric, actuatoric and ultrasonic transducer applications. Fine scale PZT fibers with five systematically adjusted Zr/Ti ratios ranging from $x = 58/42$ to $48/52$ have been prepared using a sol–gel route. The fibers were embedded in a polymer matrix to produce 1-3 composites and the effective piezoelectric and dielectric coefficients were measured. An analytical model was used to extract the corresponding values of the fibers from the effective material properties. The dependence of the coefficients on the Zr/Ti ratio shows a pronounced maximum at $x = 53/47$. This correlates with an analysis of the phase content. For $x = 53/47$ the fibers consist of 31% rhombohedral and 69% tetragonal phase, whereas the content of rhombohedral phase is 100 and 7% for $x = 58/42$ and $48/52$, respectively. For $x = 53/47$ maximum values of $\varepsilon_{33}^{T} = 1200$ and $d_{33} = 127$ pm/V were found. The latter one is about 50% of the value of corresponding bulk materials.

Keywords: Composites; Fibres; Piezoelectric properties; PZT; X-ray methods

1. Introduction and aim

Thin PZT fibers are considered to have a high potential for ultrasonic and smart material applications.[1] For a good performance of the devices it is necessary to optimize especially the electromechanical properties of the fibers.

Undoped PZT bulk ceramics show a maximum of the dielectric and piezoelectric coefficients for a Zr/Ti-ratio of 53:47, which corresponds to the morphotropic phase boundary (MPB) where the tetragonal and rhombohedral phases coexist. However, for sol–gel-derived materials like thin films sometimes a shift of the MPB or the maximum of properties with respect to the Zr/Ti-ratio was reported.[2]

Here, we report about the influence of the Zr/Ti ratio on the properties and phase content in PZT fibers prepared by a sol–gel route. By XRD measurements the content of the rhombohedral and tetragonal phase in the fibers was quantitatively analyzed. Measurements of the dielectric and piezoelectric properties of single fibers are difficult to perform due to the fact that the fibers are very thin. Therefore, it is difficult to electrode them. The fibers were embedded in a polymer matrix and the effective material properties of these 1-3 composites were measured. From these data, the dielectric and piezoelectric properties of the single fibers can be extracted using analytical approximations and modeling with the finite-element-method (FEM).

It is the aim of the paper to identify basic relationships between fiber technology and fiber properties with special emphasis on Zr content. The results were compared with data of undoped bulk PZT ceramics.

2. Preparation of 1–3 composites with PZT fiber and measurement equipment

Thin PZT fibers with diameters between 10 and 50 μm were prepared by a sol–gel route and subsequent thermal treatment as described in Ref. 3. For composite

* Corresponding author at: FB Physik, University Halle, ExPh 11, Fr-Bach-Platz 6, 06108 Halle, Germany. Tel.: +49-345-552-5548; fax: +49-345-552-7158.

E-mail address: steinhausen@physik.uni-halle.de (R. Steinhausen).

0955-2219/01/$ - see front matter
PII: S0955-2219(01)00041-3

preparation the PZT fibers were carefully aligned and infiltrated with an epoxy resin. In order to avoid bubbles and thus to get a constant dielectric coefficient of the polymer and to minimize the possibility of an electrical break-down, the resin was degassed during preparation.

Curing was carried out under pressure. According to the applied pressure, the fiber content in the composite was adjusted in the range from 13 to 65 vol.%. From optical micrographs, a statistical distribution of the fibers was observed for composites with a low fiber content of about 25 vol.%. It was found, that in composites with a fiber content higher 50 vol.% some of the fibers were broken. This was due to the applied pressure during composite preparation. Therefore, only composites with a fiber content lower than 25 vol.% were used for measurements of the dielectric and electromechanical properties.

After curing composite slices of 0.5–1 mm in thickness were cut in the way that the fiber axis was directed perpendicular to the composite surface. The samples were grounded and subsequently electroded with gold. Poling was done in oil at 80°C for 2 h with approximately 5.5 kV/mm. The poling field was kept constant during cooling to 50°C.[3]

For measurements of the piezoelectric moduli an equipment based on a capacitive detector was used.[4] The samples were placed between two rods, one of them freely movable. The upper end of the movable rod carries one plate of an air capacitor, which is a component of a HF resonance circuit. Thus a change of the sample thickness results in a change of the capacity of the capacitor and finally in a frequency modulation of the HF circuit. After demodulation a voltage proportial to the strain of the sample is available. A quartz connected mechanically in series with the sample is used for calibration and for accurate measurement of the piezoelectric moduli by a compensation technique. The measurement frequency was about 130 Hz.

The capacitance of the composites was measured at 1 kHz using an HP4194A impedance analyzer for calculation of the dielectric coefficient. The coupling coefficient k_t was calculated from impedance curves.

3. Results

3.1. Quantitative phase analysis

The quantitative phase content of unpoled fibers was determined by XRD measurements using a Philips powder diffractometer PW1710 with a diffracted-beam monochromator. High resolution measurements have been carried out of the region of the (200)-reflections. After subtraction of the background intensity the profiles were fitted by using the pseudo-voigt-function. $K_{\alpha 1}$ and $K_{\alpha 2}$ reflections were separated. The phase content of the rhombohedral phase P_{FR} was calculated from the integral intensities of the $K_{\alpha 1}$ reflections using the following equation:

$$P_{FR} = \frac{I_{FR(200)}}{I_{FR(200)} + I_{FT(200)} + I_{FT(002)}}, \quad (1)$$

where $I_{FR(200)}$ is the integral intensity of the (200)-reflection of the rhombohedral phase and $I_{FT(200)}$ and $I_{FT(002)}$ are the integral intensity of the (200)- and (002)-reflections of the tetragonal phase, respectively.

The results are shown in Fig. 1. The fibers with Zr/Ti ratio $x = 58/42$ consist of pure rhombohedral phase. With decreasing zirconium content the rhombohedral phase content also decreases and the tetragonal phase content increases. For the PZT fibers with 58% of titanate, the phase content is nearly complete tetragonal, only 7% rhombohedral phase was detected. In the middle of the investigated range, the fibers with a Zr/Ti-ratio $x = 53/47$ consist of 31% rhombohedral phase. Thus, in the fibers the MPB is located at the same Zr/Ti-ratio as in bulk ceramics.

3.2. Dielectric and electromechanical properties

3.2.1. Modeling

In order to predict the effective properties of 1-3 composites from single material properties analytical approximations were developed.[5,6]

Additionally, a finite element method (FEM) was used for modeling the quasistatic composite properties. Both, analytical approximation and FEM modeling, were experimentally verified using model structures with regularly arranged rods of a commercial PZT ceramic. For these model structures the same polymer as in the 1-3 composits with PZT fibers was used (Young's Modulus $Y_p = 3.89$ GPa and Poisson's ratio $\nu_p = 0.38$). The measured effective properties of these composites corresponded very well with the data predicted from analytical approximation and FEM modeling.[1,7]

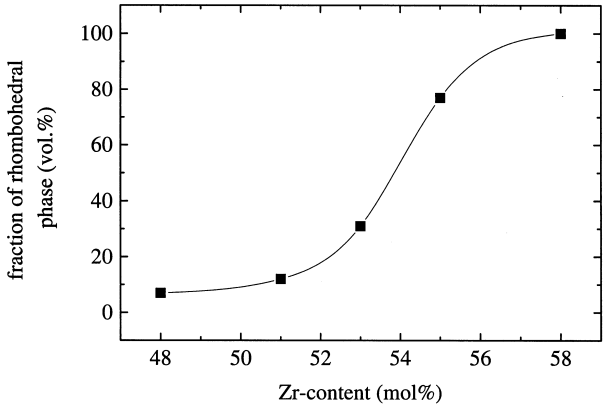

Fig. 1. Dependence of the volume fraction of rhombohedral phase on the Zr content.

Hence, it is possible to extract the dielectric and electromechanical properties of the fibers from the effective properties of the 1-3 composites by using the analytical approximations. Here, the experimental results obtained from measurements of the effective properties of the 1-3 composites were used. The piezoelectric modulus $d_{33,f}$ of the fiber can be calculated directly from the measured effective piezoelectric modulus $d_{33,eff}$ of the composite:

$$d_{33,f} = d_{33,eff}\left(1 + \frac{V_p}{V_f} s^E_{33,f} Y_p\right), \quad (2)$$

where V_p and V_f are the volume fractions of the polymer and the fibers and $s^E_{33,f}$ the elastic coefficient of the fibers, respectively. Using $d_{33,eff}$, the piezoelectric modulus $d_{31,f}$ of the fibers is determined by the formula

$$d_{31,f} = \frac{1}{V_f} d_{31,eff} + \frac{\left(\nu_p - s^E_{13,f} Y_p\right)}{\left(\frac{V_f}{V_p} + s^E_{33,f} Y_p\right)} d_{33,f}. \quad (3)$$

The dielectric permittivity $\varepsilon^T_{33,f}$ of the fiber can be calculated by the formula

$$\varepsilon^T_{33,f} = \frac{\varepsilon_{33,eff} - V_p \varepsilon_p}{V_f} + \frac{d^2_{33,f}}{s^E_{33,f} + \frac{V_f}{V_p}\frac{1}{Y_p}}, \quad (4)$$

where $\varepsilon_{33,eff}$ and ε_p are the dielectric permittivities of the composite and the polymer matrix, respectively. For calculations of the dielectric coefficient $\varepsilon_{r,f}$ of the unpoled fibers, Eq. (4) reduces to a simple parallel circuit model, because the second term is equal to zero ($d_{33,f} = 0$). Data of bulk PZT with different Zr/Ti ratios were used for the elastic coefficients $s^E_{33,f}$ and $s^E_{13,f}$ of the fibers in Eqs. (2)–(4).[8]

3.2.2. Experimental results

The piezoelectric modulus $d_{33,f}$ of the fibers in dependence of the Zr content is shown in Fig. 2. $d_{33,f}$ increases with increasing Zr content up to a Zr/Ti-ratio $x = 53/47$, then it again decreases. Thus, the maximum of the piezoelectric modulus is observed at the same Zr/Ti ratio as in bulk PZT ceramics. However, the maximum value $d_{33,f} = 127$ pm/V is much smaller than in undoped bulk PZT ceramics ($d_{33} = 270$ pm/V).

In Fig. 3, the piezoelectric modulus $d_{31,f}$ for the fibers calculated by Eq. (3) is shown. The maximum amount of $d_{31,f} = -58$ pm/V was found at a Zr content of 51%. It has to be noted, that the calculation of $d_{31,f}$ strongly depends on the volume fraction of the fibers and the material coefficients used.

In Fig. 4, the dielectric permittivity of the PZT fibers before ($\varepsilon_{r,f}$) and after poling ($\varepsilon^T_{33,f}$) are plotted versus the Zr content. The measurements of $\varepsilon^T_{33,f}$ were performed at least 24 h after poling. The dielectric coefficients of the fibers after poling are calculated from the measured effective dielectric coefficients of the composite by Eq. (4). Here, the experimentally determined piezoelectric coefficients were used.

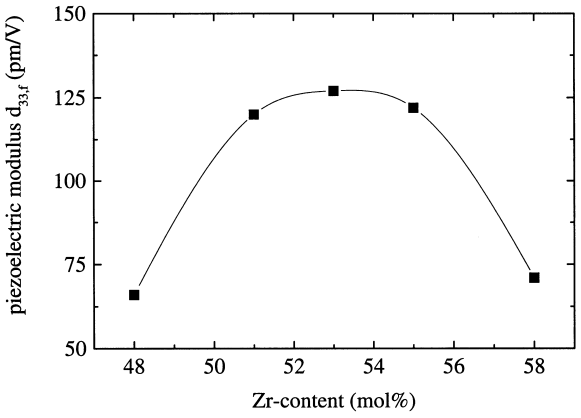

Fig. 2. Dependence of the piezoelectric modulus $d_{33,f}$ of the fibers on the Zr content.

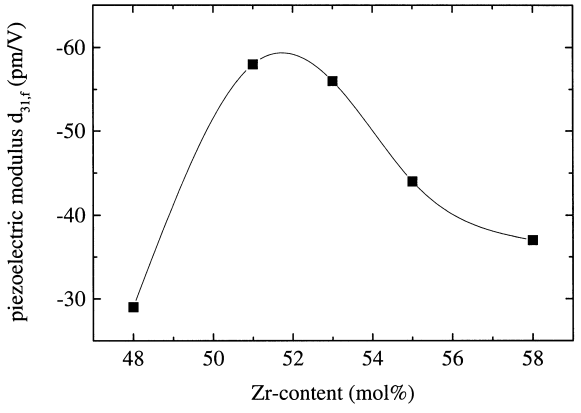

Fig. 3. Dependence of the piezoelectric modulus $d_{31,f}$ of the fibers on the Zr content.

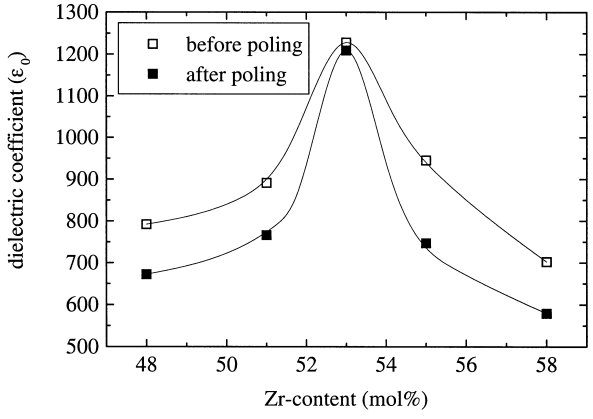

Fig. 4. Dependence of the dielectric coefficients of the fibers on the Zr content (before and after poling).

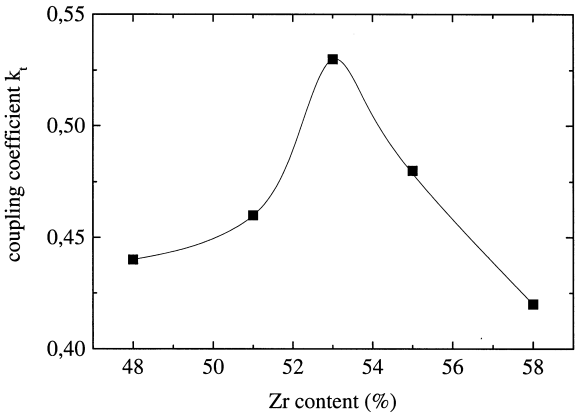

Fig. 5. Dependence of the electromechanical coupling coefficient k_t of the 1-3 composites on the Zr content of the PZT fibers.

As for $d_{33,f}$, a maximum of the dielectric permittivities $\varepsilon_{r,f}$ and $\varepsilon^{T}_{33,f}$ (1228 and 1208 ε_0, respectively) is observed at a Zr/Ti ratio $x = 53/47$. This behavior is the same in bulk ceramics. It is noteworthy, that the dielectric coefficient dropped for all measured samples after poling independent from the Zr/Ti ratio.

Additionally, the electromechanical coupling coefficients k_t of the 1-3 composites were determined. k_t was calculated from the resonance and antiresonance frequencies of the thickness mode. In Fig. 5, the dependence of k_t on the Zr content is shown. It is an effective material coefficient of the composite and depends on the volume fracture of the PZT fibers. However, in the range of $v_f \approx 20$ vol.% investigated here the influence of the volume fraction is only slight.

Like the quasistatic coefficients the coupling coefficient reaches its maximum $k_t = 0.53$ at the Zr/Ti ratio $x = 53/47$.

4. Summary

Thin PZT fibers with systematically adjusted Zr/Ti ratios ranging from $x = 48/52$ up to $x = 58/42$ were prepared by a sol–gel route and embedded in a polymer matrix.

The quantitative phase analysis of the fibers had shown, that the rhombohedral phase content increases with increasing Zr content, the tetragonal phase content increases with increasing Ti content. At a Zr/Ti ratio of 53/47 a volume fraction of the rhombohedral phase of 31% was measured.

From the dielectric and electromechanical properties of the 1-3 composites the material coefficients of the fibers were calculated using analytical approximations. As in bulk ceramics, a maximum of the dielectric and electromechanical properties was obtained ($\varepsilon_{r,f} = 1200$ ε_0 and $d_{33,f} = 127$ pm/V) at a Zr/Ti ratio 53/47.

Thus, both the location of the MPB and the maximum of the material properties are observed at the same Zr/Ti ratio as in bulk ceramics. On the other hand, the values of the piezoelectric coefficient $d_{33,f}$ of undoped PZT fibers are smaller than the values known from undoped bulk PZT ($d_{33} = 270$ pm/V), which may be for example due to an insufficient poling or a nonoptimal microstructure.

Acknowledgements

This work was supported by the Deutsche Forschungsgemeinschaft, SPP Multifunktionswerkstoffe.

References

1. Steinhausen, R., Hauke, T., Seifert, W., Beige, H., Watzka, W., Seifert, S., Sporn, D., Starke, S. and Schönecker, A., Finescaled piezoelectric 1-3 composites: properties and modeling. *J. Eur. Ceram Soc.*, 1999, **19**, 1289–1293.
2. Klee, M., De Veirman, A., Waser, R., Brand, W. and van Hal, H., Processing and electrical properties of PZT films: comparison of metallo-organic decomposition and sol–gel processing. *J. Appl. Phys.*, 1992, **72**, 1566.
3. Watzka, W., Seifert, S., Scholz, H., Sporn, D., Schönecker, A. and Seffner, L., Dielectric and ferroelectric properties of 1–3 composites containing thin PZT-fibers. In *Proceedings of 10th Int. Symp. Appl. Ferroel., ISAF '96*, Vol. 2, ed. B. M. Kulwicki, A. Amin and A. Safari, 1996, pp. 569–572.
4. Sorge, G., Hauke, T. and Klee, M., Electromechanical properties of thin ferroelectric $PbZr_{0.53}Ti_{0.47}O_3$-layers. *Ferroelectrics*, 1995, **163**, 77–88. .
5. Smith, W. A. and Auld, B. A., *IEEE Trans. Ultrasonics, Ferroelectr. And Frequ. Contr.*, 1991, **38**, 40.
6. Smith, W. A. and Auld, B. A., *IEEE Trans. Ultrasonics, Ferroelectr. And Frequ. Contr.*, 1993, **40**, 41.
7. Gebhardt, S., Schönecker, A., Steinhausen, R., Hauke, T., Seifert, W. and Beige, H., Fine scale 1-3 composites fabricated by the soft mold process: preparation and modeling. *Ferroelectrics*, 2000, **241**, 67–73.
8. Landolt-Börnstein, Numerical Data and Functional Relationships in Science and Technology, Vol. III/16a, 1981, p. 123.