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Anomalous dilatation–temperature curves of PZT–ZrO$_2$ composites

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The dilatation–temperature curves of the PZT–ZrO$_2$ composites, containing 1.3–13.2 vol% ZrO$_2$ were studied. The course of martensitic transformation (MT) of dispersed ZrO$_2$ particles in the PZT matrix was followed. Upon cooling, a spontaneous microcrack formation occurred during the MT from tetragonal to monoclinic crystal phase of ZrO$_2$. The phenomenon of intensive shrinkage above 800 °C upon heating is explained as a process of microcrack healing in the presence of the PbO-rich liquid phase.

1. Introduction

Pb(Zr, Ti)O$_3$ solid solution (PZT)-based ceramics are widely used piezoelectric materials [1]. It has been shown that the addition of ZrO$_2$ improves to a certain amount the mechanical strength of PZT–ZrO$_2$ composites relative to PZT, but at the expense of a lower piezoelectric response [2].

The use of dilatation–temperature curves has been a convenient way of recording the martensitic transformation (MT) of ZrO$_2$ particles in various ceramic composites, such as Al$_2$O$_3$–ZrO$_2$, mullite–ZrO$_2$, etc. [3]. The same procedure was used to characterize the MT of dispersed ZrO$_2$ particles in PZT–ZrO$_2$ composites. The rather unusual dilatation–temperature curves of PZT–ZrO$_2$ composites are described here.

2. Experimental procedure

PZT and PZT–ZrO$_2$ composites with the addition of 1.3, 4.0, 8.0 and 13.2 vol% ZrO$_2$ were prepared from Pb$_{0.94}$Sr$_{0.06}$(Zr$_{0.52}$Ti$_{0.48}$)O$_3$ PZT 5204 (TAM) and ZrO$_2$ SC20 (MEL) powders by classical ceramic methods, as described in detail elsewhere [2]. The samples were fired at 1250 °C for 2 h and reached approximately 95% theoretical density.

The microstructural analysis of thin sections was performed using a transmission electron microscope (TEM, Jeol 2000 FX EM).

The thermal expansion of the as-fired 25 mm long bars was recorded by a dilatometer with an Al$_2$O$_3$ measuring system (Netzsch 402 E) at a constant heating and cooling rate of 5 °C min^{-1}.

3. Results and discussion

3.1. Microstructure of the as-fired PZT–ZrO$_2$ composites

The grain sizes of PZT and ZrO$_2$ in the composites were less than 2 μm. The matrix PZT phase retained tetragonal crystal structure, the ZrO$_2$ phase was monoclinic at room temperature, confirming thereby the occurrence of the martensitic transformation of ZrO$_2$ MT (t → m) during cooling from the sintering temperature in the firing process. The presence of at least 8 vol% ZrO$_2$ in PZT–ZrO$_2$ composites led to the formation of microcracks, as a consequence of high stresses, caused by shape and volume changes accompanying the MT (t → m) of ZrO$_2$ particles in the PZT matrix (Fig. 1). In PZT–13.2 vol% ZrO$_2$, connected networks of microcracks were observed. In some radial cracks a discontinuous PbO-rich amorphous phase was found [4].

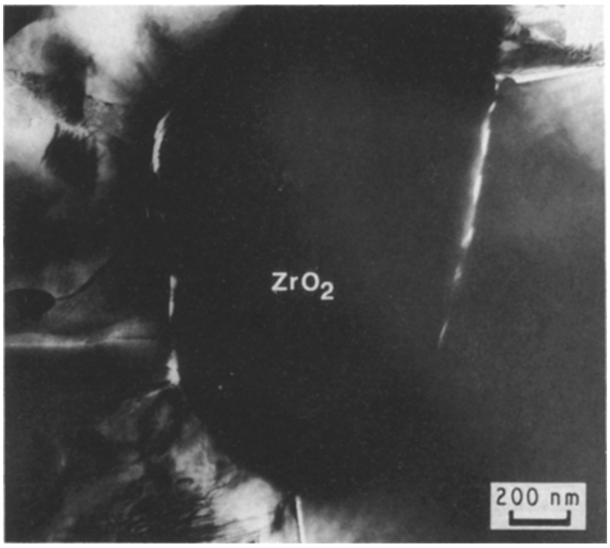

Figure 1 Transmission electron micrograph of the PZT–13.2 vol% ZrO$_2$ composite showing a ZrO$_2$ particle surrounded by PZT grains. Smaller tangential and larger radial cracks, protruding intergranularly into the matrix, are clearly visible.

3.2. Dilatation–temperature curves of PZT

The dilatometric heating and cooling curves of pure PZT with the final temperatures 1100 and 1200 °C are shown in Fig. 2. The thermal expansion coefficients of the tetragonal and the cubic phase up to 600 °C and

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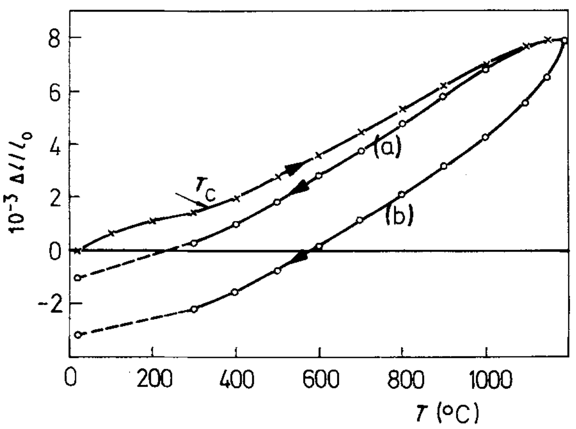

Figure 2 Heating–cooling dilatometric curves of PZT, the final temperatures being (a) 1100 and (b) 1200 °C. (▶) Heating, (◀) Cooling, T_c = Curie temperature.

Curie temperature, i.e. ferroelectric to paraelectric phase transformation temperature, are shown in Table I. The experimental values are consistent with literature data up to 600 °C [1, 5]. The measurements during cooling could be performed only to approximately 350 °C, therefore the Curie temperature upon cooling could not be determined.

The dilatation of cubic PZT upon heating constantly increased up to approximately 900 °C. Further heating resulted in a retained deformation of the samples upon cooling to room temperature, the dimensional change being systematically dependent on the final temperature. The phenomenon could be attributed to a plastic deformation of the samples, caused by the measuring rod in the dilatometer.

3.3. Dilatation–temperature curves of PZT–ZrO_2 composites

The dilatometric heating and cooling curves of PZT–ZrO_2 composites with the addition of 1.3 and 4 vol % ZrO_2 were similar to those of pure PZT, with comparable values of thermal expansion, Curie temperature and retained deformation. The characteristic temperatures of the martensitic transformation of ZrO_2 in these composites could only be determined by the use of the first derivative of change in length [6]. The experimental values were in agreement with the data for ceramic composites with dispersed unstabilized ZrO_2 particles [3] and are shown in Table II.

In order to facilitate further explanation of the dilatometric curves of PZT–ZrO_2 composites, plastic deformation of the PZT matrix in the diagrams was omitted. This correction was based on the assumption that a larger content of ZrO_2 did not have a major influence on the plastic deformation of the composites.

The dilatometric heating and cooling curves of PZT–ZrO_2 composites with the addition of 8 and 13.2 vol % ZrO_2 and the final temperature of 1200 °C markedly differed from those of pure PZT and PZT–ZrO_2 composites with 1.3 and 4 vol % ZrO_2, as shown in Figs 3 and 4.

TABLE I Experimental values of thermal expansion coefficients, α, of the tetragonal and the cubic phase and the Curie temperature, T_c, of PZT

Crystal phase	Temperature range (°C)	α (10^{-6} °C^{-1})	T_c (°C)
Tetragonal	25–200	6 ± 0.5	
Tetragonal	200–330	2.5 ± 0.5	
Cubic	350–900	8.3 ± 0.1	330 ± 10

TABLE II Characteristic temperatures of MT of dispersed ZrO_2 particles in PZT–ZrO_2 composites containing 1.3 and 4.0 vol % ZrO_2. A_s, temperature of MT (m → t) start upon heating; A_f, temperature of MT (m → t) end upon heating; M_s, temperature of MT (t → m) start upon cooling; M_f, temperature of MT (t → m) end upon cooling

ZrO_2 (vol %)	A_s (°C)	A_f (°C)	M_s (°C)	M_f (°C)
1.3	1150	–	< 500	< 500
4.0	1150	–	550	555

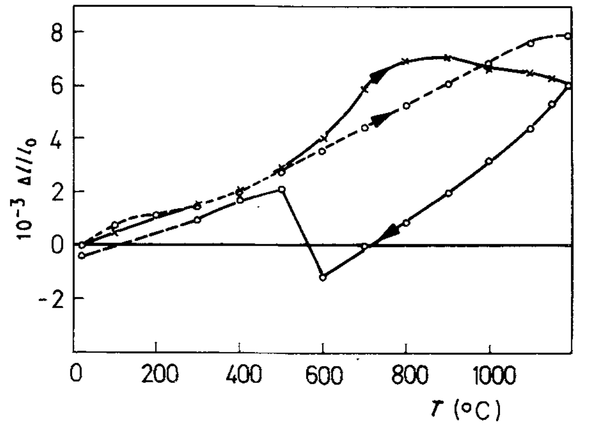

Figure 3 Heating–cooling dilatometric curve of the as-fired PZT–8 vol % ZrO_2, relative to (– – –) PZT, the final temperature being 1200 °C. (▶) Heating, (◀) Cooling.

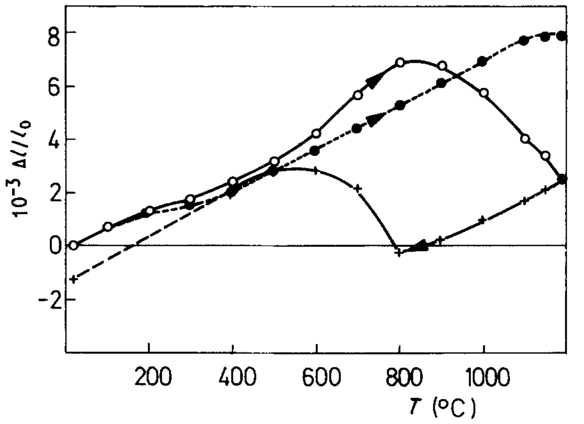

Figure 4 Heating–cooling dilatometric curve of the as-fired PZT–13.2 vol % ZrO_2, relative to (– – –) PZT, the final temperature being 1200 °C. (▶) Heating, (◀) Cooling.

The dilatation of the composites PZT–8 vol % ZrO_2 and PZT–13.2 vol % ZrO_2 upon heating to 500 °C was comparable to that of PZT, whereas in the temperature range from 500 °C to approximately 850 °C it increased considerably. Further heating to the final temperature, 1200 °C, led to an intensive shrinkage, whereby the dimensional change increased with increasing ZrO_2 content. At 1150 °C, a change of slope on both curves was determined by use of the first derivative of change in length. Upon cooling, a marked dimensional increase at 600 and 800 °C in the case of PZT–8 vol % ZrO_2 and PZT–13.2 vol % ZrO_2, respectively, led to almost closed hysteresis loops.

The thermal expansion increase in the range 500–800 °C upon heating of PZT–8 vol % ZrO_2 and PZT–13.2 vol % ZrO_2 composites has not been satisfactorily explained. The various explanations of similar phenomena, such as twin coarsening or stress relaxation [7, 8] did not seem applicable to the PZT–ZrO_2 system.

The shrinkage of the PZT–ZrO_2 composites above 800 °C upon heating could not be explained as the retained deformation of pure PZT. The former started at a lower temperature and was not retained to room temperature as in the case of PZT.

Also, the onset of shrinkage of the PZT–ZrO_2 composites at approximately 850 °C upon heating occurred at a significantly lower temperature than the expected start of the martensitic transformation from monoclinic to tetragonal crystal structure MT ($m \rightarrow t$) of the unstabilized ZrO_2 particles above 1100 °C [9]. The measured dimensional change was considerably larger than the value estimated on the reported data on the course of MT of ZrO_2 in ceramic composites containing dispersed ZrO_2 particles [3]. On the other hand, the change of slope at 1150 °C that was determined on both dilatometric curves, coincided with the experimentally determined temperature of MT ($m \rightarrow t$) of ZrO_2 in PZT–1.3 and 4.0 vol % ZrO_2 and could, therefore, be interpreted as the MT start ($m \rightarrow t$) in PZT–8 and 13.2 vol % ZrO_2.

Upon cooling, the onset of the dimensional increase at 600 and 800 °C for PZT–8 and 13.2 vol % ZrO_2, respectively, could be analogously explained as the MT start ($t \rightarrow m$). The concomitant large dimensional increase could be explained as the spontaneous microcrack formation during the MT ($t \rightarrow m$), a phenomenon also observed in other ceramic composites with ZrO_2 [3, 10]. The microcracks, originating at monoclinic ZrO_2 particles in PZT–8 and 13.2 vol % ZrO_2 composites were, in fact, observed by TEM, as shown in Fig. 1.

To summarize, the course of MT of ZrO_2 particles in PZT–ZrO_2 composites was investigated by dilatation–temperature curves. Based upon the shape of the dilatometric curves, showing an unexpected phenomenon of intensive shrinkage above 800 °C and on the MT start ($m \rightarrow t$) at 1150 °C upon heating, it was thought that at least two overlapping processes influenced the thermal behaviour of the PZT– ZrO_2 composites.

The onset of shrinkage above 800 °C upon heating coincided with the melting points of PbO at 888 and of PbO–TiO_2 eutectic at 838 °C [11]. A PbO-rich amorphous phase was found in microcracks in PZT–ZrO_2 composites by TEM [4]. Therefore, the melting of the PbO-rich phase upon heating was associated with the shrinkage of the composites. The subsequent plastic deformation of the samples, containing a liquid phase, was caused by the slight pressure of the measuring rod in the dilatometer. The extent of shrinkage increased in proportion to the amount of ZrO_2 in the composites, and therewith, as evinced by TEM [4], to the increased concentration of microcracks. It is proposed that during shrinkage a microcrack healing in the presence of the liquid phase occurred, either as a crack closure due to the high surface tension of the liquid or as a particle recombination in the presence of the liquid phase.

The heating of the as-fired composites PZT–8 and 13.2 vol % ZrO_2 to the final temperature below the anticipated MT start ($m \rightarrow t$) at 1150 °C should, therefore, lead to a different kind of dilatometric curve. That was clearly confirmed by our experiment (Fig. 5). The heating–cooling cycles with the final temperature, 1100 °C, resulted in a size reduction of the samples. The extent of retained deformation was proportional to the ZrO_2 content. The hypothesis of microcrack healing was confirmed by TEM investigations, as described later.

A repeated heating of the same samples above 1150 °C resulted in a different kind of dilatometric curve. There, as shown in Figs 6 and 7, clear courses of MT of ZrO_2 in the composites with 8 and 13.2 vol % ZrO_2 could be followed. Upon cooling, the

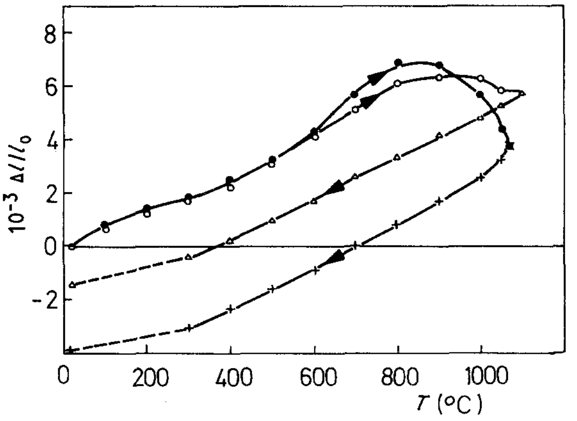

Figure 5 Heating–cooling dilatometric curves of the as-fired PZT–8 (o, △) and 13.2 (●, +) vol % ZrO_2, the final temperature being approximately 1100 °C.

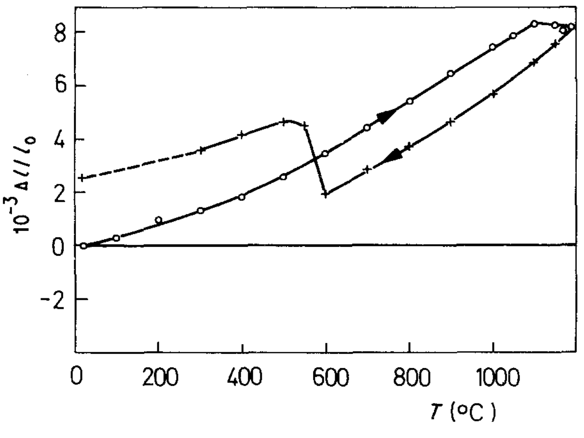

Figure 6 Repeated heating–cooling dilatometric curve of PZT–8 vol % ZrO_2 after firing the same sample to 1100 °C, the final temperature being 1150 °C. (▶) Heating, (◀) Cooling.

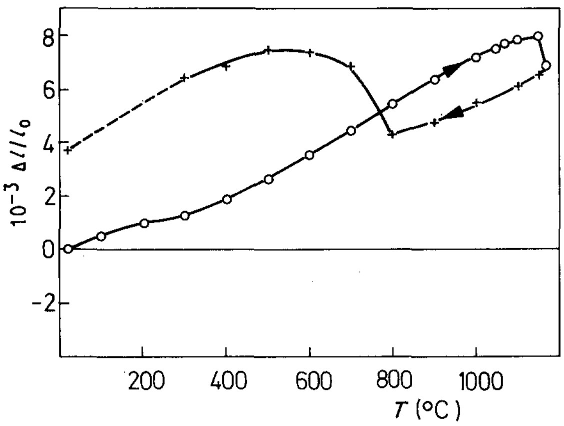

Figure 7 Repeated heating–cooling dilatometric curve of PZT–13.2 vol % ZrO_2 after firing the same sample to 1100 °C, the final temperature being 1150 °C. (▶) Heating, (◀) Cooling.

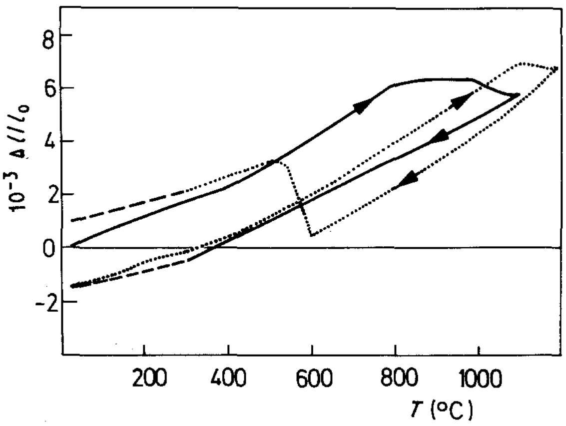

Figure 8 Dilatation–temperature curves of PZT–8 vol % ZrO_2, showing two successive heating–cooling cycles, the end point of the (——) first cycle equals the starting point of the (· · ·) second one.

spontaneous formation of microcracks during the MT (t → m) caused a dimensional increase, its extent being in proportion to the ZrO_2 content in the composites.

When comparing the two heating–cooling cycles of PZT–8 vol % ZrO_2 and PZT–13.2 vol % ZrO_2 it is worthwhile to note that the extent of plastic deformation in the first heating–cooling cycle, the result of microcrack healing (Fig. 5), corresponds in the range of the experimental error to the dimensional increase, caused by the spontaneous microcrack formation during the second heating–cooling cycle (Figs 6, 7). Both heating–cooling cycles together, with the end point of the first cycle equaling the starting point of the second one, form an almost closed hysteresis loop, see Fig. 8.

3.4. Microstructure of the additionally fired PZT–ZrO_2 composites

The microstructure of PZT–ZrO_2 composites after additional firing to 920 °C, i.e. to the temperature above the onset of the shrinkage as compared to the as-fired samples, was analysed by TEM.

Fig. 9 shows two PZT grains, separated by a thin, continuous film of amorphous phase. It is a typical configuration of a radial crack, originating at a ZrO_2 particle and extending intergranularly into the PZT matrix, in this case completely filled with the amorphous phase. Cracks, such as observed in the as-fired composites (see Fig. 1), were not found in the microstructure of the additionally fired samples.

The solidification of the PbO-rich phase upon cooling led to an approximately 10–20 nm thin amorphous film at the grain boundaries. The reason for the inhibition of the crystallization is probably, as described in the literature [12], the thinness of the intergranular phase.

4. Conclusion

The anomalous thermal expansion behaviour of PZT–ZrO_2 composites was studied. The course of the martensitic transformation of ZrO_2 in the composites was followed by dilatation–temperature curves. Also, intensive shrinkage was observed above 800 °C in the composites containing at least 8 vol % ZrO_2. The phenomenon was explained as microcrack healing in the presence of the PbO-rich liquid phase, and confirmed by the TEM analysis of additionally fired composites.

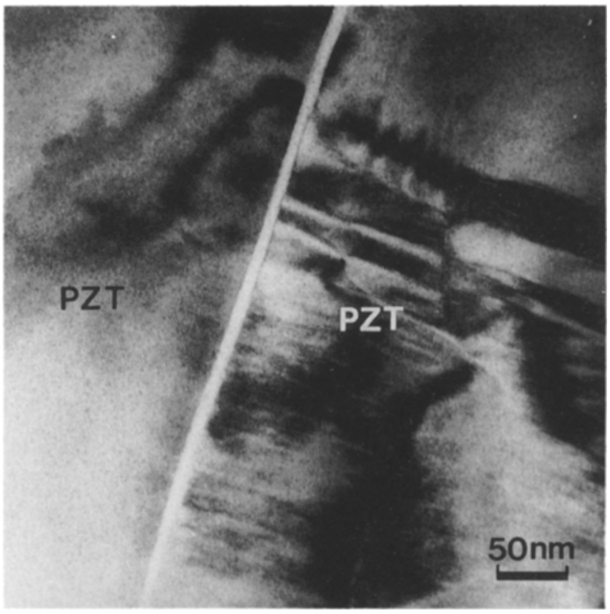

Figure 9 Transmission electron micrograph of the additionally fired PZT–8 vol % ZrO_2 composite (fired to 920 °C, 15 min) showing a continuous intergranular amorphous phase between PZT grains.

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References

1. B. JAFFE, W. R. COOK and H. JAFFE, "Piezoelectric Ceramics" (Academic Press, London, New York, 1971).
2. B. MALIČ, M. KOSEC and T. KOSMAČ, *Ferroelectrics*, **129** (1992) 147.

3. N. CLAUSSEN and M. RÜHLE, *Adv. Ceram.* **3** (1981) 137.
4. B. MALIČ, M. KOSEC, T. KOSMAČ, and V. KRAŠEVEC, *Mater. Res. Bull.* submitted.
5. D. R. BISWAS, S. CHANDRATREYA and J. A. PASK, *Ceram. Bull.* **98** (1979) 792.
6. B. MALIČ, MSc, University of Ljubljana (1990).
7. N. CLAUSSEN, F. SIGULINSKI and M. RÜHLE, *Adv. Ceram.* **3** (1981) 164.
8. W. M. KRIVEN and E. BISCHOFF, *ibid.* **12** (1983) 425.
9. E. C. SUBBARAO, H. S. MAITI and K. K. SRIWASTAVA, *Phys. Status Solidi* (*a*) **21** (1974) 9.
10. S. R. WITEK, E. P. BUTLER, *J. Amer. Ceram. Soc.* **69** (1986) 523.
11. M. K. RESER, (ed.), "Phase Diagrams for Ceramists" (American Ceramic Society, Columbus, 1969) pp. 2561 – 2.
12. E. K. W. GOO, R. K. MISHRA and G. THOMAS, *J. Amer. Ceram. Soc.* **64** (1981) 517.

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