Ceramics International 21 (1995) 391–394

Study of Phase Transition Line of PZT Ceramics by X-Ray Diffraction

A. Boutarfaia, C. Boudaren, A. Mousser & S. E. Bouaoud*

Institut de Chimie, Département de Chimie Inorganique, Université de Constantine, Route de Ain el Bey,
Constantine 25000, Algeria

(Received 12 October 1994; accepted 3 February 1995)

Abstract: The transition line between tetragonal and rhombohedral phases in PZT ceramics has been studied on the basis of X-ray diffraction data, with a view to establishing the morphotropic phase boundary (MPB). In ceramic manufacturing technology, piezoelectric PZT ceramic compositions are most likely to be near the morphotropic phase boundary. This boundary can move when even small levels of dopants are present in the PZT ceramics.

1 INTRODUCTION

The binary system $PbZrO_3$–$PbTiO_3$ has long been studied from both physical and technical points of view. $PbTiO_3$ and $PbZrO_3$ are known to be ferroelectric and antiferroelectric, respectively, and they form perovskite-type solid solutions. The ferroelectric ceramic PZT is a zirconate–titanate solid solution, and has very interesting properties. It has been shown that ceramic specimens with compositions near $Pb(Zr_x, Ti_{1-x})O_3$ are very useful for piezoelectric applications.[1]

The phase diagram of the solid solutions shows, for $x \simeq 0{\cdot}52$–$0{\cdot}55$ at room temperature, a morphotropic phase boundary (MPB) between the rhombohedral and tetragonal (T + R) phases.[2–9] It is known that compositions close to this boundary, when prepared by solid-state reaction of the oxides, display a co-existence of the tetragonal and rhombohedral phases. The composition corresponding to MPB exhibits maximum values of electromechanical properties[4] and has, therefore, been studied extensively to exploit the material from a commercial point of view.[1] However, controversies exist with respect to the MPB composition. Most studies have shown that the morphotropic phase change takes place at a specific ratio of Zr to Ti in the PZT solid solution, whereas a group of investigators[2–5] have demonstrated that there can be co-existence of tetragonal and rhombohedral phases over a wide range of compositions around the MPB.

Many authors have suggested the existence of a range of compositions where both the tetragonal and rhombohedral phases are thermodynamically stable.[2,3,5] Many authors have studied the phase transition line of the ternary system by XRD, theoretical thermodynamic analysis and measurements of piezoelectrics properties (K_r, Q_m, ϵ).[1–9]

The purpose of the present work was to determine the morphotropic phase transition of the PZT solid solution in the ternary system:

$$x\ PbZrO_3 - y\ PbTiO_3 - z\ Pb(Fe^{3+}_{0\cdot2}, Ni^{2+}_{0\cdot2}, Sb^{5+}_{0\cdot6})O_3$$

To determine the transition line in this ternary system, three compositional ranges were studied, using the 'geometrical addition' method (XRD).

2 EXPERIMENTAL

Three series of PZT compositions, $x\ PbZrO_3 - y\ PbTiO_3 - z\ Pb(Fe, Ni, Sb)O_3$, near the morphotropic phase boundary, where $x + y + z = 100\%$, were prepared from mixed oxides as given in Table 1. The mixtures were made from crystalline raw materials, viz. high purity Pb_3O_4 (99·9%), TiO_2 (99·56%), ZrO_2 (99·9%), NiO (99·9%), Fe_2O_3 (99·9%) and Sb_2O_3 (99·9%). Powders

---

*To whom correspondence should be addressed.

Ceramics International. 0272-8842/95/$9.50 © 1995 Elsevier Science Limited, England and Techna S.r.l. Printed in Great Britain

Table 1. Series of compositions and identified phases by X-ray diffraction

Section	Composition (*x/y/z*)	Temperature (°C) 850	950	1050	1150	1180
1	51·1/43·9/5	R	R	R	R	R
	50·1/44·9/5	T+R	T+R	R	R	R
	49·1/45·9/5	T+R	T+R	T+R	R	R
	48·1/46·9/5	T+R	T+R	T+R	T+R	T+R
	47·1/47·9/5	T+R	T+R	T+R	T+R	T+R
	45·1/49·9/5	T	T	T	T	T
2	47/43/10	R	R	R	R	R
	46/44/10	T+R	T+R	T+R	R	R
	45/45/10	T+R	T+R	T+R	T+R	T+R
	44/46/10	T+R	T+R	T+R	T+R	T+R
	43/47/10	T+R	T+R	T+T	T	T
	41/49/10	T+R	T	T	—	—
	39/51/10	T	T	—	—	—
3	42/43/15	R	R	R	R	R
	41/44/15	T+R	T+R	T+R	T+R	T+R
	40/45/15	T+R	T+R	T+R	T+R	T+R
	38/47/15	T	—	T	—	—

were mixed in stoichiometric ratios in an agate mortar for 6 h in distilled water and the dried powders were pressed at 10^4 kg/cm^2 into pellets. The samples for analysis after reaction were heated at the required temperature for 2 h in alumina crucibles with suitable control of ambient PbO vapor pressure. Heating rates were 1–6°C/min, and the temperature values were 850, 950, 1050, 1150 and 1180°C.

These samples were analysed by X-ray diffraction by means of a D500 Siemens diffractometer using CuK$_\alpha$ radiation with a nickel filter. The PZT phases were identified by analysis of the peaks in the range 43–46·5° two theta (2θ). The composition of the rhombohedral (R) phase of PZT was determined from the (200)-reflection and calibrated using the *d*-spacing determined as a function of composition.[1] The composition of tetragonal (T) phase was determined from the d_{200}–d_{002} tetragonal splitting. To make the difference between tetragonal, rhombohedral phases and rhombohedral–tetragonal (T+R) phase. The density of the ceramics sintered at 1180°C was 7·47 10^3 kg/m^3.

3 RESULTS AND DISCUSSION

The results obtained using XRD, for the first, second and third sections, are given in Table 1. A morphotropic phase boundary 'co-existence region' was observed (shown by duplicated (200) peaks). From the results, three types of 2θ intensity curves were obtained. Each type features differences as shown in Fig. 1. It has been reported in the literature that the splitting of these reflections into triplets takes place in conventionally-prepared

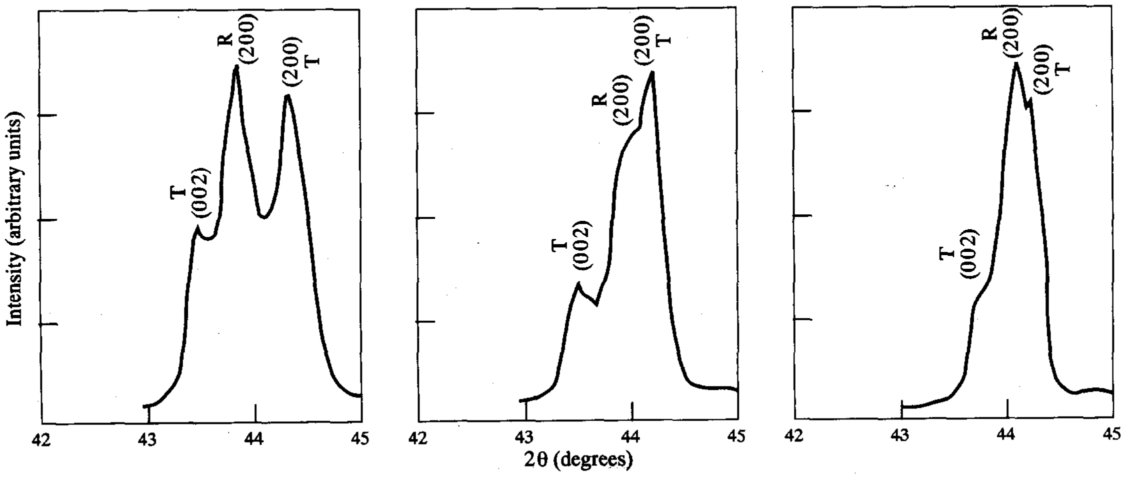

Fig. 1. Typical X-ray diffraction patterns.

Table 2. Lattice parameters (X-ray diffraction data): (a) as a function of temperature (for: 48·1/46·9/5) (b) as a function of composition (at 1180°C)

(a)

Lattice parameters	Temperature (°C) 850	950	1050	1150	1180
c_T (Å)	4·1198	4·1098	4·1154	4·1132	4·1158
a_T (Å)	4·0362	4·0374	4·0328	4·0418	4·0416
a_R (Å)	4·0812	4·0722	4·0726	4·0736	4·0704

(b)

Composition	Identified phases	Lattice parameters (Å)		
x		c_T	a_T	a_R
45·1	Tetragonal	4·1232	4·0246	—
47·1	Tetragonal + Rhombohedral	4·1218	4·0408	4·0718
48·1	Tetragonal + Rhombohedral	4·1132	4·0418	4·0736
49·1	Tetragonal + Rhombehedral	4·1276	4·0418	4·0722
50·1	Rhombohedral	—	—	4·0702

ceramics due to compositional fluctuations leading to the co-existence of the tetragonal and rhombohedral phases (T + R).[2] The morphotropic phase boundary is therefore not a line but a region in which tetratragonal–rhombohedral phases co-exist. Thus the tetragonal phase is stable from $x = 0$ to $x = x_T$ $(x_T > x_R)$[2,4] and the rhombohedral phase from $x = x_R$ to $x = 1$ $(x_T > x_R)$.[2] The region in which two phases co-exist is stable through the interval from x_T and x_R, although one of these phases can be metastable corresponding to the other phase in one part of this interval and vice versa in the other part.

The width $\Delta x = x_T - x_R$ of the 'co-existence region' from our work is close to that obtained by many authors.[6] It can be noticed that Δx varies with temperature. For example, for the second section at 850°C, $\Delta x = 8\%$; at 1150°C, $\Delta x = 6\%$; at 1180°C, $\Delta x = 3\%$. The higher the temperature the lower the value of Δx. The variation of Δx depends on the dopant concentration (z). This Δx variation is probably due to tetragonal and rhombohedral phases diffusion. Indeed, the increase of temperature facilitates the phases diffusion, shown in the homogenous kind of PZT solid solution. The homogenisation of the phases does not occur significantly at 850 and 950°C, but does occur during sintering at 1150 and 1180°C. This emphasises that higher temperatures are required for this homogenisation process.

Table 3. Average concentration x' in the PZT sample at 1180°C determined by the leverage law

Section	x	W_T/W_R	x'_i	x'
1	47·1	2·09	46·36	46·0
	48·1	5·19	45·73	
2	44	4·24	43·92	44·58
	45	0·32	45·25	
3	40	0·56	40·58	40·39
	41	0·24	41·20	

The values of the lattice parameters a_T and c_T of the tetragonal structure and a_R of the rhombohedral structure, were found to be nearly constant when varying separately the temperature and composition (Table 2).

It can be noted that the phase transition in the ceramic solid solution $Pb(Zr,Ti)O_3$ between tetragonal and rhombohedral phases is of the first order[4,5] when the Landau–Devenshire theory is applied. This is for several reasons, in particular because of the inhomogeneities associated with composition fluctuations.[4] The tetragonal and rhombohedral phases may co-exist in one grain, so that even a grain which consists mainly of one phase may contain nuclei of the other phase.[6–9]

To determine the thermodynamic equilibrium of the co-existence region, the average concentration value x' of 'T + R' phases is used. The leverage law[2] (eqn 1) is applied to obtain this concentration for each series of dopants (Table 3). It has been shown that ceramic specimens which had compositions near the above mentioned concentration, had very interesting properties.

$$\frac{W_T}{W_R} = \frac{x'_R - x'}{x'_T - x'} = \frac{I_T}{I_R} \qquad (1)$$

where:

W_T and W_R are the relative amounts of the two phases, x' is the relative weight, and x_T' and x'_R are the region edges and I_T/I_R is the ratio of the integrated intensity.

4 CONCLUSION

At 1180°C the width of the morphotropic phase boundary (MPB) of PZT ceramics has been found to be in the range ($47{\cdot}1 < x < 48{\cdot}1$, $45 < x < 44$ and $40 < x < 41$), respectively, for the first, second and third compositional sections studied. The width of MPB increases when the sintering temperature decreases and when the doping concentration is increased.

The large co-existence region of ferroelectric phases around the MPB is due to the local compositional variation in the material and due to the use of PZT powders prepared from the constituent solid oxides.

This study aimed to show the homogenisation reaction of intermediate tetragonal and rhombohedral PZT. The result is different from what has been found in other works and confirms the disagreement in the literature concerning the co-existence of tetragonal and rhombohedral phases. This is because each worker has made his samples in a different way and has achieved varying extents of compositional fluctuations which have not been removed by diffusional homogenisation.

REFERENCES

1. JAFFE, B., ROTH, R. S. & MARZULLO, S., *J. Res. Nat. Bur. Std.*, **55** (1955) 239.
2. AIR-GUR, P. & BENGUIGUI, L., *Solid State Communc.*, **15** (1974) 1077.
3. ISUPOV, V. A., *Solid State Communc.*, **17** (1975) 1331.
4. BENGUIGUI, L., *Solid State Communc.*, **11** (1972) 825.
5. CARLK, K. & HARDTL, K. H., *Phys. Stat. Sol.* (A), **8** (1971) 87.
6. ISUPOV, V. A., *Soviet Phys.-Solid State*, **10** (1970) 989.
7. ISUPOV, V. A., *Soviet Phys.-Solid State*, **18** (1976) 529.
8. ISUPOV, V. A. & STOLYPIN, Y., *Soviet Phys.-Solid State*, **11** (1970) 2062.
9. ISUPOV, V. A. & STOLYPIN, Y., *J. Phys. Soc. Japan*, (Suppl.) **28** (1970) 312.