The Morphotropic Phase Boundary in PZT Solid Solutions

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Abstract

PbZrxTi1-xO3 ceramics around the morphotropic phase boundary (MPB) have been prepared under different firing conditions using the usual ceramic techniques. The phases of the compounds have been investigated with X-ray diffraction photographs. It has been found that the MPB is not a narrow and vertically straight boundary but a region whose width depends on the firing time and temperature. The microstructures of the ceramics have been studied with a scanning electron microscope and can be correlated with the firing conditions. Measurements of lattice parameters, dielectric constants and transition temperatures are reported.

Introduction

PbTiO3 and PbZrO3 form solid solutions (PbZr_xTi_{1-x}O_3, PZT for short) over the whole composition range. The phase diagram (Fig. 1) of the system was established by a number of workers (Shirane & Takeda, 1952; Shirane, Suzuki & Takeda, 1952; Barnett, 1962). The phase diagram shows that for x \approx 0.52 there is an almost vertical boundary between a tetragonal ferroelectric phase and a rhombohedral ferroelectric phase. This boundary is nearly temperature independent and has been termed the 'morphotropic phase boundary' (MPB).

It was found by a number of workers that piezoelectric, elastic and dielectric constants rise to their maxima at x \approx 0.52 (Jaffe, Roth & Marzullo, 1954, 1955; Berlincourt, Cmolik & Jaffe, 1960). Attempts have been made from time to time to explain the occurrence of the maxima but with little success (Heywang, 1965; Isupov, 1968). Until 1968, workers in this field had thought that the rhombohedral and tetragonal phases coexisted only at a particular x, i.e. the MPB had negligible width. Employing Devonshire's (1949, 1951, 1954) theory, Isupov (1970) showed that it was possible for the tetragonal and rhombohedral phases to coexist over a range of composition. Pinczuk (1973) suggested that the rhombohedral to tetragonal transition was connected with the softening of an E(TO) mode, the mode condensing out at x \approx 0.53. This was put to experimental test by Bäuerle, Yacoby & Richter (1974) who found that, in contradiction to Pinczuk's suggestion, the frequency of the E(TO) mode softened but did not condense out at the MPB. Ari-Gur & Benguigui (1974, 1975) carried out X-ray diffraction experiments on a number of composition near the MPB and found that it extended over the composition range 0.49 \leq x \leq 0.64.

The lattice parameters of each phase were constant over the coexistence region. Recently, Isupov (1976) has shown that the MPB need not be strictly parallel or smooth. Kakegawa et al. (1977) reported that they found no coexistence of phases in materials prepared by chemical precipitation. They, however, observed coexistence in sintered ceramics prepared in the usual way. They have interpreted the coexistence in terms of compositional fluctuations.

Preparation of the samples

PbZr_xTi_{1-x}O_3 ceramics of compositions x = 0.43 to 0.65 at intervals of 2 mol % were prepared from 99.9% pure PbO, ZrO_2 and TiO_2 employing the usual ceramic techniques. The first firing was carried out at 1043 K for 2 h. X-ray diffraction revealed that the raw materials had not reacted at that temperature. After the first firing
the ceramic discs were crushed and ground and the resulting powder was divided into six portions each of which was pressed into small discs. The six discs (which were of the same composition) thus obtained were each heated for 2 h at six different temperatures 1173, 1223, 1273, 1323, 1373 and 1423 K, all ± 10 K (Fig. 2). Thus a total of 72 samples (twelve different compositions fired at six different temperatures), each one fired for 2 h, was obtained. All the samples fired at a particular temperature were then divided into two portions, one of which was reserved and the other was fired for 4 h. The fired portion was again divided into two, one part was reserved and the other fired for 22 h. The firing scheme is depicted in Fig. 2.

In order to ensure identical firing conditions for the samples, the furnace was heated to the required firing temperature, \( t_f \), and left until the temperature was steady. Then all the twelve samples, \( x = 0.43 \) to 0.65, to be fired at \( t_f \) were properly covered and gradually introduced into the furnace. After being fired, the samples were rapidly withdrawn with the furnace still at \( t_f \). This method of quenching ensured that the samples were fired at a constant temperature for the desired length of time.

Each of these samples will be denoted by \( \text{Zr/Ti}(h_f)t_f \) where \( \text{Zr/Ti} \) stands for the mol % of the Zr/Ti content of the composition, \( h_f \) for the firing time in hours and \( t_f \) the firing temperature in K.

**Investigation of the phases**

X-ray diffraction was employed for the investigation of phases of the different compounds. Debye–Scherrer photographs using Cr Ka radiation were taken. Some of the reflections occurring at high Bragg angles were weak and broad. However, the reflections given in Table 1 were reasonably sharp and with their help it was possible to determine unambiguously the phases of the compounds. Of these reflections, 200 and 310 were of particular importance in determining the coexistence of the phases, because in the tetragonal phase these two reflections are doublets appearing approximately at the following angles: 002, 67.0°; 200, 69.3°; 013, 122.4°; 310, 128.0°. In the rhombohedral phase these reflections appear approximately at 200, 68.4°; 310, 125.3°; 310, 125.3°. The Bragg angles corresponding to the reflections 310, and 310, are very close to each other and for this reason they appear as a single diffraction line. Therefore, when the two phases coexisted these reflections appeared to be split into three in the following order:

\[
002_t, 200_t, \text{ and } 013_t, (310 + 310), \text{ and } 310_t;
\]

as seen in Fig. 3. The results of the X-ray investigations are shown in Fig. 4(a)–(c). The following observations were made.

(a) Chemical reaction was not complete in the compounds fired at 1173 K for 2 h [i.e. in all \( \text{Zr/Ti}(2)1173 \)]. The same compounds fired for \( (2+4) \) h at 1173 K were a mixture of tetragonal (\( t \)) and rhombohedral (\( r \)) phases. However, their phases could not be determined when fired for \( (2+4) \) h at 1173 K, because the lines were broad and diffuse.

(b) All \( \text{Zr/Ti}(2)1223 \) were a mixture of phases \( t \) and \( r \). As the temperature was raised (for \( h_f = 2 \) h), the coexistence region reduced in width and it was confined to only 2 mol % of Zr at the highest temperature studied. Fig. 4(a) shows that the MPB is neither vertical nor symmetrical.

(c) Fig. 3 shows the diffraction patterns of \( \text{Zr/Ti} \) 51/49, 52/48, 55/45 and 56/44 fired at 1273 K for 2 h. The phases of these compounds are \( t \), \( t+r \), \( t+r \) and \( r \) respectively. This shows that with \( h_f \) and \( t_f \) constant, the structure is very sensitive to the proportion of Zr/Ti and that an addition of even 1 mol % Zr is enough to bring about a change in the phases of these compounds.

(d) The position of the MPB changes when the compounds are fired for a longer time. It has been observed that the higher the \( t_f \) and the longer the \( h_f \), the more the shift of the MPB towards the \( \text{PbZrO}_3 \) end of the phase diagram. From diffraction patterns of \( \text{Zr/Ti} \) 49/51, 51/49, 53/47, 55/45, 57/43 and 59/41 fired at 1373 K for 2 h it was seen that the MPB was 2 mol % wide. An additional firing of 4 h shifted the MPB by 2 mol % toward the \( \text{PbZrO}_3 \) end of the phase diagram and at the same time made the MPB at least 4 mol % wide. Firing for an additional 22 h made all the compounds tetragonal and the MPB was shifted outside the range of composition studied.

(e) An examination of the diffraction pattern of the end members of the coexistence region shows that the intensity of the 200, reflection is higher (compared with that of 200, and 002,) on the rhombohedral side of the

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**Table 1. Reflections in the tetragonal and rhombohedral phases**

<table>
<thead>
<tr>
<th>Reflection</th>
<th>Tetragonal ( t )</th>
<th>Rhombohedral ( r )</th>
</tr>
</thead>
<tbody>
<tr>
<td>110</td>
<td>splits into 011 and 110</td>
<td>( (110 + 110) ) appears as singlet</td>
</tr>
<tr>
<td>111</td>
<td>singlet</td>
<td>splits into 111 and 111</td>
</tr>
<tr>
<td>200</td>
<td>splits into 002 and 200</td>
<td>singlet</td>
</tr>
<tr>
<td>310</td>
<td>splits into 013 and 310</td>
<td>( (310 + 310) ) appears as singlet</td>
</tr>
<tr>
<td>222</td>
<td>singlet</td>
<td>splits into 222 and 222</td>
</tr>
</tbody>
</table>

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**Fig. 2. Firing scheme for the ceramics, \( \text{PbZr}_x\text{Ti}_{1-x}\text{O}_3 \). The hatched portions represent the portions used during the present investigation.**
MPB than on the tetragonal one. This can be seen in Fig. 3 and is consistent with having a preponderance of rhombohedral crystallites in ceramics grown on the rhombohedral side of the MPB (vice versa for the tetragonal side).

(f) All the Zr/Ti(2 + 4 + 22)1423 became tetragonal. Superimposed on the tetragonal pattern were some extra diffraction lines coming from free ZrO2 and TiO2. This happens because of Pb loss due to prolonged firing at such a high temperature (Northrop, 1968).

**Lattice-parameter measurements**

X-ray diffraction photographs were used for the determination of the lattice parameters. The reflections used were 222, 013, and 222, 222. Most of the high-angle lines were weak and broad and therefore it was not possible to use them in calculating lattice parameters. The cause of the broadening of the diffraction lines may be due to inhomogeneity of the compounds because the melting points of ZrO2 and TiO2 are 2973 and 2073 K respectively, whereas that of PbO is 1193 K. Both ZrO2 and TiO2 have low mobility even at 1423 K. This means that the homogeneity depends on the initial mixing of the raw materials. However, the reflections mentioned above were sufficient to measure the lattice parameters a, c, a, and c. It was observed that within experimental error the value of the c axis is remarkably constant except where the phase itself changes. This agrees well with the findings of Ari-Gur & Benguigui (1975). The a axis changes only slightly except for the specimens fired at 1423 K for (2 + 4 + 22) h for which it is much shorter. The average

![Fig. 3. Powder photographs of some PZT ceramics fired for 2 h at 1273 K.](image)

![Fig. 5. Average values of the lattice parameters of the PZT ceramics.](image)

![Fig. 4. Phases of the ceramics around the MPB fired at different temperatures. ○ Rhombohedral; × tetragonal; © rhombohedral + tetragonal; ◆ incomplete reaction; ○ excessive lead loss; ? phases could not be decided. (a) Firing time 2 h. (b) Firing time 2 + 4 h. (c) Firing time 2 + 4 + 22 h.](image)
value of the axial lengths, where they are nearly equal, are shown in Fig. 5. The rhombohedral angle \( \alpha \), was found to vary only slightly.

**Scanning electron microscopy**

The microstructures of the ceramics were studied with a Cambridge Stereoscan electron microscope. The microstructures obtained can be divided into three categories depending on the shape and size of the grains of the ceramics.

(i) Ceramics with grain size \( \sim 2 \mu m \) observed in Zr/Ti(2)1223 and Zr/Ti(2+4+22)1173.

(ii) Ceramics with fused globular grains of size \( \sim 7 \mu m \) observed in Zr/Ti(2)1273, Zr/Ti(2)1323, Zr/Ti(2)1373, Zr/Ti(2)1423, Zr/Ti(2+4+22)1223, Zr/Ti(2+4+22)1273 and Zr/Ti(2+4+22)1323.

(iii) Ceramics with octahedrally shaped crystallites

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![Micrographs](a) ![Micrographs](b) ![Micrographs](c)

Fig. 6. Some scanning electron micrographs of the ceramics. (a) 59/41(2)1223, average grain size \( \sim 2 \mu m \). (b) 59/41(2)1423, average grain size \( \sim 7 \mu m \). (c) 59/41(2+4+22)1423.
The following features were found.

(a) When fired at 1223 K for 2 h, the reaction was complete and the grains were the same size as those in the starting materials. An example is shown in Fig. 6(a).

(b) After 2 h firing at temperatures between 1273 and 1423 K the grains became fused together and enlarged (see Fig. 6b). They had a globular shape with smooth surfaces, and this firing condition gave additional strength to the ceramics. This type of effect is well known in many other ceramics [e.g. in periclase (Rigby, Richardson & Ball, 1946); in rutile, kaolin and porcelain (Mehmel, 1951)].

(c) When fired for (2 + 4 + 22) h, weak ceramics were formed because of loss of PbO. The prolonged sintering increased the dimensions of the ceramic pellets with a simultaneous decrease in their strength. This overfiring is known to result in a decrease in ceramic density (Haertling, 1963) and has been observed also in modified PZT (Krikorov et al. 1975).

(d) At 1173 K and (2 + 4 + 22) h firing, the reaction was complete, but the ceramics were not as good as those fired at higher temperatures (1373–1423 K) for a relatively short time (2 h). This suggests that even the most prolonged firing would not produce a sintered compact comparable to a matured product fired at a higher temperature for a shorter time (see Takahashi, 1970). In Fig. 6(c) an example of a ceramic fired for (2 + 4 + 22) h at 1423 K is shown. Note the occurrence of octahedral crystallites, which are probably in the tetragonal phase.

Discussion

It has been observed in the previous sections that the MPB is not a narrow and vertically straight boundary but a region whose width depends on the firing time and temperature. Depending upon the firing conditions, the MPB can be as narrow as 1 mol %, as observed in ceramics fired at 1273 K for (2 + 4) h and also in those fired at 1323 K for (2 + 4 + 22) h (Fig. 4b and c). This behaviour is in contradiction to the findings of Kakegawa et al. (1977). The sintered ceramics they studied were always of mixed phases. However, with chemically precipitated ceramics, they observed that the MPB was confined to within 1 mol % of Zr, viz 0.53 ≤ x ≤ 0.54, and did not alter with change in the firing time. Ari-Gur & Benguigui (1975) investigated the behaviour of the ceramics fired at 1273 K for 2 h and found that the MPB was 14 mol % wide. In contrast to this, in the present case the MPB is only 4 mol % wide under similar firing conditions (Fig. 4a). These apparent contradictions are not very surprising if one takes into account the fact that the structure of the ceramics in this region is much affected by a slight change in the sintering condition.

In the region where the two phases coexist, there may be islands of rhombohedral regions scattered in the tetragonal matrix or tetragonal regions scattered in the rhombohedral matrix. But whether they would be of the same composition or not cannot be inferred from the present study. It is probably worth mentioning that the existence of such islands of differing compositions has been postulated by Isupov (1968). With the help of this theory Isupov was able to explain the increase in polarization near the MPB although the magnitude of the increase did not completely fit experimental measurements. It is possible that by incorporating the additional factor of lattice-parameter variation this discrepancy might be reduced. When the ceramics are heated for a longer time their phases change. This means that the atoms assume different arrangements caused most probably by diffusion, which is the main mechanism by which reaction proceeds in powder-pressed and sintered (as opposed to hot-pressed at a lower temperature) ceramics (Kingery, 1958). Fig. 7 shows dielectric constant measurements on the ceramics fired at 1423 K for 2 h. The dielectric constant was found to peak in the coexistence region, and is in agreement with other authors. Fig. 8 shows the transition temperatures of the ceramics fired at 1423 K.

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Fig. 7. Dielectric constants of PZT ceramics around the MPB fired for 2 h at 1423 K.

Fig. 8. Transition temperatures of the PZT ceramics around the MPB fired for 2 h at 1423 K.
for 2 h. It can be seen that the transition temperature decreases as the Zr content increases.

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References
