

Crystal Clamping in PbTiO_3 Glass-Ceramics

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Lead titanate crystals precipitated in borate glasses by the glass-ceramic process have been found by X-ray diffraction to have abnormally low axial ratios. This has been shown to be due primarily to the stress applied by the surrounding glass matrix.

1. Introduction

Controlled nucleation and crystal growth in glasses has led to the development of materials with new combinations of crystal composition and microstructure. Often the crystalline phase formed is metastable, and difficulties are encountered in characterising its properties from phase equilibria data. In particular, the degree of solid solubility for these phases is unknown. In materials where it is not possible to separate chemically the crystalline phase it is therefore a problem to find the degree of solid solubility.

Solid solution crystals are commonly used in the production of ceramic ferroelectric materials in order to obtain more desirable properties than those of the pure crystal phases. The glass-ceramic technique offers some potential advantages in the preparation of ferroelectric materials and it is important therefore to obtain the required solid solution crystals by precipitation from a glass.

X-ray diffraction is chiefly used to analyse the crystalline phases. However, diffraction techniques have an important limitation; the crystals may be highly strained and the effects of strain may not be easily distinguished from those due to solid solution. The crystals normally grow at a temperature above the annealing temperature of the glass, and will therefore be strain-free initially. Small strains will arise from differences in expansion between the crystal and the glass below the annealing point. Much larger strains will arise if the crystal undergoes a phase change involving a substantial change of shape, such as a ferroelectric transition in lead titanate.

The purpose of the present paper is to show that large strains occur in PbTiO_3 crystals precipitated in a glassy matrix by the glass-ceramic process. The axial ratio in the tetragonal crystals is thereby considerably reduced.

2. Experimental Procedure

Glass-ceramic compositions suitable for the precipitation of the ferroelectric phase PbTiO_3 were melted in platinum crucibles using a resistance furnace at 1100°C . The glasses were composed from the oxides of lead, barium, boron and titanium, with progressive substitutions of ZnO for PbO as given in table I. Glass compositions were given identical heat-treatments of 520°C (nucleation temperature) and 610°C (crystal growth temperature) for a total of 36 h producing fine-grained materials with crystal clusters 2 to 3 μm in diameter formed from individual crystallites of about 0.5 μm across. Detailed properties of the PbTiO_3 glass-ceramics and experimental procedures have been described previously [1].

With increasing ZnO content, the lead titanate yield is reduced for a given heat-treatment. Quantitative determinations of the crystal content were made by comparing the integrated intensity of the d_{III} X-ray diffraction line to the intensity of the same line from pure PbTiO_3 , and the results are included in table I.

3. Crystallographic Observations

Angular positions of the X-ray diffraction lines for the various glass-ceramic materials were determined directly from the chart recorder of a

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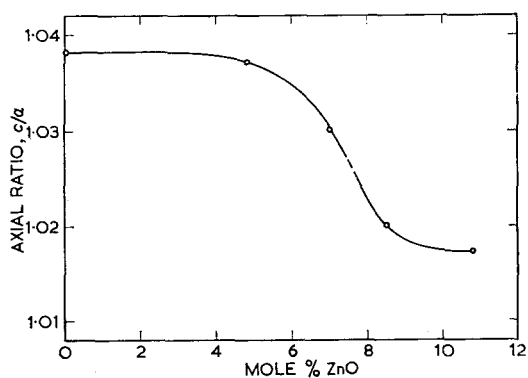
TABLE I PbTiO₃ Glass-ceramic compositions in mole %.

Composition	PbO	BaO	ZnO	TiO ₂	B ₂ O ₃	SiO ₂	Al ₂ O ₃	TeO ₂	Wt % crystal
0	23.8	20.0	0.0	23.8	25.0	3.0	3.0	1.5	64.8
1	19.0	20.0	4.8	23.8	25.0	3.0	3.0	1.5	57.0
2	16.8	20.0	7.0	23.8	25.0	3.0	3.0	1.5	50.2
3	15.3	20.0	8.5	23.8	25.0	3.0	3.0	1.5	35.5
4	13.0	20.0	10.8	23.8	25.0	3.0	3.0	1.5	28.0

Philips PW1310 diffractometer. All measurements were taken at room temperature, using a slow scanning speed of $\frac{1}{4}^\circ 2\theta/\text{min}$ and a fast chart speed of 1.2 m/h, so that the line positions could be determined within one minute of arc of 2θ . The observed d -spacings in angstroms are given in table II for forward reflection lines only since lines in the back reflection region were of low intensity and highly broadened.

Measurement of the axial ratio for the tetragonal lead titanate crystals precipitated in glass was performed graphically with the aid of a partial Hull-Davey chart. The chart was constructed by plotting the variation of the quantity $[(h^2 + k^2) + l^2/(c/a)^2]$ against c/a on semilog paper for the observed values of hkl .

The variation of the c/a ratio with ZnO content of the material is shown in fig. 1. At zero ZnO concentration (composition No. 0) the measured value was 1.038 compared with 1.063 for stress-

Figure 1 Axial ratio in PbTiO₃ glass-ceramics.

free pure PbTiO₃ at room temperature [2]. As the c/a ratio decreases the $hkl0$ spacings increase, in general, while the diffraction pattern approaches that of a simple cubic crystal, as can be seen in the Debye-Scherrer photographs in fig. 2. The photographs were taken using a camera of 114.6 mm diameter and Co K α radiation.

4. Discussion

The observed decrease in c/a ratio for PbTiO₃ crystals in the glass-ceramics might be a result of either strain or solid solution formation. PbTiO₃ and BaTiO₃ are isomorphous [3], and form a continuous series of solid solution crystals when fired together in the temperature range 1100 to 1400°C. The axial ratio at room temperature varies continuously from 1.063 for PbTiO₃ to 1.008 for BaTiO₃ caused by a progressive decrease in the c -axis length and a corresponding increase in the length of the a -axis. Very similar crystallographic changes would be expected if pure PbTiO₃ was subjected to increasing stresses opposing the cubic to tetragonal transition.

In order to separate the effects of strain from those due to solid solubility a leaching technique was employed. A specimen of the glass-ceramic containing no ZnO (No. 0) was leached for 2 h at room temperature in 5% HNO₃ in order to remove the glass fraction. The slurry was filtered, washed and thoroughly dried and the c/a ratio remeasured.

The axial ratio was seen to increase to a value of 1.052 and the difference between this value and the value of 1.063 for stress-free pure PbTiO₃ might be attributed to solid solubility of Ba for

TABLE II D -spacings in angstroms for PbTiO₃ glass-ceramics.

Composition/Line	001	100	101	110	002	200	112	211	202	220
0	4.073	3.925	2.825	2.775	2.036	1.961	1.641	1.610	1.412	1.385
1	4.067	3.911	2.823	2.780	2.033	1.963	1.638	1.611	1.411	1.387
2	4.055	3.934	2.820	2.786	2.028	1.963	1.634	1.612	1.409	1.389
3	4.019	3.951	2.812	2.782	2.011	1.965	1.631	1.613	1.406	1.392
4	3.998	3.948	2.813	2.782	2.000	1.966	1.629	1.614	1.405	1.396

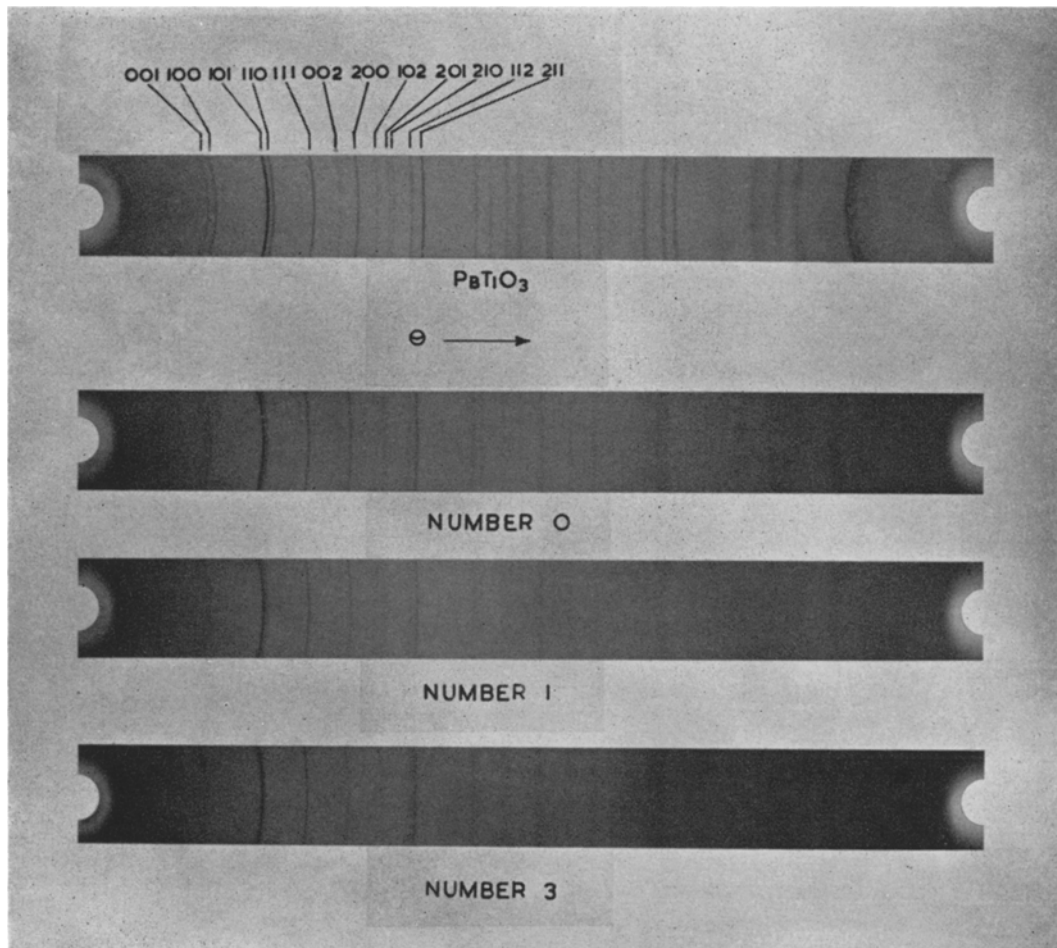


Figure 2 Debye-Scherrer photographs of lead titanate and PbTiO_3 glass-ceramics of decreasing axial ratio. Compositions are given in table I.

Pb. This analysis assumes that the removal of the glass fraction was complete and that the crystals were allowed to assume their stress-free dimensions. Measurement of the d_{III} diffraction peak height intensities for unleached, leached and pure PbTiO_3 samples indicated that most of the glass had been removed. It is possible however that a small amount of residual glass could have a disproportionate effect since the crystals grow in clusters and a small amount of glass at the centre of a cluster could restrain the crystals from assuming their proper dimensions.

Unfortunately it was not possible to separate the crystals from the glass by leaching the glass-ceramics of high ZnO content; so the strain in the crystals could not be determined. The residual glass compositions of these glass-ceramics contained more TiO_2 , since less

PbTiO_3 was precipitated, and this reduced the solubility. Even after repeated leaching in fresh acid much of the glass remained undissolved.

The distinction between the effects due to solid solubility and strain in the present system is best observed by the variation of the unit cell volume with c/a ratio shown in fig. 3. The cell volume is calculated as a^2c for the glass-ceramics from the data given in table II. The increase in cell volume in the solid solution series $(\text{Pb},\text{Ba})\text{TiO}_3$ can be attributed to the larger ionic radius of the Ba^{2+} ion (1.35 Å) to that of the Pb^{2+} ion (1.10 Å) [3]. In pure PbTiO_3 , however, the cell volume decreases with decreasing c/a ratio from room temperature to 490°C, resulting in a negative coefficient of thermal expansion as observed by Shirane and Hoshino [2].

The PbTiO_3 crystals in the glass-ceramics also

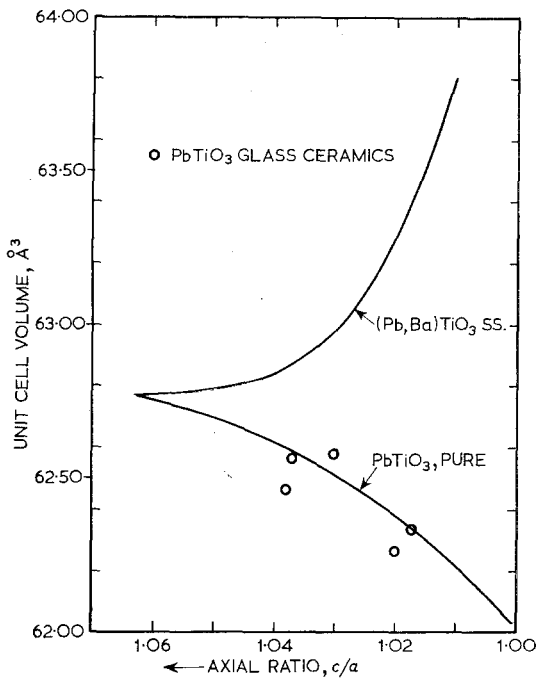


Figure 3 Unit cell volume against axial ratio in pure PbTiO_3 over the temperature range 30 to 490° , from [2], $(\text{Pb}, \text{Ba})\text{TiO}_3$ solid solutions at 30° from [3], and PbTiO_3 glass-ceramics at room temperature.

show a decrease in the unit cell volume with decreasing c/a ratio following the line for pure PbTiO_3 . It seems probable therefore that the observed reduction in axial ratio for the glass-ceramic materials is due to a clamping effect imparted by the glass matrix, rather than by a substitution of Ba for Pb.

So far no other method than X-ray diffraction has been found capable of distinguishing between solid solubility and strain in these glass-ceramics. Analysis of the chemically separated crystals for barium would have been indecisive since any barium found could equally well be attributed to residual glass as to solid solution in the crystals. Furthermore any reduction in the Curie temperature for the solid solution series $(\text{Pb}, \text{Ba})\text{TiO}_3$ can also be expected from the Clausius-Clapeyron relation, the phase transition of the pure PbTiO_3 being shifted to lower temperatures with an increase in hydrostatic pressure.

The progressive decrease of c/a due to the increasing ZnO content of the melt may have been the result of an increase in the degree of solid solubility or of an increase in the setting temperature of the glass – or both. It is unlikely that Zn

itself substitutes for Pb in the PbTiO_3 crystals, since only very limited solid solubility takes place between titanates of different structural types, such as perovskite PbTiO_3 and ilmenite ZnTiO_3 [4]. The increase of ZnO content of the melt was accompanied by a decrease of the PbO content, thereby decreasing the PbO/BaO ratio. If this ratio was the controlling factor in the degree of solid solubility, one would expect a continuous decrease in c/a against ZnO content, rather than the sharp decrease exhibited at approximately 7% ZnO as shown in fig. 1. On the other hand, the addition of ZnO to the matrix glass probably raises its viscosity, as is observed when ZnO is added to silicate glasses [5]. The annealing point of the glass is close to the Curie temperature of the lead titanate crystals (490°C), and the crystals undergo a large change in c/a in a narrow range of temperature as shown in fig. 4, taken from the work of Shirane and Hoshino [2].

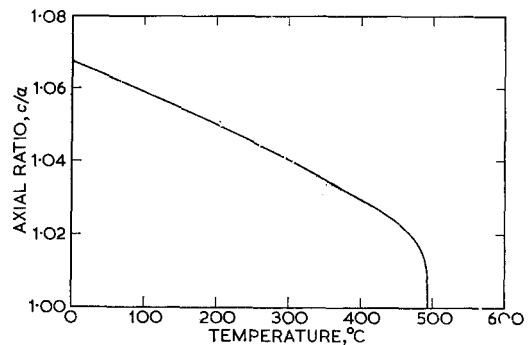


Figure 4 Temperature-dependence of the axial ratio in lead titanate (from [2]).

An increase in the viscosity of the glass will give an increase in its annealing temperature. If this is above the Curie temperature of the crystals no flow can occur in the glass to relieve the stresses, and the strain in the crystals will be a maximum. If the annealing point is below the Curie temperature some of the stresses will be relieved and there will be less strain in the crystals. The sharp decrease of c/a in the glass-ceramics at approximately 7% ZnO can be related to the setting point of the matrix glass corresponding to the Curie temperature. The locked crystals undergo a limited spontaneous strain resulting in a reduced axial ratio.

Acknowledgement

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