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# Thermal vibrations in PbTiO<sub>3</sub> single crystals

J Kwapuliński<sup>1</sup>, J Kusz<sup>1</sup>, H Böhm<sup>2</sup> and J Dec<sup>1</sup>

<sup>1</sup> Institute of Physics, University of Silesia, 40-007 Katowice, Poland

<sup>2</sup> Institut für Geowissenschaften der Universität, 55099 Mainz, Germany

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## Abstract

The structure refinement from x-ray diffraction data on PbTiO<sub>3</sub> single crystals revealed that the parameters of the mean thermal displacements for Pb ions in the high temperature paraelectric phase (SG  $Pm\bar{3}m$ ) showed large values. Therefore models with displacements of Pb ions in several relevant directions were tested. It is very likely that in the cubic phase there is disorder for the Pb occupancy on three equivalent positions off the position (0, 0, 0).

## 1. Introduction

Lead titanate (PbTiO<sub>3</sub>) has the perovskite-type structure (Shirane and Hoshino 1951). One phase transition from the paraelectric to the ferroelectric state at 493 °C was observed (Shirane and Hoshino 1951, King-Smith and Vanderbilt 1994). The ferroelectric phase is much better investigated than the paraelectric one. There are however some publications available describing the structure of the paraelectric phase. The crystal lattice dynamics has not been investigated yet. The compound has been of interest for some time because it is one of the end members of the technologically important solid-solutions series PbZr<sub>1-x</sub>Ti<sub>x</sub>O<sub>3</sub> (PZT) with their very attractive piezoelectric, ferroelectric and pyroelectric properties.

In several studies (Comes *et al* 1968, Chen *et al* 1988, Bonneau *et al* 1991, Glazer *et al* 1993, Kwapuliński *et al* 1994, 1997, 2001) the existence of ‘disorder’ has been reported in perovskites even in the paraelectric phase whose symmetry is commonly described by the  $Pm\bar{3}m$  space group. The theoretical model describing this ‘disorder’ state was first proposed by Comes *et al* (1968). This model was then applied to BaTiO<sub>3</sub> (Itoh *et al* 1985), to BaTiO<sub>3</sub> and KNbO<sub>3</sub> (Chen *et al* 1988), PbMg<sub>1-x</sub>Nb<sub>x</sub>O<sub>3</sub> (Bonneau *et al* 1991), PbHfO<sub>3</sub> (Kwapuliński *et al* 1994), PbTiO<sub>3</sub> (Kwapuliński *et al* 1997) and PbZrO<sub>3</sub> (Kwapuliński *et al* 2001). In this paper the results of model calculations based on single-crystal diffraction data on PbTiO<sub>3</sub> in the paraelectric phase are presented.

## 2. Experiment

The PbTiO<sub>3</sub> single crystals were synthesized by the flux method. A mixture of PbO, B<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> in the proportions of 62 mol%:27 mol%:11 mol% was melted in a platinum crucible

**Table 1.** Experimental details, thermal displacement parameters ( $\text{\AA}^2$ ) and bond lengths ( $\text{\AA}$ ).

	500 °C	520 °C	540 °C	560 °C	580 °C	600 °C
Lattice par. $a$ ( $\text{\AA}$ )	3.9689(7)	3.9705(8)	3.9715(8)	3.9715(8)	3.9780(8)	3.9759(8)
No. of ref.	417	417	416	455	417	271
$R_1$	0.0145	0.0161	0.0146	0.0149	0.0147	0.0395
$wR_2$	0.0287	0.0348	0.0390	0.0367	0.0292	0.0815
$s$	1.090	1.116	1.029	1.465	1.176	1.102
Ext.	0.418	0.403	0.442	0.634	0.541	0.449639
$U_{11}$ Pb ( $\text{\AA}^2$ )	0.0355(9)	0.0354(7)	0.0357(7)	0.0382(8)	0.0378(7)	0.0378(17)
$U_{11}$ Ti ( $\text{\AA}^2$ )	0.0143(9)	0.0140(7)	0.0139(7)	0.0158(7)	0.0159(6)	0.0155(15)
$U_{11}$ O ( $\text{\AA}^2$ )	0.0143(6)	0.0115(3)	0.0130(1)	0.0135(3)	0.0135(1)	0.0144(2)
$U_{\text{eq}}$ O ( $\text{\AA}^2$ )	0.022(2)	0.023(2)	0.023(2)	0.024(2)	0.022(1)	0.021(3)
$d$ (Ti–O) ( $\text{\AA}$ )	1.985(1)	1.985(1)	1.986(1)	1.986(1)	1.986(1)	1.986(1)
$d$ (Pb–Ti) ( $\text{\AA}$ )	3.439(1)	3.439(1)	3.439(1)	3.439(1)	3.449(1)	3.439(1)

at a temperature of 1000 °C for 4 h. Then the melt was cooled at a rate of 5 °C h<sup>-1</sup> to 900 °C and the solvent was poured off. A constant temperature gradient along the vertical axis of the crucible of about 10 °C cm<sup>-1</sup> was maintained throughout the synthesis. Transparent light-yellow crystals in the form of thin plates were obtained.

The x-ray experiment were performed using single crystals of good quality and with flat surfaces without cracks with nearly cube shape and dimensions of  $\sim 80 \times 80 \times 80 \mu\text{m}^3$ . Laue photographs of these crystals were taken in order to select a suitable one. The diffraction experiments were carried out on the four-circle diffractometer CAD4 (Enraf Nonius) with graphite-monochromatized Mo K $\alpha$  radiation. The crystals were mounted with cement on the tip of a quartz glass fibre. A heating device (Böhm 1995) was used for the high temperature experiments. The temperature stability was  $\pm 1$  °C. The cell parameter variation was determined by using 25 selected Bragg reflections. The data collection of the intensities was performed at 500, 520, 540, 560, 580 and 600 °C. Data were collected for  $2\theta < 60^\circ$ , with  $0 \leq h \leq 5$ ,  $-5 \leq k \leq 5$  and  $-5 \leq l \leq 5$  in  $\omega$ - $2\theta$  scans. During the data collection, three standard reflections were monitored each hour. The morphological absorption correction and data reduction was performed with the program JANA98 (Petricek and Dusek 1998). Further details about the data collection are shown in table 1.

The structures based on the standard perovskite model were refined in the SG  $Pm\bar{3}m$  using the Shelx193 (Sheldrick 1993) computer program. The  $R$ -factor fluctuated between 1.44% and 1.63% (except for 600 °C) for all 33 unique reflections. The mean square thermal displacements are shown in table 1.

### 3. Results

The temperature dependence of the lattice parameters in the paraelectric phase of PbTiO<sub>3</sub> is shown in figure 1. The error bar for each experimental point is smaller than the symbol. The values of the lattice parameters in the ferroelectric phase are similar to those obtained earlier by Glazer and Mabud (1978). This indicates the good quality of the crystals used in our research. The tetragonal to cubic phase transition occurs at about 480 °C.

Using the Shelx193 program for the data analysis we obtained the anisotropic mean square thermal displacement  $U$  for each ion in the mean position of the SG  $Pm\bar{3}m$ , i.e.  $U(\text{Pb})$ ,  $U(\text{Ti})$  and  $U(\text{O})$ , respectively. These factors  $U$  are shown in figure 2. We can see that  $U_{11}(\text{Pb}) > U_{11}(\text{Ti}) > U_{11}(\text{O})$ . Over the whole temperature range investigated the value

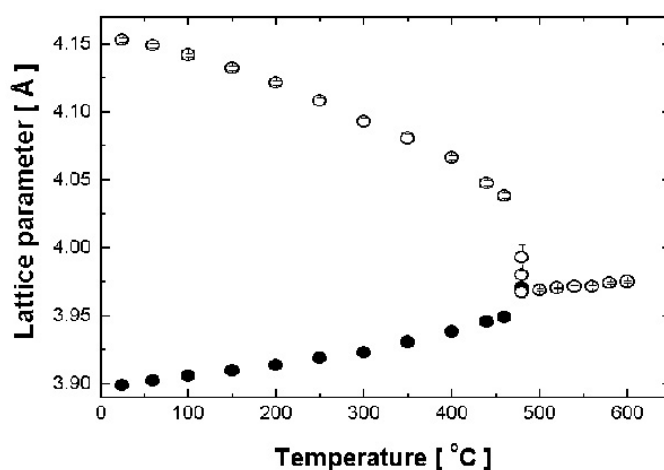


Figure 1. The variation of the lattice parameters of PbTiO<sub>3</sub> as a function of temperature.

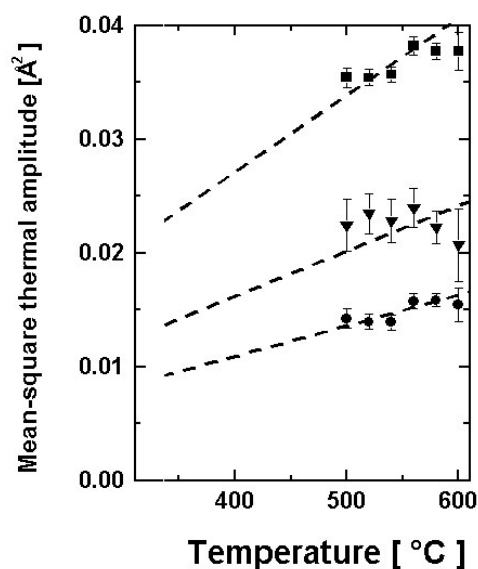
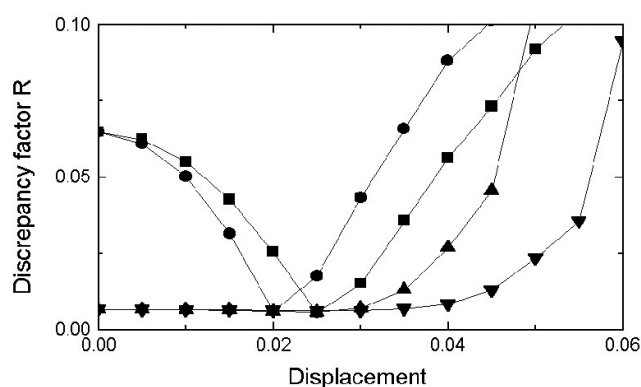


Figure 2. The mean square thermal amplitudes for the ions of PbTiO<sub>3</sub> in their standard positions in the perovskite structure ((■)— $U(\text{Pb})$ , (▼)— $U(\text{Ti})$ , (●)— $U_{\text{eq}}(\text{O})$ ).

of  $U(\text{Pb})$  is significantly larger than  $U(\text{Ti})$ . A similar relation has already been observed for other lead-containing perovskites (Glazer and Mabud 1978, Kuprianov and Kogan 1991, Kwapuliński *et al* 1994, 1997, 2001). It is surprising that the heaviest atom in the structure has the largest  $U$ -values. The masses of the Pb and Ti ions are comparable; the Pb ion is heavier than the O ion by one order of magnitude. Taking into account the ratio of the ion masses, it is very unlikely from the crystal dynamics point of view that Pb ions have  $U$ -values almost three times greater than those of the Zr ions. In figure 2 it also becomes apparent that the values of  $U(\text{Pb})$  as a function of temperature do not follow the dotted lines which extrapolate to 0 K.

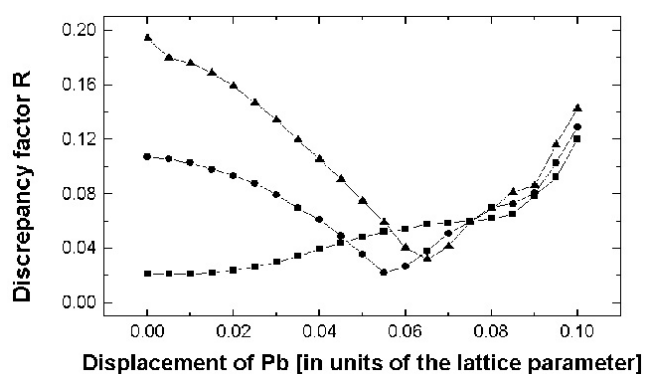


**Figure 3.** Model calculations with calculated structure factors. Shifts in the directions of [1 1 1] (▲) and [1 1 0] (▼), when  $U$  is refined; shifts in the direction of [1 1 1] (●) and of [1 1 0] (■), when  $U$  is fixed.

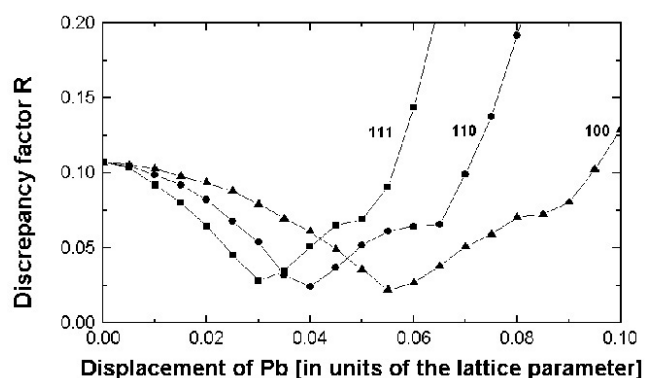
To explain the behaviour described above we assume that the mean position of the Pb ion is displaced off the (0, 0, 0) position and is distributed with equal occupancy on three symmetrically equivalent positions (in the SG  $Pm\bar{3}m$ ) (Itoh *et al* 1985, Kwapuliński *et al* 1997). Conceivable shifts are in the directions [1 0 0], [1 1 0] and [1 1 1]. According to this model the movement of Pb ions therefore consists of two simultaneous motions:

- (1) the random (independent in different cells) displacements from the (0, 0, 0) position to one of the new positions, where chaotic jumps between these positions may take place;
- (2) thermal vibration with the mean square amplitude around the new off-centre position.

Model calculations with the data from different temperatures have been performed with Pb ions displaced to one of three off-centre positions:  $(x, 0, 0)$ ;  $(x, x, 0)$  and  $(x, x, x)$  in order to find the most likely position. For such calculations it was important to avoid the correlation between an assumed shift and the thermal displacement parameter, because a false positional parameter can be compensated by a suitable thermal displacement parameter. In order to test the strategy of the refinement calculations we calculated structure factors for a model with Pb in the position (0.02, 0.02, 0.02). These structure factors we used as 'F-observed' in order to test the strategy. When the discrepancy factors  $R$  for a series of shifts are calculated refining the thermal displacement factor  $U(\text{Pb})$ , there is no minimum in the  $R$  versus displacement curve (figure 3) for the two shifts in direction [1 1 1] (up-pointing triangles) and [1 1 0] (down-pointing triangles). However, if the thermal displacement factors are kept constant with the not physically sensible value of  $U_{11}(\text{Pb}) = 0.038 \text{ \AA}^2$  (of table 1) the  $R$ -factor exhibits a minimum at the correct shift value for the direction of [1 1 1]. This model calculation only proves that, when using experimental data, one must keep the parameter  $U$  fixed when calculating  $R$ -values for the various shifts. In figure 4 the  $R$ -value is plotted against the shifts in direction [1 0 0] using experimental data and testing three different  $U$ -values: 0.038, 0.02, 0.01  $\text{\AA}^2$ . Minima are observed only for the physically sensible values of 0.02 and 0.01  $\text{\AA}^2$ . The third step of the calculation is now to test the three different directions using the data for  $T = 560 \text{ }^\circ\text{C}$  and the fixed value  $U_{11} = 0.02 \text{ \AA}^2$ . It is obvious that a minimum is attained first for the direction of [1 1 1] and the shift value for the minimum is 0.03. Therefore the Pb atom is very likely to be distributed equally on the equivalent positions of (0.03, 0.03, 0.03) (figure 5).



**Figure 4.** *R*-factor calculations for various displacements in the direction of [1 1 1] with experimental data for fixed  $U = 0.038 \text{ \AA}^2$  (■),  $U = 0.02 \text{ \AA}^2$  (●) and  $U = 0.01 \text{ \AA}^2$  (▲).



**Figure 5.** *R*-factor calculations for various displacements and for three directions with experimental data for fixed  $U = 0.02 \text{ \AA}^2$ .

#### 4. Conclusions

The results presented by Aoyagi *et al* (2002), Kuroiwa *et al* (2001) concerning disorder in the paraelectric phase of PbTiO<sub>3</sub> look correct; however there is a lack of interpretation of the values of the Debye–Waller factor. Their data concern only one temperature in the paraelectric range. Our measurements convincingly indicate the existence of disorder in the paraelectric phase of PbTiO<sub>3</sub>. This disorder appears to be different from that in PbZrO<sub>3</sub>. In PbZrO<sub>3</sub> the Pb ion has a well defined ‘off-centre’ position, but in PbTiO<sub>3</sub> it can just occupy many positions around the (000) site with equal probability. The model calculations using experimental x-ray diffraction data imply that Pb is disordered. This is consistent with early ideas given by Bersuker *et al* (1973). This interpretation is also supported by earlier refractive index (Kleemann *et al* 1986), Raman scattering (Fontana *et al* 1990) and neutron diffraction measurements (Nelmes *et al* 1990), which revealed some evidence of disorder in the paraelectric phase. The Pb is distributed equally on the equivalent positions of about (0.03, 0.03, 0.03).

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