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2001 J. Phys.: Condens. Matter 13 1461

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## Thermal vibrations in $\text{PbZrO}_3$ single crystals

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Received 3 August 2000, in final form 9 January 2001

### Abstract

The structure refinement from x-ray diffraction data of  $\text{PbZrO}_3$  single crystals revealed that the parameters of the mean thermal displacements for Pb ions in the high-temperature paraelectric phase (SG  $Pm3m$ ) showed unrealistically large values. Therefore models with displacements of Pb ions in several relevant directions were tested. A shift in the [100] direction yielded both the lowest  $R$ -value and the most sensible mean thermal displacement.

### 1. Introduction

Lead zirconate ( $\text{PbZrO}_3$ ) has the perovskite-type structure (Sawaguchi *et al* 1951 and Shirane *et al* 1951). A structural phase transition in the vicinity of 230 °C from the antiferroelectric to the paraelectric high temperature phase has been reported. Until now, the dielectric properties and the basic structure parameters have mainly been investigated for the antiferroelectric phase. There is very little structural information about the paraelectric phase. The crystal lattice dynamics have not been investigated yet. The compound has been of interest for some time because it is the end member of the technologically important solid-solution series  $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$  with their piezoelectric, ferroelectric and pyroelectric properties.

Several workers (Comes *et al* 1968, Itoh *et al* 1985, Bonneau *et al* 1991, Kwapuliński *et al* 1994, 1997) postulated the existence of a ‘disorder’ in perovskites even in the paraelectric phase whose symmetry is commonly described in the  $Pm3m$  space group. A theoretical model describing this ‘disordered’ state was first proposed by Comes *et al* (1968). This model was then applied to  $\text{BaTiO}_3$  (Itoh *et al* 1985), to  $\text{BaTiO}_3$  and  $\text{KNbO}_3$  (Chen Jun *et al* 1988),  $\text{PbMg}_x\text{Nb}_{1-x}\text{O}_3$  (Bonneau *et al* 1991),  $\text{PbHfO}_3$  and  $\text{PbTiO}_3$  (Kwapuliński *et al* 1994, 1997).

In this work, the results of model calculations based on single crystal diffraction data of  $\text{PbZrO}_3$  in the paraelectric phase are presented. The objective of this investigation is to show that a realistic parameter of the mean thermal displacement is only achieved with a shift of Pb from its high symmetric position.

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

|   | 250 °C    | 300 °C    | 350 °C    | 400 °C    | 450 °C    | 500 °C    | 550 °C    | 600 °C    |
|---|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|
| Lattice par.                              | 4.1595(4) | 4.1607(6) | 4.1629(5) | 4.1652(4) | 4.1668(5) | 4.1687(4) | 4.1703(4) | 4.1724(4) |
| $a$ [ $\text{\AA}$ ]                      |           |           |           |           |           |           |           |           |
| $R_{int}$                                 | 0.0902    | 0.0872    | 0.0892    | 0.0860    | 0.0879    | 0.0892    | 0.0901    | 0.0954    |
| $R_1$                                     | 0.0470    | 0.0470    | 0.0452    | 0.0453    | 0.0465    | 0.0489    | 0.0421    | 0.0447    |
| $WR_2$                                    | 0.1129    | 0.1175    | 0.1079    | 0.1104    | 0.1062    | 0.1095    | 0.0966    | 0.1040    |
| $s$                                       | 1.31      | 1.352     | 1.209     | 1.245     | 1.195     | 1.213     | 1.058     | 1.135     |
| Ext.                                      | 2.59      | 2.51      | 2.82      | 2.76      | 2.65      | 2.38      | 2.55      | 2.56      |
| $U_{11}(\text{Pb})$<br>[ $\text{\AA}^2$ ] | 0.066(4)  | 0.068(7)  | 0.071(4)  | 0.073(4)  | 0.074(4)  | 0.075(4)  | 0.078(8)  | 0.079(4)  |
| $U_{11}(\text{Zr})$<br>[ $\text{\AA}^2$ ] | 0.017(3)  | 0.017(3)  | 0.018(3)  | 0.019(3)  | 0.019(3)  | 0.019(3)  | 0.020(2)  | 0.022(3)  |
| $U_{eq}(\text{O})$<br>[ $\text{\AA}^2$ ]  | 0.061(12) | 0.059(12) | 0.058(11) | 0.059(11) | 0.063(11) | 0.066(12) | 0.058(9)  | 0.068(12) |
| $d(\text{Zr-O})$<br>[ $\text{\AA}$ ]      | 2.080     | 2.080     | 2.081     | 2.083     | 2.083     | 2.084     | 2.085     | 2.086     |
| $d(\text{Pb-Zr})$<br>[ $\text{\AA}$ ]     | 3.602     | 3.603     | 3.605     | 3.607     | 3.609     | 3.610     | 3.612     | 3.613     |

## 2. Experiment

The  $\text{PbZrO}_3$  single crystals were synthesized by the flux method. A mixture of  $\text{PbZrO}_3$ ,  $\text{PbO}$  and  $\text{B}_2\text{O}_3$  in the proportions of 2.4 mol%: 78.1 mol%: 19.5 mol% was melted in a platinum crucible at a temperature of 1100 °C for 4 h. Then the melt was cooled at a rate of  $-9\text{ °C h}^{-1}$  to 900 °C and the solvent was poured off. A constant temperature gradient along the axis of the crucible of about  $10\text{ °C cm}^{-1}$  has been maintained during 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 a graphite-monochromatized  $\text{Mo K}\alpha$  radiation. The crystals were mounted by a 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  $\pm 1\text{ °C}$ . The cell parameter variation was determined by using 25 selected Bragg reflections. The data collection of the intensities was performed at 250 °C, 300 °C, 350 °C, 400 °C, 450 °C, 500 °C, 550 °C and 600 °C. Data were collected for  $2\Theta < 60^\circ$ , with  $0 \leq h \leq 5$ ,  $-5 \leq k \leq 5$  and  $0 \leq l \leq 5$  by  $\omega$ - $2\Theta$  scans. During the data collection, three standard reflections were monitored each hour. The morphological absorption correction and data reduction was performed with program JANA98 (Petricek 1998). Further details about the data collection are shown in table 1.

The structures were solved in the SG  $Pm3m$  using the Shelx193 (Sheldrick 1993) computer program. The  $R$ -factor fluctuated between 4.2% and 4.9%. The mean square thermal displacements are shown in table 1.

## 3. Results

The temperature dependence of the lattice parameter in the paraelectric phase of  $\text{PbZrO}_3$  is shown in figure 1. The values are similar to those obtained earlier by Dec and Kwapuliński (1989).

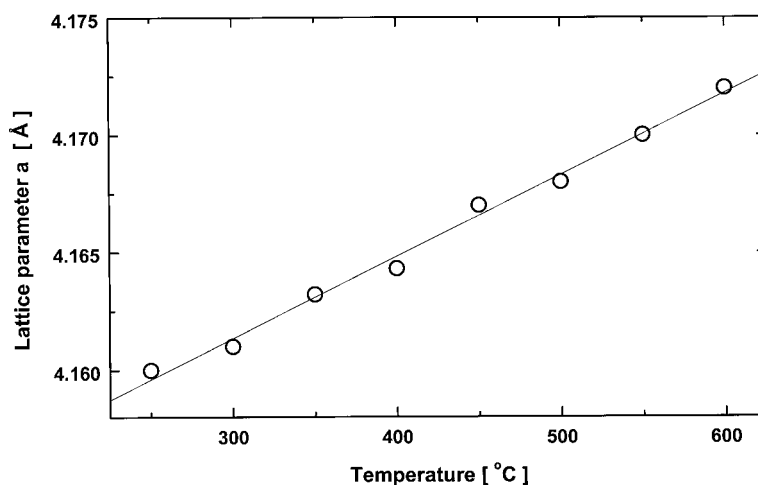


Figure 1. The variation of the lattice parameter  $a$  with temperature.

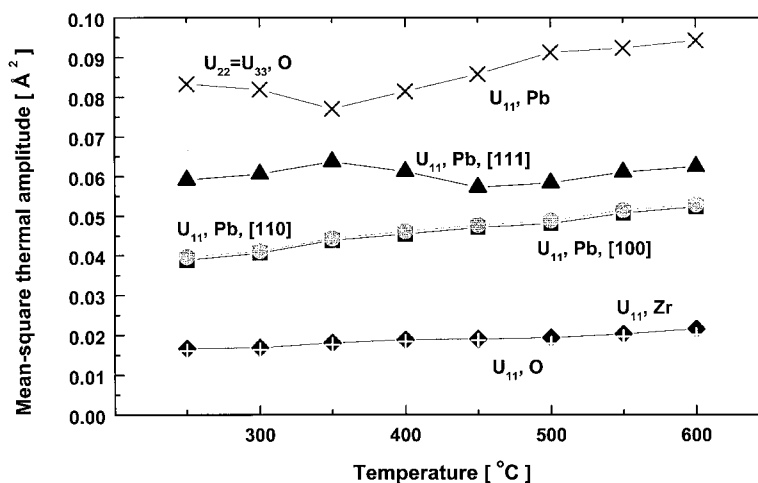
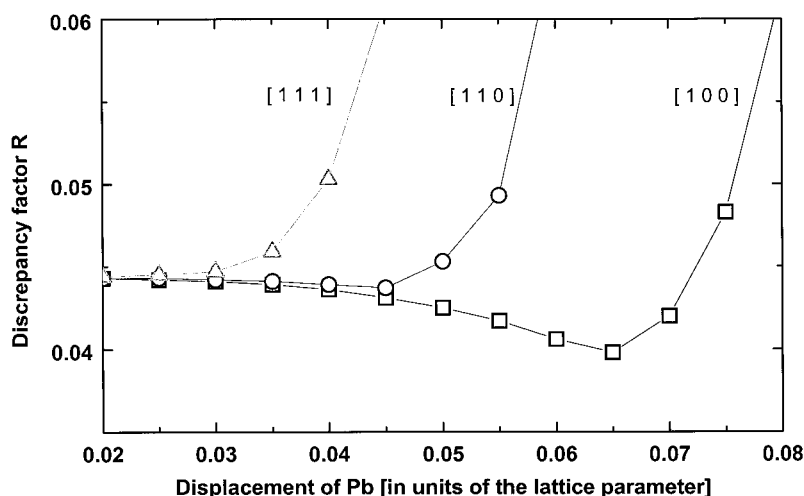


Figure 2. The mean square thermal displacement parameters for the ions in PbZrO<sub>3</sub>. The values are also plotted for Pb shifts in the directions given in brackets.

Using the Shelxl program for the data analysis we obtained the anisotropic mean square thermal displacement  $U$  for each ion in the mean position of the SG  $Pm3m$ , i.e.  $U(Pb)$ ,  $U(Zr)$  and  $U(O)$ , respectively. These factors  $U$  are shown in figure 2. We can see that  $U(Pb) > U(Zr) = U(O)$ . In the whole investigated temperature range the value of  $U(Pb)$  is significantly larger than  $U(Zr)$ . 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). It is surprising that the heaviest atom in the structure has the largest  $U$ -values. The masses of the Pb and Zr ions are comparable; the Pb ion is heavier than the O ion by one order of magnitude. From the crystal dynamics point of view and taking into account the ratio of the ion masses, it is very unlikely that Pb ions have  $U$ -values more than four times greater than the Zr ions.



**Figure 3.** The variation of the  $R$ -factor for different displacements of Pb in the three directions [111], [110] and [100] for the data set of 350 °C.

To explain the behaviour described above we assume that the mean position of the Pb ion is displaced from that given by the  $Pm3m$  space group (Itoh *et al* 1985, Kwapuliński *et al* 1994). The movement of Pb ions can be described by two mechanisms which occur simultaneously:

- (1) the random (independent in various 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 the three off-centre positions:  $(x, 0, 0)$ ;  $(x, x, 0)$  and  $(x, x, x)$ . In these calculations the shift position of Pb has been kept fixed and the mean square thermal vibration parameters have been refined. There is a variation of the final discrepancy factor  $R$  among the different models. As an example the discrepancy factors  $R$  are shown for  $T = 350$  °C in figure 3. There is a unambiguous minimum of  $R$  only for the displacement in the direction [100] at a shift of approximately 0.065. Similar curves are obtained at other temperatures. For a shift in the direction of [110] the minimum is very flat. If the mean square thermal amplitude which is determined for the model with the minimal  $R$ -value is plotted against temperature the curve exhibits a reasonably low value (figure 2), as compared with the curve for a shift in the direction [111]. But for a shift in the direction of [110] the  $U$ -value is also low. Since there is only a pronounced minimum in  $R$  for a shift in the direction [100] we may conclude that this is the most likely direction of the displacement; however, a shift in the direction [110] cannot be ruled out. Similar calculations for displacement of the Zr ion only exhibit a very flat curve for the minimal  $R$ -value for shifts between 0 and 0.055 (figure 4). For the calculation of the curves in figure 4 Pb has been assumed to be in the off-centre position 0.065 in direction of [100]. From the interpretation of that curve we must say that any shift up to this value is likely with equal probability. Since the mean-square amplitude for Zr is also reasonably low (figure 2) a Zr shift is also conceivable but there is no such strong indication as for Pb in our model calculations.

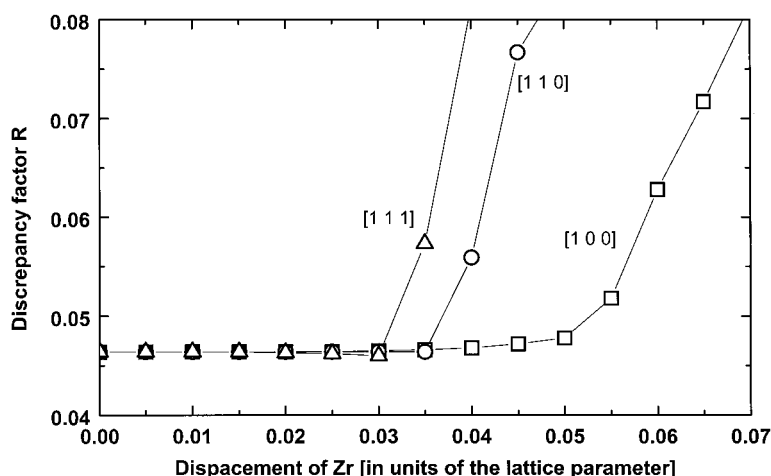


Figure 4. The variation of the  $R$ -factor for different displacements of Zr in the three directions [111], [110] and [100] for the data set of 300 °C.

#### 4. Conclusions

The unusual behaviour of lead in the perovskites may be understood when considering the nature of ion bonding in these structures. It is well known that the Pb–O bond is approximately 50% covalent whereas the Zr–O bond is covalent only by 34% (Thomann 1984, 1987). This relation between A–O and B–O bonds in lead zirconate (where the covalency of the A–O bond prevails) is just opposite to that in commonly known barium titanate where the covalency of B–O bonds is larger than the one of the A–O bond (Thomann 1984, 1987). In contrast to the ionic bonds, which are isotropic, the covalent bonds are determined by the directional valency forces which are responsible for additional potentials with a definite bond lengths. As a result local off-centre potential minima may appear, which can trap the Pb ion forming covalent bonds with surrounding oxygen atoms but swapping partners (Cohen *et al* 1992).

Our model calculations for the HT paraelectric phase indicate that the phase transition is characterized by an order/disorder transition, which is mainly triggered by the thermal activation of the Pb ion in different off-centre positions. In the ordered ferroelectric LT phase both Pb and Zr appear to be displaced from the centre position in directions [110] and [100] and Zr also has a component in the direction of [001] (Jona *et al* 1957, Soejima *et al* 1997, Glazer *et al* 1978, Yamasaki *et al* 1998). In our analysis there is only a strong indication that the displacement of Pb must be postulated in the HT phase.

#### Acknowledgment

This work was partly supported by the ‘Materialwissenschaftliches Forschungszentrum der Universität Mainz’, Germany.

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