Thermal vibrations in $PbTiO_3$ single crystals

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Introduction:

For many perowskites the existence of "disorder" has been reported in the literature even in the paraelectic phase [5]

A theoretical model describing this "disorder" state has been successfully applied by several authors to $BaTiO_3$ and other perowskites [2]. Models for $PbTiO_3$ with displacements of Pb ions in several relevant directions were tested. The results are compared with previous calculations for $PbZrO_3$[3].

Analysis

Reliability factors (R-factors) have been calculated after the Pb atom has been shifted to several relevant directions while the thermal displacement parameter has been kept constant. This strategy has been tested on small single crystal of CaF_2.

Experimental data have been collected with a CAD4 diffractometer at 500 °C,520 °C, 540 °C, 560 °C, 580 °C and 600 °C.

Phase transition for perowskite $PbTiO_3$

ferroelectric | paraelectric

493 °C

T °C

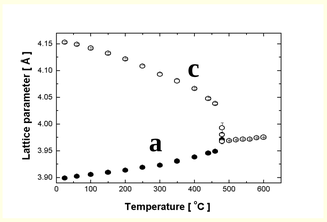
tetragonal

P4mm [1]

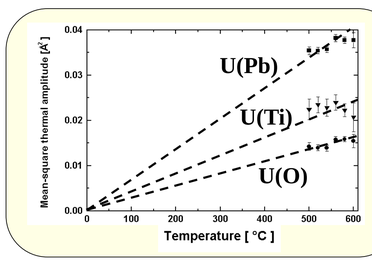
cubic

Pm3m [1]

Lattice parameter:

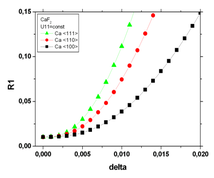


Mean square thermal displacement parameters

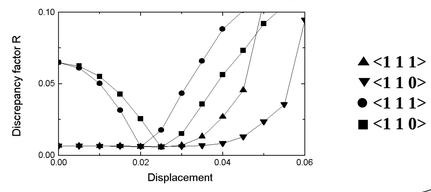


Test of the analysis

1. For a data set of CaF_2 the Ca atom has been shifted in three directions, while the thermal displacement parameter was fixed. The curve exhibits a minimum at Δ=0.

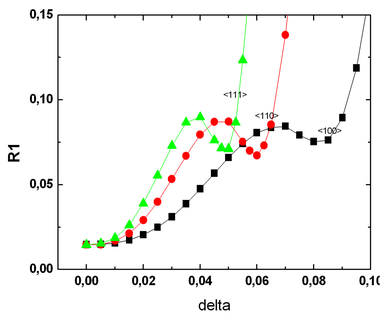


2. A model data set of $PbTiO_3$ with Pb in (0.02, 0.02, 0.02) has been tested. Pb has been shifted in two directions.
In one calculation the thermal displacement parameter was fixed, in the other one it has been refined.
The curves only exhibit minima when this parameter is fixed..



Results of the analysis.

1. The R-factor as a function of the shift Δ for three relevant directions for **$PbTiO_3$** at 540 °C



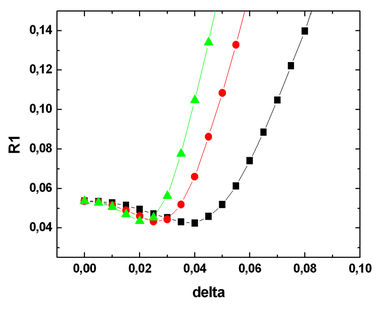
The shifts Δ for three relevant directions:

△ **<1 1 1>**
○ **<1 1 0>**
■ **<1 0 0>**

Result

For **$PbTiO_3$** there is only a global minimum at **Δ=0**

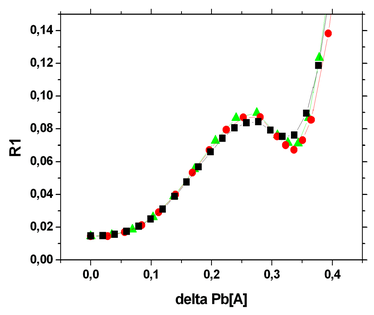
1. The R-factor as a function of the shift Δ for three relevant directions for **$PbZrO_3$** at 350 °C



Result

For **$PbZrO_3$** there are minima for the three directions for **Δ ≠ 0**

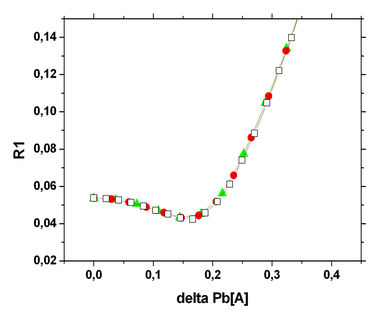
2. The R-factor as a function of the shift in Å-units for three relevant directions for **$PbTiO_3$** at 540 °C.



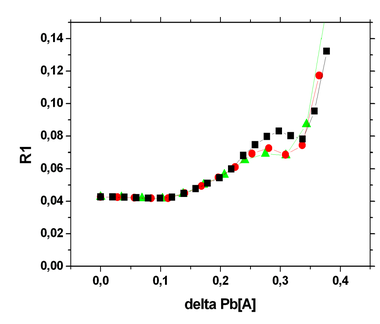
The shifts in Å-units for three relevant directions:

△ **<1 1 1>**
○ **<1 1 0>**
■ **<1 0 0>**

2. The R-factor as a function of the shift in Å-units for three relevant directions for **$PbZrO_3$** at 350 °C.



3. The R-factor as a function of the shift in Å-units for three relevant directions for **$PbTiO_3$** at 600 °C.



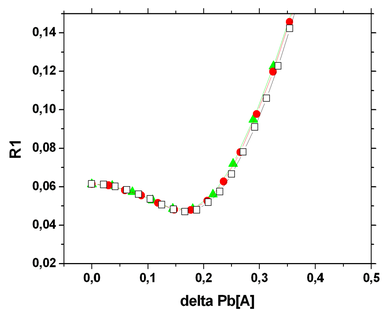
The shifts in Å-units for three relevant directions:

△ **<1 1 1>**
○ **<1 1 0>**
■ **<1 0 0>**

Result

For **$PbTiO_3$** there is only a global minimum at **Δ=0** but only for T=600 °C the minimum is very flat.

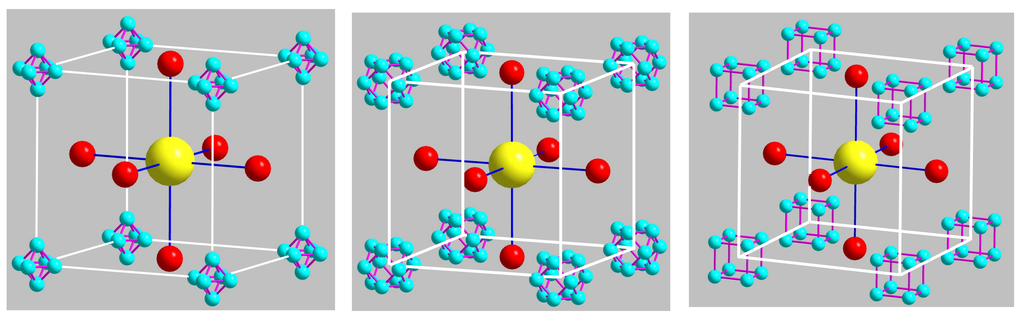
3. The R-factor as a function of the shift in Å-units for three relevant directions for **$PbZrO_3$** at 600 °C.



Result

For **$PbZrO_3$** there is one minimum for the three directions for **Δ ≠ 0**

Models of disorder:



Disorder of Pb in [1 0 0] | **Disorder of Pb in [1 1 0]** | **Disorder of Pb in [1 1 1]**

Coclusion:

1. The model calculations for $PbTiO_3$ and the test calculation for CaF_2 show that the strategy of calculation must be the following:
   The thermal displacement parameter is kept fixed. For each arbitrary shift in one of the three relevant directions the R value is calculated.
2. The calculations show that there are minima of the R-value for $PbZrO_3$ for **Δ ≠ 0** and for $PbTiO_3$ there is only one minimum for **Δ=0.**
3. The Minima are at the same absolute value of the shift in Å-units.
4. For $PbZrO_3$ there is an indication for a disorder of Pb in an off-centre position in the paraelectric phase. The calculations yield equal probability for the three relevant directions, like a distribution on a sphere.
   For $PbTiO_3$there is no indication for disorder. This is in agreement with the synchrotron irradiation experiments of S. Aoyagi et al. [4]
5. When the thermal displacement parameters are extrapolated to T=0, the extrapolation curves for $PbTiO_3$ point to zero within our experimental error, indicating that there is no static disorder (see figure above). For $PbZrO_3$, however, such curves point at a non-zero value [3].

Literature

[1] A.M. Glazer and S.A. Mabud. *Acta Cryst*. 1978, **B34**, 1065
[2] K. Itoh, L.Z. Zeng, E. Nakamura and N. Mishima. *Ferroelectrics*, 1985, **63**, 29-37
[3] J. Kwapulinski, J. Kusz, H. Böhm and J. Dec. *J. Phys. Condens. Matter*, 2001, **13**, 1461 – 66
[4] S. Aoyagi et al. *J. Phys. Soc. Japan*, 2002, **71**, 2353 – 56.
[5] Chen Jun et al. *J.Phys. C: Solid State Phys*. 1988, 21, 2255