Appendix A

Overview of the experimental data on bulk $PbTiO_3$ from literature [13, 41, 161, 162, 163]. Besides general parameters like the Curie temperature and Landau parameters, also lattice parameters and atomic positions of the tetragonal and cubic phase are listed (Pb is fixed at the origin).

critical temperature	T_c[°C]	492.2
Curie temperature	θ [°C]	478.8
Curie-Weiss constant	C [°C]	$1.5{\cdot}10^5$
dielectric stiffness coefficient	$\alpha_1[\frac{m}{F}]$	$3.8(\text{T-}478.8){\times}10^5$
higher-order stiffness coefficient	$\alpha_{11}[\frac{m^5}{FC^2}]$	$-7.3{\times}10^7$
″	$\alpha_{12}[\frac{m^5}{FC^2}]$	$7.5{\times}10^8$
″	$\alpha_{111}[\frac{m^9}{FC^4}]$	$2.6{\times}10^8$
″	$\alpha_{112}[\frac{m^9}{FC^4}]$	$6.1{\times}10^8$
″	$\alpha_{123}[\frac{m^9}{FC^4}]$	$-3.7{\times}10^9$
electrostrictive constant	$Q_{11}[m^4/C^2]$	0.089
″	$Q_{12}[m^4/C^2]$	-0.026
″	$Q_{44}[m^4/C^2]$	0.0675
elastic compliance	$s_{11}[m^2/N]$	$8.0{\times}10^{-12}$
″	$s_{12}[m^2/N]$	$-2.5{\times}10^{-12}$
″	$s_{44}[m^2/N]$	$9.0{\times}10^{-12}$

Symmetry-dependent properties			
parameter		**25°C**	**550°C**
crystal system		tetragonal	cubic
space group		$P4mm - C_{(}4v)^1$	$Pm3m - O_h^1$
lattice parameter	a[Å]	3.905	3.97
″	c[Å]	4.156	-
tetragonality	c/a [-]	1.064	1
z atomic coordinate	$z(Ti)$ [lattice units]	0.540	0.5
″	$z(O1, O2)$ [lattice units]	0.612	0.5
″	$z(O3)$ [lattice units]	0.112	0
interatomic distance	$Pb - O$[Å]	2.80; 2.53; 3.20	2.81
″	$Ti - O$[Å]	1.98; 1.78; 2.38	1.99
spontaneous polarization	P_0[C/m^2](along [001])	0.75	0
dielectric constant	ϵ_a	124.4	
″	ϵ_c	66.6	
piezoelectric coefficient	d_{31} [pC/N]	-23.1	-
″	d_{33} [pC/N]	79.1	-
″	d_{15} [pC/N]	56.1	-
elastic constant	c_{11} [GPa]	237	
″	c_{33} [GPa]	60	
″	c_{44} [GPa]	69	
″	c_{66} [GPa]	104	
″	c_{12} [GPa]	90	
″	c_{13} [GPa]	70	
piezoelectric tensor	e_{31} [C/m^2]	2.1	-
″	e_{33} [C/m^2]	5.0	-
″	e_{15} [C/m^2]	4.4	-
band gap	E_{gap} [eV]	3.5	

Appendix B

The following Matlab-script is used with a wide grid to estimate the minimum energy followed by a Gauss-Newton iteration to determine the exact energy minimum, as plotted in Figure 5.12:

```
function energy = calc_W(phi,chi,Hn)
%lattice parameters
a   =  3.905;
b   =  3.945;
c   =  4.156;
%Poisson's ratio
mu  =  0.3;
%Relative coherency Strain
sr  =  c*(b-a)/(b*(c-a));

%GRIDS
gx  =  2000;
x   =  linspace(0,-1,gx);
gy  =  2000;
y   =  linspace(0,1,gy);
```

```
%CALCULATE Q-TERM
%VARIABLES IN Q11
sxp     =       2*pi*(x+1)/chi;
sxp3    =       2*pi*(x+3)/chi;
sxm     =       2*pi*(x-1)/chi;
sx      =       ((2*pi/chi)^2)*x;
sp      =       2*pi*phi;

%Q11(phi,x3) TERMS (equation 17)[5]
cshsxp  =       cosh(sxp);
cshsxm  =       cosh(sxm);
snhsxp  =       sinh(sxp);
snhsxm  =       sinh(sxm);
csp     =       cos(sp);
Q01     =       +(1/2)*log((cshsxp-1)./(cshsxm-1));
Q02     =       +(sxp/2).*(snhsxp./(cshsxp-1));
Q03     =       -(sxp3/2).*(snhsxm./(cshsxm-1));
Q04     =       +sx./(cshsxm-1);
Q110    =       Q01+Q02+Q03+Q04; %Q11(0,x3)
Qd1     =       +(1/2)*log((cshsxp-csp)./(cshsxm-csp));
Qd2     =       +(sxp/2).*(snhsxp./(cshsxp-csp));
Qd3     =       -(sxp3/2).*(snhsxm./(cshsxm-csp));
Qd4     =       +sx.*(cshsxm*csp-1)./((cshsxm-csp).^2);
Q11d    =       Qd1+Qd2+Qd3+Qd4; %Q11(d,x3)
%INTEGRAND
dx      =       1/gx;
Intx3   =       (Q110-Q11d).*(1+x)*dx;
%INTEGRATION
iQ      =       0;
        for kx =  1:gx-1
        iQ =      iQ+Intx3(kx);
        end
```

```
%CALCULATE J-TERM
%VARIABLES IN J
jh      =       4*pi/chi;
jv      =       2*pi*phi*(1-y);

%EQUATION (A4)[5]
J1      =       +(1/(4*pi))*log((cosh(jh)-cos(jv))
                ./(1-cos(jv)));
J2      =       +(jh*sinh(jh))./(4*pi*(cosh(jh)-cos(jv)));
J3      =       -(jh^2)*(cosh(jh)*cos(jv)-1)
                ./(8*pi*(cosh(jh)-cos(jv)).^2);
Jt      =       J1+J2+J3;
%INTEGRAND
dy      =       1./gy;
Intv    =       Jt.*y.*dy;
%INTEGRATION
iJ      =       0;
        for ky =  1:gy-1
        iJ =      iJ+Intv(ky);
        end

%calculate W(DH,phi)
%W1, W2 TERMS (NO INTEGRATION)
W1      =       Hn*2*((sr*(1+mu))-1)*phi;
W4      =       2*sqrt(2)./chi;
%W2, W3 TERMS (INTEGRATION REQUIRED)
W2      =       Hn*iQ./(2*pi*chi);
W3      =       Hn.*chi.*((phi).^2)*iJ;
energy  =       W1+W2+W3+W4;
```