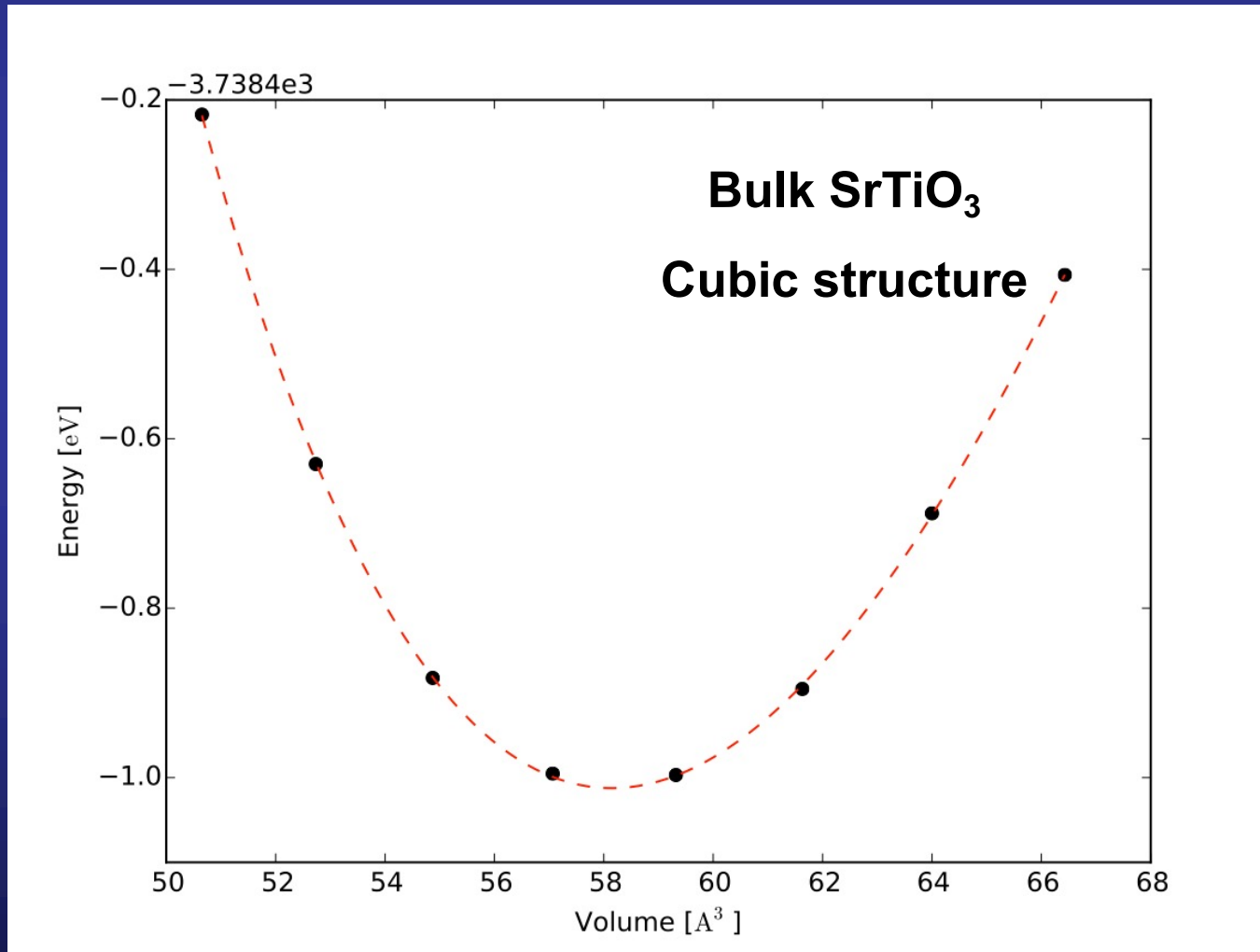


# Computing lattice constant, bulk modulus and equilibrium energies of bulk cubic $\text{SrTiO}_3$



# Information required to run a first-principles simulation

Number and species of the atoms in the unit cell,

Lattice vectors and lattice constants

Position of all the atoms

After the Born Oppenheimer approx.,  
are assumed to be fixed,  
no thermal vibrations ( $T = 0$ )



$N$



$\Omega$



$T = 0$

$S = 0$

The most convenient thermodynamic potential in first-principles theoretical analysis is the total energy  $E(N, \Omega, S)$  at  $T = 0$

It is straightforward to carry out electronic structure calculations at fixed  $\Omega$

# First test: determine theoretical predictions for $\Omega_0$ and $B$ for the known zero-pressure crystal structure

Definition of some fundamental quantities

**Energy**

$$E(N, \Omega, S)$$

**Pressure**

$$P = -\frac{dE}{d\Omega}$$

**Bulk modulus**

$$B = -\Omega \frac{dP}{d\Omega} = \Omega \frac{d^2 E}{d\Omega^2}$$

Why  $\Omega_0$  and  $B$  :

- Can be measured with great accuracy.
- Can be extrapolated at  $T = 0$

# $\Omega_0$ and $B$ can be measured with great accuracy and extrapolated at $T = 0$

**Table 3 Crystal structures of the elements**

The data given are at room temperature for the most common form, or at the stated temperature in deg K. (Inorganic Crystal Structure Database (ICSD) online.)

<b>H<sup>1</sup> 4K</b> hcp 3.75 6.12																	<b>He<sup>4</sup> 2K</b> hcp 3.57 5.83
<b>Li 78K</b> bcc 3.491	<b>Be</b> hcp 2.27 3.59											<b>B</b> rhomb.	<b>C</b> diamond 3.567	<b>N 20K</b> cubic 5.66 (N <sub>2</sub> )	<b>O</b> complex (O <sub>2</sub> )	<b>F</b>	<b>Ne 4K</b> fcc 4.46
<b>Na 5K</b> bcc 4.225	<b>Mg</b> hcp 3.21 5.21	← Crystal structure → ← a lattice parameter, in Å → ← c lattice parameter, in Å →										<b>Al</b> fcc 4.05	<b>Si</b> diamond 5.430	<b>P</b> complex	<b>S</b> complex	<b>Cl</b> complex (Cl <sub>2</sub> )	<b>Ar 4K</b> fcc 5.31
<b>K 5K</b> bcc 5.225	<b>Ca</b> fcc 5.58	<b>Sc</b> hcp 3.31 5.27	<b>Ti</b> hcp 2.95 4.68	<b>V</b> bcc 3.03	<b>Cr</b> bcc 2.88	<b>Mn</b> cubic complex	<b>Fe</b> bcc 2.87	<b>Co</b> hcp 2.51 4.07	<b>Ni</b> fcc 3.52	<b>Cu</b> fcc 3.61	<b>Zn</b> hcp 2.66 4.95	<b>Ga</b> complex	<b>Ge</b> diamond 5.658	<b>As</b> rhomb.	<b>Se</b> hex. chains	<b>Br</b> complex (Br <sub>2</sub> )	<b>Kr 4K</b> fcc 5.64
<b>Rb 5K</b> bcc 5.585	<b>Sr</b> fcc 6.08	<b>Y</b> hcp 3.65 5.73	<b>Zr</b> hcp 3.23 5.15	<b>Nb</b> bcc 3.30	<b>Mo</b> bcc 3.15	<b>Tc</b> hcp 2.74 4.40	<b>Ru</b> hcp 2.71 4.28	<b>Rh</b> fcc 3.80	<b>Pd</b> fcc 3.89	<b>Ag</b> fcc 4.09	<b>Cd</b> hcp 2.98 5.62	<b>In</b> tetr. 3.25 4.95	<b>Sn (α)</b> diamond 6.49	<b>Sb</b> rhomb.	<b>Te</b> hex. chains	<b>I</b> complex (I <sub>2</sub> )	<b>Xe 4K</b> fcc 6.13
<b>Cs 5K</b> bcc 6.045	<b>Ba</b> bcc 5.02	<b>La</b> hex. 3.77 ABAC	<b>Hf</b> hcp 3.19 5.05	<b>Ta</b> bcc 3.30	<b>W</b> bcc 3.16	<b>Re</b> hcp 2.76 4.46	<b>Os</b> hcp 2.74 4.32	<b>Ir</b> fcc 3.84	<b>Pt</b> fcc 3.92	<b>Au</b> fcc 4.08	<b>Hg</b> rhomb.	<b>Tl</b> hcp 3.46 5.52	<b>Pb</b> fcc 4.95	<b>Bi</b> rhomb.	<b>Po</b> sc 3.34	<b>At</b> —	<b>Rn</b> —
<b>Fr</b> —	<b>Ra</b> —	<b>Ac</b> fcc 5.31															
			<b>Ce</b> fcc 5.16	<b>Pr</b> hex. 3.67 ABAC	<b>Nd</b> hex. 3.66	<b>Pm</b> —	<b>Sm</b> complex	<b>Eu</b> bcc 4.58	<b>Gd</b> hcp 3.63 5.78	<b>Tb</b> hcp 3.60 5.70	<b>Dy</b> hcp 3.59 5.65	<b>Ho</b> hcp 3.58 5.62	<b>Er</b> hcp 3.56 5.59	<b>Tm</b> hcp 3.54 5.56	<b>Yb</b> fcc 5.48	<b>Lu</b> hcp 3.50 5.55	
			<b>Th</b> fcc 5.08	<b>Pa</b> tetr. 3.92 3.24	<b>U</b> complex	<b>Np</b> complex	<b>Pu</b> complex	<b>Am</b> hex. 3.64 ABAC	<b>Cm</b> —	<b>Bk</b> —	<b>Cf</b> —	<b>Es</b> —	<b>Fm</b> —	<b>Md</b> —	<b>No</b> —	<b>Lr</b> —	

# $\Omega_0$ and $B$ can be measured with great accuracy and extrapolated at $T = 0$

**Table 3 Isothermal bulk moduli and compressibilities at room temperature**

After K. Gschneidner, Jr., *Solid State Physics* 16, 275–426 (1964); several data are from F. Birch, in *Handbook of physical constants*, Geological Society of America Memoir 97, 107–173 (1966). Original references should be consulted when values are needed for research purposes. Values in parentheses are estimates. Letters in parentheses refer to the crystal form. Letters in brackets refer to the temperature:

[a] = 77 K; [b] = 273 K; [c] = 1 K; [d] = 4 K; [e] = 81 K.

Bulk modulus in units  $10^{12}$  dyn/cm<sup>2</sup> or  $10^{11}$  N/m<sup>2</sup>  
Compressibility in units  $10^{-12}$  cm<sup>2</sup>/dyn or  $10^{-11}$  m<sup>2</sup>/N

H (a)																	He (d)				
0.002																	0.00				
500																	1168				
Li	Be															B	C (d)	N (e)	O	F	Ne (d)
0.116	1.003															1.78	4.43	0.012			0.010
8.62	0.997															0.562	0.226	80			100
Na	Mg															Al	Si	P (b)	S (c)	Cl	Ar (a)
0.068	0.354															0.722	0.988	0.304	0.178		0.013
14.7	2.82															1.385	1.012	3.29	5.62		79
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga (b)	Ge	As	Se	Br	Kr (a)				
0.032	0.152	0.435	1.051	1.619	1.901	0.596	1.683	1.914	1.86	1.37	0.598	0.569	0.772	0.394	0.091		0.018				
31.	6.58	2.30	0.951	0.618	0.526	1.68	0.594	0.522	0.538	0.73	1.67	1.76	1.29	2.54	11.0		56				
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn (c)	Sb	Te	I	Xe				
0.031	0.116	0.366	0.833	1.702	2.725	(2.97)	3.208	2.704	1.808	1.007	0.467	0.411	1.11	0.383	0.230						
32.	8.62	2.73	1.20	0.587	0.366	(0.34)	0.311	0.369	0.553	0.993	2.14	2.43	0.901	2.61	4.35						
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg (c)	Tl	Pb	Bi	Po	At	Rn				
0.020	0.103	0.243	1.09	2.00	3.232	3.72	(4.18)	3.55	2.783	1.732	0.382	0.359	0.430	0.315	(0.26)						
50.	9.97	4.12	0.92	0.50	0.309	0.269	(0.24)	0.282	0.359	0.577	2.60	2.79	2.33	3.17	(3.8)						
Fr	Ra	Ac	Ce (γ)	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu					
(0.020)	(0.132)	(0.25)	0.239	0.306	0.327	(0.35)	0.294	0.147	0.383	0.399	0.384	0.397	0.411	0.397	0.133	0.411					
(50.)	(7.6)	(4.)	4.18	3.27	3.06	(2.85)	3.40	6.80	2.61	2.51	2.60	2.52	2.43	2.52	7.52	2.43					
			Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr					
			0.543	(0.76)	0.987	(0.68)	0.54														
			1.84	(1.3)	1.01	(1.5)	1.9														



# Bulk SrTiO<sub>3</sub>: a perovskite oxide that at high temperatures crystallizes in the simple cubic structure

Go to the directory where the exercise on the structure of Si is stored  
Inspect the input file, SrTiO<sub>3</sub>.fdf

More information at the Siesta web page  
<http://www.icmab.es/siesta> and follow the link Documentations, Manual

```
SystemName      Bulk SrTiO3
#               Centrosymmetric paraelectric configuration
#               LDA-CA
#               400 Ry
#               6 x 6 x 6; 0.5 0.5 0.5 MP mesh

SystemLabel     SrTiO3
NumberOfAtoms   5
NumberOfSpecies  3

%block ChemicalSpeciesLabel
  1 38 Sr
  2 22 Ti
  3  8 O
%endblock ChemicalSpeciesLabel

LatticeConstant 3.70 Ang
%block LatticeVectors
  1.000 0.000 0.000
  0.000 1.000 0.000
  0.000 0.000 1.000
%endblock LatticeVectors

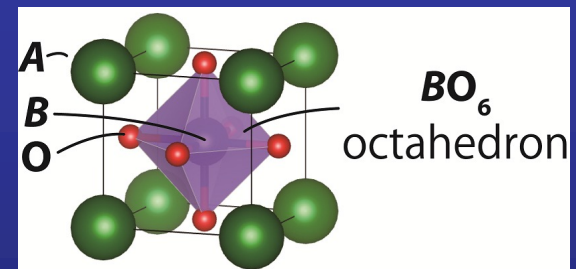
AtomicCoordinatesFormat Fractional
%block AtomicCoordinatesAndAtomicSpecies
  0.00000000 0.00000000 0.00000000 1 87.62 Sr
  0.50000000 0.50000000 0.50000000 2 47.867 Ti
  0.50000000 0.50000000 0.00000000 3 15.9994 O
  0.50000000 0.00000000 0.50000000 3 15.9994 O
  0.00000000 0.50000000 0.50000000 3 15.9994 O
%endblock AtomicCoordinatesAndAtomicSpecies

%block kgrid_Monkhorst_Pack
  6 0 0 0.5
  0 6 0 0.5
  0 0 6 0.5
%endblock kgrid_Monkhorst_Pack
```

The theoretical lattice constant of SrTiO<sub>3</sub> for this first example

Cubic SrTiO<sub>3</sub> structure:

Simple cubic lattice



+ a basis of five atoms

Sampling in k in the first Brillouin zone to achieve self-consistency

# Procedure to compute the equilibrium volume and bulk modulus

Step 1: Given a structure, compute the energy  $E$  for several values of the volume  $\Omega$

Run the code,

```
siesta < SrTiO3.fdf > SrTiO3.3.70.out
```

The name of the output file is free, but since we are running bulk SrTiO<sub>3</sub> with this lattice constant, this seems very sensible...

For this particular example, run from 3.70 Å up to 4.05 Å in steps of 0.05 Å.  
Save each output file in a different file

Save in a file the data needed to plot the energy versus volume curve

```
grep "Total =" SrTiO3.*.out > SrTiO3.evslc.dat
```

# Procedure to compute the equilibrium volume and bulk modulus

Step 1: Given a structure, compute the energy  $E$  for several values of the volume  $\Omega$

Edit the SrTiO<sub>3</sub>.evslc.dat file and leave only two columns:

cubic	
3.70	-3738.617262
3.75	-3739.029827
3.80	-3739.282341
3.85	-3739.395325
3.90	-3739.396974
3.95	-3739.295355
4.00	-3739.088046
4.05	-3738.806515

Add a first line with the kind of lattice (cubic, bcc, fcc, diamond...)

Lattice constant (in Å)

Energy of the unit cell (in eV)



# Procedure to compute the equilibrium volume and bulk modulus

Step 2: Fit to an analytic form, e. g. , the Murnaghan equation of state

$$E(\Omega) = E_0 + \frac{B_0 \Omega}{B'_0} \left[ \frac{\left(\frac{\Omega_0}{\Omega}\right)^{B'_0}}{B'_0 - 1} + 1 \right] - \frac{\Omega_0 B_0}{B'_0 - 1}$$

F. D. Murnaghan,

Proc. Nat. Acad. Sci. USA, 30, 244 (1944)

$B_0$  bulk modulus at the equilibrium volume

To do this, we have prepared an script in python

$B'_0$  pressure derivative of the bulk modulus at the equilibrium volume

If you are running SIESTA mobile in the virtual machine, load the environment of python with all the modules installed

`workon siesta_school`

If not, you have to install all the modules by yourself.

Then, type

$E_0$  total energy at the minimum

`python fit_results.py SrTiO3.evslc.dat`

# Procedure to compute the equilibrium volume and bulk modulus

Step 2: Fit to an analytic form, e. g. , the Murnaghan equation of state

$$E(\Omega) = E_0 + \frac{B_0\Omega}{B'_0} \left[ \frac{\left(\frac{\Omega_0}{\Omega}\right)^{B'_0}}{B'_0 - 1} + 1 \right] - \frac{\Omega_0 B_0}{B'_0 - 1}$$

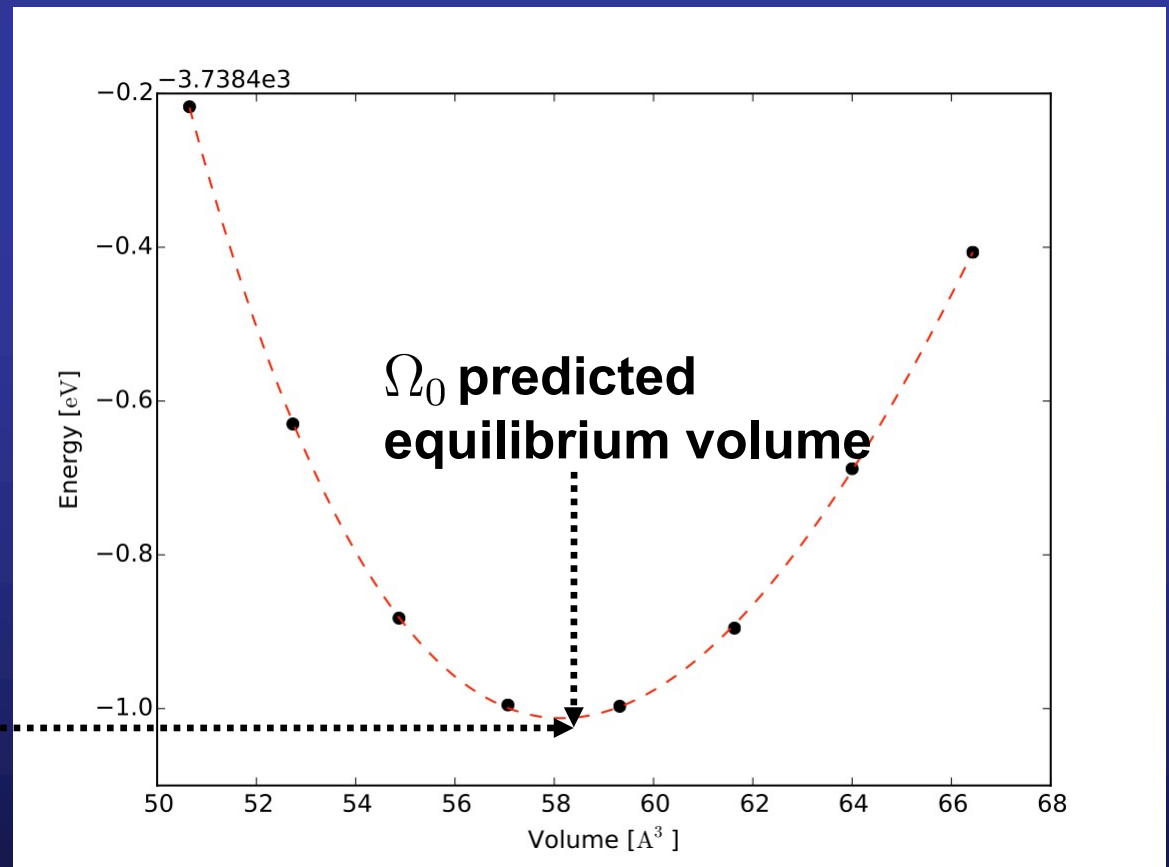
F. D. Murnaghan,

Proc. Nat. Acad. Sci. USA, 30, 244 (1944)

$B_0$  bulk modulus at the equilibrium volume

$B'_0$  pressure derivative of the bulk modulus at the equilibrium volume

$E_0$  total energy at the minimum



# Comparison of predicted equilibrium properties with experimental values are routine tests for calculations

**Table 2.** Experimental and theoretical lattice constants (in Å) of the cubic perovskite structure of various ABO<sub>3</sub> compounds

Compound	Experiment	Theory	Method	Reference
<b>I-V compounds</b>				
KNbO <sub>3</sub>	4.016	3.956 (±0.003)	DFT (LDA)	[32, 35, 36, 38]
		4.028 (±0.010)	DFT (GGA)	[35, 38]
		4.011	DFT (WDA)	[38]
NaNbO <sub>3</sub>	3.937	3.914	DFT (LDA)	[32, 36]
KTaO <sub>3</sub>	3.983	3.938 (±0.018)	DFT (LDA)	[35, 38, 115]
		4.033 (±0.002)	DFT (GGA)	[35, 38]
		3.972	DFT (WDA)	[38]
<b>II-IV compounds</b>				
CaTiO <sub>3</sub>	3.836	3.809 (±0.003)	DFT (LDA)	[32, 36]
SrTiO <sub>3</sub>	3.905	3.862 (±0.012)	DFT (LDA)	[32, 35, 36, 38, 40, 41]
		3.941 (±0.007)	DFT (GGA)	[35, 38, 40]
		3.917	DFT (WDA)	[38]
		3.94	B3LYP	[40]
		3.92	HF	[40]
BaTiO <sub>3</sub>	4.000	3.947 (±0.013)	DFT (LDA)	[28, 32, 35–38, 40, 41]
		4.028 (±0.005)	DFT (GGA)	[35, 38, 40, 41]
		4.009	DFT (WDA)	[38]
		4.04	B3LYP	[40]
		4.01	HF	[40]
CdTiO <sub>3</sub>	3.800	3.805	DFT (LDA)	[116]
PbTiO <sub>3</sub>	3.969	3.888 (±0.005)	DFT (LDA)	[29, 32, 36, 38, 97]
		3.965 (±0.005)	DFT (GGA)	[38, 40]
		3.933	DFT (GGA')	[42]
		3.941	DFT (WDA)	[38]
		3.96	B3LYP	[40]
PbZrO <sub>3</sub>	4.133	3.94	HF	[40]
		4.115 (±0.008)	DFT (LDA)	[32, 36, 89, 117]
		4.152 (±0.004)	DFT (LDA)	[32, 36, 118]
BaZrO <sub>3</sub>	4.193	4.207	DFT (GGA)	[119]
		4.17	DFT (GGA)	[119]
SrZrO <sub>3</sub>	4.101	4.17	DFT (GGA)	[119]
SrHfO <sub>3</sub>	4.069	4.069	DFT (LDA)	[120]
PbVO <sub>3</sub>			DFT (LDA)	[121, 122]
<b>III-III compounds</b>				
BiGaO <sub>3</sub>	–	3.83	DFT (LDA)	[123]
BiAlO <sub>3</sub>	–	3.75	DFT (LDA)	[123]
BiScO <sub>3</sub>	–	3.99	DFT (LDA)	[124]
YScO <sub>3</sub>	–	3.92	DFT (LDA)	[124]

```
$ python fit_results.py SrTiO3.evslc.dat
V0      = 58.1422 A^3
E0      = -3739.4125 eV
B(V0)   = 1.2868 eV/A^3
B'(V0)  = 4.2267
Theoretical lattice constant: 3.8740 A
```

Ph. Ghosez and K. M. Rabe,  
**First-Principles Studies of Ferroelectric Oxides**  
 In  
**Physics of Ferroelectrics**  
**A Modern Perspective**  
 Springer (Berlin 2007)