materials design

APPLICATION NOTE

Ferroelectric Properties of $BaTiO_3$

First-principles computations correctly describe the ferroelectric distortions and the macroscopic polarization of $BaTiO_3$ in agreement with experiment. Computations of the vibrational properties (phonons) reveal that a cubic perovskite structure of $BaTiO_3$ becomes stable under compression of the lattice. This demonstrates the usefulness of first-principles calculations in the design and optimization of ferroelectric materials.

Keywords: Ferroelectrics, perovskites, polarizability, computations

Experimental facts

$BaTiO_3$ is a prototypical ferroelectric material with a characteristic tetragonal distortion of the cubic perovskite structure. The ferroelectric distortion is facilitated by the large size of the Ba cation. Replacement of Ba by the smaller Sr leads to a perovskite with a cubic structure.

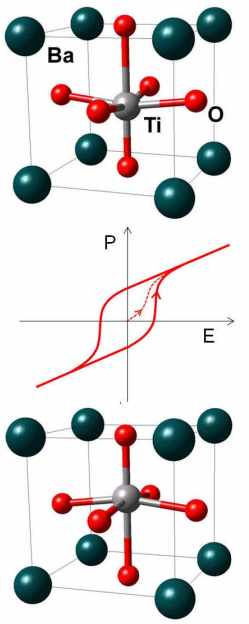

Figure 1. Displacement of atoms in $BaTiO_3$ as a function of an external electric field ***E***. As a consequence of the particular structure, the induced polarization ***P*** shows a non-linear behavior with hysteresis.

Computed structural properties

The origin of the ferroelectric property is a displacement of the Ti atoms as illustrated in Fig.1. The effect is very sensitive to the interatomic distances (lattice parameter).

The recently developed PBEsol functional gives very good agreement with the experimental values for the equilibrium volume and the relative displacement of the Ti atoms in the z-direction as shown in Fig.2.

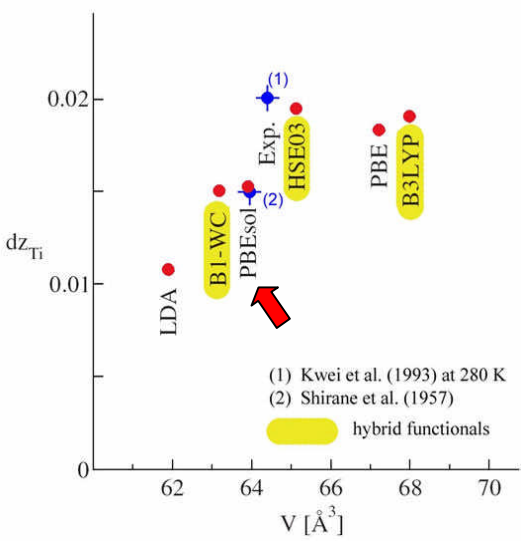

Figure 2. Computed equilibrium volume, V, and relative displacement of Ti atoms in z-direction, dz_{Ti} for various exchange-correlation potentials. The PBEsol potential gives the closest agreement with experiment (blue symbols). After Wahl *et al*. [1].

Table 1. Computed macroscopic polarization, after Ref. [1].

	LDA	PBE	PBEsol	WC	HSE	B3LYP	B1-WC	Experiment
P (C/m^2)								
Present	0.216	0.435	0.314		0.407			0.27[c]
Ref. 4	0.20	0.39		0.26		0.48	0.28	

(c) Wieder (1955)
Ref. 4: Bilc et al. (2008)

The computed macroscopic polarization obtained with PBEsol agrees well with experiment, which is consistent with the good structural values obtained with this functional.

Pressure dependence

An interesting question is the dependence of the ferroelectric displacement as a function of cell volume (i.e. pressure). The computation of the lattice vibrations (phonon dispersions) provides an answer. At ambient pressure, the phonon dispersions of the cubic form or $BaTiO_3$ show a negative eigenvalue of the dynamic matrix. This means that certain concerted displacements of the atoms lower the total energy of the system. The cubic structure is unstable. This can be seen in the middle panel of Fig. 3. Upon compression of the lattice (reduction of the cubic lattice parameter by 2%) this negative eigenvalue disappears. The cubic structure becomes stable. In fact, replacing Ba by the smaller Sr atom, which amounts to a compression of the lattice, leads to the stable cubic $SrTiO_3$. On the other hand, and expansion of the lattice aggravates the instability of the cubic structure.

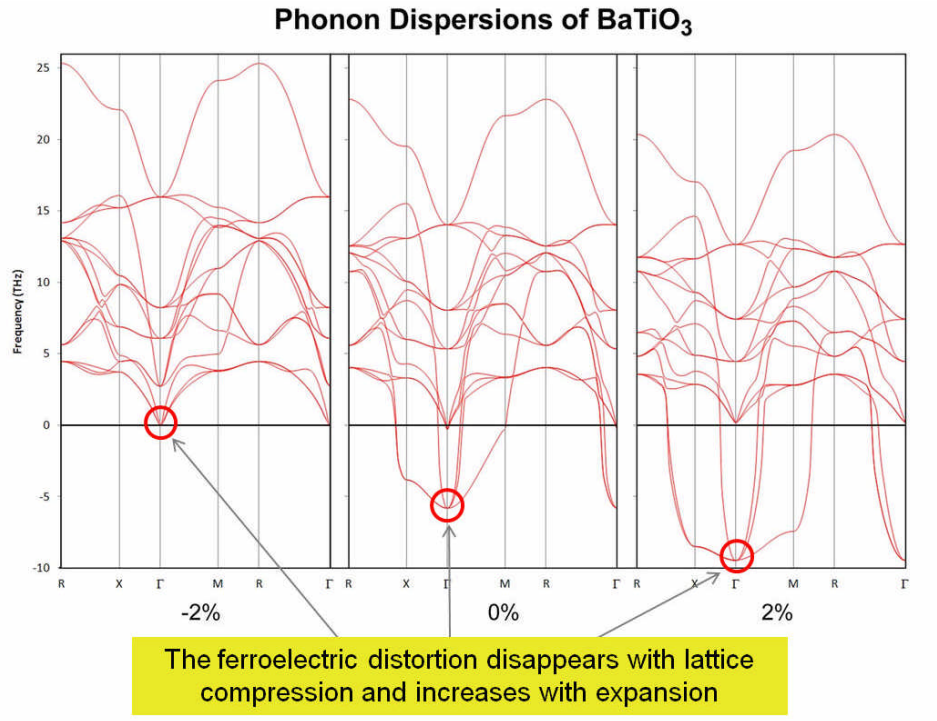

Figure 3. Computed phonon dispersions of cubic $BaTiO_3$. Note the disappearance of the negative eigenvalues upon compression of the lattice.

MedeA modules used for this application

The present calculations were performed with the MedeA platform using the following integrated modules of the MedeA software environment

- Standard MedeA framework including crystal structure builders and geometric analysis tools as well as
- JobServer and TaskServers
- InfoMaticA with structural databases (ICSD, Pearson, Pauling) – these databases contain the various phases of $BaTiO_3$ with bibliographic references
- VASP 5.2 and its graphical user interface as integrated in MedeA
- Phonon as integrated in MedeA

Comments

A critical aspect is the treatment of the many-body interactions among the electrons. Density functional theory, which was formulated in the mid 1960s, has emerged as the most common treatment of these so-called exchange-correlation effects. During the past decades a number of improvements have been developed in the form of different functionals. The functionals highlighted in yellow are so-call hybrid functionals, which are designed to improve the description of excitation energies. As can be seen, these functionals do not necessarily also improve the structural properties.

References

1. R. Wahl, D. Vogtenhuber, and G. Kresse, "$SrTiO_3$ and $BaTiO_3$ revisited using the projector augmented wave method: Performance of hybrid and semilocal functionals", Phys. Rev. B **78**, 104116 (2008)
2. H. H. Wieder, Phys. Rev. **99**, 1161 (1955)
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