ORDER-DISORDER, LOCAL STRUCTURE AND PRECURSOR EFFECTS IN BaTiO$_3$

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Interatomic potentials are determined in the framework of the nonlinear oxygen polarizability model to describe the structural behavior of BaTiO$_3$. To this purpose, the adiabatic potential is evaluated for different ferroelectric distortions and the model potential parameters are obtained by comparing with LAPW total energy calculations. The phase diagram as a function of temperature is obtained through constant pressure molecular dynamics simulations, and the non-trivial phase sequence is correctly reproduced. Calculations of the pair distribution function indicate that order-disorder is the dominant dynamics at all transitions. Precursor clusters with local polarizations correlated along Ti-O chains are determined to persist several hundreds of degrees above the para-ferroelectric transition.

Keywords BaTiO$_3$; ferroelectric transition; molecular dynamics
INTRODUCTION

Ferroelectric BaTiO$_3$ possess the simple cubic (C) perovskite structure in the high-temperature paraelectric phase at normal pressure. With decreasing temperature it becomes tetragonal (T) at 393 K, orthorhombic (O) at 278 K and rhombohedral (R) below 183 K, with spontaneous polarizations in [100], [110] and [111] directions, respectively, referred to the C phase.

Initially these transitions were interpreted in terms of a TO($\Gamma$) phonon instability, whose eigenvector in each phase has the symmetry of the ionic displacements which lead to the next lower ferroelectric phase. Indeed, such ferroelectric mode has been observed to soften in several oxide perovskites. However, it has not been clearly observed in BaTiO$_3$ and furthermore, many experimental results point out to order-disorder transition mechanisms. Recent XAFS measurements reveal a local rhombohedral environment for Ti in all phases.$^{[1]}$

During the last decade, first-principles calculations contributed greatly to understand the origins of structural transitions in perovskites. However, dynamical behaviours at finite temperature cannot be treated with these methods without some shortcomings. A feasible approach consists in constructing effective Hamiltonians, which include just the dynamical variables appropriate to the transitions of interest, and whose parameters are fitted to reproduce ab-initio results in a given material. The four phases of BaTiO$_3$ have been studied in this way$^{[2]}$. The transition temperatures, however, come out considerably lower than experimentally observed. Since volume increase favours the instabilities, this failure may be ascribed to the lack of thermal expansion within this approach.

Another interesting method which has been widely applied to the study of dynamical properties of perovskites is based on atomistic models. The modelling of interatomic forces allows in addition to study properties related to departures from perfect crystallinity. Prior to the ninetieths, these models where adjusted exclusively against measured properties. Afterwards, the availability of ab-initio results made it possible to fit them
to detailed behaviours of the total energy.

Successful descriptions of the lattice dynamics, ferroelectric soft mode, dielectric and optical properties of oxide perovskites have been given through the nonlinear oxygen polarizability model. This is a shell model initially formulated with only one nonlinear interaction, namely an anisotropic core-shell interaction at the oxygen with a quartic term in the relative core-shell displacement along the Ti-O bond. The dynamic properties of the C phase, including BaTiO$_3$ [3], were studied within a self-consistent harmonic approximation, which precludes the appearance of order-disorder phenomena. Neither can this form of the model account for the transitions. Therefore it has been recently extended, whereby the harmonic shell-shell interactions between ion pairs have been replaced by short-range Buckingham potentials. An application to KNbO$_3$ showed that this extended model is capable to describe the sequence of phases of this material, analogous to BaTiO$_3$, and the microscopic dynamics characteristic of each phase.$^{[4]}$

Our purpose is to develop a similar model for BaTiO$_3$ with parameters fitted to reproduce the LAPW total energy behaviour that we obtain under the structural distortions relevant to its various phases. Molecular dynamics simulations are then performed, which shows the appearance of the various phases and allows to study, including thermal expansion, their dynamical characteristics and local structure.

MODEL BUILDING

Details of the model have been previously given.$^{[4]}$ In order to determine its parameters for BaTiO$_3$ we evaluate the behaviour of the LAPW total energy as a function of the ferroelectric mode normal coordinate for displacements in [100], [110] and [111] directions in the C phase. For the first ones we also consider the stabilizing effects of the tetragonal distortion, which is taken from experiment. The eigenvector of the ferroelectric mode is determined through a frozen phonon calculation
of the $\Gamma_{15}$ modes. Calculations are performed at the experimental zero-temperature volume. Technical aspects of the LAPW calculation will be published separately\cite{5}.

Then we evaluate the potential energy of the model, under the adiabatic condition for the shells, by considering the same distortions. The model parameters are obtained from the comparison with the LAPW results. The agreement reached is quite satisfactory in view of the simplicity of the model\cite{5}.

The model is further proved by comparing its phonon dispersion relations with first-principles linear-response results\cite{6}. The agreement is also good, particularly with respect to a pronounced two-dimensional instability of the lowest TO branch, which suggests dynamically correlated displacements along Ti-O chains\cite{5}.

An additional achievement of the model concerns the dynamic effective charges. It reproduces the anomalously large values for Ti and O obtained from ab-initio calculations\cite{5,7}.

Finally, we compared the bulk modulus obtained from the model with the LAPW evaluation, each one calculated at the corresponding equilibrium volume for the C phase. A fairly good agreement is obtained: 226 GPa for the shell model and 195 GPa for the LAPW value, corresponding to 3.99 Å and 3.94 Å for the lattice parameter, respectively.

**MOLECULAR DYNAMICS SIMULATIONS**

To investigate the temperature behaviour of the model, with the aim to describe the different phases of BaTiO$_3$, we perform molecular dynamics calculations using the DL-POLY package\cite{8}. This employs a constant-($\hat{p}, T$) algorithm and the adiabatic condition for the shells is approximated by assigning enough small masses to them. Simulations were carried out over $7 \times 7 \times 7$ cells (1715 ions) with periodic boundary conditions, 0.4 fs time step, 2 ps of thermalization and 20 ps of total time.

The resulting lattice parameters are shown as functions of tem-
Temperature in Fig. 1. The four phases appear clearly in the correct sequence and the agreement with the experimental parameters is very good. The transition temperatures, which follow neatly from this graph, are low, and the range of existence of the ferroelectric phases is narrow, compared with experiment. This result resembles the one obtained with the effective Halmiltonian approach\cite{2}, in spite of taking correctly into account thermal expansion in our calculations. The calculated (experimental\cite{9}) values of the thermal expansion coefficient are 7.2 (5.2), 4.3 (4.6), 7.7 (6.5) and 8.5 (9.8) $10^{-6}K^{-1}$ for the R, O, T and C phases, respectively. Thus, the above discrepancy may be related to a failure in using zero-temperature ab-initio total energies for finite-temperature calculations.

To explore the nature of the dynamics in each phase we calculate the Ti - nearest oxygen pair distribution function $g(r)$. Its volume integral within a sphere of radius R provides the average number of oxygen ions included in the sphere centred at Ti. Thus $g(r)$ gives precise information on the average local environment of Ti. In addition it can be determined
Figure 2: Ti - nearest oxygen pair distribution function in the C (full line), T (dot-dashed line), O (dashed line) and R (doted line) phases of BaTiO₃. The inset shows the time evolution of a cell polarization at the same temperatures in the various phases.

from XAFS measurements. Our result, shown in Figure 2, indicates that there are oxygens located at two different distances from Ti. The integral up to the minimum between the two peaks gives 3 and the integral including both peaks amounts 6, for all phases. Therefore, in agreement with XAFS measurements[1], the environment of Ti is rhombohedral at all temperatures, with very little variation in the Ti-O distances: from the R to the C phase the shorter distance is 1.90 - 1.92 Å, while the longer one goes from 2.10 Å to 2.04 Å. We conclude that the dynamics is of relaxatory type in the C, T and O phases, with jumps among the [111] potential minima. This follows also from the observation of the time evolution of a cell polarization component, shown in the inset of Fig. 2. There we see for the above three phases that fast oscillations around a finite polarization value are interrupted by much less frequent polarization reversals. For the R
Figure 3: Longitudinal ($P_{zz}$) and transverse ($P_{xx}$ and $P_{yy}$) dynamic polarization correlations between pairs of cells as functions of the distance $d$ from each other along $z$ direction, for several temperatures in the C phase. The transverse correlations are almost insensitive to temperature. Phase only fast oscillations around a finite polarization are observed.

Finally we look for the spatial correlations of dynamic polarizations in the C phase. In the analogue material KNbO$_3$, ab-initio$^{[10]}$, atomistic$^{[11]}$ and diffuse X-ray scattering$^{[12]}$ results prove the existence of longitudinally correlated polarizations along Nb-O chains. Also in BaTiO$_3$ there is preliminary evidence of such features$^{[12]}$, in agreement with the previously mentioned suggestion from the phonon instabilities.

To verify this point we calculate the correlation functions $P_{\alpha\alpha}(d) = \langle P_{\alpha}^i(t) P_{\alpha}^{i+d}(t) \rangle$ relating the $\alpha$ polarization component in two cells separated by a distance $d$ along $z$ direction. The results are shown in Fig. 3 for several temperatures. It is seen that the correlation of transverse polarizations decays much faster than that of longitudinal ones. The curves represent a fit of the function $P_{\alpha\alpha}(d) = e^{-\frac{d}{\xi_d}}$ to the numerical results,
whereby only the nearest cell is considered to avoid the effect of the periodic boundary conditions. From this fit we obtain a correlation length \( \xi_{zz} \approx 4a \) for the longitudinal polarizations at 300 K, while for the transverse ones \( \xi_{xx} \approx \xi_{yy} \approx 0.5a \). Remarkably, there is only a moderate decrease of the longitudinal correlations 600 degrees above the first ferroelectric transition.

In conclusion, by developing an atomistic model capable to describe the four phases of BaTiO\(_3\) we verify that order-disorder is the dominant dynamic mechanism for the transitions, with the same average rhombohedral local environment of Ti in all phases. In the C phase precursor chain-like clusters appear dynamically with polarization along Ti-O chains.

References

[8] DL-POLY is a package of molecular simulation routines written by W. Smith and T.R. Forester, Daresbury and Rutherford Appleton Laboratory, Daresbury, UK.