Correspondence

Molecular Mechanics of the Ferroelectric to Paraelectric Phase Transition in Barium Titanate

AIC508116

Sir:

It has recently been shown[1] that by analyzing the temperature dependence of optical second harmonic generation (SHG) coefficients via a microscopic hyperpolarizability model[2] one can obtain detailed structural information concerning the microscopic nature of solid-state phase transitions. The aforementioned technique has been successfully applied to structural problems involving rigid-body rotations and deformations of tetrahedra[1] as well as trigonal deformations of octahedra.[3,4] In this case, $BaTiO_3$, we use the technique to describe the temperature dependence of the tetragonal deformation of the TiO_6 octahedron in ferroelectric $BaTiO_3$. Combining the same tetragonal deformation model with a microscopic Ti→O dipole model we find the same temperature-dependent deformation angle ϕ via an analysis of the temperature dependence of the spontaneous polarization P_s.

We relate the bulk SHG coefficient d to the microscopic Ti→O bond hyperpolarizability β via

$$d_{ijk} = \frac{1}{V} A_{il} A_{jm} A_{kn} \beta_{lmn} \qquad (1)$$

where the matrix **A** represents the 3 × 3 array of direction cosines which transforms the microscopic (bond) coordinate system into the macroscopic (crystal) coordinate system and V represents the volume of the unit cell.[5] We assume here that the temperature dependence of **A** is much greater than that of β, i.e., $\partial A/\partial T >> \partial\beta/\partial T$; hence any changes in d vs. temperature can be attributed to changes in **A**. This assumption that $\beta(25\ °C) \approx \beta(120\ °C)$ has been shown to be valid in the several cases,[1,3,4] thus far investigated ($LiNbO_3$, $LiTaO_3$, SiO_2, $Pb_5Ge_3O_{11}$, etc.) where some of the phase transitions are much higher in temperature than in $BaTiO_3$; for example the temperature for Tc($LiTaO_3$) is ~600 °C. Assuming a Ti→O bond of symmetry $C_{\infty v}$, which allows[2] both $\parallel$ and $\perp$ components of β, ($\beta^{\parallel} \equiv \beta_{333}$ and $\beta^{\perp} \equiv \beta_{311} = \beta_{113} = \beta_{322} = \beta_{223}$), one finds from eq 1 that

$$d_{333} = \frac{1}{V}\sum_{i=1}^{6} n_i^3 \beta^{\parallel}_i + 3n_i(1 - n_i^2)\beta^{\perp}_i \qquad (2)$$

$$d_{311} = \frac{1}{V}\sum_{i=1}^{6} l_i^2 n_i \beta^{\parallel}_i + n_i(1 - 3l_i^2)\beta^{\perp}_i \qquad (3)$$

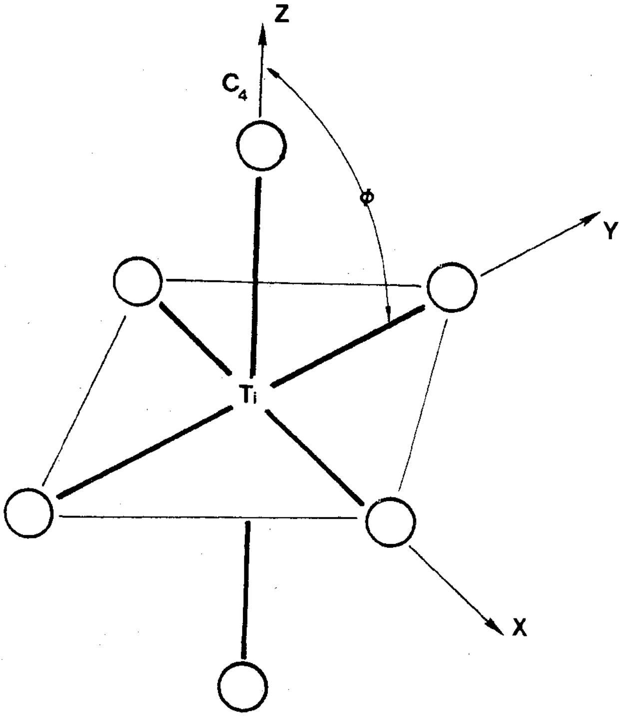

Figure 1. TiO_6 octahedron in $BaTiO_3$ showing the fourfold (z) axis and the tetragonal deformation angle ϕ.

where β_i represents the hyperpolarizability of the ith Ti→O bond[6] which has direction cosines $(l, m, n)_i$. In the case of $BaTiO_3$ there are six Ti→O bonds per tetragonal cell[7] ($P4mm$) of volume V. The cell constants for $BaTiO_3$ are a_0 = 3.992 Å and c_0 = 4.036 Å. The phase transition at 120 °C transforms the crystal from the polar ($4mm$) ferroelectric group to a centric ($m3m$) group where symmetry requires the SHG coefficients (d's) to be identically zero. We see from Figure 1 that the four Ti→O bonds in the xy plane are related by a fourfold axis and that the top and bottom (z axis) bonds are diametrically opposed for all deformation angles ϕ. Hence we only have one Ti→O bond with fourfold degeneracy to consider. Thus from eq 2 we find

$$d_{333} = \frac{4}{V}(\beta^{\parallel} \cos^3 \phi + 3\beta^{\perp} \cos \phi \sin^2 \phi) \qquad (4)$$

the range of ϕ being from ϕ = 93° at room temperature[7] to ϕ = 90° at the Curie temperature ($T \approx$ 120 °C). Since for all allowed values of ϕ (90° ≤ ϕ ≤ 93°) the coefficient of $\beta^{\perp}$ is at least 10^3 times greater than that of $\beta^{\parallel}$, we thus neglect the $\beta^{\parallel}$ term completely, giving us

$$d_{333} = \frac{12\beta^{\perp}}{V} \cos \phi \sin^2 \phi \qquad (5)$$

Combining the room-temperature SHG results[8] [d_{333} = (14 ± 1)$d_{123}(KH_2PO_4)$] with the room-temperature structural data[7] (V = 64.32 Å^3 and ϕ = 93°) via eq 5 we find $\beta^{\perp} = -14.2 \times 10^{-22}$ cm^3 × $d_{123}(KH_2PO_4)$. Hence

$$d_{333} = -265 d_{123}(KH_2PO_4) \cos \phi \sin^2 \phi \qquad (6)$$

which for 90° ≤ ϕ ≤ 93° can be approximated as

$$d_{333} = -265 d_{123}(KH_2PO_4) \cos \phi \qquad (7)$$

This now allows us to calculate the temperature dependence of ϕ from the known temperature dependence of d_{333}. This calculated dependence of ϕ on temperature is shown in Figure 2. The relation between d_{311} and ϕ is found from eq 3 to be

$$d_{311} = \frac{2}{V}[\beta^{\parallel} \cos \phi \sin^2 \phi - \beta^{\perp} \cos \phi (1 - 3 \cos^2 \phi)] \qquad (8)$$

Again using our known values[7,8] of V, ϕ, $\beta^{\perp}$, and d_{311} [d_{311} = (36 ± 3)$d_{123}(KH_2PO_4)$] at room temperature we find from eq 7 that $\beta^{\parallel} = -236.8 \times 10^{-22}$ cm^3 × $d_{123}(KH_2PO_4)$. Hence

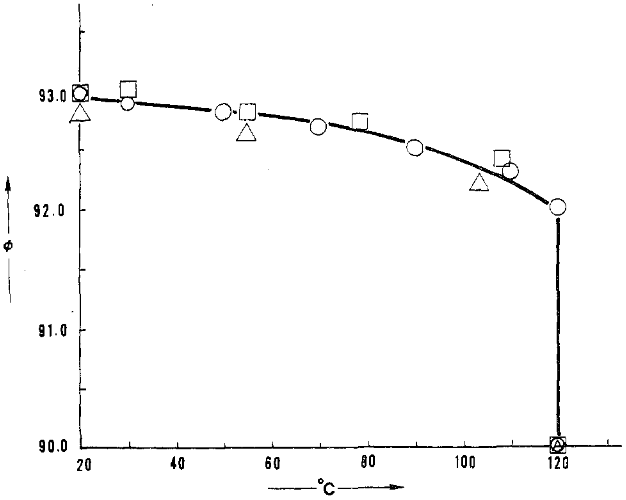

Figure 2. Tetragonal deformation angle ϕ vs. temperature for $BaTiO_3$ as calculated from the SHG coefficients d_{333} (□) and d_{311} (△) as well as from the spontaneous polarization P_s (○).

$$d_{311} = 44.16[-16.67 \cos\phi \sin^2\phi + \cos\phi(1 - 3\cos^2\phi)]d_{123}(KH_2PO_4) \quad (9)$$

which for ϕ near 90° can be approximated to

$$d_{311} = -736 d_{123}(KH_2PO_4)\cos\phi \quad (10)$$

Using the temperature dependence[8] of d_{311} we again calculate the temperature dependence of ϕ and compare the results with those found from d_{333} in Figure 2. The agreement is well within the experimental uncertainties[9] (~5%).

We further relate the observed spontaneous polarization P_s to the microscopic Ti→O bond dipole moment μ via the same formalism as eq 1, i.e.

$$P_i = \frac{1}{V}A_{ij}\mu_j \quad (11)$$

assuming again that the temperature dependence of μ is small compared to that of **A**, i.e., $\partial A/\partial T >> \partial\mu/\partial T$. From eq 11 and Figure 1 we find

$$P = \frac{4\mu}{V}\cos\phi \quad (12)$$

Using the room-temperature value[7] of the spontaneous polarization ($P_s = 26\ \mu C/cm^2$) and the previously given values of V and ϕ we find $\mu_{Ti\to O} = -24$ D. Hence

$$P_s = (-498\ \mu C/cm^2)\cos\phi \quad (13)$$

Using the temperature dependence of P_s we thus again determine the temperature dependence of ϕ. This is compared with the results via SHG coefficients in Figure 2. The agreement is excellent.

The large Ti→O dipole moment (24 D) is due in part to the fact that we have neglected the bond length dependence in eq 11. If we had taken the bond length into account, we would have found $\mu = 14$ D which is quite close to the 13-D value obtained by assuming a 1.33-electron transfer from the Ti to each of the three oxygens (i.e., 100% ionic). The usefulness of this type of a bond dipole model, beyond simplicity, can be seen for example in that we can predict ϕ for the isomorphous ferroelectric $PbTiO_3$ from the literature[10] value of $P_s = 75\ \mu C/cm^2$ and eq 13. In this case we predict ϕ to be 98.7° which is fortuitously close to that found by Shirane and co-workers,[11] viz., $\phi = 98.6°$. Another example of its utility is the demonstration that $P_s(T) \propto d_{333}(T)$, an experimental result first observed by Miller[8] which is now known to occur in a great many crystals.

In summary we have shown that detailed structural information regarding the nature of the solid-state phase transition in $BaTiO_3$ can be obtained from SHG results by using a three-dimensional hyperpolarizability model. The results are in good agreement with those found via a microscopic bond dipole model which is applied to spontaneous polarization results. We feel that since the experiment (SHG) is so straightforward[2] (laser light into the crystal–optical second harmonic detected leaving the crystal) and the theory so simple that the technique should prove highly useful as a tool for investigating the microscopic details of solid-state phase transitions. Furthermore, since SHG only arises from the acentric (bonding or valence) electrons, it is indeed possible that the individual β's will provide new information about the electronic structure of molecules.

Registry No. $BaTiO_3$, 12047-27-7.

References and Notes

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(5) The more ionic Ba–O interactions are neglected because of their small amount of directional character; i.e., spherical or core electron distributions should not reradiate at the second harmonic.
(6) Since we have neglected the local field effects, it might be more precise to call β an "effective" polarizability.
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(9) Even though the absolute values of d's are seldom known to better than ±20%, their temperature behavior is generally a well-behaved function whose relative spread is ~±5%.
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The Di-μ-hydroxo-Λ-bis(ethylenediamine)chromium(III)-Δ-bis(ethylenediamine)cobalt(III) Cation and Its Equilibria with Monobridged Systems

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Sir:

More than 60 years ago Dubsky[1] made an unsuccessful attempt to prepare a complex in which hydroxide ions bridge a chromium(III) and a cobalt(III) ion. Such an intriguing complex has gained renewed interest because of recent spectral[2] and magnetic[3] studies of bridged chromium(III) complexes. The results of these studies can be accounted for as properties of the individual chromium(III) ions superposed on a superexchange interaction[2] through the bridges. It is now important to obtain information about the properties of the individual chromium(III) ions in the same site situations but under conditions where the superexchange interaction is absent. The present mixed-metal bridged system provides such a situation. The double-hydroxo-bridged systems have further gained interest by the recent discovery[4,5] that the double-bridged system of two chromium(III) ions in solution enters into equilibrium with a monobridged system within minutes, i.e., long before other reactions take place. The mixed system therefore gains kinetic interest. The present note describes the preparation of the mixed cation di-μ-hydroxo-Λ-bis(ethylenediamine)chromium(III)-Δ-bis(ethylenediamine)cobalt(III) and its first bridge hydrolysis.