Field dependent dielectric study of PbTiO$_3$ and KNbO$_3$ ferroelectric perovskites

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An expression has been obtained for the complex dielectric constant in anharmonic pure ferroelectric crystals using double time temperature dependent Green’s function technique along with a modified Hamiltonian which includes anharmonicity up to the fourth order due to the interactions of the soft mode. The electric field, temperature and frequency dependent dielectric constant of PbTiO$_3$ and KNbO$_3$ crystals have been studied. Dielectric constant increases with increase in the applied electric field and decreases with increasing temperature in PbTiO$_3$ and KNbO$_3$ crystals. Anharmonicity is necessary in these crystals to observe these effects.

Keywords: Dielectric constant, Perovskites, Anharmonicity, Green’s function, Hamiltonian

1 Introduction

Ferroelectric materials can be phenomenologically defined as the dielectric materials with spontaneous polarization in a range of temperature. This is produced by lack of symmetry of the crystal structure with respect to higher symmetry of the paraelectric phase. Spontaneous polarization decreases with the increase in temperature up to where the phase transition occurs. The study of dielectric properties helps in understanding intra and inter molecular interactions, conformational changes in the macromolecules etc. The temperature and the frequency dependence of dielectric constant in external electric field have been the subject of much interest in the past years. The dielectric constants of PbTiO$_3$ and KNbO$_3$ are large and show Curie-Weiss law type temperature dependence. This behaviour results from a near cancellation of the short range restoring forces and the long range driving forces on the ions. Anharmonic terms in the lattice potential energy are held responsible for the dependence of the dielectric constant on the factors: temperature, frequency, etc.

Temperature dependent properties of the ferroelectrics result from the temperature dependence of the low lying transverse optic mode of vibrations. One of the very interesting property of these crystals is the electric field dependence of low frequency transverse optic mode.

The compounds PbTiO$_3$ and KNbO$_3$ possess structure at room temperature and both are based upon the mineral perovskites. Due to large value of permeability with suitable doping, these are used in capacitors with outstanding properties. Above 435°C, KNbO$_3$ exhibits a simple cubic structure. On cooling, the perovskites cell undergoes a deformation to tetragonal symmetry. Further cooling below 250°C results in another phase transition and perovskites cell possess monoclinic symmetry.

Due to their specific features, ferroelectrics are broadly employed to make small size capacitors of high capacitance, non-linear capacitor with controllable capacitance, frequency multipliers, voltage stabilizers, modulators, dielectric amplifiers etc. A considerable review on dielectric behaviour of ABO$_3$ type perovskites is available in literature.

The variation of field dependent dielectric constant with the temperature and frequency has been studied in the present paper. Double time Green’s function technique will be used to obtain thermally averaged correlation function and hence the observable quantities with the help of Silverman-Joseph modified Hamiltonian which include anharmonic effects up to fourth order. Calculated results are compared with the results of other researchers.

2 Theory

To evaluate the expressions for the various dynamic properties in the presence of the electric field, we introduced the retarded double time Green’s function for the optical phonon as:

$$G_0^0(t-t') = <<A_0^0(t), A_0^0(t')>>_{\omega + i\varepsilon}$$  \hspace{1cm} (1)
or \( G'_0(\omega + i\varepsilon) = G'(\omega) - G''(\omega), \quad \ldots (2) \)

where \( G'(\omega) \) and \( G''(\omega) \) are the real and imaginary parts of the Green’s function \( G(\omega) \).

For the study of dielectric constant, we have used Silverman-Joseph modified Hamiltonian\(^{11}\), which includes the anharmonicity up to the fourth order in the potential energy similar to our previous study for zero field case\(^{11}\). The notations used are the same and in the same sense as used in Ref. (11). The interactions of the soft mode coordinates, resonant interactions, scattering and electric dipole moment terms are considered in the Hamiltonian.

Solving the equation of the motion for the Green’s function Eq. (1) with the help of modified Silverman-Joseph Hamiltonian, Fourier transforming and writing it in the form of Dyson’s equation one obtains:

\[ G_0^0(\omega + i\varepsilon) = \omega / \pi[\omega^2 - (\nu_0^0)^2 - 2i\omega\Gamma_0^0(\omega)] \quad \ldots (3) \]

where

\[ \nu_0^0(\omega) = -\sum_k \beta^k(k) <A^k>, \]

\[ A_k^\lambda > + 96g^2\omega_0^0VE^2 - 24g\omega_0^0D'i'\epsilon_2 + \Delta_0^0(\omega). \quad \ldots (4) \]

\( \Delta_0^0(\omega) \) and \( \Gamma_0^0(\omega) \) are the field dependent shift and width for the soft mode respectively, \( \beta^k(k) \) and \( V \) are anharmonic constants. All these terms are well defined in Ref. (11).

The real part of the dielectric constant is related to the soft phonon Green’s function:

\[ \varepsilon'(\omega) = -8\pi^2N\mu^2G'(\omega) \quad \ldots (5) \]

The real part of the complex dielectric constant [with the help of Eq. (3)] is given by:

\[ \varepsilon'(\omega) - 1 = -8\pi N\mu^2(\omega^2 - \Omega^2)e_j[(\omega^2 - \Omega^2)^2 + 4\omega^2\Gamma_0^0], \quad \varepsilon_0 = \Omega \]

or \( \varepsilon'(\omega) = 8\pi N\mu^2(\Omega^2 - \omega^2)\epsilon_0/[(\Omega^2 - \omega^2)^2 + 4\omega^2\Gamma_0^0], \quad \varepsilon > 1 \)

\[ \ldots (6) \]

where \( \epsilon_0 \) is the static dielectric constant of the material, \( \mu \) the dipole moment per unit cell, \( N \) the total number of unit cells in the specimen and other symbols are as usual. The unit cell volume of PbTiO\(_3\) is 6.33 \times 10^{-29} \text{m} \quad (a=b=3.904 \text{ Å} \text{ and } c=4.152 \text{ Å}) and of KNbO\(_3\) is 6.5 \times 10^{-29} \text{m} \quad (a=b=3.997 \text{ Å} \text{ and } c=4.063 \text{ Å}) have been taken from the pages 77 and 48 of Ref. (13), respectively. The value of polarization \( P \) for PbTiO\(_3\) (81 \mu\text{C}/\text{cm}^2) and for KNbO\(_3\) (30 \mu\text{C}/\text{cm}^2) are taken from Ref. (14) and Ref. (15), respectively. We have calculated the electric dipole moment for unit cell for PbTiO\(_3\) (5.12 \times 10^{-29} \text{C/m}) and KNbO\(_3\) (1.95 \times 10^{-29} \text{C/m}) using the relation:

\[ \mu = P. \Delta V \]

where \( P \) is the polarization of the crystal and \( \Delta V \) is volume of the unit cell.

The frequency dependent dielectric constant in the range \( \omega T \leq 1 \) may be calculated using the relation (which is similar to that of Udagawa\(^{16}\)):

\[ \varepsilon'(\omega) = (\omega^2 - \omega_0^2)\epsilon_0 \omega_0^0/[(\omega^2 - \omega_0^2)^2 + 4\omega^2\Gamma_0^0], \quad \omega_0^0 = \Omega \approx \nu_0^0 \]

or

\[ \varepsilon'(\omega) = (\omega^2 - \omega_0^2)\lambda J/[(\omega^2 - \omega_0^2)^2 + 4\omega^2\Gamma_0^0] \quad \ldots (7) \]

where \( \lambda = \varepsilon_0/T_0^2 \) is a constant at a certain temperature.

The soft mode frequency is very large as compared to the microwave frequencies (as \( \omega/\Omega = 10^{-3} \)) and no relaxation effects are observed. Half width \( \Gamma_0(\omega/2\omega_0) \) is such that \( \Gamma_0(\omega) << 2\omega_0 \). Due to this appreciable difference between the microwave frequency and the normal frequency of the oscillator, the real part of the dielectric constant [Eq. (7)] can also be written as:

\[ \varepsilon' = \lambda/\omega_0^2 \text{ or } \varepsilon' = \lambda/\Omega^2 \quad \ldots (8) \]

where \( \Omega \) is soft mode frequency which depends upon anharmonicity and electric field. The square of the soft mode frequency for optic mode could be written as:

\[ (\nu_0^0)^2 = -(\omega_0^0)^2 - 2\omega_0^0V + Y_1Y_2T + Y_3T^2 \quad \ldots (9) \]

where \( Y_2 \) and \( Y_3 \) are temperature dependent coefficients of \( T \) and \( T^2 \), respectively.

From Eqs (6) and (8), \( (\nu_0^0)^2 \) is same as \( \omega_0^0 \), we conclude that:

\[ \varepsilon'(T) = \lambda / K(T-T_c+\xi T^2) \quad \ldots (10) \]

where \( K \) is temperature independent constant, \( T_c = (\alpha/\beta) \) the paraelectric phase transition temperature, \( \xi = (-\gamma/\beta) \) the non-linearity constant, \( \alpha = -(\omega_0^0)^2 - 2\omega_0^0V + Y_1 ; \beta = Y_2, \gamma = Y_3 \).

If the parameter \( \xi \) is very small and the temperature is not very high (i.e. though in paraelectric phase but in the vicinity of Curie temperature \( T_c \)), then one can neglect the term \( \xi T^2 \) from denominator of the Eq.(10) and one gets:

\[ \varepsilon'(T) = \lambda / K(T-T_c) = C / (T-T_c) \quad \ldots (11) \]

where \( C = \lambda/K \) is the Curie constant and \( T_c \) is the Curie temperature.

In general, electric field dependence of dielectric constant can be written as from [Eq. (11)]:

\[ \ldots (11) \]
\[ \epsilon'(T) = C/(T-T'_c) \]  
\[ \text{where } T'_c = T_c + \Delta T \]  
\[ \text{with } \Delta T = 1.9 \times 10^{-3} \times E \]

Here \( E \) is applied electric field in volt/cm and similar to as suggested by Merz Walter\(^{17} \). The temperature dependent soft mode frequency can be approximated as:\(^{3} \)

\[ \Omega \sim (T-T_c)^{1/2} \]

The values of Curie- temperature for PbTiO\(_3\) (\( T_c = 763K \)) and KNbO\(_3\) (\( T_c = 708K \)) crystals are taken from Ref. (13) for zero field case. By using Eqs (13) and (13a), we have calculated Curie temperature for both the crystals in the presence of electric field. Using Eqs (13) and (14), the soft mode frequency of PbTiO\(_3\) and KNbO\(_3\) crystals for different electric field strengths has been calculated. The variation of the soft mode frequency with temperature for different field strengths for PbTiO\(_3\) and KNbO\(_3\) crystals is shown in Figs 1 and 2, respectively. The curves are in good agreement with previous experimental and theoretical results of other researchers\(^{5,7,19-21} \).

Using Eq. (11), we have calculated temperature dependent dielectric constant of PbTiO\(_3\) and KNbO\(_3\) crystals in paraelectric phase for zero field case. By using Eqs (12) and (13), we have calculated the variations of dielectric constant with temperature for different electric field strengths. The value of \( C \) has been calculated from Figs (15 and 363) of Ref. (13) by the best fit of data. Calculated values of dielectric constant for PbTiO\(_3\) and KNbO\(_3\) crystals are given in Tables 1 and 2, respectively. The variation for PbTiO\(_3\) and KNbO\(_3\) crystals in Figs 3 and 4, respectively. As temperature increases, dielectric constant decreases. It is also evident from Figs 3 and 4 that taking any temperature as reference, dielectric constant increases with increase of electric field.

By using Eq. (14), we have calculated the soft mode frequency of PbTiO\(_3\) and KNbO\(_3\) crystals for the different electric fields. Using Eq. (7), we have calculated the dielectric constant at room temperature in the frequency range \( 10^6-10^{11} \) Hz for different field strengths. The variation of dielectric constant with frequency for different electric fields in Figs 7 and 8, respectively. The curves are in agreement with previous experimental and theoretical results\(^{5,7,19-21} \).

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**Table 1 — Calculated dielectric constant with respect to temperature at different field strengths in PbTiO\(_3\) crystal**

<table>
<thead>
<tr>
<th>T(K)</th>
<th>800</th>
<th>810</th>
<th>820</th>
<th>830</th>
<th>840</th>
<th>850</th>
<th>860</th>
<th>870</th>
<th>880</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dielectric constant</td>
<td>E=0KV/cm</td>
<td>1.10</td>
<td>0.90</td>
<td>0.70</td>
<td>0.61</td>
<td>0.53</td>
<td>0.47</td>
<td>0.42</td>
<td>0.38</td>
</tr>
<tr>
<td>(( \epsilon' \times 10^4 ))</td>
<td>E=5KV/cm</td>
<td>1.48</td>
<td>1.09</td>
<td>0.86</td>
<td>0.71</td>
<td>0.61</td>
<td>0.53</td>
<td>0.47</td>
<td>0.42</td>
</tr>
<tr>
<td></td>
<td>E=10KV/cm</td>
<td>2.30</td>
<td>1.50</td>
<td>1.10</td>
<td>0.84</td>
<td>0.71</td>
<td>0.60</td>
<td>0.53</td>
<td>0.46</td>
</tr>
<tr>
<td></td>
<td>E=15KV/cm</td>
<td>4.75</td>
<td>2.20</td>
<td>1.43</td>
<td>1.10</td>
<td>0.84</td>
<td>0.70</td>
<td>0.60</td>
<td>0.52</td>
</tr>
</tbody>
</table>

**Table 2 — Calculated dielectric constant with respect to temperature at different field strengths in KNbO\(_3\) crystal**

<table>
<thead>
<tr>
<th>T(K)</th>
<th>740</th>
<th>750</th>
<th>760</th>
<th>770</th>
<th>780</th>
<th>790</th>
<th>800</th>
<th>810</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dielectric constant</td>
<td>E=0KV/cm</td>
<td>51.11</td>
<td>41.90</td>
<td>35.50</td>
<td>30.80</td>
<td>27.20</td>
<td>24.30</td>
<td>22.02</td>
</tr>
<tr>
<td>(( \epsilon' \times 10^2 ))</td>
<td>E=5KV/cm</td>
<td>63.95</td>
<td>50.14</td>
<td>41.24</td>
<td>35.02</td>
<td>30.40</td>
<td>26.9</td>
<td>24.10</td>
</tr>
<tr>
<td></td>
<td>E=10KV/cm</td>
<td>85.40</td>
<td>62.40</td>
<td>49.20</td>
<td>40.60</td>
<td>34.56</td>
<td>30.10</td>
<td>26.60</td>
</tr>
<tr>
<td></td>
<td>E=15KV/cm</td>
<td>128.50</td>
<td>82.80</td>
<td>60.90</td>
<td>48.30</td>
<td>39.90</td>
<td>34.10</td>
<td>29.70</td>
</tr>
</tbody>
</table>
3 Discussion and Conclusions

In the present study, the Hamiltonian proposed by Silverman has been designed in terms of creation and annihilation operators. The normalized Hamiltonian has been obtained using the Green’s function technique and Dyson’s equation treatment to evaluate the higher order correlation functions. We have numerically estimated the dielectric constant of PbTiO$_3$ and KNbO$_3$ crystals and shown the comparative variation of dielectric constant with frequency and temperature at different field strengths.

It is evident from Eq. (6) that the field dependence of dielectric constant is a clear consequence of the field dependence of soft mode frequency. Figures 1 and 2 show the variation of soft mode frequency with temperature for different electric fields in PbTiO$_3$ and KNbO$_3$ crystals, respectively. The soft mode frequency increases with increase in temperature as well as electric field. At any temperature and electric field as reference, the soft mode frequency for KNbO$_3$ is greater than for PbTiO$_3$ crystal. The curves are in good agreement with experimental and theoretical results of other researchers$^{10,19,21}$.

Figures 3 and 4 show the variation of the dielectric constant with temperature ($T-T_c$) for different electric fields for PbTiO$_3$ and KNbO$_3$ crystals in paraelectric phase, respectively. At any temperature and electric field as a reference, the dielectric constant of pure PbTiO$_3$ perovskite is greater than that of KNbO$_3$ crystal. The present results indicate that the dielectric constant increases sharply as ($T-T_c$) decreases and has the highest value as $T\rightarrow T_c$. Dielectric constant decreases as we go away from the Curie temperature and has small value at high temperature side. The trend is the same for different electric field strengths. For simplicity, we have included here the experimental results of researchers$^{22,23}$ in Figs 5 and 6 for PbTiO$_3$ and KNbO$_3$ crystals, respectively.
Different researchers using different approaches and parameters have shown the variation of dielectric constant with $T$ or $(T-T_c)$ and have shown that in the paraelectric phase the dielectric constant decreases. Thus our results are in good agreement with experimental results observed by Remeika and Glass\textsuperscript{22} and Shirane \textit{et al.}\textsuperscript{23} for PbTiO$_3$ and KNbO$_3$ crystals, respectively.

Figures 7 and 8 show the variation of dielectric constant with frequency for different electric fields in case of PbTiO$_3$ and KNbO$_3$ crystals. The dielectric constant remains constant for the frequencies $10^6$-$10^9$ Hz and above this range dielectric constant suddenly decreases. For both the crystals, the same variation is obtained. Also it is evident from Figs 7 and 8 that by taking any frequency as a reference the dielectric constant increases with increase in electric field. The curves are in good agreement with experimental and theoretical results of other researchers\textsuperscript{4,10,11,24}.

Strong phonon phonon interaction due to vanishingly small frequency of the soft mode is held responsible for it. Anharmonicity is necessary in these crystals to observe these effects. Recently, we have applied Green’s function technique in obtaining expression for field dependent dielectric constant\textsuperscript{9}, tangent loss\textsuperscript{25} and specific heat\textsuperscript{26} in Ba$_x$Sr$_{1-x}$TiO$_3$ ferroelectric perovskites.

**References**