Electric field on Dielectric & acoustic Properties of Ferroelectric crystal $PbHPO_4$

Mayank Joshi & Trilok Chandra Upadhyay
Physics Department,
H.N.B. Garhwal University Srinagar (Garhwal) Uttarakhand-246174
Email-Mayankphysics@Gmail.Com

Abstract

The third and fourth order phonon anharmonic interactions and external electric field terms are added in the two-sublattice pseudospin model for $PbHPO_4$ crystal. By using double time thermal Green's function method modified model, theoretical expressions for soft mode frequency, dielectric constant, shift, width and tangent loss are evaluated for $PbHPO_4$ crystal. Temperature and field variations of soft mode frequency, dielectric constant and loss tangent are calculated numerically. Present theoretical results agree with experimental results of Smutney and Fousek for dielectric constant of $PbHPO_4$

1. Introduction

Due to their promising application in the field of electronics and technology ferroelectric crystals are continuously being attracted to both physicists and material scientists. Memory devices, infrared and pyroelectric detectors, transducers, display devices piezoelectric devices are some common uses of these materials [1].

Lead hydrogen phosphate ($PbHPO_4$) crystal and its isomorphs ($PbAsPO_4$, $CaHPO_4$, $BaHPO_4$, $CaHPO_4$ etc.) from an interesting group of quasi-one dimensional hydrogen bonded ferroelectric crystals. In $PbHPO_4$ the direction of spontaneous polarization is almost parallel to the direction of the H-bonded O-H...O projecting on the (010) plane unlike in KH_2PO_4**.** The PO_4 groups are bound to one another by the O-H...O bonds in the from of a one dimensional chain along c-axis[2] Raman spectroscopic studies showed the value of tunneling integral for $PbHPO_4$ crystal very small although very large changes of curie temperature and Curie-Weiss constant occur on deuteration [3]. According to Cochran[3] the frequency of some of the normal mode of vibration of crystal called soft mode becomes zero at the transition temperature. It is this soft mode that largely determines the dielectric and scattering properties in ferroelectric crystals.

The acoustic experiments of Litov and Garland [4] clearly showed that external electric field has pronounced effect on temperature dependence of ultrasonic attenuation and elastic measurements on ferroelectric crystals. Baumgartner[5]. Choi and Lockwood[6] and Silverman[7] have carried out experiments on effects of electric field on dielectric measurements in KDP and $BaTiO_3$.

Ohno and Lockwood[8] have measured Raman Spectra in $PbHPO_4$ crystal in the temperature range 100K to 350K. Tezuka et al[9] have made experimental studies of soft mode spontaneous polarization in $PbHPO_4$ crystal. Ratajezak et al [10] have studied structural and second harmonic generation studies in $PbHPO_4$ crystal. Mahadevan et al[11] have grown $PbHPO_4$ crystal and measured its dielectric constant and loss.

Wesselinowa[12] has considered pseudospin-lattice coupled mode modal with third and forth order phonon interaction terms to study dynamical structure factor of central peak in $PbHPO_4$, crystal using Tsernikov's Green's function. This model is over simplified for the case of $PbHPO_4$ crystal since it does not explain salient features of these systems such as low value of tunneling integral etc. Their work is quite different to our approach. Chaudhuri et al [13] have used a two sub lattice ~~pseudo spin~~ lattice coupled mode model with a fourth order phonon anharmonic term. But they failed to consider third order phonon anharmonic term which is very important. Moreover they decoupled the correlation at an early stage so that some important cross terms disappeared from their calculated results.

In the present study a two sub lattice pseudospin lattice coupled mode (PLCM) Model along with third and fourth order phonon anharmonic interactions is considered for $PbHPO_4$ crystal using Green's function method[15] the field dependent shift, width, soft mode frequency dielectric constant and loss tangent have been calculated for, values for $PbHPO_4$ crystal, temperature dependence of the above quantities have been calculated in the presence of electric field and compared with experimental results of Smutny and Fousek[16].

2. Model Hamiltonian

Mitsui[17] and Blinc and Zeks [18] proposed a two-sublattice pseudospin model, which was applied to the case of $PbHPO_4$ and isomorphous crystals . For $PbHPO_4$ type crystals we have, extended their two-sublattice pseudospin-lattice coupled mode model[4] by adding third and fourth order phonon anharmonic interaction terms [14] as well as external electric field term which is expressed as

$$H = -2\Omega\sum_i \left(S_{1i}^x + S_{2i}^x\right) - \sum_{ij} J_{ij}\left[\left(S_{1i}^z S_{2i}^z\right) + \left(S_{2i}^z S_{2i}^z\right)\right] - \sum_{ij} K_{ij}\left(S_{1i}^z S_{2i}^z\right) - 2\mu E\sum_i (S_{1i}^z + S_{2i}^z)$$

$$+\frac{1}{4}\sum_k \omega_k\left(A_k A_k^+ + B_k B_k^+\right) \qquad (1)$$

In Eq.(1) above Ω is proton tunneling frequency between O-H…O double well potential,

J_{ij} is exchange interaction between neighboring lattice dipoles, and k_{ij} that in same lattice μ is dipole moment of O-H…O bond, E is external electric field, is phonon frequency, A_k and B_k are position and momentum operators and S^x and S^z are components of spin variable.

Chaudhari et al[13] have modified above model by following Kobayashi [19] by adding pseudospin-lattice interaction terms

$$H_{s-p} = -\sum_{ik} V_{ik} S_{1i}^z A_k - \sum_{ik} V_{ik} S_{2i}^z A_k^+$$

(2)

In Eqs(2) above V_{ik} is spin lattice interaction constant.

We add the third and the fourth-order phonon anharmonic interaction terms[14] as

$$H_{anh} = \sum_{k_1 k_2 k_3} V^{(3)}\left(k_1, k_2, k_3\right) A_{k_1} A_{k_2} A_{k_3} + \sum_{k_1 k_2 k_3 k_4} V^{(4)}\left(k_1, k_2, k_3, k_4\right) A_{k_1} A_{k_2} A_{k_3} A_{k_4} ,$$

(3)

$V^{(3)}$ (k_1,k_2,k_3) and $V^{(4)}$ (k_1,k_2,k_3,k_4) are third and fourth-order atomic forces constants given by Born and Huang[20].

Green’s functions, Width and Shift Equations

For the evaluation of expressions, soft mode frequency, dielectric susceptibility, dielectric constant and loss tangent we consider the evaluation of Green's function[15]

We consider the Green's function

$$G_{ij}(t-t') = \left\langle\left\langle S_{1i}^z(t); S_{1j}^z(t')\right\rangle\right\rangle = -i\theta(t-t')\left\langle\left[S_{1i}^z(t); S_{1j}^z(t')\right]\right\rangle,$$

(4)

in which θ(t- t') is unity for t<t' and zero otherwise. The angular bracket is ensemble average.

The Green's function (GF) is differentiated twice first with respect to time t and then with respect to t' , Fourier transforming the Green's function and putting in the or of Dyson's equation,

$$G_{ij}(\omega) = G_{ij}^0(\omega) + G_{ij}^0(\omega) P(\omega) G_{ij}^0(\omega)$$

(5)

where $G_{ij}^0(\omega)$ is unperturbed Green's function given as

$$G_{ij}^0(\omega) = \frac{\Omega\left\langle S_{1i}^x\right\rangle \delta_{ij}}{\pi\left(\omega^2 - 4\Omega^2\right)}$$

(6)

and $\tilde{P}(\omega)$ is polarization operator given by

$$\tilde{P}(\omega) = \pi f + \pi^2 \left\langle\left\langle F_{1i}(t); F_{j1}(t') \right\rangle\right\rangle$$
(7)

where $f = \dfrac{i\left\langle\left[F, S_{1j}{}^{y}\right]\right\rangle}{\Omega\left\langle S^{x}{}_{1i}\right\rangle}$ and (8)

$$F_{i1}(t) = 2\Omega\left(S_{1i}{}^{x} S_{1j}{}^{z} + S_{1j}{}^{z} S_{ij}{}^{x}\right) - 2\Omega K_{1j}\left(S^{X}{}_{1J} S^{Z}{}_{1J}\right) + 2\Omega V_{ik} S_{1i}{}^{x} A_k + 2\Omega V_{ik} S_{1i}{}^{x} A^{+}{}_{k}$$
(9)

The Green's function $G(\omega)$ is then obtained as

$$G(\omega) = G^0(\omega)\left[1 - G^0(\omega)\tilde{P}(\omega)\right]^{-1}$$
(10)

This gives the values of Green's function (4)

$$G_{ij}^{0}(\omega) = \frac{\Omega\left\langle S_{1i}^{x}\right\rangle \delta_{ij}}{\pi\left(\omega^2 - \tilde{\Omega}^2 - 2i\Omega\Gamma(\omega)\right)}, \qquad (11)$$

where $\tilde{\Omega}^2 = 4\Omega^2 + \left\langle S^x \right\rangle^{-1} f$
(12)

$$\tilde{\tilde{P}}(\omega) = \frac{\pi}{\left\langle S_1^x \right\rangle}\left\langle\left\langle F_i(t); F_j'(t)\right\rangle\right\rangle,$$
(13)

where <<F_i(t);F_j(t')>> are higher order Green's functions. They are evaluated by decoupling them using decoupling scheme <abcd>=<ab><cd>+<ac><bd>+<ad><bc>

$\tilde{\tilde{P}}(\omega)$ after evaluation is resolved into its real and imaginary parts using formula

$$\lim_{m\to 0} \frac{1}{x + im} = \left(\frac{1}{x}\right) \pm i\pi\delta(x)$$
(14)

The real part is called shift $\Delta(\omega)$ and the imaginary part is called half width $\Gamma(\omega)$

We therefore obtain shift and width as

$$\Delta(\omega) = \Delta_1(\omega) + \Delta_2(\omega) + \Delta_3(\omega) + \Delta_4(\omega)$$
(15)

where

$$\Delta_1(\omega) = \frac{a^4}{2\Omega\left(\omega^2 - \tilde{\Omega}^2\right)}$$
(16)

$$\Delta_2(\omega) = \frac{V_{ik}^2 N_k a^2}{2\Omega\left(\omega^2 - \tilde{\Omega}^2\right)}$$
(17)

$$\Delta_3(\omega) = \frac{4\mu^2 E^2 a^2}{2\Omega\left(\omega^2 - \tilde{\Omega}^2\right)}$$
(18)

$$\Delta_4(\omega) = \frac{2V_{ik}^2 \langle S_{1i}^x \rangle \omega_k \delta_{kk^i} \left(\omega^2 - \tilde{\tilde{\omega}}_k^2\right)}{\left[\left(\omega^2 - \tilde{\tilde{\omega}}_k^2\right)^2 + 4\omega_k^2 \Gamma_k^2(\omega)\right]}$$
(19)

and width

$$\Gamma(\omega) = \Gamma_1(\omega) + \Gamma_2(\omega) + \Gamma_3(\omega) + \Gamma_4(\omega),$$
(20)

$$\Gamma_1(\omega) = \frac{\pi a^4}{4\Omega\tilde{\Omega}}\left[\delta\left(\omega - \tilde{\Omega}\right) - \delta\left(\omega + \tilde{\Omega}\right)\right]$$
(21)

$$\Gamma_2(\omega) = \frac{V_{ik}^2 N_k a^2}{4\Omega\tilde{\Omega}}\left[\delta\left(\omega - \tilde{\Omega}\right) - \delta\left(\omega + \tilde{\Omega}\right)\right],$$
(22)

$$\Gamma_3(\omega) = \frac{4V_{ik}^2 \langle S_{1i}^x \rangle \omega_k \delta_{k\_k'} \left(\omega^2 - \tilde{\tilde{\omega}}_k^2\right)}{\left[\left(\omega^2 - \tilde{\tilde{\omega}}_k^2\right)^2 + 4\omega_k^2 \Gamma_k^2(\omega)\right]}$$
(23)

$$\Gamma_4(\omega) = \frac{2\pi\mu^2 E^2 a^2}{4\Omega\tilde{\Omega}}\left[\delta\left(\omega - \tilde{\Omega}\right) - \delta\left(\omega + \tilde{\Omega}\right)\right]$$
(24)

In Eqs.(19) and (23) $\tilde{\tilde{\omega}}_k$ and $\Gamma_k(\omega)$ are phonon frequency and phonon half width which are obtained by solving phonon Green's Function(in a similar way)

$$G_{kk'}(t - t') = \ll A_k(t), A_{k^1}(t') \gg = -i\theta(t - t') \ll A_k(t), A_{k^1}(t) \gg$$
(25)

which gives $G_{ij'}(\omega)=\dfrac{\omega_k\delta_{kk'}}{\pi\left[\omega^2-\tilde{\tilde{\omega}}^2{}_k-2i\Gamma_k(\omega)\right]}$

(26)

where

$$\tilde{\tilde{\omega}}_k^2=\tilde{\omega}_k^2+2\omega_k\Delta_k(\omega)$$

$$\tilde{\omega}_k{}^2=\omega_k+A_k \qquad (27a, b)$$

Phonon shift

$$\Delta_k(\omega)=\operatorname{Re}P^0(k,\omega)$$

$$=18P\sum k_1k_2\left|V^{(3)}(k_1,k_2,-k)\right|^2$$

$$\frac{\omega_{k1}\omega_{k2}}{\tilde{\omega}_{k1}\tilde{\omega}_{k2}}\left\{\left(n_{k_1}+n_{k_2}\right)\frac{\tilde{\omega}_{k1}+\tilde{\omega}_{k2}}{\omega^2-(\omega_{k1}+\omega_{k2})^2}+\left\{\left(n_{k_2}+n_{k_1}\right)\frac{\tilde{\omega}_{k1}+\tilde{\omega}_{k2}}{\omega^2-(\omega_{k1}+\omega_{k2})^2}\right.\right.$$

$$+48P\sum\left|V^{(4)}(k_1,k_2,k_3,-k\right|^2\frac{\omega_{k1}\omega_{k2}\omega_{k3}}{\tilde{\omega}_{k1}\tilde{\omega}_{k2}\tilde{\omega}_{k3}}$$

$$\left\{\left(1+n_{k1}n_{k2}+n_{k2}n_{k3}+n_{k3}n_{k1}\right)\frac{\tilde{\omega}_{k1}+\tilde{\omega}_{k2}+\tilde{\omega}_{k3}}{\omega^2-(\tilde{\omega}_{k1}+\tilde{\omega}_{k2}+\tilde{\omega}_{k3})^2}\right.$$

$$+3\left(1-n_{k2}n_{k1}+n_{k2}n_{k3}-n_{k3}n_{k1}\right)\frac{\tilde{\omega}_{k1}+\tilde{\omega}_{k2}+\tilde{\omega}_{k3}}{\omega^2-(\tilde{\omega}_{k1}+\tilde{\omega}_{k2}+\tilde{\omega}_{k3})^2}$$

+ highter terms }

(28)

Phonon width

$$\Gamma_k(\omega)=\operatorname{Im}P(k,\omega)$$

$$=9\pi\sum\left|V^{(3)}(k_1,k_2,-k\ )\right|^2\frac{\omega_{k1}\omega_{k2}}{\tilde{\omega}_{k1}\tilde{\omega}_{k2}}$$

$$\left\{\left(n_{k2}+n_{k1}\right)\begin{bmatrix}\left[\ \delta(\omega+\tilde{\omega}_{k1}+\tilde{\omega}_{k1})-\delta(\omega-\tilde{\omega}_{k1}-\tilde{\omega}_{k1})\right)\\ +\left(n_{k2}-n_{k1}\right)\delta(\omega+\tilde{\omega}_{k1}+\tilde{\omega}_{k1})-\delta(\omega+\tilde{\omega}_{k1}+\ \ \}\tilde{\omega}_{k1})\end{bmatrix}\right.$$

$$+48\pi\sum\left|V^{(3)}(k_1,k_2,k_3,-k_4)\right|^2$$

$$X\{1+n_{k1}n_{k2}+n_{k2}n_{k3}+n_{k3}n_{k4}\}$$

$$X\left[\delta(\omega+\tilde{\omega}_{k1}+\tilde{\omega}_{k2}+\tilde{\omega}_{k3})-\left[\delta(\omega-\tilde{\omega}_{k1}-\tilde{\omega}_{k2}-\tilde{\omega}_{k3})\right]\right]$$

(29)

In Eq(28) and (29) $n_{ki}=Coth\left(\dfrac{\tilde{\omega}_{ki}}{k_BT}\right)$ and P stand for principal part.

In Eq.(8)is solved by using means field approximation for co-relation i.e. second term in Eq.(12) is evaluated using mean field approximation, i.e. correlations are finite, i.e.

$$\frac{\left\langle S_{1i}^{z}\right\rangle}{a}=\frac{\left\langle S_{1i}^{x}\right\rangle}{b}=\frac{1}{2\tilde{\Omega}}\tanh\beta\frac{\tilde{\Omega}}{2}, \qquad (30)$$

which gives

$\tilde{\Omega}^2=a^2+b^2-bc$ (first frequency)

(31)

where $a=2J_0\left\langle S_1^z\right\rangle+K_0\left\langle S_2^z\right\rangle,$

(32)

$$b=2\Omega; \qquad (33)$$

and $\boldsymbol{c}=2\boldsymbol{J}_0\left\langle\boldsymbol{S}_1^x\right\rangle+\boldsymbol{K}\left\langle\boldsymbol{S}_2^x\right\rangle$

(34)

Therefore, the Green's function finally takes the from

$$G_{ij}(\omega)=\frac{\Omega\left\langle S_{1i}^{x}\right\rangle\delta_{ij}}{\pi\left(\omega^2-\hat{\Omega}^2-2\Omega i\Gamma(\omega)\right)}$$

(35)

$$\hat{\Omega}^2=\tilde{\Omega}^2+2\Omega\Delta(\omega) \qquad (36)$$

In Eq.(35) and (36) $\Gamma(\omega)$ and $\Delta(\omega)$ are liven by Eq.(20) and (15) respectively.

Solving Eq.(36) one gets

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$$\hat{\Omega}_{\pm}^2=\frac{1}{2}\left(\tilde{\tilde{\omega}}_k^2+\tilde{\tilde{\Omega}}^2\right)\pm\frac{1}{2}\left[\left(\tilde{\tilde{\omega}}_k^2-\tilde{\tilde{\Omega}}^2\right)^2+8V_{ik}^2\left\langle S_{1i}^x\right\rangle\Omega\right]^{½}$$

(37)

The Curie temperature is given by

$$T_c = \frac{\eta}{2k_B \tanh^{-1}\left(\frac{\eta^3}{4\Omega^2 J'}\right)}$$
(38a)

Where $\eta^2 = (2J-K)^2\sigma^2 + 4\Omega^2$
(38b)

$$J^* = (2J+K) + \frac{2V_{ik}^2 \tilde{\tilde{\omega}}_k^2}{\left[\tilde{\tilde{\omega}}_k^4 + 4\omega_k \Gamma_k^2\right]}$$
(38c)

Acoustic Attenuation

Acoustic attenuation is a measure of the energy loss of sound propagation in media.The acoustic attenuation provides an important clue about phase transition. At T_c is abruptly increase showing anomalous behavior. According To Tani & Tsuda[20] attenuation is given by $\alpha = \frac{\Gamma(\omega)}{\nu}$
(39)

Where $\Gamma(\omega)$ is acoustic width and ν is sound velocity.

Dielectric constant and Loss

The response of a ferroelectric crystal to the external electric field is expressed dielectric susceptibility χ which is related to Green's function as

$$\chi = -\lim_{\in\to 0} 2\pi N\mu^2 G_{ij}(\omega + i\in)$$
(40)

The dielectric constant $\in$ is related to electrical susceptibility as

$$\in = 1 + 4\pi\chi \qquad (41)$$

By putting value of Green's function from Eq.(39) and (40) we obtain

$$\in(\omega) = \left(-8\pi N\mu^2\right)\left\langle S_1^x\right\rangle\left(\omega^2 - \hat{\Omega}^2\right)\left[\left(\omega^2 - \hat{\Omega}^2\right)^2 + 4\Omega^2\Gamma^2\right]^{-1}$$
(42)

The dissipation of power in dielectric material is called tangent loss which expressed as

$$\tan\delta = \frac{\in''}{\in'} \qquad (43)$$

Where $\in''$ and $\in'$ are imaginary and real parts of dielectric constant

$$\tan\delta = -\frac{2\Omega\Gamma(\omega)}{\left(\omega^2 - \hat{\Omega}^2\right)} \qquad (44)$$

Where $\Gamma(\omega)$ and $\hat{\Omega}$ are half width and soft mode frequency given by Esq. (20) and (37) respectively. By using model values of various quantities in expression for $\Delta(\omega), \Gamma(\omega), \tilde{\Omega}, \hat{\Omega}, \in, \alpha$ and $\tan\partial$ for $PbHPO_4$ crystal from literature their electric field and temperature dependences $\hat{\Omega}, \in$ and $\tan\delta$ near transition temperature are calculated, which are shown in figs.1, 2, 3and 4.

Figures For crystal

Calculated electric field and temperature dependences for $PbHPO_4$ crystal

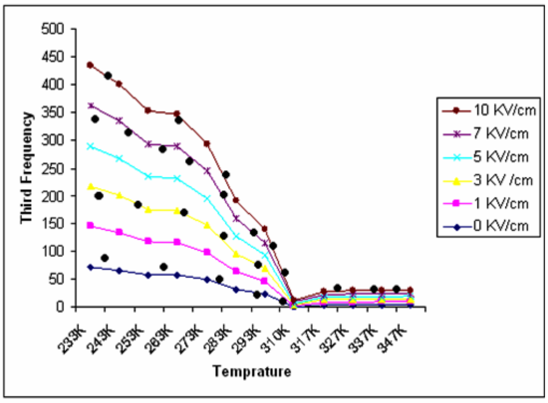

Fig 1. Soft mode frequency in $PbHPO_4$ crystal (Present calculation, ● Experimental results)

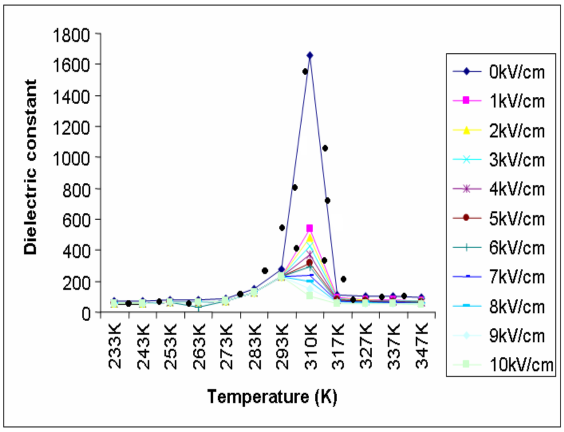

Fig.2. Dielectric constant in $PbHPO_4$ crystal (Present calculation,● Experimental results)

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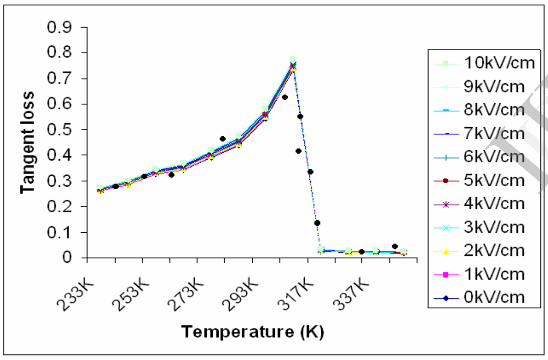

Fig 3. Tangent loss in $PbHPO_4$ crystal (Present calculation, ● Experimental results)

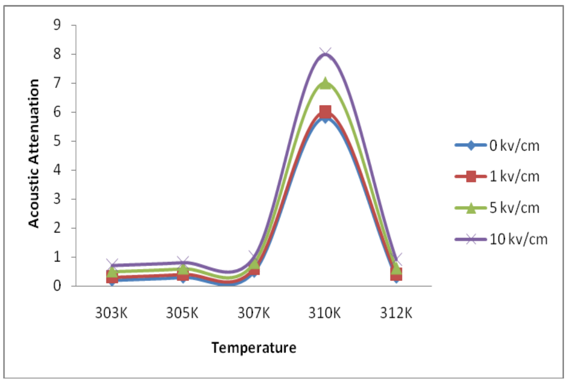

Fig.4 Acoustic Attenuation in $PbHPO_4$ crystal((Present calculation,● Experimental results

Conclusion

In the present work the effect of electric field on the dielectric properties of $PbHPO_4$ crystal has been studied .The two sub-lattice pseudo spin-lattice coupled mode model is extended by adding third and forth order phonon anharmonic interaction terms and external electric field term. With the help of double-time Green's function method, theoretically the field dependent expression for shift, width, soft mode frequency dielectric constant and loss tangent have been obtained. By fitting model values of physical quantities appearing in the expressions derived, field and temperature dependences of soft mode frequency, dielectric constant width shift and loss tangent have been calculated. Theoretical results have been compared with experimental result of Smutney & Fousek. [16] Previous workers have not considered the third order interaction an electric field terms in their calculation. Chaudhari et al [13] have not considered third-order-phonon anharmonic interaction terms in their model. This term is essential to explain linear temperature dependence (A) of soft mode frequency square $(i.e.\hat{\Omega} = AT + BT)$ since third order anharmonic term gives linear temperature dependence. Therefore, our calculation provides much better results to fit the experimental data. Secondly Chaudhuri et al [13] has decoupled the cor-relations in the early stage while we have decoupled them at a proper stage. As a result some important interactions disappeared from their calculations. If third order-phonon anharmonic terms are neglected from our expressions, these at once reduce to the expressions of previous workers. Present study shows that the electric field has pronounced effect on ferroelectric and dielectric properties of $PbHPO_4$-type crystal. The soft mode frequency increase while dielectric constant and loss tangent decrease with increase in electric field strength. It can be seen from our expressions that our frequency $\tilde{\Omega}$ is same with the initial frequency of Chaudhuri et al [See Eqs(31)]. However, our soft mode frequency $\tilde{\Omega}$ contains extra terms $\Delta(\omega)$ [given in Eqs (15)]. Our soft mode frequency $\hat{\Omega}$ contains extra terms in $\tilde{\tilde{\omega}}_k and \Gamma_k(\omega)$ applying in $\Gamma_k(\omega)$ (Eq.27a)].These extra terms are given $\left|V^{(3)}(k_1,k_2,-k_3)\right|^2$ in $\Delta_k(\omega)$ [Eqs. (28)]and $\left|V^{(3)}(k_1,k_2,-k_3)\right|^2$ term given in $\Gamma_k(\omega)$ (Eq.29-)]. . These terms differentiate our expressions with the expressions given in the work of Chaudhuri et al[13]. Attenuation increase with electric field strength both below and above T_c in $PbHPO_4$ crystal. This is in agreement with experimental results of Litov & Garleand[21]. So far we could not find experimentally data for electric field dependence for $PbHPO_4$ crystal. This Is quite similar to other ferroelectric crystal like KH_2PO_4 Experimentally.

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