# COMPOSITION DEPENDENCE OF
# SOFT MODE IN $Pb_xSr_{1-x}tio_3$ferro-Electric MIXED CRYSTALS

Sunil Kumar[*]
M S Yadav[**]
Neetu Sharma[***]
S C Deorani[****]

## ABSTRACT

*The composition dependence of soft mode in $Pb_xSr_{1-x}TiO_3$ (PST) single crystals has been theoretical investigated in para-electric phase for various compositions. Using model Hamiltonian [ For pure anharmonic crystal in presence of defect (impurity)] and Green's functions technique. Soft mode is estimated for various values of x. As x increases value of soft mode frequency decreases at constant temperature and as T increases the value of soft mode frequency increases at constant x.*

***Keywords:** Model Hamiltonian, Green's Functions Technique, Soft Mode Frequency, Anharmonic Crystal, Single Crystal.*

_____

## Introduction

Solid solutions of lead strontium titanate (PST) are very interesting ferro-electric materials which gain considerable attention due to useful in broad range of electric devices such as pyro-electric detector, DRAM capacitors, tunable microwave devices etc. PST is the most promising material because it is good insulator with large value of relative dielectric constant and low value of dielectric loss near ambient temperature.

It is easy to control the dielectric properties of the PST by adjusting [Pb/Sr] ratio. Pure $SrTiO_3$is intrinsic quantum para-electric. It is known that permittivity peaks can be induced in $SrTiO_3$by introducing substitutional impurities into the lattice[1]. In the present paper, $Pb_xSr_{1-x}TiO_3$ with Pbcontents x varies from 0 to 1.0. (Pb, Sr)$TiO_3$ solid solutions belong to ferro-electric materials of the form $(A'A'')BO_3$type. Both constituents of this solution are ferro-electric.

This work is aimed at the determination of an influence of the ferro-electric components PT and ST on physical properties like. Softmode of PST as well as a character.

Perovskites are known to exhibit a lot of useful properties[2]. They possess high dielectric co-efficients over a wide temperature and frequency range. They are used as dielectrics in integrated or surface mounted device capacitors. The remarkable piezo-electric effect is applied in a variety of electromechanical sensors, actuators and transducers. Infrared sensors need a high pyro-electric co-efficient which is available with this class of materials[3]. Tunablethermistor properties in semiconducting ferro-electrics are used in positive temperature co-efficient resistors (PTCR)[4].

Lead Strontium titanate$Pb_xSr_{1-x}TiO_3$ (PST) which is known to adopt ABO$_3$type solution, is a continuous solid solution of $PbTiO_3$ (PTO) and $SrTiO_3$ (STO) over the whole concentration range. The properties of $Pb_xSr_{1-x}TiO_3$are known to depend on the composition x[5,6,7]. $SrTiO_3$ is usually added to $PbTiO_3$ as a shifter in order to move the Curie-point $T_C$ to lower temperatures. It is well established that $T_C$ of $PbTiO_3$ decreases linearly with the amount of Sr in place of Pb. For bulk$Pb_xSr_{1-x}TiO_3$, the Curie-point varies from $-236^0$C to $490^0$ C whereas the dielectric constant (measured at room temperature and frequency of 1KHz) increases from $\varepsilon \sim 300$ To$\varepsilon \sim 1100$ for x from x =0.0 to x=$1.0^{8,9,10,11}$ .

_____
[*] Department of Physics, R. R. College, RRBM University, Alwar, Rajasthan, India.
[**] Department of Physics, R. R. College, RRBM University, Alwar, Rajasthan, India.
[***] Department of Physics, R. R. College, RRBM University, Alwar, Rajasthan, India.
[****] Department of Physics, R. R. College, RRBM University, Alwar, Rajasthan, India.

In the present paper, an expression for the soft mode frequency in $Pb_xSr_{1-x}TiO_3$ ferro-electric crystals has been derived by designing a model Hamiltonian for anharmonicferro-electric crystal and then modified by adding a defect (impurity) term for $Pb_xSr_{1-x}TiO_3$. The mass and force constant changes are taken into account. The variation of soft mode frequency with temperature and impurity concentration x (ofPb) in pure $SrTiO_3$ crystal has been theoretically studied using Green's function technique.

**Theory**

**Hamiltonian and Green's Function**

The Hamiltonian which includes the anharmonicity upto fourth -order in the potential energy due to interaction of soft mode coordinates, resonant interaction and scattering terms are considered. The impurities introduced are characterized by different mass than the host atoms and with modified nearest neighbour harmonic force constants around their sites. The influence on the anharmonic coupling coefficients in the Hamiltonian, being small is neglected. The modified Hamiltonian of a mixed perovskite, in para-electric phase which includes defects (substitutional impurity) is used in present study and is exactly similar as used earlier[12] is given

$$H' = H + H_D \dots \quad (1)$$

where H is Hamiltonian for pure crystal and $H_D$ is the contribution by the defect in Hamiltonian which involves the effect of mass change and harmonic force constant change between the impurity and host lattice atoms due to substitutional defects.

Where

$$H = \sum_k \frac{\hbar\omega_k^a}{4}(A_k^{a+}A_k^a + B_k^{a+}B_k^a) + \sum_k' \frac{\hbar\omega_k^0}{4}(A_k^{0+}A_k^0 + B_k^{0+}B_k^0) -$$

$$\frac{\hbar\omega_0^0}{4}(A_0^{0+}A_0^0 + B_0^0 B_0^0) + \sum_k \hbar F(k)A_0^0 A_k^{0+}A_k^a + \sum_k \hbar\beta^a(k)A_0^{02}A_k^{0+}A_k^0 +$$

$$\sum_k \hbar\beta^0(k)A_0^{02}A_k^{a+}A_k^a + \sum_{k_1 k_2 k_3}\hbar\varphi(k_1 k_2 k_3)A_0^0 A_{K_1}^0 A_{k_1}^a A_{k_3}^a +$$

$$\sum_{k_1 k_2 k_3}\hbar\psi(k_1 k_2 k_3)A_0^0 A_{K_1}^0 A_{k_1}^0 A_{k_3}^0 + \hbar V A_0^{04} +$$

$$\hbar E$$

$$\{-\alpha A_0^0 +$$

$$\sum_k A(k)A_k^a A_0^{0+} + \sum_{k,\lambda}B^\lambda(k)A_0^0 A_k^{\lambda+}A_k^\lambda + \sum_{k_1 k_2 k_3}C(k_1, k_2, k_3)A_{K_1}^0 A_{k_2}^a A_{k_3}^a +$$

$$\sum_{k_1 k_2 k_3}D_1(k_1, k_2, k_3)A_{K_1}^0 A_{k_2}^0 A_{k_3}^0 - D_1(0,0,0)A_0^{03}\}$$

$$= H_1 + H_2 + H_0 + H_3 + \dots\dots H_{14}, \quad \dots\dots(2)$$

Where

$$F(k) = \frac{P(k)}{\sqrt{N}}\cdot\frac{1}{(\omega_k^0 \omega_k^a)^{\frac{1}{2}}}\dots\dots\dots\dots(2a)$$

$$\beta^a(k) = \frac{G^0(k)}{N}\cdot\frac{1}{\omega_k^0}\dots\dots\dots\dots(2b)$$

$$\beta^0(k) = \frac{G^a(k)}{N}\cdot\frac{1}{\omega_k^a}\dots\dots\dots\dots\dots\dots(2c)$$

$$\varphi(k_1, k_2, k_3) = \frac{1}{\sqrt{N}}Y(k_1, k_2, k_3)\frac{\hbar^{\frac{1}{2}}}{(\omega_{k_1}^0 \omega_{k_2}^a \omega_{k_3}^a)^{\frac{1}{2}}}\dots\dots\dots\dots\dots(2d)$$

$$\psi(k_1, k_2, k_3) = \frac{1}{\sqrt{N}}\mu(k_1, k_2, k_3)\frac{\hbar^{\frac{1}{2}}}{(\omega_{k_1}^0 \omega_{k_2}^0 \omega_{k_3}^0)^{\frac{1}{2}}}\dots\dots\dots\dots(2e)$$

$$A(k) = \frac{A'(k)}{(\omega_k^0 \omega_k^a)^{\frac{1}{2}}}\dots\dots\dots\dots\dots\dots(2f)$$

$$B^\lambda(k)= \frac{B'^\lambda(K)}{\sqrt{N}}\cdot\frac{1}{\omega_k^\lambda}\dots\dots\dots\dots\dots\dots\dots\dots(2g)$$

$$C(k_1, k_2, k_3) = C'(k_1, k_2, k_3)\frac{\hbar^{\frac{1}{2}}}{(\omega_{k_1}^0\ \omega_{k_2}^a\ \omega_{k_3}^a)^{\frac{1}{2}}}\dots\dots\dots\dots\dots\dots\dots\dots(2h)$$

$$D(k_1, k_2, k_3) = D'(k_1, k_2, k_3)\frac{\hbar^{\frac{1}{2}}}{(\omega_{k_1}^0\ \omega_{k_2}^0\ \omega_{k_3}^0)^{\frac{1}{2}}}\dots\dots\dots\dots\dots(2i)$$

$$V=\Psi(0, 0, 0)$$
$$\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (2j)$$

$$D_1' = D_1(0, 0, 0)$$
$$\dots\dots\dots\dots\dots\dots\dots\dots\dots (2K)$$

In the above equations $G^0(k)$ and $G^a(K)$ are the Fourier transforms of 3rd order anharmonic force constants, $Y(K_1, K_2, K_3)$ and $\mu(K_1, K_2, K_3)$ are the Fourier transformed 4th order anharmonic force constants. $(\alpha)$; $A(K)$, $B^\lambda(K)$ and $C'(K_1, K_2, K_3)$, $D'(K_1, K_2, K_3)$ represent the linear, second and third-order electric moment co-efficients respectively. The primed sum in $H_2$ is taken for $k \neq 0$.

$H_D$ is the contribution by the defect in Hamiltonian which involves the effect of mass change and harmonic force constant change between the impurity and host lattice atoms due to substitutional defects and is given by[13]

$$H_D = -\hbar C(0,0)\,B_0^0 B_0^0 + \hbar D(0,0)A_0^0 A_0^0 - \hbar B_0^0 X + \hbar A_0^0 Y + \hbar Z, \dots\dots\dots\dots\dots\dots\dots(3)$$

With

$$X = \sum_{k,\lambda} C(k^\lambda, 0)B_k^\lambda\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(3a)$$

$$Y = \sum_{k,\lambda} D(k^\lambda, 0)A_k^\lambda\dots\dots\dots\dots\dots\dots\dots\dots\dots(3b)$$

And

$$Z = \sum_{k_1,k_2,\lambda}[D(k_1^\lambda, k_2^\lambda)A_{k_1}^\lambda A_{k_2}^\lambda - C(k_1^\lambda, k_2^\lambda)B_{k_1}^\lambda B_{k_2}^\lambda]$$
$$+ \sum_{k_1,k_2}[D(k_1^a, k_2^0)A_{k_1}^a A_{k_2}^0 - C(k_1^a, k_2^0)B_{k_1}^a B_{k_2}^0]\dots\dots\dots\dots\dots\dots(3c)$$

Here $\lambda$= a ,0 are for acoustic and optic modes respectively. The defect parameters $C(k_1, k_2)$ and $D(k_1, k_2)$ depend upon the changes in the mass and force constants due to the substitutional defects respectively and are given by

$$C(k_1, k_2) = \frac{1}{2\mu}(M_0/2N)(\omega_{k_1}\omega_{k_2})^{\frac{1}{2}}e(k_1)e(k_2)$$

$$\times\{\sum_\ell^n f \exp[i(k_1 + k_2).R(\ell)] - \sum_\ell^n \exp[i(k_1 + k_2).R(\ell)]\}$$
$$\dots\dots\dots\dots\dots(3d)$$

and

$$D(k_1, k_2) = \frac{1}{4N}(\omega_{k_1}\omega_{k_2})^{-\frac{1}{2}}\times\sum_{\ell\alpha\ell\beta}[\Delta\phi_{\alpha\beta}(\ell\ell')/M_0]\times e(k_1)\,e(k_2)$$

$$\times \exp.[i\{k_1.R(\ell)+k_1.R(\ell')\}], \dots\dots\dots\dots\dots\dots(3e)$$

where e(k) is the polarization vector, R($\ell$) the equilibrium position vector of the $\ell$-th atom,

$C(k_1, K_2)$ vanishes when n is either zero or N. $\Delta\varphi$ denotes the force constant change, $\ell$ and $\ell'$ refer to the impurity and its nearest neighbours and $\mu = [M M'/(M'-M)]$. $M_0$ is the weighted harmonic mean of the masses of all atoms and is defined by the relation

$$\frac{1}{M_0} = \frac{f}{M'} + \frac{1-f}{M}\dots\dots(3f)$$

with $f=\frac{n}{N}$. Here N is the total number of atoms in the crystal whose (N-n) lattice sites are occupied by atoms of mass M while n sites are occupied by randomly distributed substitutional impurities each of mass M' .

In order to get the effect of defect on soft mode frequency, we transform the Hamiltonian H' as given by Naithani et. al[13]. The transformed Hamiltonian is obtained as

$H_T = H + H_D + \hbar\omega_0^0 g A_0^0$ ...........................................................(4)

Where $g = \frac{\alpha}{\omega_0^0}$ .

The retarded Green's function $G_0^0$ (t- t') for optic phonon is defined as

$G_0^0$ (t -t') =<<A(t); A(t')>>ω + iε (5)     or $G_0^0$ ( ω+ iε) = G'(ω)−iG"(ω)

(6) The real (ε ') and imaginary parts (tan δ ) of dielectric constant are related to Green's function as

ε'(ω) −1 =−8 π² Nμ² G'(ω)     (7)     and tan δ=G"( ω)/ G'(ω)

(8)

The equation of motion for Green's function is

$i\hbar\frac{d}{dt}$G(t, t') = $\hbar\frac{d}{dt}\theta\left(t-t'\right) <$ [A (t),B(t') ]>

+<<[A(t),H_T];B(t') >>(9) Using this equation of motion, modified Hamiltonian, Fourier transforming and shaping in Dyson's equation form, we get

$G_0^0$( ω+ iε) = $\frac{\omega_0^0}{\pi[\omega^2-\nu^2(\omega)+i\Gamma_0^0(\omega)]}$          (10)

Here     $\nu^2(\omega)=\nu_0^2(\omega)+\Delta(\nu_D^2(\omega))$          (10a) where

$\nu_0^2(\omega)=-(\omega_0^0)^2 + 4\omega_0^0\bar{Q}+\Delta_0(\omega)$          (10b)

and

$\Delta(\nu_D^2(\omega))$ =4$\omega_0^0$ D(0,0) + 4 $\omega_0^0\sum_{k,\lambda}$ D²(k,0)[$\tilde{\omega}_k^\lambda$ /ω² −( $\tilde{\omega}_k^\lambda$)² ] - 4(ω²/ ω₀⁰) $\sum_{k,\lambda}$ C² (k,0) [$\tilde{\omega}_k^\lambda$ /ω² −( $\tilde{\omega}_k^\lambda$)² ]+ 4 $\sum_{k,\lambda}$ C(k,0)D*(k,0)          × [$\tilde{\omega}_k^\lambda$ /ω² −( $\tilde{\omega}_k^\lambda$)² ] - 4 $\sum_{k,\lambda}$ C*(k,0) D(k,0) [$\tilde{\omega}_k^\lambda$ /ω² −( $\tilde{\omega}_k^\lambda$)² ] +96V² × ω₀⁰ ([1+3(N⁰₀)²]*3Ω/ ω²−(3Ω)²-[1-((N⁰₀)²)]*Ω/ ω²−(3Ω)²)          ... (10c)

The notations used here are in the same sense as used by Yadav et al[12] and Naithani et al[13].

Temperature dependence of ν²(ω) can be written as

ν² (ω)=− ( $\omega_0^0$)²+$\gamma_1$ T+γ₂T² +Δ ($\nu_D^2$ )                    ...(11)

where $\Delta_0(\omega)$ (shift in phonon frequency corresponds to pure crystal, $\Delta(\nu_D^2(\omega))$ is temperature independent part due to defect and γ₁ and γ₂ are temperature dependent parts in ν² (ω) and depend on anharmonic force- constant and electric dipole moment terms.

Thus from equation (11), we conclude

$\frac{\nu2(\omega)}{\gamma_1}$=--$\frac{(\omega_0^0)2}{\gamma_1}$+$\frac{\gamma_1}{\gamma_1}T$+$\frac{\Delta(\nu_D^2(\omega))}{\gamma_1}$ +$\frac{\gamma_2 T^2}{\gamma_1}$

$\frac{\nu2(\omega)}{\gamma_1}$=(T-T_c'+ξT²) ... (11a)

Where $T_c'$= - -$\frac{(\omega_0^0)2}{\gamma_1}$+$\frac{\Delta(\nu_D^2(\omega))}{\gamma_1}$ and ξ =$\frac{\gamma_2}{\gamma_1}$(non linearity constant).

Equation (11a) can be reduced now as

ν²(ω)= γ₁ (T-T_c'+ ξT²)                    ............(12)

or ν²(ω) =γ₁(T-Tc') and ξ = -1.49x10⁻³ cm⁻¹ k⁻² is negligible for ST[14].          ................. (13)

Here Tc'=T_c+ Δ(T_c) is the new Curie-temperature in presence of defect impurity.

Here, Δ(T_c)=- $\frac{\Delta(\nu_D^2(\omega))}{\gamma_1}$          ............. (13a)

Thus $T_c$ is one of the parameters which is very sensitive to impurity (x).The above results show that $T_c$ varies linearly with x.

Equation 13 shows that the change in Curie temperature depends on substitutional impurity.

$\Delta (v^2{}_D(\omega))$ (temperature independent part due to defect) and $\gamma_1$ (anharmonic coupling constant) and hence $\Delta T_c$ is a function of mass change due to defect and anharmonic constants.

- **Composition dependence of soft mode frequency**

Using relation $v = \gamma_1^{\frac{1}{2}}(T - T_c')^{\frac{1}{2}}$ as stated above (taking $\gamma_1^{\frac{1}{2}}$=1.548 x $10^{11}$ $H_z$ from G.Shirane et.al.[14] and $T_C$ from the reference[11,15]), softmode frequency $v$ for $Pb_xSr_{1-x}TiO_3$ crystals are calculated for various values of x at 800K. The values are given in table 1.The variation of soft mode frequency versus impurity parameter x in $Pb_xSr_{1-x}TiO_3$ have been shown in figure 1.

**Table 1:Soft mode frequency versus composition at T=800K.**

| X | $T_C$(K) | $v = \gamma_1^{\frac{1}{2}}(T - T_c')^{\frac{1}{2}}$ ($\times 10^{12}$ Hz) |
|---|---|---|
| 0 | 37 | 4.276 |
| 0.1 | 109.6 | 4.067 |
| 0.2 | 182.2 | 3.848 |
| 0.3 | 254.8 | 3.615 |
| 0.4 | 327 | 3.367 |
| 0.5 | 400 | 3.096 |
| 0.6 | 472.6 | 2.801 |
| 0.7 | 545.2 | 2.471 |
| 0.8 | 617.1 | 2.094 |
| 0.9 | 690.4 | 1.621 |
| 1.0 | 763 | 0.942 |



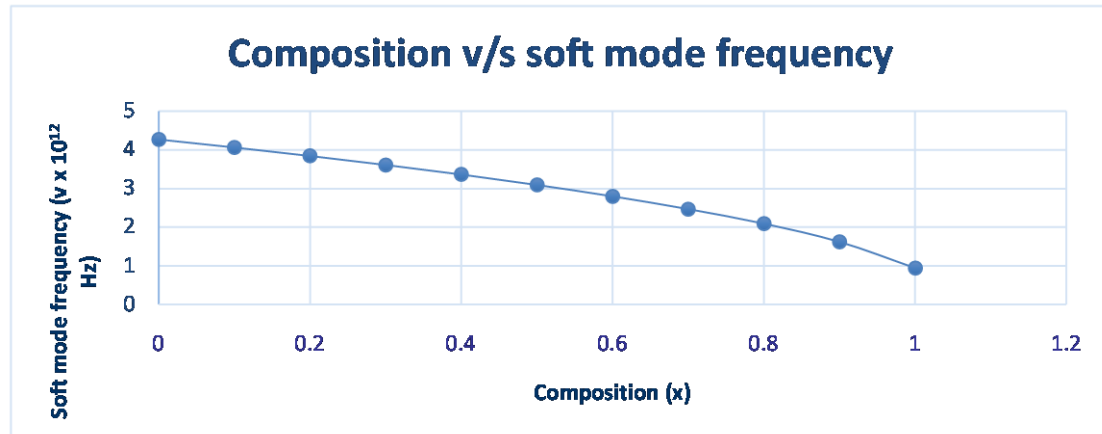**Fig. 1: Variation of soft mode frequency with composition x in $Pb_xSr_{1-x}TiO_3$**

- **Soft mode frequency as a function of temperature**

For different value of x, $v$ is calculated as a function of temperature using the relation $v = \gamma_1^{\frac{1}{2}}(T - T_c')^{\frac{1}{2}}$. The various calculated values are given in table 2(a) to 2(k) and are shown in figure 2.

**Table 2(a):** Soft mode v/s temperature of $SrTiO_3$, $T_C$ = 37K, x=0

| T(K) | 50 | 60 | 70 | 80 | 90 | 100 | 300 | 400 |
|---|---|---|---|---|---|---|---|---|
| $v \times 10^{11}$Hz | 5.58 | 7.42 | 8.89 | 10.15 | 11.27 | 12.29 | 25.10 | 29.49 |

**Table 2(b):Soft mode v/s temperature of $Pb_{0.1}Sr_{0.9}TiO_3$, $T_C$ = 109.6K, x=0.1**

| T(K) | 110 | 120 | 130 | 140 | 150 | 200 | 300 | 400 |
|---|---|---|---|---|---|---|---|---|
| $v \times 10^{11}$Hz | 0.98 | 4.99 | 6.99 | 8.54 | 9.84 | 14.72 | 21.36 | 26.38 |

**Table 2(c): Soft mode v/s temperature of $Pb_{0.2}Sr_{0.8}TiO_3$, $T_C$ = 182.2K, x=0.2**

| T(K) | 190 | 200 | 210 | 220 | 230 | 300 | 400 | 500 |
|---|---|---|---|---|---|---|---|---|
| $\nu \times 10^{11} Hz$ | 4.32 | 6.53 | 8.16 | 9.52 | 10.70 | 16.80 | 22.85 | 27.60 |

**Table 2(d): Soft mode v/s temperature of $Pb_{0.3}Sr_{0.7}TiO_3$, $T_C$ = 254.8K, x=0.3**

| T(K) | 260 | 270 | 280 | 290 | 300 | 400 | 500 | 600 |
|---|---|---|---|---|---|---|---|---|
| $\nu \times 10^{11} Hz$ | 3.53 | 6.04 | 7.77 | 9.18 | 10.41 | 18.65 | 24.24 | 28.76 |

**Table 2(e): Soft mode v/s temperature of $Pb_{0.4}Sr_{0.6}TiO_3$, $T_C$ = 327K, x=0.4**

| T(K) | 330 | 340 | 350 | 360 | 370 | 400 | 500 | 600 |
|---|---|---|---|---|---|---|---|---|
| $\nu \times 10^{11} Hz$ | 2.68 | 5.58 | 7.42 | 8.89 | 10.15 | 13.23 | 20.36 | 25.58 |

**Table 2(f): Soft mode v/s temperature of $Pb_{0.5}Sr_{0.5}TiO_3$, $T_C$ =400K, x=0.5**

| T(K) | 410 | 420 | 430 | 440 | 450 | 500 | 600 | 700 |
|---|---|---|---|---|---|---|---|---|
| $\nu \times 10^{11} Hz$ | 4.90 | 6.92 | 8.48 | 9.79 | 10.95 | 15.48 | 21.89 | 26.81 |

**Table 2(g): Soft mode v/s temperature of $Pb_{0.6}Sr_{0.4}TiO_3$, $T_C$ =472.6K, x=0.6**

| T(K) | 480 | 490 | 500 | 510 | 520 | 600 | 700 | 800 |
|---|---|---|---|---|---|---|---|---|
| $\nu \times 10^{11} Hz$ | 4.21 | 6.46 | 8.10 | 9.47 | 10.66 | 17.47 | 23.34 | 28.01 |

**Table 2(h): Soft mode v/s temperature of $Pb_{0.7}Sr_{0.3}TiO_3$, $T_C$ = 545.2K, x=0.7**

| T(K) | 550 | 560 | 570 | 580 | 590 | 600 | 700 | 800 |
|---|---|---|---|---|---|---|---|---|
| $\nu \times 10^{11} Hz$ | 3.39 | 5.96 | 7.71 | 9.13 | 10.36 | 11.46 | 19.26 | 24.71 |

**Table 2(i): Soft mode v/s temperature of $Pb_{0.8}Sr_{0.2}TiO_3$, $T_C$ = 617.1K, x=0.8**

| T(K) | 620 | 630 | 640 | 650 | 660 | 700 | 750 | 800 |
|---|---|---|---|---|---|---|---|---|
| $\nu \times 10^{11} Hz$ | 2.64 | 5.56 | 7.41 | 8.88 | 10.14 | 14.09 | 17.85 | 20.94 |

**Table 2(j): Soft mode v/s temperature of $Pb_{0.9}Sr_{0.1}TiO_3$, $T_C$ = 690.4K, x=0.9**

| T(K) | 700 | 710 | 720 | 730 | 740 | 750 | 800 | 850 |
|---|---|---|---|---|---|---|---|---|
| $\nu \times 10^{11} Hz$ | 4.80 | 6.85 | 8.42 | 9.74 | 10.90 | 11.95 | 16.21 | 19.56 |

**Table 2(k): Soft mode v/s temperature of $PbTiO_3$, $T_C$ = 763K, x=1.0**

| T(K) | 770 | 780 | 790 | 800 | 850 | 900 | 950 | 1000 |
|---|---|---|---|---|---|---|---|---|
| $\nu \times 10^{11} Hz$ | 4.10 | 6.38 | 8.04 | 9.42 | 14.44 | 18.12 | 21.17 | 23.83 |
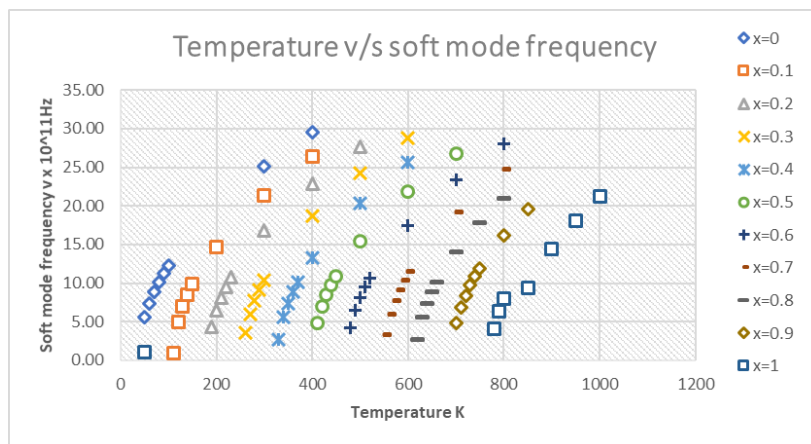


**Fig. 2: Variation of soft mode frequency with Temperature in $Pb_xSr_{1-x}TiO_3$**

**Discussion**

        In the present study, we have calculated the soft mode frequency and its temperature and composition dependence in a doped displacive anharmonic crystal using Green's function technique. Both the mass and force constant change due to substitutional impurity have been taken into account in the crystal Hamiltonian augmented with the higher order anharmonic terms.  The softmode which has an imaginary frequency in harmonic approximation is renormalized and the lowest order anharmonic interaction that can stabilize the mode, is the fourth order. The soft mode frequency is impurity dependent (indirectly $T_C$) and depends upon the relative magnitudes and sign of the defect parameters C and D. The present study deals with the variation of the soft mode with an increasing component of Pb and temperature both in an anharmonic displaciveferro-electrics.It is clear that soft mode frequency is stabilized in presence of impurity and higher-order anharmonicity. If anharmonicity and impurity effects are neglected, soft mode frequency is imaginary due to cancellation effects of competing forces. From section 2, it is clear that soft mode frequency increases with increasing impurity contents and increasing temperature in the said range of the temperature. In the high temperature para-electric phase, the soft mode frequency (equation 12) can be rationalized   as

$$\nu^2 = A_1 + A_2 T + A_3 T^2,$$

        where $A_1$, $A_2$ and $A_3$are temperature independent co-efficients and in the vicinity of Curie temperature, softmode is approximated (neglecting $A_3$ being very-very small) as

$$\nu = K\left(T - T_c'\right)^{\frac{1}{2}}; \quad T_c' = -\frac{A_1}{A_2}; \quad K = A_2^{\frac{1}{2}}.$$

        From the text, it is also clear that impurity changes Curie-temperature ($T_C$).

        The quantitative dependence of the soft mode frequency discussed here agrees with the previous experimental and theoretical values[16]. The treatment adopted here leads one to see the comparative variation of the softmode frequency with variation of defects and temperature in presence of anharmonicity. From figure 1, it is clear that softmode frequency varies with the variation of Pb content concentration on the pure Strontium titanate crystal. The soft mode frequency has the highest value for a pure Strontium titanate crystal and continuously decreases when impurity of lead increases. The soft mode frequency shows a sharp decrease at x=0.6, which is due to large value of defect parameter and has the lowest values for x= 1.0 in the calculated one. Figure 2, indicates that softmode variations with temperature are of similar trends for all compositions.

**References**

1.      Chen. Ang, Yu z.; Scott, J. ;Loidle, A. ; Gou, R. and Bhall, A. S.-J. Phys. Chem. Solids, 61, 191 (2000).
2.      Xu, Y.- "Ferro-electric materials and their application", North Holland, New York, (1991)
3.      Liu, S.; Liu, M.; Zeng, Y. and Huong, Y.-Mater. Sci. Eng. B, 20, 149 (2002)
4.      Bomlai, P.; Sirikulrat, N. and Tunakasiri, T.-Mater. Lett., 59, 118 (2005).
5.      Peng-ZuGe , Xiao-Dong Jian , Xiong-Wei Lin , Xin-Gui Tang , *, Zhi Zhu ,Qiu-Xiang Liu , Yan-Ping Jiang , Tian-Fu Zhang , Sheng-Guo Lu ,- Journal of Materiomics  5 (2019) 118-126
6.      M. Jain, P. Bhattacharya, Yu.I. Yuzyuk, R.S. Katiyar, and A.S. Bhalla,-Mat. Res. Soc. Symp. Proc. Vol. 784 (2004).
7.      M. Tarnaoui, N. Zaim, M. Kerouad, A. Zaim,-Computational Materials Science 183 (2020) 109816
8.      Wodecka, B. D.; Lisinska, A. C. and Orkisz, T.-Mater. Sci., Polland, 25,791 (2007).
9.      Vijendra A. Chaudhari and Govind K. Bichile,-Hindawi Publishing Corporation Smart Materials Research Volume 2013
10.     F. M. Pontes, E. J. H. Lee, E. R. Leite, E. Longo, -Journal of Materials Science**35** (2000) 4783 – 4787
11.     Ying Chen, Genshui Wang, Junyu Zhu, XiaodongTang,-Applied Physics Letters · February 2011
12.     Yadav, M. S.; Singh, Parminder; Kumar, S. and Deorani, S. C. –J. of Pure and Applied Physics, 22, 2 (2010)
13.     Naithani, U. C. and Baluni, G. N. –Indian Journal of Pure and Applied Physics, 24, 446 (1986).
14.     Shirane, G. and Yamada, Y.-J. Phys. Soc., Jpn. 26, 396 (1969).
15.     Sunil Kumar ,M. S. Yadav,Neetu Sharma and S. C.Deorani,-"Curie-Temperature Variation in Pervoskite $SrTiO_3$ Containing Pb as Substitutional Impurities (In Press).

❖◆❖