

Substitutional effect on Dielectric constant and Soft Mode Frequency in $\text{Ca}_x\text{Sr}_{1-x}\text{TiO}_3$ ferro-electric mixed crystals

Sunil Kumar¹, M S Yadav², Neetu Sharma³ and S C Deorani⁴
Department of Physics, R. R. College, RRBM University, Alwar 301001 (India)

Abstract

Soft mode and Dielectric constants in $\text{Ca}_x\text{Sr}_{1-x}\text{TiO}_3$ (CST) single crystals have been theoretical investigated in para-electric phase for various composition and temperature. In our calculations, double time temperature-dependent Green's function technique along with a modified Hamiltonian for the crystals is used which includes anharmonicity up to the fourth order due to the interactions of the soft mode. Fourier transformation and Dyson's equation treatment is used in arriving the result. Temperature and composition dependent dielectric constants and soft mode of $\text{Ca}_x\text{Sr}_{1-x}\text{TiO}_3$ (CST) have been estimated. The soft mode frequency decreases and Dielectric constant increases with increase in the composition x at constant temperature and the value of soft mode frequency increases and Dielectric constant decreases with increasing temperature at constant value of x .

Keywords:- *Soft mode frequency, Dielectric constant, Single crystal, Perovskites, anharmonicity, Retarded Green's function, Hamiltonian, Fourier transform, Dyson's equation.*

Date of Submission: 26-08-2022

Date of Acceptance: 10-09-2022

I. Introduction

In 1839, in the Ural Mountains of Russia, new mineral CaTiO_3 was discovered by Gustav Rose and named perovskite after Russian mineralogist L.A. Perovski. Later this name was used for a designation of large class of compounds with the same (ABO_3) crystalline structure. ABO_3 - type compounds are interesting for materials science because of their ferroelectric and piezoelectric properties. Perovskite-type ferroelectrics are important materials for many technological applications, this is why they have been intensively investigated for a long time [1–4]. Development of new lead-free materials with good piezoelectric properties is a challenging problem. Chemical modification is the common approach for tuning dielectric and electromechanical properties of ferroelectrics.

We know a lot of classical ferroelectrics belong to this ABO_3 family. SrTiO_3 , KTaO_3 and CaTiO_3 have a polar soft mode, but do not exhibit a ferroelectric phase transition. This is explained by the stabilization of their Para-electric phase by quantum fluctuations [5] (similar to quantum liquids ^4He and ^3He , where a crystalline state does not form under normal conditions). SrTiO_3 and CaTiO_3 “founding father of perovskites” are quantum para-electric or incipient ferroelectrics (6). They may be, in a certain sense, classified as marginal systems which are at the limit of their para-electric phase stability. An arbitrarily Small external influence can upset the stability and induce a ferroelectric phase. It appears (7-8) that impurities with concentration around 10^{-3} can also destroy the stability of paraelectric phase and induced a ferroelectric phase. The Substitution of Sr^{2+} by Ca^{2+} is known [7,9] to stabilize the ferroelectric (FE) phase against quantum fluctuations.

In the incipient ferroelectrics the dielectric constant increases as the temperature decreases and saturates at low temperatures. This behaviour as well as the large value of the dielectric constant is a “finger print” of the incipient ferro-electricity [10]. In perovskites, doping generally involves the replacement of either A- or B-type cations.

Solid solutions of Calcium strontium titanate (CST) 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. CST 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.

Perovskites are known to exhibit a lot of useful properties [11]. They possess high dielectric coefficients 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 [12]. Tunable thermistor properties in semiconducting ferro-electrics are used in positive temperature co-efficient resistors (PTCR) [13].

It is easy to control the dielectric properties of the CST by adjusting [Ca/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 [14]. In the present paper, $\text{Ca}_x\text{Sr}_{1-x}\text{TiO}_3$ with Ca contents x varies from 0 to 1.0. (Ca, Sr) TiO_3 solid solutions belong to ferro-electric materials of the form (A'A'') BO_3 type.

Calcium Strontium titanate $\text{Ca}_x\text{Sr}_{1-x}\text{TiO}_3$ (CST) which is known to adopt ABO_3 type solution, is a continuous solid solution of CaTiO_3 (CTO) and SrTiO_3 (STO) over the whole concentration range. The properties of $\text{Ca}_x\text{Sr}_{1-x}\text{TiO}_3$ are known to depend on the composition x [15-17]. CaTiO_3 is usually added to SrTiO_3 as a shifter in order to move the Curie-point T_C to higher temperatures. It is well established that T_C of SrTiO_3 increases linearly with the amount of Ca in place of Sr. For bulk $\text{Ca}_x\text{Sr}_{1-x}\text{TiO}_3$, the Curie-point varies from 37^0K to 743.2^0K [18] for x from $x=0.0$ to $x=1.0$.

The dielectric constant in perovskite structures has been investigated [19], at microwave frequencies over a wide range upto 1000^0K on a series of perovskites ($\text{CaTiO}_3, \text{SrTiO}_3, \text{BaTiO}_3, \text{PbTiO}_3$ and KTaO_3) and their mixtures.

This work is aimed at the determination of an influence of the ferro-electric components CT and ST on physical properties like, Soft mode frequency, Dielectric constant and Curie Temperature of CST as well as a character.

In the present paper, Expression for the soft mode frequency and the Dielectric constant in $\text{Ca}_x\text{Sr}_{1-x}\text{TiO}_3$ ferro-electric crystals have been derived by designing a model Hamiltonian for anharmonic ferro-electric crystal and then modified by adding a defect (impurity) term for $\text{Ca}_x\text{Sr}_{1-x}\text{TiO}_3$. Double time thermal Green's function method is used to obtain observable quantities with the help of model Hamiltonian considering anharmonic effects up to fourth-order with substitutional defects. The mass and force constant changes are taken into account. For simplicity the ions are assumed non polarizable. Such a formulation is particularly interesting as the real part of dielectric constant ϵ' will lead to an expression for the change in the Curie-temperature resulting from the presence of impurities. We have taken into account the contribution of the temperature and defects (impurities) towards dielectric constant. The effect of defects (impurities) on the real part of dielectric constant of a displacive ferroelectric materials in para-electric phase is discussed. The variation of soft mode frequency and the Dielectric constant with temperature and impurity concentration x (Ca) in pure SrTiO_3 crystal has been theoretically studied and thus theoretical results obtained are compared with previous results available elsewhere.

II. 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 earlier²⁰ is given

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

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

$$H = \sum_k \frac{\hbar\omega_k^a}{4} (A_k^{a+} A_k^a + B_k^{a+} B_k^a) + \sum_k' \frac{\hbar\omega_k^0}{4} (A_k^{0+} A_k^0 + B_k^{0+} B_k^0) - \frac{\hbar\omega_0^0}{4} (A_0^{0+} A_0^0 + B_0^{0+} B_0^0) + \sum_k \hbar F(k) A_0^0 A_k^{0+} A_k^a + \sum_k \hbar \beta^a(k) A_0^{02} A_k^{0+} A_k^0 + \sum_k \hbar \beta^0(k) A_0^{02} A_k^{a+} A_k^a + \sum_{k_1 k_2 k_3} \hbar \varphi(k_1 k_2 k_3) A_0^0 A_{k_1}^0 A_{k_2}^a A_{k_3}^a + \sum_{k_1 k_2 k_3} \hbar \psi(k_1 k_2 k_3) A_0^0 A_{k_1}^0 A_{k_2}^0 A_{k_3}^0 + \hbar V A_0^{04} + \hbar E \{ -\alpha A_0^0 + \sum_k A(k) A_k^a A_k^{0+} + \sum_{k,\lambda} B^\lambda(k) A_0^0 A_k^\lambda + A_k^\lambda A_k^\lambda + \dots \dots \dots \} + H_1 + H_2 + H_3 + \dots \dots \dots H_{14}, \dots \dots \dots (2)$$

Where

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

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

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

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

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

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

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

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

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

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

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

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. (α) ; $A(K)$, $B^\lambda(K)$ and $C'(K_1, K_2, K_3)$, $D'(K_1, K_2, K_3)$ represent the linear, second and third-order electric moment coefficients 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 by²¹

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

With

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

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

And

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

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

$$C(k_1, k_2) = \frac{1}{2\mu} (M_0/2N) (\omega_{k_1} \omega_{k_2})^{\frac{1}{2}} e(k_1) e(k_2) \times \{ \sum_{\ell}^n f \exp. [i(k_1 + k_2) \cdot R(\ell)] - \sum_{\ell}^n \exp. [i(k_1 + k_2) \cdot R(\ell)] \} \dots\dots\dots(3d)$$

and

$$D(k_1, k_2) = \frac{1}{4N} (\omega_{k_1} \omega_{k_2})^{-\frac{1}{2}} \times \sum_{\ell\alpha\ell\beta} [\Delta\phi_{\alpha\beta}(\ell\ell')/M_0] \times e(k_1) e(k_2) \times \exp. [i\{k_1 \cdot R(\ell) + k_1 \cdot R(\ell')\}], \dots\dots\dots(3e)$$

where $e(k)$ is the polarization vector, $R(\ell)$ the equilibrium position vector of the ℓ -th atom, $C(k_1, K_2)$ vanishes when n is either zero or N . $\Delta\phi$ denotes the force constant change, ℓ and ℓ' 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

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

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. Al²¹. The transformed Hamiltonian is obtained as

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

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

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

$$G_0^0(t-t') = \langle\langle A(t); A(t') \rangle\rangle \omega + i\epsilon \quad \dots\dots\dots (5)$$

$$\text{or } G_0^0(\omega + i\epsilon) = G'(\omega) - iG''(\omega) \quad \dots\dots\dots (6)$$

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

$$\epsilon'(\omega) - 1 = -8\pi^2 N\mu^2 G'(\omega) \quad \dots\dots\dots (7)$$

and

$$\tan \delta = G''(\omega) / G'(\omega) \quad \dots\dots\dots (8)$$

The equation of motion for Green's function is

$$i\hbar \frac{d}{dt} G(t, t') = \hbar \frac{d}{dt} \theta(t - t') \langle [A(t), B(t')] \rangle$$

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

$$G_0^0(\omega + i\epsilon) = \frac{\omega_0^0}{\pi[\omega^2 - v^2(\omega) + i\Gamma_0^0(\omega)]} \quad (10)$$

$$\text{Here } v^2(\omega) = v_0^2(\omega) + \Delta(v_D^2(\omega)) \quad \dots\dots\dots (10a)$$

where

$$v_0^2(\omega) = -(\omega_0^0)^2 + 4\omega_0^0 \bar{Q} + \Delta_0(\omega) \quad \dots\dots\dots (10b)$$

and

$$\Delta(v_D^2(\omega)) = 4\omega_0^0 D(0,0) + 4\omega_0^0 \sum_{k,\lambda} D^2(k_\lambda, 0) [\tilde{\omega}_k^\lambda / \omega^2 - (\tilde{\omega}_k^\lambda)^2] - 4(\omega^2 / \omega_0^0) \sum_{k,\lambda} C^2(k_\lambda, 0) [\tilde{\omega}_k^\lambda / \omega^2 - (\tilde{\omega}_k^\lambda)^2] + 4\omega \sum_{k,\lambda} C(k_\lambda, 0) D^*(k_\lambda, 0) \times [\tilde{\omega}_k^\lambda / \omega^2 - (\tilde{\omega}_k^\lambda)^2] - 4\omega \sum_{k,\lambda} C^*(k_\lambda, 0) D(k_\lambda, 0) [\tilde{\omega}_k^\lambda / \omega^2 - (\tilde{\omega}_k^\lambda)^2] + 96V^2 \times \omega_0^0 [(1+3(N_0^0)^2) * 3\Omega / \omega^2 - (3\Omega)^2 - [1 - ((N_0^0)^2)] * \Omega / \omega^2 - (3\Omega)^2] \quad \dots\dots\dots (10c)$$

The notations used here are in the same sense as used by Yadav et al²⁰ and Naithani et al²¹.

Temperature dependence of $v^2(\omega)$ can be written as

$$v^2(\omega) = -(\omega_0^0)^2 + \gamma_1 T + \gamma_2 T^2 + \Delta(v_D^2) \quad \dots\dots\dots (11)$$

where $\Delta_0(\omega)$ (shift in phonon frequency corresponds to pure crystal, $\Delta(v_D^2(\omega))$ is temperature independent part due to defect and γ_1 and γ_2 are temperature dependent parts in $v^2(\omega)$ and depend on anharmonic force-constant and electric dipole moment terms.

Thus from equation (11), we conclude

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

$$\frac{v^2(\omega)}{\gamma_1} = (T - T_c) + \xi T^2 \quad \dots\dots\dots (11a)$$

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

Equation (11a) can be reduced now as

$$v^2(\omega) = \gamma_1 (T - T_c) + \xi T^2 \quad \dots\dots\dots (12)$$

$$\text{or } v^2(\omega) = \gamma_1 (T - T_c) \text{ and } \xi = -2.7 \times 10^{-5} \text{ K}^{-1} \text{ is negligible for } ST^{22,25,26} \quad \dots\dots\dots (13)$$

Here $T_c = T_c + \Delta(T_c)$ is the new Curie-temperature in presence of defect impurity.

$$\text{Here, } \Delta(T_c) = -\frac{\Delta(v_D^2(\omega))}{\gamma_1} \quad \dots\dots\dots (13a)$$

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. $\Delta(v_D^2(\omega))$ (temperature independent part due to defect) and γ_1 (anharmonic coupling constant) and hence ΔT_c is a function of mass change due to defect and anharmonic constants.

In the, high temperature para-electric phase, the soft mode frequency (equation (12)) can be rationalized as [U C Deorani et al²³]

$$v^2(\omega) = A + BT + CT^2 \quad \dots\dots\dots (13b)$$

Here A, B and C are temperature independent co-efficients but dependent on anharmonic force constants and $T_c = (-A/B)$ is para electric phase transition temperature, $\xi = (-C/B)$ is non linearity constant and is very small of the order of $-2.7 \times 10^{-5} \text{ K}^{-1}$ for ST. The value of A is evaluated using $A = -B * T_c$ and value of C is calculated using $C = \xi * B$ and is constant for all concentration and also temperature independent and $B = 2.676 * 10^{22} \text{ Hz}^2 \text{ K}^{-1}$ [20, 22-27] and in the vicinity of Curie temperature, soft mode frequency is approximated.

$$\text{Hence, for CST, the result is approximated as } x = a[T_c(x) - 37], \quad \dots\dots\dots (14)$$

Where a is constant and it is determined by interpolating the values of $(T_c)CT$ and $(T_c)ST$ from the references [18, 23] and comes out to be as $a = 1.416 \times 10^{-3} \text{ K}^{-1}$.

The real part of the complex dielectric constant [with the help of Eq. (7) and (10)] is given by:

$$\epsilon'(\omega) - 1 = -8\pi N\mu^2 (\omega^2 - v^2) \epsilon_s / [(\omega^2 - v^2)^2 + 4\omega^2 \Gamma_0^2]$$

$$\text{or } \epsilon'(\omega) = 8\pi N\mu^2 (v^2 - \omega^2) \epsilon_s / [(v^2 - \omega^2)^2 + 4\omega^2 \Gamma_0^2], \quad \epsilon' \gg 1$$

$$\dots\dots\dots (15)$$

Neglecting second term (being small) in comparison to the first term in the denominator, as $\omega\tau \leq 1$, $\nu \gg \omega$, (the soft mode frequency is very large as compared to the microwave frequencies as $\omega/\nu = 10^{-3}$)

So the real part of the frequency dependent dielectric constant in the range $\omega\tau \leq 1$ can be written as

$$\epsilon'(\omega) = 8\pi N\mu^2\epsilon_s/\nu^2 \dots\dots\dots (16)$$

or $\epsilon'(\omega) = \lambda/\nu^2 \dots\dots\dots (17)$

here, ν is the soft mode frequency which depend upon anharmonicity, temperature, defects and electric field. ϵ_s is the static dielectric constant of the material, μ is the dipole moment per unit cell, N the total number of unit cells in the specimen, and $\lambda = 8\pi N\mu^2\epsilon_s$ is a constant independent of temperature and equal to $2.05 \times 10^{27} \text{Hz}^2$ from reference²² and other symbols are usual.

III. Calculations

3.1 Calculation of Curie-temperature

Using equation (14) as $x = a[T_c(x) - 37]$, where a is constant and it is determined by interpolating the values of $(T_c)_{CT}$ and $(T_c)_{ST}$ from the references [18,23] and comes out to be as $a = 1.416 \times 10^{-3} \text{K}^{-1}$. Curie-temperature is calculated and summarized in Table 1 and drawn in Fig.(1).

Table 1: Defect concentration with Curie-Temperature

(x)	0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1
(T _c)(K)	37.0	107.6	178.2	248.9	319.5	390.1	460.7	531.4	602.0	672.6	743.2

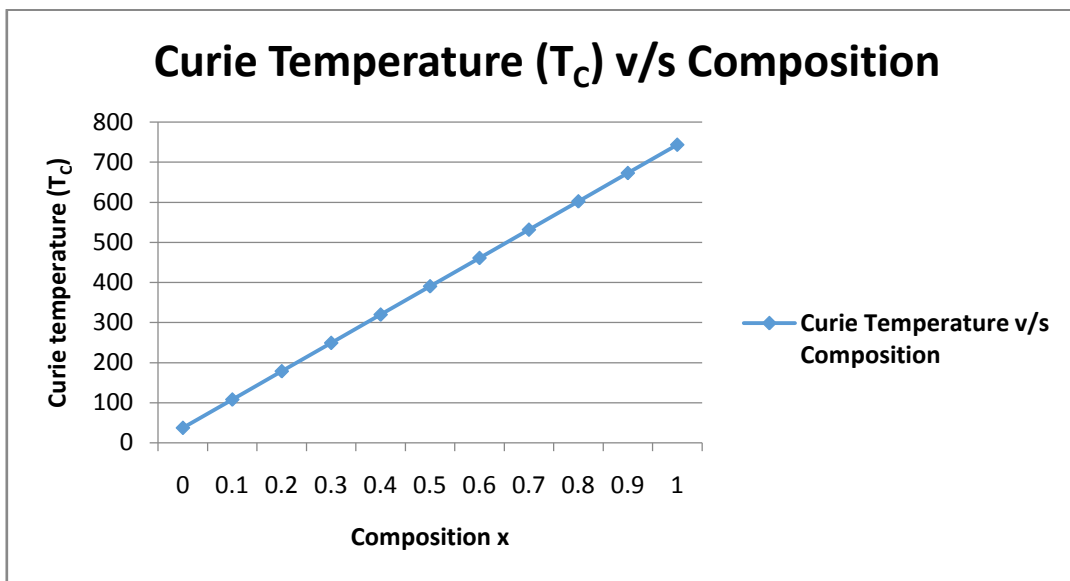


Fig.1. Variation of Curie Temperature with composition of $\text{Ca}_x\text{Sr}_{1-x}\text{TiO}_3$

3(ii) Composition dependence of soft mode frequency and Dielectric constant: -

Using relation $\nu(\omega) = (A + B\omega + C\omega^2)^{1/2}$ and $\epsilon'(\omega) = \lambda/\nu^2$ as stated above (taking $B = 2.676 \times 10^{22}$, $A = -B \times T_c$, $C = -\xi \times B$ and $\xi = 2.705 \times 10^{-5}$, T_c calculated above in table 1 and $\lambda = 2.05 \times 10^{27} \text{Hz}^2$ [20,22-27]), soft mode frequency (ν) and Dielectric constant (ϵ) for $\text{Ca}_x\text{Sr}_{1-x}\text{TiO}_3$ crystals are calculated for various values of x at 760K. The values are given in table 2. The variation of soft mode frequency versus impurity parameter x in $\text{Ca}_x\text{Sr}_{1-x}\text{TiO}_3$ have been plotted in figure 2 and the variation of Dielectric constant versus impurity parameter x in $\text{Ca}_x\text{Sr}_{1-x}\text{TiO}_3$ have been plotted in figure 3.

Table 2
Soft mode frequency and Dielectric constant versus composition at T=760K.

X	$T_c(\text{K})$	$\nu=(A+BT+CT^2)^{1/2} \times 10^{12} \text{ Hz}$	$\epsilon=\lambda/\nu^2$
0	37.0	4.35	108.30
0.1	107.6	4.13	120.31
0.2	178.2	3.89	135.32
0.3	248.9	3.64	154.60
0.4	319.5	3.37	180.30
0.5	390.1	3.08	216.24
0.6	460.7	2.76	270.08
0.7	531.4	2.39	359.62
0.8	602.0	1.95	537.97
0.9	672.6	1.39	1067.25
1.0	743.2	0.18	66145.00

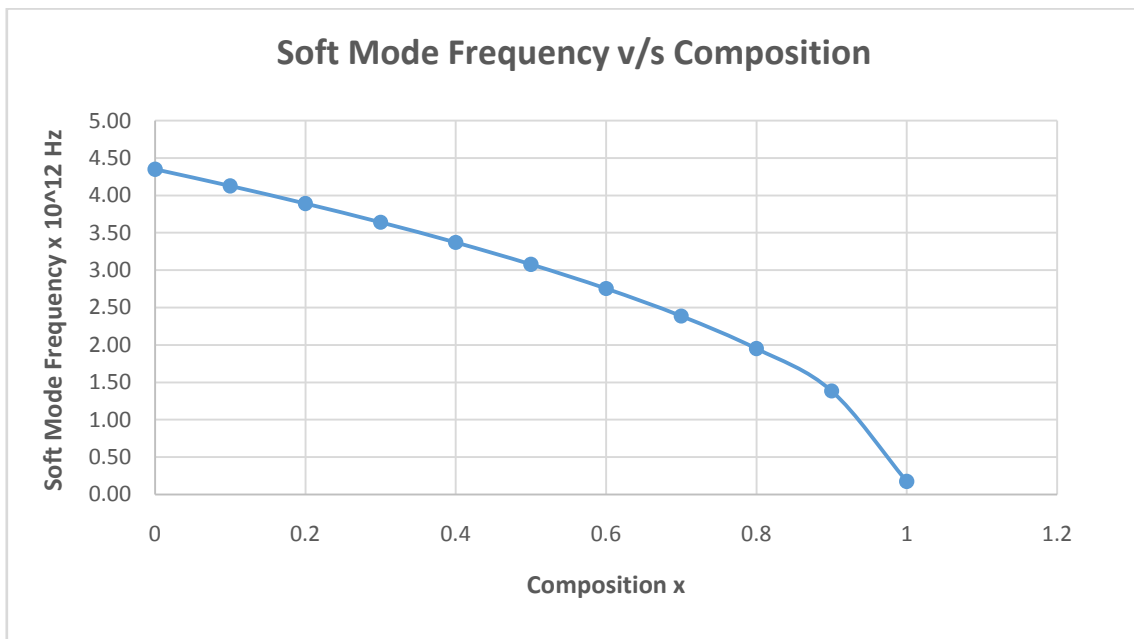


Fig.2. Variation of soft mode frequency with composition x in $\text{Ca}_x\text{Sr}_{1-x}\text{TiO}_3$

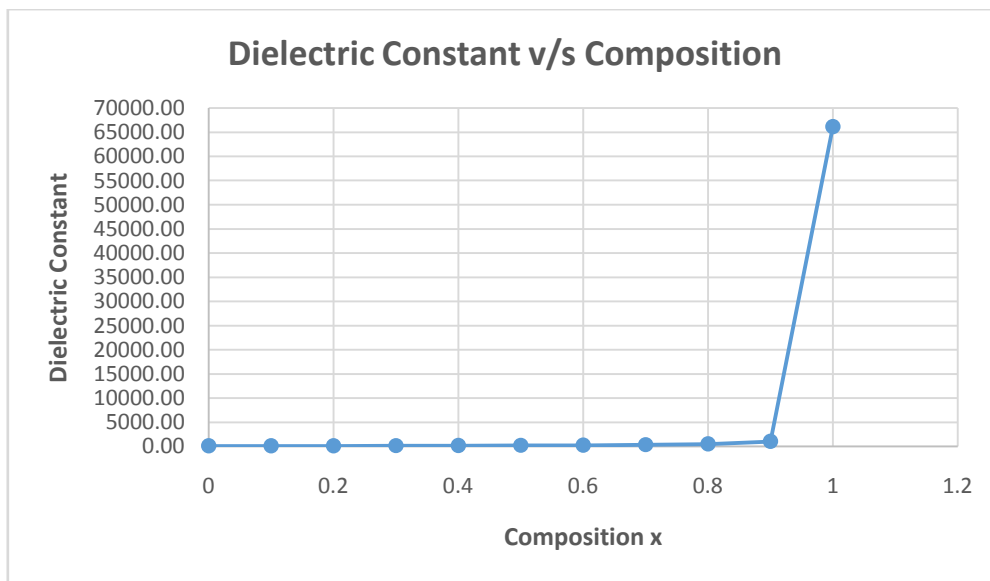


Fig.3. Variation of Dielectric constant with composition x in $\text{Ca}_x\text{Sr}_{1-x}\text{TiO}_3$

3(ii) Soft mode frequency and Dielectric constant as a function of temperature: -

For different value of x, ν and ϵ is calculated as a function of temperature using the relation $\nu = (A+BT+CT^2)^{1/2}$ and $\epsilon'(\omega) = \lambda/\nu^2$ respectively. The various calculated values are given in table 3(a) to 3(k) and are shown in figure 4 and 5.

Table 3(a)

Soft mode and Dielectric constant v/s temperature of $SrTiO_3$, $T_C = 37K$, $x=0$

T(K)	50	60	70	80	90	100	300	400
$\nu \times 10^{11}$	5.88	7.83	9.38	10.71	11.88	12.96	26.41	30.98
ϵ	5923	3345	2331	1789	1451	1221	294	214

Table 3(b)

Soft mode and Dielectric constant v/s temperature of $Ca_{0.1}Sr_{0.9}TiO_3$, $T_C = 107.6K$, $x=0.1$

T(K)	110	120	130	140	150	200	300	400
$\nu \times 10^{11}$	2.34	5.66	7.66	9.23	10.57	15.63	22.55	27.76
ϵ	37382	6391	3495	2406	1834	839	403	266

Table 3(c)

Soft mode and Dielectric constant v/s temperature of $Ca_{0.2}Sr_{0.8}TiO_3$, $T_C = 178.2K$, $x=0.2$

T(K)	190	200	210	220	230	300	400	500
$\nu \times 10^{11}$	5.37	7.44	9.04	10.40	11.60	17.87	24.12	29.03
ϵ	7107	3705	2507	1894	1522	642	352	243

Table 3(d)

Soft mode and Dielectric constant v/s temperature of $Ca_{0.3}Sr_{0.7}TiO_3$, $T_C = 248.9K$, $x=0.3$

T(K)	260	270	280	290	300	400	500	600
$\nu \times 10^{11}$	4.99	7.16	8.81	10.20	11.42	19.82	25.57	30.23
ϵ	8231	3998	2640	1971	1573	522	313	224

Table 3(e)

Soft mode and Dielectric constant v/s temperature of $Ca_{0.4}Sr_{0.6}TiO_3$, $T_C = 319.5K$, $x=0.4$

T(K)	330	340	350	360	370	400	500	600
$\nu \times 10^{11}$	4.50	6.82	8.53	9.95	11.19	14.28	21.56	26.92
ϵ	10121	4406	2816	2070	1636	1006	441	283

Table 3(f)

Soft mode and Dielectric constant v/s temperature of $Ca_{0.5}Sr_{0.5}TiO_3$, $T_C = 390.1K$, $x=0.5$

T(K)	410	420	430	440	450	500	600	700
$\nu \times 10^{11}$	6.41	8.20	9.66	10.93	12.07	16.61	23.14	28.17
ϵ	4993	3050	2196	1716	1408	743	383	258

Table 3(g)

Soft mode and Dielectric constant v/s temperature of $Ca_{0.6}Sr_{0.4}TiO_3$, $T_C = 460.7K$, $x=0.6$

T(K)	480	490	500	510	520	600	700	800
$\nu \times 10^{11}$	5.91	7.81	9.33	10.63	11.79	18.62	24.59	29.35
ϵ	5876	3364	2357	1814	1474	591	339	238

Table 3(h)

Soft mode and Dielectric constant v/s temperature of $Ca_{0.7}Sr_{0.3}TiO_3$, $T_C = 531.4K$, $x=0.7$

T(K)	550	560	570	580	590	600	700	800
$\nu \times 10^{11}$	5.29	7.35	8.94	10.29	11.48	12.56	20.39	25.93

ϵ	7319	3799	2565	1937	1556	1300	493	305
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Table 3(i)

Soft mode and Dielectric constant v/s temperature of $Ca_{0.8}Sr_{0.2}TiO_3$, $T_C = 602.0K$, $x=0.8$

T(K)	620	630	640	650	660	700	750	800
V X10 ¹¹	4.52	6.80	8.49	9.90	11.12	15.06	18.85	21.99
ϵ	10039	4430	2843	2093	1657	904	577	424

Table 3(j)

Soft mode and Dielectric constant v/s temperature of $Ca_{0.9}Sr_{0.1}TiO_3$, $T_C = 672.6K$, $x=0.9$

T(K)	700	710	720	730	740	750	800	850
V X10 ¹¹	6.15	7.98	9.45	10.73	11.86	12.90	17.16	20.55
ϵ	5414	3223	2295	1782	1457	1232	696	485

Table 3(k)

Soft mode and Dielectric constant v/s temperature of $CaTiO_3$, $T_C = 743.2K$, $x=1.0$

T(K)	770	780	790	800	850	900	950	1000
V X10 ¹¹	5.36	7.38	8.95	10.28	15.28	19.00	22.09	24.79
ϵ	7129	3769	2562	1941	878	568	420	333

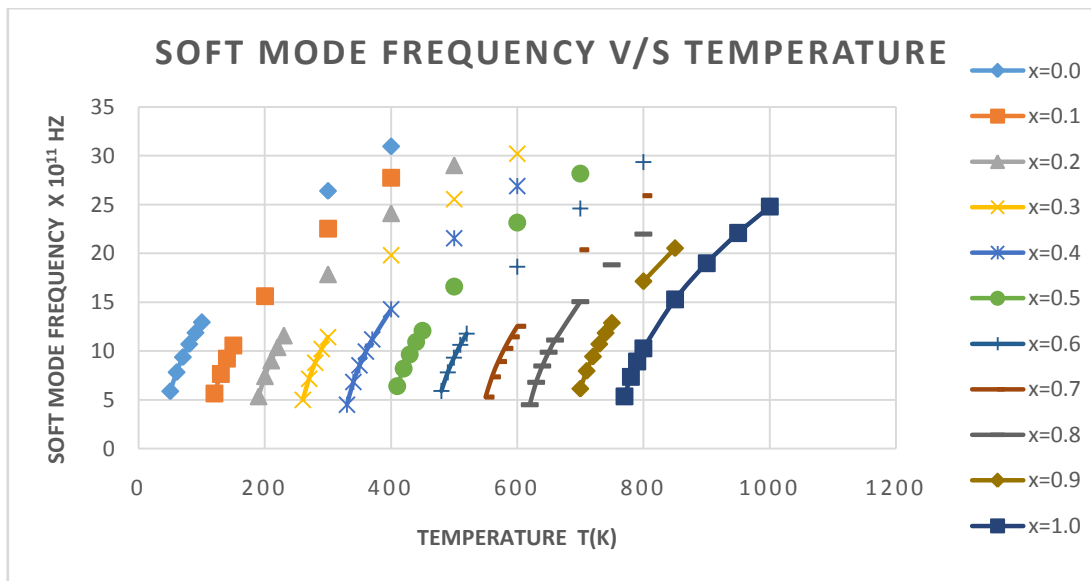


Fig.4. Variation of soft mode frequency with Temperature in $Ca_xSr_{1-x}TiO_3$

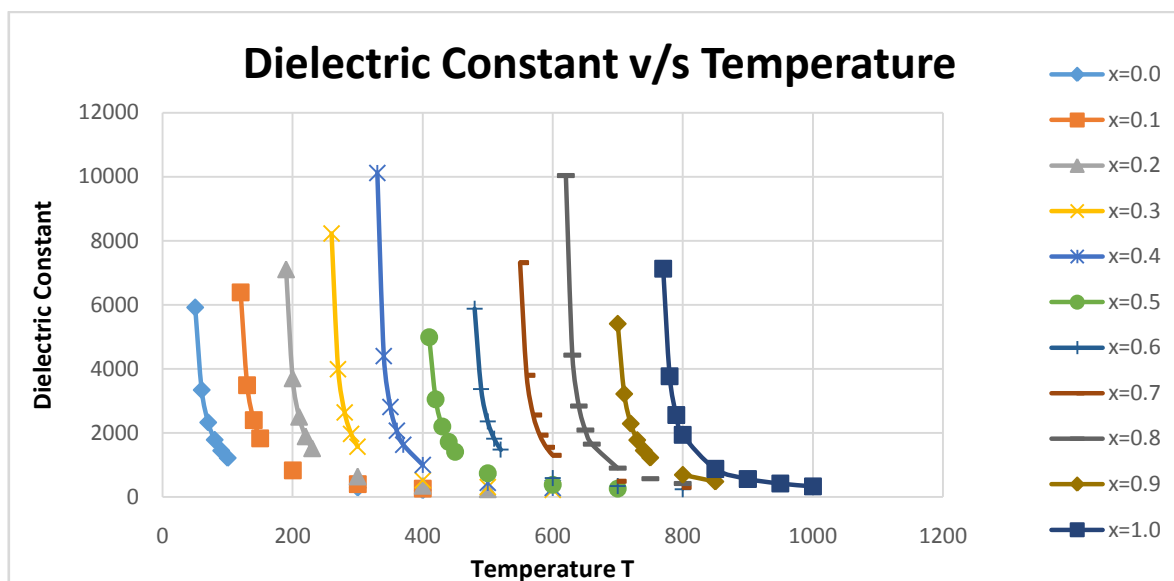


Fig.5. Variation of Dielectric constant with Temperature in $\text{Ca}_x\text{Sr}_{1-x}\text{TiO}_3$

IV. Discussion

It is easy to control the dielectric properties of CST by adjusting [Ca/Sr] ratio. The present study deals with the variation of the Curie Temperature, soft mode frequency and Dielectric constant with 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. It is clear from table 1 that the Curie temperature (T_c) varies with variation of Ca concentration in the pure strontium titanate crystal and it continuously increases when impurity of Ca increases. The Curie-point varies nearly from 37K to 743.2K for $x=0.0$ to $x=1.0$. The T_c in ST increases approximately 7.06K for each 1% increase Ca concentration.

The soft mode 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 variation of the soft mode with an increasing component of Ca and temperature both in an anharmonic displacive ferro-electrics. The 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.

The soft mode frequency has the highest value for a pure Strontium titanate crystal and continuously decreases when impurity (Ca) increases and temperature decreases in the said range of the temperature.

The treatment adopted here leads one to see the comparison of dielectric constant with the variation of composition x , and temperature T of $\text{Ca}_x\text{Sr}_{1-x}\text{TiO}_3$. It is clear from equations (11) that the substitutional impurity dependence of dielectric constant is a clear consequence of defect (substitutional impurity) dependence of Soft mode frequency. The dielectric constant of pure SrTiO_3 has the lowest value as compared to dielectric constant for mixed crystals. Figure 3 shows the increment in dielectric constant with the increase of impurity concentration of Ca is due to the fact that the Curie temperature (T_c) increases (or soft mode decreases) with the increase of impurity of Ca on SrTiO_3 . It is also evident that in case of pure SrTiO_3 , dielectric constant increases sharply as soft mode (ν) decreases and has highest value as $T \rightarrow T_c$ and dielectric constant decreases as temperature goes away from T_c in para-electric phase. Thus anomalous behaviour of dielectric constant near T_c can be explained by equation $\epsilon'' = \lambda/\nu^2$ as soft mode (ν) tends to zero as $T \rightarrow T_c$. Fig.4 and Fig.5 shows the variation of soft mode and dielectric constant with temperature of $\text{Ca}_x\text{Sr}_{1-x}\text{TiO}_3$ for different impurity concentration x in Para-electric phase respectively. The variation in soft mode and dielectric constant for all values of x are of similar trend and we calculated the dielectric constant of pure SrTiO_3 is 294 at room temperature.

The quantitative dependence of the soft mode frequency and dielectric constants are in a good qualitative and close agreement with the previous experimental and theoretical values [16,22,28-31].

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Sunil Kumar, et. al. “Substitutional effect on Dielectric constant and Soft Mode Frequency in $\text{Ca}_x\text{Sr}_{1-x}\text{TiO}_3$ ferro-electric mixed crystals.” *IOSR Journal of Applied Physics (IOSR-JAP)*, 14(5), 2022, pp. 24-33.