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Curie-temperature variation and microwave absorption in perovskites containing substitutional impurities

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ABSTRACT

Using thermal-double time Green's function method, Fourier transform and Dyson's equation, theoretical expressions are obtained for Curie-temperature and microwave absorption coefficient for a ferroelectric cubic crystal containing defect (substitutional impurities). Chang in Curie-temperature occures due to impurity content in the crystal. Microwave loss deviates from Curie-Wiess law at high temperature due to $\hat{I}T^2$ term being significant.

Key words: Curie-temperature, Green's function, Hamiltonion, Microwave loss, Dyson's equation.

INTRODUCTION

The investigation of dielectric properties provides an approach to the understanding of intra and inter molecular interactions, modes of motion and confirmational change in the macromolecules. It is well known that there are interesting temperature-dependent properties of ferroelectrics which results from the temperature-dependence of the low lying transverse optic mode of vibration i.e. soft mode.Lattice defect with substitutional impurities have a major influence on the static dielectric properties. The Curie-temperature and microwave losses are also affected by substitutional impurities. $SrTiO_3$ (ST) is paraelectric above 37 K. The change in Curie-temperature can not be accounted for simply by considering change in lattice parameters or polarisability of the defect (impurity) ions.The temperature and defect dependence of dielectric loss in perovskites has been the subject of much interest due to their wide use in optical communication, memory display unit, temperature control devices and ceramic industry.

Microwave losses in displacive ferroelectrics have been reported experimentally and theoretically by many workers[1-4]. The defect dependence of the Curie-temperature and microwave losses in ferroelectric crystals is discussed by Rita Bahadur and P.K.Sharma[4] considering the change in mass and harmonic force constants between the impurity atom and the host lattice atoms. In our previous paper[5] we have discussed soft mode variation of $Ba_xSr_{1-x}TiO_3$ with impurity concentration. $Ba_xSr_{1-x}TiO_3$(BST) solid solutions are basic materials for microwave devices. Curecheriu et al[6] studied temperature-dependent tunability data and modelling in the paraelectric $Ba_{0.7}Sr_{0.3}TiO_3$ solid solutions. Structural parameters, crystalline size and bulk densities were determined in BST by Ioachim *et al.,*[7] Kajtoch *et al.,*[8] studied experimentally the structural and dielectric properties of polycrystalline $Ba_{0.9}Sr_{0.1}TiO_3$. BST($Ba_{0.6}Sr_{0.4}TiO_3$) ceramic were characterized in terms of the crystalline structure , chemical composition and dielectric properties within the temperature region of ferroelectric-paraelectric

phase transition by Wodecka-Dus *et al*[9] . Kukreti et al[10] studied theoretically the electric field dependent dielectric behavior of BST.

In the present study ,we will discuss the impurity concentration dependence of Curie-temperature and microwave losses in an anharmonic displacive ferroelectric crystal in paraelectric phase. Double-time thermal Green's function method is used to obtain observable quantities with the help of model Hamiltonian considering anharmonic effects upto fourth - order with substitutional defects. For simplicity , the ions are assumed non-polarizable. Such a formulation is particularly interesting as the real part of dielectric constant º' 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 soft- mode frequency towards Curie-temperature and dielectric losses. Impurity-impurity interaction is neglected.

Hamiltonion and Green's function

The modified Hamiltonion for displacive ferroelectrics which includes defects, third and fourth-order anharmonicity and higher order electric moment terms can be written as[11,12]

$$H' = H+H_D . \qquad ...(1)$$

Naithani *et al.,*[12] have given

$$H = \sum_k \frac{\hbar\omega_0^0}{4}\left(A_k^{+}A_k^{+}+B_k^{+}B_k^{+}\right)+\sum_k{}' \frac{\hbar\omega_0^0}{4}\left(A_k^{+}A_k^{0}+B_k^{+}B_k^{0}\right)-\frac{\hbar\omega_0^0}{4}\left(A_k^{0}A_k^{0}+B_k^{0}B_k^{0}\right)$$

$$+\sum_k \hbar F(k)A_k^{0}A_{-k}^{+}A_k^{+}+\sum_k \hbar\beta^{+}(k)A_k^{+}A_{-k}^{+}A_k^{+}+\sum_k \hbar\beta^{0}(k)A_k^{+}A_{-k}^{+}A_k^{0}$$

$$+\sum_{k_1+k_2+k_3} \hbar\varphi(k_1,k_2,k_3)A_{k_1}^{0}A_{k_2}^{0}A_{k_3}^{+}A_{k_4}^{+}+\sum_{k_1+k_2+k_3} \hbar\psi(k_1,k_2,k_3)A_{k_1}^{0}A_{k_2}^{0}A_{k_3}^{0}A_{k_4}^{+}$$

$$+\hbar VA_0^{+}+\hbar E\{-\alpha A_0^{+}+\sum_k A(k)A_k^{0}A_{-k}^{+}+\sum_{k_1k_2} B^{+}(k)A_{k_1}^{0}A_{k_2}^{+}A_{-k}^{+}+\sum_{k_1k_2k_3} C(k_1,k_2,k_3)A_{k_1}^{0}A_{k_2}^{0}A_{k_3}^{0}$$

$$+\sum_{k_1k_2k_3} D_1(k_1,k_2,k_3)A_{k_1}^{0}A_{k_2}^{0}A_{k_3}^{0}-D_1(0,0,0)A_0^{03}\}=H_1+H_2$$

$$+H_0+H_3+.....H_{14}\,, \qquad ...(2)$$

And

$$H_D = -hC(0,0)B_0^{0}B_0^{0}+hD(0,0)A_0^{0}A_0^{0}-hB_0^{0}X+hA_0^{0}Y+hZ \qquad ...(3)$$

The Transformed Hamiltonian is obtained as

$$H_T = H+H_D+\hbar\omega_0^{0}gA_0^{0} \qquad ...(4)$$

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

$$G_0^0(t-t') = << A(t);A(t') >> \omega+i\varepsilon \qquad ...(5)$$

or

$$G_0^0(\omega+i\varepsilon) = G'(\omega)-iG''(\omega) \qquad ...(6)$$

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

$$\varepsilon'(\omega)-1 = -8\pi^2 N\mu^2 G'(\omega) \qquad ...(7)$$

and

$$\tan\delta = G''(\omega)/G'(\omega) \qquad ...(8)$$

$\Delta_0(\omega)$

The equation of motion for Green's function is given as

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

$$+<<\left[A(t),H_T\right];B(t')>> \qquad ...(9)$$

Using this equation of motion, modified Hamiltonian, Fourier transforming and shaping in Dyson's equation form, we get

$$G_0^0(\omega+i\varepsilon) = \frac{\omega_0^0}{\pi\left[\omega^2-\nu^2(\omega)+i\Gamma_0^0(\omega)\right]} \qquad ...(10)$$

Here

$$\nu^2(\omega) = \nu_0^2(\omega)+\Delta\left(\nu_D^2(\omega)\right), \qquad ...(10a)$$

where

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

Here ω^0_0 and are width and shift in optical phonon frequency and $\Delta(\nu_D^2(\omega))$ is as given

in our paper[11]. Temperature dependence of $\nu^2(\omega)$ can be written as

$$\nu^2(\omega) = -(\omega_0^0)^2 + \gamma_1 T + \gamma_2 T^2 + \Delta(\nu_D^2) \quad ...(11)$$

$\Delta_0(\nu_D^2(\omega))$ is temperature independent part due to defect and γ_1 and γ_2 are temperature-dependent parts in $\nu^2(\omega)$ and depend on anharmonic force-constant and electric dipole moment terms.

Thus from equation (11), we conclude

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

$$\frac{\nu^2(\omega)}{\gamma_1} = (T - T_c' + \xi T^2), \quad ...(11a)$$

where $T_c' = -\frac{(\omega_0^0)^2}{\gamma_1} + \frac{\Delta(\nu_D^2(\omega))}{\gamma_1}$ and $\xi = \frac{\gamma_2}{\gamma_1}$

(non-linearity constant).

Equation (11a) can be reduced now as

$$\nu^2(\omega) = \gamma_1(T - T_c' + \xi T^2) \quad ...(12)$$

or

$$\nu^2 \alpha (T - T_c' + \xi T^2) \quad ...(12a)$$

Here

$$T_c' = T_c + \Delta(T_c) \quad ....(12b)$$

T_c' is the new Curie-temperature in presence of defect.

Here

$$\Delta(T_c) = -\frac{\Delta(\nu_D^2(\omega))}{\gamma_1} \quad ...(12c)$$

Table 1.

x	$\Delta(T_c)$	Calculated T_c(K)	Experimentally observed T_c(K) ref 1,2
0	0	37	37
0.2	67.90	104.90	105
0.4	148.15	185.15	185
0.6	246.85	283.85	283
0.8	287.19	324.60	324
1.0	358.14	395.14	395

Curie-temperature

Equation (12c) shows that the change in Curie-temperature depends on impurity i.e. on $\Delta(\nu_D^2)$ and γ_1 (anharmonic coupling constant). It is evident that the change in Curie- constant, $\Delta(T_c)$ is a function of mass change due to defect and anharmonic constants.We have so far not considered the influence of defects on the dipole moment coefficient and have assumed that the introduction of defects changes only the nearest neighbour force constants as explained by Naithani *et al.,*[13]. Since we are dealing with the displacive ferroelectrics in paraelectric phase, one can see that the change in T_c cannot be explained without anharmonicity .

Using equations (12b), (12c) and values of $\Delta(\nu_D^2)$ and from our previous paper[5], we have calculated Curie-temperatures for various compositions of $Ba_xSr_{1-x}TiO_3$ crystal which are given in table1. The results are close to experimental results[1,2,6-9].

Microwave absorption

Using Green's function given by equations (8) and (10), the expression for loss tangent can be expressed as

$$\tan\delta(\omega) = -\omega_0^0(\omega) / \omega^2 - \nu^2(\omega) = \omega_0^0(\omega)/\nu^2(\omega)$$

[as for microwave photons ($\omega << \nu(\omega)$ i.e. $\omega/\nu = 10^{-3}$)] ...(13)

$\Gamma(\omega)/2\nu(\omega)$ corresponds to the half width associated with the damping of Cochran soft mode. The damping of microwaves therefore arises from the creation of a virtual Cochran polarization mode excited by the transverse electromagnetic radiation and the subsequent decay into real phonon by scattering from lattice imperfections and third and fourth-order anharmonicity.

Naithani *et al.,*[14], has given

$$\Gamma_0^0(\omega) = a + bT + cT^2 \qquad ...(14)$$

Using equation (12), we get

$$\gamma_1 (T - T_c^{'} + \xi T^2) \tan\delta = a + bT + CT^2$$

or

$$(T - T_c^{'} + \xi T^2) \tan\delta = \alpha + \beta T + \gamma T^2 \qquad ...(15)$$

$$(T\text{-}T_c) \tan\delta = \alpha + \beta T + \alpha T^2 \qquad ...(16)$$

where $\alpha = \frac{a}{\gamma_1}, \beta = \frac{b}{\gamma_1}, \gamma = \frac{c}{\gamma_1}$ and ξ is very small

(Panwar[15])

Equation (16) gives the microwave tangent loss in defect ferroelectrics. The parameter α depends on the impurity contents (Ba) in the anhamonic crystal and is zero for a pure single crystal. and γ are intrinsic properties of the lattice.

We[11] have recently discussed dielectric losses in $Ba_xSr_{1-x}TiO_3$ above phase transition.

DISCUSSION

Our results show that the Curie-temperature changes due to the presence of defects in anharmonic ferroelectric crystal. Anharmonicity is also necessary in these crystals to observe the Curie-temperature change. Change in T_c caused by an impurity depends on the changes in the harmonic force constants between the impurity and host lattice atoms and mass change due to impurity and can be negative or positive[4].

Microwave loss tangent depends on the impurity contents in the lattice . It follows from equation (16) that microwave loss tangent for these crystals strictly depends on anharmonicity and defect. In these crystals ($Ba_xSr_{1-x}TiO_3$), the deviations in microwave loss from the Curie-Weiss law at high temperature are characterized by parameter î. The introduction of defects in the crystal changes Curie-temperature T_c to $T_c^{'}$, the Curie-law remains valid in paraelectric phase.

≈ 10^{-16} forSrTiO$_3$

It is easy to control the dielectric properties of BST ($Ba_xSr_{1-x}TiO_3$) by adjusting [Ba]/[Sr] ratio. The Curie-temperature of BT shifts below room temperature with increasing Sr contents thus making BST a paraelectric with low microwave loss at room temperature[11]. For bulk $Ba_xSr_{1-x}TiO_3$ ceramic, the Curie-point varies nearly from -236^0 C to 122^0 C for x=0 to x=1.0 .We have discussed here the impurity dependence of $\Delta(T_c)$ and tanä of an anharmonic ferroelectric crystal in a qualitative way.

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