



CHANGES IN FERROELECTRIC PROPERTIES OF MASD ALUM ALONG WITH TEMPERATURE BY USING PLCM MODEL

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Abstract: With addition of third-and fourth-order phonon anharmonic interactions, and extra spin-lattice interaction term into pseudospin-lattice coupled mode (PLCM) model, MASD alum has been studied. Employing double time temperature dependent Green's function technique expressions for shift and width of response function, normal mode frequency, dielectric constant and loss stangent have been derived for MASD alum. Numerical calculation has been done. Theoretical results have been compared with experimental results of Pepinsky et al. [16]. A good agreement has been found.

Keywords: Ferroelectrics, green's function, dielectric constant, loss tangent, anharmonicity.

Introduction

Ferroelectric substances have been found useful in electronics and technology. Memory devices, infrared detectors, optical modulators etc. are some examples. Ronald et al. [1] worked on organic non-volatile memory devices based on ferroelectricity and suggested the use of low-cost solution-based processing techniques to make integrated memory circuits that consist of crossbar arrays of ferroelectrics capacitors e.g., by ink-jet printing metal contacts, conductive polymer interface layers etc. Some alums show ferroelectric behaviour.

Methyl ammonium aluminium alum (MASD), $(\text{CH}_3\text{NH}_3)\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ becomes ferroelectric below 177K temperature. In ferroelectric state CH_3NH_3 groups are arranged in dumbbell shape. They are in ordered state. In paraelectric phase they are oriented in disordered fashion. Venkatesh et al. [2] have done spectroscopic studies of ferroelectric MASD alum. They observed that sulphate or selenate ions do not undergo any distortion in low temperature phase. Griffith and Powell [3] have measured dielectric constant at

different temperatures. Rao et al. [4] have measured dielectric constant of MASD alum. They observed phase transition near 177K. Derby [5] has done growth studies of different alums. Weber [6] has made dielectric measurements on alums. Boujelbene and Mihiri [7] have done Raman spectroscopic studies on MASD alums. Sachdeva et al. [8] have done growth studies on alums. Gu and Li [9] have done spectral studies of alums. Gu and Hao [10] have studied electrolytic coloration below 0°C and spectral properties of ammonium alum crystals using a pointed anode. Zhang et al. [11] have carried out experimental study on hysteresis curves on alums. Basara et al. [12] have done electric conductivity studies on alums. Singh et al. [13] have done synthesis and characterization studies on alums. Sajan et al. [14] have studied physical properties of polymer mixed alums. Ghanew et al. [15] have studied experimentally effects of doping of different polymers on alums. Pepinsky et al. [16] have measured dielectric constant of MASD alums at different temperatures. They observed that



dielectric constant reaches maximum at 177K anomalously (abruptly) showing phase transition at this temperature. Shaxin et al. [17] have studied application of alum in inorganic synthesis. Petrusevski [18] has carried out experimental study of vibrational spectra of selenate and related alums. Bow et al. [19] have done alums adjuvant action studies. Mansingh et al. [20] have done work on low frequency electrical behaviour of ferroelectric MASD alum. Cha and Strauss [21] together worked on local structure and tunnelling kinetics of ammonium aluminium alum by infrared hole-burning. Hao and Tsu [22] have worked on dimorphism in methylammonium aluminium alum studied by X-ray diffraction and electron paramagnetic resonance. O' Reilly and Tsang [23] have worked on magnetic resonance studies of ferroelectric Methylammonium alum. Chaudhury et al. [24] gave phenomenological explanation of the anomalous dielectric behaviour of alums with pseudo-spin-lattice coupled-mode model.

Theoretical studies to understand phase transition and dielectric behaviour of MASD alums were initiated by Choudhuri et al. [24]. They have considered pseudospin-lattice coupled mode model along with fourth-order phonon anharmonic interaction term. They have not considered third-order phonon anharmonic interaction term. They have decoupled correlations at an early stage. In the present work, we have considered pseudo-spin lattice coupled mode model along with third-and fourth-order phonon anharmonic interactions terms. With the help of modified model and double-time Green's function method, expressions for shift, width, ferroelectric mode frequency, dielectric constant and loss tangent have been derived. By fitting model values in expressions temperature dependences of ferroelectric mode frequency, dielectric constant and loss tangent have been calculated, for MASD alum. Theoretical results have been compared with experimental results of Pepinsky et al. [16].

Model Hamiltonian

For ferroelectric MASD crystal, the pseudo-spin lattice coupled mode model (earlier used by Chaudhury et al. [23] by adding third-and fourth order phonon anharmonic interactions and other terms. The pseudo-spin lattice coupled mode model is expressed as:

$$H_1 = -2\Omega \sum_i S_i^x - \frac{1}{2} \sum_{ij} J_{ij} S_i^z S_j^z + \frac{1}{4} \sum_{ik} \omega_k (A_k^+ A_k + B_k^+ B_k) - \sum_{ik} V_{ik} S_i^z A_k, \quad (1)$$

we shall add:

$$H_2 = \sum_{ijk} V^{(3)}(k_1, k_2, k_3) A_{k_1} A_{k_2} A_{k_3} + \sum_{k_1 k_2 k_3 k_4} V^{(4)}(k_1, k_2, k_3, k_4) A_{k_1} A_{k_2} A_{k_3} A_{k_4} - \sum_{ik} V_{ik} S_i^x A_k, \quad (2)$$

where, Ω is proton tunnelling frequency between double well potential O-H...O bonds, S_i^x is x-component of the spin variables, J_{ij} is exchange interaction constant, S_i^z is z-component of pseudospin variable S, V_{ik} is spin- lattice interaction constant, A_k and B_k are position and momenta co-ordinates. $V^3(k_1, k_2, k_3)$ and $V^4(k_1, k_2, k_3, k_4)$ are the third and fourth order phonon anharmonic interactions terms. The third term in Eq.(2) describes an indirect coupling between the tunnelling motion of one proton and other proton. This term describes the modulation of distance between the two equilibrium sites in the O-H...O bonds. This modulates Ω by non polar optic phonons. We shall consider the total Hamiltonian:

$$H = H_1 + H_2, \quad (3)$$

for our study of MASD crystal.

Green's function, Width and Shift



Following Zubarev [25], we consider the Green's function:

$$G_{ij}(t-t') = \langle\langle S_i^z(t); S_j^z(t') \rangle\rangle = -i\theta(t-t') \langle [S_i^z(t), S_j^z(t')] \rangle, \tag{4}$$

where θ is step function, $\theta=0$ for $t < t'$ and $\theta=1$ for $t > t'$. Differentiation of Green's function (4) with respect to time t and t' two times using model Hamiltonian (3), Fourier transforming and putting into Dyson's equation form:

$$G_{ij}(\omega) = G_{ij}^0(\omega) + G_{ij}^0(\omega) \tilde{P}(\omega) G_{ij}^0(\omega), \tag{5}$$

we obtain,

$$G_{ij}(\omega) = \frac{\Omega \langle S_i^x \rangle \delta_{ij}}{\pi[\omega^2 - \tilde{\Omega}^2 - \tilde{P}(\omega)]}, \tag{6}$$

where,

$$G_{ij}^0(\omega) = \frac{\Omega \langle S_i^x \rangle}{\pi(\omega^2 - 4\Omega^2)} \tag{7}$$

$$\tilde{\Omega}^2 = (J_{ij} \langle S_i^z \rangle)^2 + 4\Omega^2 - 2\Omega J_{ij} \langle S^x \rangle, \tag{8}$$

and,

$$\tilde{P}(\omega) = \frac{\pi}{\Omega \langle S_i^x \rangle} \langle\langle F_i(t); F_j(t') \rangle\rangle, \tag{9}$$

where,

$$F_i(t) = -\Omega \sum_i \sum_{ij} J_{ij} S_i^x S_j^z - \Omega \sum_i \sum_{ij} J_{ij} S_i^z S_i^x - 2\Omega \sum_i \sum_{ik} V_{ik} A_k S_i^x + 4\Omega \sum_i \sum_{ik} V_{ik} A_k S_i^z - \frac{1}{2} \sum_{ik} \sum_{ij} V_{ik} A_k J_{ij} S_i^x S_j^z - \frac{1}{2} \sum_{ik} \sum_{ij} V_{ik} A_k J_{ij} S_i^z S_i^x - \sum_{ik} V_{ik}^2 A_k^2 S_i^x + \sum_{ik} V_{ik}^2 A_k^2 S_i^z. \tag{10}$$

Solving Eq. (8) we obtain:

$$\tilde{\Omega}^2 = a^2 + b^2 - bc, \text{ where:} \tag{11}$$

$$a = J \langle S_i^z \rangle$$

$$b = 2\Omega$$

$$c = J \langle S_i^x \rangle. \tag{12}$$

$\tilde{P}(\omega)$ contains higher order Green's functions like $\langle\langle AB; CD \rangle\rangle$, $\langle\langle ABC; DEF \rangle\rangle$. These are decoupled using symmetric decoupling scheme. Due to it product of operators single out. The decoupling is done as follows:

$$\langle\langle AB; CD \rangle\rangle = \langle AC \rangle \langle\langle B; D \rangle\rangle + \langle AD \rangle \langle\langle B; C \rangle\rangle + \langle BC \rangle \langle\langle A; D \rangle\rangle + \langle BD \rangle \langle\langle A; C \rangle\rangle$$

We obtain simple Green's functions like $\langle\langle A; B \rangle\rangle$, $\langle\langle C; D \rangle\rangle$ etc. These are solved and substituted. We therefore obtain value of $\tilde{P}(\omega)$. Resolution of $\tilde{P}(\omega)$ into real and imaginary parts is done by following scheme:

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



it gives shift $\Delta(\omega)$ and width $\Gamma(\omega)$ functions. We obtain:

$$\Delta(\omega) = \frac{a^4}{(\omega^2 - \tilde{\Omega}^2)^2} + \frac{b^2 c^2}{(\omega^2 - \tilde{\Omega}^2)^2} + \frac{V_{ik}^2 N_k a^2}{(\omega^2 - \tilde{\Omega}^2)^2} + \frac{2bV_{ik} \langle S_i^x \rangle \omega_k (\omega^2 - \tilde{\omega}_k^2) \delta_{k,k'}}{[(\omega^2 - \tilde{\omega}_k^2)^2 + 4\omega_k^2 \Gamma_k^2(\omega)]} + \frac{4b^2 V_{ik}^2 N_k}{(\omega^2 - \tilde{\Omega}^2)^2} + \frac{8aV_{ik}^2 \langle S_i^z \rangle \omega_k (\omega^2 - \tilde{\omega}_k^2) \delta_{k,k'}}{[(\omega^2 - \tilde{\omega}_k^2)^2 + 4\omega_k^2 \Gamma_k^2(\omega)]}$$

$$+ \frac{c^2 V_{ik}^2 N_k}{(\omega^2 - \tilde{\Omega}^2)^2} + \frac{V_{ik}^2 N_k a^4}{b^2 (\omega^2 - \tilde{\Omega}^2)^2} + \frac{2V_{ik}^4 N_k \langle S_i^x \rangle \omega_k (\omega^2 - \tilde{\omega}_k^2) \delta_{k,k'}}{\Omega [(\omega^2 - \tilde{\omega}_k^2)^2 + 4\omega_k^2 \Gamma_k^2(\omega)]} + \frac{6V_{ik}^4 N_k \langle S_i^z \rangle \omega_k a (\omega^2 - \tilde{\omega}_k^2) \delta_{k,k'}}{b\Omega [(\omega^2 - \tilde{\omega}_k^2)^2 + 4\omega_k^2 \Gamma_k^2(\omega)]}$$
(13)

and,

$$\Gamma(\omega) = \frac{a^4}{2\Omega} \{ \delta(\omega - \tilde{\Omega}) - \delta(\omega + \tilde{\Omega}) \} + \frac{b^2 c^2}{2\tilde{\Omega}} \{ \delta(\omega - \tilde{\Omega}) - \delta(\omega + \tilde{\Omega}) \} + \frac{V_{ik}^2 N_k a^2}{2\tilde{\Omega}} \{ \delta(\omega - \tilde{\Omega}) - \delta(\omega + \tilde{\Omega}) \}$$

$$+ \frac{2bV_{ik} \langle S_i^x \rangle \omega_k \delta_{k,k'} \{ 2\omega_k \Gamma_k(\omega) \}}{[(\omega^2 - \tilde{\omega}_k^2)^2 + 4\omega_k^2 \Gamma_k^2(\omega)]} + \frac{4b^2 V_{ik}^2 N_k \{ \delta(\omega - \tilde{\Omega}) - \delta(\omega + \tilde{\Omega}) \}}{2\tilde{\Omega}} + \frac{8aV_{ik}^2 \langle S_i^z \rangle \omega_k \delta_{k,k'} \{ 2\omega_k \Gamma_k(\omega) \}}{[(\omega^2 - \tilde{\omega}_k^2)^2 + 4\omega_k^2 \Gamma_k^2(\omega)]}$$

$$+ \frac{c^2 V_{ik}^2 N_k \{ \delta(\omega - \tilde{\Omega}) - \delta(\omega + \tilde{\Omega}) \}}{2\tilde{\Omega}} + \frac{V_{ik}^2 N_k a^4 \{ \delta(\omega - \tilde{\Omega}) - \delta(\omega + \tilde{\Omega}) \}}{2\tilde{\Omega} b^2}$$

$$+ \frac{2V_{ik}^4 N_k \langle S_i^x \rangle \omega_k \delta_{k,k'} \{ 2\omega_k \Gamma_k(\omega) \}}{\Omega [(\omega^2 - \tilde{\omega}_k^2)^2 + 4\omega_k^2 \Gamma_k^2(\omega)]} + \frac{6V_{ik}^4 N_k \langle S_i^z \rangle \omega_k \delta_{k,k'} \{ a 2\omega_k \Gamma_k(\omega) \}}{b\Omega [(\omega^2 - \tilde{\omega}_k^2)^2 + 4\omega_k^2 \Gamma_k^2(\omega)]}$$
(14)

In Eqs(13) and (14) $\tilde{\omega}_k$ and $\Gamma_k(\omega)$ are phonon frequency and phonon width respectively. These are obtained when we solve $\langle\langle A_k; A_{k'} \rangle\rangle$ Green's function. This appear when we decouple $\langle\langle F(t); F(t') \rangle\rangle$ for obtaining value of $\tilde{P}(\omega)$. Phonon Green's function is obtained as:

$$\langle\langle A_k(t); A_{k'}^+(t') \rangle\rangle = \frac{\omega_k \delta_{kk'}}{\pi [\omega^2 - \tilde{\omega}_k^2 - 2i\omega_k \Gamma_k(\omega)]}$$
(15)

with,

$$\tilde{\omega}_k^2 = \tilde{\omega}_k^2 + 2\omega_k \Delta_k(\omega)$$
(16)

The phonon shift $\Delta_k(\omega)$ is obtained as:

$$\Delta_k(\omega) = \text{Re } P_k(\omega) = 18P \sum_{k_1 k_2} |V^{(3)}(k_1, k_2, -k)|^2 \times \frac{\omega_{k_1} \omega_{k_2}}{\tilde{\omega}_{k_1} \tilde{\omega}_{k_2}} \left\{ \begin{aligned} & (n_{k_1} + n_{k_2}) \frac{\tilde{\omega}_{k_1} + \tilde{\omega}_{k_2}}{\omega^2 - (\tilde{\omega}_{k_1} + \tilde{\omega}_{k_2})^2} \\ & (n_{k_2} - n_{k_1}) \frac{\tilde{\omega}_{k_1} - \tilde{\omega}_{k_2}}{\omega^2 - (\tilde{\omega}_{k_1} - \tilde{\omega}_{k_2})^2} \end{aligned} \right\}$$

$$+ 48P \sum_{k_1 k_2 k_3} |V^{(4)}(k_1, k_2, k_3, -k)|^2 \frac{\omega_{k_1} \omega_{k_2} \omega_{k_3}}{\tilde{\omega}_{k_1} \tilde{\omega}_{k_2} \tilde{\omega}_{k_3}} \times \left\{ \begin{aligned} & (1 + n_{k_1} n_{k_2} + n_{k_2} n_{k_3} + n_{k_3} n_{k_1}) \frac{\omega_{k_1} + \omega_{k_2} + \omega_{k_3}}{\omega^2 - (\tilde{\omega}_{k_1} + \tilde{\omega}_{k_2} + \tilde{\omega}_{k_3})^2} \\ & + 3(1 - n_{k_1} n_{k_2} + n_{k_2} n_{k_3} - n_{k_3} n_{k_1}) \frac{\omega_{k_1} - \omega_{k_2} - \omega_{k_3}}{\omega^2 - (\tilde{\omega}_{k_1} - \tilde{\omega}_{k_2} - \tilde{\omega}_{k_3})^2} \end{aligned} \right\}$$

+ higher terms .

(17)

and the phonon width $\Gamma_k(\omega)$ is:



$$\Gamma_k(\omega) = \text{Im } P_k(\omega) = 9\pi \sum_{k_1 k_2} V^{(3)}(k_1, k_2, -k)^2 \times \frac{\omega_{k_1} \omega_{k_2}}{\tilde{\omega}_{k_1} \tilde{\omega}_{k_2}} \left\{ \begin{array}{l} \left(n_{k_1} + n_{k_2} \right) \begin{bmatrix} \delta(\omega + \tilde{\omega}_{k_1} + \tilde{\omega}_{k_2}) \\ -\delta(\omega - \tilde{\omega}_{k_1} + \tilde{\omega}_{k_2}) \end{bmatrix} \\ \left(n_{k_2} - n_{k_1} \right) \begin{bmatrix} \delta(\omega + \tilde{\omega}_{k_1} - \tilde{\omega}_{k_2}) \\ -\delta(\omega - \tilde{\omega}_{k_1} + \tilde{\omega}_{k_2}) \end{bmatrix} \end{array} \right\}$$

$$+ 48\pi \sum_{k_1 k_2 k_3} |V^{(4)}(k_1, k_2, k_3, k_4)|^2 \times \begin{bmatrix} \delta(\omega + \tilde{\omega}_{k_1} + \tilde{\omega}_{k_2} + \tilde{\omega}_{k_3}) \\ -\delta(\omega - \tilde{\omega}_{k_1} - \tilde{\omega}_{k_2} - \tilde{\omega}_{k_3}) \end{bmatrix} + \text{higher terms.} \quad (18)$$

$$\times \left[\left(1 + n_{k_1} n_{k_2} + n_{k_2} n_{k_3} + n_{k_3} n_{k_1} \right) \frac{\omega_{k_1} \omega_{k_2} \omega_{k_3}}{\tilde{\omega}_{k_1} \tilde{\omega}_{k_2} \tilde{\omega}_{k_3}} \right]$$

The Green's function (6) finally takes value:

$$G_{ij}^{(\omega)} = \frac{\Omega \langle S_i^x \rangle \delta_{ij}}{\pi[\omega^2 - \hat{\Omega}^2 - 2\Omega i\Gamma(\omega)]} \quad (19)$$

$$\text{Where, } \hat{\Omega}^2 = \tilde{\Omega}^2 + \Delta(\omega) \quad (20)$$

Ferroelectric mode frequency

Cochran [26] has suggested that ferroelectric transition occurs due to becoming small of one of normal mode frequency of crystal at transition temperature. Solving Eq(20) we obtain:

$$\hat{\Omega}^2 = \frac{1}{2} \left(\tilde{\omega}_k^2 + \tilde{\Omega}^2 \right) \pm \frac{1}{2} \left[\left(\tilde{\omega}_k^2 - \tilde{\Omega}^2 \right)^2 + 4 \left(\frac{2bV_{ik} \langle S_i^x \rangle \omega_k \delta_{kk'} + 8aV_{ik}^2 \langle S_i^z \rangle \omega_k \delta_{kk'}}{\Omega} + \frac{2V_{ik}^4 N_k \langle S_i^x \rangle \omega_k \delta_{kk'}}{\Omega} + \frac{6V_{ik}^4 N_k \langle S_i^z \rangle \omega_k \delta_{kk'}}{b\Omega} \right) \right]^{\frac{1}{2}}, \quad (21)$$

Frequency corresponding to negative sign is the ferroelectric mode frequency of MASD alum.

Curie Temperature

At transition or Curie temperature (T_c) $\tilde{\Omega} \rightarrow 0$, so that we obtain from Eq(8)

$$T_c = \frac{\Omega}{2k_B \tanh^{-1} \left(\frac{4\Omega}{J} \right)} \quad (22)$$

where,

$$J = J + \frac{2V_{ik}^2 \omega_k^2}{\tilde{\omega}_k^2} \quad (23)$$

Dielectric Constant



Following Zubarev [25] we have:

$$\chi = -\lim_{x \rightarrow 0} 2\pi N \mu^2 G_{ij}(\omega) \tag{24}$$

χ is related to dielectric constant ϵ as:

$$\epsilon = 1 + 4\pi\chi \tag{25}$$

From Eqs(19),(24) and(25) we obtain:

$$\epsilon = \frac{8\pi N \mu^2 \Omega \langle S_i^x \rangle}{[(\omega^2 - \hat{\Omega}^2) - 2\Omega i \Gamma(\omega)]} \tag{26}$$

Dielectric loss tangent

In all ferroelectric crystals some power is lost in the form of heat which is called loss tangent ($\tan\delta$):

$$\tan \delta = \frac{\text{imaginary}\epsilon}{\text{real}\epsilon} \tag{27}$$

from Eq(26) we have

$$\tan \delta = \frac{2\Omega \Gamma(\omega)}{(\omega^2 - \hat{\Omega}^2)} \tag{28}$$

Numerical Calculations & Results

By substituting model values for MASD alum, given in table-1, we calculate temperature dependence of $\tilde{\Omega}$, $\tilde{\tilde{\Omega}}$, $\hat{\Omega}$, ϵ , $\tan\delta$. Theoretical results have been compared with experimental results of Pepinsky et al [16]. Calculated values have been shown in figures 1-3.

Table 1- Model values of physical quantities for MASD alum:

$\Omega(\text{cm}^{-1})$	$J(\text{cm}^{-1})$	$J^*(\text{cm}^{-1})$	$V_{ik}(\text{cm}^{-1})$	$T_c(\text{K})$	$\omega_k(\text{cm}^{-1})$	$C(\text{K})$	$\mu * 10^{18}(\text{cgs})$	$A_k * 10^{17}(\text{erg/K})$
0.11	366.75	488.99	60.41	177	5	540	3.513	37.66

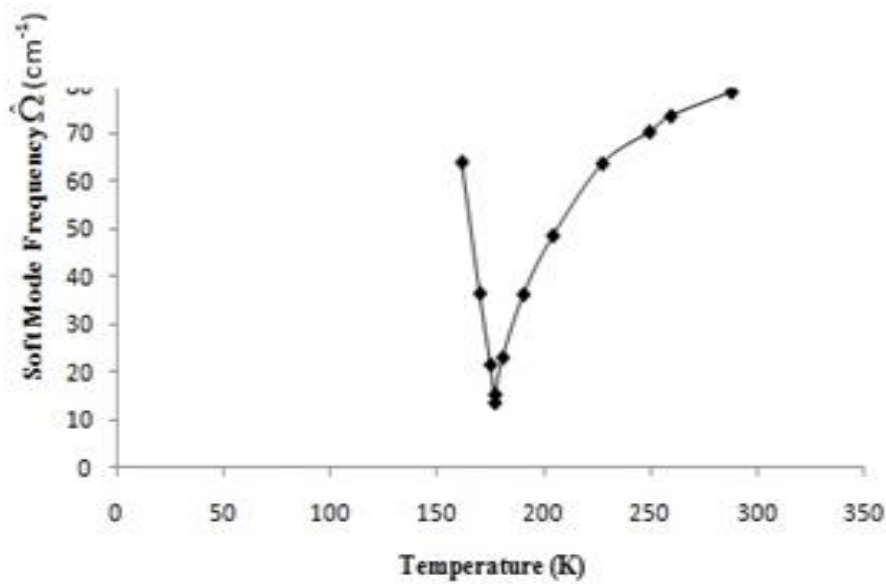


Figure 1. Temperature dependence of soft mode frequency $\hat{\Omega}$ (cm⁻¹) of MASD alum (Our calculation, Correlated values with experimental values of Pepinsky et al. [16]).

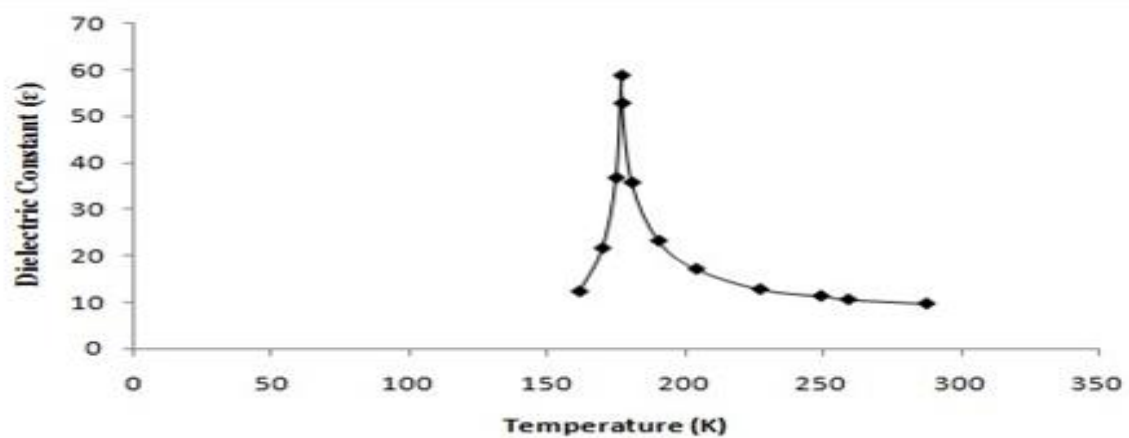


Figure 2. Temperature dependence of dielectric constant (ϵ) of MASD alum (Our calculation, Correlated values with experimental values of Pepinsky et al. [16]).

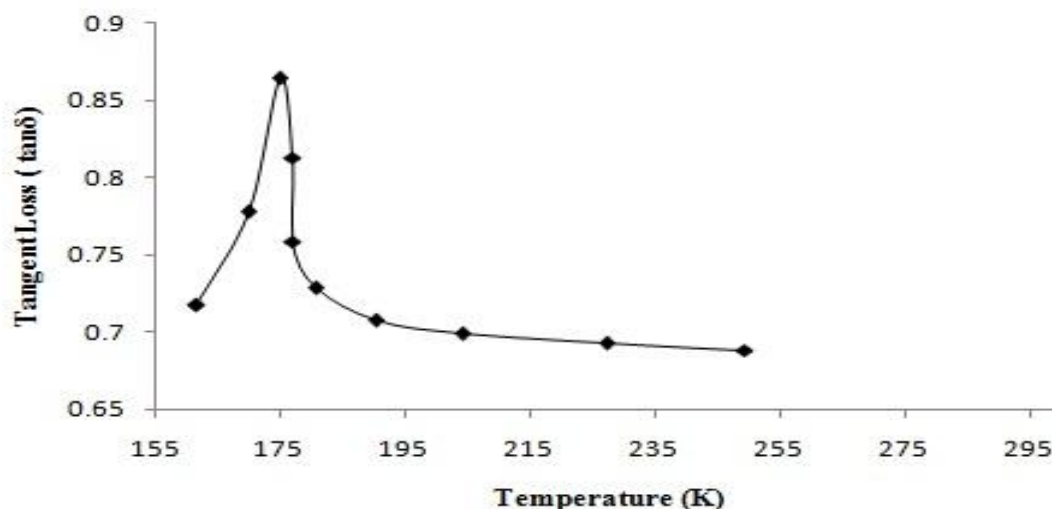


Figure 3. Temperature dependence of loss tangent ($\tan\delta$) of MASD alum (Our calculation, Correlated with experimental values of Pepinsky et al. [16]).

Discussion

Our expression (21) for ferroelectric mode frequency shows that as temperature is increased from below T_c , the frequency decreases and becomes small at T_c while above T_c it increases. The phonon anharmonic terms contribute in both ferroelectric as well as paraelectric phases. Our expression (26) for dielectric constant shows that as temperature is increased from below it increases sharply becoming largest at T_c and then decreases. This is due to the fact that dielectric constant is inverse squarely proportional to ferroelectric mode frequency and directly proportional to total width. Our expression (28) for loss tangent shows that as temperature is increased from below, it increases, becoming largest at T_c and then decreases. Our predictions are in quite agreement with experimental observations for MASD alum.

Conclusions

Present study shows that modified model explains adequately the ferroelectric transition and dielectric behaviours of MASD alum. With the help of formulae obtained in present study we may

explain transition and dielectric properties of similar other alums such as AFeSD, ACrSD, ANdSD alums.

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