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Study of ferroelectric and dielectric properties of potassium dihydrogen phosphate crystal

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A simple pseudospin lattice coupledmode model with addition of third and fourth-order phonon anharmonic interactions terms and direct spin-spin interactions terms and external electric field term has been considered for investigation of transition phenomena and dielectric properties of classic ferroelectric Potassium Dihydrogen Phosphate **(**KDP) crystal. A double-time thermal Green's function method has been used for derivation of response function. From response function shift, width and soft mode frequency have been derived for KDP crystal. Response function is also related to dielectric constant which has been obtained. Unlike previous authors, some different simple approximations have been used to obtained results quite different to them. By fitting model values of different parameters in the expressions, temperature variations of normal mode frequency, dielectric constant and loss tangent have been calculated numerically for KDP crystal. Our theoretical results are compared with experimental results. It is observed that our theoretical results agree with the experimental results of Kaminow& Harding[2].

Therefore, it can be concluded that the simple model with still simplest approximation is quite suitable to explain transition and dielectric properties of classic KDP crystal. Present expressions can be used for similar other crystals also.

Keywords: Green's function, Dielectric constant, Potassium dihydrogen phosphate.

1 Introduction

Ferroelectric inorganic salt potassium Dihydrogen phosphate KH_2PO_4(KDP) crystal have been widely known for a long time but researchers continue to develop theories and experimental study because of a unique set of properties. Including ferroelectric hysteresis (used in non-volatile memory), High permittivity (used in capacitors), high piezoelectric effects (used in sensors, resonant wave devices, actuators), High pyroelectric coefficients (used in infra-red detectors)[1]. Potassium dihydrogen phosphate (KDP) shows phase transition at 123 K. It changes its phase from ferroelectric to paraelectric after Curie temperature[2].

Extensive studies in both Experimental and Theoretical areas are being done to explore more about KDP crystal. Kaminow and Harding have studied phase transitions in KDP crystal. Darinskaya and Koldaeva[3]studied Relaxation Kinetics of the Microhardness of KDP Crystals in Magnetic field. Sheeja and Mahadevan[4] studied Effect of ZnS as impurities on the Physical Properties of KDP Single Crystals and examined their X-ray diffraction, atomic absorption, and Fourier transform infrared spectral measurements. Milinskii and Baryshnikov[5] studied dielectric and ferroelectric properties of nanocomposites based on deuterated KDP crystal. Xie and Qi *et al.*[6] have grown deuterated KDP crystal with about 70% deuterium level by a rapid horizontal growth method. Liu *et al.*[7] have studied Intercalated hybrid of kaolinite with KH_2PO_4 and showed high conductivity at room temperature. Graczyk *et al*[8]. has studied temperature dependencies of magnetization of KH2PO4 ferroelectric substrates.

Theoretical studies on KDP crystal were initiated by Ganguli *et al.*[9] they have considered Green's function theory of Ramakrishnan and Tanaka for studying ferroelectric phase transitions using pseudo-spin-lattice coupled mode(PLCM) model by including phonon anharmonicity. They decoupled correlation at an early stage. So there we were not able to obtain convincing and precise results. In Present work, we have considered third and fourth-order anharmonic interaction term with some additional terms in our Hamiltonian. We have obtained different parameters of phase transitions, soft mode frequency, dielectric constant, loss tangent for KDP crystal. Theoretical results show good agreement with experimental results of Kaminow and Harding[2].

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2 Calculations and Results

We have modified the pseudo-spin-lattice coupled mode model given by Ganguli *et al.*[9] by adding anharmonic terms of third and fourth-order. Spin-spin interactions terms, external electric field term and some other terms. The pseudo-spin lattice couple mode model is expressed as:

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

We shall add

$$H_2 = \sum_{k_1 k_2 k_3} V^{(3)}(k_1, k_2, k_3) A_{k_1} A_{k_2} A_{k_3} + \sum_{k_1 k_2 k_3 k_4} V^{(4)}(k_1, k_2, k_3, k_4) A_{k_1} A_{k_2} A_{k_3} A_{k_4} - \sum_{ik} V_{ik} S_i^x A_k + \frac{1}{2}\sum_{ij} B_{ij} S_i^x S_j^x - \sum_{ik} V_{ik} S_i^x A_k - \sum_{ik} V_{ik} S_i^x A_k^2 - 2\mu E \sum_i S_i^z \quad \text{... (2)}$$

Where Ω is proton tunnelling frequency between double well potential O-H---O bonds, $S^{\alpha}(\alpha = x, y, z)$ is the α^{th} component of the pseudo-spin variable, i,j run over proton ordering. V_{ik}, A_k, B_k are spin-lattice interaction constant, position and momentum co-ordinates respectively.V^3 (k_1,k_2,k_3) and V^4(k_1,k_2,k_3,k_4) are anharmonic interactions of third and fourth order. B_{ij} represents interaction of the transverse field with one proton to another proton.

We shall consider the total Hamiltonian:

$$H = H_1 + H_2$$

We have differentiated Green's function[10]twice with respect to time t and t'.Using this Hamiltonian which is then set into Dyson's equation form, Green function is obtained as:

$$G(\omega) = \pi^{-1}\Omega\left\langle S_i^x \right\rangle \delta_{ij}[(\omega^2 - \hat{\Omega}^2) + 2i\Omega\Gamma(\omega)]^{-1} \quad \text{... (3)}$$

The pseudo-spin frequency, modified pseudo-spin frequency, soft mode frequency are related as:

$$\hat{\Omega} = \tilde{\Omega}^2 + \Delta(\omega), \quad \text{... (4)}$$

$$\tilde{\Omega}^2 = a^2 + b^2 - bc, \quad \text{... (5)}$$

$$a = J_{ij}\left\langle S_j^z \right\rangle - Bij\left\langle S_i^z \right\rangle + 2E\mu$$

$$b = 2\Omega \quad \text{... (6)}$$

$$c = J_{ij}\left\langle S_j^x \right\rangle - B_{ij}\left\langle S_i^x \right\rangle \quad \text{... (7)}$$

In equations (4) and (5), $\Delta(\omega)$ and $\Gamma(\omega)$ are shift and width respectively which are given in our earlier paper.[10]

$\tilde{\Omega}^2$ is modified soft mode frequency which is given as:

$$\hat{\Omega}_{\pm}^2 = \frac{1}{2}\left[\left(\tilde{\tilde{\omega}}_k^2 + \tilde{\tilde{\Omega}}^2\right) \pm \left\{\begin{matrix}\left(\tilde{\tilde{\omega}}_k^2 - \tilde{\Omega}^2\right)^2 + 16V_{ik}\left\langle S_i^x \right\rangle \Omega \\ +6V_{ik}^2 J_{ij}\left\langle S_j^x \right\rangle \left\langle S_j^z \right\rangle \omega_k + ...\end{matrix}\right\}^{\frac{1}{2}}\right] \quad \text{... (8)}$$

The expression for dielectric constant is obtained as:

$$\varepsilon = (-8\pi N\mu)(S_i^x)(\omega^2 - \hat{\Omega}^2)\left[\left(\omega^2 - \hat{\Omega}\right)^2 + 4\Omega^2\Gamma^2\right]^{-1} \quad \text{... (9)}$$

And loss tangent is given by,

$$\tan\delta = \frac{2\Omega\Gamma(\omega)}{\hat{\Omega}^2} \quad \text{... (10)}$$

We have used different model values of physical quantities for KDP crystal here shown in Table 1. We have calculated temperature dependence of ferroelectric mode frequency, dielectric constant and loss tangent. We have shown our results in Figs. 1-3. Our calculated results are compared with experimental values of Kaminow and Harding[2].

Table 1 — Model values of different physical quantities[9].

Tc(K)	J*, cm^{-1}	J*,cm^{-1}	V_{ik}, cm^{-1}	Ω, cm^{-1}	ω_k , cm^{-1}	C, K	μ, esu	A_k, (erg/K)
123	440	334	0.229	82	150	254	1.8	9.763

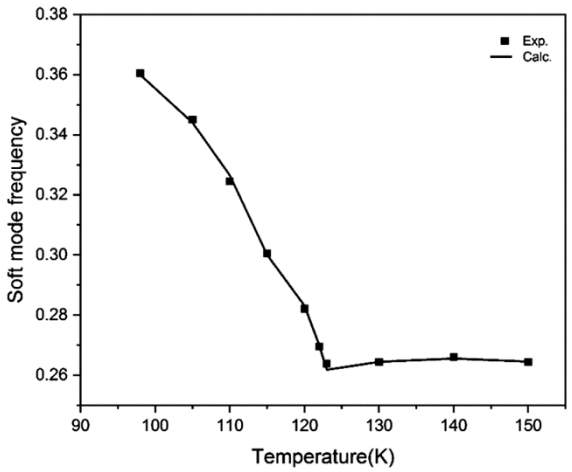

Fig. 1 − Calculated temperature dependence of soft mode frequency in KH_2PO_4 crystal compared with experimental data of others.

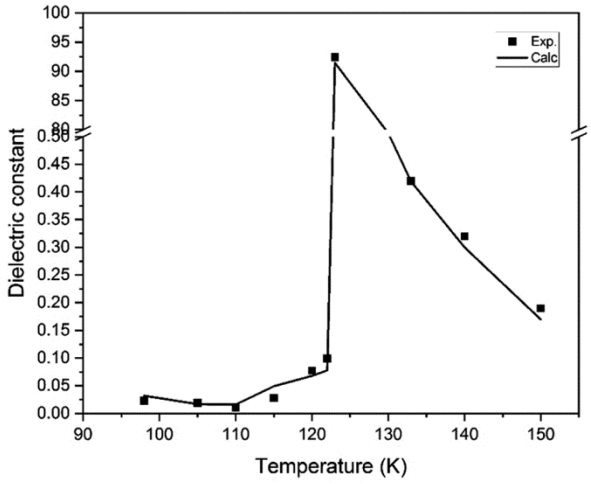

Fig. 2 − Calculated temperature dependence of dielectric constant with KH_2PO_4 crystal compared with experimental data of others.

3 Discussion

In our present study, we have fitted various model values in our obtained expressions from equation (3) to equation (10). Using our obtained expressions, we have calculated soft mode frequency, dielectric constant and loss tangent. For validation, we have compared our obtained data to experimental data of Kaminow and Harding[2]. As we can define, soft mode as a collective excitations whose frequency decrease anomalously as the transition point is reached[1]. This behaviour of softmode can be seen in Fig. 1, where soft mode frequency is decreasing and

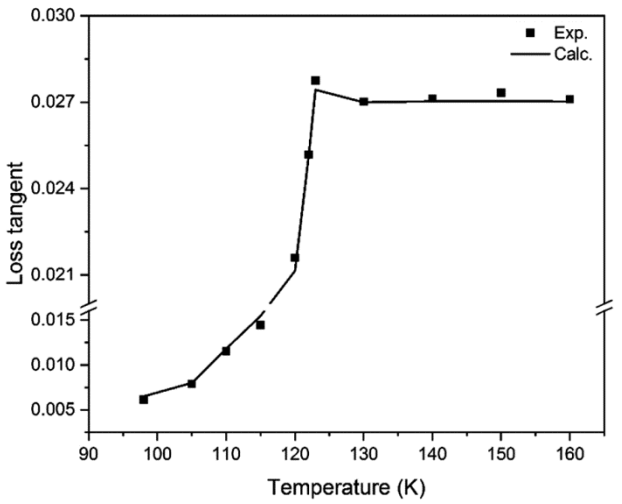

Fig. 3− Calculated temperature dependence of loss tangent in KH_2PO_4 crystal compared with experimental data of others.

approaching to a minimum value at T_c.at transition temperatureT_c(123K), KDP crystal co-exist in both form in equilibrium. Hence the expressions we have obtained for KDP crystal shows can fairly explain soft mode frequency, dielectric constant, loss tangent. Also, its shows good applicability of the modified pseudo spin lattice coupled mode model for explanation of phase transition in KDP crystal system.

4 Conclusions

Present work reveals that by adding third and fourth-order anharmonic terms, interactions terms and some other terms can explain quantitatively well the ferroelectric and dielectric behaviours of KDP crystal. Theoretical results agree with experimental results of Kaminow and Harding[2] which show applicability of modified Hamiltonian for KDP crystal.

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