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Temperature and frequency dependence of width in sodium potassium niobate mixed system

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Considering a quadratic anharmonic model Hamiltonian and using double time temperature dependent Green's function method and Dyson's equation treatment, expressions for the width in the frequency response for mixed perovskite type ferroelectrics have been obtained. Using the experimentally observed dielectric constant and loss tangent for $Na_{1-x}K_xNbO_3$ [where x = 0, 0.4, 0.5], the temperature dependence of soft mode width in these samples at 10 and 100 kHz has been calculated. Anomaly has been observed in the behaviour of soft mode width, near the transition temperatures in these compounds.

[**Keywords:** Ferroelectricity, Piezoelectricity, Soft mode frequency]

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1 Introduction

The occurrence of ferroelectricity in perovskite-type crystals such as $KNbO_3$ has been investigated both theoretically and experimentally. The perovskite structure is very commonly found in the compounds of general formula ABO_3 and many of these materials have interesting and important properties, such as ferroelectricity, piezoelectricity and non-linear optical behaviour. Many perovskites undergo a structural change in which the octahedra are rotated or tilted (100) directions of the cubic phase. Nearly all of these changes are caused by the condensation of one or more modes at the R and/or M-points of the cubic Brillion zone. The modes have wave vectors (1/2 ½ ½) and (0 ½ ½) and symmetry-related positions, respectively. The mode at the R point is triply degenerated and at the M-point is a singlet. Pytte[1] has constructed a model Hamiltonian, for the ferroelectric transition in the perovskite structure in terms of localized-strain and soft-normal-mode coordinates and temperature-dependent model parameters, which was used in our theoretical investigations to study the physical properties of perovskite ferroelectrics. Authors[2] studied the temperature dependence of width and soft mode frequency of the $KNbO_3$ and $NaNbO_3$ using their earlier theoretical[3-6] and experimental results[7]. $Ba_xSr_{1-x}TiO_3$ mixed system has also been studied by correlating theoretical and experimental values[8].

In the present study, temperature (150 to 440 °C) and frequency (0.1 to 1000 kHz) dependence of phonon width for $Na_{1-x}K_xNbO_3$ [x = 0, 0.4, 0.5] ceramic samples have been calculated by using the theoretical expressions[5,6] and experimental results[7] on dielectric measurements. The theoretical expressions[3] for soft mode phonon frequency and width in the frequency response have been obtained by using the model Hamiltonian[3-6] proposed by Pytte[1], and are solved with the help of double time thermal Green's function technique and Dyson's equation[9] treatment.

2 Theory

Soft mode frequency and width: Using the Kubo formalism and Hamiltonian[1,9], the general expression for complex dielectric susceptibility[3,10] is given as:

$$\chi_{\mu\nu}(\omega) = lim_{\varepsilon\to 0} -\frac{2\pi}{\varepsilon_0} G_{\mu\nu}(\omega + i\varepsilon) \qquad \ldots(1)$$

where $G_{\mu\nu}(\omega)$ is the Fourier transform of the retarded double time thermal Green's function between μ and ν components and can be expressed as:

$$G_{\mu\nu}(\omega+i\varepsilon)=\frac{N\mu^2}{\varepsilon_0\eta}\frac{\omega_k}{\left[\left(\omega^2-\Omega_k^2\right)+2i\omega_k\Gamma_k(w)\right]}$$

So, $$\chi_{\mu\nu}(\omega)=-\frac{2N\mu^2}{\varepsilon_0\eta}\frac{\omega_k}{\left[\left(\omega^2-\Omega_k^2\right)+2i\omega_k\Gamma_k(w)\right]} \quad \ldots(2)$$

Separating its real and imaginary parts and writing these together, we have

$$\chi_{\mu\nu}(\omega)=-\frac{2N\mu^2}{\varepsilon_0\eta}\frac{\omega_k\left[\left(\omega^2-\Omega_k^2\right)-2i\omega_k\Gamma_k(w)\right]}{\left[\left(\omega^2-\Omega_k^2\right)^2+4\omega_k^2\Gamma_k^2(w)\right]} \quad \ldots(3)$$

where, the symbols have their usual meanings[3-6]

or

$$\chi_{\mu\nu}(\omega)=\chi'_{\mu\nu}+i\chi''_{\mu\nu}$$

where $\chi'_{\mu\nu}$, the real part and χ''_{μ}, the imaginary part are given as below:

$$\chi'_{\mu\nu}=-\frac{2N}{\hbar\varepsilon_0}M_\mu N_\mu\frac{\omega_k\left[\left(\omega^2-\Omega_k^2\right)\right]}{\left[\left(\omega^2-\Omega_k^2\right)^2+4\omega_k^2\Gamma_k^2(w)\right]}$$

$$\chi''_{\mu\nu}=\frac{4N}{\varepsilon_0\eta}M_\mu N_\mu\frac{\omega_k^2\Gamma_k(w)}{\left[\left(\omega^2-\Omega_k^2\right)^2+4\omega_k^2\Gamma_k^2(w)\right]}$$

For small Γ <<w as compared to frequency, Eq. (3) can be written as

$$\chi'_{\mu\nu}=-\frac{2N\mu^2}{\hbar\varepsilon_0}\frac{\omega_k}{\left[\left(\omega^2-\Omega_k^2\right)\right]} \quad \ldots(4)$$

We know

$$T_C=\frac{N\mu^2}{9K_B\varepsilon_0}, Hence\frac{N\mu^2}{\varepsilon_0}=9K_BT_C,$$

Substituting this value in above equation, we get

$$\chi'_{\mu\nu}=-\frac{18K_BT_C}{\eta}\frac{\omega_k}{\left[\left(\omega^2-\Omega_k^2\right)\right]}$$

Static part of dielectric constant (w = 0) is

$$\chi'_{\mu\nu}=\frac{18K_BT_C}{\eta}\frac{\omega_k}{\left[\left(\Omega_k^2\right)\right]} \quad \ldots(5)$$

Soft mode frequency can be expressed as:

$$\Omega^2=-\frac{18K_BT_C}{\eta}\frac{\omega_k}{\chi'} \quad \ldots(6)$$

and tangent loss is given by the following well known[3-6] expression

$$\frac{\chi''_{\mu\nu}}{\chi'_{\mu\nu}}=\frac{\omega_k^2\Gamma_k(\omega)}{\omega_k\left(\omega^2-\Omega^2\right)},$$

$$\tan\delta=\frac{\omega_k\Gamma}{\left(\omega^2-\Omega^2\right)} \qquad \Omega^2>>\omega^2$$

$$\tan\delta=-\frac{\omega_k\Gamma}{\left(\Omega^2\right)}$$

and width is given by

$$\Gamma=-\frac{\tan\delta\Omega^2}{\omega_k}$$

With all the terms having their values given by above expressions

So, we have

$$\Gamma=-AT_c\frac{\tan\delta}{\chi}$$

where A is a constant having its value = 23.635 × 10^{11} s^{-1} k^{-1}

Therefore,

$$\Gamma=23.635\times10^{11}\frac{T_C\tan\delta}{\chi} \quad \ldots(7)$$

We have calculated the width of the ceramic sample of mixed $Na_{1-x}K_xNbO_3$ system [where x = 0, 0.4 and 0.5] by substituting the experimental value of tan δ and X' at different temperatures varying from 150-440 °C at frequencies 10 and 100 kHz in the above Eq. (7). The results have been tabulated in

Tables 1 and 2 and have been plotted in Figs 1 and 2 respectively.

The variation of width with frequency from 0.1 to 1000 kHz at room temperature have also been calculated, using our theoretical expressions[7-10] and experimental results[13] and the results have been tabulated in Table 3 and plotted in Fig. 3.

3 Results and Discussion

Using our[7] experimental results for dielectric constant and tangent loss for $NaNbO_3$, $Na_{0.6}K_{0.4}NbO_3$ and $Na_{0.5}K_{0.5}NbO_3$ and with the help of Eq. (7), temperature and frequency dependence of width in the frequency response, for these mixed systems, have been calculated, in continuation with our previous paper[2]. The temperature dependence of width at 10 and 100 kHz frequency has been shown in Tables 1 and 2 and Figs 1 and 2 respectively. It is observed that the width increases with the increase of temperature up to (orthorhombic-tetragonal) transition temperature for these systems, thereafter it decreases and further increase up to the second transition temperature (tetragonal to cubic). In the temperature range (370 ± 20 °C) and (460 ± 20 °C) anomalous behaviour has been observed, due to phase transitions. The width is associated with the damping of the soft mode. The damping of microwave in a crystal may be understood to arise due to the creation of a virtual polarization

Table 1 — Variation of width with temperature for $Na_{1-x}K_xNbO_3$ at 10 kHz

Temp. (°C)	Dielectric constant (10kHz) (χ)			Tangent loss (10kHz) ($\tan\delta$)			Width (Γ) × 10^8 kHz		
	$NaNbO_3$	$Na_{.6}K_{.4}NbO_3$	$Na_{.5}K_{.5}NbO_3$	$NaNbO_3$	$Na_{.6}K_{.4}NbO_3$	$Na_{.5}K_{.5}NbO_3$	$NaNbO_3$	$Na_{.6}K_{.4}NbO_3$	$Na_{.5}K_{.5}NbO_3$
150	149.21	393.09	344.01	0.009	0.042	0.051	0.498	0.479	0.683
170	163.49	628.73	414.84	0.010	0.038	0.065	0.505	0.271	0.721
190	180.67	662.46	716.05	0.016	0.036	0.041	0.732	0.244	0.263
195	190.00	659.21	722.35	0.017	0.036	0.037	0.740	0.490	0.236
210	203.94	640.89	696.73	0.018	0.039	0.036	0.730	0.546	0.488
230	229.74	622.65	667.22	0.022	0.048	0.039	0.792	0.692	0.552
250	255.31	616.90	648.07	0.030	0.065	0.049	0.972	0.946	0.714
270	290.63	625.70	641.91	0.046	0.084	0.068	1.309	1.205	1.001
290	320.35	646.90	648.99	0.063	0.108	0.104	1.626	1.499	1.514
310	349.90	686.14	673.79	0.101	0.151	0.148	2.387	1.976	2.076
330	464.50	771.59	713.93	0.136	0.223	0.216	2.422	2.595	2.860
350	649.11	1029.94	794.49	0.155	0.282	0.295	1.975	2.459	3.510
370	648.18	2723.54	959.75	0.248	0.229	0.368	3.165	0.755	3.624
380	641.08	3508.07	1285.29	0.291	0.221	0.369	3.713	0.565	2.714
390	631.68	3422.88	2981.14	0.347	0.249	0.244	4.477	0.653	0.773
400	628.23	2793.06	3568.81	0.405	0.378	0.244	5.303	1.215	0.646
410	626.45	2379.64	3028.96	0.465	0.565	0.331	6.122	2.132	1.033
420	626.79	2260.12	2626.17	0.498	0.595	0.441	6.576	2.364	1.587
430	632.80	2114.31	2287.13	0.524	0.615	0.661	6.915	2.612	2.732
440	634.98	2022.52	2031.13	0.572	0.725	1.165	7.477	3.219	5.422

Table 2 — Variation of width with temperature for $Na_{1-x}K_xNbO_3$ at 100 kHz

Temp. (°C)	Dielectric constant (100 kHz) (χ`)			Tangent loss (100 kHz) (tan δ)			Width (Γ) × 10^8 kHz		
	$NaNbO_3$	$Na_{.6}K_{.4}NbO_3$	$Na_{.5}K_{.5}NbO_3$	$NaNbO_3$	$Na_{.6}K_{.4}NbO_3$	$Na_{.5}K_{.5}NbO_3$	$NaNbO_3$	$Na_{.6}K_{.4}NbO_3$	$Na_{.5}K_{.5}NbO_3$
150	135.99	435.14	361.76	0.009	0.024	0.029	0.547	0.247	0.359
170	147.02	689.14	615.36	0.008	0.027	0.031	0.450	0.175	0.239
190	161.38	691.81	672.43	0.008	0.030	0.033	0.410	0.194	0.226
195	164.25	683.85	665.77	0.008	0.035	0.035	0.402	0.471	0.220
210	177.35	670.28	639.01	0.009	0.034	0.040	0.419	0.467	0.484
230	199.57	636.55	619.19	0.010	0.034	0.045	0.414	0.492	0.576
250	218.99	639.10	612.43	0.011	0.050	0.050	0.415	0.721	0.669
270	244.70	645.33	618.99	0.015	0.060	0.057	0.506	0.857	0.752
290	266.45	658.64	642.98	0.020	0.077	0.074	0.620	1.077	0.848
310	295.85	691.69	676.10	0.034	0.088	0.096	0.950	1.172	1.060
330	360.66	766.63	756.94	0.048	0.114	0.123	1.10	1.370	1.308
350	634.78	904.69	914.07	0.023	0.091	0.138	0.299	0.927	1.497
370	541.24	2325.25	3411.54	0.023	0.060	0.094	0.351	0.444	1.391
380	538.10	2904.30	3539.78	0.023	0.056	0.124	0.353	0.221	0.335
390	532.20	2524.25	2953.07	0.023	0.075	0.151	0.357	0.238	0.393
400	523.81	2000.00	2559.79	0.023	0.130	0.185	0.363	0.474	0.577
410	514.21	1747.28	2087.28	0.164	0.456	0.296	2.63	2.101	1.06
420	503.18	1654.35	1886.71	0.384	0.546	0.421	6.31	2.880	1.859
430	498.25	1585.21	1644.98	0.415	0.625	0.556	6.89	3.482	2.716
440	490.69	1502.63	1448.46	0.496	0.722	0.667	8.36	4.198	3.737

Table 3 — Variation of width with frequency for $Na_{1-x}K_xNbO_3$ at room temperature

Freq. kHz	Dielectric constant (room temp.) (χ`)			Tangent loss (room temp.) (tan δ)			Width (Γ) × 10^8 kHz		
	$NaNbO_3$	$Na_{.6}K_{.4}NbO_3$	$Na_{.5}K_{.5}NbO_3$	$NaNbO_3$	$Na_{.6}K_{.4}NbO_3$	$Na_{.5}K_{.5}NbO_3$	$NaNbO_3$	$Na_{.6}K_{.4}NbO_3$	$Na_{.5}K_{.5}NbO_3$
0.1	19.99	294.35	235.07	0.047	0.117	0.076	19.449	1.784	1.451
1	20.7	284.55	218.87	0.012	0.065	0.040	4.795	1.025	0.820
10	20.53	277.94	207.11	0.007	0.025	0.020	2.820	0.403	0.433
100	20.37	270.9	207.11	0.007	0.020	0.013	2.842	0.403	0.281
1000	21.65	264.77	205.8	0.016	0.022	0.019	6.113	0.373	0.414

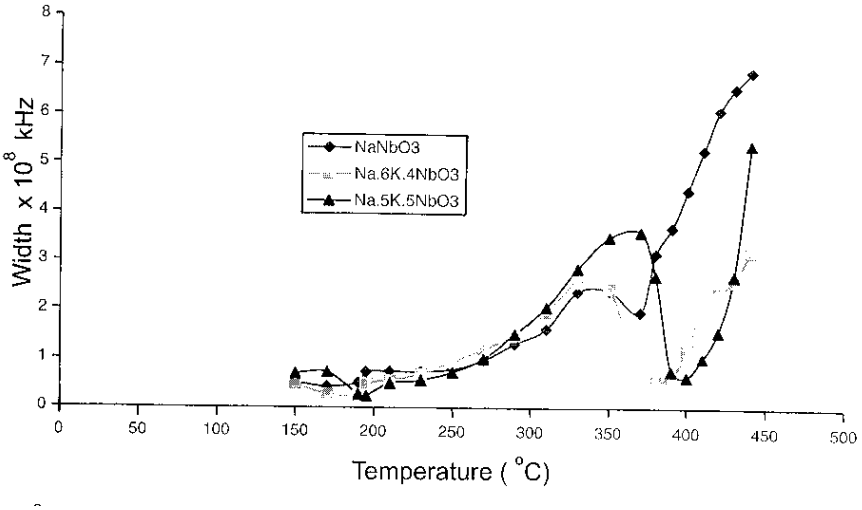

Fig. 1 — Variation of width with temperature for $Na_{1-x}K_xNbO_3$

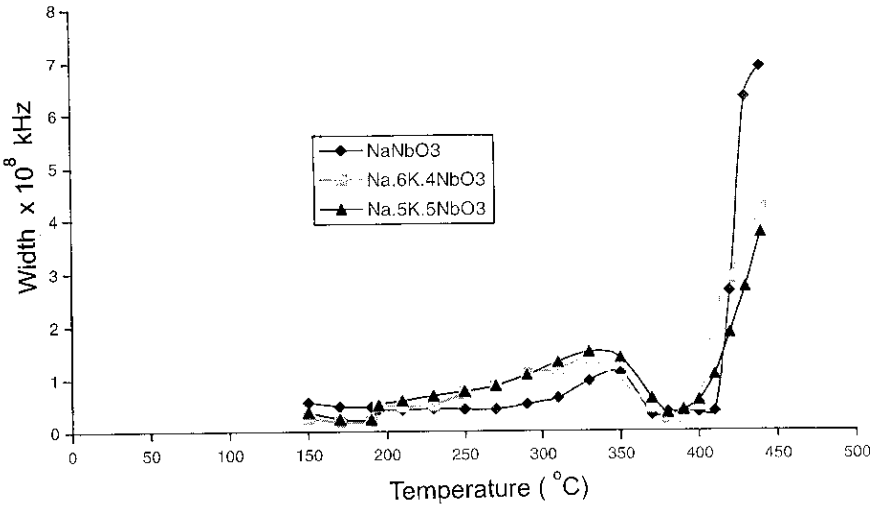

Fig. 2 — Variation of width with temperature for $Na_{1-x}K_xNbO_3$

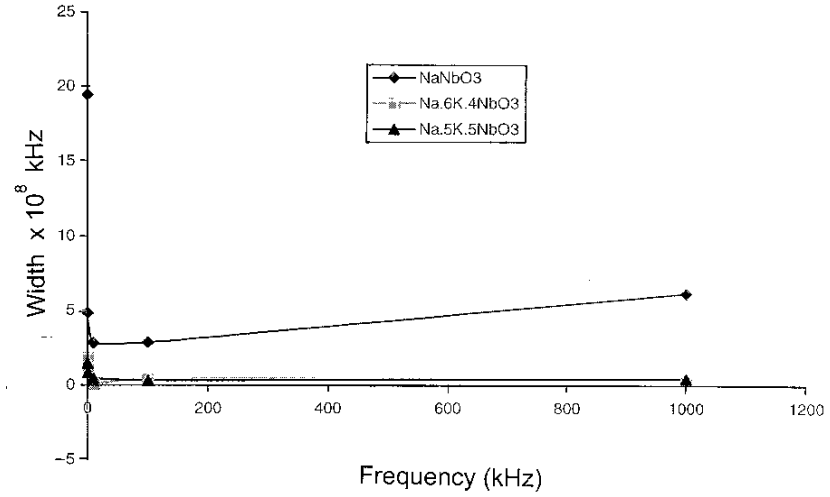

Fig. 3 — Variation of width with frequency for $Na_{1-x}K_xNbO_3$ at room temperature

mode excitation by the transverse electromagnetic radiation and the subsequent decays into real phonons by scattering from lattice imperfections and third and fourth order anharmonicity. Soft mode phonons are held responsible for this anomalous behaviour near transition temperature. The phase transition in perovskite crystals is assumed to be due to the instability of the temperature dependent low frequency optical phonons at transition temperature[6]. Depending on the relative magnitude of anharmonic interaction coefficient, different structural phases occur. Table 3 and Fig 3 show the frequency dependence of width for $NaNbO_3$, $Na_{.6}K_{.4}NbO_3$ and $Na_{.5}K_{.5}NbO_3$ systems at room temperature. Small dispersion is seen to exist; otherwise the variation is not very strong. At present we have experimental results of only three compositions, i.e., $K_{1-x}Na_xNbO_3$ (x = 0, 0.2, 0.4). So we have presented the calculation for only these compositions. Other dilute compositions may result in some interesting results.

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