

Vibrational Study of Structural Phase Transition in H-Bonded Mixed Crystals of $K_x(NH_4)_{1-x}PO_4$ (KDP-ADP)

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Abstract. Vibrational studies of structural phase transition (SPT) in strongly H-bonded mixed KDP-ADP system are reported. In the light of the structural evidences, doubts were raised about the present understanding of microscopic mechanism of phase transition in these systems. In our studies, some interesting results have been obtained leading to much more important role of molecular ions play in the phase transition. It is concluded that PO_4^{3-} site environment is of C_2 symmetry. Mixed crystals in the range $0.20 < x < 0.80$ show glassy behaviour. The behaviour of O-H...O bands is also analysed.

Introduction

KDP undergoes PE to FE phase transition at 123 K with space group changing from D_{2d}^{12} [I42d] to C_{2v}^{19} [Fdd2]. Large number of papers are reported in the literature dealing with the experimental investigation of KDP type system. It includes IR¹, Raman^{2,3}, Magnetic resonances⁴, Dielectric⁵, electro-optic⁶, X-ray⁷, neutron diffraction⁸, etc. The main emphasis of the vibrational studies have been to study the low lying B_2 symmetry soft mode, to understand the nature of vibrational modes associated with O-H...O bond and to investigate the nature of coupling of soft mode with other optic modes. Due to the large deuteration effect of T_c and on other ferroelectric properties, the role of protons were considered central in the mechanism of ferroelectricity in these crystals⁸. However, O-H...O bonds connecting each PO_4 with four neighbouring PO_4 lies very nearly in the basal plane. Thus restricting the proton motion to ab plane. In FE phase, P_s is parallel to c-axis and essentially perpendicular to the proton motion. Fe properties thus can not be accounted for by the proton motion alone. The ferroelectric mechanism picture is that the protons move between the minima of a double well potential on the O-H...O bonds in the PE phase. The transition is accompanied by the ordering of the protons in one minima of this double well potential. The proton motion is strongly coupled to an optic mode of the lattice, when the protons order, this proton-lattice interaction causes a distortion of the K- PO_4 sub-lattice to produce the spontaneous polarization. Therefore, a number of theoretical models have been suggested based on proton motion, lattice motion or the coupling between them⁹. Much attention is however, not paid to the hard modes associated with PO_4^{3-} internal motions. Recent Raman scattering experiments¹⁰ and neutron diffraction studies¹¹ have suggested that H_2SO_4 group centre of mass motion follows the proton motion and O-O distance in H-bond also changes with temperature in

addition to change in the direction of bond. The heavily damped low frequency mode in Raman spectra above T_c is shown to be associated with librational motion of PO_4^{3-} tetrahedra which much couple with polarization fluctuations. These results suggested a new view point regarding the phase transition. Accordingly the distorted PO_4^{3-} units carry the peramanent local dipole moment and order at T_c . This is similar to the molecular distortion type picture suggested by Bajpai et. al.^{12,13} in Ammonium Sulphate family crystal. It is therefore important to know what role PO_4^{3-} ion play in the phase transition. In mixed crystals, the ferroelectric ordering will change with increasing coccentration of NH_4^+ ion in KDP. Moreover, a comparison of KDP and ADP spectra will help in assigning PO_4^{3-} mode unambiguously. Another intresting aspect in the nature of H-bond and site potential of molecular species which is still a matter of controversy, systematic vibration studies become extremely relevant. We have planned these studies and in this paper present our results followed by a critical discussion.

Results and Discussion

The DRIFT spectra of KDP and ADP as well as those of mixed crystals are shown in fig. 1.

The observed mode are presented in Table 1 along with their assignments.

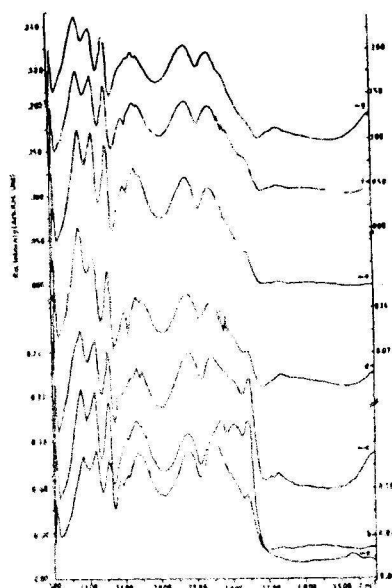


Fig. 1: Diffuse Reflectance Infrared Fourier Transform (DRIFT) Spectra of $\text{K}_x(\text{NH}_4)_{1-x}\text{H}_2\text{PO}_4$; Composition x in (a) 0.0 (b) 0.70, (c) 0.75, (d) 0.80, (e) 0.89, (f) 0.95 & (g) 0.99.

Table 1. Observed vibrational modes in KDP-ADP mixed system

X=1	X=0.95	X=0.89	X=0.80	X=0.75	X=0.70	X=0.00	Mode Assignments
539	539	540	541	539	541	539	ν_3 (PO ₄)
760(sh)	760	—	760	—	—	920	ν_3 (PO ₄)+ γ O-H
898	898	910	900	900	907	1098	ν_4 (PO ₄)
1096	1098	1098	1098	1100	1092	1284	δ O-H
1283	1286	1296	1286	1270	1286	1443	—
1502	1502	1541	1520	1502	1541	1542	ν_{as} (NH ₄)
1533	1528	—	1622	1520	—	1602	ν_4 (NH ₄)
1683	1610	1684	1684	1684	1684	1684	—
1752	1682	1749	1749	1749	1749	1750	—
2400	1754	2403	2403	2403	2398	2403	ν_5 (O-H...O)
2720	2400	2731	2714	2724	2745	2724	2ν (O-H...O)
3240	2736	3218	3218	3224	3214	3224	$2\nu_4$ (NH ₄)
3550	3216	3616(vw)	—	3616	3640	3643	—
3678	3661	3688	3694	3643	—	4020	—
4090	4090	—	3900	4090	4306	—	—
4900(s)	4900(w)	4900	4900	4900	4900	—	3ν (O-H...O)

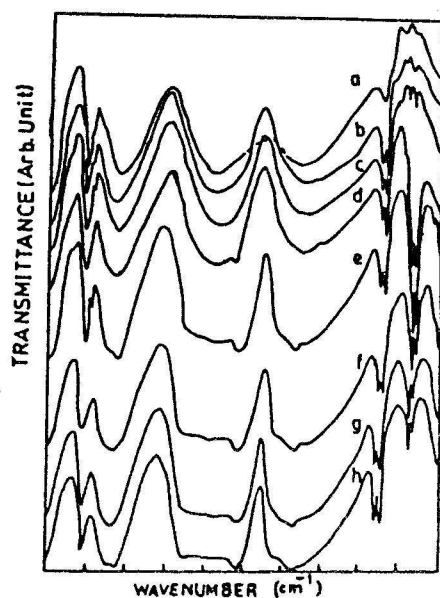
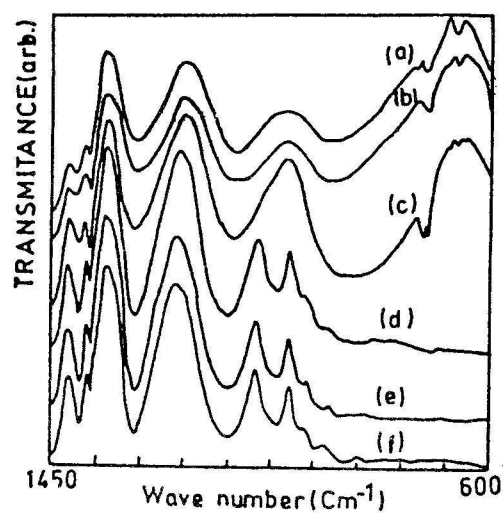


Fig. 2. Temperature dependence of IR spectra of KDP powder (a) 300K, (b) 148K, (c) 128K, (d) 123K (e) 118K (f) 98K & (h) 88K

Fig. 3. Temperature dependence of IR spectra of $K_x(NH_4)_{1-x}H_2PO_4$ ($x = 0.01$) (a) 300K, (b) 148K, (c) 128K, (d) 123K (e) 118K (f) 198K

IR transmission spectra were also recorded for these samples and the temperature dependence of various modes were investigated. Representative spectra for KDP and $\text{K}_{0.01}(\text{NH}_4)_{0.99}\text{H}_2\text{SO}_4$ are shown in Fig. 2 and Fig. 3, respectively, for various temperatures.

The Raman spectra for various samples are shown in Fig. 4 in the range $50\text{--}1200\text{ cm}^{-1}$. The representative deconvolution spectra in the range $650\text{--}250\text{ cm}^{-1}$ are given in Fig. 5 for KDP and ADP.

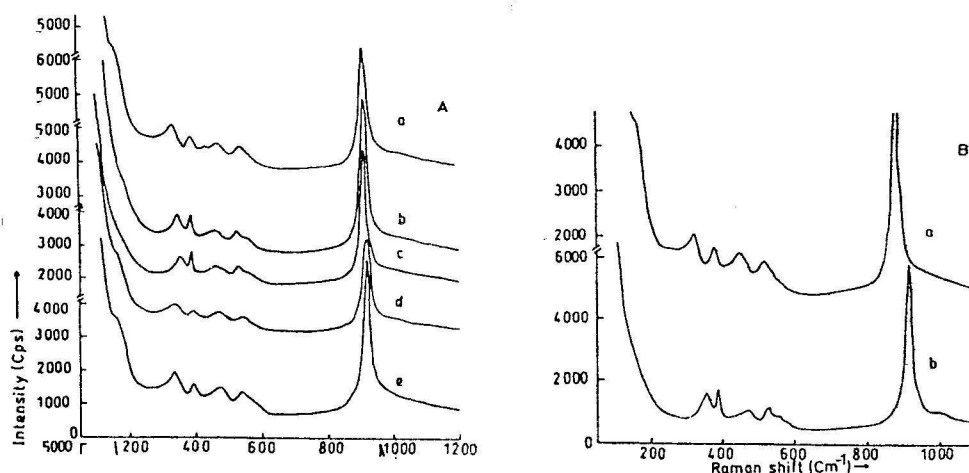


Fig. 4. Observed Raman Spectra in PO_4^{3-} internal mode range ($50\text{--}1200\text{ cm}^{-1}$) for KADP_x with x varying from (a) to (e) as 0.95, 0.89, 0.80, 0.75 and 0.50 respectively. The lower spectra is that of (a) ADP and (b) KDP.

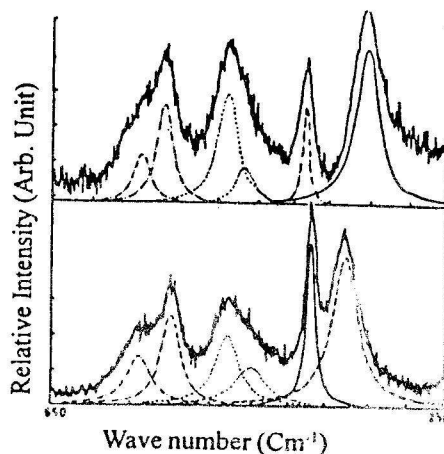


Fig. 5. Deconvoluted Raman spectra of ADP and KDP (Lower Spectra).

The results of deconvolution are summarized in Table 2. The convolution is done considering mixed Lorentzian and Gaussian character of bands and the χ^2 fitting was used with a background subtraction using a deconvolution programme developed by us.

Table 2. Mode parameters for mixed crystals (600-250 cm⁻¹) as obtained from deconvolution of Raman spectra.

Crystal	Band Position (cm ⁻¹)	FWHM ($\Delta\nu$)	Peak Int. I_p (%)	Band Int. I_{Band} (%)
ADP	560	10.6	8.95	8.89
	537	9.8	18.10	16.61
	475	12.0	19.98	22.40
	456	10.8	6.9	6.98
	396	4.0	17.75	6.71
	334	14.5	28.29	38.41
KDP	561	14.84	8.76	10.95
	529	11.35	15.91	15.21
	473	14.53	12.37	15.13
	449	18.92	6.72	10.70
	388	5.27	29.39	13.03
	356	15.51	26.85	34.98
$K_{.95}(NH_4)_{0.05}H_2PO_4$	563	13.33	10.85	12.82
	538	11.03	18.43	18.02
	474	14.14	19.09	23.86
	452	13.07	4.02	4.64
	396	4.27	19.47	7.37
	337	13.33	28.19	33.30
$K_{.90}(NH_4)_{0.10}H_2PO_4$	559	13.55	10.57	13.43
	537	9.81	17.17	15.77
	477	11.26	17.48	18.44
	458	10.94	10.72	10.99
	396	4.01	17.49	6.60
	337	14.01	26.49	34.77
$K_{.80}(NH_4)_{0.20}H_2PO_4$	559	14.47	8.83	10.57
	529	11.54	15.54	14.84
	470	17.28	14.83	21.14
	445	16.21	5.05	6.78
	388	5.21	29.71	12.79
	354	15.71	26.07	33.88
$K_{.50}(NH_4)_{0.50}H_2PO_4$	559	11.84	8.29	8.77
	531	11.30	16.19	16.35
	472	13.56	14.97	18.09
	449	12.09	6.24	6.74
	390	4.95	26.97	11.95
	350	15.60	27.32	38.09

Crystal	Band Position (cm ⁻¹)	FWHM ($\Delta\nu$)	Peak Int. I_p (%)	Band Int. I_{Band} (%)
$K_{.05}(NH_4)_{0.95}H_2PO_4$	564	10.17	8.82	8.46
	538	10.97	19.03	19.60
	472	13.98	20.16	26.60
	442	2.22	3.96	0.80
	396	3.80	18.50	6.63
	336	13.55	29.52	37.75

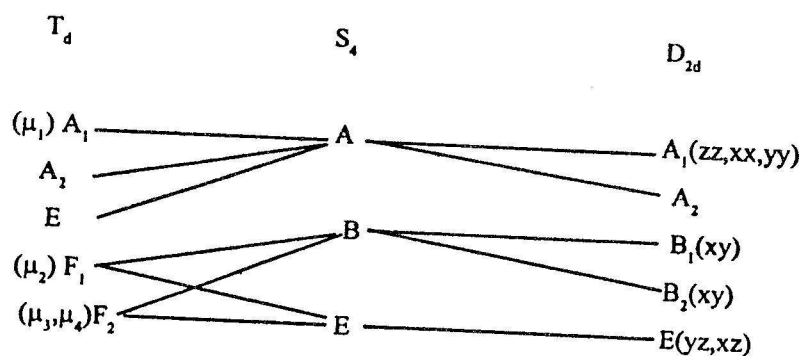
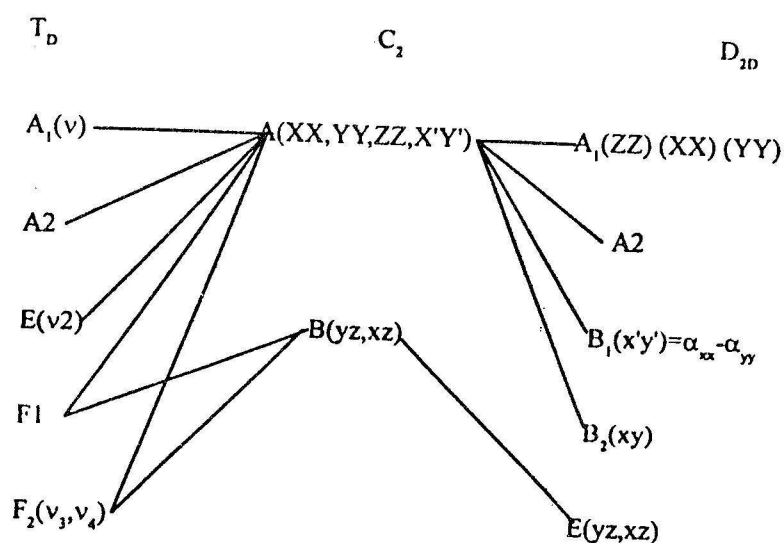
The relative intensity ratios of some modes and relative (%) intensities deduce from deconvolution are given in table 3.

Table 3. Relative intensity ratios and relative (%) intensities of modes as deduced from deconvolution

MODE POSITION cm ⁻¹	560/537	475/456	396/334	560+537	475+456	396+334
ADP	0.54	3.20	0.175	25.5	29.38	45.12
$K_{.05}(NH_4)_{.95}$	0.43	32.53	0.176	28.14	27.40	44.38
$K_{.5}(NH_4)_{.5}$	0.54	2.68	0.311	25.12	24.83	49.04
$K_{.8}(NH_4)_{.2}$	0.71	3.12	0.377	25.41	27.92	46.67
$K_{.9}(NH_4)_{.1}$	0.85	1.68	0.190	29.20	29.43	41.37
$K_{.95}(NH_4)_{.05}$	0.71	5.14	0.221	30.84	28.50	40.67
KDP	0.72	1.41	0.373	26.16	25.83	48.01

The unit cell of KH_2PO_4 Contain 32 atoms with four formula unit per unit cell. A group theoretical analysis of the total number of vibrations transforming as a given irreducible representation has been worked out.

Accordingly, in PE phase, there will be a total number of $4A_1 + 4A_2 + 7B_1 + 7B_2 + 13E$ irreducible modes whereas in FE phase, one will have $(11A_1 + 11A_2 + 13B_2 + 13B_2)$ modes, out of which internal modes in PE phase will be of $(3A_1 + 3A_2 + 5B_1 + 5B_2 + 7E)$ type and in FE phase of $(8A_1 + 8A_2 + 7B_1 + 7B_2)$ type. B_2 and E mode in PE and A_1 , B_1 and B_2 type mode in FE phase will be IR active whereas all modes except A_2 Type (In PE phase) will be Raman active. In order to confirm the site of each molecular species, the correlation tables considering different sites can therefore be analysed. PO_4^{3-} in free state belongs to T_d and has four distinct frequencies $\nu_1(A_1)$ 937 cm⁻¹ $\nu_2(E)$ at 420 cm⁻¹ and $\nu_3, \nu_4(F_2)$ at 560 and 1022 cm⁻¹. All vibrations being active in Raman and ν_3, ν_4 being simultaneously active in IR spectra. Similarly, NH_4^+ also show $\nu_1(3022\text{cm}^{-1}), \nu_2(1666)\text{cm}^{-1}, \nu_3(3128\text{cm}^{-1})$ and $\nu_4(1397\text{cm}^{-1})$. Both these ions can occupy either S_4 , or C_2 site. The correlation diagram for them under D_{2d} space group are given in Table 4 and 5.

Table 4. Correlation Table for PO_4^{-3} in KDP (S_4 site)Correlation Table for PO_4^{-3} in KDP (C_2 site)

It is clear from the table that A_1 and E under C_2 are correlated to A whereas F_2 to $A + B$. On the other hand assuming S_4 site $A_1 \rightarrow A$, $E \rightarrow A + B$ and $F_2 \rightarrow B + E$. Similar correlation can also be established for O-H..O molecular entity. There can be two different sites possible for it viz. C_2 and C_i depending upon, whether the H-bond is linear or not. It may be noted that structural evidences give indication of some bending of H-atom in O-H bond. This will change the potential of H-atom whose displacement is considered as the major triggering agent in phase transition till now.

In the Raman spectra ν_1 is observed as a strong symmetric mode at 916 cm^{-1} in

KDP and 921 cm^{-1} in ADP, whereas ν_4 is observed as a very weak broad response $\cong 1020\text{ cm}^{-1}$.

They could not be used for site determination. However, ν_2 and ν_3 show some symmetry and after deconvolution can be resolved. ν_3 has two component at 560 and 537 cm^{-1} in ADP with relative intensity ratio of $\cong (1:2)$, whereas in KDP it is at 563 and 538 cm^{-1} with intensity ratio $\cong (1:1.5)$; ν_2 appears at 475 and 456 cm^{-1} with 475 component being very strong. The band width $\nu_{1/2}$ is also same for both components of the same modes. Under C_2 site, ν_2 should have two components of almost equal intensity. Whereas, for S_4 site it should have one component (A type) stronger than other, The precise ratio of $1:2$ for ν_3 mode and their behaviour in mixed crystals suggest that site should be preferably C_2 and not S_4 . The apparent contradiction in $\nu_{1/2}$ component not having same intensity ratio may be resolved if one consider either 396 cm^{-1} as a component of ν_2 otherwise 475 cm^{-1} mode having some contribution from combination modes of lower symmetry. The remaining two modes at 396 and 334 cm^{-1} in Raman spectra can be assigned only after considering their behaviour in mixed crystals. The parameter of these modes for mixed crystals of ADP and KDP are summarised in Table 2. It is obvious from the table that the behaviour of all these modes changes in going from the KDP to ADP. However, the frequency of only three modes changes. The notable change are ; the band intensity ratio of three pairs of band $560/537$; $475/456$ and $396/334$ are different for KDP and ADP for mixed crystals of $K_x(\text{NH}_4)_{1-x}\text{H}_2\text{PO}_4$ for $x < 20$, the behaviour is either costant or changes systematically similarly, for $x > .90$ changes matches with ADP features. However, for $x \cong 20$ and $.50$ the changes are completely different.

In order to understand the significance of these changes, the structural changes in mixed crystals can be analysed. Mixed crystals of KDP-ADP are not studied thoroughly due to problem of growing mixed crystals owing to lattice parameter mismatch. However, dielectric, electrical conductivity and X-ray and IR spectra of these crystals were reported recently. No significant change in the IR spectra of mixed systems that from ADP could be observed. Lattice constant, however, increase with increasing concentration of ADP. Effect of ADP and KDP impurities on the dielectric behaviour are also reported by a number of workers at low frequency and impurity concentration. T_c and domain wall freezing temperatures are lowered with the concentration of ADP in KDP. Structural studies on $(\text{NK}_4)_{1-x}\text{K}_x\text{H}_2\text{PO}_4(\text{KADP}_x)$ have also been reported. Boukhris et al¹⁶. It has been established to be analogous to RADP_x , the widely investigated mixed crystal of the family. Accordingly, KADP_x may show ferroelectricity or antiferroelectricity depending upon the range of x . In some concentration range these crystals may show a glassy behaviour analogous to spin glass system. For the range $0.23 < x < 0.85$ the disappearance

of the FE or AFE phase transition is observed by Fukami et al.¹⁷. In the in between concentration shows glassy behaviour with tetragonal crystal structure which remains upto 20K. The disappearance of FE or AFE phase has been observed in the composition range $0.20 < x < 0.85$ for KADP_x and dielectric measurement has shown the glassy low frequency dispersion. Furthermore, structural studies have established that these mixed crystals maintained their I 42d structure up to 20K^{18,19}. High resolution crystal structural data for $\text{KADP}_{0.11}$ at different temperature revealed that crystal structure is closer to ADP with elongation of c-parameter. No significant shift of the average of the heavy atom positions as a function of temperature is observed, P-O distance remaining independent of temperature. The O-O distance decreases by $0.01 \text{ \AA}$ at 154K in comparison to 300K. The apparent changes are related with contraction of a(b) cell parameter and slight increase of the Θ .

On the basis of the change in the average P-O-H(O) angle, it is argued that the behaviour of H-atom is not same in pure and mixed systems. In KDP one has assymetric configuration of the H-bands O...H(O)--O and O-H(O)... O. This H(O) H(O) distance implies a very short distance between the two possible H-sites. The NH_4 is linked to four of the eight neighbouring PO_4 tetrahedron by hydrogen bonds N...O., which are shown to be temperature independent in mixed system. On other hand, analysis of changes associated with PO_4 in both ADP and KDP_x (0.89), i.e. the P-O..N^b and O-O..O^c angles, the changes were attributed to the deformation of the PO_4 tetrahedron. In the mixed systems therefore one aspects the disorder motion of PO_4 Tetrahedron to be reduced, whereas the distribution increasing with increased composition of $\text{NH}_4\text{H}_2\text{PO}_4$. In the glassy phase, however, the distribution will be random resulting into less distortion, Distortion PO_4 will increase the line width of all the modes shown in table-2 for KDP in comparison to ADP. Interestingly, for mixed crystal upto $x=0.90$, the linewidth of all the modes decrease as expected, whereas for $x=0.05$, the width are almost similar to ADP. However, for intermediate compositions $x = 0.20$ and 0.50 , the width are similar to KDP. This can be taken as as evidence of glassy structure in these compositions. This indicates that all the bands reported in table 2 are associated with PO_4 ion. The relative percentage intensity of 334 cm^{-1} band is however insensitive to composition change, whereas 396 cm^{-1} mode is having almost twice intensity in KDP in comparison to ADP (See Table 3). Another interesting aspects is the appearance of these bands at distinct position. In KDP, the two band are at 388 and 356 cm^{-1} , whereas in ADP these are at 396 and 334 cm^{-1} . For $x = 0.50$ the position is some what in between i.e. at 390 and 350 cm^{-1} . Thus the observed spectral data corroborate the inferences drawn from structural results and are in good agreement.

O-H..O BANDS IN MIXED CRYSTALS :

Hydrogens in KDP family crystals are well known to form strong H-bands and the

complicated vibrational spectra of O-H...O exhibit very interesting precursor aspects of phase transition. It is well known that the four H-bonds in the primitive unit cell of the KDP crystal are correlated to form the collective tunneling modes of A_2 , B_2 and E symmetric in the PE phase, compatible with the D_{2d} lattice symmetries. The soft mode, which is of B_2 symmetry is well known to be a coupled mode between the proton tunneling mode B_2 phono mode carrying the c-axis lattice polarization. The high frequency vibrational Raman bands of O-H...O with peaks around 27,00, 2400 and 1800 cm^{-1} have been observed only in A_1 and B_1 mode spectra²⁰ and analysed in terms of the single particle tunneling. The interpretation of three bond structure of O-H...O bonds in KDP crystal has not been clearly explained. However attempts have been made to explain its origin as proton tunneling and Fermi resonance between the O-H stretching mode and an overtone of the bending mode $2y^{\text{OH}}$ or $2d^{\text{OH}}$. In 1983 Kim and Choi proposed an explanation based on strong coupling theory involving the anharmonic interaction between the stretching vibrations of H-atom (O - H - O) and the stretching vibration of H-bond (O-H...O). They observed no change in the bond structure in B_1 and A_1 symmetry spectra either in the PE or FE phase. Even in melt system the bond spectra remains intact. This has been taken as an evidence of O-H...O bond shape being independent of the lattice part of spectrum. From there results, it is concluded that the intensity enhancement of ν_s (P-O-P) and decrease in the intensity of 188 cm^{-1} mode associated with zero phonon bond in strong coupling theory in melt can then be taken as the characteristic of glassy structure in KDP type system. This is due to the sensitivity of zero phonon bond to coupling strength which will reduce in glassy structure which may be taken as diluted low concentration system of O-H-O bonds in melting comparison to crystalline one.

These inferences can be taken as the basis for analysing the bond structure appearing in DRIFT spectra for mixed system of $(\text{NH}_4)_x\text{K}_{1-x}\text{H}_2\text{PO}_4$.

In all the mixed systems analysed by us, three bands are observed at 1752, 2400 and 2720 cm^{-1} in DRIFT spectra (fig. 1). The lowest band frequency is unchanged in all the systems, whereas the other two bands shifts slightly (10 cm^{-1} in going from KDP to ADP). However the intensity pattern changes in a more systematic way. The intensity of 1752 cm^{-1} band increasing in intermediate compositions. These changes can immediately be correlated with glassy structure as discussed above. This is further supported by the fact that PO_4 internal modes also gain intensity as expected in the glassy phase. From these correlations the systems with $x = .20$ or above are essentially the glassy structures. Moreover, the independence of band positions with composition can be taken as their origin being essentially single particle motion. The position correlation suggest the linear nature of H-bond.

The IR temperature dependent data also gives the similar trend for these modes. The other notable changes in KDP in going from PE to FE phase is the appearance of a doublet at 656 and 648 cm^{-1} alongwith a broad band peaking around 1305 cm^{-1} getting

symmetric and two peaks at 1045 and 910 cm^{-1} gaining intensities. In the spectra of ADP this doublet does not appear whereas in ADP having 11% KDP it is visible as a very weak band at low temperature. Thus the origin of this may lie in PO_4 internal mode coupled with K- PO_4 sublattice. This observation is the direct proof of PO_4 tetrahedra being involved in ferroelectricity. In ADP, a strong band at 1397 cm^{-1} is observed which is absent in KDP, thus associated with NH_4 . The more symmetrical nature of 1281 and 1089 cm^{-1} modes in ADP at low temperature and the latter being splitted into two absorption minima clearly indicate the decoupling of H-motion with optic phonon in ADP whereas the same is coupled in KDP. Thus our assignment of 1286 cm^{-1} band due to H-bonding is further corroborated. Further intensity enhancement of ν_1 and $\nu(\text{PO}_4)$ mode at low temperature clearly reveals the PO_4 getting more ordered in FE phase supporting the picture that order-disorder type transition is connected with PO_4 distorted tetrahedra getting ordered in FE phase.

Conclusion

The present study leads to the following conclusions :

The observed DRIFT spectra of mixed crystals reflects the formation of glassy phase in intermediate composition range. The PO_4 internal modes becomes bands and gains intensity in glassy structure.

The site of the PO_4 as well as the nature of the O-H-O bond is deduced from the observed changes. The possibility of tetrahedra occupying C_2 site is supported by the present results.

Temperature dependent spectral changes support the order-disorder model where ordering of tetrahedral ions leads to ferroelectricity.

The nature of coupling of H-bond motion in ADP and KDP is different and the motion is decoupled in ADP at low temperature phase.

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