

## Raman studies on potassium-ammonium dihydrogen phosphate systems [(KDP)<sub>1-x</sub>(ADP)<sub>x</sub>]

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We have studied pressed-pellet samples of potassium-ammonium dihydrogen phosphate [(KDP)<sub>1-x</sub>(ADP)<sub>x</sub>] by Raman scattering for  $x=0$ ,  $x=0.5$ , and  $x=1$  at room temperature and liquid-nitrogen temperature. The liquid-nitrogen-temperature spectra of pure KDP and ADP pellets showed the characteristics of their ferroelectric and antiferroelectric phases, respectively. However, the low-temperature spectra of the (KDP)<sub>0.5</sub>(ADP)<sub>0.5</sub> pellets showed features that were characteristic of a structural glass formation as found previously in single-crystal samples of rubidium-ammonium dihydrogen phosphate [(RDP)<sub>1-x</sub>(ADP)<sub>x</sub>], such as the persistence of the continuum soft-mode structure and local freezing of NH<sub>4</sub><sup>+</sup> units.

### INTRODUCTION

Mixed crystals of the potassium dihydrogen phosphate (KDP) family have attracted much attention recently as illustrative systems in which we can study the physics of competing interactions.<sup>1,2</sup> The representative crystals of this family, ferroelectric KH<sub>2</sub>PO<sub>4</sub> (KDP) and antiferroelectric NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> (ADP), cannot be grown into a large mixed single-crystal (KDP)<sub>1-x</sub>(ADP)<sub>x</sub> in the full range of  $x$  due to a large mismatch in lattice constants between the two mixing crystals. Consequently, (KDP)<sub>1-x</sub>(ADP)<sub>x</sub> mixed crystals have been studied only at the two ends near  $x=0$  and  $x=1$ ,<sup>3-6</sup> leaving out many interesting phenomena such as dipole glass formation, structural frustration, etc., as found in the mixed crystal Rb<sub>1-x</sub>(NH<sub>4</sub>)<sub>x</sub>H<sub>2</sub>PO<sub>4</sub>, which can be grown in the full range of  $x$  and has been studied extensively in detail by many research workers.<sup>7-20</sup>

However, solid solutions of (KDP)<sub>1-x</sub>(ADP)<sub>x</sub> can be made for the full range of values of  $x$  and can be used to study something of the competing interactions in these solid solutions. Competing interactions influence the lattice dynamics of the system, which can be studied by Raman scattering. Raman studies of the single-crystal Rb<sub>1-x</sub>(NH<sub>4</sub>)<sub>x</sub>H<sub>2</sub>PO<sub>4</sub> indeed elucidated the freezing dynamics of the paraelectric crystal into the glass state.<sup>16,17</sup>

We report here our results of Raman studies on the pressed-pellet samples of K<sub>1-x</sub>(NH<sub>4</sub>)<sub>x</sub>H<sub>2</sub>PO<sub>4</sub> for  $x=0$ ,  $x=0.5$ , and  $x=1$ . Raman spectra of pure KDP ( $x=0$ ) and pure ADP ( $x=1$ ) pellets also deserve attention because the previous studies of KDP Raman spectra were mostly concerned with the  $B_2$ -symmetry soft mode,<sup>21,22</sup> the  $E$ -mode plateau band<sup>23-25</sup> and O—H···O bands,<sup>26,27</sup> while most previous studies of ADP Raman spectra were limited until very recently<sup>28</sup> to the paraelectric phase<sup>29</sup> because of powdery shattering of the ADP crystals at the antiferroelectric phase transition. Raman spectra of KDP crystals have recently been reexamined carefully to determine the correct site symmetries of PO<sub>4</sub> in the crystal.<sup>30</sup>

### EXPERIMENT

Raman spectra were obtained at both room temperature and liquid-nitrogen temperature by use of an argon-

ion laser (Spectra Physics 165) operated at 4880 Å, a double-grating spectrometer (Spex 1401), and photon-counting system (Spex). An interference filter was used to block out laser-tube plasma lines and the Brewster-angle method was employed by a proper control of the polarization and the angle of incidence of the laser. The spectra were completely free of stray light and spurious plasma lines above 50 cm<sup>-1</sup> away from the exciting laser line, and meaningful data could be collected to within a few cm<sup>-1</sup> of the laser line. For pellet samples of (KDP)<sub>0.05</sub>(ADP)<sub>0.5</sub> homogeneous solutions of (KDP)<sub>0.5</sub>(ADP)<sub>0.5</sub> were slowly evaporated at a temperature of about 90°C until all the water was removed. The dried mixture was composed of microcrystallites which were then ground in a mortar, and pressed under vacuum to a pressure of about 30 tons per square inch to form pellets of 6 mm diameter and 1 mm thickness which had glassy-looking surfaces. Pure KDP and ADP pellets were made directly from the crystalline powders as supplied by B. D. H. Laboratory Chemicals, Ltd. Sample homogeneity was good to the degree that we did not see any change in the Raman spectra as the incident laser spot was moved on the surface from the center to the rim of the mixture pellet.

### RESULTS AND DISCUSSIONS

#### Pure KDP and ADP Pellets

We show in Figs. 1(a) and 1(b) the room-temperature Raman spectra of KDP and ADP pellets. We expect both translational and rotational optical-phonon bands in the lattice vibrational spectra of the KDP-family crystals.<sup>31</sup> Using the assignments favored by previous work on KDP-family crystals,<sup>16,32,33</sup> the 91-cm<sup>-1</sup> KDP band and the corresponding 68-cm<sup>-1</sup> ADP band may be assigned as the transverse-optic phonons corresponding to K-PO<sub>4</sub> and N-PO<sub>4</sub> translatory vibrations along the  $c$  axis. The frequency difference comes mainly from force-constant changes produced by the different K-P and N-P distances in the KDP and ADP crystals, respectively. The broad 182-cm<sup>-1</sup> KDP band and 174-cm<sup>-1</sup> ADP band may be assigned to the PO<sub>4</sub> librational bands. The very weak shoulder band at around 280 cm<sup>-1</sup> in the ADP sample

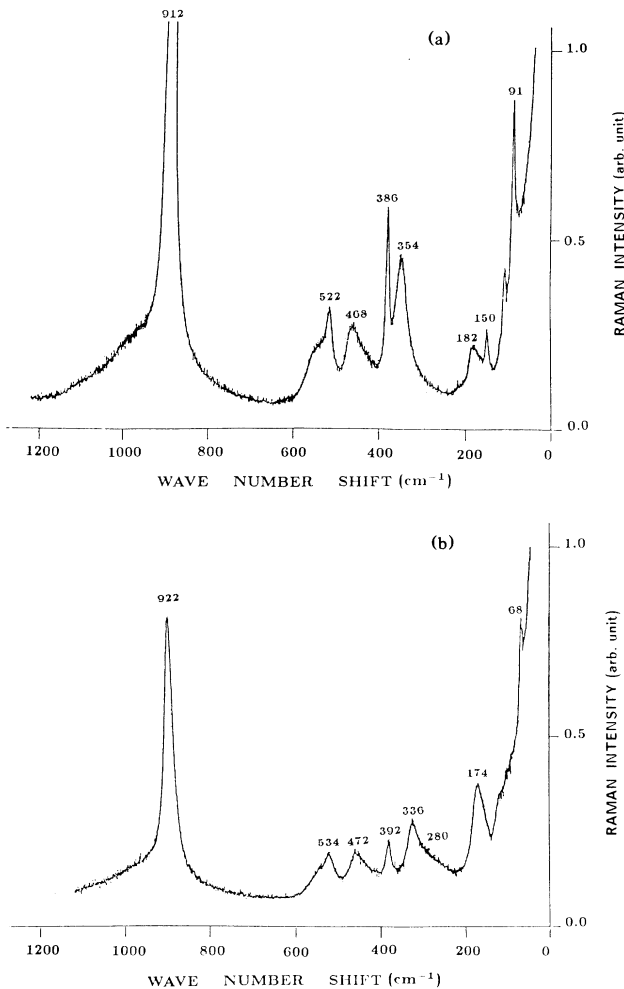


FIG. 1. (a) Room-temperature Raman spectra of KDP pellet. (b) Room-temperature Raman spectra of ADP pellet.

may correspond to the  $\text{NH}_4$  librational band. The narrow bandwidth of the translational modes in the completely random polycrystalline powder samples may imply a very flat dispersion curve near the zone center for the translational optic phonons, while the broad bandwidth of the librational modes implies that the rotational optic phonons are susceptible to anharmonic phonon-phonon interactions and the dispersion curves are not flat near the zone center. With two molecular units in the primitive unit cell and possible transverse-optic (TO)-longitudinal-optic (LO) splittings of the polar lattice modes several other lattice vibrational bands are expected, although some of them may be degenerate or very weak. We can easily see in the KDP spectra a broad Rayleigh-wing band, which may be attributed to the  $B_2$ -symmetry soft mode or the Slater configurational mode. In the ADP spectra many lattice bands are observed to be much weaker than the corresponding bands of KDP, which is usually considered to be a result of the hydrogen-bonding interactions between  $\text{PO}_4$  groups and  $\text{NH}_4$  groups in ADP crystals.<sup>16,34</sup>

Raman bands in the region from 320 to  $1000\text{ cm}^{-1}$  show the internal modes of vibration of the  $\text{PO}_4$  groups

which are influenced by the site symmetries of the  $\text{PO}_4$  group in the microcrystallites. The dominant band, due to the totally symmetric stretching model of  $\text{PO}_4$  is observed at  $922\text{ cm}^{-1}$  in ADP and is much weaker and broader than the corresponding  $912\text{-cm}^{-1}$  band of KDP. This may be due to the hydrogen-bonding interactions between  $\text{PO}_4$  and  $\text{NH}_4$  groups in ADP, particularly as the other  $\text{PO}_4$  vibrational bands in ADP also seem to be broader and weaker than those of KDP.

In Figs. 2(a) and 2(b) we show the Raman spectra of pure KDP and ADP pellets observed at liquid-nitrogen temperatures. The KDP spectra show lattice modes below  $250\text{ cm}^{-1}$  while ADP lattice modes are observed between 50 and  $320\text{ cm}^{-1}$ . The  $294\text{-cm}^{-1}$  band, appearing only in ADP spectra, may be assigned to the  $\text{NH}_4$  librations. In the low-temperature ferroelectric phase of KDP we expect more lines to appear than in the room-temperature paraelectric phase spectrum. This is due to splitting of the degenerate  $E$  modes of the  $D_{2d}$ -symmetry paraelectric phase into  $B_1$  and  $B_2$  modes of the  $C_{2v}$ -symmetry ferroelectric phase and Raman-inactive  $A_2$  modes of the  $D_{2d}$ -symmetry phase becoming Raman active in the  $C_{2v}$ -symmetry phase at temperatures below the ferroelectric transition.<sup>31</sup> In ADP spectra, in addition to the splittings and new lines due to the structural transformation from  $D_{2d}$  symmetry to  $C_{2v}$  symmetry as for KDP, we expect more new lines to appear because the unit cell is doubled from two to four molecules in the primitive unit cell due to the additional antiferroelectric ordering in ADP. Even though we have a translational mode as low as  $68\text{ cm}^{-1}$  for ADP already at room temperature in the paraelectric

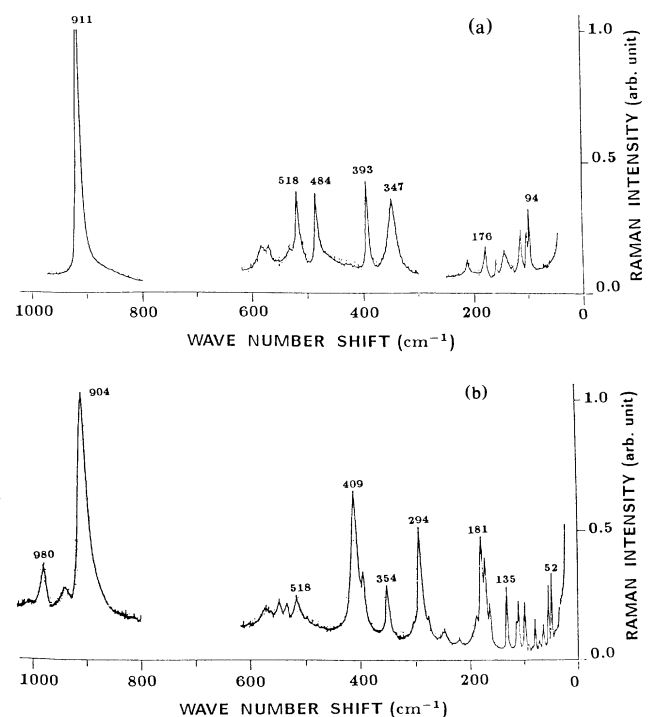


FIG. 2 (a) Raman spectra of KDP pellet at liquid-nitrogen temperature. (b) Raman spectra of ADP pellet at liquid-nitrogen temperature.

phase, some of the low-frequency bands in the low-temperature antiferroelectric phase may stem from the zone-boundary folded acoustic-branch phonons of the paraelectric phase. The broad Rayleigh-wing band in the lattice spectrum of paraelectric KDP is seen to vanish completely in the low-temperature spectra of ferroelectric KDP.

Internal vibrational modes of  $\text{PO}_4$  groups are observed above  $350\text{ cm}^{-1}$ . The totally symmetric stretching band of  $\text{PO}_4$  becomes much stronger and narrower (note in the figures the changes in photon counter gains and scan rates) at low temperature for KDP, but the corresponding  $\text{PO}_4$  band of ADP remains broad and weak at low temperature, probably due to the persistence of the interactions with  $\text{NH}_4$  groups through hydrogen bonds. Splittings of the bands and the appearance of new bands in the low-temperature spectra of  $\text{PO}_4$  internal modes in both KDP and ADP seems to imply different site symmetries for the  $\text{PO}_4$  groups between the tetragonal and orthorhombic phases<sup>16,33</sup> rather than the same site symmetry of  $\text{PO}_4$  in the two different phases.<sup>29,30</sup> However, there seems to be a perturbative distortion of  $C_2$  ( $C_1$  for ADP) symmetry already in the paraelectric phase, which may give some leakage of lower symmetries in the paraelectric Raman bands of  $\text{PO}_4$  internal modes.<sup>16</sup>

#### (KDP)<sub>0.5</sub>(ADP)<sub>0.5</sub> mixed pellet

Figures 3(a) and 3(b) show the Raman spectra of a (KDP)<sub>0.5</sub>(ADP)<sub>0.5</sub> pellet observed at room temperature and liquid-nitrogen temperature. The room-temperature lattice-mode spectra seem to indicate that the mixed microcrystals in the pellet have the same structure as pure KDP (or ADP) but with a lattice constant partway between that of KDP and ADP. Some lattice modes are seen to show the one-mode behavior. For example, the translational lattice band is observed at around  $75\text{ cm}^{-1}$ , intermediate between the corresponding  $68\text{-cm}^{-1}$  band of ADP and the  $91\text{-cm}^{-1}$  band of KDP; the  $\text{PO}_4$  librational band at around  $180\text{ cm}^{-1}$ , intermediate between the corresponding  $174\text{-cm}^{-1}$  band of ADP and the  $182\text{-cm}^{-1}$  band of KDP, etc. We can also see the Rayleigh-wing band overlapped underneath the lattice bands and very weak  $\text{NH}_4$  librational band as a shoulder to the lowest-frequency internal band. Bands due to the internal modes of the  $\text{PO}_4$  groups all show one-mode behavior, with the frequencies falling between those of pure KDP and ADP. This also seems to indicate that the microcrystallites in the (KDP)<sub>0.5</sub>(ADP)<sub>0.5</sub> pellets do have lattice constants in between those of KDP and ADP crystals. The internal-mode bands, especially the  $\text{PO}_4$  symmetric stretching band, are as weak as those of pure ADP but closer in frequencies to those of pure KDP.

At low temperature the lattice-mode spectrum continues to show the broad Rayleigh-wing band (Slater configurational mode) in contrast to the low-temperature spectra of pure KDP and pure ADP. This persistence of the  $B_2$ -symmetry soft-mode band was previously observed in the crystalline dipole glass of  $\text{Rb}_{1-x}(\text{NH}_4)_x\text{-H}_2\text{PO}_4$ .<sup>16,17</sup> Several new bands emerge between  $90$  and  $180\text{ cm}^{-1}$  in the low-temperature spectrum, which seems to indicate that the  $\text{NH}_4$  units get frozen near the liquid-

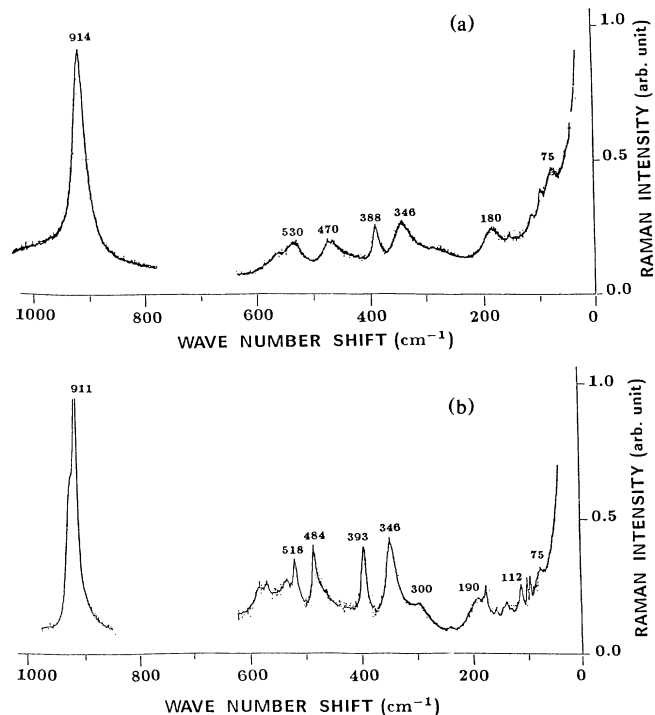


FIG. 3 (a) Raman spectra of (KDP)<sub>0.5</sub>(ADP)<sub>0.5</sub> pellet at room temperature. (b) Raman spectra of (KDP)<sub>0.5</sub>(ADP)<sub>0.5</sub> pellet at liquid-nitrogen temperature.

nitrogen temperature and no longer give the paraelectric random-phase perturbations below the freezing point.<sup>1</sup> These new lattice bands seem to correspond more to low-temperature ferroelectric KDP bands, rather than ADP bands associated with the antiferroelectric structure. However, the  $75\text{-cm}^{-1}$  translational lattice band and the  $190\text{-cm}^{-1}$   $\text{PO}_4$  librational band remain to show the same room-temperature characteristics in bandwidth and intensity. The low-temperature  $\text{NH}_4$  librational band also remains as a broad single band at around  $300\text{ cm}^{-1}$ , in contrast with the corresponding  $294\text{-cm}^{-1}$  band of the pure ADP which shows the correlation splitting at liquid-nitrogen temperature.

The internal-mode spectra, which at room temperature shows more resemblance to the ADP spectrum, seems at liquid-nitrogen temperature to have more resemblance to the KDP spectrum. The symmetric  $\text{PO}_4$  stretching band is seen to be split into two peaks at  $911$  and  $919\text{ cm}^{-1}$  at liquid-nitrogen temperature. The  $911\text{-cm}^{-1}$  band is stronger and narrower, as for the KDP band, while the  $919\text{-cm}^{-1}$  band is weaker and broad, as for the ADP band. The internal-mode spectra of the (KDP)<sub>0.5</sub>(ADP)<sub>0.5</sub> pellet thus seem to suggest that the  $\text{PO}_4$  groups in the mixture pellet may have at liquid-nitrogen temperature the same site symmetry as in the ferroelectric KDP even though the persisting Rayleigh-wing soft-mode band suggests no ferroelectric ordering at this low temperature. In the scale of microcrystallites the (KDP)<sub>0.5</sub>(ADP)<sub>0.5</sub> system thus seems to have average lattice constants between those of pure KDP and ADP crystals. The low-temperature lattice structure of the mixed microcrystallites may favor a

slightly orthorhombic ( $C_{2v}$ ) distortion as for pure KDP and ADP crystals, but the Slater configurations of protons remain disordered as if the competing interactions between the two ordering fields of the ferroelectric KDP and antiferroelectric ADP lattices frustrate any preferred ordering of the Slater proton configurations at low temperature. The weak orthorhombic distortion of the mixed  $(\text{KDP})_{0.5}(\text{ADP})_{0.5}$  system may thus bring about orthorhombic signature for some vibrational modes but not strong enough for some other vibrational modes, such as the translational optic phonon at around  $75 \text{ cm}^{-1}$ , the  $\text{PO}_4$  librational mode at around  $190 \text{ cm}^{-1}$ , the  $\text{NH}_4$  librational mode at around  $300 \text{ cm}^{-1}$ , the  $\text{PO}_4$  symmetric stretching modes, and most important the Rayleigh-wing soft mode (Slater configurational mode), which all continue to show the tetragonal signatures.

### CONCLUSION

Raman spectra of  $(\text{KDP})_{1-x}(\text{ADP})_x$  pressed-pellet samples are found to depict important features characteristic of the structural glass formation as observed previously in the well-characterized but expensive samples of single-crystal  $(\text{RDP})_{1-x}(\text{ADP})_x$ .<sup>16,17</sup> Low-temperature changes in the Raman spectra of pure KDP, pure ADP, and  $(\text{KDP})_{0.5}(\text{ADP})_{0.5}$  pellet samples seem to reveal that

the lattice constants and  $\text{NH}_4$ -bond concentrations are among the most important parameters fixing the proton-ordering configurations and the degree of structural distortions at low temperatures. The simultaneous occurrence of the proton ordering and the displacive lattice distortions observed in pure KDP crystals<sup>35</sup> does not seem to be obvious in the mixed  $(\text{KDP})_{0.5}(\text{ADP})_{0.5}$  system. A recent suggestion by Ishibashi and Suzuki<sup>36</sup> of a possible ferroelectric ordering with a [110] polarization in the  $(\text{RDP})_{1-x}(\text{ADP})_x$  single-crystal system in the glass-forming range of  $x$  seems to have some bearing on our low-temperature spectra of the  $(\text{KDP})_{0.5}(\text{ADP})_{0.5}$  system, although the theory was found incompatible with the low-temperature dielectric constant measurements along the [110] direction in the  $(\text{RDP})_{0.61}(\text{ADP})_{0.39}$  crystal.<sup>37</sup> The degree of low-temperature orthorhombic distortion in the  $(\text{KDP})_{1-x}(\text{ADP})_x$  system, and thus the freezing point and the glass-transition temperature, should be a function of mixing concentration  $x$ , temperature, and pressure, which will be studied in detail separately in cooperation with the x-ray diffraction studies for a quantitative characterization of the pellet samples.

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