

## Dielectric, NMR and X-ray Diffraction Study of $\text{Cs}_{1-x}(\text{NH}_4)_x\text{H}_2\text{PO}_4$

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Mixed crystals  $\text{Cs}_{1-x}(\text{NH}_4)_x\text{H}_2\text{PO}_4$  of the ferroelectric  $\text{CsH}_2\text{PO}_4$  (CDP) and the antiferroelectric  $(\text{NH}_4)\text{H}_2\text{PO}_4$  were grown with  $x=0.2$  (CADP0.2) in solution. The structural properties of the crystal were analyzed by means of x-ray diffraction. Dielectric measurements at several temperatures and frequencies have been performed along the three crystallographic axes in this sample and also in the fully deuterated CADP0.2 sample (DCADP0.2). NMR experiments were also performed.

### I. INTRODUCTION

$\text{CsH}_2\text{PO}_4$  (CDP) is known to have one dimensional ferroelectric order below  $T=159$  K and a superionic transition at  $T=504$  K on heating [1], whereas  $(\text{NH}_4)\text{H}_2\text{PO}_4$  (ADP) is antiferroelectric below  $T=148$  K [2]. In addition, their paraelectric phases have different structures; CDP is monoclinic with the space group  $P2_1/m$  and ADP is tetragonal with the space group  $I4_2d$ .

In this work we present x-ray, dielectric and NMR results in undeuterated and deuterated  $\text{Cs}_{1-x}(\text{NH}_4)_x\text{H}_2\text{PO}_4$  crystals with  $x=0.2$  in solution.

Crystal quality, a concern for mixed crystals, was excellent. The lattice structure and the space group of CADP0.2 was found to be identical to that of pure CDP at room temperature, monoclinic with the space group  $P2_1/m$ . The obtained lattice parameters were:  $a=7.893(67)$  Å,  $b=6.383(46)$  Å,  $c=4.876(13)$  Å, and  $\beta=107.56(06)$  deg. These values were very close to those in the pure compound [3], with the most significant variation being a small increase in length ( $\sim 0.02$  Å) along the ferroelectric b-axis. The upper limit for  $x$  in the crystals was found to be  $x=0.1\pm 0.1$ . Further chemical analysis of the crystals showed the ammonium concentration to be  $x=0.0473\pm 0.0024$ .

### II. EXPERIMENTAL METHOD

The crystals were grown by controlled evaporation from aqueous solution of 20% molar concentration of ADP and 80% of CDP. In order to perform the x-ray transmission experiments small semi-spherical samples ( $\sim 1$  mm<sup>3</sup>) were prepared. For the dielectric measurements, samples in the shape of thin slides ( $< 1$  mm) were cut perpendicular to the three crystallographic axes, optically polished and silver painted. The temperature (25 K-320 K) and frequency (10 Hz-1 MHz) dependencies of  $\epsilon'$  and  $\tan \delta (= \epsilon''/\epsilon')$  were measured. For the NMR measurements several crystals were pulverized and desiccated. The variation of the spin-lattice relaxation time as a function of temperature was measured.

### III. RESULTS

#### 1. X-ray Transmission Scattering Measurements

#### 2. Dielectric Measurements

Both of the anomalies in  $\epsilon'_b(T)$  and  $\epsilon''_b(T)$  are pretty similar to those observed in the pure compound (Fig. ??). The measured transition temperature ( $T_c=159.3$  K) and the frequency dependence of the anomalies do show small changes due to the amount of ammonium impurities. The transition temperature is shifted  $\sim 3$  K to higher temperatures. The fit parameters of the quasi-1D-Ising model [4,5] suffer significant variations within the increase of concentration: the interactions along the chains decrease from 305 K to 150 K whereas the interactions between the chains increase from 3.6 K to 14 K [6]. At the same time the dielectric permittivity along the c- and a-axes clearly show anomalies around the transition temperature into the ferroelectric phase. These anomalies do not exist in the pure compound.

A striking feature observed in the dielectric measurements is the apparently thermally activated conductivity within the paraelectric phase along the a- and c-axes. Similar dielectric anomalies occur both in many other

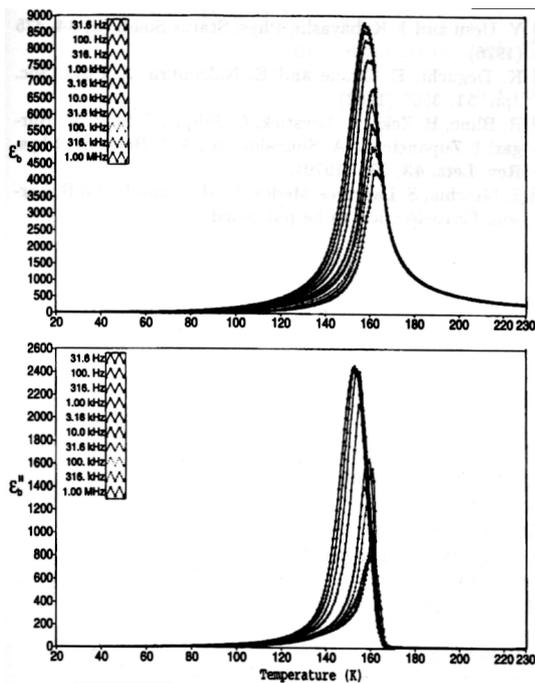


Fig. 1.  $\epsilon'_b(T)$  and  $\epsilon''_b(T)$  for CADP0.2 at several frequencies.

mixed crystals isomorphs of KDP containing ammonium and in pure ADP. Comparison with our results from NMR suggests that the large anomaly is related to conductivity arising from the acid protons or deuterons. The large change in transition temperature resulting from deuteration of CDP and CADP0.2 further suggests conduction by hydrogen. Cycling the experiments several times demonstrates that the conductivity effects present a very large ( $\sim 40$  K) and anomalous thermal hysteresis that depends on the thermal history of the crystal: in the heating runs the conductivity starts at lower temperatures than it stops in the cooling runs. The effect of deuteration in CADP0.2 is similar to that in pure CDP: the transition temperature is shifted from 159.3 K to 276 K, as compared to a shift from 156 K to 268.3 K in the pure compound [4]. The changes in shape, the anisotropy and the frequency dispersion are as described for the undeuterated sample [6]. The temperature and shape of the conductivity effects remain almost independent of the amount of deuteration.

### 3. Nuclear Magnetic Resonance Measurements

The primary mechanism for the  $T_1$  relaxation in our sample is dipolar coupling between hydrogen (H) and phosphorus (P) nuclei in the lattice. H is the more mobile nuclear species, implying that the relaxation time  $\tau$  is characteristic of a specific motion of the H-atom. Assuming liquid-like motion of the hydrogens, for a static NMR field  $H_0$  giving 28 MHz resonant frequency for  $^{31}\text{P}$

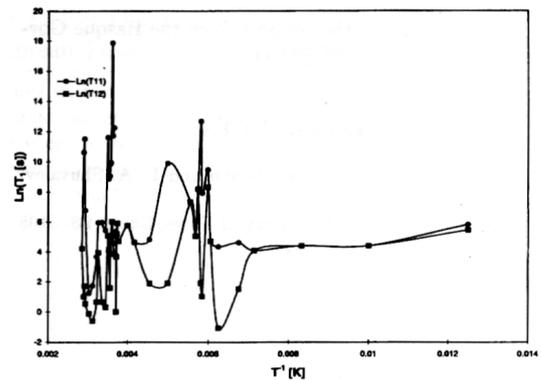


Fig. 2. Natural logarithm of  $T_{11}$  and  $T_{12}$  versus inverse temperature.  $T_{11}$  and  $T_{12}$  correspond to the  $T_1$  value of the two different processes.

and nuclear separation  $r$ , yields  $T_1(\text{min}) = (8.89 \times 10^{57} \text{ m}^{-6} \text{ s}) r^6$ .

The molecular radius of the ammonium ions is considerable smaller than that of the Cs atoms for which they substitute, thus for small concentrations of ammonium the molecular structure will be that of CDP with the ammonium ions free to move within the larger  $\text{Cs}^+$  cation space. Since there is sufficient separation between the oxygen atoms ( $1.4 \times 10^{-10}$  m) for the H atoms in the ammonium groups to fit easily in between, the distance of closest approach will be slightly longer than that of a typical P-H bond (P-H for  $\text{PH}_3 = 1.42 \times 10^{-10}$  m). This distance yields a  $T_1$  value of 0.07 s at the minimum.

We calculated the distance of closest approach for the ammonium atoms from the law of cosines by knowing the length ( $0.958 \times 10^{-10}$  m) and angle ( $104^\circ$ ), obtaining  $2.63 \times 10^{-10}$  m. This yields a  $T_1$  minimum of 2.9 s. We tentatively associate the minimum in the graph of  $\ln(T_1)$  versus temperature (Fig. ??) at 162 K with ammonium hindered rotation at the minima at 328 K with H-interbond motion. We expect that the effect of intrabond motion is too small to detect by  $^{31}\text{P}$  relaxation. By minimizing  $T_1$  as a function of temperature, the frequency  $f$  of the processes at these minima is determined to be 38.9 MHz.

Assuming an activated process with activation energy  $E_A$ , the relaxation times  $\tau$  of the motions at arbitrary temperatures can be calculated from  $\tau = \tau_0 \exp(E_A/kT)$ . Setting the energy of motion equal to the thermal energy at the minimum, we obtain  $E_A = kT \ln(kT/hf)$ , where  $k$  is the Boltzmann's constant and  $h$  is the Planck's constant. This equation yields values of 0.35 eV at 328 K, and 0.16 eV at 162 K. The experimental activation energies  $E_A$  as determined from the slope of the  $\ln(T_1)$  versus reciprocal temperature curves near the minima systematically diverge from these results with increasing temperature. We obtain  $E_A = 0.46$  eV for the acid relaxation at 328 K, and  $E_A = 0.19$  eV for the ammonium relaxation at 162 K. Since intrabond motion has little effect on  $T_1$ , then the process near 328

K most probably corresponds to an actual mobility between lattice sites.

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### REFERENCES

[1] A. I. Baranov, V. P. Khiznichenko and L. A. Shuvalov, *Ferroelectrics* **100**, 136 (1989).

[2] K. Eichele and R. E. Wasylshen, *J. Phys. Chem.* **98**, 3108 (1994).  
[3] Y. Uesu and J. Kobayashi, *Phys. Status Solidi (a)* **34**, 475 (1976).  
[4] K. Deguchi, E. Okaue and E. Nakamura, *J. Phys. Soc. Jpn.* **51**, 3569 (1982).  
[5] R. Blinc, B. Zeks, A. Levstick, C. Filipic, J. Slak, M. Burgar, I. Zupancic, L. A. Shuvalov and A. I. Baranov, *Phys. Rev. Lett.* **43**, 231 (1979).  
[6] S. Meschia, S. Lanceros-Médez, V. H. Schmidt and R. Larson, *Ferroelectrics*, to be published.