PROTONIC CONDUCTIVITY OF MIXED $K_{1-x}(NH_4)_xH_2PO_4$ AND $Rb_{1-x}(NH_4)_xH_2O_4$ "PROTON GLASS" CRYSTALS

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1. Introduction

Crystals of the KDP group are almost pure protonic conductors with proton transfer number $t_p = 1$ [1,2]. Most experimental results indicate intrinsic conductivity at high temperature (over 400K) and extrinsic conductivity at moderate temperature (270 to 400K) [1-5]. The ferroelectric properties of these crystals are due to the intrabond proton motion, but the protonic conductivity involves both the intrabond and interbond proton motion [3-5]. Much research is being devoted to the investigation of proton dynamics of mixed $Rb_{1-x}(NH_4)_xH_2PO_4$ (RADP) [6,7] and $K_{1-x}(NH_4)_xH_2PO_4$ (KADP) [8] crystals. These crystals reveal random freezeout of the protons between two possible positions in O-H...O bonds, because competition between ferroelectric and antiferroelectric ordering acts within the acid-hydrogen-bond network. Moreover, the nonsymmetrical positions of the NH_4 ions change the double well potentials of the acid protons. This means that the enthalpy of formation of hydrogen bonds changes in a random manner too. Taking into account that long range proton diffusion is accompanied by creation and breaking of hydrogen bonds, we expected some peculiarities of conductivity in the mixed crystals.

The purpose of this work is to investigate the effect of Rb-NH_4 and K-NH_4 substitution on protonic conductivity in RADP and KADP crystals. The study was carried out in the temperature range from 140 to 380K.

2. Experimental Details

The experiments were performed on samples of $Rb_{1-x}(NH_4)_xH_2PO_4$ with x = 0.50, 0.77, 0.80, 1.00 and $K_{0.4}(NH_4)_{0.6}H_2PO_4$. The plates of $0.7 \times 0.7 \times 0.08$ cm^3 and $0.5 \times 0.5 \times 0.125$ cm^3 were cut perpendicular to the tetragonal direction and coated with silver paint electrodes. Complex impedance measurements were carried out in the frequency range from 11 Hz to 100 kHz, using a General Electric 1616 bridge. The temperature was stabilized to within ± 0.1K.

3. Experimental Results and Discussion

3.1 d.c. Conductivity

The complex admittance of the sample can be written as

$$Y^*(\omega) = Y'(\omega) + iY''(\omega) = [G(\omega) + \omega C(\omega)]d/s \qquad (1)$$

where $G(\omega)$ and $C(\omega)$ are the conductance and capacitance of the sample, and d and s are its thickness and area, respectively. Figure 1 shows some typical frequency dependences of admittance plotted in the complex plane. The low-frequency parts of these dependences represented by arcs of semicircles display marked dependence on thickness and bulk conductivity. For example, at T = 376K RADP 0.5 and RADP 0.8 have approximately the same bulk conductivity but different thickness (Fig. 1). Therefore this part of the $Y^*(\omega)$ dependence should be related to the admittance of the electrode-crystal boundary. At the low frequency limit the frequency dependence of the bulk conductivity $\sigma(\omega)$ is fit by a

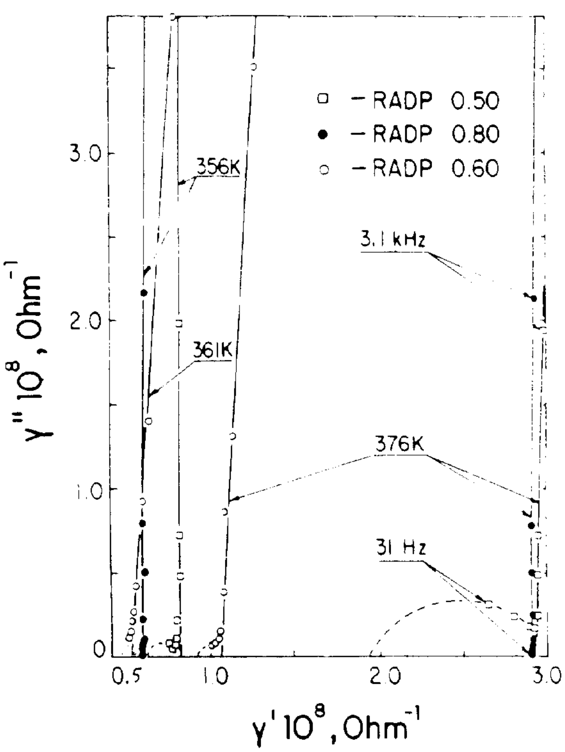

Fig. 1. Complex admittance plots for RADP 0.5, RADP 0.8, and KADP 0.6.

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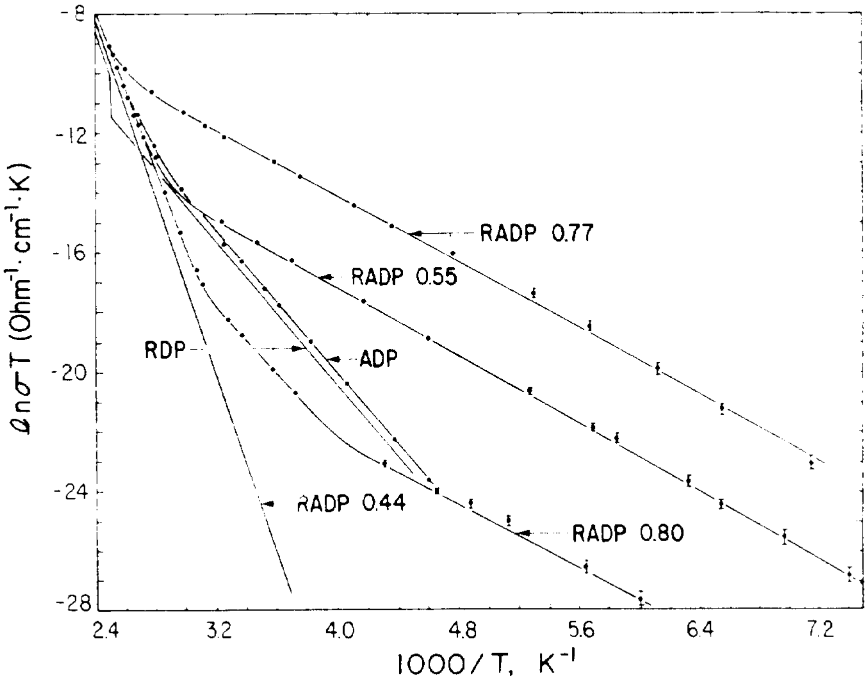

Fig. 2. Arrhenius plots of the d.c. bulk conductivity for different crystals of RADP, RDP and ADP. The RADP 0.44 results are from ref. [9].

Table 1

Activation Enthalpies H_a and Prefactors A in the Arrhenius Law for the Investigated Crystals of KDP Group.

		Intrinsic		Extrinsic I		Extrinsic II	
Crystal	NH_4 concentr.	H_a (eV)	A (Ohm^{-1} cm^{-1} K)	H_a (eV)	A (Ohm^{-1} cm^{-1} K)	H_a (eV)	A (Ohm^{-1} cm^{-1} K)
RDP	0	1.04	$8x10^9$	0.50	25	-	-
RADP	0.4	1.02	$9x10^9$	-	-	-	-
RADP	0.50	1	10^9	-	-	0.24	$3x10^{-3}$
RADP	0.77	1	10^9	-	-	0.23	$3x10^{-2}$
RADP	0.80	0.95	$2x10^9$	0.49	1.5	0.23	$3x10^{-6}$
ADP	1.00	1.05	$5x10^9$	0.51	37	-	-
KDP	0	0.82	$3x10^5$	-	-	-	-
KADP	0.60	-	-	0.48	8.1	-	-

straight line and the d.c. bulk conductivity $\sigma_{dc} = \sigma(O)$ is determined as the point of intersection of this line with the real axis (Fig. 1).

In accord with the results of more early works [3,4,9] the temperature dependences of σ_{dc} for pure RDP and ADP are quite similar and display two temperature regions where they can be fit by Arrhenius laws

$$\ln \sigma_{dc}T = A\exp(-H_a/kT) \qquad (2)$$

with different values of prefactor A and activation enthalpy (Fig. 2, Table 1). In the high temperature region the values of A and H_a are typical for proper (intrinsic) conductivity. The low temperature region is sensitive to wrong-valence impurities [2,4], therefore conductivity of this region can be characterized as extrinsic. The similar values of H_a and A in corresponding temperature regions for RDP and ADP indicate similarity of the structural mechanisms of the proton conductivity in both crystals and an unimportant role of the ammonium protons for long range proton transport.

In contrast to pure RDP and ADP the mixed RADP crystals reveal dramatic change of σ_{dc} with composition in the extrinsic region (Fig. 2) due to decrease of the contribution of the extrinsic conductivity mechanism with H_a = 0.5 eV. For Rb-rich compositions this conductivity mechanism is not observed at all [9], but for compositions with x over 0.5 a new extrinsic mechanism with very low activation enthalpy near 0.25 eV appears (Fig. 2, Table 1). The impurity origin of this mechanism is confirmed by nonmonotonic concentration dependence of the prefactor A. Thus one concludes that small concentration of NH_4 leads to frustration of proton long range diffusion paths existing in pure crystals, but large concentration (0.5<x<0.8) leads to creation of new diffusion paths.

The KADP 0.6 crystals reveal some features of a nonequilibrium state in the first heating experiment and after cooling to room temperature σ_{dc} decreases by 30% (Figs. 3, 4). At 240<T<360K these crystals show the same extrinsic conductivity mechanism as pure ADP (Table 1).

3.2 ac Conductivity

The bulk ac conductivity $\sigma_{ac}(\omega)$ can be described phenomenologically by the sum of the diffusion $\sigma_D(\omega)$ and dielectric relaxation $\sigma_r(\omega) = \omega\varepsilon''(\omega)$ parts. As shown in Fig. 3 the temperature dependences of σ_D are characterized by an activation enthalpy as well as d.c. conductivity enthalpy. The relaxation part of the conductivity is related to noncritical local ion motion though low potential barriers and one has weak temperature dependence (Figs. 3-5).

For all investigated crystals the high temperature dependences $\sigma_{ac}(\omega)$ are similar: σ_D slightly increases with temperature but σ_r has strong frequency dependence

$$\sigma \sim \omega^{\upsilon} \qquad (3)$$

with $1<\upsilon<1.5$. However, at T 260K some distinctions of $\sigma(\omega)$ dependences appears for various compositions. KADP 0.6 at T<240K reveals strong frequency dependence of σ over the whole investigated frequency range. These dependences are fit by Eqn. (3) with constant υ for given temperature values (Fig. 4). When temperature decreases υ increases from 0.3 to 1.0. At 240>T>180K the temperature dependences of

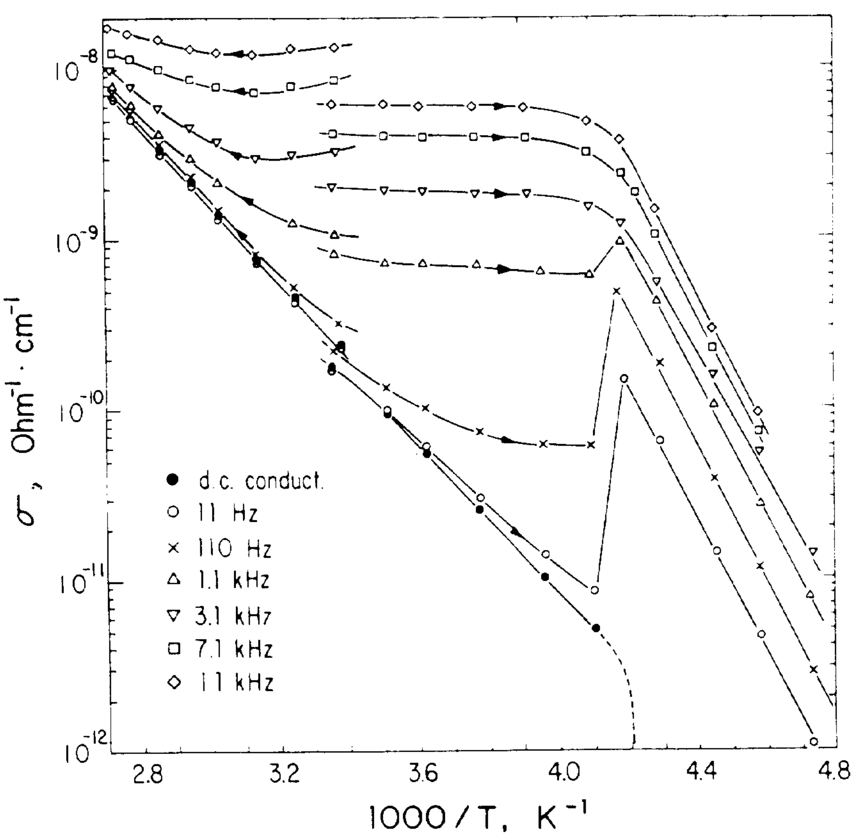

Fig. 3. Arrhenius plots of the d.c. bulk conductivity and a.c. conductivity for KADP 0.6.

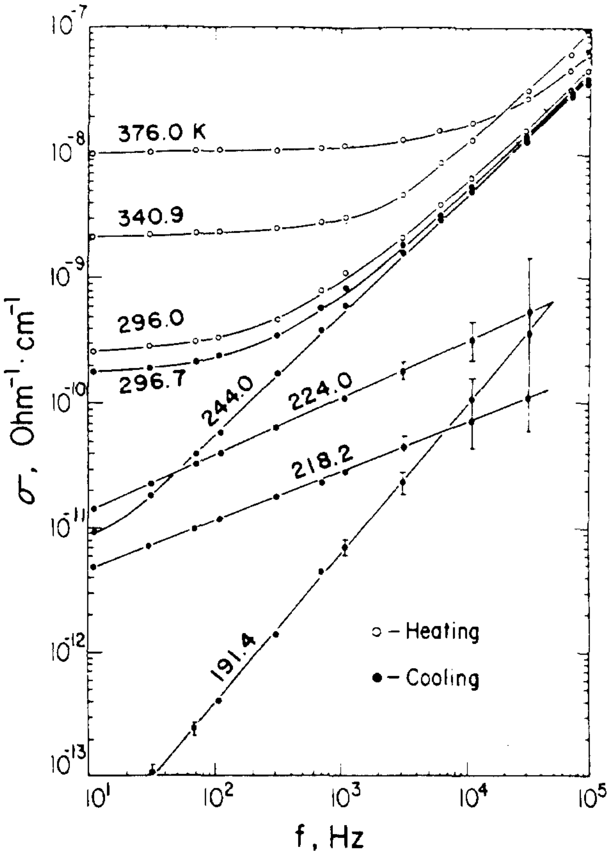

Fig. 4. Frequency dependences of the a.c. conductivity for KADP 0.6.

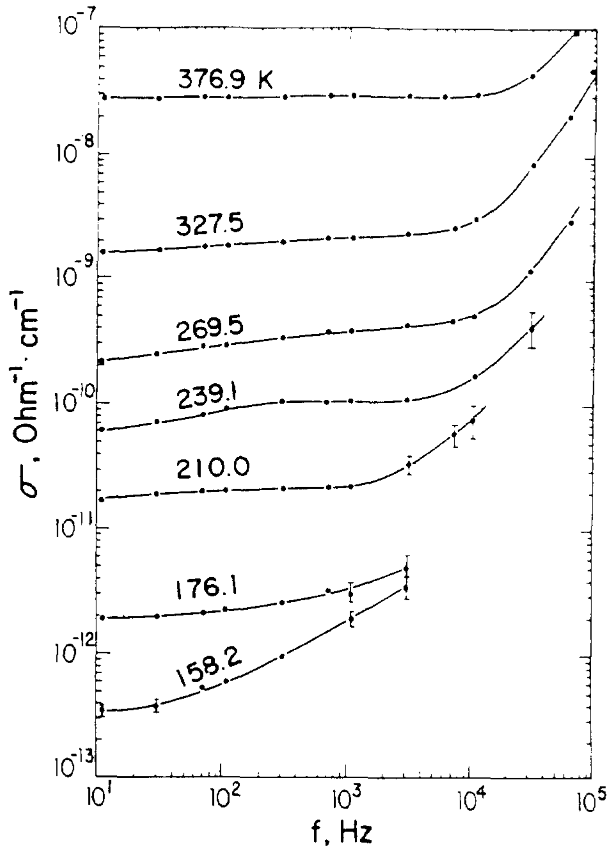

Fig. 5. Frequency dependences of the a.c. conductivity for RADP 0.5.

σ for fixed frequencies are fit by an Arrhenius law [2] with high activation enthalpy near 0.7 eV characteristic of the intrinsic conductivity of pure KDP (Table 1).

This anomalous behavior of σ_D is somewhat similar to that observed in certain amorphous semiconductors [10] and one-dimensional ionic conductors with random distribution of activation barriers [11]. For KDP-type crystals amorphous-like proton diffusion indicates random distribution of the activation barriers for intrabond and interbond proton jumps. Such randomization seems to be due to the freezing of the NH_4 groups in nonsymmetrical position in a random manner below 240K.

In contrast to KADP 0.6 the RADP crystals reveal essentially more weak anomalies of $\sigma(\omega,T)$ in the vicinity of T = 240K. For example, RADP 0.5 shows only a weak maximum at f = 300 Hz (Fig. 5).

4. Conclusion

We have reported a proton conductivity investigation of some mixed RADP and KADP crystals. It is shown that both d.c. and ac conductivities reveal specific features which are not observed for corresponding pure crystals:

1. The RADP crystals show strong dependence of the d.c. conductivity on composition. For some compositions, conductivity differs by three orders at moderate temperatures. Therefore these materials represent a tool for obtaining low conductivity specimens in electro-optic devices.

2. The a.c. conductivity of the KADP 0.6 crystal shows amorphous-like behavior below 240K.

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