

Proton transport in KDP-family of ferroelectric materials

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Abstract. Proton transport in potassium dihydrogen phosphate (KDP) and ammonium dihydrogen phosphate (ADP) is briefly reviewed. The experimental results of Wagner's polarization measurement, coulometry, infrared spectroscopy, transient ionic current measurement, the variation of electrical conductivity with temperature and electrogravimetric analysis for KDP and ADP are reported. H^+ and OH^- ions are ascertained as the mobile ionic species. A new mechanism for the proton transport in KDP and ADP is suggested: A three-fold rotation of $H_2PO_4^-$ units about any of the axes of PO_4 tetrahedra leads to a configuration like $O...H...H...O$, the rearrangement of which provides $H...O...H$ bridge that gets electrodisassociated on the application of a d.c. electric field.

Keywords. Proton transport; KDP-type ferroelectrics; coulometry; electrogravimetry.

1. Introduction

The ferroelectric material potassium dihydrogen phosphate (KDP) and the antiferroelectric material ammonium dihydrogen phosphate (ADP) are well established proton conductors. The motion of structural protons controls both the ferroelectric/antiferroelectric properties and the proton transport in these materials. KDP and ADP remain in the paraelectric phase at room temperature with tetragonal $142d$ symmetry (Slater 1941; Ueda 1948; Frazer and Pepinsky 1953; Tenzer *et al* 1958). Both ADP and KDP have four molecules per unit cell with almost identical phosphate lattice. The phosphate (PO_4) groups are tetrahedrally attached with four other PO_4 groups via hydrogen bonds. On an average, each PO_4 group has two protons forming a network of $H_2PO_4^-$ ions ionically bonded with K^+/NH_4^+ ions. In the case of KDP, only one type of hydrogen bond network exists associated with PO_4 group whereas in the case of ADP, two types of hydrogen bond networks are present; one is associated with PO_4 group and the other with NH_4^+ ions. Various proton transport mechanisms in KDP and ADP have been suggested earlier invoking the involvement of different types of defects in the hydrogen bond network. These defects are in general the ionization defects and the orientational defects, i.e. L- and D-defects (O'Keefe and Perrino 1967).

According to Murphy (1964), proton migrates through the hydrogen bond network by alternate interbond and intrabond proton jumps between $H_2PO_4^-$ units, i.e. L- and D-defects migration. Harris and Vella (1973) attributed the L- and D-defects to proton transport in KDP, but considered the additional A-defects (proton vacancies in ammonium lattice) to ADP. Sharon and Kalia (1977) suggested a synchronized rotation of $H_2PO_4^-$ units around the three-fold axes of PO_4 tetrahedra leading to a possible unstable situation like $O...H...H...O$ between $H_2PO_4^-$ units and forcing them to revert back to the initial position by bidirectional axial rotation. This to-and-fro movement of the proton can be restricted to a direction by applying a d.c. electrical field across the KDP/ADP sample.

Our experimental investigations, viz. coulometry, gas chromatography, infrared

study, transient ionic current measurement, electrical conductivity measurement and electrogravimetric analysis (EGA) on KDP and ADP have led us to propose a mechanism (Chandra and Kumar 1990a, 1991) of proton transport in KDP and ADP.

2. Experimental

Experimental studies on KDP and ADP were performed on polycrystalline pellets pressed at 10,000 lbs/cm².

The ionic transference numbers of KDP and ADP were determined directly by two experiments: (i) Wagner's polarization measurement (Wagner and Wagner 1957) and coulometry (Chandra 1988; Chandra *et al* 1986a, 1989). In the first measurement, one blocking and one non-blocking electrodes are required. However, in the present case, no suitable blocking or non-blocking electrode could be identified and therefore a thick silver coating was deposited as blocking electrode on each of the faces of the KDP/ADP polycrystalline pellet using vacuum evaporation technique. The results obtained, i.e. current vs time plots at fixed potential have been taken as a guide to Wagner's polarization behaviour. This method fails to separate the contributions due to anionic/cationic species in the total transference number.

In the coulometric experiment, the sample pellet (KDP/ADP) was mounted on a specially designed double-arm electrolysis cell or coulometer (Chandra *et al* 1986a, 1989). A constant d.c. current was passed through KDP and ADP pellets. The volume of the gases evolved at the cathode and anode was observed as a function of time. The cathode side gas (hydrogen) was gas chromatographically tested (Tracor Instruments, model 540).

Infrared (IR) spectral studies on the original and electrolyzed KDP/ADP samples were carried out to identify the electrodisociable groups and the corresponding mobile ionic species. Almost equal amounts of the original KDP/ADP material and the materials scraped from the anode and cathode sides of the electrolyzed KDP/ADP pellet were separately dispersed in the potassium bromide (KBr) matrix in the ratio 1:100. Thin pellets were made and their IR spectra recorded using a spectrophotometer (Perkin Elmer IR, model 783).

The transient ionic current (TIC) was measured on KDP/ADP pellet to determine the number of mobile ionic species and their respective mobilities. Both the faces of the sample pellet were thickly coated with silver to block the mobile ionic species. A d.c. voltage was first applied across the sample to polarize it. After some time, the polarity was reversed. Current vs time was monitored. The experimental details were reported earlier (Chandra *et al* 1988).

The a.c. electrical conductivity was measured in the temperature range 294–490 K at frequencies ranging 100 Hz to 100 kHz using a Hewlett-Packard LCR meter (model 4274A). The bulk electrical conductivity at different temperatures was deduced from the complex admittance plots.

EGA is a new analytical technique developed by us to study proton conducting solids (Chandra and Kumar 1989, 1990b). During our experiments with some of the proton conductors (Chandra 1984, 1988, 1989; Chandra *et al* 1986b, 1989; Chandra and Kumar 1990a), we have noted that gases like H₂, O₂, NH₃, Cl₂ etc. are discharged at the respective electrodes on the application of d.c. electric field because of the vehicular transport of ionic species such as H⁺, NH₄⁺, OH⁻, Cl⁻ etc resulting in a

change in the mass of the sample. This change is monitored as a function of time and d.c. electric field in the EGA technique similar to the thermogravimetric analysis (TGA) where the change in mass of the sample is monitored as a function of time and temperature. In the EGA experiment, the sensitive electrical balance of Linseis TGA/DTA unit (TYP 2045) fitted with a special EGA sample holder (see figure 6a) was used. Metallic grid/mesh electrodes were fixed to both faces of KDP pellet to allow gas evolution (if any) on electrodisassociation. This sample pellet was then mounted on the EGA sample holder. A fixed voltage was applied across the sample and the change in mass was monitored as a function of time. The experimental details were discussed earlier (Chandra and Kumar 1989, 1990b).

3. Results and discussion

3.1 Transference number

3.1a *Wagner's polarization measurement:* Wagner's polarization curves for KDP and ADP are shown in figure 1. The total ionic transference numbers of KDP and ADP calculated from these curves are 0.98 and 0.99 respectively. This implies that both KDP and ADP are essentially ionic conductors.

3.1b *Coulometry:* On passing a constant d.c. current through KDP and ADP pellets, guses were evolved at both the cathode and anode. Figure 2 shows the plots

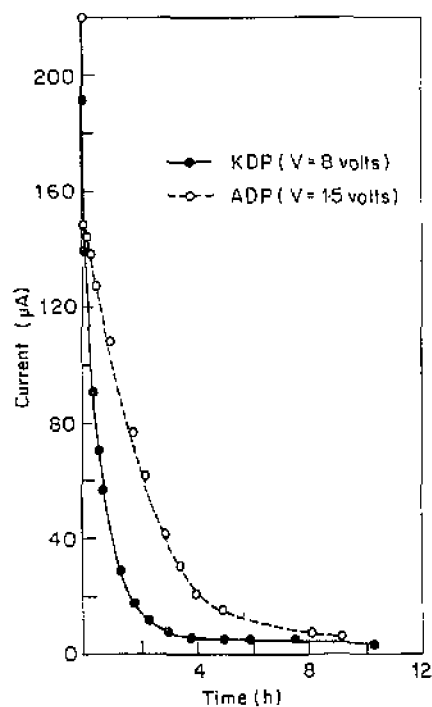


Figure 1. Wagner's polarization plots for KDP and ADP polycrystalline pellets.

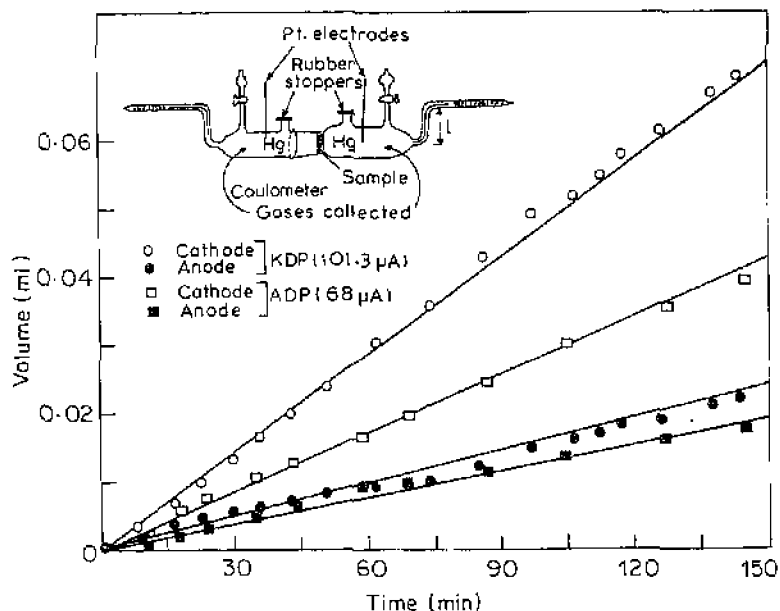


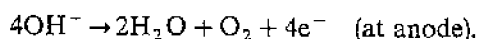
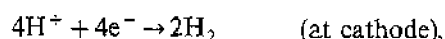
Figure 2. Volumes of the evolved gases observed in the coulometer as a function of time for KDP and ADP.

Table 1. Transference numbers for H^+ and OH^- ions.

Materials	t_{H^+}	t_{OH^-}	Total transference number
KDP	0.64	0.16	0.80
ADP	0.54	0.16	0.70

of evolved volume of gases for KDP and ADP. The cathode side gas was gas-chromatographically tested and found to be hydrogen. The anode side gas (supposed to be $O_2 + H_2O$) could not be tested due to lack of facility.

The evolution of gases at both the electrodes on the application of d.c. electrical field across KDP and ADP samples suggests the possible electrodisassociation of $H...O...H$ bridges formed due to the rotation of $H_2PO_4^-$ units about the three-fold axes of PO_4 tetrahedra generating H^+ and OH^- as the mobile ionic species according to the following reactions (Chandra and Kumar 1991):



The transference numbers evaluated for H^+ and OH^- from the observed volumes of evolved gases can be summarized as given in table 1, where t_{H^+} and t_{OH^-} are the transference numbers of H^+ and OH^- ions respectively. We expect the total transference number (t_i) to be less than 1 even if the total transference is by ionic transport, because the actual volume of gases measured during coulometric experiment would be less than the evolved gases due to the loss for various reasons like adsorption

of gases in mercury of the coulometer, possibility of small leakage, electrode reaction like $\text{Hg}^+ + 1/2 \text{O}_2 \rightarrow \text{HgO}$ etc.

3.2 IR-spectral studies

The IR spectra of the original as well as the electrolyzed KDP and ADP samples are shown in figure 3. The salient changes in the IR-spectra because of ion migration under d.c. electrical field are as follows:

(I) KDP: (a) Disappearance of the peaks at 3560, 3240, 1730, 1645 and 820 cm^{-1} after electrodisassociation. These have been attributed to electrolysis of H...O...H bridges formed due to rotation of H_2PO_4^- units as shown in figure 7. (b) Appearance of a strong peak at 930 cm^{-1} superimposed over a broad 950 cm^{-1} peak which has been assigned to the growth of symmetric P-O-P bond after electrodisassociation (see figure 7). (c) Appearance of a new peak at 535 cm^{-1} after electrodisassociation. This has also been assigned to the symmetric P-O-P bond formed by the process illustrated in figure 7 (discussed later). (d) Disappearance of the peak at 485 cm^{-1} after electrodisassociation. It is reported (Blinic *et al* 1968) that in KDP at higher temperatures H_2PO_4^- unit rotates and acquires such a configuration that intrabond proton tunnelling between H_2PO_4^- units ceases and the corresponding peak (450 cm^{-1}) becomes weak. In the present case, it seems that a similar situation is created on the application of d.c. field through a process of H_2PO_4^- group rotation and subsequent electrodisassociation (as shown in figure 7) resulting in the disappearance of the 485 cm^{-1} peak.

(II) ADP: (a) Disappearance of peak at 1650 cm^{-1} after electrodisassociation of H...O...H bridges as discussed for KDP. (b) Appearance of a new peak at 525 cm^{-1}

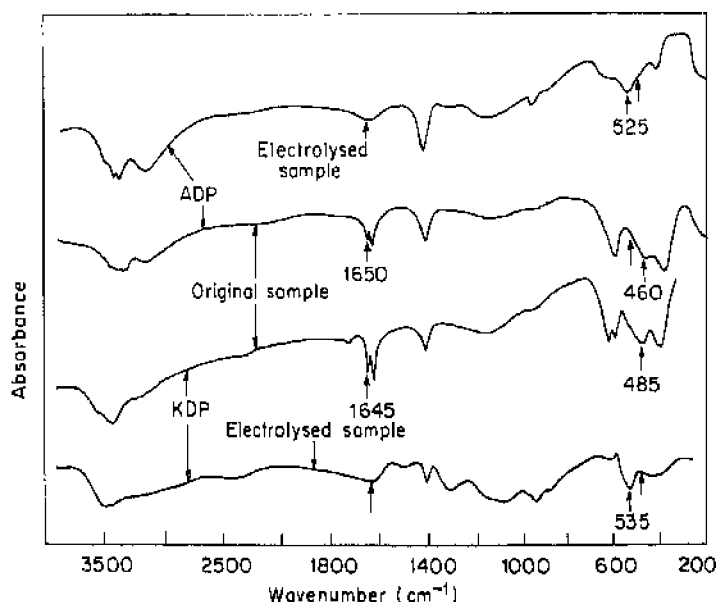


Figure 3. IR-spectra of the original and the electrolyzed samples of KDP and ADP polycrystalline materials.

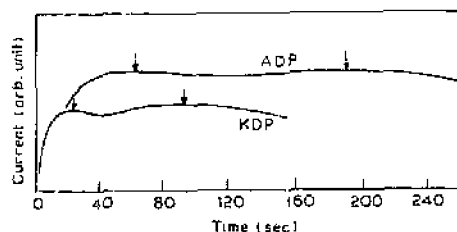


Figure 4. TIC plots of KDP and ADP polycrystalline pellets.

Table 2. TIC results for KDP and ADP.

Materials	KDP	ADP
No. of peaks	2	2
Possible mobile species	H ⁺ and OH ⁻	H ⁺ and OH ⁻
Mobility values	$\mu_{\text{H}^+} = 3.6 \times 10^{-5}$ $\mu_{\text{OH}^-} = 9.3 \times 10^{-6}$	$1.34 \times 10^{-4} \text{ cm}^2/\text{Vs}$ $3.30 \times 10^{-5} \text{ cm}^2/\text{Vs}$

after electrodisassociation corresponding to the symmetric P–O–P bond formed by the process shown in figure 7 (discussed later). (c) Disappearance of 460 cm^{-1} peak after electrodisassociation because the intrabond proton tunnelling between H_2PO_4 units possibly ceases on the application of d.c. electric field as discussed for KDP in (d).

3.3 Transient ionic current measurement (TIC) for mobility

In this experiment, the sample was first polarized by applying a fixed d.c. potential. After some time, the polarity was reversed. Current vs time was monitored. The number of peaks provides the number of mobile ionic species. The time taken for peaking is related to the mobility (Chandra *et al* 1988). The TIC plots for KDP and ADP are shown in figure 4. The results are summarized in table 2, where μ_{H^+} and μ_{OH^-} are the mobilities of H⁺ and OH⁻ ions, respectively.

3.4 Electrical conductivity

Figure 5 shows the temperature dependence of bulk electrical conductivity (σ) of KDP and ADP in the ambient atmosphere. The bulk conductivity was evaluated using the complex impedance spectroscopy technique. The initial decrease in the value of bulk conductivity of KDP and ADP with increase in temperature is an artifact because of the loss of surface adsorbed water (Chandra and Kumar 1990, 1991). The onset of a dip in KDP after 423 K has been assigned to the structural change from tetragonal to monoclinic (Chandra and Kumar 1991).

3.5 Electrogravimetric analysis

The EGA experiment on KDP polycrystalline pellet was carried out in vacuum to avoid any confusion from changes in mass because of varying surface hydration due

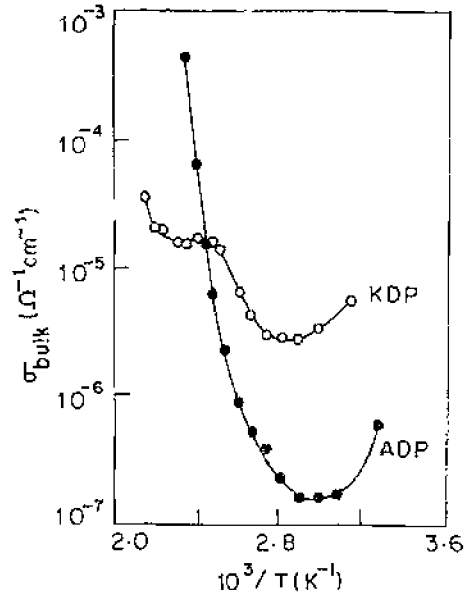


Figure 5. Variation of the bulk electrical conductivity of KDP and ADP polycrystalline pellets in the ambient atmosphere.

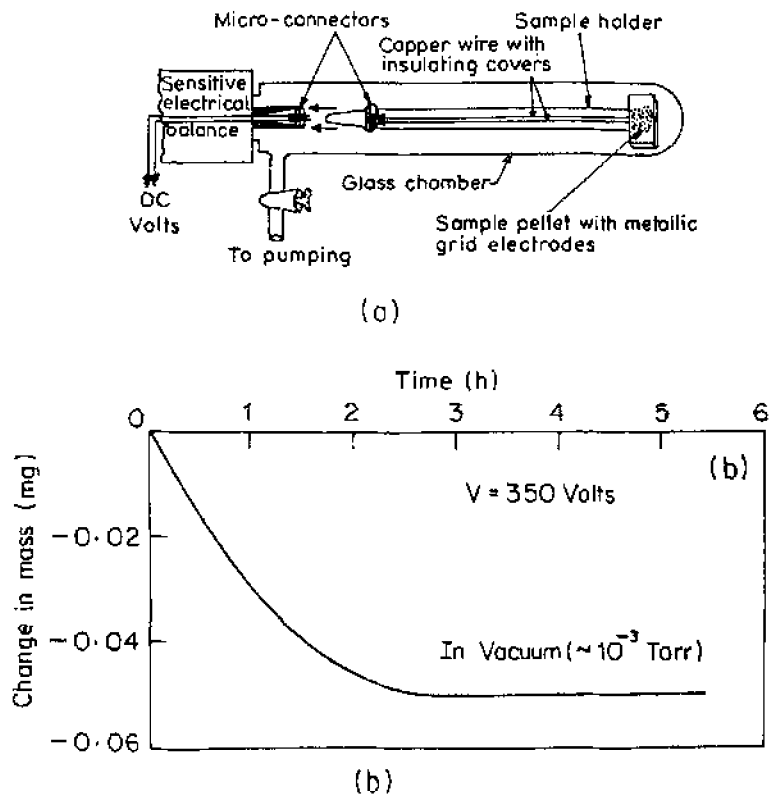


Figure 6. (a) Schematic diagram of the sample holder used for EGA experiment, and (b) loss in mass of the KDP sample (initial mass ≈ 220 mg).

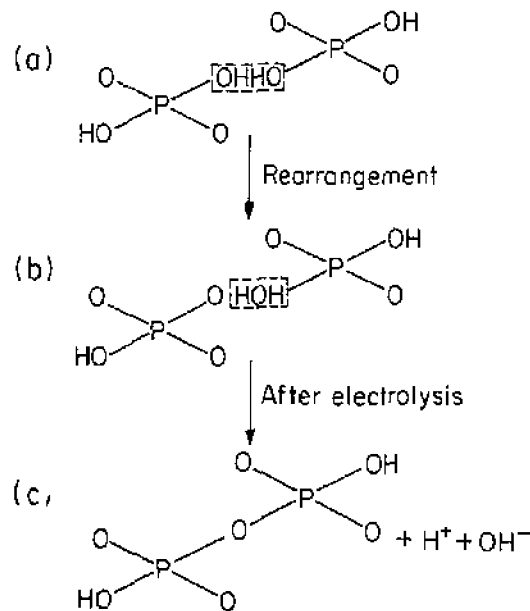


Figure 7. Schematic illustration of the proton transport mechanism in KDP and ADP.

to minor changes in ambient humidity. Figure 6b shows the EGA results of KDP in vacuum. On the application of 350 volts across the sample, the mass of the sample decreases and ultimately equilibrates after nearly 2.5 h following the electrolysis of H...O...H bridges (formed due to the process shown in figure 7) producing H^+ and OH^- as the mobile ionic species.

On the basis of the above experimental results, the suggested proton transport mechanism for KDP and ADP is: A three-fold rotation of H_2PO_4 units about any of the axes of PO_4 tetrahedra results in a situation like O...H...H...O (the D-defect) as shown in figure 7a. It rearranges itself in an unstable configuration as H...O...H...O (figure 7b) which ultimately gets electrodisassociated on the application of the d.c. electrical field generating H^+ and OH^- as the mobile ionic species and as a result a P-O-P bond is formed between the electrodisassociated H_2PO_4^- units as illustrated in figure 7c.

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