Proton transport mechanism in ammonium dihydrogen phosphate

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Coulometric, transient ionic current, electrical conductivity and IR investigations on polycrystalline and single crystal of ammonium dihydrogen phosphate (ADP) have been carried out. During coulometry, gases evolved both at the cathode (mostly H_2) and at anode (O_2) indicating the electrolysis of the H–O–H bridge. Transient ionic current study suggests the likely presence of two types of mobile ionic charge carriers (H^+ and O^{2-}) with mobilities of 1.3×10^{-4} and 3.3×10^{-5} cm^2 V^{-1} sec^{-1}. A comparative study of the IR spectra of the original and the electrolysed samples also supports the idea of possible electrolysis. The temperature dependence of the electrical conductivity have also been studied and interpreted in terms of possible deammoniation reaction and phase transformation. Finally, a mechanism for ionic transport in ADP is suggested.

1. Introduction

Ammonium dihydrogen phosphate (ADP) has long been of interest because of its strong piezoelectric activity, optical frequency doubling and protonic conductivity. The crystal structure of ADP has been given by many workers [1–4]. In the paraelectric phase, it has a tetragonal structure belonging to the space group $\bar{1}42d$, $a = b = 0.7502$ nm, $c = 0.7546$ nm. There are four $NH_4H_2PO_4$ formula units per unit cell. The hydrogen bond networks of ADP can be classified into two groups [5]. One is associated with the phosphate group; whereas, the other with the ammonium group. Each phosphate group is linked by four hydrogen bonds. Some additional secondary hydrogen bonds are also present in which each ammonium ion has four hydrogen bonds linked with oxygen at the phosphate lattice.

Many workers [5–8] have suggested different possible mechanisms of proton transport in ADP. According to Murphy [6], the proton migration through the hydrogen bond network of ADP is mediated by alternate interbond and intrabond jumps between the $H_2PO_4^-$ unit (i.e. L- and D-defects migration). Harris and Vella [5] suggested that the proton conduction in ADP is not only through the hydrogen bonds between of phosphate groups but the hydrogen bonds of the ammonium group are also involved in the conduction process. At temperatures above 40° C, the $NH_4H_2PO_4$ may decompose into NH_3 and H_3PO_4 and the generated proton vacancies (A-defects) may also migrate along with L-defects. Sharon and Kalia [8] proposed a synchronized rotation mechanism for proton conduction in which the $H_2PO_4^-$ unit can rotate around three fold axes of PO_4 tetrahedra [9] and one of these reorientations may create a situation like the O–H–H–O bond between two $H_2PO_4^-$ units. The O–H–H–O situation is unstable because in ADP the distance between two possible sites for hydrogen in the O–H–O bond does not allow the accommodation of another hydrogen. This non-existing situation may be forced to revert back to such a configuration, by bidirectional axial rotation, which will have the O–H–O situation between two $H_2PO_4^-$ units. Under these rotations, the proton may migrate from one $H_2PO_4^-$ to another $H_2PO_4^-$ group. This to- and fro- movement of protons can be restricted to be one direction by a d.c. electric field.

This paper presents a new look at the proton transport mechanism following the coulometry, transient ionic current (TIC), infrared and electrical conductivity studies on ADP. Results suggest a possible electrolysis of the H–O–H bridges which are formed as a consequence of the reorientation of $H_2PO_4^-$ units about the axis of PO_4 tetrahedra.

2. Experimental details

The powder sample of ADP was pressed at 10 000 lbs cm^{-2} to make polycrystalline pellets. The single crystal of ADP was grown by slow evaporation of its saturated aqueous solution.

The transference number was determined by two methods (a) Wagner's polarization technique [10, 11]; and (b) Tubandt's direct electrolysis method or coulometry [11–14]. In the polarization method, the potentiostatic current was monitored as a function of time across the cell Ag/ADP/Ag. But this method fails to tell whether (and which) cation or anion is responsible for the ion transport. The coulometric investigation was carried out to determine the mobile species using the specially designed d.c. electrolysis cell. The full details of electrolysis cell have been reported earlier [12–14]. The hydrogen at cathode side gas was tested by using the gas chromatograph of Tracor Instruments model "540".

The transient ionic current (TIC) measurement technique was used to detect the number of different
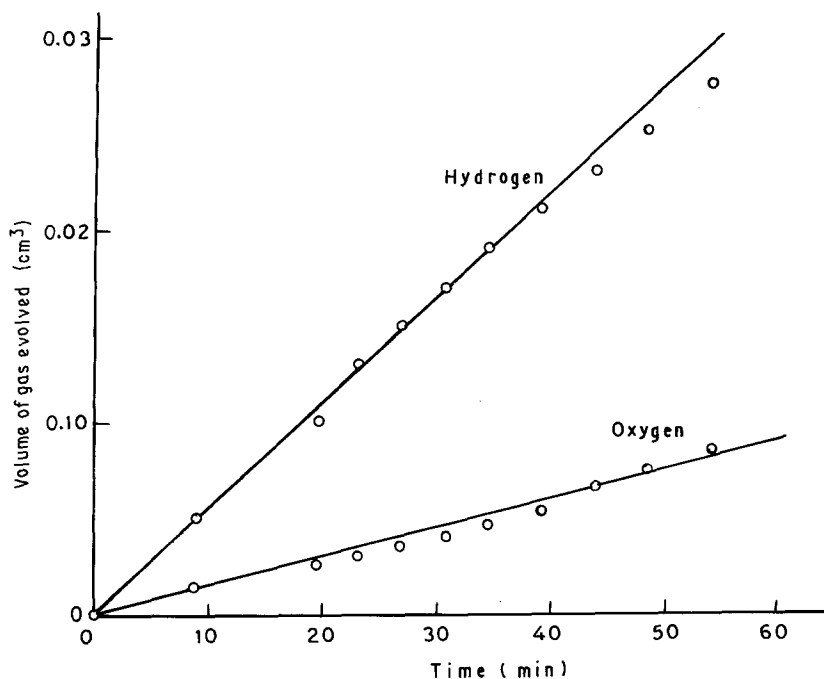
Figure 1 The volume of gas evolved from the polycrystalline sample for a constant current $(100\,\mu A)$ as a function of time.

types of mobile ionic species and to evaluate their mobility. In this method, the sample is first polarized and then the transient ionic current is monitored as a function of time after reversing the polarity of the polarizing field. Details of the experimental technique has been reported elsewhere [15].

The infra-red spectrum of the cathode and anode side sample was recorded along with the original sample using Perkin-Elmer spectrophotometer model "783". The spectra were recorded in KBr pellets.

The a.c. conductivity was measured in the temperature range from 305 to 433 K and in the frequency range from 100 Hz to 100 kHz with the help of Hewlett-Packard LCR meter model "4274A". The true bulk conductivity was computed by complex admittance plot (i.e. B–G plot) at different temperatures.

3. Results and discussion
3.1. Transference number and mobility measurement

First, the ionic transference number of ADP has been estimated by using Wagner's polarization method [11, 14]. The value of ionic transference number t_{ion} is found to be $\simeq 0.989$. So, it is concluded that the conduction in ADP is mainly ionic. But, this method fails to tell whether (and which) cation or anion is responsible for the ion transport. For this purpose, the coulometric investigation on polycrystalline pellet of ADP have been made using d.c. electrolysis cell (or coulometer). Following results are obtained:

1. On passing the current $(100\,\mu A)$ through the sample placed in the coulometer, gases evolved both at the cathode and anode ends. The volumes of the gases evolved are shown in Fig. 1.

2. The gas collected at the cathode has been tested using gas chromatography and found to be hydrogen. For comparison purpose, the gas chromatographs of the standard hydrogen and the cathode side gas are shown in Fig. 2. The anode side gas was not tested as we did not have the facility to detect the oxygen.

3. The cathode side gas was tested chemically also and no indication of ammonia evolution was found.

The evolution of gases at both the electrodes suggests that H–O–H bridges are somewhere getting electrolysed and H^+ and O^{2-} ions are generated as charge
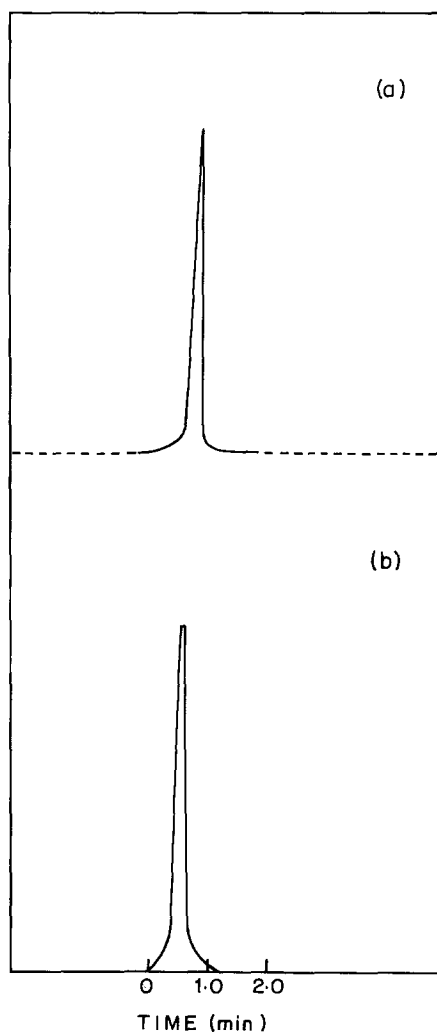

Figure 2 The gas chromatograph of (a) the 0.1 ml of standard H_2; and (b) 0.2 ml of cathode side gas.
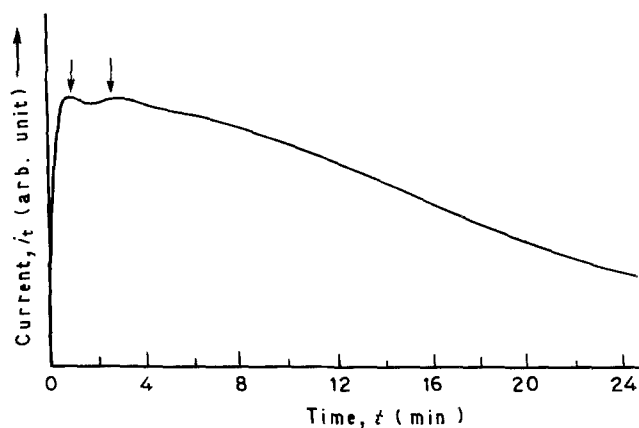
2460

Figure 3 Transient ionic current (i_t) against time (t) plot.

carriers. As a result H_2 and O_2 gases evolve at the cathode and anode ends, respectively, as electrolysis products. These H–O–H bridges may be formed due to the reorientation of $H_2PO_4^-$ units about the axis of PO_4 tetrahedra, discussed later in Section 3.2. The H_2 and O_2 gases may evolve at the two electrodes following the charge transfer reaction given below:

$$2H^+ + 2e^- \rightarrow H_2\uparrow \qquad : \text{at cathode}$$

$$2O^{2-} \rightarrow O_2\uparrow + 4e^- \qquad : \text{at anode}$$
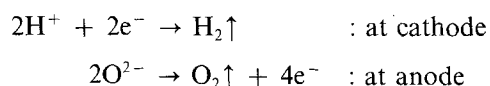
The transference numbers for hydrogen and oxygen have been calculated (based on Faraday's law of electrolysis) as:

$$t_{H^+} \simeq 0.69 \quad \text{and} \quad t_{O^{2-}} \simeq 0.42 \text{ within } \pm 10\%$$

The coulometry has also been performed on the single crystal of ADP along a- (or b-) and c-axes. More gases evolve at the cathode and very small but finite volume of gases at the anode, when the charge trans-

ference was along c-axis. This shows an anisotropic behaviour.

The number of mobile ionic species has also been confirmed by transient ionic current (TIC) measurement. As explained by Chandra et al. [15] the number of peaks tell about the number of types of charge carriers. Two peaks, observed in transient ionic current (i_t) against time (t) plot as shown in Fig. 3, are indicative of two types of mobile ionic species. The two likely mobile ions are H^+ and O^{2-}. The mobility μ of these ionic species have been calculated using the formula:

$$\mu = d^2/\tau V$$

where d is the thickness of the sample, τ is time of flight and V is the voltage applied. The calculated mobilities are given below:

$$\mu_1 = 1.3 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ sec}^{-1}$$

$$\mu_2 = 3.3 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ sec}^{-1}$$

We could not identify unambiguously the ionic species to be associated with μ_1 and μ_2. However, on the basis of relative ionic radii and charge of the two likely species H^+ and O^{2-}, it can be assumed that the larger mobility μ_1 corresponds to hydrogen (μ_{H^+}) while μ_2 refers to the mobility of oxygen $(\mu_{O^{2-}})$.

3.2. IR spectral studies
The IR spectra of the cathode and anode side samples have been recorded and compared with the original sample (Fig. 4). Some distinctive features between the IR spectra of the original and electrolysed samples are:

1. the 460 cm^{-1} peak associated with P–O–H vibration disappears;
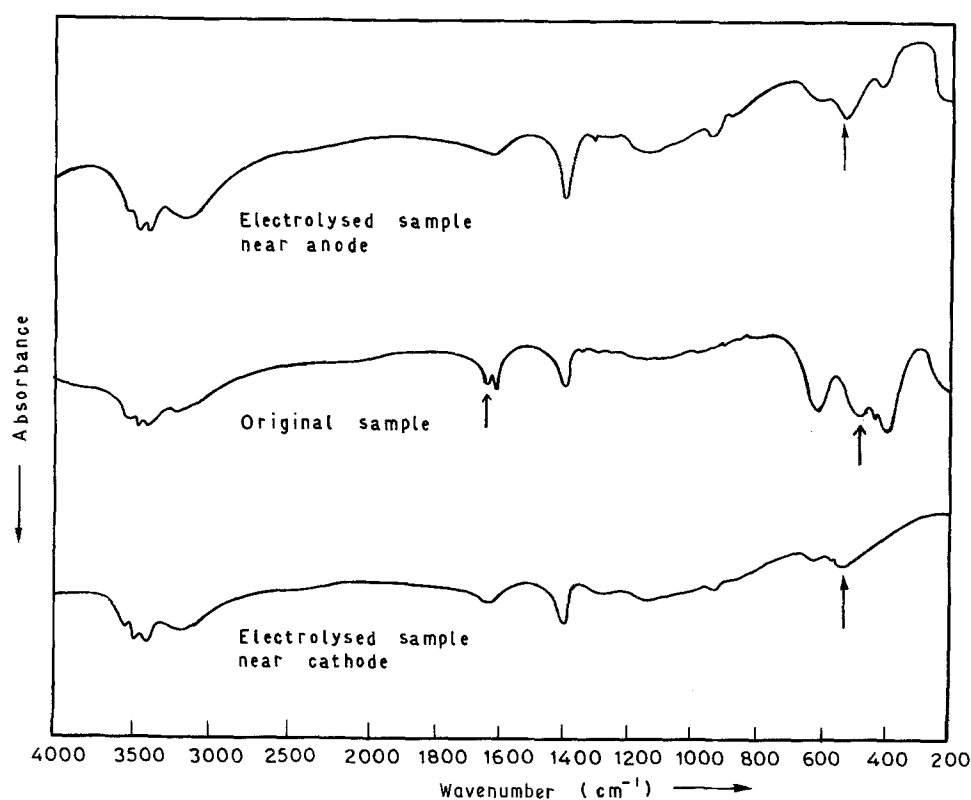

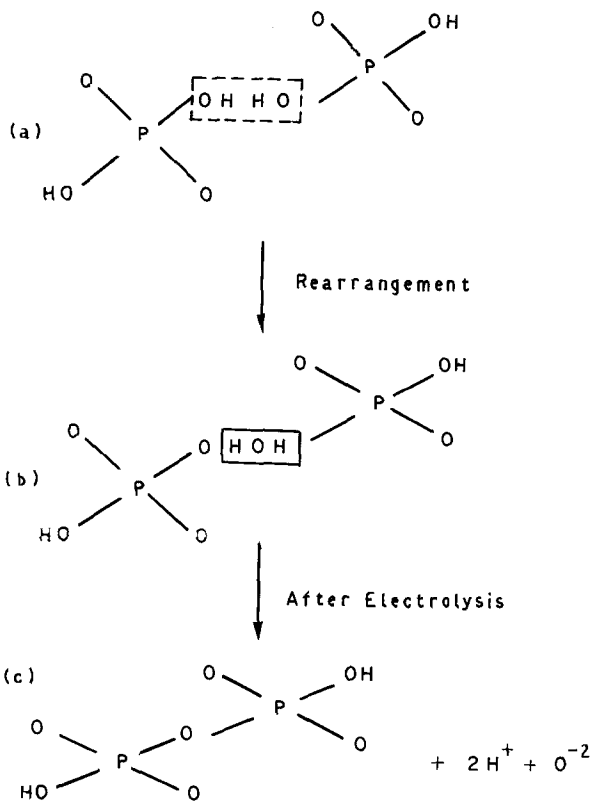Figure 4 IR absorption spectra of original sample along with electrolysed materials near cathode and anode.

2461

Figure 5 Electrolysis mechanism of ADP.

2. a new peak at 525 cm⁻¹ appears. This has been assigned by us to P–O–P vibration; and

3. 1650 cm⁻¹ peak disappears which is due to H–O–H bending.

We propose a model to explain the above spectral changes and also the earlier observations of H_2/O_2 evolution during coulometry under d.c. field. The proposed model is given in Fig. 5. It is known that $H_2PO_4^-$ unit can rotate in KDP about the axis of PO_4 tetrahedra [9], and similar situation is likely to occur in the isostructural material ADP. Thus, as a first step, $H_2PO_4^-$ group would rotate and lead to a rearrangement, as shown in Fig. 5b, to obtain a configuration O–H–O–H. This is highly unstable. On application of the d.c. electric field H–O–H unit goes out as in Fig. 5c. Thus according to this model, on electrolysis (1) P–O–P bond is formed giving 525 cm⁻¹ peak (2) P–O–H bond and H–O–H vibration disappear and (3) electrolysis products H_2 and O_2 are obtained.

3.3. Electrical conductivity

Fig. 6 shows the bulk conductivity calculated from complex admittance (B–G) plots as a function of temperature. The conductivity decreases initially after 305 K, shows a minima at 330 K and rises rapidly after 400 K. In this temperature range from 305 to 400 K
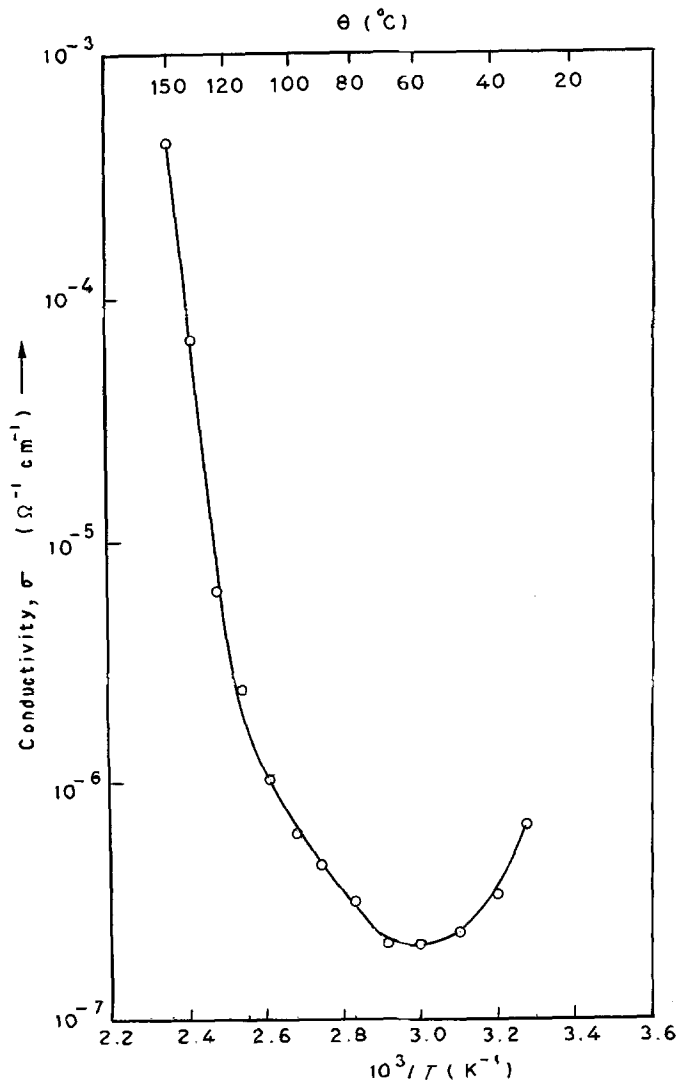

Figure 6 The bulk conductivity of polycrystalline sample as a function of temperature.
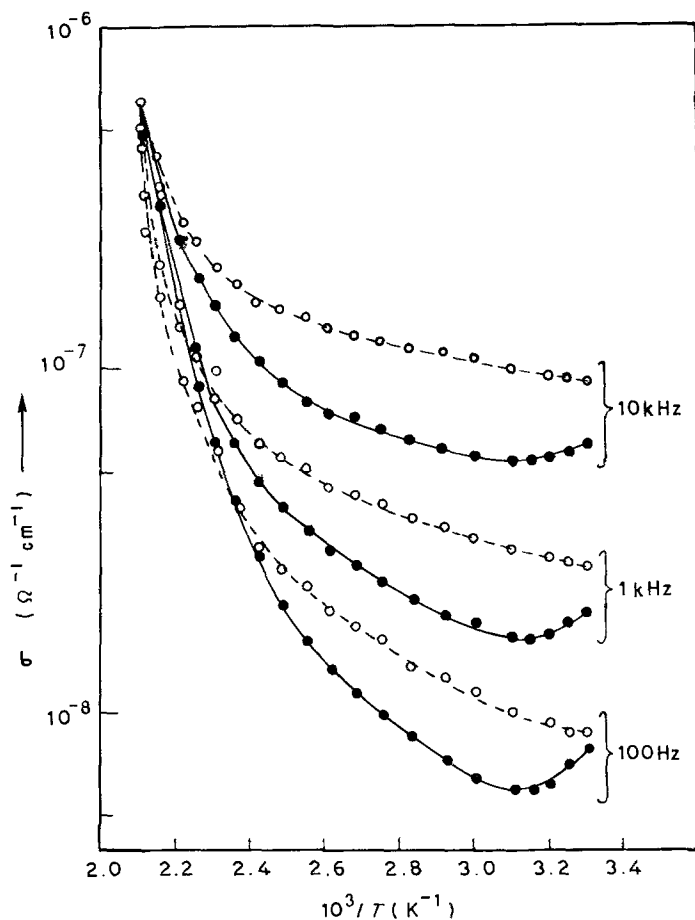
2462

Figure 7 The a.c. conductivity of single crystal of ADP as a function of temperature along *a*- (or *b*-) and *c*-axes, at different frequencies. (O) *c*-axis; (●) *a*-axis.

the variable composition phase of ADP occurs following the reaction of deammoniation [5]:

$$NH_4H_2PO_4 \rightarrow NH_3\uparrow + H_3PO_4$$

Therefore, the minima in σ against $1/T$ plot (Fig. 6) is an artifact of kinetic origin. Such an artifact has also been observed by Mari *et al.* [16] in $HTaWO_6 \cdot H_2O$ following the reaction of dehydration. The rapid increase in conductivity after 400 K is related with the structural phase transition [17].

The conductivity measurements were also carried out on the single crystal of ADP along *a*- (or *b*-) and *c*-axes. The temperature dependence of conductivity along *a*- (or *b*-) and *c*-axes is shown in Fig. 7. The conductivity is anisotropic with $\sigma_{c\text{-axis}} > \sigma_{a\text{-axis}}$. Such an anisotropy was also noted during the coulometric studies (see Section 3.1).

4. Conclusion

From the electrical, thermal and spectroscopic studies on ADP described above, the following conclusions can be drawn regarding the ion transport mechanism in ADP. As evidenced from TIC experiment, two types of ionic charge carriers are responsible for ion transport in ADP. Electrolysis of the H–O–H bridge, formed due to orientation of $H_2PO_4^-$ units about the axis of rotations of PO_4 tetrahedron, provides the proton for transport, along with O^{-2} ions. The O–H–H–O linkage present between two neighbouring $H_2PO_4^-$ groups can be rearranged as O–H–O–H to form H–O–H bridge through the process of a possible three fold rotation of $H_2PO_4^-$ units. The bridge can break to give H^+ and O^{-2} for transport. Thus, after

charge transfer the linkage between two $H_2PO_4^-$ units is via the P–O–P bond.

The temperature dependence of electrical conductivity shows a phase transition at 400 K. The σ against $1/T$ behaviour from room temperature to 400 K is essentially an artifact due to a variable composition phase. The coulometry and conductivity measurements on single crystal show an anisotropic behaviour. The ionic transport is more favoured along *c*-axis in comparison to *a*- (or *b*-) axis.

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