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AC conductivity, electric modulus analysis of $KLi(H_2PO_4)_2$ compound

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ABSTRACT

In this paper, the potassium lithium dihydrogenphosphate, $KLi(H_2PO_4)_2$, has been investigated by X-ray powder diffraction (XRD), scanning electron microscopy (SEM) and electrical impedance spectroscopy. The X-ray diffraction analysis indicated the little compound was found to crystallize in the monoclinic system with space group $P2_1/c$. Electrical properties were studied using complex impedance spectroscopy as a function of frequency (4–7 MHz) at various temperatures (300–420 K). The impedance plots show semicircle arcs at different temperatures and an electrical equivalent circuit has been proposed to explain the impedance results. The equivalent circuit built up by a parallel combination of resistance (*R*), fractal capacitance (*CPE*) and capacitance (*C*). Single relaxation peak is observed in the imaginary part of the electrical modulus, suggesting the response of grain. Moreover, the frequency dependence of the conductivity is interpreted in term of Jonschers law: $\sigma = \sigma_{DC} + f^n$. The near activation energies, obtained from the impedance, modulus spectra and conductivity confirms, that the transport is through a proton hopping mechanism in investigated materials.

1. Introduction

Alkali metal dihydrogen phosphate MH_2PO_4 (M = K, Li, Rb, Cs or NH_4) type compounds are well known crystal family for their significance in scientific and technological applications such as fuel cell, proton batteries, electrochemical sensors [1–6].

These crystals are unique in the class of proton conductors, since the superprotonic conductivity at which the proton conductivity jumps by 3–4 orders of magnitude to a “superprotonic” state with conductivity [7–10], is related to the structural features of these compounds possess of superprotonic behaviour. In fact, these acids solid characterized by tetrahedral oxyanions PO_4 occurs upon disordering of the hydrogen-bond network. The conductivity are a result of rapid tetrahedral reorientation in combination with a high rate of proton transfer between tetrahedra groups [11–15]. In particular, crystalline materials of cesium dihydrogen phosphate (CsH_2PO_4, CDP) have attracted much attention because of their relatively simple structures and conduction mechanisms [16,17].

In the present paper, we report the results of the impedance spectroscopy, the temperature and frequency dependence of the electrical and dielectric properties of $KLi(H_2PO_4)_2$ compound.

2. Experimental details

The $KLi(H_2PO_4)_2$ sample crystals were synthesized as reported in Ref. [18].

The X-ray powder diffraction pattern was recorded using a Phillips powder diffractometer operating with copper radiation $\lambda = 1.54187$ Å over a wide range of Bragg angles ($10° \leq 2\theta \leq 60°$). Structural analysis was carried out using the standard Rietveld method [19,20].

The morphologies of the obtained ceramics were observed by scanning electron microscopy (SEM) on a Hitachi S4100-1, on the free and fracture surfaces. The samples were covered with carbon before microscopic observation. The particle size was estimated by image processing of SEM's pictures using ImageJ software [21].

The electrical measurements were performed using a two electrode configuration. The $KLi(H_2PO_4)_2$ sample was pressed into pellets of 8 mm diameter and 1.6 mm thickness using 3 t/cm^2 uniaxial pressures Impedance measurements were carried using the HP 4284A spectrometer in the frequency range of 10^4–10^7 H. A

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source of 50 mV was applied to the electroded pellet samples. The temperature variation was performed using a programmable Thermolyne heater with a temperature stability of ±0.1 °C. Silver electrodes were deposited on the two circular faces of the sample to get the capacitor shaped samples.

3. Results and discussions

3.1. Structure analysis

The results of the X-ray diffraction (XRD) study at room temperature of our sample indicate that our compound were found to be single phase and crystallize in the monoclinic structure with $P2_1/c$ space group, with $Z = 4$. Fig. 1 shows typical XRD patterns registered at room temperature $KLi(H_2PO_4)_2$ sample. The structural parameters are refined by Rietveld's profile-filling method. The quality of the refinement is evaluated through the goodness of the fit indicator $\chi^2 = 1.85$. The lattice parameters in unit cell dimensions: $a = 7.5170$ Å, $b = 12.8979$ Å *and* $c = 7.3901(6)$ Å, $\beta = 98.4970°$, which are in good agreement with the results obtained by X-ray single crystal [18]. This feature structure, consists of LiO_4 tetrahedra linked by corners with H_2PO_4 groups to form infinite layer running along *(ab)* plane. In the interlayer, KO_8 polyhedra form layers parallel to the same plane as represent in Fig. 2.

Fig. 3 shows the SEM micrographs of the sample at room temperature. The morphology of the powders were approximately spherical and they were formed as fine nano-metric particles around 500 nm.

3.2. Impedance spectroscopy

The impedance spectroscopy technique is used to study the electrical behaviour of the system. It enables us to separate the real and imaginary components of the electrical parameters and hence provides a true picture of the materials properties.

Fig. 4 shows the Nyquist plots (Z'' vs. Z') of $KLi(H_2PO_4)_2$ compound measurements taken over at several temperatures (300 K–420 K). The radius of semicircles decreases with the increase in temperature. The presence of a single semicircular arc

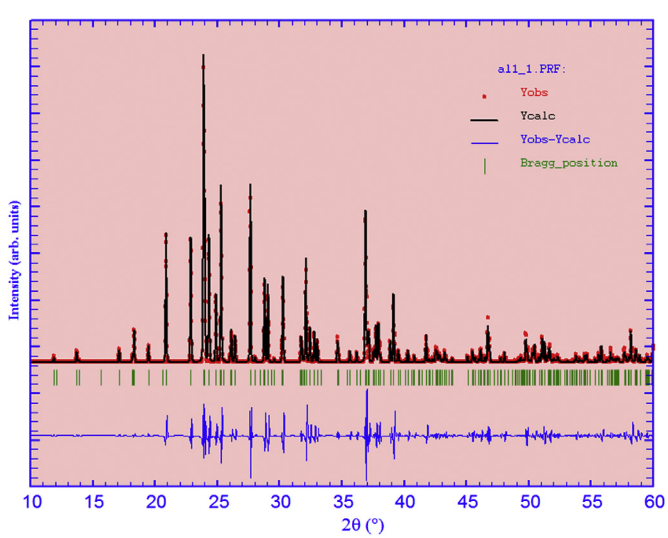

Fig. 1. Rietveld refinement for $KLi(H_2PO_4)_2$: experimental data are shown in red; calculated data in black; difference between them in blue; and Bragg positions in green. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

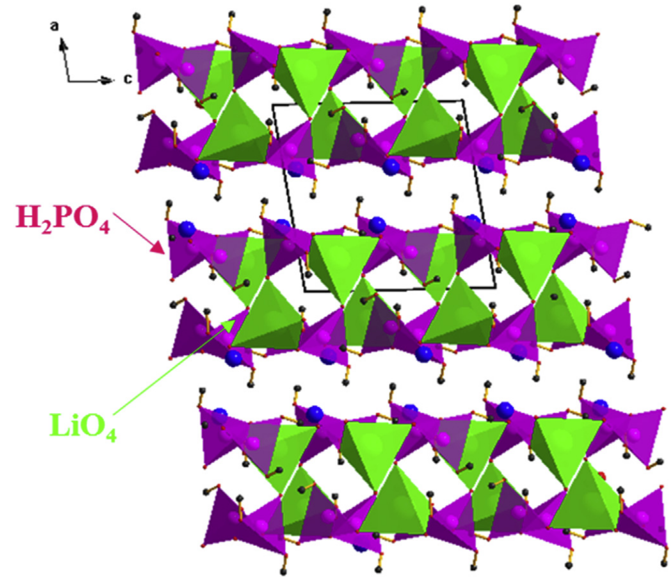

Fig. 2. Crystal Structure of the $KLi(H_2PO_4)_2$, view along the "b" axis.

indicates that the electrical processes in the material arise essentially due to the contribution from grain interiors, which is expected from the sample where no grain boundaries are involved [22–24]. These plots are fitted using the Z-view software and the best fit is obtained when employing an equivalent circuit. Those spectra were successfully modeled by an equivalent circuit, consists of a parallel combination of resistance (*R*), fractal capacitance (*CPE*) and capacitance (*C*). With the impedance of the fractal capacitance (*CPE*) is distributed element that produces impedance having a constant phase angle in the complex plane. The CPE impedance is given by the relationship [25]:

$$Z_{CPE} = \frac{1}{(jQ\omega)^{\alpha}} \tag{1}$$

where, Q indicates the value of the capacitance of the *CPE* element, and α is the deviation degree with respect to the value of the pure capacitor. If α equal to 1, the element is an ideal capacitor, if $\alpha = 0$, it behaves as a frequency independent ohmic resistor. The values of the equivalent circuit elements have been evaluated and listed in Table 1. It is obvious that all the capacitance values Q are in the pF range, revealing that the observed semicircle represented the bulk response of system [26]. Moreover, the grain resistance *R* decreases with rise in temperature due to the increase of the mobility of charge carriers that adds to the conduction process [27].

The expressions of the real and imaginary components of the whole impedance were calculated according to the following equations:

$$Z' = \frac{R^{-1} + Q\omega^{\alpha} + \cos\left(\alpha\frac{\pi}{2}\right)}{\left(R^{-1} + Q\omega^{\alpha}\cos\left(\alpha\frac{\pi}{2}\right)\right)^2 + \left(C\omega + Q\omega^{\alpha}\sin\left(\alpha\frac{\pi}{2}\right)\right)^2} \tag{2}$$

$$-Z'' = \frac{C\omega + Q\omega^{\alpha} + \sin\left(\alpha\frac{\pi}{2}\right)}{\left(R^{-1} + Q\omega^{\alpha}\cos\left(\alpha\frac{\pi}{2}\right)\right)^2 + \left(C\omega + Q\omega^{\alpha}\sin\left(\alpha\frac{\pi}{2}\right)\right)^2} \tag{3}$$

Fig. 5 shows the variation of real part of impedance (Z') with frequency at different temperatures. The spectra are characterized by magnitude of Z' decreases with rise in temperatures and frequencies which indicates the possibility of an increase in the ac conductivity with increasing temperature and frequency [23]. At