NEW AMORPHOUS PHASE $K_nH_2P_nO_{3n+1}$(n>>1) IN KH_2PO_4

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Abstract

Thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) and impedance spectroscopy (IS) were used to examine the high-temperaure phase equilibria of KH_2PO_4 (KDP). The tested samples (named as KDP*) were prepared by heating KDP crystals up to 260°C. On subsequent heating the solid samples from room temperature, it was apparent thermal dehydration reactions of KDP* into polyphosphates, $K_nH_2P_nO_{3n+}1(n>1)$. If the sample is heated above 300°C, such that all the constitutional water is released as a consequence of the dehydration reaction, then, a single solid phase (i.e. Kurrol's salt C, $K_nH_2P_nO_{3n+}1(n>>1)\cong(KPO_3)_n$ is present in it, which is stable up to 800°C. An analysis of the frequency dependence of the electrical conductivity showed different effects of correlation on ion jumping in the various phases of KDP*. In particular, different mechanisms were infered from the temperaure variation of the "stretching" exponemtial parameter, β, and the cossover frequency to the dispersive region of the ionic conductivity, ω_p, indicating a stable solid phase of KDP* below 260°C and a highly viscous phase above this transition temperature. The polyphospate phase or the inorganic polymer shows high proton conductivity whose optimization may find application in mid- to high-temepertaure use in the fuel cell emerging technology.

Keywords: *KDP, Kurrol's salt C, Electrical relaxation, Phase behavior*

Resumen

Análisis termogravimétrico (TGA), calorimetría diferencia de barrido (DSC) y espectroscopia de impedancia (IS) fueron usados para examinar el equilibrio de fases a altas temperaturas del KH_2PO_4 (KDP). Las muestras estudiadas (que designadas KDP*) fueron preparadas por calentamiento de cristales de KDP hasta 260°C. Calentando estas muestras sólidas desde el ambiente, llegaron a ser evidentes reacciones de deshidratación del KDP* para formar polifosfatos, $K_nH_2P_nO_{3n+\ 1}$ (n> 1). Calentando la muestra por encima de 300°C, tal que toda el agua constitucional se liberara como consecuencia de la reacción de deshidratación, se estabilizó una sola fase: la sal de Kurrol's C, $K_nH_2P_nO_{3n+}1(n>>1)\cong(KPO_3)_n$, estable hasta 800°C. Del análisis en frecuencia de la conductividad eléctrica, diferentes mecanismos se infirieron de la variación con la temperatura del parámetro de estiramiento exponencial, β, y de la frecuencia de corte al régimen dispersivo de la conductividad iónica, ω_p, indicando una fase estable del KDP* por debajo de 260°C, y una fase altamente viscosa por encima de esta temperatura. La conductividad iónica dc fue del orden de 10^{-4} $(\Omega cm)^{-}1$por encima de 300°C. El polifosfato o polímero inorgánico encontrado tiene características de electrolito protónico que puede tener aplicaciones a altas temperaturas en la tecnología emergente de las celdas de combustible.

Palabras Claves: KDP, Sal de Kurrol's C, Relajación eléctrica, Comportamiento de fases.

1. INTRODUCTION

Ammonium dihydrogen phosphate $NH_4H_2PO_4$ (ADP) and potassium dyhydrogen phosphate KH_2PO_4 (KDP) are well known antiferroelectric and ferroelectric crystal, respectively, belonging to the KDP family compounds [1]. KDP is the most investigated hydrogen bonded crystal, and its low-temperature phase behaviour has attracted the attention of many researchers. It is, for example, well known that KDP has a structural orthorhombic-tetragonal phase transition at the Curie temperature T_c =-150°C (under normal presure) [2], and it is attributed to ordering of the H-bonds. At higher temperatures, different experiments performed on this compound indicate a hight degree of disorder

with increasing temperature and a solid–solid phase transition near a characteristic T_p = 180°C can be seen in electrical conductyvity [3,4], dielectric constant [5] and specific heat [6] measurements.
A structural high–temperature phase transition (HTPT) from tetragonal to monoclinic symetry has been claimed for some KDP–type crystals [5] at a characteristic temeperature, T_p, wich is not far from thermal descomposition. But T_p is scattered more widely than one would expect and there are considerable differences in the published reports concerning high–temperature behavior. Its has been reported that the phase change is indicated by an anomaly in the electrical conductivity curve [3], dielectric constant [7] and other quantities around 180°C [8, 9], or by an abrupt increase in the conductivity at 171°C [10] or a dip in the conductivity around 150°C [11].

In addition, some authors claimed another anomaly of KDP around 110 ±10°C (T'_p) in addition to the 180°C (T_p) transition, by showing a knee in the conductivity at around this temperature [12].

It has been established that protons are the main charge carrier, and in order to explain the electrical conductivity in the temperature region below and above T_p and the mechanism of HTPT, various proton transport models have been proposed. The single particle approximation model of Imry, Pelah and Wiener [13], where the effective potencial for the proton in the hydrogen bond is an asymetric double–minimum potencial well having a fluctuating asymetry, is especially interesting because it predicts an additional phase transition at high temperature**,** T_p**.** According to this dynamical model, an abrupt change occur in the hydrogen bond at temperature T_p. Proton tunnelling almost stops and the hydrogen approaches one of thr oxygens in the hydrogen bond. As a result, the bond is drastically weakened, and thus the bonding of the PO_4 thetrahedron to its neighbours is weakened, and it might turn around its c–axis. This model also predicts that the force constant of the O–O bond tends to zero at the phase transition. Since the H–bonds are in the ab-plane, the macroscopic force constant in that plane will tend to zero.

Since Imry, Pelah and Wiener predicted the posibility of an HPTP in KDP [3], proton transport [3, 4, 14], disordered hindered rotation of H_2PO_4 tetrahedra [15, 16] and proton migration through synchronous rotation of PO_4 radicals [11] have been proposed in order to explain the electrical conductivity below T_p and the mechanism of the HTPT. Nevertheless, it has recently been reported by Choi and Chung [17] that conductivity data in the transition region could be interpreted solely as a chemical descomposition which occurs near 190°C. They showed, for instance, that the conductivity of KDP increases papidly near 190°C on the first heating run of a fresh sample, but on the subsequent thermal cycles, the ionic conductivity falls to a final value which follows the classical Arrhenius law. They also showed that at a constant temperature of 190°C the conductivity first increases rapidly with time and then decreases slowly with the progress of the dehydration. The highest protonic conductivity is obtained when the decomposition process is most active since there may be many defects available for hydrogen conduction.

In a previous paper, Lee [18] concluded that the thermal dedydration

$$nKH_2PO_4(s) \rightarrow K_nH_2PO_{3n+1}(s) + (n-1)H_2O(\nu) \quad n>1 \qquad (1)$$

takes place for T> T_p, where n is the number of molecules participating in the thermal decomposition, s and ν denote solid or vapour state, respectively. This means that a polymerization of the phosphate salt takes place forming KPO_3 repeating units.It was further proposed that the polymerization sets in at particular sities on the surface. Thus, Lee suggested that the term HTPT at T_p should be replaced by the term “onset of partial polymerization” at reaction sities on the surface”. Recently, Park et al. supported the Lee´s proposal that the high–temperature phenomenom is not related to the HTPT but chemical change by thermal decomposition [19]. But, there are still controversies about the existence of structural phase transition and thermal decomposition of KH_2PO_4.

In this work we report a study of the phase behavior of KDP above the reported HTPT-like phenomena at about 180°C, with the purpose to investigate proton transport in its controversial high-temperature phase.

2. ELECTRICAL RELAXATION

Two alternative formalisms are usually employed in the analysis of the electrical conductivity relaxation in materials with disordered structure [20], the

conductivity formalism in the frequency domain, and the electric modulus formalism which uses electric modulus data to obtain the decay function in the time domain. From de impedance data, $Z = Z' + Z'', (i = \sqrt{-1})$, the real part of the conductivity, σ´(ω), can be calculated from

$$\sigma'(\omega) = \frac{d}{A}\frac{Z'}{(Z'^2 + Z''^2)} \quad (2)$$

where $\omega = 2\pi f$ / Hz is the angular frequency, *A* is the electrode-electrolyte contact surface and *d* the distance between electrodes in a flat M|electyrolyte|M (M= metal) configuration.

The real and amamginary part of the electric modulus, *M (ω)*, are calculated from

$$M' = \frac{\omega A \varepsilon_0 Z''}{d} \quad (3)$$

$$M'' = \frac{\omega A \varepsilon_0 Z'}{d} \quad (4)$$

where ε_0 is the permittivity of free space. In time domain, an alternative representation of the electric modulus has been made in terms of a decay function Φ(t), which is related to relaxation of the electric field at constant displacement vector. Kohlrausch-Williams-Watts (KWW) "stretched" exponential decay functions of the form

$$\Phi(t) = \exp\left[-(t/\tau^*)^{\beta}\right] \quad (5)$$

have been observed in ionic conductors [21], where τ* is a temperature activated relaxation time and 0<β<1,the electric modulus is then expressed as

$$M(\omega) = M_{\infty}\left[1 - \int_0^{\infty} -\frac{d\phi(t)}{dt}\exp(-i\omega t)dt\right] \quad (6)$$

where M_∞ is the inverse of the high-frequency dielectric permittivity. Some models [22; 23] have proposed to explain the non-Debye behavior of the conductivity relaxation in structurally disordered solids, suggesting that a slowing of the relaxation process occurs as a result of correlated ion hopping. The stretched exponential parameter β may represent an index of correlation of ion motion, so that one would expext this parameter to be closet o zero for strong correlated systems and 1 for random Debye-like hops.

From the real part of conductivity, *σ´(ω)*, the dc conductivity , i.e. the limit for very low frequencies, can be extracted and, by comparison with simple equivalent circuits, contributions of diferent structural elements of the sample may be discriminated [24]. The Nernst-Einstain equation gives a direct relationship between dc conductivity *σ´(0)* and the diffusion coefficient *D*, from which the temeperature temperature dependence of the dc conductivity is often described empirically by and Arrhenius relation

$$\sigma(0) = A\exp\left[-\frac{E_A}{k_B T}\right] \quad (7)$$

where A is a pre-exponential factor, k_B is the Boltzmann constant and *T* is the temperature.

3. EXPERIMENTAL METHODS AND RESULTS

Monocrystals of KDP was grown by slow evaporation from an aquous solution of fine powder of comercial KDP (Aldrich).

Differential scanning calorimetry (DSC) and thermogravimetric analysisi (TGA) were performed with a TA instruments 2920 Modulated DSC and a 2950 TGA, respectively, using a heating rate of 10°C /min under a dry N_2 flux.

The electrical characterization of the samples was done by impedance spectroscopy (IS) using a two electrode configuration Pt|sample|Pt and a home-built temperature and atmosphere controlled cell for measurements. Polycrystalline pellets were prepared from finely ground single crystals pressed in a 5 mm die under 2.5 tons during 45 min. The electrode-electrolyte contact surface (A) and the distance between electrodes (d) were measured using a micrometer. No corrections for thermal expansion of the cell were carried out. The measuremets were carried out with a computer controlled Wayne Kerr 6420 LCR meter in the frequency range of 25 Hz -5 MHz, in the isothermal or in the heating cooling modes.

The electrical measurements were done under the

ambient air atmosphere, from room temperatre up to 360°C.

On heating a fresh KDP crystal in air up to 260°C, it is observed that after keeping the crystal at this temperatura for 20 minutes, it transforms to a transparent and highly viscous liquid. After this time, the sample turns to a milky-white color with numerous microscopic cracks [2,3,6,10,13,17]. On further heating the sample, the sample starts to dehydrate and becomes solid. It is important to point out that the samples used for the subsequent measurements were those obtained at 260°C when is still a transparent liquid and then cooled to room temperature and dehydrated to a solid phase under vacuum. The tested sample will be designated as KDP*.

Figure 1 shows the first heating DSC and the weight loss curves for the powdered sample, KDP*. From these figures one can observe, when the sample is heated at constant heating rate, that a major variations in the weight loss start to occur at about 225°C which corresponds well to the endothermic DSC peak. Notice that the transformation enthalpy of pure KDP at about 180°C has been reduced drastically, because the sample was previously thermally treated up to 260°C. On the other hand, the two-peak anomaly in the DSC curve at about 225°C consists of an endothermic-type peak followed by an exothermic-type peak. Moreover, the TGA curve shows that the total weight loss on heating the sample up to 400°C is about 10 %. If this weight loss is attributted to water removal from a pure KDP sample, which a product of the reation (1), then, considering in this reaction the case n>>1, the ratio of scaped product, for the total dehydration reaction of the sample, is

$$\frac{M((n-1)H_2O)}{M(nKH_2PO_4)} \cong \frac{M(H_2O)}{M(KH_2PO_4)} \times 100 = 13\% \quad (8)$$

where M is the atomic weight. The difference between the calculated value for total decomposition (13%) of pure KDP and the experimental one (10%) is explained by the fact that the original sample is not pure KH_2PO_4 but a mixture of KDP and a polyphosphate ($K_nH_2PO_{3n+1}$(s), n>1).

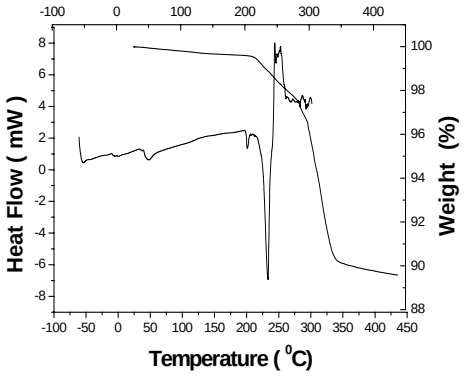


Figure 1. DSC and TGA first heating curves for the powdered sample KDP*.

Figure 2 shows the Nyquist plots, -Im Z vs Re Z, for the impedance behavior of KDP* at select temperatures between 200 and 300°C. A tipical spectra consist of two parts; (a) a high–frequency non–ideal arc of a semicircle associated to the bulk electrical response of the sample and (b) a low–frequency linear variation due to the sample-electrode interface effects.

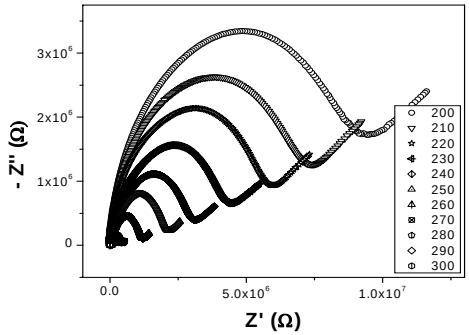


Figure 2. Typical impedance spectra for KDP* at temperatures between 200 and 300°C.

Figure 3 shows tipical plots of the frecuency dependence of the real part of conductivity $\sigma'(\omega)$ at severals isotherms between 90 and 300°C for KDP*. Note that $\sigma'(\omega)$ approaches a flat region at low frecuencies (with zero slope), which is associated to $\sigma'(0)$, the bulk dc the conductivity of the sampe at temperature T, $\sigma_0(T)$. As temperature T is increased, the value $\sigma_0(T)$ increases.

For a fixed tempearure, $\sigma'(\omega)$ increases with increasing frecuency after a characteristic crossover frecuency, $f_p = \frac{\omega_p}{2\pi}$, that also increases with

temperature.

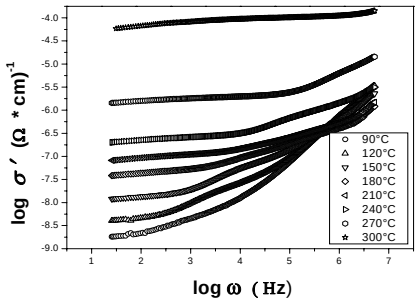


Figure 3. Frequency dependence of the real part of the conductivity $\sigma'(\omega)$ at temperatures between 90°C at 300°C.

The conductivity $\sigma'(0)=\sigma_0$, was then obtained from the asymptotic behavior of $\sigma'(\omega)$ as $\omega \to 0$, and the calculated σ_0 for each isotherm is presented in Arrhenius form in figure 4. Notice two different regimes of variation of $\sigma_o(T)$, with a change of activation energy at T =124°C. Above T =260°C, σ_0 increases rapidly with temperature, indicating the growing of the liquid phase in the sample, due to the water product of the dehydration reaction of KDP* (Eq.1), such that it is obtained an aqueous solution of Kurrol's salt C

$$(K_nH_2PO_{3n+1}) \square (KPO_3)n$$

$$n >> 1 \qquad (9)$$

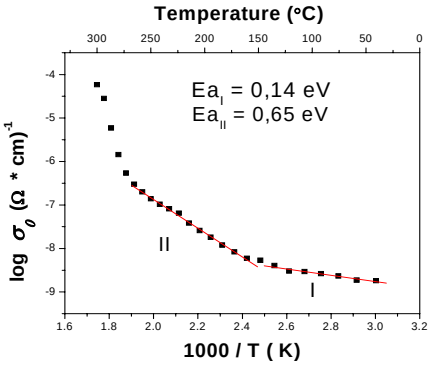


Figure 4. Arrhenius plot of the temperature dependence of the dc conductivity, $\sigma'(0)$ in the temperature range 30 – 300°C. The solid lines are least square fitting to segment of data points in three different temperature regions.

Further information regarding the conduction mechanism in the investigated ionic system is provided by analyzing the electric modulus formalism which is used to obtain the time decay funtion of the form expresed in Eq (6).

Figure 5 shows typical plots of the frequency depence of the imaginary part of the electric modulus, $M''(\omega)$, at several isotherms between 90 at 300°C for KDP*. The date is presented in a double logaritmic scale to bring out the power–law behavior at both side of the maximun, showing the strong non–Debye characters of the relaxation process, mainly at high frequencies with a slop lower than -1 (Debye value).

The time decay function $\phi(t)$ can be obtained from modulus data according to expression (6), which relates electric modulus to the Fourier transform of the time derivative of the decay function. Then, on the basis of a KWW dependence of $\phi(t)$, the parameter β and τ^* characterizing the relaxation mechanism can be obtained.

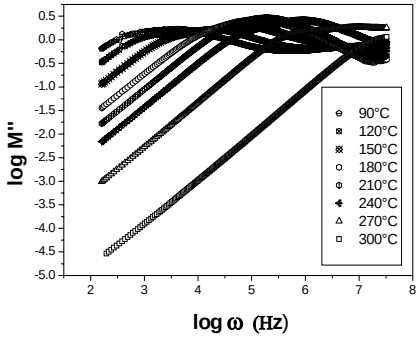


Figure 5. Frequency dependence of the imaginary part of the electric modulus, $M''(\omega)$ at temperatures between 90 and 300°C.

Figure 6 shows the temperature variation of β obtained by using the time domain representation de $M''(\omega)$. Notice that β shows there different regime with increasing temperature indicating different correlations of proton jumping's. At low temperature β decreases form 0.67 to 0.64 as the temperature increases. This indicates that proton jumping become more correlated in increasing temperature, probably because the proton transport is taking place on the surface of the sample due to a moisture in layer whose thickness is reduced on heating the sample, thus a smaller free volume is available for ion diffusion.

At the intermediate temperature region between 100°C and 225°C, β increases with increasing temperature from 0.54 to 0.64. At about T = 225°C

a step jump to a lower value (0.59) is observed, and from this temperature up to 300°C, β increasing again with temperature reaching a value of □ 0.7 at 300°C. Thus, this behavior of β indicate less correlation among moving ions as the temperature increase, but at about T=225°C a different regime of proton transport is evident, then supporting the view that at around this temperature, probably a dehydration reaction, as that predicted by Eq. (1), is taking place. This observation is also correlated with the temperature variation of the crossover frequency, f_p, plotted in Figure 7, which was calculated from the inverse correlation time, $1/\tau^*$, obtained from the fitting of $M''(\omega)$ to Eq. (6).

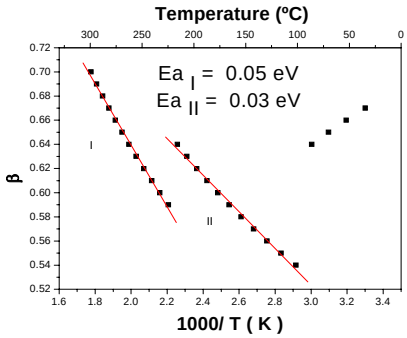


Figure 6. Temperature dependence of the "stretched"exponential parameter, β, obtained by fitting the $M'(\omega)$ data to Eq.(6).

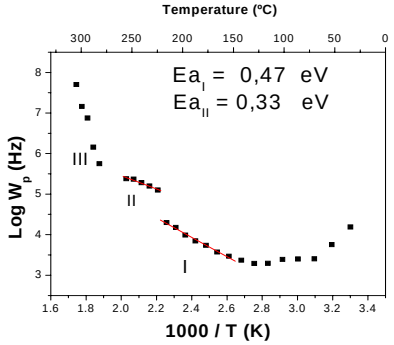


Figure 7. Arrhenius plot of the temperatura dependence of the cross – over frequency ω_p in the temperature range 30-300°C. The solid lines are least equare fitting to segment of data points in three different temperature regions.

4. ANALYSIS AND DISCUSSION OF THE RESULTS

Our results, based on thermal analysis (DSC and TGA) and electrical relaxation measurements indicate that the phase behavior of KH_2PO_4 is very sensible to thermal treatments and points defects that can be modified in presence of moisture in the surrounding gas phase.

The activation energies associated with ion transport (dc conductivity) and the crossover frequency for electrical relaxation, show similar variation with temperature, indicating that they obey similar transport mechanism. On increaing temperaure, a first region is apparent in which ion transport may take place on the surface of the sample due to moisture since all the transport parameters decrease on heating indicating less long-range conduction (lower dc-conductivity), higher correlation among moving ions (lower "stretching" exponemtial parameter, β) and lower cossover frequency to the dispersive region of the ionic conductivity (ω_p). On further increasing the temperature a second region is exhibited, in which a revesrse trend of behavior is observed in the previous parameters. Finally, a high-temperature region is found above 260°C after an abrupt change of the parameters in which their variations with increasing temperature is higly anomalous indicating a completely new phase in the sample, which by optical inspection shows a hihly viscous liquid with milky-white color.

Then, the two-peak anomaly observed in the DSC curve (Fig.1), which is well correlated with the starting of a rapid weight loss of the sample, is associated to the thermal decomposition of KDP* which is completed at higher temperaures due the scanning rate of temperaure used in these experiments (10°/min). Assuming that the scaped product is water during the DSC and TGA experiments (done under a dry N_2 atmosphere), then our calculation based on the reaction (1) for n>>1, gives a ratio of scaped product of 13% is of the order of that given by the experiment (10%), so this result confirm that on prolongued period of time of treating KDP above 230°C, Currol´s salt C is obtaines as final product. This salt under a humid atmosphere form a highly viscous phase with fast proton conduction. Therefore, the results of TGA indicate that the high temperature phenomena exhibited by KDP above T_p should be imterpreted as indicating the onset of partial polymerization at reaction sites on the surface, that propagates to the whole sample on increasing temperature. Thus, we considerer the electrical conductivity mechanisms above T_p for KDP including the partial break up of H-bonds and the formation of H_2O molecules by thermal decomposition at the crystal surface. Two

mechanisms of impedance relaxation in KDP at high temperature can involve crystal defects induced by water molecules and dehydration at the surface that it is reflected in the low frequency relaxation of conduction or low "stretching" exponential parameter, β.

5. CONCLUSIONS

In summary, the high temperature transformation of KDP, previously treated thermally at 260°C, was studied by means of impedance spectroscopy, differential thermal analysis and thermogravimetric measurements. An analysis of the frequency dependence of the electric modulus has allow us to obtain different effects of correlate ion motion on the electrical conductivity relaxation in various phases of KDP, showing difference mechanism in a stable solid phase below 230°C and a liquid - like-phase above this transition temperature. Dispersive conductivities in the frequency domain of the exponential form $\sigma' = \sigma_0(1+(\omega/\omega_p)^n)$ have been also found, where the crossover frequency ω_p is temperature dependent. The relaxation parameter β and an average relaxation time τ^* were compared with the inverse of the crossover frequency, $\tau = 1/\omega_p$, showing very good agreement and they are correlated for the various phases present in KDP. In particular, the results support the existence of a liquid like phase above 260°C that forms an aqueous solution of Currol's salt $C(KPO_3)n$, (n<<1) . In contact with air humid atmosphere (air with high relative humidity), this phase exhibits the highest proton conductivity ($\sim 10^4(\Omega cm)^{-1}$).

6. ACKNOWLEDGEMENTS

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