Preparation, Characterization and Electrical Conductivity of Condensed Sodium Phosphates

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Abstract

Condensed phosphates are generally prepared from their simple phosphates by heating at high temperature. The formation, structure and the morphology of the resultant condensed phosphates depend on the kind of inorganic cations as well as the conditions of preparation, temperature, heating time, and cooling rate of the melt.

Condensed sodium phosphates were prepared by thermal treatment of NaH_2PO_4, the effect of calcinated temperature, also was studied. The products were characterized by X-ray diffraction, IR spectrum, Transmission electron microscope (TEM).The results indicate that the produced phosphate depends on the heat of calcinations. The electrical conductivity of the product was measured in range from room temperature up to 300 ^{0}C. The measurements show that the condensed phosphates tend to be a semiconductor material.

Introduction

Phosphates have been used for ceramic materials, catalyst, metal surface treatments, fertilizers, food additives, etc [1]. Condensed phosphates are generally produced from simple phosphates by dehydration – condensation at elevated temperature [2]. The formation and the structure of the resultant condensed phosphates depend on the kind of the inorganic cations as well as reaction temperatures, heating time, cooling rate of the melt, and water vapor pressure through the dehydration processes. In general there are three types of the condensed phosphates, poly phosphate, cyclophosphate and ultra phosphate. Poly phosphate has a chain structure in which PO_4 unit shares two oxygen atoms, cyclophosphate has a cyclic structure and ultra phosphate has a network structure [3]. Depending on the chemical activity towards the acid and the base, the three types of the condensed phosphates can be distinguished.

In previous works, the authors prepared and characterized different types of simple and metal phosphates such as: sodium phosphate for detergents and feed animals [4, 5], iron and aluminium phosphates [6, 7] and rare earth phosphates as sensors [8]. Also, they prepared some tetra valent (Zr,Ti) phosphates as ion exchangers and semiconductor materials [9, 10] by applying the traditional and the sol-gel methods. As continuation to our policy, this paper aimed to study the preparation and characterization of sodium condensed phosphate and study the effects of dehydration temperature on the structure and morphology of the products. The electrical conductivity of the produced phosphates and the precursor materials were measured at different temperature to draw some light on the semiconducting properties of the condensed phosphate.

Material and methods

The starting material of this work was sodium dihydrogen phosphate, $NaH_2PO_42H_2O$ (mark). The condensed phosphates were prepared by dehydration process. In this work the precursors material ($NaH_2PO_4.2H_2O$) was denoted as sample (I). Two samples of the condensed phosphate were prepared. The first one (sample II) was prepared by

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ignited NaH_2PO_4 at 1000 ^{0}C for ~ 2hrs, the second sample (sample III) was prepared by firing sample II at 520 ^{0}C for 12hrs.

The three samples (I, II, III) were characterized by using X-ray diffraction technique to detect the formed phases and the crystallinity states of the materials, IR spectra and the transition electron microscope (TEM) to detect the morphology of the materials. Also the electrical conductivity of the produced and the precursors material was measured at different temperatures. The conductivity was measured using AG 4311B RLC-Meter, Japan in the temperature range from 25 to 200^{0}C. The values of conductivity (σ) was obtained after recording the resistance (R) and using the following equation.

$$\sigma\ (\Omega^{-1}\ cm^{-1}) = 1/\rho\ \rho = R.A/d \quad (1)$$

where ρ the receptivity, R the measured resistance, A is the surface area of the sample and d is the thickness.

Results and discussion

The produced phosphates at different temperature as well as the start material were characterized to follow the formation of the condensed phosphates. Fig 1(a, b, c) represents the X-ray diffraction of the compounds. Fig 1a shows that the start material was sodium dihydrogen phosphate $NaH_2\ PO_4.2H_2O$ in well crystalline form according to the card no. (10-0198 o). By heating sample I up to 1000^{0}C the material diffused and goes to form poly phosphate in amorphous state as shown in Fig 1b. When the resultant material fired at 520 C for 12hr, Fig 1c, the amorphous phosphate converted to crystalline poly phosphate having chemical formula $Na_3P_3O_9$ according to card no. (72-1628 c).

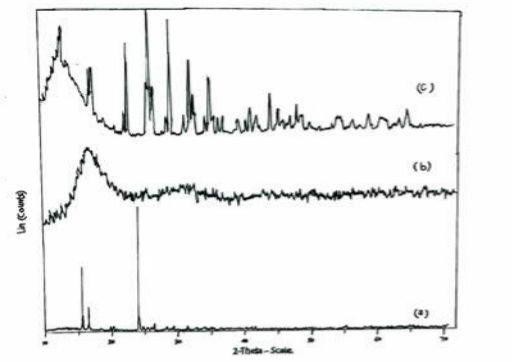

Fig. 1. (a,b,c) : X-ray diffraction of sodium phosphate samples a) sample I b) sample II c) sample III

The IR spectra of the three samples was recorded in Fig 2(a, b, c). The IR absorption of $NaH_2PO_42H_2O$ shows different absorption peaks at 615, 959, 527, 1254, 1045, and 1155 corresponding to the $(P_3O_9)^{-3}$, P-O-P, O-P-P, $(PO_3)^{-2}$ respectively. There peaks characterized the formation of the phosphate compounds [11]. In addition a peak at 3742 was appeared characterizes the O-H groups. By heating sample I at 1000^{0}C for 2hrs, the IR spectrum shows the same phosphate groups, but the deepness of the peaks at 1045,1245,1155 $(PO_3)^{-2}$ were increased indicating to the formation of poly phosphate. From other hand the depth of the peak of the hydroxyl group was decreased indicating to the dehydration of the phosphate. The IR spectrum of the sample (III) shows that:

1. The specific peaks of the phosphate compounds still appeared;
2. Two peaks at 1045, 1245, 1155 characterized to $(PO_3)^{-2}$ were identified;
3. The peaks characterized to the presence of the water content tend to disappear.

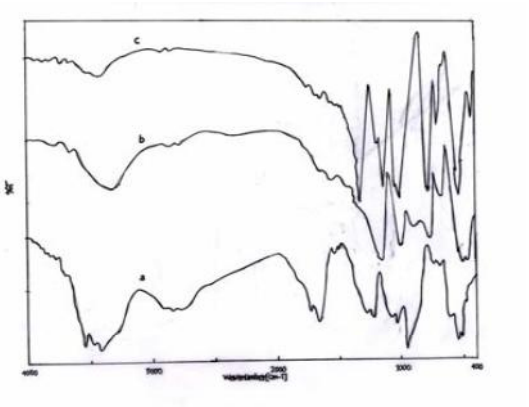

Fig. 2. (a,b,c) : IR spectrum bands of sodium phosphate samples a) sample I b) sample II c) sample III

The results of the transmission electron microscope (TEM) for the three samples were represented in Fig 3(a ,b, c). For sample I, Fig 3a, the TEM shows that this material have a well arranged crystalline and having nearly the same particle size in the range of 16 nm to 82 nm. Also the boundary of the grains well defined.

By heating the sample I to obtain sample II the general TEM shape shows that sample I is converted to amorphous with some clusters formations without considerable change in the size.

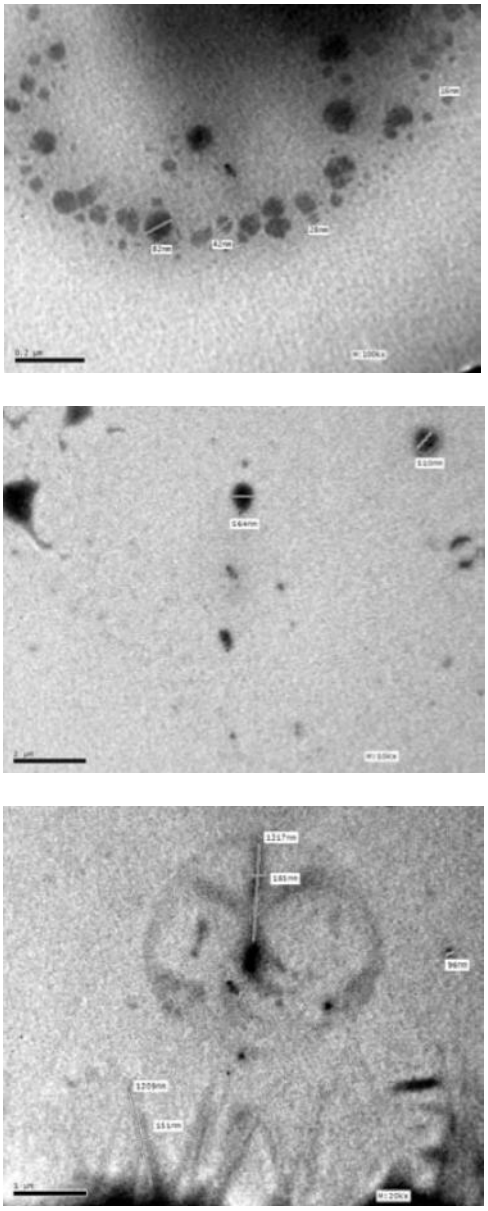

Fig. 3. (a, b, c): TEM of sodium phosphate samples
a) sample I b) sample II c) sample III

For sample III the TEM graph 3c shows that:

1. A nanotubes shape was appeared.
2. The appearance of a circle shape with specific one needle that may be corresponding to the condensed phosphate formation.

To study the behavior of electrical conductivity of the starting material as well as the resultant condensed phosphate, the electrical conductivity was measured in the temperature range from 25 to 200 ^{0}C at 1KHz. Fig 4 (a, b, c) represents the variation of log conductivity (σ Ω^{-1} cm $^{-1}$) with reciprocal of absolute temperature (k^{-1}). It is noteworthy that the three samples behave as semiconducting material with some variation according to their structure. Fig 4a for NaH_2 PO_4, three region on the curve of log σ – 1/T can be specified. The first region between 25 to ~ 70^{0}C where the values of electrical conductivity increase with temperature which is the typical behavior of the semi conducting materials. This behavior may be due to the protonic conductivity which increase the mobility of charge carriers. So hopping model is the most suitable one to be applied, where the charge carriers jump from one localized state to an other until they reach the conduction band. The second region between 70 to ~ 150^{0}C, where the electrical conductivity is nearly independent on the temperature. This region may be corresponding the melting of NaH_2PO_4 where the thermal energy consumed in the fusion of the start material. The third part, inspire of the values of the electrical conductivity lies in the range of the semiconducting material, it tends to loss this property due to a change in the phases under consideration as illustrated for X-ray. The formation of non-conducting layer at the inter-granular spacing similar to that formed on the ceramic materials when heated [12].

For the other two samples II and III (Fig 4 b, c) the values of the electrical conductivity is affected slightly by the temperature. On other hand, this behavior may due to the losses of the hydration water and reducing the movement of the rotated groups by condensation. In comparison, it is observed that the values of the electrical conductivity for the three samples behave as the following sequence.

NaH_2PO_4 > crystalline condensed phosphate > amorphous condensed phosphate

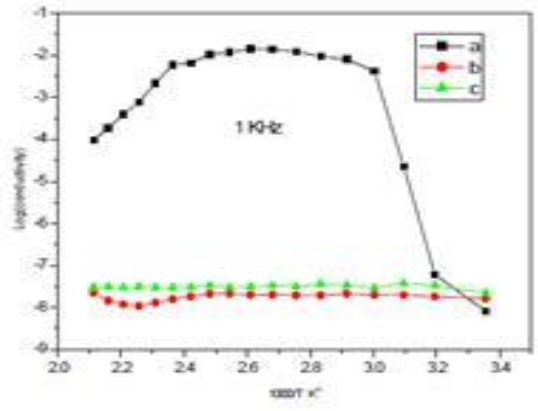

Fig.4. The variation of AC-electrical conductivity with temperature for sodium phosphate samples a) sample I
b) sample II c) sample III

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