



Studies on obtaining of Zinc phosphate powders

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Abstract

In most of the pigments, we find those of Zinc based on phosphates, the pigments have wide application in painting, corrosion and surface treatment, the method of synthesis of $Zn_{3-x}Co_x(PO_4)_2$ powders with ($x = 0, 1, 2$) solidly from the solid state reagents ammonium phosphates, Zinc oxide and cobalt nitrates, the powders were treated at between $200^\circ C$ and $950^\circ C$ then air cooling.

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1. Introduction

The main purpose of these powders is the use in the paint as a pigment and anticorrosive additive and a substrate on the surfaces against the entry of air, the most frequently used pigments, having very good anticorrosive properties, included lead and zinc chromate. However, both pigments belong to very dangerous and very toxic substances. With regard to the ecological reasons, these pigments are removed from the paint composition and environmentally friendly pigments replace them, zinc phosphate finds the widest application. This compound is non-toxic the anticorrosive properties of zinc phosphate depend, largely, on the particle size distribution. Therefore, it is intended to obtain pigments having the appropriate size already in the technological process or they are subjected to micronization [1].

There are several methods for the preparation of phosphate-based zinc materials based on different raw materials has been developed. However, the products obtained in this approach can hardly be classified in materials [2-5].

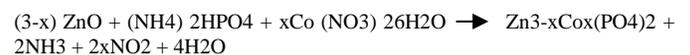
The purpose of these studies was to develop a new zinc phosphate material with the very small size of crystallites as possible and the use of inorganic compounds as precursors.

2. Experimental

The reagents of the analytical grades were used in these studies. The zinc phosphate was prepared from the oxides and hydrogen phosphate ammonium necessary for the preparation of $Zn_{3-x}Co_x(PO_4)_2$ with ($x = 0, 1, 2$) the reactants are mixed

in stoichiometric proportions then grinding for one hour to obtain a homogeneous mixture. The powder is then ground in a mortar and heat-treated at $200^\circ C$, $400^\circ C$, $600^\circ C$, $800^\circ C$, $900^\circ C$ and $1000^\circ C$ for 24 hours in an oven.

The solid-state reaction allowing the formation of the following $Zn_{3-x}Co_x(PO_4)_2$:



The obtained products were examined by X-ray diffraction analysis. The studies were performed on a X'Pert PRO (Philips) diffractometer using the X-ray tube with a cobalt anode. The phase composition and the average of crystallite size of obtained compounds were determined. The changes of crystallites average size were determined using Scherrer's equation [3-4].

Table 1: Table gives the colors of $Zn_{3-x}Co_x(PO_4)_2$ when the % mass is varied.

% of mass	formula	color
x=0	$Zn_3(PO_4)_2$	creamy white
x=1	$Zn_2Co_1(PO_4)_2$	purple
x=2	$ZnCo_2(PO_4)_2$	purple

The powders obtained for x% mass substitutions (see table above) were characterized by X-ray diffraction (Fig.1)

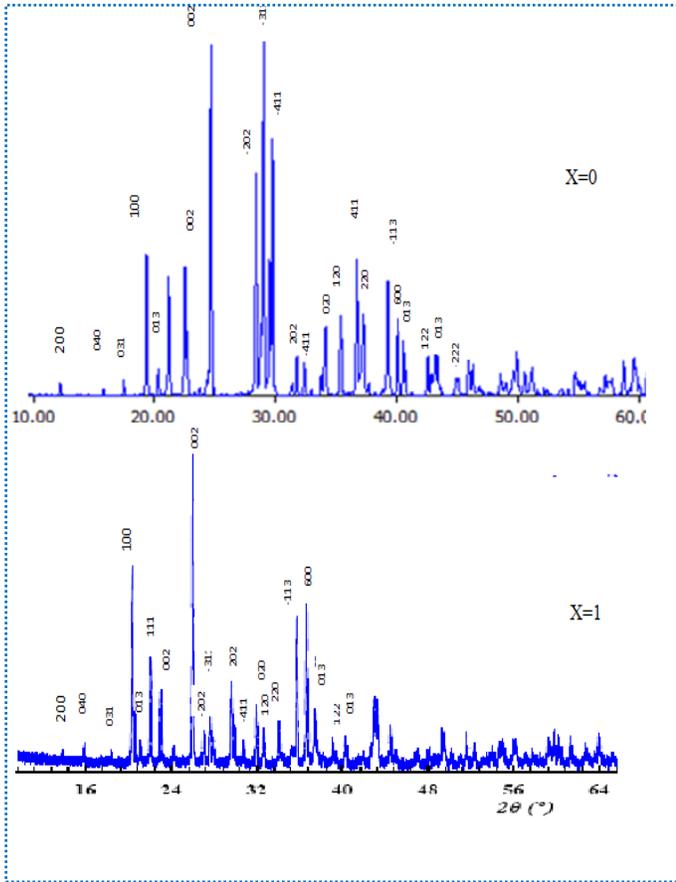


Figure 1: X-ray powder diffraction pattern $Zn_{3-x}Co_x(PO_4)_3$ with ($x = 0$ and 1) of Co

Table 2: Cell parameters of powders $Zn_{3-x}Co_x(PO_4)_3$ with ($x = 0$ and 1) of Co

Samples	A(Å)	B(Å)	C(Å)	B(°)
$Zn_3(PO_4)_2$	15.261	5.641	6.309	70.11
$Zn_2Co_1(PO_4)_2$	12.866	5.253	7.764	97.89
$ZnCo_2(PO_4)_2$	11.189	7.253	7.690	90.45

3. Result and Discussion

When a substitution of the initial phase by the Cobalt transition element, which is responsible for the coloring of the powders by virtue of these physical and chemical properties, it has been seen that the parameters of the mesh decrease this variation of the phosphates $Zn_{3-x}Co_x(PO_4)_2$ with ($x = 0, 1$ and 2) depending on the composition x table 2. This steady evolution shows that we have a continuous solid solution across the entire $0 \leq x \leq 1$ domain. We observe an increase of the parameters a, b and c. These variations can be explained in the framework of the crystalline structure of these phosphates, formed by a three-dimensional sequence of PO_4 groups, linked by the vertices (fig.2). The increase of the parameters a, b and c can be related to the size of the Co^{2+} ion ($r = 0.65 \text{ \AA}$) smaller than that of the Zn^{2+} ion ($r = 0.74 \text{ \AA}$). Moreover, this increase is related to the elasticity of the network formed by groups linked only by

vertices. Any compression in one direction induces expansion in the perpendicular direction.

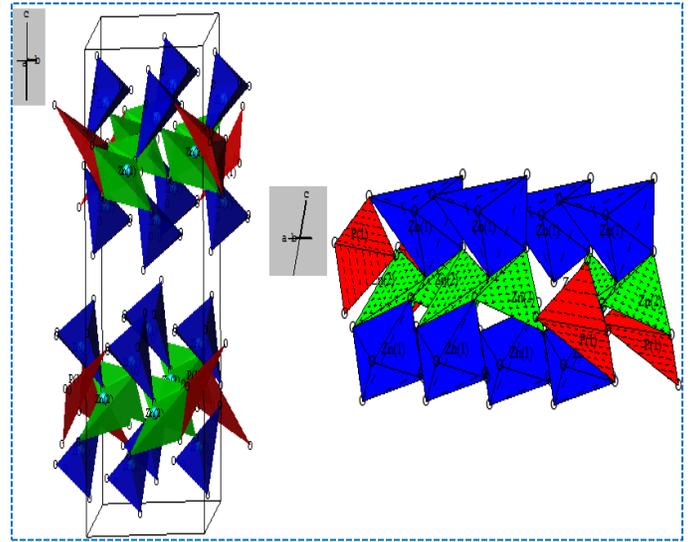


Figure 2: shows the structure of $Zn_3(PO_4)_2$ and represents the sequence of $Zn(1)O_6$ - $Zn(2)O_5-PO_4$ polyhedra

The XANES spectra of $Zn_3(PO_4)_2$, $Zn_2Co(PO_4)_2$ and $ZnCo_2(PO_4)_2$ are presented in fig.3, we observe two features: a first weak peak and a second intense peak and a second intense peak.

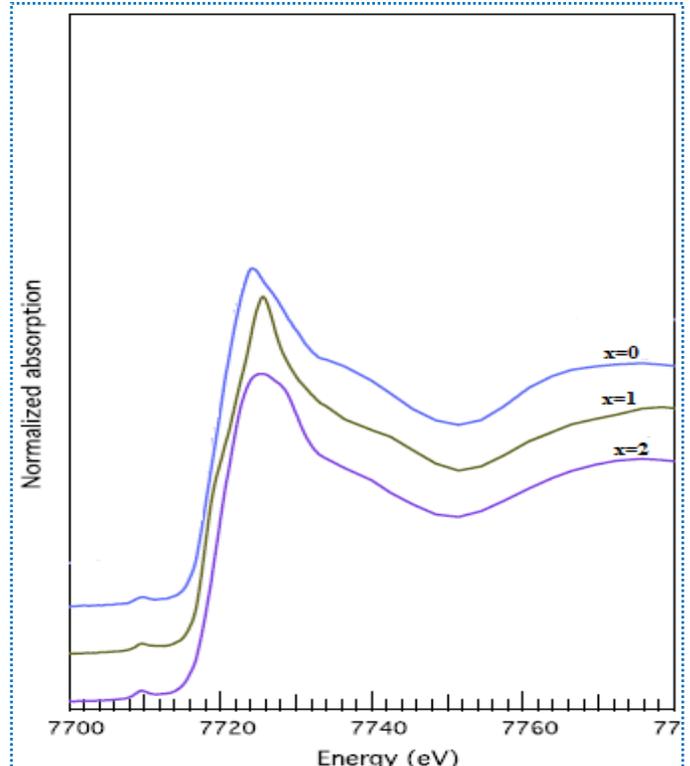


Figure 3: XANES spectra of $Zn_{3-x}Co_x(PO_4)_2$ with $x=0, 1$ and 2

In $Zn_3(PO_4)_2$, $Zn_2Co(PO_4)_2$ and $ZnCo_2(PO_4)_2$ the multiple transitions observed arise from energy level splitting and may be labeled in (C_{2v}) symmetry. Spectroscopic data confirm that (D_{3h}) and (C_{4v}) symmetries may be distinguished upon the intensity of the optical absorption bands and crystal field splitting values. We discuss the influence of the geometrical distortion and of the nature of the next nearest neighbors as shown in fig.4.

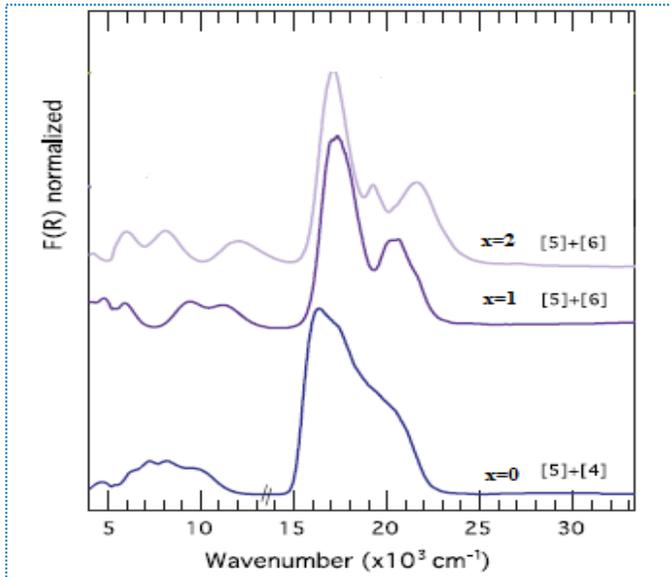


Figure 4 Diffuse reflectance spectra of sample powders $Zn_{3-x}Co_x(PO_4)_2$ with $x=0, 1$ and 2 Normalized intensity

The microstructure and morphology have an important role in determining the magnetic and electric transport properties and these were examined by a high-resolution scanning electron microscope. SEM images are shown in fig.5, The figure 5 shows an SEM picture of Fe_3PO_7 of the sample synthesized by solid state method Compared the particle size is much smaller, and secondary particles are less than $1 \mu m$.

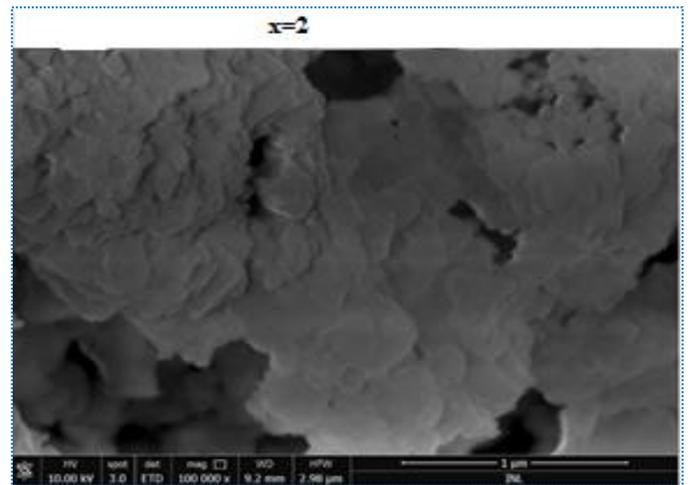
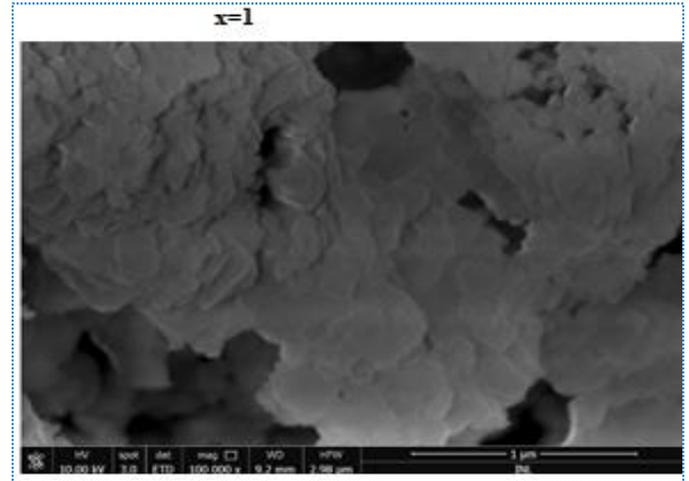
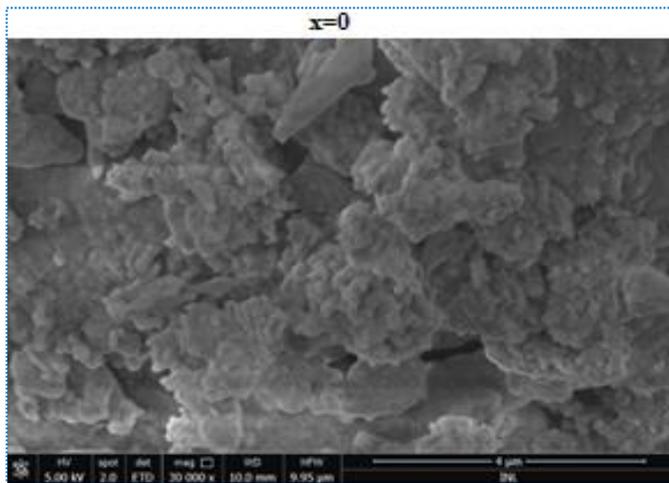


Figure 5: SEM image of of sample powders $Zn_{3-x}Co_x(PO_4)_2$ with $x=0, 1$ and 2

Porous structure and submicron grains characterize each sample. The porosity is entirely intergranular, the pores are interconnected to form pore channels. Since the pores are channeled and do not have well defined shape, it is difficult to give a particular dimension of the pores. In the sample, one can observe submicron grains, a uniform grain size distribution and the absence of the grain agglomerates as shown in fig.5.

The infrared spectrometric analysis of the samples was made via a Shimadzu IR solution 1.30 FTIR type spectrometer with a wavenumber between 4000 and 600 cm^{-1} . The preparation of the pellets to be examined is carried out as follows: about 2 mg of the powder to be analyzed is mixed with 98 mg of dry KBr. The results of the Infrared Absorption Spectroscopy (FTIR) analysis of the powders synthesized at different temperatures are shown in fig.6, while Table 3 summarizes the positions and assignments of the noted absorption bands. Fig.6 shows the infrared absorption spectrum of the powders synthesized at 900°C .

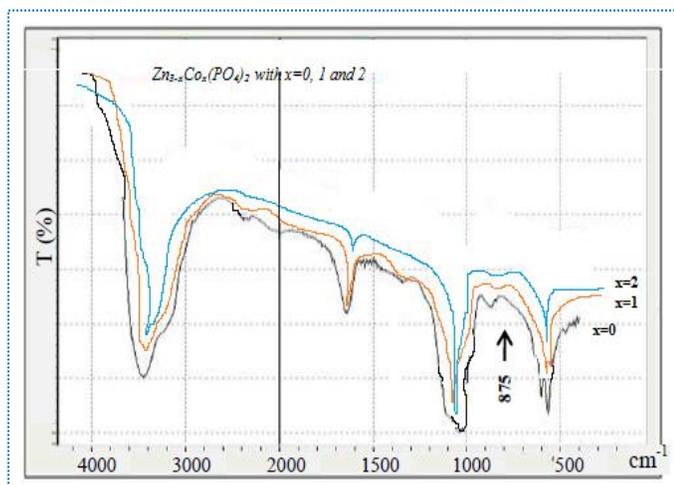


Figure.6: Infrared absorption spectra of the products obtained of $Zn_{3-x}Co_x(PO_4)_2$ with $x=0, 1$ and 2

The phosphate is identifiable by the vibration bands of PO_4^{3-} : 474-571-601-962- 1046-1087 cm^{-1} [7] groups. During the crystallization of $Zn_{3-x}Co_x(PO_4)_2$ with $x=0, 1$ and 2 , the internal hydrolysis of a PO_4^{3-} [7, 8] group occurs simultaneously. Thus, a characteristic band of HPO_4^{2-} groups is observed at 875 cm^{-1} . Phosphate at 900 ° C gives rise to the formation of the phosphate phase. Fourier transform infrared spectroscopy (fig.6) of $Zn_{3-x}Co_x(PO_4)_2$ with $x=0, 1$ and 2 calcined at 900 ° C shows several absorption bands, among which those at 552, 594, 606, 945, 972, 1025, 1042, 1120 cm^{-1} are characteristic of PO_4^{3-} groups [6].

Table 3: Position and assignment of the infrared absorption bands of phosphate $Zn_{3-x}Co_x(PO_4)_2$ with $x=0, 1$ and 2

Position of bands (cm-1)	allotment
474	PO_4^{3-} (symmetrical deformation)
530	HPO_4^{2-} (HO- PO_3 deformation)
571 - 601	PO_4^{3-} (antisymmetric deformation)
630	OH^- (libration band)
875	HPO_4^{2-} (P-OH elongation)
962	PO_4^{3-} (symmetrical elongation)
1046-1087	PO_4^{3-} (antisymmetric elongation)
1180-1200	HPO_4^{2-} (deformation in the plane of OH groups)
1630	H_2O (deformation of the molecules of water bound by bridges H)
3000-3400	H_2O (symmetrical elongation of water molecules bound by bridges H)
3560	OH^- (symmetrical elongation)

4. Conclusion

It was found that a nanocrystalline zinc phosphate tetrahydrate (about 2 nm) can be obtained in the following processes: the synthesis of $Zn_3(PO_4)_2 \cdot 4H_2O$ from diammonium phosphate and zinc nitrate, a low-temperature calcination of precipitated phosphate and the hydration of intermediate. Whereas an anhydrous zinc phosphate with the average crystallite size of

about 3 nm can be obtained in the process of a two-stage calcination (initially at a low temperature, and subsequently at a higher temperature) of the gel obtained. Finely dispersed powders were produced by solid-state method; XRD and SEM. investigated the structure and morphology of the heat-treated samples. The obtained results show that by suitable heat treatment of the combusted powder it is possible to control the structural characteristics, porosity, grain size and specific surface area, these materials can be classified as a phosphate anode material and provides a new idea on cathode and / or anode materials design.

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