SYNTHESIS OF mono- or di-VALENT CATIONS SUBSTITUTED Al- or Fe-PHOSPHATES AND THEIR ELECTRICAL CONDUCTIVITY

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Abstract Substituted AlPO_4 and FePO_4 with Na^+ and Cd^{+2} were synthesized by sol-gel method from H_3PO_4 and the chloride salts using ethylene oxide as a gelating agent. Chemical analysis, Infra red spectra and x-ray diffraction were measured for characterizing the products. Electrical conductivity of the samples, dried and sintered at 550°C , was performed.

The results of characterization indicate that the substitution process depends on the mole % of the substituant cations where they improved the crystallinity of the formed phases. The electrical conductivity measurements indicated that the prepared phosphates behave as semiconductor materials and its value depends on the nature of cations, and the thermal treatment.

INTRODUCTION

Due to the importance of metal phosphates especially aluminium phosphates, for their structural similarity to SiO_2 , large surface area, and high surface acidity, on the catalytic properties, many studies have been done. Itoh et al.¹ found that metal substitution enhanced the catalytic activities of M-Al-P-O due to the increase of the basic sites, while the amount of acid sites slightly changed. Alkali aluminophosphate, prepared from $\text{Na}_2\text{O-Al}_2\text{O}_3\text{-P}_2\text{O}_5$, has a glass transition temperature under 400°C and thermal expansion coefficient greater than $150 \times 10^{-7}/^\circ\text{C}$ and so they are used for special hermetic seals^{2,3}.

Phosphate-based Materials containing alkali metals are of interest for their ionic conductivity, which can easily reach values of the order of $10^{-12} \text{ ohm}^{-1} \text{ cm}^{-1}$ near room temperature⁴. Also, their materials have a great stability and a good capacity of charge substitution, so their

electrical properties may be modulated by just varying their chemical compositions and structures by substitution with alkali metals⁵.

A mesoporous preparation of iron and substituted iron phosphates were investigated by different authors to be used as a catalyst in dehydration of alcohols^{6,7}.

In a previous work⁸, AlPO_4 and FePO_4 were prepared with different methods depending on the precursor materials. The characterization of the products showed that the crystallinity and the formed phases depend on the method of preparation as well as the temperature and the time of sintering. This work is aimed to study the effect of substitution with mono- and divalent cations on the structure and the electrical properties of AlPO_4 and FePO_4 prepared by the sol-gel technique.

EXPERIMENTAL

Substituted aluminium and iron phosphates having the general formula $\text{M}_x\text{Al}_{1-x}\text{PO}_4$ and $\text{M}_x\text{Fe}_{1-x}\text{PO}_4$ ($\text{M} = \text{Na}, \text{Cd}$ and $x = 0.2, 0.5$ and 0.8 mole %) were prepared directly from H_3PO_4 and metal chloride salts in presence of ethylene oxide as a gelating agent. NaCl or CdCl_2 was added to the gel solution with continuous stirring. The products after drying under vacuum were fired at 550°C for 20h. The method of preparation was described in detail⁸.

The obtained products were characterized by using the chemical analysis, infrared spectra, and x-ray diffraction.

The electrical conductivity of the products sintered at 550°C was performed as a function of temperature using LCR Hioki Hitester 3532 instrument (Japan). The samples were ground, pressed to discs of 11mm diameter and 2-3 mm thickness under pressure of 5000 kg cm^{-2} .

RESULTS AND DISCUSSION

Table 1 shows the chemical analysis of the prepared samples determined by atomic absorption spectroscopy (AAS). The results indicate that:

- 1- For AlPO_4 substituted with Na, the percentage of both Na and phosphate ions are in agreement with the theoretical values, where there is some deviation in the concentration of Al, which disappeared in case of Cd substitution.
- 2- For iron phosphate substituted with 0.2 mole Na or Cd, there is a large deviation between the experimental and the theoretical values, while a good ratios were obtained at $x = 0.5$ and 0.8 . This means that the increase of sodium or cadmium contents stabilized the stoichiometric chemical ratios.

Fig. 1A represents the infrared spectra of AlPO_4 , $\text{Na}_{0.2} \text{Al}_{0.8} \text{PO}_4$, $\text{Na}_{0.5} \text{Al}_{0.5} \text{PO}_4$ and $\text{Na}_{0.8} \text{Al}_{0.2} \text{PO}_4$. This figure shows that the main bands of O-P-O, P-O, H-OH, P-O-H and O-H, which characterized AlPO_4 were appeared⁸. On the other hand, a new band at $\sim 800 \text{ cm}^{-1}$ specific for P-O-P⁹⁻¹¹ starts to appear with 0.2 mole Na, this peak sharpened with 0.5 and 0.8 mole% Na, while the P-O band ($\sim 1100 \text{ cm}^{-1}$) becomes sharp and well defined. Another band appears at $\sim 600 \text{ cm}^{-1}$ corresponds to $(\text{P}_3\text{O}_9)^{10,11}$.

For AlPO_4 substituted with Cd, Fig 1B, an additional band was appeared at 630 cm^{-1} and attributed to formation of pyrophosphate¹⁰. Fig. 1(C and D) related to FePO_4 substituted with Na or Cd indicate that the absorption peaks characteristic of phosphates P-OH, H-OH, P-O, O-P-O in addition to Fe-O (600 cm^{-1}) were appeared.

TABLE 1 The chemical analysis of the prepared samples

Sample	gm%				
	Al	Na	Cd	Fe	PO ₄
Na Al PO ₄ (0.2 Na)	18.18	3.72	-	-	64.99
Na Al PO ₄ (0.5 Na)	17.13	8.53	-	-	62.95
Na Al PO ₄ (0.8 Na)	15.43	13.35	-	-	63.93
Cd Al PO ₄ (0.2 Cd)	15.2	-	16.3	-	64.73
Cd Al PO ₄ (0.5 Cd)	9.31	-	35.5	-	63.97
Cd Al PO ₄ (0.8 Cd)	5.73	-	48.68	-	62.31
Na Fe PO ₄ (0.2 Na)	-	0.51	-	41.35	68.51
Na Fe PO ₄ (0.5 Na)	-	7.5	-	36.36	61.91
Na Fe PO ₄ (0.8 Na)	-	12.35	-	30.54	51.08
Cd Fe PO ₄ (0.2 Cd)	-	-	19.8	33.88	56.82
Cd Fe PO ₄ (0.5 Cd)	-	-	40.08	29.00	46.83
Cd Fe PO ₄ (0.8 Cd)	-	-	53.50	16.36	41.57

FIGURE 1 The infra-red spectra of the prepared samples

Fig. 2A represents the XRD patterns of the gel Na-Al-P-O system heated at 550°C. The results indicate that amorphous phases were formed at $x = 0$ and $x = 0.2$ mole % sodium. In case of higher Na additions ($x = 0.5$ and $x = 0.8$), the diffraction peaks due to AlPO_4 , sodium aluminium pyrophosphates, $\text{Al}_6\text{P}_6\text{O}_{18} \cdot 9.5 \text{H}_2\text{O}$ (ASM card No. 37-02110) and NaAlPO_4 ($2\theta = 23.44, 28.84$ and 31.2) in addition to traces of NaCl attached to phosphate groups were developed. By raising the sintering temperature up to 660°C for the sample $\text{Na}_{0.5}\text{Al}_{0.5}\text{PO}_4$ the crystallinity of the formed phosphates was developed.

By substitution with Cd ions, the amorphous AlPO_4 was converted to a crystalline phase and the formation of CdClPO_4 was indicated, while formation of CdAlPO_4 is not observed Fig. 2B.

For FePO_4 substituted with Na ions, Fig 2C, NaFePO_4 was slightly observed at 0.2 mole Na. The crystallinity were developed and sharpened by Na/Fe substitution regardless of the heat treated atmosphere beside formation of $\text{FeH}_2\text{P}_2\text{O}_7$ and $\text{Fe}_4(\text{P}_2\text{O}_7)_3$ species. These results were in agreement with the findings obtained by Itoh et al¹², where the x-ray patterns showed that FePO_4 is reduced to condensed iron phosphate by heating up to 500°C in vacuum.

A series of compounds, CdCl_2 , FeCl_3 , CdPO_4 , $\text{FeH}_2\text{P}_2\text{O}_7$, $\text{Fe}_4(\text{P}_2\text{O}_7)_3$, FePO_4 and Fe_2O_3 were observed in case of substitution with Cd ions, Fig. 2D.

Both Al and Fe phosphates series showed semiconductive behavior, where the electrical conductivity increases approximately linearly with temperature, following Arrhenius law, Fig 3. A relative high conductivity value of iron phosphates sample ($1.2 \times 10^{-6} \text{ ohm}^{-1}\text{cm}^{-1}$) compared with that of aluminium phosphates series ($\sim 3.2 \times 10^{-8} \text{ ohm}^{-1}$

FIGURE 2 The x-ray patterns of the prepared samples

FIGURE 3 The electrical conductivity of the prepared samples.

cm⁻¹) was recorded. This is explained by the possibility of ready electron exchange of di- and tri-valence iron ions¹³.

The temperature-conductivity dependence of substitution of Na or Cd cations for Al or Fe in their phosphate compounds, $M_x Al_{1-x} PO_4$ or $M_x Fe_{1-x} PO_4$ at $x = 0.5$ mole, has been investigated. Arrhenius plots of the electrical conductivity of the two compound series were shown in Fig 3. The results indicate that replacing Al^{3+} by Na^+ increases the conductivity (σ) at room temperature up to 150°C where it decreases slightly with temperature, then increases and comes back to the value of the un-substituted sample. As Cd substitutes Al in its Al-P compounds, σ has still higher values than that of Al-P, but less than that of Na-Al P, and has nearly the same trend with temperature.

In case of Fe-P compounds substituted by Na or Cd, σ increases but $\sigma_{Cd/FeP} > \sigma_{Na/FeP} > \sigma_{FeP}$. As the temperature increases $\sigma_{Na/FeP}$ increases regularly and $\sigma_{Cd/FeP}$ was observed to be temperature independent. These results show that a particular mixture of ionic and electronic conductivity mechanisms occurred with different cation substitution as well as at low and high measuring temperatures¹⁰.

CONCLUSION

$Na_x Al_{1-x} PO_4$, $Cd_x Al_{1-x} PO_4$, $Na_x Fe_{1-x} PO_4$ and $Cd_x Fe_{1-x} PO_4$ compounds were synthesized using the ethylene oxide, H_3PO_4 and metal salts, where $x = 0.2, 0.5$ and 0.8 mole %. The electrical conductivity of the products was measured and discussed.

These results indicated that:

1- Sodium aluminium phosphate, sodium iron phosphate and cadmium iron phosphate were formed at high concentration of Na and Cd, while

cadmium aluminium phosphate was not observed. Also a pyrophosphate salts were formed at 550°C.

2- The additives of Na or Cd cations improved the crystallinity of the formed phases.

3- The electrical conductivity of the substituted and unsubstituted samples depend on the nature of cations, their mole percentage and the heat treatment.

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