SOL-GEL SYNTHESIS OF AlPO_4 AND FePO_4

MOHAMED Sh. KHALIL, ADLY A. HANNA*, MARWA A. EL-SAYED

Inorganic chem. Dept., National Research Center, Dokki, Cairo, Egypt.

Abstract The aim of this work is to prepare and characterize AlPO_4 and FePO_4 with different methods depending on the precursors materials. Al PO_4 was prepared from aluminium ethoxide Al (OEt)_3 and phosphoric acid, Al (OEt)_3 and ethyl phosphate $(\text{Et})_3 \text{PO}_4$ and aluminium chloride with phosphoric acid in presence of ethylene oxide gas as a gelating agent. Fe PO_4 was prepared by dissolution of Fe_2O_3 in H_3PO_4 and from FeCl_3 with H_3PO_4 in presence of ethylene oxide.

The prepared samples were characterized by chemical and thermal analyses, x-ray diffraction and infrared spectroscopy. Infra-red charts indicate that the specific groups of the phosphate salts are appeared in all samples. X-ray diffraction patterns show that the crystalline phases of the product depend on the precursors material, the method of preparation and the temperature and time of sintering. The DTA curves indicate that no changes are observed between 300-700°C.

INTRODUCTION

Because the phosphate compounds have wide applications in many technological fields such as non linear optics, electronics industry, biocompatible materials, super-ionic conductors, ion exchangers and in low thermal expansion materials, different trials were done for preparation of some specific phosphates¹⁻⁴. Among the different methods of preparation, sol-gel route was considered as the most preferable one because of their homogeneity, purity and lower temperature of sintering of the products⁵⁻⁸.

Aluminum phosphate powders⁹ were prepared by simultaneous admixture of aluminum nitrate, sodium polyphosphate and ammonium hydroxide. The characterization of the products by elemental analysis, x-ray diffraction, infrared spectroscopy, scanning electron microscopy and thermal conductimetric analysis show that the properties of the

powder are strongly dependent on the chemical composition, specially on the P/Al mol. ratio.

In alcoholic system, Ruren et al¹⁰ studied the influences of some main factors such as organic amine template, alcohol solvent, crystallization, temperature and time of heating, etc. on the phosphate product. They concluded that some amines particularly diamine and medium size primary amines, as templates were favored for the formation of layered aluminum phosphate. Based on the reaction between ethanolic complex of AlCl_3 and H_3PO_4 , Birchall and Kelly¹¹ prepared Al PO_4 glass form using the sol-gel technique. Kearby prepared Al PO_4 gel with high surface area from aqueous solution Al Cl_3 and H_3PO_4 using ethylene oxide as a gelating agent.

Porous and fine particles of iron phosphate were prepared from $\text{FeCl}_3 \cdot 6 \text{H}_2\text{O}$ and orthophosphoric acid using a modified sol-gel method in presence of propylene oxide as a gelating agent¹³.

The aim of this work is to prepare and characterize Al PO_4 and Fe PO_4 using different methods depending on the precursors materials. For choice of the most suitable method of preparation, the products were characterized by using the chemical and thermal analysis, infra red spectra and x-ray diffraction.

EXPERIMENTAL

Trials were done to prepare Al PO_4 and FePO_4 by different precursors materials and using different methods. Al PO_4 was prepared by three methods as naming a, b and c. For method (a): aluminium alkoxide Al (O Et)_3 and $\text{H}_3 \text{ PO}_4$, (b) Al(O Et)_3 and ethyl phosphate $(\text{Et})_3 \text{ PO}_4$ and for method (c) AlCl_3 and $\text{H}_3 \text{ PO}_4$ in presence of ethylene oxide gas as a gelation agent.

For FePO_4 the following methods were used: 1- The starting materials were Fe_2O_3 and H_3PO_4 and, 2- FeCl_3 , $\text{H}_3 \text{ PO}_4$ and ethylene oxide gas. Table 1 summarized a brief account for the methods of preparation and the last column contains a brief description of the solid products. Products were characterized by chemical analysis, thermal analysis, infra-red spectroscopy and x-ray diffraction analysis.

TABLE I Summary of the used methods of preparation of the phosphate samples.

Compound	Input Material	Methods of Preparation	Product
AlPO_4	(a) $\text{Al}(\text{OEt})_3 + \text{H}_3\text{PO}_4$ (org-inorg)	H_3PO_4 was added to $\text{Al}(\text{OEt})_3$ with molar ratio and stirring. Two layers were formed, with continuous stirring a solid product was precipitated. The product was separated by filtration and dried at 280°C for 9-10h. it is notice that the product is white crystal powder.	Powder white
	(b) $\text{Al}(\text{OEt})_3$ $(\text{Et})_3\text{PO}_4$ (org-org)	$(\text{Et})_3\text{PO}_4$ was added to $\text{Al}(\text{OEt})_3$ under N_2 conditions with stirring and leaved over night. A suspension solution was formed, by continuous stirring at room temperature, a fine white crystal was precipitated. The product was separated by filtration and dried at 280°C for 9-10 h.	Very fine powder
	(c) $\text{AlCl}_3 + \text{H}_3\text{PO}_4 +$ ethylene oxide gas + H_2O (inorg – inorg + E.O)	AlCl_3 was dissolved in H_3PO_4 and cooled to 0°C . Ethylene oxide gas was passed gradually with shaking, and continuous coaling to zero temperature. A white transparent gel was formed. The gel was dried under vaccum at 50°C , then fired at 550°C for 20h in air.	White transparent gel
FePO_4	(a) $\text{Fe}_2\text{O}_3 + \text{H}_3\text{PO}_4$ (inorg. + inorg.)	Dissolve Fe_2O_3 in part of H_3PO_4 with stirring at $60\text{-}80^\circ\text{C}$, and the other part is added gradually. Cool the solution to the room temperature and keep it for one hour. Filter the product and dried at 160°C .	Brown powder
	(b) $\text{FeCl}_3 + \text{H}_3\text{PO}_4 +$ ethylene oxide gas + H_2O (inorg – inorg + E.O)	Dissolve FeCl_3 in water with gentle heating, then add H_3PO_4 with stirring and coaling . Ethylene oxide gas passes through the solution fastly to facilitate penetration through the solution with stirring. The formed brown gel, dried under vacuum at 60°C . for 20 h. The dried product was fired 550°C /at 20 h. in air.	Brown transperant gel.

All the raw materials, and reagents were of spec-pure grade. The solvents were purified according to the required uses.

RESULTS AND DISCUSSION

Observations show that AlPO_4 prepared by both methods (a) and (b) give a white precipitate powder while method (c) gives a white gel transparent material.

Table 2 represents the aluminum and the phosphate contents for the obtained AlPO_4 determined by atomic absorption spectroscopy (AAS). The results indicate that: in case of using methods a and b, there were a considerable difference between the theoretical and the actual values for Al content while for the PO_4 part, the difference is acceptable. These findings indicate that the reaction of $\text{Al}(\text{OEt})_3$ with H_3PO_4 and $\text{Al}(\text{OEt})_3$ with ethyl phosphate is not completed. Using method (c), the difference between the theoretical and the actual values of Al and PO_4 ratios is almostly neglected. Results indicate that method (c) is the more proper one for preparation of AlPO_4 gel.

TABLE 2 Comparison between theoretical and actual values of Al and PO_4 contents by different methods:

Elemetns	A		B		C	
	Theoretical	Experiments	Theoretical	Experiments	Theoretical	Experiments
Al	10.622%	8.08%	10.7%	7.9%	22.31%	20.9%
P	37.57%	34.82%	30.153%	31.22%	66.188%	63.1%

Fig 1A shows the ir spectra of the prepared aluminum phosphate using the three methods and Table 3 tabulates the specific bands for the products in comparison with the literature values^{9, 14-17}. The obtained results indicate that:

1- AlPO_4 prepared by methods (a) and (c) a specific band at $\sim 500\text{cm}^{-1}$ characterized O-P-O group is appeared, while it shifts to $\sim 550\text{cm}^{-1}$ for sample (b). The broadness of this band increased from $c > a > b$.

FIGURE 1 The infra-red spectra of aluminium phosphates (A) and iron phosphates

(B).

2- Appearance of band between 1000 to 1240 cm^{-1} was characterized to P-O group. This band becomes broad for sample (c) and splits to sharp band and small shoulder for sample (a).

3- For samples (c) and (b), sharp bands at 1620 and 1680 cm^{-1} were specified to the H-O-H groups.

4-Two sharp bands appear between 2200 and 2400 cm^{-1} correspond to P-OH group.

5-Appearance of a broad band (3000-3650 cm^{-1}) characterized to O-H groups bonded to the Al-phosphate product.

6-By firing at 660°C, the absorption band characterized to the OH-group decreased. This may be due to the volatilization of the moisture content.

In comparison with the ir data recorded in references, it is observed that:

*Lima et al.*⁹ observed a band at (600-530 cm^{-1}) specified to Al-O bonds. This finding attributed to the resulting of Al oxide accompanied the thermal decomposition of aluminum nitrate during the reaction with sodium polyphosphate and ammonium hydroxide. *M. Tatsumisago et al.*¹⁴, found a band at (980-1330 cm^{-1}) and (630-1330 cm^{-1}) specified the pyrophosphate group $(\text{PO}_4)^{3-}$, $(\text{PO}_2)^{2-}$, and $(\text{P}_3\text{O}_9)^{3-}$ which were not observed in the present work.

In sample (b), two bands at (2980 and 3440 cm^{-1}) specified the O-H groups while the first band disappears in (a) and (c). This behavior can be attributed to the non-uniform distribution of the H_2O molecules of crystallization among the AlPO_4 molecules¹⁷. The obtained ir bands summarized in Table 3 are in agreement with the literature values carried by Itoh et al.¹⁸, where they used ethylene oxide as a gelating agent.

Fig. 2A representing the x-ray pattern of of AlPO_4 samples fired at 280, 550 and 660°C. indicates that samples prepared by methods a and b show amorphous phases after

FIGURE 2 The x-ray patterns of aluminium phosphates (A) and iron phosphates (B)

TABLE 3 The ir-bands of the AlPO_4 samples.

Structure	Bands					Results		
	Ref.	Ref.	Ref.	Ref.	Ref.	a) AlPO_4	b) AlPO_4	c) AlPO_4
	(14)	(15)	(9)	(16)	(17)	org-inorg	org-org.	gel
P-($\backslash$)-P	840-1060	900-940	1750-970	-	-	-	-	-
$(\text{PO}_4)^{3-}$	980-10000	1002+2	-	-	-	-	-	-
$(\text{PO}_3)^{2-}$	1030-1230	(i)1089 $\pm$ 5 (ii) 164 $\pm$ 5	-	-	-	-	-	-
$(\text{PO}_2)^{2-}$	1080-1330	1202 $\pm$ 3	-	-	-	-	-	-
O-P-O	520-570	552 $\pm$ 1	-	-	-	500	550	500
$(\text{P}_3\text{O}_9)^{3-}$	630-650	638 $\pm$ 3	-	-	-	-	-	-
P-O-H	-	-	-	1785-2330	-	2200-2400	2200-2400	2200-2400
O-H	-	-	3000-36000	-	2840-3410	3000-36000	3040-3600	3000-3650
P-O	-	-	1600-1250	-	-	1000-1220	1000-1160	1000-1240
H-O-H	-	-	1620	-	-	1620-1680	1620-1680	1620-1660
Al-O	-	-	600-530	-	-	-	-	-

drying or even heating up to 550°C/20 h. Samples prepared by method c gives initial crystallinity at 550°C. On raising sintering temperature to 660°C/3 h, the crystallinity was developed and sharp peaks were obtained. This is in agreement with the results obtained by Complete et al¹⁹ where they observed that the crystallinity of Al PO₄ increases when preparing it from AlCl₃·6H₂O + (NH₄) H₂PO₄ and propylene oxide as a gelating agent, with heating at 950°C for 20 days. Haber and Szybalska²⁰ reported that the heat treatment of AlPO₄ during the preparation increases the growth of crystallinity.

On the other hand, *Itoh et al.*²¹, prepared aluminium phosphate by mixing aqueous solution of AlCl₃·6H₂O with phosphoric acid in stoichiometric ratio in presence of ethylene or propylene oxide with ammonia solution as neutralization agent. The x-ray pattern of the prepared samples showed that the obtained AlPO₄ is still amorphous until heating to 750°C^{22, 23}.

DTA curves of the prepared samples, Fig 3A, show that samples a, b and c behave nearly the same trend. They exhibit two endothermic peaks below ~ 200°C, due to the volatilization of the water content and the elimination of organic groups. At ~ 290°C an exothermic peak is appeared due to formation of some phases at high temperature. No changes were observed between ~ 300 – 700°C, where stable phosphates were obtained.

For iron phosphate samples the chemical analysis of FePO₄ (gel) prepared by the reaction of FeCl₃ and H₃PO₄ in presence of ethylene oxide shows that the experimental to the theoretical ratio of Fe is 41.13/37.09 = 1.11, while the phosphate ratio 50.95/62.9=0.81. In case of the FePO₄ samples prepared by dissolution of Fe₂O₃ in phosphoric acid a great deviation for the percentage of PO₄ is observed ($\text{Fe} = \frac{55.65}{96.35} = 1:1.66$ and $\text{PO}_4 = 16.68/38.5 = 1:2.3$).

The ir curves Fig. 1B of Fe PO₄ prepared by both methods indicate that the absorption peaks characterized to the main groups of phosphate, P-OH, H-OH, P-O, O-P-O and Fe-O were appeared.

FIGURE 3 The DTA curves of aluminium phosphates (A) and iron phosphates (B)

The x-ray chart Fig. 2B indicates that sample (a) dried at 280°C is in the amorphous phase. By raising the temperature 550°C, crystalline phases and other compounds start to be formed. The analysis of the observed peaks indicates the presence of: FePO_4 , $\text{FeH}_2\text{P}_2\text{O}_7$, $\text{Fe}_4(\text{P}_2\text{O}_7)_3$ and Fe_2O_3 . At 660°C, the most predominant compound is $\text{Fe}_4(\text{P}_2\text{O}_7)_3$. The appearance of the crystalline phases of the phosphate gel in the high temperature may be attributed to the arrangement of FePO_4 units during the preparation owing to the presence of ethylene oxide as a gelating agent. This finding is in agreement with the results obtained by Rouimi et al²², where they observed that the precipitated gel when calcined between 300-1000°C, the amorphous gel is converted partially to crystalline phase. For sample FePO_4 formed by dissolution of Fe_2O_3 in H_3PO_4 , dried at 160°C and fired at ~ 60°C, the x-ray patterns show that the resultant compounds are: Fe_2O_3 , FePO_4 and $\text{Fe}_4(\text{P}_2\text{O}_7)_3$ and Fe_2O_3 compound is the predominant.

Fig. 3B represents the DTA curves of the FePO_4 prepared by the reaction of Fe_2O_3 or FeCl_3 with H_3PO_4 in presence of ethylene oxide as a gelating agent.

In case of using Fe_2O_3 , the DTA curve Fig. 3B, exhibits two endothermic peaks, at 97°C and 150°C corresponding to the elimination of water molecules²⁴. An exothermic peak at 583°C is observed, which may attribute to the formation of phosphate species at high temperature. In case of using FeCl_3 and a gelating agent, a large endothermic peak is observed instead. At 177°C, on the other hand, a set of exothermic peaks at 551, 572 and 612°C were obtained which may due to the thermal decomposition of the organic content and formation of phosphate, phases²⁵.

It could be concluded that:

- 1- The preparation of aluminium and iron phosphates depends on the precursor materials, method of preparation, temperature and time of sintering. The most convenient methods of preparation of AlPO_4 and FePO_4 were from their chlorides and phosphoric acid in presence of a gelating agent.
- 2- Crystallinity of the prepared phosphates was favored by the presence of a gelating agent and increased by raising the sintering temperature.
- 3- The prepared phosphate samples are thermally stable between 300-700°C.

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