Chemical preparations, crystal data for monophosphates and condensed phosphates associated to strontium and IR studies of their anions

Rachida Oubouaza[1], Hamza Marouani[1], Soufiane Zerraf[1], Mustafa Belhabra[1], Ali Ouasri[2], MalikaTridane[1,3], Said Belaaouad[1]

[1] Laboratory of Chemistry-Physics of Materials, Faculty of Sciences Ben M'Sik B. P. 7955, Hassan II University of Casablanca, Casablanca, Morocco.

[2] Regional Center for Education and Training Trades, Madinat Al Irfane, Souissi,BP 6210 Rabat, Morocco.

[3] Regional Center for Education and Training Trades, Bd Bir Anzarane Casablanca. Morocco.

ABSTRACT

Chemical preparations and main crystallographic data are reported for the Monophosphates and the condensed phosphates associated to strontium. These compounds constituting an important part of phosphate chemistry have been subject to many studies and applications in many fields of research on materials and industry. The subject of this paper is to collect unit-cell parameters of these compounds to build a database of the different formulas which are known until now, to have an idea about their preparations and also about characterization by infrared vibration spectrometry for anions, PO_3^- in α-$Sr(PO_3)_2$, PO_4^{3-} inγ-$SrHPO_4$, $P_2O_7^{4-}$ in $Sr_2P_2O_7$, $P_3O_9^{3-}$ in $SrKP_3O_9 \cdot 3H_2O$, $P_4O_{12}^{4-}$ in $SrK_2P_4O_{12}$, $P6O_{18}^{6-}$ in $Sr_2(NH_4)_2P_6O_{18}.7H_2O$ and $P_3O_{10}^{5-}$ in $Sr_3P_3O_{10}Cl$.

Key words : Chemical preparation, monophosphates, strontium, infrared vibration spectrometry-ray diffraction.

1.   INTRODUCTION

Before we start reviewing and discussing the chemical preparation and crystallographic data of phosphate we first try to explain what we commonly call a phosphate. A general and rather abstract definition can be given by saying that phosphates are salts of both the monophosphoric acid H_3PO_4 and its various condensed or polymeric forms. The corresponding anions have varied geometries, but one common feature: they are all built up by pentavalent phosphorus atoms surrounded by more or less distorted tetrahedra made of four oxygen atoms. Monophosphate known as orthophosphates is the only phosphates known to be naturally occurring because of the hydrolysis of condensed phosphates. The condensed phosphoric anion in which P-O-P bonds exist is a condensed phosphoric anion. The condensed phosphates and monophosphates associated to strontium, the subject of this paper, contained in the important condensed phosphates and monophosphates that have been the subject of research and apply in the industry. The present work assembled the majority of the phases prepared for condensed phosphates and monophosphates associated to strontium to get ideas about their preparation, their crystallographic data, and their vibrational characteristics [1].

2. Monophosphates PO_4^{3-}

2.1 Synthesis protocols

α-SrHPO$_4$

It is easily obtained by dissolving 2.1 g of $Sr(NO_3)_2$ and 1.4 g of $NH_4H_2PO_4$ in 200 cm^3 of water. After three days, after evaporation at room temperature, crystals appear of $SrHPO_4$, polyhedral and colourless form, stable at room temperature and are very soluble in water [2].

β-SrHPO$_4$

The β-$SrHPO_4$ was prepared via a controlled hydrothermal method. $Sr(NO_3)_2$ and $(NH_4)_2HPO_4$ were dissolved in 50 ml deionized water with a molar ratio of 0.03:0.0001:0.02 under mechanical stirring for 2h. Then the mixed solution was transferred into a 100 ml Teflon bottle. The bottle was held in a stainless steel autoclave and kept at 180°C for 12h. Finally, the obtained white $SrHPO_4$ powders were filtered, washed for three times with deionized water and twice with ethanol and then dried in a vacuum oven at 60°C for 12h [3].

γ-SrHPO$_4$

They were prepared from a mixture comprising Li_2CO_3 (599.5%), $SrCO_3$ (598%), H_3PO_4 (85%) and distilled water in molar ratio Li/Sr/P/H_2O=1/1/3/190. The reactants were introduced in a Teflon-lined Parr hydrothermal bomb, with a fill factor of approximately 50%. The bomb was heated at 180°C under auto-geneous pressure for 6 days, and then slowly cooled to room temperature over 24 hours. The bomb contents were recovered by vacuum filtration and drying in

air. Repeated attempts to prepare γ-SrHPO$_4$ hydrothermally from SrCO$_3$, H$_3$PO$_4$, and H$_2$O (Sr/P/H$_2$O=1/1.9/60, T=140°C, 2 days) allowed the authors to obtain a white microcrystalline powder for this phase [4].

Sr$_{1.9}$Cu$_{4.1}$(PO$_4$)$_4$, Sr$_3$Cu$_3$(PO$_4$)$_4$, Sr$_2$Cu(PO$_4$)$_2$and Sr$_{9.1}$Cu$_{1.4}$(PO$_4$)$_7$

Samples in the Sr$_{3-x}$Cu$_x$(PO$_4$)$_2$ system were synthesized from stoichiometric mixtures of CuO (99.9%), SrCO$_3$(99.999%), and NH$_4$H$_2$PO$_4$(99.999%) by the solid state method. Stoichiometric mixtures were heated very slow up to 600°C and then annealed at 900°C (120 h, ground every 30 h) under air in alumina crucibles. The samples with x=0, 0.289, 0.4, 0.414, 0.429, 1, 1.05, 1.25, 1.5, 1.75, 2, 2.05, 2.075, 2.125, 2.5, and 3 were obtained. After annealing, the samples were quenched at room temperature. For synthesis of solid solutions Sr$_{9.1-x}$Ca$_x$Cu$_{1.4}$(PO$_4$)$_7$(0≤x≤9.1),Sr$_{2-x}$Ba$_x$Cu(PO$_4$)$_2$(0≤ x ≤2) and Sr$_{3-x}$Ba$_x$Cu$_3$(PO$_4$)$_4$(0≤x≤1.5), we used also CaCO$_3$ (99.0%) and BaCO$_3$(99.0%). Solid solutions Sr$_{9.1-x}$Ca$_x$Cu$_{1.4}$(PO$_4$)$_7$ (0≤x≤9.1) were synthesized at 900-920°C followed by quenching in air. Solid solutions Sr$_{2-x}$Ba$_x$Cu(PO$_4$)$_2$ (0≤x≤2) and Sr$_{3-x}$Ba$_x$Cu$_3$(PO$_4$)$_4$ (0≤x≤1.5) were synthesized at 840°C followed by quenching in air.

Make some remarks about the synthesis of the three new compounds in the Sr$_{3-x}$Cu$_x$(PO$_4$)$_2$ system with x=0.4, 1, and 2.05. The single-phased samples Sr$_{1.9}$Cu$_{4.1}$(PO$_4$)$_4$(x=2.05) and Sr$_2$Cu(PO$_4$)$_2$ (x=1) could be obtained at 900°C. Annealing of the sample Sr$_{1.9}$Cu$_{4.1}$(PO$_4$)$_4$ at 950°C resulted in the appearance of a liquid phase. This specimen contained I-Sr$_3$Cu$_3$(PO$_4$)$_4$, Cu$_3$(PO$_4$)$_2$, and traces of unidentified phases. A long treatment of Sr$_{1.9}$Cu$_{4.1}$(PO$_4$)$_4$at 950°C resulted in the growth of I-Sr$_3$Cu$_3$(PO$_4$)$_4$ single crystals.

Annealing of the blue specimen Sr$_2$Cu(PO$_4$)$_2$ at 1020°C resulted in a green powder, which consisted of an unidentified phase (phase I with six strongest lines: d=2.657, 3.121, 2.800, 3.098, 2.784, and 2.702 Å) and traces of Sr$_{9.1}$Cu$_{1.4}$(PO$_4$)$_7$ and I-Sr$_3$Cu$_3$(PO$_4$)$_4$. Traces of phase I, Sr$_{9.1}$Cu$_{1.4}$(PO$_4$)$_7$, and I-Sr$_3$Cu$_3$(PO$_4$)$_4$appeared when Sr$_2$Cu(PO$_4$)$_2$ was annealed at 920°C.

Our attempts to synthesize at 900°C the compound Sr$_{9.1}$Cu$_{1.4}$(PO$_4$)$_7$ (x=0.4) from SrCO$_3$ (99.999%) were not successful, even when platinum crucibles and quenching in liquid nitrogen were used.

The specimens in these cases were blue and consisted of three phases, Sr$_3$(PO$_4$)$_2$, Sr$_{9.1}$Cu$_{1.4}$(PO$_4$)$_7$ and Sr$_2$Cu(PO$_4$)$_2$, in comparable amounts. When the specimen Sr$_{9.1}$Cu$_{1.4}$(PO$_4$)$_7$ was cooled in a furnace, it was light-gray and also consisted of the three phases. The compound Sr$_{9.1}$Cu$_{1.4}$(PO$_4$)$_7$ (with traces of Sr$_3$(PO$_4$)$_2$) could be obtained by quenching from 1000°C into air in a platinum crucible. The single-phased sample Sr$_{9.1}$Cu$_{1.4}$(PO$_4$)$_7$(x=0.4) in the amount of 0.1 g was obtained in a corundum crucible by quenching from 9003C into air when we used SrCO$_3$ (98.0%), CuO (99.9%), and NH$_4$H$_2$PO$_4$(99.999%) in synthesis. It seems that impurities can stabilize the Sr$_{9.1}$Cu$_{1.4}$(PO$_4$)$_7$ phase [5].

SrCu$_2$(PO$_4$)$_2$

SrCu$_2$(PO$_4$)$_2$ was synthesized by the solid-state method from stoichiometric mixtures of Sr$_3$(PO$_4$)$_2$ and Cu$_3$(PO$_4$)$_2$ at 1153K in a Pt crucible for 200 h with five intermediate grindings. The green-blue product was cooled in a furnace. SrCu$_2$(PO$_4$)$_2$containedSr$_3$Cu$_3$(PO$_4$)$_4$ (1.2%) impurities. The mass fraction of the impurity in the sample was calculated from the scale factors refined in the Rietveld analysis described below. Single-phased Cu$_3$(PO$_4$)$_2$ and Sr$_3$(PO$_4$)$_2$ were prepared from mixtures of CuO (99.99%), NH$_4$H$_2$PO$_4$ (99.999%), and SrCO$_3$(99.999%) by the solid-state method. The mixtures were heated under air while the temperature was very slowly increased from room temperature (RT) to 873 K; then, they were reground and allowed to react at 1153K for Cu$_3$(PO$_4$)$_2$, and 1273 K for Sr$_3$(PO$_4$)$_2$ for 120 h with four intermediate grindings [6].

KSrPO$_4$

KSrPO$_4$:Dy^{3+} (x = 0.03, 0.04, 0.05, 0.06, 0.07, and 0.08) phosphors were synthesized using a solid-state reaction method. Highly pure K$_2$CO$_3$, SrCO$_3$, (NH$_4$)$_2$HPO$_4$(99.9%), and Dy$_2$O$_3$ (99.99%) obtained from Sinopharm Chemical Reagent, Co. Ltd., Shanghai China, were used as the starting materials. Stoichiometric amounts ofK$_2$CO$_3$, SrCO$_3$,(NH$_4$)$_2$HPO$_4$ (99.9%), and Dy$_2$O$_3$ (99.99%) were mixed thoroughly in alcohol by ball milling using an agate mortar. Additional 5% K$_2$CO$_3$ was used to compensate the losses due to evaporation during the synthesis. They were sintered at 1150°C for 6 h in air, and then, the samples were ground into powder for characterization [7].

KSrFe$_2$(PO$_4$)$_3$

Single crystals of KSrFe$_2$(PO$_4$)$_3$ were grown in a flux of potassium dimolybdate K$_2$Mo$_2$O$_7$ with molar ratio of product: flux =2:1 starting from 2.043 g of KNO$_3$, 1.506 g of SrCO$_3$, 8.203g of Fe(NO$_3$)$_3$.9H$_2$O, 4.002 g of (NH$_4$)$_2$HPO$_4$ and 1.454 g of MoO$_3$. These reactants were mixed in nitric acid and the resulting solution was evaporated to dryness by heating at 353K. The obtained dry residue was ground in an agate mortar and then heated for 24 h at673K in order to remove the decomposition products: NH$_3$, CO$_2$.

The process was then followed by a further heating for 12hat 873 K with intermediate grinding. After being reground, the product was melted for 1h at 1373 K, and then slowly cooled at a rate of 10 K.h^{-1}to 673K, then at a rate of 50K.h^{-1} to room temperature. The crystals obtained by washing the final product with warm water, in order to dissolve the flux, are essentially composed by yellowish and irregularly shaped crystals. Their qualitative microprobe analysis indicated the exclusive presence of K, Sr, Fe and P in an atomic ratio approximating 1:1:2:3, in accordance with the KSrFe$_2$(PO$_4$)$_3$ composition After its structure determination, the title compound was prepared in the powder form by the conventional solid state reaction. After an initial treatment similar to that undertaken for the synthesis of the single crystals until 873K, the sample was subjected to final calcinations at 1273K for 48h with

intermittent grinding. Yellowish powder was obtained by quenching in air [8].

$SrCo_2(PO_4)_2$

A stoichiometric mixture of $SrCO_3$, $CoCO_3$, and $(NH_4)_2HPO_4$ of high purity. (>> 99%) was heated to 1173 K to effect decarbonation, then heated to fusion (1473 K) in a platinum crucible followed by slow cooling(10°C/h). The product contained two types of crystals distinguishable by their color: rose and blue. Those of blue color correspond to the powder of composition $SrCo_2(PO_4)_2$ [9].

β-$SrCo_2(PO_4)_2$

All reagents were used as received without further purification except α-$Co_2P_2O_7$ which was synthesized by solid state reaction. Single crystal of β-$SrCo_2(PO_4)_2$ was prepared through a facile hydrothermal synthesis route. A mixture of α-$Co_2P_2O_7$ (0.0584 g, 0.2 mmol), $Sr(NO_3)_2$ (0.0846 g, 0.4 mmol) and5 mL H_2O was stirred for 10 min in air. The obtained mixture was then transferred into a 28 mL Teflon-lined autoclave and heated at 230°C in an oven for 120 h. The autoclave was cooled down to room temperature at a rate of 0.1 °C/min, and purple rhombus-shaped crystals of b-$SrCo_2(PO_4)_2$ were isolated, washed with distilled water and dried in air at 60°C [10].

$Sr_5(PO_4)_3(CuO_2)_{1/3}$

$SrCO_3$, $NH_4H_2PO_4$ and CuO (99,99 %) thoroughly ground and mixed in a 5.05:3: x molar ratio (x≤1) were heated stepwise at400, 600 and 850 °C for 32 h with intermediate regrindings. The powders were pressed in pellets, annealed in air at 1100 °C for 24 hours and air quenched .The samples had blue-violet color that became lighter for low copper content. XRD patterns of specimens with 0.1 < x 0.8 corresponded to practically pure apatite phase (0.6 % max peak intensity of impurities) [11].

* Crystallographic data

Table 1: Main Crystallographic data for the monophosphates associated to strontium

Formula	a(Å) α°	b(Å) β°	c(Å) γ°	Space Group	Z
α-$SrHPO_4$	7.184 94.7	6.790 104.9	7.256 88.7	P-1	4
γ-$SrHPO_4$	8.131	9.258	18.084	Pbca	16
$Sr_5(PO_4)_3(CuO_2)_{1/3}$	9.7815	9.7815	7.3018	P6₃/m	2
$SrCo_2(PO_4)_2$	5.014 118.04	8.639 75.09	9.691 86.90	P-1	2
$BaCu_2(PO_4)_2$	9.226 106.76	9.271 101.69	10.516 115.70	P-1	4
$KSrPO_4$	7.35	5.56	9.64	Pnma	4

$SrCu_2(PO_4)_2$	7.94217	15.36918	10.37036	Pccn	8
β- $SrCo_2(PO_4)_2$	5.503 110.235	6.703 101.15	9.238 98.29	P-1	2
$Sr_2Cu(PO_4)_2$	11.5155	5.07543 106.3563	6.57487	C2/m	2
$Sr_3Cu_3(PO_4)_4$	9.2010	4.94104 122.8952	17.8998	P21/c	2
$Sr_2Cu_3(PO_4)_4$	10.6119	10.6119	19.7045	R-3₁m	3
$KSrFe_2(PO_4)_3$	9.809	9.809	9.809	P2₁3	4

* Characterization of PO_4^{3-} in γ-$SrHPO_4$ by IR vibration spectrometry
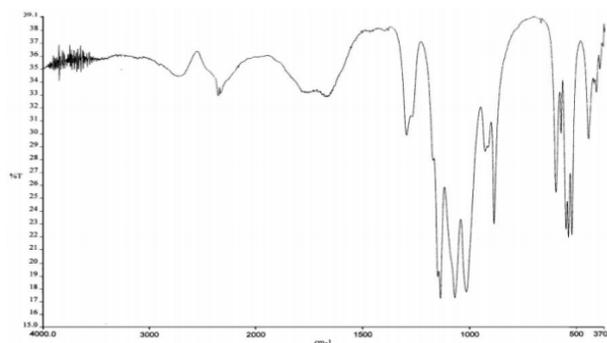
Figure 1: Infrared spectrum of γ-$SrHPO_4$ recorded at room temperature between 370 and 4000 cm^{-1}.

Table 2: Frequencies (cm^{-1}) of IR absorption bands for γ-$SrHPO_4$

Frequencies (cm^{-1})	Vibrations
1298	δP-O-H
1170, 1146, 1137	asymmetric (ν_3)
887	P-O(H)
1070, 1016, 929, 915	symmetric (ν_1)
600-520	antisymmetric (ν_4)
450-370	symmetric (ν_2)

The IR spectrum of γ-$SrHPO_4$ is reported in Fig.1. Previous workers [11,12] have found that the vibrational bands of inorganic phosphates are generally not very sensitive to the cations in the structure, which tend just to shift the band frequencies slightly rather than to create new bands. Thus, the IR spectrum is dominated by the HPO_4^{2-} modes.

The 2800-1700 cm^{-1}range corresponds to the OH modes of HPO_4^{2-} groups characterized by three broad bands of ABC type. Similar bands have been observed in strong hydrogen bonded crystals, such as $CaBa(HPO_4)_2$ and $PbHPO_4$. The presence of bands in the region 1400-1200 cm^{-1} is characteristic of hydrogen monophosphate groups**.**

They are assigned to δP-O-H in plane bending modes, two bands 1298 and 1267 cm^{-1}are observed for these modes. In the range 1200-800 cm^{-1}appear the PO_4^{3-} stretching modes: the high-frequency bands (1170, 1146, 1137cm^{-1}) are assigned to the asymmetric (v_3) mode, whereas the symmetric stretching mode of P-O(H) is observed for the low-frequency 887cm^{-1}.

The remaining bands (1070, 1016, 929, 915 cm^{-1}) are attributed to the symmetric (v_1) mode. The bands in the range 600-370 cm^{-1} are due to PO_4^{3-} bending modes. According to previous data, the two well-defined subdivisions of 600-520 and 450-370 cm^{-1} arise from the antisymmetric (v_4) and symmetric (v_2) modes, respectively [4].

3. CONDENSED PHOSPHATES

3.1 Synthesis protocols

3.1.1. $P_2O_7^{4-}$:

SrCrP$_2$O$_7$

Equimolar mixtures of the starting materials, $Cr_2P_2O_7$ and $Sr_2P_2O_7$ [obtained from $SrCO_3$ and $(NH_4)_2HPO_4$ by slowly increasing the temperature to 1273 K], were sealed in evacuated silica ampoules (l≤10cm, d≤1.6 cm) with iodine (100 mg) and CrP (5 mg) as mineralizes and heated at 1223K for 10 d. The addition of CrP was intended to ensure reducing conditions.

Furthermore, we have observed an improved recrystallization via the gas phase, and even chemical vapor transport reactions for many phosphates, using iodine as a mineraliser/transport agent in combination with reducing agents such as metal, phosphorus or metal phosphide. The reaction products were washed with dilute NaOH and water, and dried at 393K. The experiments led to light blue powders of $SrCrP_2O_7$ which always contained small amounts of well recrystallized CrP and $Cr_2P_2O_7$ as by-products.

Occasionally, growth of prismatic crystals of $SrCrP_2O_7$ with an edge-length of up to1 mm was observed. Chemical vapor transport experiments in a temperature gradient (1323K 1223K), aimed at purification and crystallization of $SrCrP_2O_7$, led to decomposition of the mixed phosphate; $Cr_2P_2O_7$ was deposited at the lower temperature region, while $Sr_2P_2O_7$ remained at the higher temperature zone.

$SrCrP_2O_7$ is remarkably stable in air and against mild oxidizing agents. By heating$SrCO_3$ with $MnCO_3$ or ZnO and stoichiometric amounts of$(NH_4)_2HPO_4$ in air slowly to 1073K, single-phase powders of the isotypic diphosphates $SrMnP_2O_7$ and $SrZnP_2O_7$ have also been synthesized [12].

α-Sr$_2$P$_2$O$_7$

Crystals of the form α of strontium pyrophosphate are obtained from an almost saturated solution of strontium carbonate, in a melt of sodium metaphosphate at 800°C [13].

Sr$_2$P$_2$O$_7$

During the production of $Sr_2P_2O_7$, solid powders of strontium carbonate ($SrCO_3$) and ammonium dihydrogen phosphate ($NH_4H_2PO_4$), from Merck and Aldrich, were used.

Stoichiometric amounts of the reactants were calculated with the help of the following formula:

$$SrCO3(s) + 2NH_4H_2PO_4(s) \longrightarrow Sr_2P_2O_7(s) +3H_2O (g) +2NH_3 (g) +2CO_2 (g)$$
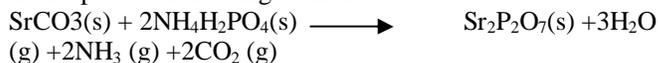
In order to obtain 5 g of $Sr_2P_2O_7$ product, at the beginning 4.227 g of $SrCO_3$ and 3.294g of $NH_4H_2PO_4$ were weighed. Two materials were then mixed homogeneously in an agate mortar by grinding. The mixture was put into furnace and was heated up to 900°C with a heating rate of 700°C/hr. Retention time was set as 14.5h. At the end of this process, when the temperature was reduced to room temperature, the product was reground nicely in an agate mortar [14].

SrZn(P$_2$O$_7$)

$SrZnP_2O_7$ powders were prepared using a conventional solid-state reaction method. High purity $SrCO_3$ (99.0%), ZnO (99.5%) and $NH_4H_2PO_4$ (99.90%) were used as raw materials. Stoichiometric mixtures of starting materials were homogenized by ball-milling with ZrO_2 balls in acetone for 24 h, and then calcined at 850–900 8C for 2h to investigate the formation process of $SrZnP_2O_7$ phase. The calcined powders were then milled again, dried and sieved. PVA (9wt.%) was added into sieved powders and was granulated, and then uniaxially pressed into pellets with a diameter of 16mm. The compacts were sintered at a temperature range from 900 8C to 980 8C in order to investigate the sintering behaviors.

A mixture of 44.3 mg [0.300 mmol; for $Sr_2(P_2O_7)$, 0.6 mmol] of strontium carbonate (Alfa Aesar, 97.5%), 24.3 mg [0.300 mmol; only for $SrZn(P_2O_7)$] of zinc oxide, 1.0 mg (0.003 mmol, doping concn 1.9%) of europium oxide Eu_2O_3 (KristallhandelKelpin, 99.9%), 2.5 mg (0.013 mmol, doping concn 4.3%) of manganese nitrate $Mn(NO_3)_2 \cdot 4H_2O$ (Merck, 98.5%), and 83.2 mg (0.630 mmol) of ammonium dihydrogen phosphate (ABCR, 98%) was transferred into an alumina boat. The latter was then heated under a hydrogen/nitrogen (10/90) flow (2 Lh^{-1}) to 1070K at a rate of 60Kh^{-1}. After 18 h, the mixture was cooled to room temperature at a rate of 180 Kh^{-1}. Finally, $SrM(P_2O_7)$:Eu,Mn was obtained quantitatively as a crystalline, colorless, and non-hygroscopic powder. According to their powder diffraction patterns, all samples presented herein were single-phase. The composition of obtained samples was checked by energy-dispersive X-ray spectroscopy and confirmed the respective M/P (M) Sr, Zn) ratios[15].

SrNiP$_2$O$_7$ et SrNi$_3$(P$_2$O$_7$)$_2$

Powder samples of $SrNiP_2O_7$and $ANi_3(P_2O_7)_2$ (A = Ca, Sr, Ba), 2 g each, were synthesized from stoichiometric amounts of nickel, alkaline earth carbonate and $(NH_4)_2HPO_4$. After dissolution of the starting materials in nitric acid the homogenous solutions have been evaporated to dryness on a heating stirrer. The residues were ground and heated in air at increasing temperatures (600, 800, 1000 and finally to 1100°C), each period lasting one day. The purity of thus obtained powder samples has been controlled by Guinier photographs. The colours of the powdery materials vary from red-orange ($SrNiP_2O_7$) over pale orange-yellow

($BaNi_3(P_2O_7)_2$), yellow ($SrNi_3(P_2O_7)_2$) to pale yellow ($CaNi_3(P_2O_7)_2$).

Single crystals of $SrNiP_2O_7$ and $SrNi_3(P_2O_7)_2$ have been obtained by a different procedure. A mixture of $SrCO_3$ (4.4288 g, 3 mmol), NiO (2.2410 g, 3 mmol) and $(NH_4)_2HPO_4$ (7.9233 g, 6 mmol) was ground thoroughly in a mortar and transferred to a ceramic crucible. The sample was then heated to 1173 K in a tube furnace, to effect decomposition of the carbonate, followed by melting (1473 K) in a platinum crucible. After controlled cooling (rate $10°C. h^{-1}$) to 773 K the sample was quenched to room temperature. The product was found to contain red-orange crystals of $SrNiP_2O_7$ and a few yellowishgreen ones, which turned out to be $SrNi_3(P_2O_7)_2$ [16].

SrFeP₂O₇

Single crystals of $SrFeP_2O_7$ were obtained by hydrothermal growth starting from the reactants SrF_2 and Fe_2O_3 in the molar ratio 2:1 in an aqueous solution of phosphoric acid (7 M). The mixture was sealed in a platinum tube (filling level 40%) and heated at 956 K for 24 h. The maximum pressure reached was 186 MPa. The resulting product was filtered off, washed with distilled water and dried in air at room temperature. The main by-product was unreacted SrF_2 [17].

(M,Cu)P₂O₇ (M =Mg,Ca,Sr)

The solid-solution $M_{2-x}Cu_xP_2O_7$ with M = Mg, Ca, Sr, and Ba($0 \leq x \leq 2$)were prepared at 1173 K from powder starting materials $M_2P_2O_7$ and $Cu_2P_2O_7$ which are obtained by two processes :The dry and wet methods.
Dry method. Stoichiometric amounts of diammonium phosphate $(NH_4)_2HPO_4$ and oxide (MgO, CuO) or carbonate (CaCO_3, SrCO,, BaCO,) were mixed, ground in a mortar, and then heated slowly to 1173 K in an alumina crucible. Several heatings of pressed pellets were used to obtain pure powders.

Wet method. The starting diphosphates could be prepared also by precipitation from an aqueous solution $Na_4P_2O_7$ with an excess of metal nitrate or chloride. The precipitate was filtered, washed with cold water and then heated at 1173K [18].

SrCoP₂O₇

Crystals were synthesized from a mixture of $SrCO_3$,$CoCO_3$ and $(NH_4)_2HPO_4$ in stoichiometric ratios, heated first in air at 893K to decompose the phosphate and carbonates. After grinding, the resulting product was heated for several days at 1323K in an evacuated silica ampoule [19].

CdSrP₂O₇

Single crystals of $CdSrP_2O_7$(I) were prepared by heating a stoichiometric mixture of $CdCO_3$, $SrCO_3$, and $(NH_4)_2HPO_4$ to liquid state (1350 K) in a platinum carrier, followed by a period of slow cooling (4 Kh^{-1}) to 1170 K and further cooling (10Kh^{-1}) to 473K [20].

SrMgP₂O₇

A powder has been prepared, according to the chemical formula $SrMgP_2O_7$, starting from equimolar mixtures of the starting materials $SrCO_3$, $MgCO_3$ and $(NH_4)_2HPO_4$. The mixture was heated progressively in air at increasing temperatures up to 1173K [21].

SrK₂P₂O₇, SrRb₂P₂O₇, and SrCs₂P₂O₇

Single crystals of the potassium salt(melting point : mp= 1348K) were prepared by slow cooling of a melt prepared from a stoichiometric mixture of K_2CO_3, $SrCO_3$, and $NH_4H_2PO_4$ first heated at 773 K for 30hbefore melting. A complete determination of the atomic arrangement was reported. This compound is isotypic with $CaK_2As_2O_7$. The same authors performed the crystal structure determination of $SrRb_2P_2O_7$ and $SrCs_2P_2O_7$. These last two compounds are isotypic but not is amorphous with the potassium salt [1].

* Crystallographic data

Table 3: Main Crystallographic Data for the Monophosphates associated to strontium

Formula	a(Å) α°	b(Å) β°	c(Å) γ°	Space Group	Z
SrCrP₂O₇ (monoclinic)	5.422	8.3254 90.39	12.542	P2₁/n	4
α-Sr₂P₂O₇ (orthorhombic)	8,9104	5,4035	13,1054	Pna2₁	4
Sr₂P₂O₇ (orthorhombic)	8.9459	5.4133	13.2114	Pnma	4
SrZn(P₂O₇) (monoclinic)	5,31	8.2	12.72	P2₁/n	4
SrNiP₂O₇	5.2691	8.2674 90.246	12.6140	P2₁/n	4
SrNi₃(P₂O₇)₂	7.4092	7.6594	9.4474	P21/c	2
SrCoP₂O₇	5.3165	8.2574 90.133	12.6755	P2/n	4
SrCuP2O7	12.455	8.129 90.59	5.369	P21/c	4
SrCdP₂O₇	5.414	8.615 90.01	12.878	P2₁/n	4
SrMgP₂O₇	5.309	8.299 10.06	12.68	P2₁/n	4
SrZnP₂O₇	5.299	8.189 90.0	12.72	P2₁/n	4
SrFeP₂O₇	5.370	8.268 90.37	12.693	P2₁/n	4
SrK₂P₂O₇	9.168	5.712 105.79	14.720	P21/c	4
SrRb₂P₂O₇	10.270	5.867 116.48	14.413	C2/c	4
SrCs₂P₂O₇	10.528	6.081 118.34	14.766	C2/c	4

*Characterization of $P_2O_7^{4-}$ in $Sr_2P_2O_7$ by IR vibration spectrometry.
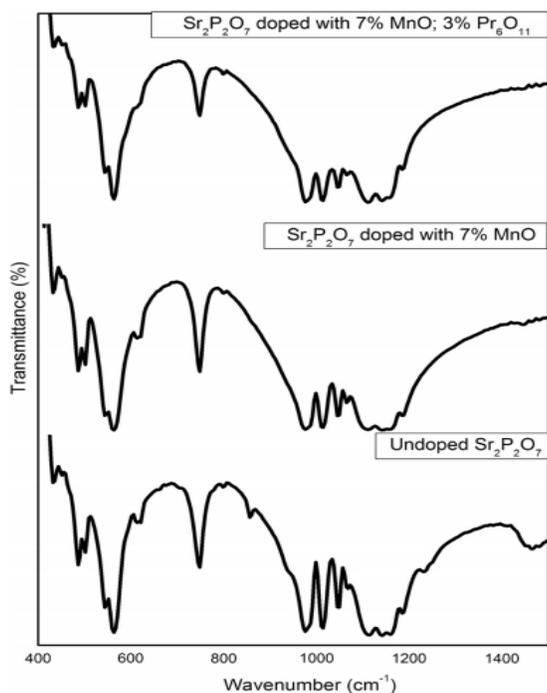
Figure 2. FTIR analysis of undoped, MnO and MnO-Pr_6O_{11} doped $Sr_2P_2O_7$ samples [14].

Table 4: IR Frequency characteristics (in cm^{-1}) for $P_2O_7^{4-}$ anions [43]

Vibrations	Frequencies (cm^{-1})
v_{as} (PO_3)	1060
	1000
v_s(PO_3)	1000
	900
v_{as}(POP)	825
	700
δ_{as} (PO_3)	656
	535
δ_s (PO_3)	520
	420

In Fig.2, FTIR analysis of samples undoped $Sr_2P_2O_7$ and doped with MnO and Pr_6O_{11} are given. $P_2O_7^{4-}$ vibrational modes were observed within the range of 1500–400 cm^{-1} which was consistent with the literature. The anion $P_2O_7^{4-}$ contains the PO_3^{2-} radical and the P–O–P bridge. For the symmetrical and asymmetrical stretching, frequencies are expected within 900–1000 and 1000– 1100 cm^{-1}.
In Fig. 2, which is the FTIR of strontium pyrophosphate sample, peaks of asymetrical PO_3^{2-} radical bending mode was seen around 1000 and 1060 cm^{-1}. The P-O-P bridge peaks were observed around 700–825 cm^{-1}. These peaks proved the presence of pyrophosphate within the structure.

In the IR plot of undoped $Sr_2P_2O_7$, the band around 1400 cm^{-1} can be assigned as the remaining impurity of dibasic orthophosphate, HPO_4^{2-} which is common in pyrophosphate formation and not present in the doped samples which were heated at higher temperature than undoped samples for longer time. The overall peak structure was consistent with the undoped strontium pyrophosphate structural peaks.

3.1.2. $P_3O_{10}^{5-}$

$Sr_3P_3O_{10}Cl$

The chemicals used in this work were all analytical-grade and were purchased from commercial suppliers and used without further purification. P_2O_5 (Aldrich, 98%), MgO (Alfa Aesar, 99.9%), $SrCl_2$ (Alfa Aesar, 99.9%), SrO (Alfa Aesar, 99.9%), and NaCl (Alfa Aesar, 99.9%), $SrCO_3$ (Alfa Aesar, 99.9%), $NH_4H_2PO_4$ (Alfa Aesar,99.9%).
 Crystals of title compound were grown by employing the NaCl and $SrCl_2$ flux in a fused quartz ampule. The reactants were ground and loaded in an Ar purged drybox and then flame-sealed under vacuum prior to heating. In the reaction, MgO, SrO and P_2O_5 were mixed in a 2:1:3 mol ratio (ca.~0.3 g) and added to a $SrCl_2$/NaCl (in a 1:1 mol ratio) eutectic flux equal to 3 times the mass of oxides reactants.
 The mixture were heated to 850°C at a rate of 3°C/min, held for 12 h, and then slowly cooled, at a rate of 0.1°C/min, to 300°C, followed by furnace-cooling. The colorless transparent crystals were retrieved from the flux by washing the products with deionized water using suction filtration. The colorless crystals were collected with about 20% yield (based on P). The crystals appear to be relatively stable in air and water [22].
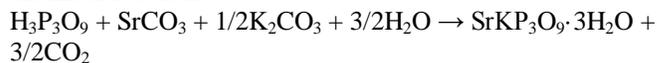
3.1.3. $P_4O_{13}^{6-}$, $P_5O_{16}^{7-}$

Until now, there are no oligophosphate associated to strontium for such anions$P_4O_{13}^{6-}$ and $P_5O_{16}^{7-}$.

3.2 Cyclophosphates $(P_nO_{3n})^{n-}$

3.2.1.$P_3O_9^{3-}$

$SrKP_3O_9 \cdot 3H_2O$

Polycrystalline samples of $SrKP_3O_9 \cdot 3H_2O$ are prepared by adding dilute cyclotriphosphoric acid to an aqueous solution of strontium carbonate and potassium carbonate with a stoichiometric ratio Sr/K = 1, according to the following chemical reaction:
$H_3P_3O_9 + SrCO_3 + 1/2K_2CO_3 + 3/2H_2O \rightarrow SrKP_3O_9 \cdot 3H_2O + 3/2CO_2$
The so-obtained solution is then slowly evaporated at room temperature until polycrystalline samples of $SrKP_3O_9 \cdot 3H_2O$are obtained. The cyclotriphosphoric acid used in this reaction was prepared from an aqueous solution of $Na_3P_3O_9$passed through an ion-exchange resin "Amberlite IR 120" [23].

SrKP$_3$O$_9$

A Polycrystalline sample of SrKP$_3$O$_9$ was obtained as polycrystalline samples by total dehydration ofSrKP$_3$O$_9 \cdot$3H$_2$O under atmospheric pressure between 250 and 350°C according to the following chemical reaction [23]

SrKP$_3$O$_9 \cdot$3H$_2$O $\longrightarrow$ SrKP$_3$O$_9$ + 3H$_2$O

SrNH$_4$P$_3$O$_9 \cdot$3H$_2$O

SrNH$_4$P$_3$O$_9 \cdot$3H$_2$O was prepared by the metathesis reaction of Boulle using silver cyclotriphosphate monohydrate as starting material. An aqueous solution of SrCl$_2 \cdot$6H$_2$O and NH$_4$Cl in stoichiometric proportions is added with the corresponding amount of Ag$_3$P$_3$O$_9 \cdot$H$_2$O, according to the following chemical reaction [24]
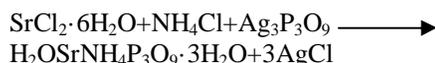
SrCl$_2 \cdot$6H$_2$O+NH$_4$Cl+Ag$_3$P$_3$O$_9$ $\longrightarrow$
H$_2$OSrNH$_4$P$_3$O$_9 \cdot$3H$_2$O+3AgCl
After filtration, to eliminate the insoluble silver chloride, the resulting solution is kept at room temperature until the formation of prismatic crystals of SrNH$_4$P$_3$O$_9 \cdot$3H$_2$O with hexagonal section.

SrTlP$_3$O$_9 \cdot$3H$_2$O

Polycrystalline samples of SrTlP$_3$O$_9 \cdot$3H$_2$O were prepared by the method of ion exchange resin"Amberlite IR 120" with a stoichiometric ratio Sr:K = 1, according to the following chemical reaction [25]
H$_3$P$_3$O$_9$ + SrCO$_3$ + 1/2Tl$_2$CO$_3$ + 3/2H$_2$O $\rightarrow$ SrTlP$_3$O$_9 \cdot$3H$_2$O + 3/2CO$_2$

SrTlP$_3$O$_9$
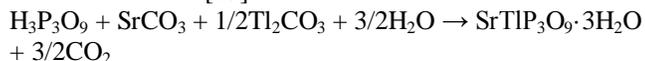
A Polycrystalline sample of SrKP$_3$O$_9$ was obtained as polycrystalline samples by total dehydration of SrKP$_3$O$_9 \cdot$3H$_2$O under atmospheric pressure between 300 and 650°C according to the following chemical reaction [25]

SrTlP$_3$O$_9 \cdot$3H$_2$O $\longrightarrow$ SrTlP$_3$O$_9$ + 3H$_2$O
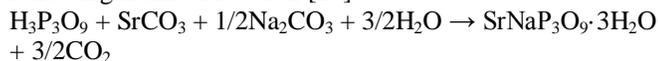
SrNaP$_3$O$_9$.3H$_2$O

Polycrystalline samples of SrNaP$_3$O$_9 \cdot$3H$_2$O were prepared by the method of ion exchange resin "Amberlite IR 120" with a stoichiometric ratio Sr/K = 1, according to the followingchemical reaction [27] :
H$_3$P$_3$O$_9$ + SrCO$_3$ + 1/2Na$_2$CO$_3$ + 3/2H$_2$O $\rightarrow$ SrNaP$_3$O$_9 \cdot$3H$_2$O + 3/2CO$_2$

Sr$_3$(P$_3$O$_9$)$_2$.7H$_2$O

Polycrystalline Sample of the title compound, Sr$_3$(P$_3$O$_9$)$_2$.7H$_2$Owas prepared by adding slowly dilute cyclotriphosphoric acid to aqueous solutions of strontium carbonate according to the following chemical reaction [28]
2H$_3$P$_3$O$_9$+3SrCO$_3$+4H$_2$O $\rightarrow$ Sr$_3$(P$_3$O$_9$)$_2$.7H$_2$O + 3CO$_2$
The so-obtained solution was then slowly evaporated at room temperature until a polycrystalline sample of Sr$_3$(P$_3$O$_9$)$_2$.7H$_2$O was obtained.

SrRbP$_3$O$_9 \cdot$3H$_2$O

Polycrystalline samples of SrRbP$_3$O$_9 \cdot$3H$_2$Owere prepared by the method of ion exchange resin with a stoichiometric ratio Sr/Rb=1, according to the following chemical reaction [29]
H$_3$P$_3$O$_9$ + SrCO$_3$ + 1/2Rb$_2$CO$_3$ + 3/2H$_2$O $\rightarrow$ SrRbP$_3$O$_9 \cdot$3H$_2$O + 3/2CO$_2$.
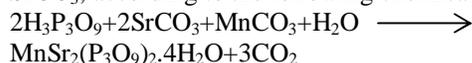
SrRbP$_3$O$_9$

SrRbP$_3$O$_9$ was obtained as polycrystalline samples by total dehydration of SrRbP$_3$O$_9 \cdot$3H$_2$O under atmospheric pressure between 300 and 400 °C according to the following chemical reaction [29].
SrRbP$_3$O$_9 \cdot$3H$_2$O $\longrightarrow$ SrRbP$_3$O$_9$ + 3H$_2$O.
With further increase in temperature, SrRbP$_3$O$_9$ was found to be stable and then melted at 760°C.

MnSr$_2$(P$_3$O$_9$)$_2$.4H$_2$O

Through a column of ion exchange resin (Na$^+$ by H$^+$), "Amberlite IR 120" . A concentrated solution of Na$_3$P$_3$O$_9$ is slowly added. The cyclotriphosphoric acid H$_3$P$_3$O$_9$ thus obtained is immediately neutralized with a mixture of stoichiometric amounts of carbonates [26], MnCO$_3$ and SrCO$_3$, according to the following chemical reaction:
2H$_3$P$_3$O$_9$+2SrCO$_3$+MnCO$_3$+H$_2$O $\longrightarrow$
MnSr$_2$(P$_3$O$_9$)$_2$.4H$_2$O+3CO$_2$
The solution abandoned for a few days, MnSr$_2$(P$_3$O$_9$)$_2$.4H$_2$O is obtained in the form of crystals and powder having a pinkish white color [30,44].

* Crystallographic data

Table 5: Main Crystallographic Data for the cyclotriphosphates associated to strontium

Formula	a(Å) α°	b(Å) β°	c(Å) γ°	Space Group	Z
SrKP$_3$O$_9 \cdot$3H$_2$O	9.082	8.133	15.009	*Pnma*	4
SrKP$_3$O$_9$	14.957	8.372 102.27	7.909	*P2$_1$/m* or *P2$_1$*	4
SrNH$_4$P$_3$O$_9 \cdot$3H$_2$O	9.126	8.157	15.256	*Pnma*	4
SrTlP$_3$O$_9 \cdot$3H$_2$O	9.147	8.180	15.458	*Pnma*	4
SrTlP$_3$O$_9$	14.544	8.639	7.727	P2$_1$/m or P2$_1$	4
MnSr$_2$(P$_3$O$_9$)$_2 \cdot$4H$_2$O	6.653	7.110	5.123	P-1	1
SrNaP$_3$O$_9$.3H$_2$O	16,167	12,013	10,645	Pnma	4
Sr$_3$(P$_3$O$_9$)$_2$.7H$_2$O	16.05	12.33	10.87	Pnma	4
SrRbP$_3$O$_9$	14.958	8.503	8.503	P2$_1$/m or P2$_1$	4
SrRbP$_3$O$_9$.3H$_2$O	9.120	8.141	15.234	Pnma	4
MnSr$_2$(P$_3$O$_9$)$_2$.4H$_2$O	6,653 103,37	7,110 95,81	5,123 93,04	P-1	1

* Characterization of P₃O₉³⁻ inSrKP₃O₉·3H₂Oby IR vibration spectrometry
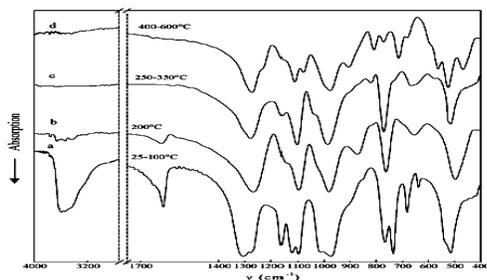
Fig. 3. IR spectra of the phosphates (a) $SrKP_3O_9·3H_2O$, (b) amorphous phase,(c) $SrKP_3O_9$ and (d) $SrK_2P_4O_{12}$ + $\gamma[Sr(PO_3)_2]$ [23, 42]

Table 6: Frequencies (cm⁻¹) of IR absorption bands for $SrKP_3O_9·3H_2O$

Frequencies (cm⁻¹)	Vibrations
3416	ν OH
1616	δ HOH
1307 1271	ν_{as} OPO
1159 1120 1103	ν_s OPO
983 871	ν_{as} POP
744 688	ν_s POP
645 635 526	δ OPO + ρ OPO

The IR absorption spectra of $SrKP_3O_9·3H_2O$ and $SrKP_3O_9$are reported in Fig.3. In the domain 4000–1600 cm⁻¹, the spectrum (a) (Fig. 3a) shows three bands at 3568, 2400 and 1611 cm⁻¹. The band at 3568 cm⁻¹ is attributed to the stretching vibrations of water molecules (νO–H).
The band at 2400 cm⁻¹ corresponds to hydrogen bonding [23].
The band at 1611 cm⁻¹ represents the bending vibration of water molecules (δHOH). The domain 1400–650 cm⁻¹, characteristic of the valence vibration bands of the cycle.Among these bands can be distinguished:
- The vibration bands of the (OPO) end groups at high frequencies: 1180 <ν_{as} OPO < 1340 cm⁻¹ and 1060 <ν_s OPO < 1180 cm⁻¹;
- the valency vibrations of the (P-O-P) ring groups at : 960 <ν_{as}POP< 1060 cm⁻¹ and
660 <ν_s POP < 960 cm⁻¹;

3.4 P₄O₁₂⁴⁻

SrNa₂P₄O₁₂.6H₂O

Polycrystalline samples of $SrNa_2P_4O_{12}.6H_2O$ were readily prepared by mixing concentrated solutions of $Na_2P_4O_{12}.4H_2O$ and $Sr(NO_3)_2$ in an equimolar ratio and allowing the mixture to evaporate at room temperature for a few days[31] [32].

SrK₂P₄O₁₂

$SrKP_3O_9$ leads between 400 and 650 °C, to a mixture of $SrK_2P_4O_{12}$crystallized and β[Sr(PO₃)₂] amorphousphase in X-ray diffraction. This mixture is stable until the melting points at 696 °C of $SrK_2P_4O_{12}$ see above the figure.3 [23].

Sr(NH₄)₂P₄O₁₂,

$Sr(NH_4)_2P_4O_{12}$, $SrTl_2P_4O_{12}$, and $SrRb_2P_4O_{12}$.These three salts isotypic with $SrK_2P_4O_{12}$.
Fiften mmol (4,82g) of anhydrous (NH₄)₄P₄O₁₂, obtained from $Na_4P_4O_{12}.4H_2O$,were dissolved in 60cm³ of water.fiften-cm³ (7,5mmol) of the 0.5 mol dm⁻³ strontium stirred.After 1h,the precipitate was filtered off and dried as described above. At least 92% of the P atoms were in the form of cyclo-tetraphosphate. [33]

Cs₄Sr₃H₂(P₄O₁₂)₃

During experiments to optimize the chemical preparations of the tetrametaphosphate-polyphosphate of Cs-Sr, $Sr_2Cs_3(P_4O_{12})(PO_3)_3$,and of the Cs-Pb polyphosphate $PbCs_2(PO_3)_4$ frequently observed the formation of tetrahedra slightly soluble in water. This solubility proves that the compound is not a polyphosphate but probably a Cs-rich cyclophosphate. The structural analysis shows that this salt is $Cs_4Sr_3H_2(P_4O_{12})_3$.[34]

Sr[NH₃(CH₂)₂NH₃]P₄O₁₂.5H₂O

The process for the preparation of the title compound is identical to that used for all the salts of the series. Crystals were prepared by adding strontium carbonate and ethylenediamine in a stoichiometric ratio to a water solution of cyclo-tetraphosphoric acid kept at low temperature (T < 278 K); after slow evaporation large prisms with rectangular section are obtained [35]

* Crystallographic data

Table 7: Main Crystallographic Data for the cyclo-tetraphosphates associated to strontium

Formula	a(Å) α°	b(Å) β°	c(Å) γ°	Space Group	Z
$SrNa_2P_4O_{12}.6H_2O$	9.838	9.838	5.003	*P4/nbm*	2
$SrK_2P_4O_{12}$	7.445	7.445	10.17	I-4	2
$Sr(NH_4)_2P_4O_{12}$	7.575	7.575	10.26	I-4	
$SrTl_2P_4O_{12}$	7.608	7.608	10.25	I-4	2
$SrRb_2P_4O_{12}$	7.585	7.585	10.28	I-4	2
$Cs_4Sr_3H_2(P_4O_{12})_3$	14.544	15.455	15.455	I-43d	2
$Sr[NH_3(CH_2)_2NH_3]P_4O_{12}.5H_2O$	17.863	15.317	13.109	Pbca	8

3.5 $P_6O_{18}^{6-}$

$Sr_2(NH_4)_2P_6O_{18}.7H_2O$

Ammonium strontium cyclo-hexaphosphatehepta hydrate $Sr_2(NH_4)_2P_6O_{18}.7H_2O$,five mmol (3.045g) of $(NH_4)_2P_6O_{18}.1,5H_2O$ were dissolved in $30cm^3$of water. Then the solution was mixed with $20cm^3$(10mmol) of the 0.5 mol dm^{-3}strontium chloride solution. The mixture was stirred for 30min.the precipitate was then filtered off, washed, and dried as above found Sr,21.87;N,3.32;P,23.03;H_2O,15.57%.Calcd for
$Sr_2(NH_4)_2P_6O_{18}.7H_2O$:Sr,21.61;N,3.45;P,22.91;H_2O,15.53%. At least 97% of the P atoms were found as cyclo-$P_6O_{18}^{6-}$ ions [33].

3.6 Long chain polyphosphates $(PO_3^-)_n$

$Sr(PO_3)_2\beta$ andγ forms

Single crystals of β-Sr $(PO_3)_2$ and γ-$Sr(PO_3)_2$ were obtained from mixtures of $NH_4H_2PO_4$, $SrCl_2$ and Y_2O_3 taken respectively in molar ratios Y: Sr: P = 1: 20: 150 and Y: Sr: P = 2: 40: 100 and brought respectively to 623 K and 773 K for 16h, then cooled slowly (0.2 K min^{-1}) [36].

$Sr(HOOCC_6H_4PO_3H)_2,\alpha$-phase

To 60mL of a mixture of water and ethanol (1/1 v/v) was added 0.44 g $(2\times10^{-3}$mol) of 4-carboxyphenylphosphonicacid monohydrate, $HOOCC_6H_4PO_3H_2.H_2O$. The mixture was heated under stirring until the acid dissolved. To this solution, cooled to room temperature, 0.42g of $Sr(NO_3)_2$ $(2\times10^{-3}$mol) dissolved in 10mL of water was added. Immediately after mixing a precipitate was formed. The reaction mixture was stirred for additional 10 min. The product was obtained in a 63% yield (0.308g). Elemental analysis (%) for $C_{14}H_{12}O_{10}P_2Sr$ (489.8): calculated C 34.30, H2.45; found C 34.82, H 2.28 [37].

$Sr_3(OOCC_6H_4PO_3)_{2.5}.7H_2O$

Using an automated burette, 65.9mL of $0.315MNH_4OH$ solution was added to 1.32 g $(6\times10^{-3}$mol) of 4-carboxyphenylphosphonic acid monohydrate in 20mL of water and 20mL of ethanol to adjust pH to 9. To this solution, 1.902 g of $Sr(NO_3)_2$ $(9\times10^{-3}$mol) in 20mL of water was added. Slowly formed precipitate was dried overP_2O_5 in a dessicator. The yield of the product was 1.47 g(67%). Elemental analysis calculated (%) for $C_{14}H_{19.4}O_{15.7}P_2Sr_3$(763.6): C 22.00, H 2.54; found C 21.27, H 2.54 .[37]

$Sr_3(OOCC_6H_4PO_3)_2.4H_2O$

About 0.1386 g of $Sr_3(OOCC_6H_4PO_3)_{2.5}.7H_2O$ $(1.8\times10^{-4}$mol) prepared according to the above given procedure was dissolved in 8mL of water. The reaction mixture was heated under auto-geneous pressure at 180°C for 48 h. The yield was 0.076 g (57%). The same compound, but in a distinctly lower yield, can be obtained by heating an aqueous solution of the starting compound until precipitation. Elemental

analysis calculated (%) for $C_{14}H_{16}O_{14}P_2Sr_3$ (733.1): C 22.92,H 2.18; found C 21.12, H 1.95.[37]

$Sr(PO_3)_2$

Thilo and Grunze also investigated the thermal condensation of $Sr(H_2PO_4)_2$ and found its course very similar to that observed in the case of calcium.$Sr(PO_3)_2$ produced by calcination of $Sr_3(P_3O_9)_2\cdot7H_2O$ at temperatures higher than873 K was identified as the βform, isotypic with calcium and lead polyphosphates. [28]

$SrNa(PO_3)_3$

$SrNa(PO_3)_3$ appears as an incongruent melting compound decomposing at 1023K in the $NaPO_3$-$Sr(PO_3)_2$, phase-equilibrium diagram elaborated. The crystal data reported by these authors showed this salt to be isotypic with $PbLi(PO_3)_3$.[38]

$SrLi(PO_3)_3$

Samples for powder studies were prepared by calcining at 700°C a mixture of suitable proportions of lithium carbonate, strontium carbonate and biamonic phosphate.the single crystals are prepared by calcining for 24h H_3PO_4 (85%) in which 2g of strontium carbonate and 2g of lithium carbonate have been introduced. The crystals obtained are in the form of very short oblic prisms with a square base or square platelets [39].

$SrNa(PO_3)_3$

Monocrystals of the compound are easily prepared by attacking a stoichiometric mixture of carbonates with an excess of orthophosphoric acid and calcining the liquor obtained between 300 and 400°C for 24 hours. Polycrystalline samples can be prepared by calcining a stoichiometric mixture of carbonates and diammonium monophosphate at 650°C for strontium salt [40].

* Crystallographic data
Table 8: Main Crystallographic Data for the polyphosphates associated to strontium

Formula	a(Å) α°	b(Å) β°	c(Å) γ°	Space Group	Z
β-$Sr(PO_3)_2$	7,209	7,9527 90,64	17,414	$P2_1/c$	8
γ-$Sr(PO_3)_2$	4,498	10,911 91.56	10,375	$P2_1/c$	4
$SrLi(PO_3)_3$	7.163 100.07	7.360 98.49	6.767 83.59	P-1	8
$Sr(PO_3)_2$	7.204	7.936	17.40	$P2_1/c$	4
$SrNa(PO_3)_3$	7.162 99.68	7.73 97.29	6.831 83.84	P-1	2
$Sr(HOOCC_6H_4PO_3H)_2,\alpha$-phase	38.736	5.834 95.94	7.808	$P2_1/a$	4
$Sr_3(OOCC_6H_4PO_3)_2.5,7H_2O$	21.59	3.294 114.40	12.34	$P2_1/m$	4
$Sr_3(OOCC_6H_4PO_3)_2.4H_2O$	13.640	5.864 99.02	13.466	$P2_1/n$	4
$Sr(HOOCC_6H_4PO_3).H_2O$	24.480	8.166	5.689	$P2_1/c$	4

		125.670			
$Sr(HOOCC_6H_4PO_3H)_2,\beta$-phase	46.58	7.868 123.30	5.603	$P2_1/c$	4
$SrHOOCC_6H_4PO_3$	19.902	5.629 96.090	7.743	$C2/c$	4

* Characterization of PO_3^- in α-$Sr(PO_3)_2$ by IR vibration spectrometry
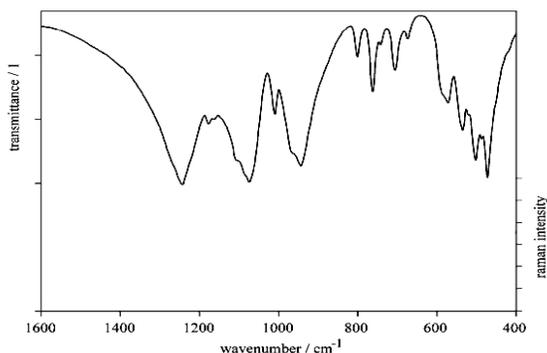
Figure 4: Infrared vibrational spectrum of α-$Sr(PO_3)_2$.

Table 9: Frequencies (cm^{-1}) of IR absorption bands for α-$Sr(PO_3)_2$

Fréquences (cm^{-1})	Vibrations
1310 1243	$\nu_{as} OPO^-$
1074	$\nu_s OPO^-$
944	$\nu_{as} POP$
792 746 705	$\nu_s POP$
611 607 520	$\delta OPO^- + \rho OPO^-$

Fig.4. shows the IR spectrum of the title compound α-$Sr(PO_3)_2$. The IR spectrum of catena-polyphosphates are not significantly different from those of catena-oligophosphates. The only characteristic bands should be found in the region between 800 and 650 cm^{-1}, where the number of bands should correspond to the periodicity of the phosphate chain. Unfortunately, this holds quite reliably only for low chain periodicities. In α-$Sr(PO_3)_2$, the characteristic frequencies of catena–polyphosphate chains such as the $\nu_{as}(PO_2)$ are detected between 1200 and 1310 cm^{-1} with a maximum at 1243 cm^{-1}, the very intense $\nu_{as}(POP)$ at 944 cm^{-1} and $\nu(PO_{term})$ ranging from 1019 up to 1100 cm^{-1}. Thus the observed vibrational data are in good agreement with the expected values [41].
\

4. CONCLUSION

In this work we have tried to review the different methods of preparation for condensed phosphates and monophosphates (classical methods, ion-exchange resins, Boulle's process, flux methods, thermal methods as dehydration and hydrothermal method). Furthermore, we have collected crystallographic data for the various condensed phosphates and monophosphates associated to strontium with known structures. Especially there anions, were characterized by infrared vibration spectrometry. Until today there are no condensed phosphates studied with the following anions: cyclophosphates $P_nO_{3n}^{n-}$ (3 types of anions: $P_5O_{15}^{5-}$, $P_8O_{24}^{8-}$, $P_{12}O_{36}^{12-}$) and oligophosphates $(P_nO_{3n+1})^{(n+2)-}$ (2 types of anions : $P_4O_{13}^{6-}$, $P_5O_{16}^{7-}$).

REFERENCES

[1] Durif, André. Crystal chemistry of condens phosphates.Springer Science & Business Media, 2013.

[2] Boudjada.A, Masse.R, and Guitel.J. C. Structure cristalline de l'orthophosphate monoacide de strontium: $SrHPO_4\alpha$: forme triclinique. Acta Crystallographica Section B: Structural Crystallography and Crystal Chemistry, 1978, 34, 9, 2692-2695. DOI :https://doi.org/10.1107/S0567740878009036

[3] Weiwei.C, Zhenzhen.L,Ruiqin.T, Shihui.T, Wei.X, Weijie.S, Junhua.Z.Comparativestudy on Pb^{2+} removalusing hydrothermal synthesizedβ-$SrHPO_4$, $Sr_3(PO_4)_2$, and $Sr_5(PO_4)_3(OH)$ powders. Powder Technology, 2018, 329,420-425. DOI:https:// /pii/S003259101830086X

[4] Taher.L, Smiri.L, Laligant.Y and Vincent.M. Investigation of the alkaline earth phosphates: synthesis and crystal structure of a new strontium hydrogen phosphate form. Journal of Solid State Chemistry, 2000,152, 2, 428-434. DOI:10.1006/jssc.2000.8700

[5] Belik.A.A,Malakho.A.P, and Lazoryak.B.I. Synthesis and X-ray Powder Diffraction Study of New Phosphates in the $Cu_3(PO_4)_2$–$Sr_3(PO_4)_2$ System: $Sr_{1.9}Cu_{4.1}(PO_4)_4$, $Sr_3Cu_3(PO_4)_4$,$Sr_2Cu(PO_4)_2$, and $Sr_{9.1}Cu_{1.4}(PO_4)$. Journal of Solid State Chemistry, 2002, 163, 1,121-131. DOI:doi.org/10.1006/jssc.2001.9380

[6] Alexei A.B, Masaki.A,Akira.M,Myung-Hwan.W, Hyun Joo.K,Jun.K,Tomoyuki.K,Susumu.O, Hitoshi.O,Koichi.K,andMikio.T.Investigation of the crystal structure and the structural and magnetic properties of $SrCu_2(PO_4)_2$. Inorganic chemistry, 2005, 44, 19, 6632-6640. DOI:Doi :org/10.1021/ic051079h

[7] Zhi-wei.Z, Ai-jun.S, Shi-tao.S, Jian-ping.Z, Wei-guo.Z,and Dong-jun.Synthesis and luminescence properties of novel $KSrPO_4$: Dy^{3+} phosphor. Journal of Alloys and Compounds, 2015,629,32-35. DOI :org/10.1016/j.jallcom.2014.12.066

[8] Hidouri.M,LuisaLópez.M, Pico.P,Wattiaux.A,andBen Amara.M.Synthesis and characterization of a new iron phosphate $KSrFe_2(PO_4)_3$ with a langbeinite type

structure. Journal of Molecular Structure, 2012,1030,145-148. DOI :doi.org/10.1016/j.molstruc.2012.04.002

[9] Elbali.B,Boukhari.Ali,Holt.E.M.,and J.Aride. Strontium dicobalt orthophosphate. Journal of crystallographic and spectroscopic research, 1993, 23,12, 1001-1004.
DOI :10.1007/BF01185551

[10] Yang.M, Zhang.S, Guo.W, and Zhangzhen.H. Hydrothermal synthesis and magnetic properties of a New phase of $SrCo_2(PO_4)_2$. Solid State Sciences, 2016,52,7277.
DOI:doi.org/10.1016/j.solidstatesciences.2015.12.013

[11] Pavel E. K, AndreyS.K,Martin.J, Jürgen.N, and YuryD.T.Crystal structure and properties of strontium phosphate apatite with oxocuprate ions in hexagonal channels. Zeitschriftfüranorganischeund allgemeine Chemie, 2003, 629, 2,344-352.
DOI: https://doi.org/10.1002/zaac.200390055

[12] Maass.K and Glaum.R. Strontium chromium (II) diphosphate, $SrCrP_2O_7$.Acta Crystallographica Section C: Crystal Structure Communications, 2000,56,4,404-406.DOI: 10.1107/S0108270100000226

[13] Grenier.J and Masse.R. Structure cristallographique de α-$Sr_2P_2O_7$.Bulletin de Minéralogie, 1967,90, 3,285-292. DOI :https://doi.org/10.3406/bulmi.1967.6124

[14] İlkay.L,Ozbayoglu.G, and Yilmaz.A.Synthesis, characterizations and investigation of thermoluminescence properties of strontium pyrophosphate doped with metals. Radiation Physics and Chemistry, 2014,104,55-60.
DOI :doi.org/10.1016/j.radphyschem.2014.04.028

[15] Guo.T, Wu.W, Wang.Y, andYongxiang.L.Relations on synthesis, crystal structure and microwave dielectric properties of $SrZnP_2O_7$ceramics. Ceramics International, 2012, 38,S187-S190.
DOI:https://doi.org/10.1016/j.ceramint.2011.04.080

[16] El-bali.B,Boukhari.A,Aride.J,and Maaß.K, Wald.D, Glaum.R,and Abraham.F.Crystal structure and colour of $SrNiP_2O_7$ and $SrNi_3(P_2O_7)_2$. Solid state sciences, 2001, 3, 6, 669-676.
DOI:https://doi.org/10.1016/S1293-2558(01)01176-1

[17] Le Meins.J.-M. and Courbion.G. $SrFeP_2O_7$, a new homologue in the AMP_2O_7series.Acta Crystallographica Section C: Crystal Structure Communications, 1999,55, 4, 481-483..
DOI:https://doi.org/10.1107/S0108270198017375

[18] Boukhari.A, Moqine.A, and Flandrois.S. Synthesis and characterization of new copper (II) mixed diphosphates $(M, Cu)_2P_2O_7$ with M= Mg, Ca, Sr, and Ba. Journal of Solid State Chemistry, 1990, 87, 2, 251-256.
DOI :https://doi.org/10.1016/0022-4596(90)90026-T

[19] Riou.D, and Raveau.B. Structure of $SrCoP_2O_7$.Acta Crystallographica Section C: Crystal Structure Communications, 1991, 47, 8, 1708-1709.
DOI:https://doi.org/10.1107/S0108270191000884

[20] Alaoui El Belghiti.A,Boukhari.A, and Holt.E. M. Structures of $CdSrP_2O_7$ and $CdBaP_2O_7$. Acta Crystallographica Section C: Crystal Structure Communications, 1991,47, 3, 473-477.
DOI:https://doi.org/10.1107/S0108270190008575

[21] Tahiri.Aziz.A, El Bali.B,Lachkar.M,Ouarsal.R,and Zavalijb.P.$SrMgP_2O_7$. Acta Crystallographica Section E: Structure Reports Online, 2002,58,1,i9-i11.
DOI :https://doi.org/10.1107/S1600536801020633

[22] Gao.J,Liu.X,Song.L,Sha.X,Zhao.P and Guo.P. Synthesis and structure of a new halophosphate $Sr_3P_3O_{10}Cl$ with the flexible $[P_3O_{10}]^{5-}$anions.Solid State Sciences, 2016, 55, 159-163.
DOI:10.1016/j.solidstatesciences.2016.03.008

[23] Belaaouad.S, Charaf.A,Elkababi.K,and Radid.M. Chemical preparation, crystallographic characterization, thermal behavior and IR studies of two new cyclotriphosphates $SrKP_3O_9·3H_2O$ and $SrKP_3O_9$. Journal of Alloys and Compounds, 2009, 468, 1-2, 270-274 DOI:https://doi.org/10.1016/j.jallcom.2007.12.100

[24] Belaaouad.S,Sbai.K, and Jouini.A. Chemical preparation, thermal behavior and crystal structure of a new cyclotriphosphate: $SrNH_4P_3O_9·3H_2O$. Solid state sciences, 2000, 2, 6, 655-661.
DOI :https://doi.org/10.1016/S1293-2558(00)01069-4

[25] Sbai.K,Belaaouad.S,Abouimrane.A,and Moutaabid.M. Chemical preparation, crystallographic characterization, thermal behavior and IR studies of a new cyclotriphosphate $SrTlP_3O_9·3H_2O$. Materials research bulletin, 2002, 37, 5, p. 915-924.
DOI :https://doi.org/10.1016/S0025-5408(02)00710-9

[26] Hamza Marouani, Rachida Oubouaza, Soufiane Zerraf, Ali Ouasri, MalikaTridane And Said Belaaouad. Chemical preparations, crystal data for monophosphates and condensed Phosphates associated to manganese and IR studies of their anions.International Journal of Emerging Trends in Engineering Research,2020,8,8, 4784-4797.DOI: 10.30534/ijeter/2020/116882020

[27] Zilber.R, Tordjman.I, Durif.A,and Guitel.J. Structure cristalline du trimetaphosphate de strontium-sodium trihydrate: $SrNaP_3O_9·3H_2O$. ZeitschriftfürKristallographie-CrystallineMaterials, 1974, 140, 5-6,350-359.
DOI :10.1524/zkri.1974.140.5-6.350

[28] Tace.El.M,Charaf.A,Fahim.I,Moutaabbid. M,Kheïreddine.A,Ouaalla.F.-E,Tridane.M, Sbai.K,Radid.M,and Belaaouad.S. Chemical Preparation, Thermal Behavior, Kinetic, and IR Studies of $MnK_4(P_3O_9)_2.2H_2O$.Crystallographic Data of a New Cyclotriphosphate $MnK_4(P_3O9)2$, and Quantum Chemical Calculations for the $P_3O_9^{3-}$Ion. Phosphorus, Sulfur, and Silicon and the Related Elements, 2011, 186,7, 1501-1514.
DOI: https://doi.org/10.1080/10426507.2010.520173

[29] Fahim.I,Kheireddine.A, Tridane.M,and Belaaouad.S. Chemical preparation and XRD data for a new triphosphate $CuNa_3P_3O_{10}$ and two cyclotriphosphates $SrRbP_3O_9·$ $3H_2O$ and $SrRbP_3O_9$. Powder Diffraction, 2011,26, 1, 78-81.
DOI :https://doi.org/10.1154/1.3553180

[30] ElMakhloufy. S,Tridane.M, Majdi.E, Marouani.M, Zerraf.S, Belhabra.M,Cherqaoui.A and Belaaouad.S.Chemical preparation, thermal behavior and infrared studies of the new cyclotriphosphatetetrahydrate of manganese and

distrontium, $MnSr_2(P_3O_9)_2.4H_2O$.Mediterranean Journal of Chemistry,2019, 9, 4, 280-289.
Available online at www.medjchem.com

[31] Santha, N. and Nayar.V. U. Vibrational spectra of $SrNa_2P_4O_{12}\cdot 6H_2O$ and $CaNa_2P_4O_{12}\cdot$ 5.5 H_2O. Journal of Raman spectroscopy, 1990, 21, 8, 517-519.
DOI: 10.1002/jrs.1250210808

[32] Durif.A, Averbuch-Pouchot.M. T, and Guitel.J. C. Structure of disodium strontiumTetrametaphosphate hexahydrate, $SrNa_2P_4O_{12}.6H_2O$. Acta Crystallographica Section C: Crystal Structure Communications, 1983, 39, 7,812-813.DOI: 10.1107/s0108270183006447

[33] Takenaka.A,Motooka.I, and Nariai.H. The thermal decomposition of ammonium strontium cyclo-tri-, cyclo-tetra-, and cyclo-hexaphosphate. Bulletin of the Chemical Society of Japan, 1989, 62, 9,2819-2823.
DOI:https://doi.org/10.1246/bcsj.62.2819

[34] Averbuch-Pouchot.M.T, and Durif.A. $Cs_4Sr_3H_2(P_4O_{12})_3$, a new derivative of $Al_4(P_4O_{12})_3$. Acta Crystallographica Section C: Crystal Structure Communications, 1985,41,11, 1557-1558.
DOI: 10.1107/s010827018500854x

[35] Bagieu-Beucher.M,Durif.A, and Guitel.J.C. Structure of A strontium ethylenediammoniumcyclo-tetraphosphate hydrate.Acta Crystallographica Section C: Crystal Structure Communications, 1988, 44, 12, 2063-2065.
DOI:10.1107/s0108270188008479

[36] Graia.M, Driss.A,and Jouini.T.Polyphosphates de strontium $Sr(PO_3)_2$ formes β et γ. Acta Crystallographica Section C: Crystal Structure Communications, 1999, 55, 9,1395-1398.
DOI :https://doi.org/10.1107/S0108270199003637

[37] Zima.V,Svoboda.J,Benes.L,Melanova.K,Trchova.M,and Dybal.J. Synthesis and characterization of new strontium 4-carboxyphenylphosphonates. Journal of Solid State Chemistry, 2007, 180, 3,929-939.
DOI :https://doi.org/10.1016/j.jssc.2006.12.021

[38] Durif-Varambon .A,Bagieu-Beucher.M,Martin.C,and Jean claude.G. Données cristallographiques sur un trimétaphosphate de strontium hydraté: $Sr_3(P_3O_9)_2\cdot 7H_2O$ et sur le polyphosphate de strontium: $Sr(PO_3)_2$. Bulletin de Minéralogie, 1972, 95, 1,146-148.
DOI: https://www.persee.fr/doc/bulmi_0037-9328_1972_act_95_1_6659

[39] Martin.C and Durif-Varambon.A. Données cristallographiques sur le trimétaphosphate de lithium-strontium: $LiSr(PO_3)_3$. Détermination du diagramme d'équilibre $LiPO_3$-$Sr(PO_3)_2$. Bulletin de Minéralogie, 1969,92, 5,489-490.
DOI :https://doi.org/10.3406/bulmi.1969.6402

[40] Martin.C and Durif-Varambon.A. Étude des systèmes $NaPO^{3-}Ba$ $(PO_3)_2$ et $NaPO^{3-}Sr(PO_3)_2$. Données cristallographiques sur $NaBa(PO_3)_3$, $SrNa$ $(PO_3)_3$, $BaNa(PO_3)_3\cdot 4H_2O$ et $SrNa(PO_3)_3\cdot 3H_2O$. Bulletin de Minéralogie, 1972,95,1,149-153.
DOI :https://doi.org/10.3406/bulmi.1972.6660

[41] Höppe.H.A.The synthesis, crystal structure and vibrational spectra of α-Sr $(PO_3)_2$ containing an unusual catena-polyphosphate helix.Solid state sciences, 2005,7, 10,1209-1215.
DOI: 10.1016/j.solidstatesciences.2005.06.014

[42] Zerraf.S,Tridane.M, and Belaaouad. S. Data of infrared vibration spectroscopy of cyclotriphosphates.Data in brief, 2019, 25, 104075.
DOI: https://doi.org/10.1016/j.dib.2019.104075

[43] Belhabra.M,Fahim.I,Atibi.A,ElKababi.K, Ouasri.A, Zerraf.S, Tridane. M, Radid. M, and Belaaouad.S.Vibrational study and thermal behavior of dihydrogenotriphosphate trihydrate of 4-aminobenzoic acid and its anhydrous new form fertilizer type NP. Mediterranean Journal of Chemistry, 2019,8, 4, 270-282.DOI:http://dx.doi.org/10.13171/mjc841905308mb

[44] Hamza Marouani,Malika Tridane,El Mehdi Majdi, Soufiane Zerraf , Mustafa Belhabra and Said Belaaouad.characterization and Thermal Behavior of two new cyclotriphosphates International Journal of Emerging Trends in Engineering Research , 2020,8, 1.
DOI :https://doi.org/10.30534/ijeter/2020/30812020