THE PHOSPHATES OF THE WORLD AND THE WORLD OF PHOSPHATES

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ABSTRACT

Nature was the first inorganic phosphate "material maker". The world phosphate resources are distributed, according to their type, approximately as follows: 75% from sedimentary marine deposits, 15–20% from igneous, metamorphic and weathered deposits, and 2–3% from biogenic sources (bird and guano accumulations). Apatite [$Ca_5(PO_4)_3(F,Cl,OH)$] is the most common naturally occurring P containing mineral in the Earth's crust. The largest deposits of phosphorites in the World are found in Morocco, USA, Kazakhstan, China and Tunisia.

Usually in inorganic phosphates the P atoms are surrounded tetrahedrally by four oxygen atoms. Such structural entities, isolated in minerals, can be linked by common corner in several synthetic crystals or glasses.

In phosphate materials three functions can be associated with the various phosphate units:

1) Possible transfer of Phosphorus between two phases. Phosphorus is uptaken by plants from fertilizers (*95% of the world phosphate rock consumption*) in water-soluble forms as $H_2PO_4^-$, HPO_4^{2-} and PO_4^{3-}. Such transfer occurs also in biomaterials.

2) Structuring role: in materials the phosphate group is only a building entity: e.g. in *zeolithe for catalyst, matrix for waste storage, low thermal expansion ceramics, composites for high temperature uses with $LaPO_4$, etc.*

3) Inductive effect: the final property of the phosphate is connected to the covalent character of the P-O bond. Such effect is found in electrochemical systems (e.g. *$LiFePO_4$ -like electrodes*) and in optical materials (e.g. *$KTiOPO_4$* and phosphate glasses).

1. INTRODUCTION

Basically phosphate can be understood as a salt of phosphoric acid but also as compounds which contain P-O linkages. The most important inorganic phosphate materials are the calcium orthophosphates which are the calcium salts of orthophosphoric acid. Such salts are used as fertilizers but also are the essential components of bones, teeth etc.

Phosphate rock is formed in oceans in the form of calcium phosphate, called phosphorite. Phosphates from deep waters, brought to the surface through coastal upwelling, are deposited in extensive sedimentary layers, formed in offshore marine conditions on continental shelves that cover thousands of square miles. In phosphorites the calcium phosphates are present as fluorapatite $Ca_5(PO_4)_3F$ (figure 1) or hydroxyapatite $Ca_5(PO_4)_3OH$ but the geochemistry of phosphates is more complex and the phosphate minerals include more than 200 crystals. In addition to the sedimentary phosphate deposits (≈75%), there are some igneous rocks that are also rich in phosphate minerals(≈25%). The largest deposits of phosphorites in the World are found in Morocco, USA, Kazakhstan, China and Tunisia. Large amounts of phosphates were also obtained from guano deposits on small islands such as Christmas Island and Nauru.

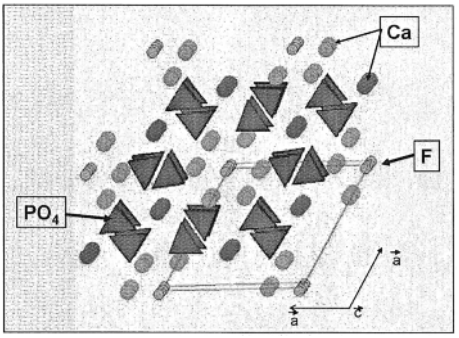

Figure 1. Structure of the calcium fluorapatite $Ca_5(PO_4)_3F$

The oldest inorganic phosphate material is probably the fossil turquoise odontolite which was used to decorate reliquary objects and that consists of blue coloured apatite. The origin of the colour is related to the trace of Mn^{5+} in a distorted tetrahedral oxygenated environment (manganese in the phosphorus site of apatite) (1)).

One of the most fascinating stories about inorganic phosphate material is the discovery in 1972 of the Oklo Fossil Fission Reactors. 16 individual reactor zones have been found in the Oklo/Okelobondo area in Gabon. The concentration and configuration of the natural uranium and surrounding materials, about 2.10^8 years ago, had been just right to sustain fission. Uranium ore are inundated in the ground water which acts as neutron moderator. Such geological system leads to the reactor formation. Many elements extracted from the reactor material are clear isotopic signatures of ^{235}U and ^{239}Pu fission and neutron capture reaction. The average power of each reactor is about 100kW, equivalent to a small research reactor.

Different types phosphates were found in the clays and in the core of reactors. The most important are hydroxyapatites which have trapped fissiogenic nuclides as Nd, Sm, Sr and ^{235}U giving evidence for ^{239}Pu retention. Such elements are found as inclusions or in the structure. Cerium and lanthanum florencite - $La(Ce)Al_3(PO_4)_2(OH)_6$ -were also observed in the clays of the reactors which can contain fission products (Zr, Ce and Sr) and large concentrations of fission Xe and Kr (2) .

The occurrence of self-sustaining fossil reactor has several implications: (i) storage of nuclear wastes in geological environments, (ii) the verification of long time variability - about 2 billion years ago - of fundamental physical constants : Planck constant, charge of electron etc. (3).

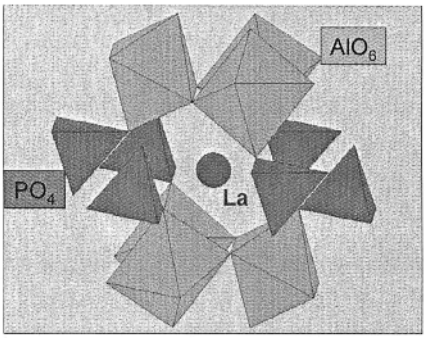

Figure 2. Structure of the florencite $LaAl_3(PO_4)_2(OH)_6$. Captured fission Xe and Kr and are associated with the cycling operation of the reactor.

2. HOW THE PHOSPHATE WORKS ?

The area of solid state chemistry of phosphate has shown remarkable grown over the past century. Therefore the parameters connected to the phosphate groups and explaining the properties of inorganic phosphate materials are clearly identified. Three parameters will be considered to understand "How the phosphate works?"

1) The exchange or inter phase transfer of the phosphate units. Such processes are observed in fertilizers and biophosphates.

2) The structural role of the phosphate entities concomitant with the involvement of the dimensionality of the structure.

3) The "inductive effect" of the phosphate groups which is related to the covalent character of the phosphorus- oxygen bond.

3. EXCHANGE OR INTER PHASE TRANSFER IN PHOSPHATES

3-1 Examples of exchanges in biomaterial phosphates

Apatitic and related calcium phosphates are the main constituents of mineralised tissues (bone, dentine etc.). Therefore synthetic calcium phosphates are largely investigated as biomaterials in several dental and medical applications. There are different types depending on the origin or production procedure. They have some features in common: non toxic, biocompatibility, biodegradation, bioresorption and strong bond to the bone and to the soft tissues.

The ion exchanges in calcium phosphates of apatite type have been explained by the group of Toulouse (4). Assuming the calcium phosphate hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$

as a model compound for studying biological mineralization in the frontier of apatite crystal and solution, the substitution of a PO_4^{3-} group by bivalent species such as HPO_4^{2-} or CO_3^{2-} is compensated by the formation of cationic vacancy and anionic vacancy in the hydroxyl site leading to the simplified formula $Ca_{10-x}(PO_4)_{6-x}(HPO_4^{2-}$ or $CO_3^{2-})_x(OH)_{2-x}$. This approach was completed by Brown (5) which introduced the concept of hydrated domains at

the surface of crystals explaining especially the ion – exchange properties with the possible formation of the octacalcium phosphate $Ca_8(PO_4)_4(HPO_4)_2.5H_2O$ formed by a succession of apatite-like and hydrated layers.
Such a layers can be considered as a reserve of mineral ion of the crystal surface nourishing the slow growth of apatite domains. The figure 3 schematises the ions exchange including also the charged groups of the protein and the growth of apatite domains.

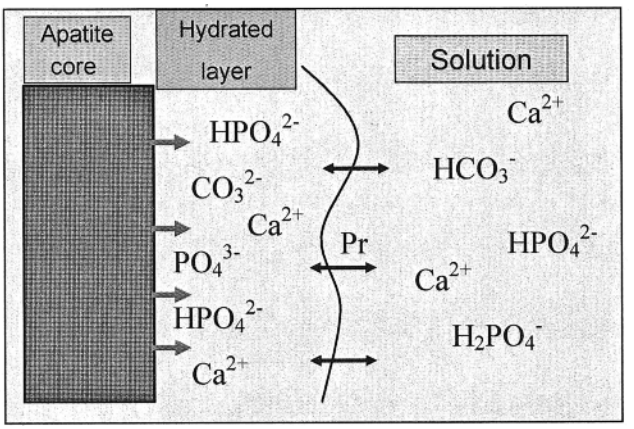

Figure 3. Schematisation of ion exchange at the surface of apatite crystal and the growing apatite domain (red arrows). Adapted from C. Rey et al. Mat.-u. Werkstoffech.,38 n°12(2007).

3-2 Examples of exchange in fertilizers phosphates (6).

According to the Glossary of Soil Science Terms, Fertilizer is "any organic or inorganic material of natural or synthetic origin that is added to a soil to supply one or more plant nutrients essential to the growth of plants": phosphate fertilizers are a plant-essential nutrient.

About 93% of the extracted phosphate rock are used to produce mineral fertilizers, essentially:
- the monoammonium phosphate $NH_4H_2PO_4$ (MAP),
- the diammonium phosphate $(NH_4)_2HPO_4$, (DAP)
-the single superphosphate (SSP) which results from the reaction of the concentrated sulphuric acid on powdered phosphate rock according to the reaction:

$$Ca_3(PO_4)_2(s) + 2\ H_2SO_4(aq) \rightarrow 2\ CaSO_4 + Ca(H_2PO_4)_2(aq))$$

- the triple superphosphate(TPS) produced by the action of concentrated phosphoric acid on ground phosphate rock according to the reaction:

$$Ca_3(PO_4)_2(s) + 4\ H_3PO_4(aq) \rightarrow 3Ca^{2+}(aq) + 6\ H_2PO_4^{1-}(aq) \rightarrow 3\ Ca(H_2PO_4)_2(aq)$$

The active ingredient of SSP and TPS is the monocalcium phosphate. The interaction between fertilizer, soil and plants is complex and in part biochemical. Nevertheless the assimilation of phosphorus by plant occurs mainly by the transport of the small phosphate groups $H_2PO_4^-$ and HPO_4^{2-} : initial solubilisation of fertiliser attacks the surface of the soil with the formation of various crystalline or amorphous phosphates (e.g. calcium, iron, magnesium phosphates). Actually these phosphates are for a long period of time the nutrient sources of the plant.

4. THE STRUCTURING ROLE OF PHOSPHATES ENTITIES.

The simplest structural unit of the phosphates is formed of isolated $[PO_4]$ tetrahedra in which the distance P-O is ≈ 1.55 Å. In more complex structures these tetrahedra can be connected by sharing corner with a chain or cycle configurations. In phosphate materials the role of the structural entities is often related to the dimensionality of the structure and/or the possibility to prepare composites with different functions.

A) Example of one dimensional phosphate.

Typical example of 1D system is the lanthanum metaphosphate LaP_3O_9 with infinite helicoidally chain. In this structure the closest distance between lanthanum atoms are large (4.35Å). Such a long distance allows to optimize the luminescent properties as the lanthanum is replaced by active optical ion (e.g. Nd^{3+}, Sm^{3+}, Eu^{3+}) by inducing a low concentration quenching of the luminescence (7).

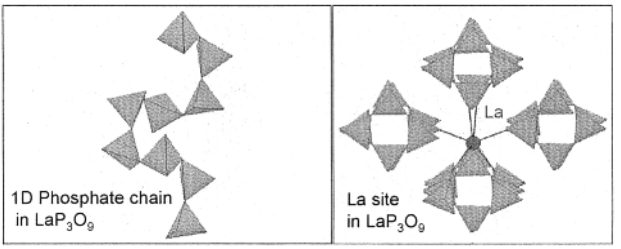

Figure 4. Helicoidally chain and lanthanum site in LaP_3O_9. The lanthanum atom is connected to 4 helicoidally chains (adapted from J. Maruszewski, J. Solid State Chem., **75**, n°2,285-90(1988)).

B) Examples of two dimensional phosphates

Two dimensional phosphates have been investigated for their specific physical properties (e.g. 2D magnetism in $BaNi_2(PO_4)_3$) (8) or for chemical implication especially in layered structures found in zirconium phosphates.

The chemistry of 2D zirconium phosphates began in 1964 when the first crystalline member of this class $\alpha Zr(HPO_4)_2.H_2O$ (αZrP) was obtained by Clearfield and Stynes(9) and its layered structure was clearly established.

The covalent layers of α-ZrP with the composition $Zr(HPO_4)_2$ are made up of ZrO_6 octahedron sharing common corners with six phosphate groups (Fig 5). Each PO_4 tetrahedron share three of its coordinating oxygen with zirconium oxygen octahedra, the fourth oxygen can interacts with the interlayer organic or inorganic molecules. The inter layer distances can be readily expanded to accommodate both small and large guest species.

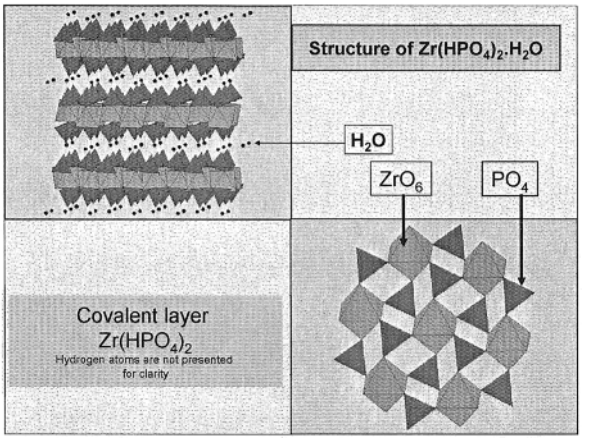

Figure 5. Structure of $Zr(HPO_4)_2.H_2O$ with the covalent layer $Zr(HPO_4)_2$. (adapted from (9))

This phosphate is representative of closely related layer compounds of general formula $M(HXO_4)_2.nH_2O$ where M = Si, Ti, Zr ,Ge and X = P or As with n = 0,1,2. These 2D phosphates exhibit several remarkable properties: inorganic cation exchange, ionic conductivity, resistance to ionizing radiation, catalysts, nanoencapsualtion for delivery application, flame retardant etc (10 – 14).

C) Examples of three dimensional phosphates.

Three types of 3D phosphate materials can be characterized: phosphate with a dense structure, phosphate with open channel or cage structure and composite systems.

The calcium phosphates which are representative of the first type, play a major role in fertilizer technology and as biomaterials.

Phosphates with a three dimensional channel structure have been developed for their good fast-ion conduction properties. The typical example is the sodium zirconium monophosphate $NaZr_2(PO_4)_3$ first member of the NASICON (Sodium Super Ionic Conductor) family. The structure is built from PO_4 and ZrO_6 units and contains two possible sodium sites. Substitution of SiO_4 tetrahedral groups for the phosphate groups give solid solutions with general formula $Na_{1+x}Zr_2(PO_4)_{3-x}(SiO_4)_x$ in which the extra negative charge is progressively compensated by the introduction of more sodium into the empty cation sites (15). Nasicon can be prepared as dense ceramic or thin film. In addition to the development as solid electrolyte, several compositions of the Nasicon type have been investigated as low thermal expansion ceramics (16).

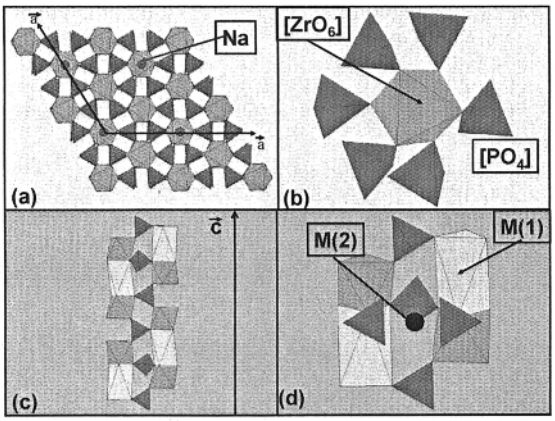

Figure 6. The crystal structure of $NaZr_2(PO_4)_3$ (a) the covalent framework, (b) the environment of ZrO_6 octahedron, (c) the environment of the phosphate groups,(d) the location of possible sodium sites usually called M(1) and M(2) (adapted from L. Hagman and P. Kierkegaard, Acta Chem. Scand., 22,1822(1968)).

In these open structures by increasing the site of the cavity are created the family of zeolite phosphates. For instance PO_4 group can be incorporated in silicate frameworks of Faujasite, Analcime etc. These materials can be prepared hydrothermally or solvothermally using organic molecules acting as templates to determine the pore size and consequently to tailor the application requirement. Synthetic zeolites are studied for many applications e.g. catalyst in petrochemical industry, ion exchange materials for water purification etc.

D) Examples of composite materials.

The development of composite systems is mainly related with the characteristics of the monazite – like compounds ($LaPO_4$ type).

(i) Lanthanum phosphate is a host lattice for rare earth luminescent ions. Green luminescence is obtained from cerium/terbium codoped $LaPO_4$. For potential biological application as biolabelling, nanocrystal of SiO_2@$LaPO_4$:Ce^{3+},Tb^{3+} can be prepared via sol gel process (17). Theoretically unlike of most molecular lanthanide complex these "nano" crystals exhibit a higher photoluminescence quantum yield.

(ii) In the context of the elaboration of structural composite material, $LaPO_4$ presents interesting properties: refractory nature (melting point 2074°C), stability in oxidizing environments, compatibility with other refractory oxides: alumina, garnet, mullite, zirconia. The effectiveness of the Al_2O_3 /$LaPO_4$ composite ceramics has been studied in three types of materials porous ceramics, machinable ceramics, ceramics stable at high temperature (18, 19).

5. THE INDUCTIVE EFFECT OF THE PHOSPHATE GROUP.

Usually the inductive effect is understood as a transmission of charge through a chain of atoms or molecular entities by electrostatic induction. It induces a bond polarization where the more

electronegative atom have a slight "extra" negative charge (δ^-) and the other entity has a slight "extra" positive charge (δ^+). In phosphate connected to a transition metal ion M the phosphate group has a more negative charge and the metal ion a more positive charge than formally expected. Therefore the covalent character of the P-O bond increases the ionic character of the opposite M-O bond i.e. decreases the electronic density at the transition element. Such inductive effect is of industrial importance in electrochemical systems as well as in non linear optical materials.

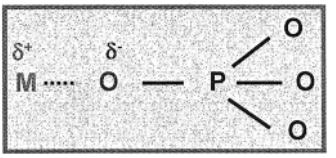

Figure 7. Scheme of the inductive effect in transition metal phosphate

5-1 Electrochemical systems.

Lithium iron phosphate $LiFePO_4$ and related compounds are promising positive-electrode materials for the next generation of lithium-ion batteries that will be used in electric and plug-in hybrid vehicles. The development of this phosphate is the consequence of the pioneering work of J.Goodenough and co-workers (20): by considering the redox potential of transition metal ions in isostructural family of compounds, the position of the redox couple energy relative to the Fermi energy of lithium –in electrochemical lithium system – can be determined.

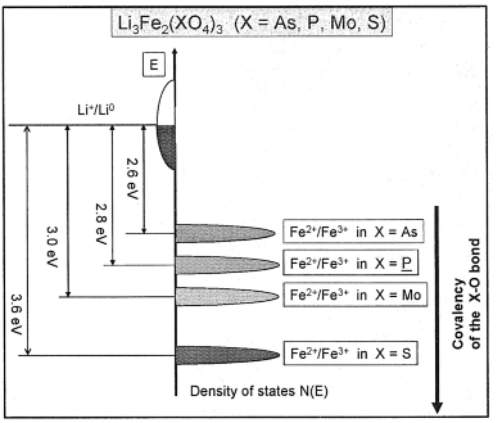

Figure 8. Position of the Fe^{3+}/Fe^{2+} redox couples relative to the Fermi energy of lithium in lithium Nasicon related compounds (adapted from J.B. Goodenough et al. Chem. Mater. 22,3(2010)587.)

The figure 8 illustrates the evolution of this energy difference in the case of the $Li_3Fe_2(XO_4)_3$ (X = As, P, Mo, S) nasicon-like compounds: the difference between the Fermi energy of lithium and the energy of the Fe^{2+}/Fe^{3+} redox couples increases with the covalent character of the X-O bond.

5-2 Optical systems

Transparent materials (crystals or glasses) with relatively large optical non linearities are promising material for all- optical communication systems. The nonlinear optical properties of materials under an electromagnetic field E result from the generation of a polarization P which can be expressed as a power serie in E:

$$P = \chi^{(1)} E + \chi^{(2)} E.E + \chi^{(3)} E.E.E. + \ldots .$$

where $\chi^{(1)}$ is the linear susceptibility which accounts for the linear index, $\chi^{(2)}$ and $\chi^{(3)}$ correspond respectively to the second – and third- order nonlinear susceptibilities. $\chi^{(2)} = 0$ in centrosymmetric material as glasses but $\chi^{(3)}$ is never 0. This last property opens the non linear optics to all dielectric materials with no- symmetry condition.

The choice of composition is mainly dictated by the possibility of increasing the non linear index n_2 (or the third-order susceptibility $\chi^{(3)}$). The main problem is to prepare new materials (including phosphates) with a high proportion of polarizable and hyperpolarizable entities while maintaining very low absorption in a broad spectral range. In crystals high nonlinear indices have been reported for titanium oxides such as TiO_2 and $SrTiO_3$ (21) (Table). In glasses the introduction of "d^0" ion increases the non linear index by one order of magnitude. Such properties can be explained the bond orbital theory introduced by M. E. Lines to explain the dielectric properties of transparent transition-metal oxides (22).

This model adopts a local picture resulting from interactions between the nearest-neighbours metal and oxygen. For the transition-metal-oxide series, an empty *d* level progressively falls below the *sp* conduction band as the metal oxygen distance *r* decreases. In fact, the *d* orbital contribution appears negligible if *r* is greater than 2.3 Å while for shorter distances lower than 2 Å it generally exceeds the orbital *sp* contribution and its role becomes significant. In this context , phosphates (crystals or glasses) containing transition metal ions with empty d^0 shell like Ti^{4+}, Nb^{5+} with short metal oxygen distances have been investigated (23,24).

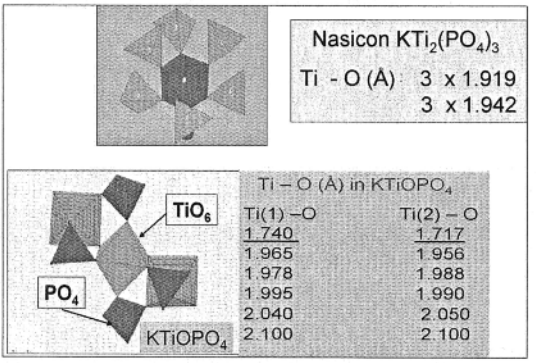

Figure 9. Comparison of the Titanium-oxygen distances in $KTi_2(PO_4)_3$ and $KTiOPO_4$.
(adapted from E.S.Lunesheva et al. *Soviet Physics Crystllography* 34(5)1119-22(1989) and I. Tordjman, et al. *Zeit. fur Kristallographie*, 139, 103-115 (1974)).

The creation of such structural property is mainly related to the topology of the phosphate groups around the $M(d^0)$ oxygenated polyhedron. This effect is illustrated in the figure 9 where are compared the structures and the titanium-oxygen distances in $KTi_2(PO_4)_3$ of the Nasicon type and $KTiOPO_4$. In

the first compound the TiO_6 octahedra are connected with six phosphate group sharing common corner by six PO_4 groups and the Ti-O distances are
very close. In contrast in $KTiOPO_4$ the TiO_6 octahedra are connected only with four phosphate groups. Therefore two oxygens are not are not subjected to the inductive effect of the phosphate groups which give rise to a very distorted octahedral with involving very short and very long titanium oxygen distances.
Such structural features are common to the majority of "d^{0}" metal oxyphosphates e.g. $A_3Nb_5O_{11}(PO_4)_2$ (A = Na,K, Tl) (25), $Rb_2MgWO_2(PO_4)_2$(26) etc.

Table 1. Linear and non linear index of dielectric crystals (21).

Crystals	linear-index n (λ = 1.06 μm)	non-linear index n_2 (10^{-13} esu)
NaF	1.321	0.34
NaCl	1.531	1.59
NaBr	1.623	3.26
CaO	1.83	5.20
SrO	1.81	5.07
TiO_2	2.48	55.8
$SrTiO_3$	2.31	26.7
KH_2PO_4	1.460	0.72
$KTiOPO_4$	1.73	5.73

Table 1 collects the linear and non linear index of dielectric crystals. The polarizabilities and hyperpolarizabilities of anions are larger than that of cations. Nevertheless the cations with d^0 low – lying empty shell (here Ti^{4+}) give anomalous oxygen polarizabilities and hyperpolarizabilities which can be explained by the model of Lines in agreement with the influence of the inductive effect in the case $KTiOPO_4$.

This model was successfully applied to explain the optical linear and non linear responses of titanium and niobium borophosphate glasses (23,27). As a consequence second harmonic generation wich is not expected to take place in centrosymmetric materials as glasses was observed in bulk glasses submitted to thermal poling treatment in which the creation of an internal dc field Edc in the material induces a non zero second order optical nonlinearity $\chi^{(2)}$ through the relation : $\chi^{(2)} \alpha \chi^{(3)}E_{dc}$ and the possibility of observing a second harmonic generation. In these glasses the applied electric field produces a migration of sodium ions from the anode to the cathode and a reorganization of the network former with a formation of a negative charged depletion zone at the anode side. Such materials could be produced either as thin film for electro-optical device developments (28).

6. CONCLUSIONS: TOWARDS HIGH VALUES INORGANIC PHOSPHATE MATERIALS.

High value material including phosphates can result from: (i) major efforts to maintain and possible improve the quality of education, (ii) cross disciplinary approach (Chemistry, Physics, Geology, Biology etc.), (iii) implementation of new concepts which are able to push back the technological frontiers e.g. composite, laser processing, functionalization of surface, template effect etc. .

A non-exhaustive list of typical high value phosphate materials resulting from cross-disciplinary approach and new material engineering concepts can be given.

-Composites for high temperature uses with $LaPO_4$ (Geology, Chemistry, Mechanics, High temperature)(17,18,19).
-Electrode for battery of $LiFePO_4$ type (Composite, Chemistry, Electrochemistry, Surface reaction, Nano- size particles) (20,29)
-Chemical bonded phosphate ceramics: cements for low temperature environments (Chemistry, Mechanics and Geology) (30).
- Phosphate glass laser for fusion energy (Chemistry of glasses, Optics, Mechanics) (31).
-Phosphates for second harmonic generation (Chemistry, Crystal growth, Crystallography, Optics, Composite) (32).
-Photonic component for information storage (Phosphate chemistry, Materials Laser Processing, Aggregates, Optics) (33)
-Biomaterials (Chemistry, Biology, Medicine, Ceramics) (4)
-Waste storage (Chemistry, Geology, Mechanics) (34)
-Phosphors(Chemistry, Optics) (35)

Finally the extension of the world of phosphate depends also on the imagination of the solid state chemist.

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