Nasicon - type solid solution in the system Ca - Na - Ti - (PO₄) :
Application for the elaboration of multicomponent phosphate bioceramics.

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Abstract Nasicon type compounds in the system Ca - Na - Ti - (PO₄) may be obtained by soft chemistry way. We use the phosphate coacervate route and we obtain the same results as by solid chemistry methods. The coacervate route permits us to obtain multicomponent ceramics that may be used in medical applications. This study of the formation of Nasicon solid solution shows the possibility of a sodium ratio control in the glass phase of multicomponent phosphate ceramic obtained by coacervate process. Thus it is possible to obtain adaptable durability of phosphate ceramic in biomedical application.

INTRODUCTION

Bioactive glasses in the phosphate system are used as implant materials for medical device. We presently observe the development of bioglass ceramics like CaO / P₂O₅ glasses containing TiO₂. Titanium oxide is used to form biocompatible Nasicon like compounds [1] [2]. We develop biomaterials from soft chemistry precursor: the polyphosphates coacervates.

EXPERIMENTAL

The starting materials are Graham's salt ((NaPO₃)_n), calcium chloride, magnesium chloride and anatase (TiO₂) [Merck]. After dissolution of Graham's salt in a pyrex beaker (3M solution), we slowly added calcium chloride

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solution (2M). The polyphosphates precipitate in a viscous phase called "coacervate" [3],[4]. We eliminate the supernatant liquid and we put a solution (1M) of magnesium chloride to exchange sodium with magnesium during 20 hours [3].

When adding anatase in suspension in the solution of Graham's salt, the coacervate precipitates with the totality of TiO_2 . After drying and grinding, we obtain a ceramic after heating at 900°C [4] [5].

This process permits us to have an homogeneous powder before the heating treatment. The chemical composition of products that has been determined by elementary analysis, is $13,5\text{CaO}$, 12MgO , $8\text{Na}_2\text{O}$, $31,5\text{TiO}_2$, $34\text{P}_2\text{O}_5$.

THERMAL EVOLUTION OF BIOMATERIAL PRECURSOR

The evolution of these systems have been studied by

FIGURE 1
Thermal évolution
of precursors by D T A

spectroscopic and thermal investigations.

The figure 1 shows the comparative thermal evolution of dried coacervate without and with anatase filler. The thermal evolution can be summarized as following [2] [4]: In a first step, the phopshate chains are subjected to hydrolysis and led to amorphous hydrogen phosphate at 130°C. Afterwards thermal condensations and crystallisations occur at 400°C. The free and bonded

FIGURE 2
R X studies of precursor heating at different temperatures

waters are released between 80 and 400°C. For the coacervate without anatase, we obtain at 500°C two major compounds: Calcium sodium trimetaphosphate and magnesium sodium trimetaphosphate and also a little calcium metaphosphate [2] [4]. With anatase, we have a reaction above 700°C which gives sodium titanium orthophosphates - $\text{NaTi}_2(\text{PO}_4)_3$ Nasicon like compound [6]. This reaction may be followed by X ray diffraction ($\text{Cu K } \alpha$, Ni filter) - Figure 2. In view of biological applications, this multicomponent ceramic has been implanted in subcutaneous, supraparietal and supracranial position of Swiss mice in order to study the tissue behavior. It seems that the properties of surface change and the durability of ceramic is affected after ten days of implantation. Thus we observe a negative tissue response that we explain by an increase of solubility of glass phases [2], if the length of heating treatment is too short. In fact for this case, the good solubility may be explained by the high sodium concentration in the glass phases.

The formation of a Nasicon phase must be controlled in order to obtain a good biomaterial by this way. This leads us to study more particularly the behavior of these orthophosphates in the system $\text{Ca} - \text{Na} - \text{Ti} - (\text{PO}_4)$

STUDY OF $\text{Ca}_{1-x}\text{Na}_x\text{Ti}_4(\text{PO}_4)_6$ SOLID SOLUTION.

A complete solid solution has been prepared between $\text{CaTi}_4(\text{PO}_4)_6$ and $\text{Na}_2\text{Ti}_4(\text{PO}_4)_6$ by solid state reaction from stoichiometric mixture of Na_2CO_3 , $\text{Ca}_3(\text{PO}_4)_2$, TiO_2 and $(\text{NH}_4)_2\text{HPO}_4$ at 970°C during 16 hours. The a unit cell parameter increases linearly from $x=0$ to $x=1$ - Figure 3-. On the contrary, the c parameter decreases. The Nasicon structure may be described as made of ribbons parallel to the c axis. (Figure 4), these ribbons are connected together by PO_4 tetrahedra. In $\text{Na}_2\text{Ti}_4(\text{PO}_4)_6$ ($x=1$), space group $\text{R}\bar{3}\text{c}$, the M1 octahedra sites are all occupied while in $\text{CaTi}_4(\text{PO}_4)_6$, ($x=0$), space group $\text{R}\bar{3}$ vacancies and Ca atoms alternate along the c axis; this half occupancy of

FIGURE 3

Left evolution of unit cell parameters with the Na/Ca ratio
 Right evolution of IR spectra with the Na/Ca ratio

the M1 site allows a decrease of the inter ribbon electrostatic repulsion, and results in a repulsion between oxygen of the empty M1 site which is not compensated by attraction due to the Na⁺ ions. In the range $0.5 < x < 1$, the X ray powder patterns are indexed with the space group $R\bar{3}c$, on the contrary, in the range of $0 < x < 0.5$, extra lines led us to reassign the space group $R\bar{3}$, thus Ca and Na atoms are partly ordered.

Infra Red study confirm the existence of a complete solid solution - figure 3-.

Sodium ions can be totally exchanged for calcium in $\text{CaTi}_4(\text{PO}_4)_6$ using molten NaNO_3 at 350°C . Reverse exchange failed.

Figure 4
Structure of NASICON

CONCLUSION

This study of the formation of Nasicon solid solution shows the possibility of sodium ratio control in the glass phase of multicomponent phosphate ceramic obtained by coacervate process. Thus it is possible to obtain adaptable durability of phosphate ceramic in biomedical application.

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