DEVELOPMENT OF FUNCTIONAL INORGANIC PHOSPHORUS MATERIALS SCIENCE

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Abstract: This paper reviews the studies achieved by the author and his research group on functional inorganic phosphorus materials, in commemoration of the distinguished contribution award from The Japanese Association of Inorganic Phosphorus Chemistry (JAIPC) in 2019. The focus of the review is on the development both of electrically functionalized hydroxyapatite and new Na⁺ conduction ceramics and glass-ceramics. It is therefore to be stated here that the present review clearly differs from conventional journal-reviews which summarize related papers and collect their related references with critical comments.

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INTRODUCTION

The author carried out the studies on inorganic phosphorus materials during 1984 to 2019, a part of which was done under supervision of Emeritus Professors Takafumi Kanazawa (TK) and Takao Umegaki at Tokyo Metropolitan University. The important discipline on inorganic phosphorus chemistry by TK was the elemental relationship of P with Si and S in Periodical Table. The unique characteristics of P arises from tetrahedral ionic group of (PO₄)³⁻, similar to tetrahedral (SiO₂)⁴⁻ in the structure of metaphosphates. The author has undertaken the fundamental study on the electric properties of hydroxyapatite, well-known bioceramics as artificial bones. At that time there were few reports on electrical fundamentals of the material, although the phenomena related to in vivo phenomena such as dissolution and growth were well studied. The first work by the author was the discovery of the unique electric properties of hydroxyapatite as purely protonic semi-conductor at high temperatures. Based on the electric property, successfully produced were the bioceramic electrets, which showed various invaluable bioactivity. This paper introduces the electric properties of hydroxyapatite ceramics and the characteristics of the electrets.

The second achievement was the discovery of Na⁺ superionic conductor, Naprio in the system Na₂O-R₂O₃-P₂O₅-SiO₂ (R: rare earth elements). The crystal structure consisted of 12-(PO₃)-(SiO₂)-tetrahedra membered rings and the conductivities were 10⁻⁸ and 10⁻¹ Scm⁻¹ at 25 and 300°C, respectively, as high as the front-running solid electrolytes. As detailed below, the main constituent of the composition is Si, however, the
inclusion of a few % P instead of Si led to the success in the production of the unreported glass-ceramics of Na⁺ superionic conductors.

**HYDROXYAPATITE ELECTRET**

**Characteristics of hydroxyapatite ceramics as calcium phosphate and hydroxide compounds**

The chemical formula of Ca₁₀(PO₄)₆(OH)₂ indicates that hydroxyapatite (HAp) belongs not only to calcium phosphate (CP) family but also to hydroxide compounds. Contrastingly, another representative CP ceramics, α- and α-tricalcium phosphates (Ca₃(PO₄)₂, TCP), do not include any hydroxide ions nor water molecules in the structures. Resultantly, HAp exhibits much different characteristics from TCP’s: HAp can stay long in vivo, whereas TCP is rather bio-resolvable. However, the difference in the chemical composition between the two calcium phosphates is only 2H in the formula of Ca₁₀(PO₄)₆(OH)₂, equivalent to only ca. 0.2 wt%, in addition to Ca/P atomic ratio of 1.67 (HAp) vs 1.5 (TCP). Such small amount of difference in [H] gives remarkably different chemical, physical and biomedical properties to HAp from TCP.

Ceramic processing techniques for HAp have developed in pace with the production of commercial biomaterials. Frankly speaking, it is indeed true that hydroxide ions in HAp are fairly stable, because commercial HAp ceramics are sintered at temperatures of up to 1300°C in air. We have, however, experimentally proved that HAp partially decomposes to oxyhydroxyapatite, Ca₁₀(PO₄)₆[OH]₁₂-₂xO₂x⁻x₁ + xH₂O(g), where x denotes uncharged vacancies during sintering at a temperature of 1100 to 1300°C in air. Further dehydration results in the decomposition of oxyhydroxy- to oxy-apatites (Ca₁₀(PO₄)₆O).

Considering the partial dehydration at elevated temperatures, we improved the process of sintering in water vapor stream to obtain dense and stoichiometric hydroxyapatite ceramics. As detailed below, thus obtained HAp ceramics exhibited excellent and surprising chemical, physical and biological properties.

**Electric properties of hydroxyapatite**

Although available data on the electric characteristics of ceramic HAp were limited before our study, some of the few studies had already reported catalytic ability of nonstoichiometric HAp and the mechanism of dental caries. HAp was also reported to function as sensors of humidity, CO₂, and various alcoholic gases. An assumption was supported at that time that electrical conduction in HAp could be achieved by either protons or hydroxide ions transport penetrating through the center of so-called Ca²⁺ triangle planes along the c-axes of the hexagonal structure with the space group P6₃/m. However, vacancies are required for OH⁻ conduction to change positions with OH in an electric field, as is theoretically proved unrealistic. The dielectric measurements were also carried out at the early stage for the understanding of the bioactive characteristics of HAp. As a result, HAp ceramics were proved to exhibit dielectric relaxation below ca. 500°C. Concerning the dielectric relaxation characteristics of HAp ceramics, our colleague, Horiuchi³⁵,³⁶ conducted a series of excellent studies and successfully clarified that the rotation of protons between or around OH⁻ ions gives rise to the orientational or space charge polarization, respectively.

First of all, we have revealed both the semi-ionic conduction properties of HAp ceramics above ca. 600 to 1000°C, and the dielectric characteristics below 500°C. We have also observed an unusual phenomenon of the time-dependent conductivity σ (Scm⁻¹) of HAp ceramics sintered in water vapor stream at higher temperatures (Fig. 1).

![Figure 1](image-url)  
**FIGURE 1** Aging-conductivity characteristics of hydroxyapatite ceramics measured at 700 and 800°C. Sintering condition and thickness of HAp specimens should be referred to the following text.

The measured conductivity of HAp specimens changed with time in a wide range from 10⁶ to only 10⁻¹ Scm⁻¹ at high temperatures. The figure shows some examples of the aging characteristic to HAp sintered under steam stream at 700 (A₁, B₁) and 800°C (A₂, B₂), while HAp sintered in air did not show aging behavior (C₁, C₂). The aging characteristics also showed thickness-dependence as was determined using bulky (A₁, B₁) and thinner (A₂, B₂) sintered HAp ceramic with 1 mm and 100 μm thickness, respectively.
The thickness dependence of $\sigma$ is considered to arise from the diffusion or evaporation process in solids. It was therefore proved that the electrical properties of HA\textsubscript{p} can depend upon the constituents such as H\textsuperscript{+}, OH\textsuperscript{-}, O\textsuperscript{2-}. Taking into account of the result, we measured the electromotive force generated using a hydrogen concentration cell of HA\textsubscript{p} ceramics. The purely thermodynamic study confirmed that mass transport in HA\textsubscript{p} takes place due to the migration of protons (Fig. 2). The protonic conduction was found to closely relate to biocompatibility of HA\textsubscript{p}, as mentioned below.

**Hydroxyapatite electret and the biomedical effects**

Based on the above-mentioned electric properties due to the proton movements, we succeeded in the polarization of HA\textsubscript{p} and proved that HA is an excellent electret which behaves like ferro- or piezo-electric ceramics. Electrostatic force compares to magnetic one in respect of an independent and spontaneous or autonomous power, which can be semi-permanently irradiated to surroundings without continuous power supply. Using the thermally stimulated depolarization current measurements, HA\textsubscript{p} electret was evaluated to store a few tens of $\mu$C\textpercm\textsuperscript{2}, depending on the polarization conditions (Fig. 3). Hydroxyapatite ceramic electrets have chemical, physical, and biological effects upon their surrounding constituents in vivo as well as in vitro. Using the HA\textsubscript{p} electrets, we observed that crystal growth from a simulated body fluid can be accelerated or decelerated, and that microorganism can be manipulated on the surfaces of hydroxyapatite, depending upon the electric signs (Fig. 4).

Various kinds of cells with different biological functions have been proved to behave differently on electret- and usual-surfaces from one another. HA\textsubscript{p} electrets were demonstrated to effectively behave in vivo. In consideration both of the excellent biocompatibility in vitro and in vivo, the manipulation of biointerfaces by electrets is reasonably considered to effectively work. The manipulation of an interface between a surface of a material and its surrounding medium is important in biomedical applications, because the properties of the interface dominate in vivo phenomena. The primary interfacial zone is generally considered to be on the order of 0.1 to 1 nm. Phenomena are largely initiated by the adsorption of inorganic ions, proteins, and polysaccharides on material’s surface at the early stage after implantation in vivo. Various kinds of blood cells including embryo cells are attracted to a surface of a implanted material through the adsorbed substances. These phenomena are considered to determine the successive in vivo reactions. A possible reason is briefly explained below.

Under a certain circumstance such that a force is intended to act on a given spot in a closed system, an external field such as magnetic, sonic or electric one is

![FIGURE 2 Electromotive measurement of HA\textsubscript{p} ceramic using concentration cell. Dotted line shows the theoretical relationship and solid marks indicate measured results.](image-url)

![FIGURE 3 Thermally stimulated depolarization currents of HA\textsubscript{p} ceramics polarized under various temperatures, inserted in the figure (1 kV\textpercm\textsuperscript{1}).](image-url)

![FIGURE 4 Effects of HA\textsubscript{p} electrets surfaces on various cells behaviors for different tissues.](image-url)
applied to the whole system. The application of such field actually arouses some competitive reactions. For such condition, independent forces are expected to bring great benefit because they can irradiate locally. In a biological condition surrounded with water, typical electrolytic substance, local electrostatic influence is sometimes desirable. Electret works in vivo due to electrostatic force. We have proved in a long series of studies that HAp electrets are much more biocompatible and bioactive than bioceramic HAp.

SODIUM ION CONDUCTOR Narpsio \(^{37,77}\)

**Introduction to Narpsio**

Another target of my study was the development of polycrystalline and glass-ceramic electrolytes, and we have developed Na\(_3\)YSi\(_6\)O\(_{18}\)-type new fast sodium ionic conductors of sodium yttrium silicophosphates with the composition Formula 1 and the representative structure (Fig. 5), as will be detailed below. The materials were actually the compounds derived from Na\(_3\)YSi\(_6\)O\(_9\) with the pseudo-cubic Ca\(_3\)Al\(_2\)O\(_6\) (C\(_3\)A)-type structure. The mother silicates belong to the family (Formula 2), comprised of 3 kinds of compounds (Formula 2) where the values of the parameters x and y correspond to Formula 2.

- Na\(_{2+3x}\)Y\(_{1.5}\)PySi\(_{1.5}\)O\(_9\) (Formula 1)
- Na\(_{2+4.5x}\)Y\(_{3}\)Si\(_3\)O\(_{16}\) (Formula 2)
- Na\(_3\)YSi\(_6\)O\(_9\) (x=4),
- Na\(_{3.6}\)YSi\(_6\)O\(_{12}\) (x=3),
- Na\(_{3.6}\)YSi\(_6\)O\(_{18}\) (x=2) (Formula 3)

We have successfully synthesized Na\(_3\)YSi\(_6\)O\(_{12}\)^\(_{-}\), Na\(_3\)YSi\(_6\)O\(_{12}\)^\(_{0.6}\), and Na\(_3\)YSi\(_6\)O\(_{18}\)^\(_{-}\)-type sodium yttrium silicophosphates with the appropriate combination of the composition parameters x and y. Some of these compounds were found to exhibit a high Na\(^+\)-conductivity of \(10^{-1}\) to \(10^{-3}\) Scm\(^{-1}\) at 300°C, comparable with the conventional sodium ionic conductors such as β and β’-aluminas, and Na\(_2\)Zr\(_2\)PSi\(_2\)O\(_{12}\).

The present materials family were designated as Narpsio, and the Na\(_3\)YSi\(_6\)O\(_{12}\) and Na\(_3\)YSi\(_6\)O\(_{18}\)-type silicophosphates are referred hereafter to as N\(_3\)YPS and N\(_3\)YPS, respectively, and for convenience Na\(_3\)YSi\(_6\)O\(_9\)-type compounds are also symbolized as N\(_3\)YPS in place of C\(_3\)A-type NASICON. Structurally, N\(_3\)YPS and N\(_3\)YPS, and N\(_3\)YPS may be characterized by the 6- or 12-membered rings of SiO\(_4\) and PO\(_4\) tetrahedra, respectively. In considering practical applications such as sodium/sulfur and all-solid-state batteries, the present Narpsio materials have advantages over the alumina both in lowering the sintering temperatures (<1150°C) and in fabricating various shapes because of the easiness of glass-making.

Figure 6 shows the phase-composition relationship in the [Y]-[P] diagram, where [Y] and [P] express the contents of yttrium and phosphorus, or 1- x and y in formula 1, respectively. As can be seen from the diagram, these phases were obtained as follows.

- N\(_3\)YPS or N\(_3\)YPS: 0.6-0.5[P]<[Y], [P]<0.8
- N\(_3\)YPS: 0.5-0.5[P]<[Y]<0.8-0.5 [P], [P]<0.7
- N\(_3\)YPS: 0.5-0.5[P]<[Y]<0.8-0.5 [P], [P]<0.4

FIGURE 6 Phase relationship with composition parameters of Narpsio family.

The region where N\(_3\)YPS was obtained as a single phase was limited between the two lines P and Q, which are mathematically expressed with [Y] = 0.5-0.5[P] and [Y] = 0.75-0.5[P], respectively. The compositions on these lines relate to vacancies of Na-site (V\(_{Na}\)) and of the center of SiO\(_4\)-PO\(_4\) ring. Line P and Q correspond to the composition expressed with \(1-2x+y=0\) and \(0.5-2x+y=0\), respectively. In the region of higher [Y] and above line P, N\(_3\)YPS was predominantly obtained.
Figure 7 shows the phase-conductivity relationship in the [Y]-[P] diagram. The high conductivity-region ($\sigma_{300} > 10^3$ Scm$^{-1}$) almost corresponds to the whole region of Na$_2$YPS and some parts of Na$_3$YPS, where $\sigma_{300}$ is the conductivity at 300, while the region of the medium conductivity ($10^1$ Scm$^{-1} > \sigma_{300} > 10^4$ Scm$^{-1}$) roughly corresponds to those of Na$_2$YPS and of Na$_3$YPS. The low conductive materials ($\sigma_{300} < 10^3$ S/cm) were obtained in the remaining region. The mixtures of Na$_2$YPS and Na$_3$YPS also exhibited higher conductivity with the increasing ratio of Na$_2$YPS to Na$_3$YPS. The activation energy for conduction ($E$) was also strongly dependent on the type of phase and composition, and the values obtained ranged between 20.1 and 87.3 kJmol$^{-1}$.

As in the case of Na$_2$YPS, the conduction properties of Na$_3$YPS-type compounds were much improved compared with those of the mother silicate Na$_3$YSi$_3$O$_{12}$; the substitution of SiO$_4$ and Na$^+$ for PO$_4$ and Y$^{3+}$, respectively, in Na$_2$YPS structure lead to enhancement of conductivity. The conductivity and activation energy of Na$_2$YPS and Na$_3$YPS were strongly dependent on the composition and were in the range of $5 \times 10^{-5}$ Scm$^{-1} < \sigma_{300} < 10^{-2}$ Scm$^{-1}$ and 45 kJmol$^{-1} < E < 85$ kJmol$^{-1}$ for Na$_2$YPS, and $4 \times 10^{-4}$ Scm$^{-1} < \sigma_{300} < 10^{-3}$ Scm$^{-1}$ and 42 kJmol$^{-1} < E < 60$ kJmol$^{-1}$ for Na$_3$YPS, respectively. The enhancement of conductivity in Na$_3$YPS given by the replacement of SiO$_4$ by PO$_4$ is at present believed to be explicable by the same reason: exclusion of Y$^{3+}$ disturbing the migration of Na$^+$ and creation of vacancies for charge compensation.

**Glass-ceramics of Narpsio and the conduction properties**

Glass-ceramics are polycrystalline materials which are produced by controlled crystallization of glasses. In addition to their easy fabrication into desired shapes, glass-ceramics generally have the advantages over conventional sintered ceramics in mechanical properties and chemical durability because of their pore-free and small grained (<1 μm) microstructure. Glass-ceramics of Na-fast ionic conductors are therefore expected to overcome the difficulties in the fabrication of practical devices, as mentioned above. To date, the conventional Na-fast ionic conductors, however, have not yet been produced in the form of glass-ceramics; β- and β"-aluminas have high melting points because of high inclusion of Al$_2$O$_3$, the general formulæ of which are written as NaAl$_{11}$O$_{17}$ and NaAl$_9$O$_{19}$, respectively. While Nasicon (Na$_2$Zr$_2$Si$_2$O$_{12}$) also suffers inhomogeneous melting from a high content of ZrO$_2$ (46.5 weight percent), although Na$_2$O-P$_2$O$_5$-SiO$_2$ is a system suitable for glass making. Alternatively, Nasicon-like glass-ceramics were synthesized using the composition with lower content of ZrO$_2$ (mNa$_2$O·xZrO$_2$·yP$_2$O$_5$·(100-m-x-y)SiO$_2$ (m=20, 30 mol percent), however, the conductivities attained were, at most, as high as $\sigma_{300} = 2 \times 10^{-2}$ Scm$^{-1}$ at 300°C with E, 30 kJmol$^{-1}$. These low conductivities were attributed to the crystallization of the poorly conductive rhombohedral phase in the NASICON-like materials. A pioneering work on Na$_3$YS-type glass-ceramics has
been performed by Banks et al. on the family of \(N_5YS\)-type materials by substituting \(Y\) with Er, Gd, or Sm. However, their results were not completely satisfactory because of the relatively lower conductivities of \(\sigma_{300} < 2 \times 10^{-2} \text{ S} \text{cm}^{-1}\) than the reported values of \(N_5YS\). This discrepancy may possibly have arisen from the occurrence of a less conductive metastable phase during crystallization.

Contrary to the previous works, we have successfully produced glass-ceramics with \(\sigma_{300} = 10^{-1} \text{ S} \text{cm}^{-1}\) and \(E = 20 \text{ kJmol}^{-1}\) on the basis of the phosphorus-containing \(N_5YS\)-type materials discovered in the \(Na_2O-Y_2O_3-P_2O_5-SiO_2\) system. As mentioned above, these \(N_5YS\)-type materials have been obtained with the composition formula originally derived for \(N_5YS\)-type solid solutions.

With the aim of searching for more conductive glass-ceramic \(N_5YS\)-type materials, other kinds of rare-earth \(N_5YPS\)-type glass-ceramics were studied according to Formula 5.

\[
\text{Na}_{3+3x} \text{R}_{1-x} \text{PySi}_{3-x} \text{O}_9 \quad (\text{R: rare-earth elements})
\]

(Formula 5)

The trivalent ions employed here for R were Sc, Er, Gd, Sm, Eu, Nd, and La as well as Y. These results were interpreted in terms of the effect of the rare-earth ions on the crystallization of \(N_5YS\)-type phase in glasses; \(N_5YS\)-type structure was obtained in all of the compounds with Formula 5, and \(N_5YS\) of elements with larger ionic radii gave higher conductivities.

We have developed another family of Narpsio according to composition Formulae 6 and 7.

\[
\text{Na}_{3+3x} \text{Y}_{1-x} \text{VySi}_{3-x} \text{O}_9 \quad (\text{Formula 6})
\]

\[
\text{Na}_{3+3x} \text{Y}_{1-x} \text{MoySi}_{3-x} \text{O}_9 \quad (\text{Formula 7})
\]

Figure 8 shows the diagrams of phase-composition-crystallization temperature of \(Na_2O-Y_2O_3-V_2O_5-SiO_2\) (NYVS) and \(Na_2O-Y_2O_3-MoO_2-SiO_2\) (NYMS) systems. \(N_5YS\)-type NYVS and NYMS were obtained as a stable phase at high-temperatures.

The crystallization of \(N_5YS\)-type single phase was strongly dependent both on the contents of yttrium and vanadium or molybdenum ions, \(i.e.,\) the values of \(x\) and \(y\) in the Formulae 6 and 7. \(N_5YS\)-type and \(N_5YS\)-type phases crystallized as the high-temperature stable phases at the regions of rather lower \([Y]\) and higher \([Y]\), respectively. The effect of sodium content seems insignificant, because the value of \([Na]\) is subordinately determined as \([Na]= 6-3[Y] (=3+3x)\) depending on the content of yttrium. It was reasonably assumed that the skeleton structures of \(N_5YS\)- and \(N_5YS\)-type phases may consist of 6-(\(SiO_4\), \(VO_4\) or \(MoO_4\))-tetrahedron-membered rings, while \(N_5YS\)-type phase has 12-tetrahedron-membered skeleton structure. The results shown in Fig. 8 were observed in various systems of \(Na_2O-R_2O_3-M_2O_5-SiO_2\) (R: rare earth and Fe elements; M: P, Mo, V, B, Ge, Al). As can be seen in the figure, \(N_5YS\)-type phase appears at higher temperatures, while \(N_5YS\)- and \(N_5YS\)-type ones are observed at lower temperatures. The results indicate the phase relationship of the three; \(i.e.,\) \(N_5YS\)- and \(N_5YS\)-type are rather metastable phases and the superionic conducting phase \(N_5YS\) is the most stable during crystallization.

The microstructure of a glass-ceramic, including neck growth among grains as well as grain size, is generally affected by the crystallization process. As the above mentioned devices utilize dc conduction properties of Na-fast ionic conductors, the microstructural effects are important on the conduction properties of a whole glass-ceramic. Special attention was paid to the analysis of grain boundary properties using the \(Na_2O-Y_2O_3-P_2O_5-SiO_2\) system. Generally, the total conductivities of \(\sigma\) (T) at higher temperatures were determined by those of crystalline grains of \(\sigma\) (G), while \(\sigma\) (T) were strongly affected by grainboundary conduction \(\sigma\) (GB) at lower temperatures. Therefore, the applications of Na/S batteries require higher \(\sigma\) (G), while all-solid state ones need improved \(\sigma\) (GB) for practical devices.

**SUMMARY**

We have developed new functional inorganic phosphate-based materials of hydroxyapatite electrets and silicophosphate ceramic and glass-ceramic Narpsio conductors. I hope these materials will open new materials science and practical devices.
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