Development of environmental purification materials with smart functions

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Abstract For an environmental-friendly sustainable society, the global environmental problems should be solved. Here we outline our recent results of environment purification materials with smart functions. For the effective adsorbent for remediation process, zeolite coated with layered double hydroxide (LDH) was prepared by the precipitation of LDH on zeolite-LTA under hydrothermal treatment. This multifunctional material has a possible application for simultaneous uptake of harmful cations and anions, and minimizes environmental pollution during municipal and industrial water management. For novel material for the nuclear waste management, zeolite with hydroxyapatite layers on its surface was obtained by a hydrothermal method on the basis of the cation exchange of Ca^{2+} in zeolite for NH_4^+ in solution. The novel nanocomposite is an ideal material for adsorbing and fixing radioactive elements for geological time-scale.

Key words apatite • environmental purification • layered double hydroxide • nanocomposite • nuclear waste • zeolite-LTA

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Introduction

The global environmental problems and ecological change of today were brought about by the rapid expansion of human and industrial activities. In order to solve them and survive in the 21st century, it is essential for us to convert the present society to an environmental-friendly sustainable society. Under these circumstances, one of the research targets is the development of environmental function material. The environmental function material is identified newly in Ecomaterials Center, NIMS, as the eco-function material, which is the environment purification materials with smart functions, that is, high-sensibility and intelligent response to harmful pollutants. The production of eco-function materials for improving environmental quality can take two approaches. One strategy is to tailor the material as the catalyst for decomposing polluting products, that is, to make new photocatalysis. The second and more desirable strategy is to establish the effective adsorbent and separator for remediation process and correcting already polluted environments.

The present paper focuses on the second approach. Two topics were reviewed in this paper. One is the establishment of the effective adsorbent for remediation process in geosphere and biosphere, that is, water and soil environments in the earth. The other topic is the development of novel material for the nuclear waste management.
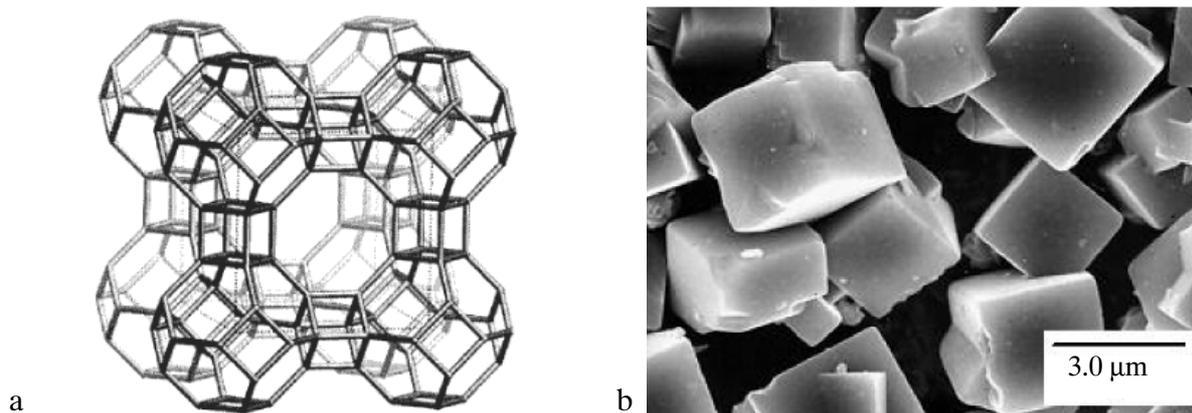
Fig. 1. Schematic representation of the framework structure (a) and scanning electron microscopy (SEM) image (b) of zeolite-LTA.

Establishment of the effective adsorbent for remediation process

The eutrophication was generated by the considerable amounts of ammonium and phosphate ions in domestic wastewater. The groundwater and soil system were also contaminated with arsenic anion, cadmium and lead cations. Zeolite has a high cation exchange capacity, ion adsorption, especially high selectivity for ammonium and heavy metal ions, and the possibility of releasing them over time. Layered double hydroxide (LDH) is expected to be one of the potential treatment agents for phosphate and arsenic removal, because of their anion exchange property. We synthesized zeolite coated with LDH by precipitation of LDH on zeolite-LTA under hydrothermal treatment [24]. The results showed that this multifunctional material has a possible application for simultaneous uptake of harmful cations and anions, and minimizes environmental pollution during municipal and industrial water management.

Structure of zeolite-LTA

Zeolite is crystalline, hydrated aluminosilicate with exchangeable cations. The aluminosilicate portion of the structure is a 3-dimension open framework consisting of a network of AlO_4 and SiO_4 tetrahedra linked to each other by sharing all the oxygen [2]. They have periodic and molecular-sized pores and channels in their structures. They have high cation exchange capacity, ion adsorption, and especially high selectivity for ammonium ion and heavy metal ions.

More than 100 different species of zeolites have been identified [1]. Linde type A zeolite (zeolite-LTA), which is a type of zeolite, has the framework structure shown schematically in Fig. 1a. In the zeolite-LTA structure, a large cage (α-cage) with an inner diameter of ~ 11 Å is surrounded by eight β-cages (sodalite cage) linked through double 4-rings. The α-cages are arrayed in a simple cubic structure and are connected by shared windows with an inner diameter of ~ 5 Å. Zeolite-LTA with Na^+ as an exchangeable cation, whose general formula is $Na_{12}Al_{12}Si_{12}O_{48}\cdot 27H_2O$, has the minimum Si/Al ratio among zeolites and high cation-exchange capacity. Zeolite-LTA is easily synthesized with well-shaped cubic morphology, smooth surface and a few μm in size (Fig. 1b).

Structure of layered double hydroxide (LDH)

Layered double hydroxide (LDH), the so-called anionic clay, is a class of layered materials with the ideal formula $[M_{1-x}^{2+}M_x^{3+}(OH)_2][X_{x/m}^{m-}]nH_2O$, where M^{2+} and M^{3+} are metal cations and X^{m-} is an intercalated exchangeable anion [3, 5, 12]. The structure consists of positively charged brucite-like layers with edges sharing $M^{2+}(OH)_6$ and $M^{3+}(OH)_6$ octahedra. Partial M^{2+} to M^{3+} substitution induces a positive charge for the layers, balanced with the presence of the interlayer exchangeable anions that are usually hydrated (Fig. 2a).

The interlayer anion can be exchanged for other inorganic or organic anions, thus imparting new functionality to the LDH. They have been used as catalysts and catalyst precursors, as sorbents and scavengers for halogens and weak acids [15, 17], and more recently for storing and delivering biologically active materials [4]. They are also expected to be one of the potential water treatment agents for phosphate removal. LDH is easily synthesized with well-shaped hexagonal plate morphology, whose size is dependent on the synthetic conditions (from a few hundred nm to a few μm in size) (Fig. 2b).

Preparation of LDH-coated zeolite-LTA

Zeolite-LTA coated with LDH was prepared by the co-precipitation of LDH on zeolite-LTA and a hydrothermal treatment. A typical synthetic procedure is as follows: 50 ml of the homogeneous magnesium (3×10^{-2} M) and aluminum chloride solution (1×10^{-2} M) added dropwise to 100 ml of a zeolite-LTA with Na^+ ion suspension (0.1 wt.%) at a constant pH of 10 adjusted by NaOH solution (3×10^{-2} M). The suspensions were subsequently aged at room temperature for 24 h, and then placed in a teflon cup fitted into a stainless steal pressure vessel and heated in an oven at 150°C and autogeneous pressure for 24 h. After cooling to room temperature,
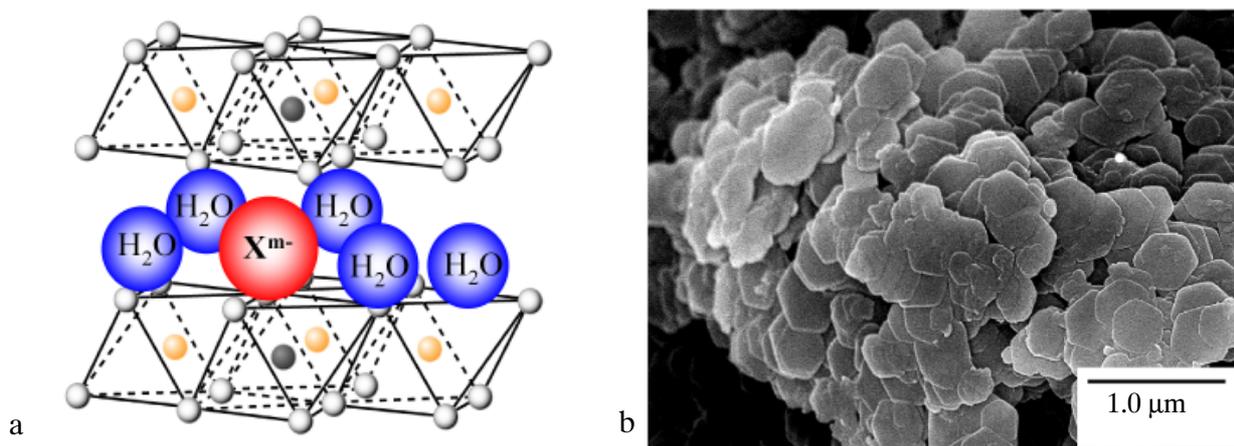
Fig. 2. Schematic representation of the crystal structure (a) and SEM image (b) of layered double hydroxide (LDH).

the product was filtered with a 0.45 µm membrane filter, washed with 500 ml deionized water, and dried at 50°C in an oven. The concentration of solution and reaction temperature were changed for investigating their effects on the products.

The products were characterized by the powder X-ray diffraction (XRD) method, scanning electron microscopy (SEM) fitted with an energy dispersive spectrometer (EDS), and also transmission electron microscopy (TEM) and the selected area electron diffraction (SAED) method.

Characterization of LDH-coated zeolite-LTA

The SEM images of the obtained product from the typical synthesis procedure are shown in Fig. 3. After the hydrothermal treatment, the cubic automorphism of the original zeolite-LTA was not destroyed, but its surface morphology was completely changed from the original smooth surface. It is covered homogeneously by tiny platy crystals of 100–150 nm in diameter and 15 nm in thickness, whose morphology was very similar to that of typical LDH. A comparison between the EDS data of the original zeolite-LTA and the treated product indicated that the Mg:Al ratio of platy particles (3:1) was similar to that of general LDH. The XRD patterns

of the product after hydrothermal treatment indicated that the sharpness of zeolite-LTA in the product was maintained, and was stable, and the broad and weak peak of LDH coexisted. TEM image and SAED revealed that the platy particles that grow on the surface of zeolite-LTA were LDH. The observations by SEM-EDS, XRD, TEM and SAED confirmed that the present product was a novel zeolite-LTA coated with platy LDH.

The amount of platy particles grown on the surfaces of zeolite-LTA increases with higher concentrations of the solutions used in the synthesis ($1 \times 10^{-2} - 3 \times 10^{-2}$ M for $MgCl_2$ solution and $1/3 \times 10^{-2} - 1 \times 10^{-2}$ M for $AlCl_3$ solution) and the particles sizes of LDH on the surface of zeolite-LTA changed from 100 nm to 300 nm in diameter, depending on the temperature of hydrothermal treatment (25°C–200°C). The results indicated that the sizes of LDH particles on the surface are controllable by changing the concentration of starting solutions and/or the synthetic temperature during hydrothermal treatment.

The present nanocomposite was not obtained using a concept applied to an ion-exchange reaction. But the cation exchange capacity of zeolite-LTA might play an important role to gather Mg^{2+} and Al^{3+} cations and form LDH nanocrystals. The present material should be promising one for removing both harmful cations and anions at the same time.
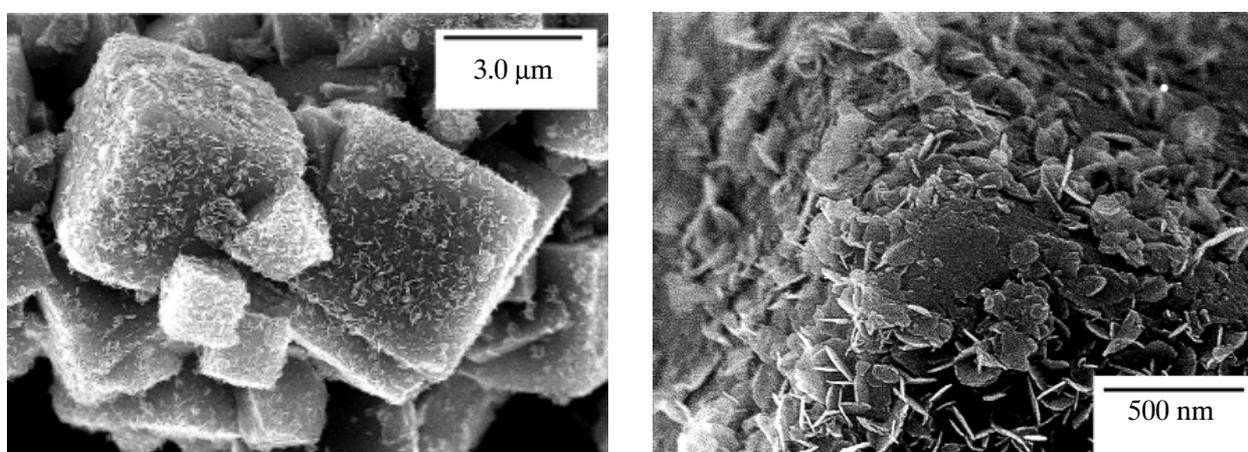

Fig. 3. SEM images of LDH-coated zeolite-LTA by a hydrothermal treatment.
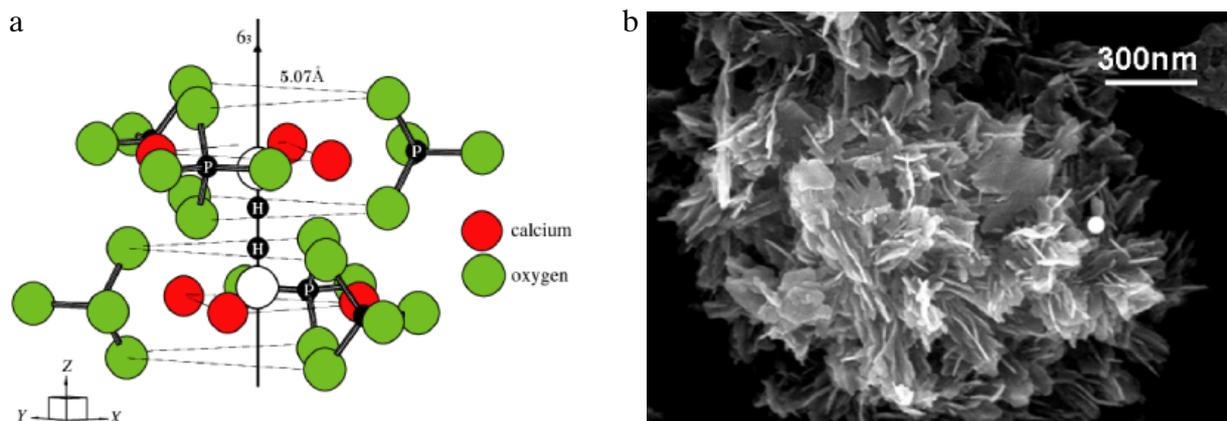
a

b

Fig. 4. Schematic representation of the crystal structure (a) and SEM image (b) of apatite.

Development of novel material for the nuclear waste management

The disposal of radioactive waste generated by the nuclear fuel cycle is among the most pressing and potentially costly environmental problems of the 21st century, a heritage from the Atomic Age of the 20th century. Proposed disposal strategies are complicated, not only because of the large volumes and activities of waste, but also because of the political and public-policy issues associated with the long times required for containment and disposal (10^4 to 10^6 years). The development and use of highly durable waste forms, materials that have a high chemical durability and resistance to radiation damage effect, can simplify the disposal strategy [7].

Zeolite-LTA is widely used as an ion exchanger for ammonium and cadmium [22, 23], and also considered to be utilized for the adsorption of radioactive elements, such as cesium and iodine [11, 16]. Hydroxyapatite $[Ca_{10}(PO_4)_6(OH)_2]$ (Hap) has a very low solubility product of under 1×10^{-100}, and shows particularly high stability in alkaline solutions [13]. We prepared a novel zeolite with Hap layers on its surface by a hydrothermal method on the basis of the cation exchange of Ca^{2+} in zeolite for NH_4^+ in solution and discussed the formation mechanism of Hap on the surface [20, 21]. The novel nanocomposite obtained is an ideal material for adsorbing and fixing radioactive elements for geological timescale. We also applied the pulse electric current sintering (PECS) method to the fabrication of zeolite, Hap and fluorapatite (Fap) sintered bodies that should be long-term assurance materials for the disposal of radioactive waste [19].

Structure of apatite

Apatite $[Ca_5(PO_4)_3(OH, F, Cl)]$ is of importance in a greater variety of fields, particularly is significant in earth science, life science, and material science. Apatite is the most abundant naturally occurring phosphate on the earth. In the realm of biology, hydroxyapatite is the main mineral constituent of human bones, teeth, and many pathological calcifications [6, 9, 10].

The structure of apatite can be visualized as a series of phosphate 'tubes' internally lined by calcium ions.

In fluorapatite, each F atom is surrounded by three Ca atoms at one level, and, in addition, Ca-O columns are linked with PO_4 groups forming a hexagonal network. In other word, PO_4 tetrahedra are linked with two Ca polyhedra: Ca_1O_9 and Ca_2O_6X (where X is the F, OH or Cl anion) crystallographically (Fig. 4a). The structure and chemistry of apatite allow for numerous substitutions, including a multitude of metal cations (i.e., K, Na, Mn, Ni, Zn, Sr, Pb, Cd, Y, REEs, U) that substitute for Ca in the structure, and anionic complexes (i.e., AsO_4^{3-}, SO_4^{2-}, CO_3^{2-}, SiO_4^{4-}, etc.) that replace PO_4^{3-}. Because of its ability to incorporate rare earth elements and actinides, apatite has been investigated as a potential nuclear waste form, as well as a host phase for toxic metals. In geological system, apatite typically forms hexagonal, prismatic crystals, elongated or rather stubby, often terminated by bipyramidal faces. In biological systems, its form is lamellar or thin platy of a few hundred nm in size (Fig. 4b).

Preparation of Hap coated zeolite-LTA

Zeolite-LTA with Ca^{2+} (Ca-LTA) was obtained washing 5.0 g of zeolite-LTA with Na^+ three times in 500 ml of 0.5 M $CaCl_2$ solution. The resultant solid was filtered with a 0.45 μm membrane filter, washed with distilled water to remove excess cations and dried at 100°C for 24 h. The Hap coating by hydrothermal treatment was conducted as follows: 0.3 g of the Ca-LTA powder was immersed in 20 ml of 1 M ammonium phosphate $[(NH_4)_3PO_4]$ solution in a 100 ml teflon cup fitted into a stainless steal pressure vessel. The pH of the solution was controlled to 9 by the addition of an ammonium solution and heated at 120°C for 8 h. The sample was cooled and washed three times in distilled water and dried at 100°C for 24 h. The obtained samples were characterized by XRD, SEM, Fourier-transform infrared spectroscopy (FT-IR) and TEM equipped with EDS. The chemical composition of products before and after treatment (Si, Al, Ca and P) and the ion exchange ability of typical element (NH_4^+ and Na^+ ions on LTA) were measured by using inductively coupled plasma atomic emission spectroscopy (ICP-AES) and an ammonium specific ion electrode.
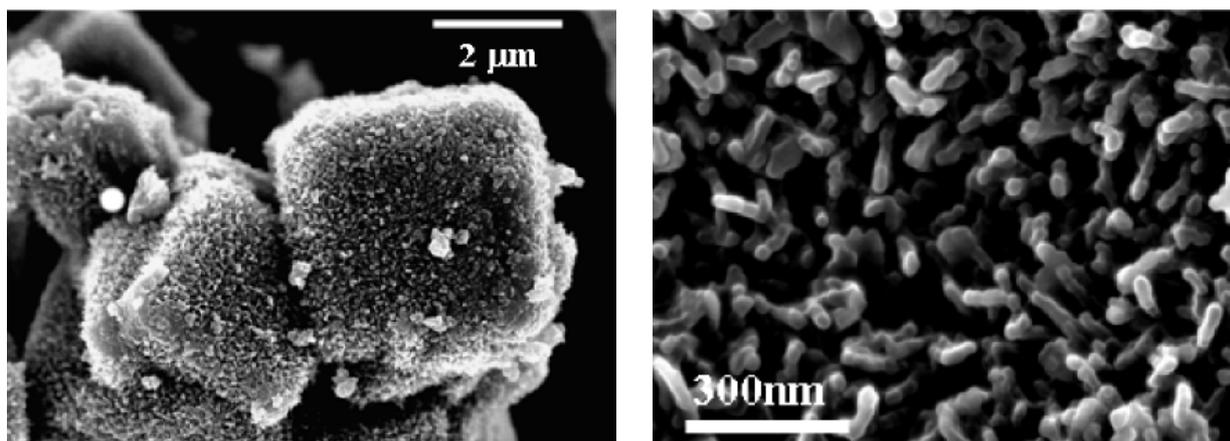
Fig. 5. SEM images of zeolite-LTA with hydroxyapatite layers on its surface by a hydrothermal method.

Characterization of Hap coated zeolite-LTA

After the hydrothermal treatment, the cubic automorphism of Ca-LTA was not destroyed. But the original smooth surface was completely changed to be covered with scaly particles (Fig. 5). The scaly particles aggregated became needle-like crystals from 100 nm to 200 nm in diameter and 30 nm in thickness. The crystal morphology was very similar to that of Hap obtained under hydrothermal treatment as reported in previous studies [8].

The XRD patterns of products after the hydrothermal treatment of Ca-LTA showed a combination of the sharp peaks agreed with those of zeolite-LTA replaced by NH_4^+ and the broad peaks corresponded closely to those of Hap. This result indicates that cation sites in the Ca-LTA were occupied by NH_4^+ during the hydrothermal treatment. The XRD patterns also demonstrated that there was no significant difference in the sharpness of zeolite-LTA before and after the hydrothermal treatment. These results indicate no change of LTA structure. From the results of SEM and XRD, the zeolite-LTA structure is stable in 1 M ammonium phosphate solution heated at 120°C.

In FT-IR spectra of the product after hydrothermal treatment, the absorption bands attributed to double rings and (Si, Al)-O bend in the zeolite-LTA structure (542 and 460 cm^{-1}), and those to asymmetric and symmetric stretches of the framework aluminosilicate in the zeolite-LTA (1130/1055/998 and 742/705/665 cm^{-1}) were observed. These results indicated that the framework of zeolite-LTA was not affected by the hydrothermal process, which was comparable to the results obtained by XRD. The characteristic absorption bands of Hap for the ν_2, ν_3, and ν_4 vibration of PO_4^{3-} (474 cm^{-1}, 1092/1045 cm^{-1} and 602/572 cm^{-1}, respectively) and OH$^-$ (632 cm^{-1}) were observed. An absorption band at 1400 cm^{-1} attributed to NH_4^+ was obtained, which was caused by the cation exchange of Ca^{2+} for NH_4^+ and agreed with the results of XRD.

TEM with EDS and SAED analyses of the scaly particles revealed that the scaly particles growing in the direction roughly perpendicular to the surface were Hap. The Hap had about 30 nm in thickness and a sharp interface with the zeolite-LTA, indicating that the Hap grew toward the outside solution without marked dissolution of zeolite-LTA.

The chemical analyses of the hydrothermal product indicated that the Si/Al molar ratio was not changed to be nearly 1.0, which was an ideal value of zeolite-LTA, and Ca/P molar ratio was 1.7 which was compared to that of the theoretical Hap. NH_4^+ ions were exchanged for Ca^{2+} ions on zeolite-LTA. From these results, we propose the following formation mechanism of Hap layer on zeolite-LTA. The ion exchange of Ca^{2+} on zeolite-LTA for NH_4^+ in an ammonium phosphate solution is the driving force for the formation of Hap and then the discharged Ca^{2+} reacted with phosphate ions on the surface of zeolite-LTA due to Ca^{2+} supersaturation at the local area.

The nanocomposite, Hap coated zeolite-LTA was obtained by a new concept which makes use of the intrinsic exchange properties of one of the starting compounds. The nanocomposite obtained is a novel material for the adsorption and capsulation of radioactive ions, possessing excellent characteristics of both zeolite and hydroxyapatite.

Densification of zeolite/apatite composites by PECS method

The Hap and/or Fap sintered bodies have been studied as one of the long-term assurance matrices for preserving the radioactive elements [25]. The PECS method can fabricate the dense Hap sintered bodies with approximately 100% of relative density at lower temperature and shorter duration compared to the conventional sintering method due to the rapid heating rate [14, 18].

The zeolite-LTA with Hap thin layers and the spherical Fap powder were mixed at a weight ratio of 3/7. The obtained powder was sintered by using the PECS method. The sample was pressed uniaxially at 50 MPa in a vacuum of 0.6×10^{-2} Pa throughout the sintering process. The temperature was increased to 900°C at a rate of 50°C/min. After keeping at 900°C for 10 min, the sample was slowly cooled to 600°C at a rate of 5°C/min. The sample was cooled further to room temperature after stopping the electric current and releasing the pressure. The sintered bodies of zeolite-
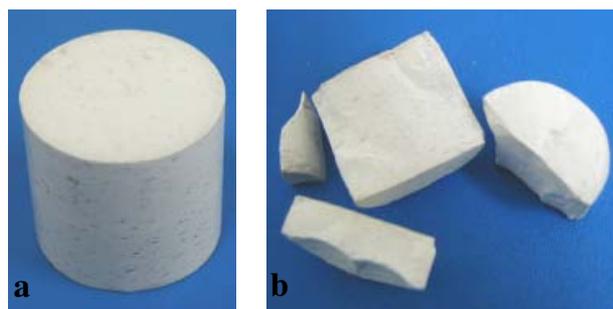
Fig. 6. Photographs of zeolite/apatite sintered composite by PECS method from the mixed powder of Fap and zeolite-LTA with Hap thin layers (a) and without Hap thin layers (b).

LTA with Hap thin layers and Fap fabricated by using the PECS method were characterized by XRD, SEM-EDS and scanning transmission electron microscopy (STEM).

The XRD indicated that the structure of zeolite-LTA has changed to the amorphous. The zeolite-LTA powder was well dispersed in the Fap matrix as the results of element mapping analyses by SEM-EDS. STEM observations indicated that amorphous zeolites-LTA were covered with needle-like Hap crystals whose layer completely coupled with sintered Fap grains. The Fap crystals in the sintered bodies were well sintered, and the grain size was small (< 300 nm). Micropores were not observed among the three different phases. This indicates that the three different phases are completely sintered, and the Hap layers play an important role for improving the affinity between Fap and amorphous zeolite-LTA. When the mixed powder of zeolite-LTA without Hap thin layers and Fap was sintered under the same conditions, the sintered bodies obtained were with cracks and/or destroyed in ejecting (Fig. 6).

The obtained zeolite/apatite composite, zeolite, Hap and Fap sintered bodies, should be long-term assurance materials for the disposal of radioactive waste.

Conclusion

The developments of environment purification materials with smart functions in Ecomaterials Center, NIMS were reviewed. One is a zeolite coated with LDH for the effective adsorbent for remediation process. This material should be promising nanocomposite for removing harmful cations and anions simultaneously, and minimizes environmental pollution in water system. The other is a zeolite with hydroxyapatite layers on its surface for the nuclear waste management. This novel nanocomposite has a high chemical durability and resistance to radiation damage effect. The sintered body of zeolite/apatite composite should be long-term assurance materials for the disposal of radioactive waste. These materials should help to solve the global environmental problems and make an environmental-friendly sustainable society in the 21st century.

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