Novel potentials of calcium silicate ceramics for environment-friendly material applications are briefly described based on experimental and computational simulation methods. Calcium phosphate clusters were successfully incorporated into the structure of tobermorite under hydrothermal reaction conditions. The incorporation of the cluster resulted in changes in the crystal structure and density of states of tobermorite, thereby improving the biocompatibility of the resulting material. The chemical composition of the hydrogarnet could be controlled using a potassium solution during hydrothermal reaction in a \( \text{CaO-SiO}_2-\text{Al}_2\text{O}_3-\text{H}_2\text{O} \) system. This afforded tailoring of the content of the surface hydroxyl groups. Consequently, this led to enhanced adsorption abilities towards organic compounds in solution.

1. Introduction

Calcium silicate ceramics have been widely used in various applications, e.g., biomaterials and environment-friendly materials, owing to calcium and silicon elements with large Clarke numbers.\(^1\)\(^-\)\(^10\) Wollastonite (\( \text{CaSiO}_3 \)) has been investigated on artificial bone substitutes for more than 20 years.\(^11\)\(^-\)\(^14\) They are known to be biocompatible and show higher degradability than calcium phosphate ceramics.\(^15\),\(^16\) To improve its biocompatibility, cations, such as strontium, have been incorporated into the structure.\(^17\) Calcium silicate hydrate ceramics, such as tobermorite \( \text{Ca}_5\text{Si}_6\text{O}_{18}\text{H}_2\cdot4\text{H}_2\text{O} \), have been reported to feature high removal properties of toxic heavy metal ions.\(^18\)\(^-\)\(^20\) Substitution with aluminum in the structure is known to enhance the cation exchange properties because of charge compensation.\(^21\)

Thus, these reports have suggested that incorporation of cations into the calcium silicate ceramics plays an important role in improving the properties of the final ceramics.

It is well known that the electronic state of a material strongly influences the material properties. The strategy for realizing novel potentials of calcium silicate ceramics in environment-friendly material applications is to tune the electronic state of the ceramics using experimental and computational simulation methods. This paper describes two approaches to tuning the electronic states of the materials for application as biomaterials and in environmental remediation purpose.

2. Incorporation of molecular clusters into calcium silicate ceramics for biomaterial applications

Recently, there has been interest in a new approach to enhancing bone formation on materials via the use of osteogenic ions.\(^22\),\(^23\) The effect of osteogenic ions is well established, as reviewed elsewhere.\(^24\) It is well known that calcium ion is one of the key ions in bone formation. Many researchers have reported that silicate ions released from the materials, such as Bioglass\(^10\), show stimulatory effect on bone formation and cell compatibility.\(^25\)\(^-\)\(^27\) We believe that calcium silicate ceramics, with calcium and silicate ion releasing abilities, owing to their dissolution, are a potential candidate as bone substitutes.

Tobermorite is a form of crystalline calcium silicate hydrate and comprises calcium polyhedral layers running parallel to the \( (001) \) plane and silicate layers with double chains running parallel to the \( b \)-axis as shown in Fig. 1. The interlayer region in the silicate layer has nanovoids with exchangeable cations, i.e., calcium ion and water molecules.\(^28\) Lin et al. first reported that tobermorite forms hydroxycarbonated apatite after soaking in simulated body fluid,\(^29\) which is a buffer solution typically employed to evaluate apatite-forming abilities on the surface of artificial materials according to the International Organization for Standardization. Additionally, it has been reported that silver ions incorporated into the structure of tobermorite via cation exchange.

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exchangeable properties have been used to induce antimicrobial effects.30)

Proteins and/or cells first react with the surface of biomaterials following their implantation into bone defects. Subsequent activation for interaction between the proteins and materials at their interface plays an important role in improving the performance of biomaterials. The strategy employed for activating protein adsorption properties is to form adsorption sites by incorporating molecular clusters. It is well known that hydroxyapatite, crystalline calcium phosphate, is the mineral phase of bone. Thus, calcium phosphate was examined herein as a molecular cluster.

Tobermorite incorporating calcium phosphate clusters was hydrothermally prepared using a slurry consisting of quartz, calcium hydroxide, sodium dihydrogen phosphate and dilute hydrochloric acid. The X-ray diffraction (XRD) pattern of the prepared tobermorite showed peaks corresponding to tobermorite and quartz; peaks corresponding to calcium phosphate were not observed (Fig. 2). The solvent, hydrochloric acid, suppressed the dissolution of quartz. The lattice constant, as determined using the (002), (220) and (400) peaks, indicated that the dissolution of quartz, calcium hydroxide, sodium dihydrogen phosphate as phosphate source, and dilute hydrochloric acid as solvent. These materials were mixed at a molar ratios of Ca/Si = 0.83 and P/(P+Si) = 0.10, and mass ratio of solid/liquid = 0.3. In the hydrothermal reaction, calcium phosphates are prone to precipitate in the presence of both calcium ions and phosphate species.31) The solvent plays an important role in preventing formation of calcium phosphate crystals during the hydrothermal reaction.

The X-ray diffraction (XRD) pattern of the prepared tobermorite showed peaks corresponding to tobermorite and quartz; peaks corresponding to calcium phosphate were not observed (Fig. 2). The solvent, hydrochloric acid, suppressed the dissolution of quartz. The lattice constant, as determined using the (002), (220) and (400) peaks, indicated that the c-axis (2.288 nm) of the prepared tobermorite is larger when compared with that (2.256 nm) of tobermorite (JCPDS #45-1480). The phosphate content in the prepared tobermorite was determined to be 0.05 [evaluated as P/(Si+P) molar ratio] using X-ray fluorescence analysis. The Fourier transform infrared spectroscopy spectrum of the prepared tobermorite showed an absorption band at 580 cm\(^{-1}\) attributed to P-O bonds at the orthophosphate Q\(_{ph}\) sites.32) The 31P magic angle spinning nuclear magnetic resonance (MAS-NMR) spectrum of the prepared tobermorite showed a peak at 2.8 ppm corresponding to the Q\(_{ph}\) group with a 3.4-ppm full-width at half-maximum (FWHM).32) The FWHM of the prepared material was twice as large as that of hydroxyapatite (1.7 ppm).33) PO\(_4\) groups present in clusters are known to be distorted when compared with those in the bulk material.34) These results imply that the phosphate species exist as Ca\(_3\)(PO\(_4\))\(_2\) clusters considering the prediction based on charge compensation and size of the nanovoid in the silicate layer of tobermorite.

The structure of tobermorite incorporating calcium phosphate clusters was evaluated by first-principle projector augmented-wave method using the Quantum Materials Simulator (QMAS) software.35) The isolated tricalcium phosphate cluster had D\(_{3h}\) symmetry with the lowest energy, as consistent with previous reports.36) Considering the experimental results, the calcium phosphate cluster was arranged into the nanovoids in the silicate layers. A preliminary structure with a super cell arrangement (3 \(\times\) 2 \(\times\) 1) was selected as the major axis of the cluster, running parallel to the c-axis. For simplification and minimization of calculations, the cluster was only present in the nanovoid of tobermorite, and exchangeable calcium ions and water molecules were excluded. Figure 3 shows a calculated structure of tobermorite incorporating a cluster. It was clear that the structure of tobermorite was maintained even after incorporation of the cluster. Relative to the initial structure, the cluster was tilted towards the ab-plane in the nanovoid. The cluster underwent contraction and had an asymmetric structure when compared with the isolated calcium phosphate cluster, as shown in Fig. 4. The asymmetric structure caused distortion at the position where the phosphorous element is located in the calcium phosphate cluster, as consistent with the 31P MAS-NMR result. Lysozyme was used as a model protein for the protein adsorption tests. The tobermorite incorporating the cluster had a higher protein adsorption property (55 mg/g) than that (44 mg/g) of tobermorite, which was prepared under the same hydrothermal treatment using a slurry consisting of quartz, calcium hydroxide and distilled water.
water as solvent. The incorporation of the cluster in the material was believed to activate the protein adsorption property of the material.

3. Effect of the chemical composition of hydrogarnet on the content of hydroxyl groups on the surface

Surface hydroxyl groups have been suggested to be one of the key functional groups to organic dye and polymer compound adsorption.37-39 Amorphous calcium silicate hydrate gels (C-S-H gels) consist of monomer silicate anions with silanol groups. We have successfully prepared composites containing C-S-H gels with various silicate anion chain lengths for the removal of color derived from organic dye methylene blue in solution.40 The presence of various hydroxyl groups could induce many interactions with these compounds, resulting in improvement of the adsorption performance for environmental purification.

The hydrogarnet series Ca₃Alₓ(SiO₄)₉₋ₓ(OH)ₓ (0 ≤ x ≤ 3) is a solid solution comprising grossular (x = 0, Ca₃Al₂Si₃O₁₂) and katoite [x = 3, Ca₃Al₂(OH)₁₂]. Figure 5 shows the structure of grossular and katoite. Katoite has a three-dimensional framework consisting of Al(OH)₆ octahedra and Ca(OH)₈ dodecahedra. The presence of 4(OH)⁻ caused the substitution of (SiO₄)₄⁻ in the structure, leading to the formation of intermediate compositions between Ca₃Al₂Si₃O₁₂ and Ca₃Al₂(OH)₁₂. The ability to tune the structure, leading to the formation of intermediate compositions, was believed to activate the protein adsorption property of the material.41

The hydrogarnet prepared using potassium alumina as starting materials.42 The preparation of hydrogarnet with x = 2.24 was reported at hydrothermal temperatures above 200°C.43 The chemical composition in the miscibility gap shows a higher energy relative to that of other compositions on the Gibbs energy curve. Hydrothermal preparation was conducted under alkali conditions to control the Gibbs energy, which depends on the activity of ions in the system. The hydrogarnet was hydrothermally prepared using a slurry with a molar ratio of Ca:Al:Si = 3:2:1 and a mass ratio of solid:solvent 3:2:1 and a mass ratio of solid:solvent = 1:10, containing silica gel, calcium hydroxide and γ-alumina as starting materials. Distilled water and dilute potassium hydroxide solution were used as solvent to control the ionic activity. The hydrothermal treatment was conducted at 150°C for 6 h.

Figure 7 shows the XRD patterns of the hydrogarnet prepared using different solvents. Peaks corresponding to hydrogarnet were observed together with a peak corresponding to calcite. The chemical composition of hydrogarnet was estimated from the equation: d-spacing of 420 = 0.0567 × x-value + 2.6416, obtained by plotting the x-value in the hydrogarnet series formula against the d-spacing of the major peak (420) at approximately 32° (as determined from the known hydrogarnet pattern available in the International Centre for Diffraction Data database).45 The hydrogarnet prepared using distilled water as solvent featured one x-value (2.58). The hydrogarnet prepared using potassium hydroxide solution as solvent comprised three x-values (1.69, 2.54 and 2.83). This finding suggests that the use of potassium hydroxide afforded control over the chemical composition of the prepared hydrogarnet during the hydrothermal reaction. The hydrogarnet ratio in the samples was estimated to be closely similar to that determined by the internal standard XRD technique.46 The specific surface areas of the two types of hydrogarnet were determined to be around 30–35 m²/g using nitrogen gas sorption analysis.

Changes in the amounts of hydroxyl groups on the surface of the hydrogarnet were examined using X-ray photoelectron spectroscopy (XPS). The resulting Al₂p spectra were deconvoluted into two component peaks, corresponding to Al-OH at 74.4 eV47 and Al-O-Si at 74.8 eV48. The relative ratios of the
The humic acid adsorption capacity of hydrogarnet was in proportion to the number of hydroxyl groups on the surface. Humic acid was prepared using distilled water. This suggests that control over the content of the hydroxyl groups on the surface, using potassium hydroxide solution as solvent during the hydrothermal reaction, demonstrated that improve adsorption abilities on material surfaces were possible by tuning the density of states and functional groups of the materials.

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