Electrical conductivity of polycrystalline hydroxyapatite and its application to electret formation

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A B S T R A C T

Hydroxyapatite (HAp), a type of calcium phosphate found in bones and teeth, exhibits proton conductivity. In this study, its conductivity is investigated by measuring the complex permittivity of polycrystalline hydroxyapatite samples obtained via a sintering process. The dielectric dispersions measured from samples with different grain sizes are successfully explained using the Maxwell-Wagner interfacial polarization model. The results show that polycrystalline hydroxyapatite consists of both a high impedance grain boundary and a proton-conductive grain that has a conductivity of about 1.0×10^{-7} S cm^{-1} at 573 K. The interfacial polarization is confirmed using thermally stimulated depolarization current measurements. Additionally, electrets are prepared with the polycrystalline HAp via a poling process, and it is demonstrated that the electret formation is caused by the interfacial polarization.

1. Introduction

In contrast to magnets, which produce external magnetic fields, electrets generate external electric fields. The electrets have been used in microphones and air filters [1]. Recently, their applications have extended to new areas. For example, power generators utilize electrets in their system for energy harvesting [2]. In addition, electrets are attracting attention from biomedical fields [3,4]. Living tissues interact with electrets at their interfaces. The electrostatic fields generated by these electrets induce biological reactions, representing a new approach in biomedical device engineering. Hydroxyapatite (HAp), a well-known biomaterial, can be polarized [5–18] and converted into an electret [19,20]. HAp has similar composition and structure to those of the main inorganic components of hard vertebrate tissues. The high biocompatibility of HAp is utilized in biomedical fields because polarized-HAp (HAp electret) surfaces have favorable effects on living tissues and cells [21–26]. For example, artificial bones consisting of HAp electrets promote new bone formation [21,22]. The uses of HAp electrets are not limited to biomedical fields; they can be employed in power generating systems, as already mentioned [27].

Although the HAp electret is a promising material for various applications, the mechanism that forms the HAp electrets is still obscure. In particular, it is unclear how electric fields are generated on their surfaces. A variety of electric phenomena have been reported with

regards to HAp [28–30]. One is the polarizations derived from the crystal phase change due to the orientation changes of OH$^-$ ions in the HAp crystals. The critical phenomenon that occurs at its phase transition temperature was reported, which implies the possibility of ferroelectricity [13,31,32]. Pyroelectric [7] and piezoelectric [8,11,12] measurements also suggested that the ferroelectric polarization in HAp. Piezoelectric hysteresis loops which suggest the ferroelectricity in HAp were reported in the literatures [11,12]. In addition to these experimental reports, computational studies also showed the presence of the polar phases of HAp which has the ordered OH$^-$ ion arrangements [14–18]. The results by Bystrov et al. indicated that the ordered and disordered phase can coexist, and they calculated piezoelectric coefficient d_{33} of 16 pC/N [17]. Hu et al. reported the value of theoretical ferroelectric polarization of 7–10 μC/cm^2 [18]. Furthermore, ion conduction has been reported in HAp crystals, for example, a proton conductivity of 10^{-4} S cm^{-1} was reported in polycrystalline HAp at temperature of 700 °C by Yamashita et al. [33], and an even higher conductivity of 10^{-2} S cm^{-1} was observed in yttrium-doped hydroxyapatite membranes at 700 °C by Yates et al. [34]. The possible proton conduction paths in these cases were investigated via neutron and X-ray diffraction studies [35,36]. Thermally stimulated depolarization current (TSDC) measurements suggested that proton conduction induced polarization in the polycrystalline HAp [6,9,10]. However, in these papers, the external electric fields which are generated around the

materials are do not confirmed. That means that it is still obscure whether or not electrets can be really formed by the polarization. In addition to above, Some reports also indicated that O^{2-} and OH^- ions were conductive at higher (700–1000 °C) temperatures [37,38].

As mentioned above, various electric properties have been reported in HAp. Its electric responses to external stimuli are diverse; an external electric field transports O^{2-} (OH^-) ions and protons, and inverts dipoles of OH^- ions. Although many literatures refer to the polarizations in HAp, the relationships of the polarizations and electret formations are not reported. Therefore, with respect to the formation of electrets, it is unclear which response is dominant. This study reveals that polycrystalline HAp consists of highly resistive grain boundaries and proton-conductive grain by using complex impedance spectroscopy on samples with varying grain sizes. In addition, in this study, we measure the potential differences which are generated by the electrets in order to evaluate electret performance using the Kelvin probe method. Furthermore, we provide evidence that interfacial polarization, which is induced at the grain boundaries by proton conduction, is the primary cause of electret formation.

2. Experiment

Ceramic pellets of HAp with different sintering conditions were prepared using raw HAp powder that was synthesized via the same method used in a previous study [32]. The raw powder was calcined at 1073 K for 2 h. The calcined powder was pressed into pellets uniaxially, which were then sintered at different temperatures (1423–1653 K) and times (2 h or 9 h). The heating processes described above were performed under flowing oxygen gas with water vapor. Prior to making electrical measurements, the surfaces were polished and coated with platinum using a sputtering machine (IB-2; EIKO Engineering Co., Ltd.).

The grain sizes were evaluated by their surface morphologies observed by a scanning electron microscope (S-3400NX; Hitachi, Ltd.). The average grain sizes were determined after evaluating at least 130 grains. The crystal structures were characterized by their powder X-ray diffraction (XRD) patterns, which were obtained using a diffractometer (D8 Advance; Bruker AXS GmbH) with nickel-filtered Cu $K\alpha$ radiation at a voltage of 40 kV and a current of 40 mA. Infrared (IR) spectra were measured using the KBr method with a Fourier transform infrared spectrometer (FTIR4700; Jasco Corp.). Dielectric measurements were performed using an impedance analyzer (1260; Solartron Analytical) in the frequency domain (1 Hz–1 MHz) at temperatures between 373 and 823 K. The TSDC measurements were performed as follows. A sample was poled (polarized) by applying a direct-current (DC) electric field E_{poling} at a poling temperature T_{poling} for time t_{poling}. The electric field was applied until the sample was cooled to room temperature (300 K). Thereafter, the electrodes were short-circuited and connected to an electrometer (Model 6514 Electrometer; Keithley Instruments, Inc., Cleveland, OH). The TSDC was recorded as a function of temperature at a constant heating rate of $b = 5$ K min^{-1}. The dielectric and TSDC measurements were carried out in air atmosphere without control of humidity. The measurements were performed in the temperature range from 300 to 833 K.

In the temperature range, effects of atmosphere is negligible because dehydration starts at temperatures above 1073 K [39]. The HAp ceramic electrets obtained via the poling process were evaluated using a Kelvin probe system [20]. In the Kelvin probing method, the potential difference (V_{PD}) produced by charge on the electret surfaces was measured. Prior to the potential difference measurements, the platinum electrodes were removed by polishing.

3. Results and discussion

3.1. Grain size evaluation

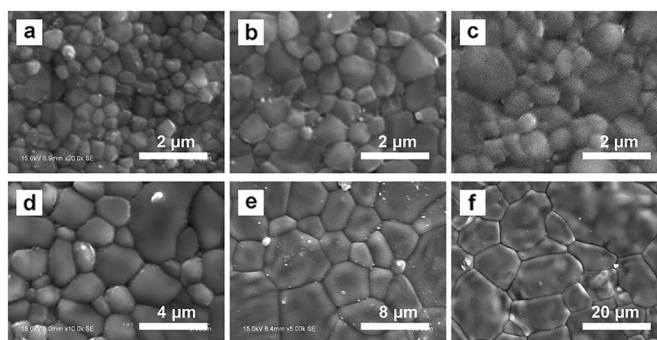The surface morphologies of the samples under different sintering

Fig. 1. Surface morphology of HAp under different sintering conditions: (a) 1423 K, 2 h, (b) 1473 K, 2 h, (c) 1533 K, 2 h, (d) 1593 K, 2 h, (e) 1593 K, 9 h, (f) 1653 K, 9 h.

conditions are shown in Fig. 1(a)–(f). These surfaces exhibit no remarkable open pores, indicating that the dense, sintered compacts were prepared successfully. The relative densities of the samples were all greater than 97%; thus, the effects of porosity on the electrical properties were negligible. The average grain sizes presented in Table 1 represent a gradual increase in grain size with increasing temperature and time for the sintering process.

3.2. X-ray diffraction analysis and infrared spectroscopy

The X-ray diffraction patterns (shown in Fig. S1) had no peaks that indicated secondary phases (e.g., $Ca_3(PO_4)_2$ or CaO), suggesting that the samples had a single apatite structure phase. The IR absorption spectra of the samples under various sintering conditions are shown in Fig. S2(a). The peaks located at 3570 cm^{-1} and 630 cm^{-1} are attributed to the stretching and libration of the OH^- ions, respectively, while the peaks located from 900 cm^{-1} to 1200 cm^{-1} and from 550 cm^{-1} to 650 cm^{-1} are attributed to the vibrations of the PO_4^{3-} ions. It was noted that absorption, which indicates the presence of impurities (e.g., carbonate ions), was not observed. A comparison of the peak intensities of OH^- and PO_4^{3-} provided quantitative information about the OH^- ion concentration. The calculated peak intensity ratios (A3570/A1040) are presented in Fig. S2(b). These results indicate that the sintering conditions affected the number of OH^- ions in HAp. A higher sintering temperature resulted in a lower number of OH^- ions. Under high temperature conditions, dehydration occurred and OH^- vacancies were induced in the HAp crystal lattice [33,40]. Therefore, the number of OH^- ions decreased as the sintering temperature increased, as illustrated in Fig. S2(b). However, an exception was observed: the ratio of the sample sintered at 1423 K for 2 h was smaller than that of the one sintered at 1473 K for 2 h. The reason for this exception is not clear. It may be attributed to either differences in crystallinity or effects of the grain boundaries.

3.3. Dielectric spectroscopy

Fig. 2(a)–(f) show the frequency dependences of the permittivities for HAp under different sintering conditions at different temperatures. These consist of two types of Debye-like relaxations, which agree with the findings of previous studies [32,40,41]. For convenience, the two types of relaxations located at lower and higher frequency ranges are represented as A and B, respectively. The relaxation times for both relaxations (τ_A and τ_B) were derived from the peak frequency (f_p) using $\tau = (2\pi f_p)^{-1}$. The values obtained are shown in Fig. 2(g) as functions of inverse temperature T^{-1}, which indicates that τ follows the Arrhenius law $\tau = \tau_0 \exp(-E/k_B T)$, where τ_0 is the prefactor, E denotes the activation energy for the responses, and k_B is the Boltzmann constant. The activation energies were determined based on the slopes shown in the figure. Those of relaxation A were in the range 0.64–0.71 eV, which corresponded to what previous studies had reported [32,40]. For