# Pyroelectric surface charge in hydroxyapatite ceramics

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Surface charge of pyroelectric nature is measured in poled hydroxyapatite ceramics. The average pyroelectric constant can range from 0.1 to 40 nC cm$^{-2}$ K$^{-1}$ at temperatures of 300–500 °C, while at 27–60 °C the value ranges from 15 to 64 nC cm$^{-2}$ K$^{-1}$. The higher temperature values are comparable to conventional pyroelectric ceramics such as LiTaO$_3$ or PZT. The lower temperature values are four orders higher than those observed in bone and tendon. © *2009 American Institute of Physics.* [doi:10.1063/1.3262628]

Hydroxyapatite, the main inorganic constituent of bone, is an important material for synthetic bone grafts, tissue culture scaffolds, protein chromatography, DNA separation, and implant coatings. From crystallographic considerations, hydroxyapatite is not currently considered as a pyroelectric material.[1] Recent theoretical and experimental results have contested the nonpyroelectric crystal structure of hydroxyapatite[2,3] and claimed that ceramic hydroxyapatite is piezoelectric.[4] Hydroxyapatite was polarized to induce surface charge that had mimicked the growth of bone apatite[5] and improved bone bonding.[6] A model describing the origin of such surface charge assumed a spontaneous polarization in hydroxyapatite[5] and was linked to biomineralization on its surface.[7] In bone, surface charge is known to occur from a mechanical stress (piezoelectricity[8] and electrokinetic phenomenon measured as streaming potentials[10]) or a temperature change (pyroelectricity[9] and electret polarization[11]). Here we demonstrate significant surface charge of pyroelectric origin appearing in polarized hydroxyapatite ceramics. The results confirm our predictions that hydroxyapatite can be pyroelectric[2,3] and can help to explain biomimetic growth, as it has been observed, on hydroxyapatite.

Yamashita *et al.*[5] have measured thermally stimulated depolarization current (TSDC) density that originated from the stored charge injected into hydroxyaptite ceramics during the poling process. This capacity of hydroxyapatite to store charge demonstrates its electret nature. This electret nature, when considered in conjunction with our crystallographic arguments that polycrystalline hydroxyapatite can be belong to a polar crystal class,[2] led us to the hypothesis that hydroxyapatite is pyroelectric.[2,3]

Hydroxyapatite exhibits the characteristics of a dipolar insulator, the dipole being the hydroxyl (OH) ion, which lies along the crystallographic *c*-axis within the tunnel formed by phosphate (PO$_4$) tetrahedra[2] and floats just over the imaginary triangle formed by three calcium (Ca) ions. Within a given tunnel there are two OH ions pointing to the same direction. The OH ions in the neighboring tunnel can be oriented in an antiparallel (a nonpolar monoclinic 2/m crystal class) or in a parallel arrangement (a polar monoclinic 2 or polar hexagonal 6). The antiparallel arrangement was found to be the lowest energy state.[2] The energy differences between these phases were small (a few kJ mol$^{-1}$) thus allowing either a nonpolar to polar phase transition[3] or a stabilization of the polar phase,[2,12] if not already present [Fig. 1(a)]. On this basis we expected that thermally stimulated surface charge from hydroxyapatite should show a polarity reversal when the sign of the thermal gradient changes sign.

Evidence of such a polarity change occurring in hydroxyapatite can be seen from Fig. 2, where we show typical TSDC density profiles of hydroxyapatite ceramics prepared
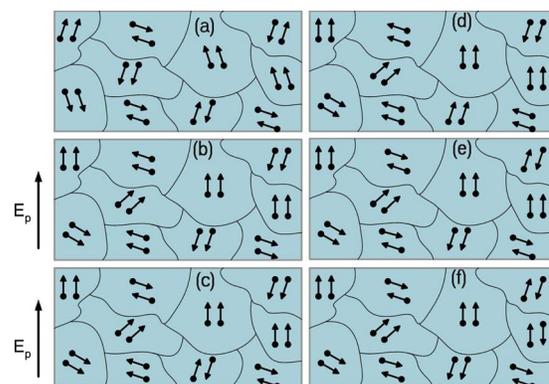


FIG. 1. (Color online) A schema of the origin of pyroelectricity in hydroxyapatite. The polar and nonpolar nature of individual HA grains are represented by parallel and antiparallel arrows, respectively. (a) Ground state: HA with both polar and nonpolar grains; net polarization is zero. (b) Polarization above 212 °C: polar grains try to orient along the direction of the applied electric field; nonpolar grains undergo a polar phase transition. (c) Freezing of polarization under field: polar grains retain their orientations when cooled under the applied electric field to room temperature. Some of the grains returns back to their nonpolar ground state. Net polarization is still zero. (d) Heating at 300–500 °C: nonpolar grains become polar due to thermal reorientations; net polarization is not zero anymore as spontaneous polarization appears. HA exhibits pyroelectricity. (e) Cooling at 500–300 °C: some polar grains become nonpolar due to thermal flip-flop; net polarization is still nonzero due to the presence of polar grains. (f) Cooling between 300 °C and room temperature: some polar grains retain polar nature, while some lose polar nature due to thermal flip-flop; net polarization is zero despite the presence of polar grains.

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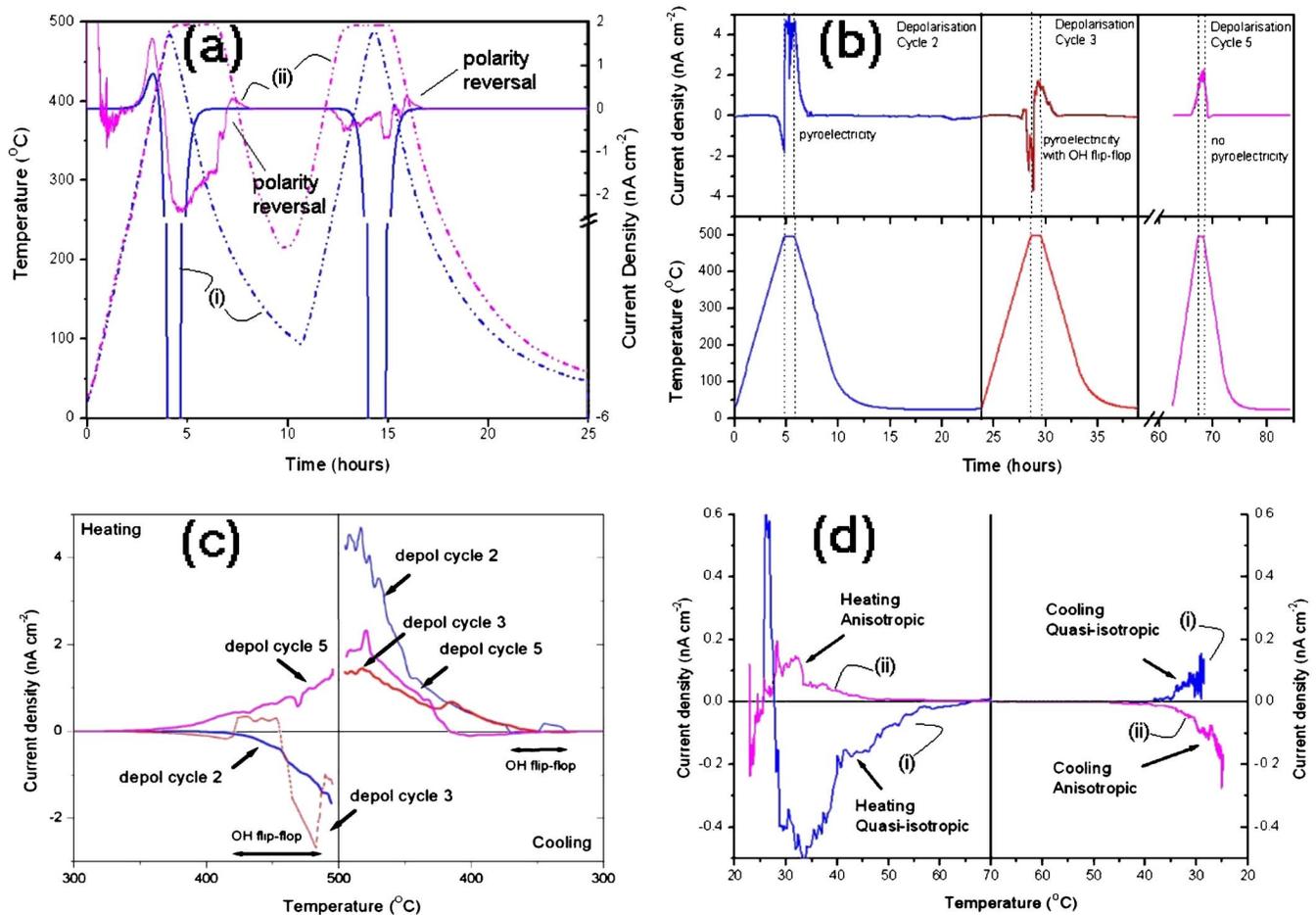
FIG. 2. (Color online) (a) Depolarization cycles for quasi-isotropic hydroxyapatite ceramics showing the effect of thermal cycle patterns. The curves marked (i) represent a sample that showed polarity reversal in the first depolarization cycle but not in the second one. The (ii) curves represent a sample for which polarity reversal was observed in both depolarization cycles. These samples were poled along the pressure axis. (b) Depolarization cycles for a typical anisotropic hydroxyapatite ceramic showing the effect of thermal cycle patterns. The polarity reversal was seen during depolarization cycles, e.g., in cycle 2 and cycle 3 but eventually became very small (e.g., cycle 5). The sample was polarized along the pressure axis. (c) The depolarization current densities of the sample described in (b) as a function of temperature and depolarization cycles. The discontinuities in the heating and cooling cycles are due to independent reorientations of OH ions. (d) Depolarization current densities of a quasi-isotropic (i) and an anisotropic sample (ii) exhibiting polarity reversal between 27 and 60 °C during heating and cooling. The quasi-isotropic sample was polarized along the pressure axis, while the anisotropic sample was polarized perpendicular to the pressure axis.

from calcined HA powders sintered in both conventional and spark plasma sintering (SPS) methods. The sintered bodies were subjected to different duration and magnitude of thermal treatments, before, during and after the polarization treatment. In contrast to previously reported TSDC results,[5,13] the TSDC density measured at HA surface during the cooling phase is also given (Fig. 2). This allowed a clear demonstration of the reversal of polarity of the current when the sign of the thermal gradient changed from heating to cooling. Unpoled hydroxyapatite ceramics, unpoled and poled $\beta$-tricalcium phosphate ceramics and a poled alumina ceramic did not show any polarity reversal on cooling.

The TSDC was measured by a HP 4140B picoammeter with the baseline current measured within the TSDC rig of the order of femtoampere. The sample holder was heated in a muffle furnace. A heating/cooling rate of either 1.67 or 5 °C/min was used for preconditioning, poling and depoling. Anisotropic samples were preconditioned at 500 °C and then cooled to room temperature at the same rate. The structural purity of hydroxyapatite ceramics was measured by

conventional x-ray diffraction (XRD), while the presence of OH ions was checked by Fourier transform infrared spectroscopy on ground ceramic samples.

A total of eleven samples were sintered using a conventional sintering technique where uniaxially pressed pellets of hydroxyapatite powder were fired at 1200 °C in air for 6 h. The ceramics contained phase pure hydroxyapatite. A comparison of intensities of the (002) and (004) reflections in XRD showed a small amount of anisotropy ($\sim$10%) in the sintered pellets when referenced to their ground powders. The pellets were somewhat deficient in OH ions as a result of the sintering. All but one of these samples was prepared from pure hydroxyapatite supplied by CAM Implants Ltd., The Netherlands, while the remaining sample was SRM 2910™ sourced from National Institute of Standards and Testing (NIST), USA.

Prior to the polarization operation, all samples studied here received a thermal preconditioning by heating to 200–500 °C at a heating/cooling rate of 1.67 or 5 °C/min. Samples which were not preconditioned did not exhibit po-

larity reversal. Poling was carried out by heating the sample to the poling temperature (350–375 °C) at a heating rate of 5 °C/min. An electric field of 2–2.27 kV cm$^{-1}$ was then applied. The samples were then cooled in the electric field to room temperature. The field was then removed at which point they were short circuited prior to the thermal depolarization. When these conventional ceramics were depolarized, ten samples including SRM 2910™ demonstrated polarity reversal typically between 300 and 500 °C in either the first or second depolarization cycles.

The pyroelectric current density was however complicated by the contributions from dipole relaxation, defect charge mobility and sporadic release of charges trapped at defect sites. Contributions to TSDC from these processes are exhausted if the poled sample is held for a length of time short circuited at a somewhat higher temperature than the poling temperature.[14] A second heating cycle may cleanse the effect of relaxation and lower the magnitude of the TSDC.[15] Subsequent cooling can then show polarity reversal in the TSDC if the material is pyroelectric. This however runs the danger of diminishing the poling effect in polycrystalline material.[14] This is shown in Fig. 2(a), where the pyroelectric current in quasianisotropic hydroxyapatite has been cleansed of relaxation effects in the first cycle revealing TSDC of lesser extent in the second cycle [lines (ii) Fig. 2(a)].

When the degree of anisotropy in hydroxyapatite ceramics was increased by using a SPS, a process known to yield texturing in the crystallographic *c*-axis,[16] a clear polarity reversal in the TSDC response was observed [Figs. 2(b) and 2(c)]. This was repeated for a total of four depolarization cycles, after which the material did not show any polarity reversal. The SPS process had oriented the tunnel axis of hydroxyapatite (crystallographic *c*-axis) along the uniaxial pressure axis [001]. Furthermore, as the sample was also sintered rapidly (10 min) at a lower temperature (1000 °C), it retained more OH ions than the eleven conventionally sintered ceramics. When such a sample was polarized along the pressure axis, the OH dipoles were "frozen in" much better than if the same sample had been polarized along the perpendicular ([100]) direction or along the pressure axis in conventional ceramics. A combination of texturing, retention of stoichiometry and poling in the direction of OH dipole orientation is thus necessary for hydroxyapatite ceramics to exhibit pyroelectricity. It is prudent to recall here that piezoelectricity in hydroxyapatite was found to be very weak[4] and can be safely ignored as a contributing factor as pseudopyroelectric effect (caused by lattice expansion, not reorientation) to the pyroelectricity measured here.

There can however appear some discontinuities in the pyroelectric current in around 350–450 °C during the heating and/or cooling process [Fig. 2(c)]. Hitmi *et al.*[12] recognized that at these temperatures the OH dipoles can reorient "at will" independent of the OH ions in the neighboring tunnel so that a dynamic stabilization of the structure may occur. This thermal "flip-flop" of OH ions did not occur in unpolarized samples. In polarized samples it happened during heating as well as during cooling, thus indicating its independence from the sign of thermal gradient. Figures 1(a)–1(f) explain how dipole orientations in hydroxyapatite ceramic are influenced by thermoelectric polarization and independent reorientation of OH ions. On repeated thermal cycling, such reorientation at will can acquire enough energy to compensate for the induced polarization to the extent that the pyroelectric effect can eventually disappear.

Despite this, the polarity change in the TSDC density profiles in Figs. 2(a)–2(d) clearly shows that hydroxyapatite is pyroelectric at 300–500 °C. Two samples exhibited pyroelectricity at lower temperature [27–60 °C, Fig. 2(d)] indicating a largely metastable nature of the pyroelectric phase, which may have been stabilized under suitable conditions unknown to us at present. In the temperature range of 60–300 °C there was limited measurable TSDC. The average pyroelectric constant can range from 0.1 to 40 nC cm$^{-2}$ K$^{-1}$ at 300–500 °C and from 15–64 nC cm$^{-2}$ K$^{-1}$ at 27–60 °C. The higher temperature values are comparable to conventional pyroelectric ceramics used for high temperature applications such as LiTaO$_3$ or PZT. The lower temperature values are four orders higher than those observed in bone and tendon.[1,9]

The observation of pyroelectricity in hydroxyapatite ceramics at these temperatures would seem to be a corollary of the low temperature pyroelectric effect in bone and merits further investigation.

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