

Performance of bone materials for chemical sensing

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This project is focused to develop chem-bio sensors using electrical properties



Performance of bone materials for chemical sensing

Outlines....

- Objectives
- Background
- Material System
- Experimental Methods
- Results
 - Pure material
 - Effect of chemical/bioagent on capacitance and resistance
- Summary

Goal was to use polarizability (dielectric) based chem-bio sensing



Performance of bone materials for chemical sensing

Objectives:

There were two major objectives:

1. Determine suitability of electrical properties of perovskites for chemical and biological sensing
2. Effect of disruptive chemistry on the electrical characteristics of synthetic bone materials (polarity and hence self healing)

Material system: We synthesized hydroxyapatites by using CaCO_3 , Na_3PO_4 , SiO_2 , KOH , MgO , Ga_2O_3 , and TiO_2
Studied the effect of acetone and methanol on the capacitance and resistance

Composition: Composition was chosen based on commercial materials suggested by Prof. Larry Hench et al, American Ceramic Society Bulletin, Vol 94, 27- 31 August 2015

Goal was to use polarizability (dielectric) based chem-bio sensing



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Background:

- The sensitivity of a sensor depends on the activity of the sensing materials on the surface to be determined.
- The sensitivity is very much dependent on the variation of properties used for the detection.
- It is very important if the sensor can be inexpensive, fast as well as reusable without much processing.
- We have studied electrical properties and observed that these properties are significantly affected by the traces of chemicals.
 - Resistivity
 - Dielectric constant
- In addition, in some cases utilization of selenium flux lowered the temperature of processing significantly. In this paper we present the sensing effect of chemicals such as acetone and methanol for sensing by measuring the capacitance and resistance.

Goal was to use polarizability (dielectric) based chem-bio sensin

Bonding mechanisms with existing bones

- Although there is evidence that BGs can attach to various soft tissues, the mechanisms responsible for these observations have not been fully described
- The mechanism of bonding between BGs and soft and hard tissues is governed by well-established dissolution and precipitation reactions
- A local pH increase caused by increased concentration of various ions at the BG-fluid interface results in formation of a carbonated HA layer at the interface. This helps
- Although there is evidence that BGs can attach to various soft tissues, the mechanisms responsible for these observations have not been fully described
- It has been reported that polarity is a major factor, in addition, to other factors regeneration of bones.
- We have been working with crystalline and glassy synthetic bone materials to determine the polarity since it is an important property which plays roles in growth and merging when material is implanted into body.

- We tried to evaluate effects of chemicals on polarity (dielectric constant) of this distorted perovskite also by using acetone and naphthalene
- **Materials choice**
- : Generally perovskites have reasonably large dielectric constant
 - Several experiments have been performed by replacing Ca^{2+} with other elements (Mandal and Singh et al)
- **Experimental approach**
 - **Organic was used for detection**
 - Sample preparation
 - Characterization of dielectric constant and resistivity
- **Morphology and its effect of solidification on morphology and dielectric constant (we will not focus on morphology in this presentation)**
- We will focus on sensing properties

We synthesized compounds in-house

- We tried to evaluate effects of chemicals on polarity (dielectric constant) of this bone materials and effect of acetone and naphthalene

Materials choice

- For the synthesis we used CaCO_3 , Na_3PO_4 , SiO_2 , KOH , MgO , Ga_2O_3 , and TiO_2 to prepare the desired stoichiometry.
- We used small components of sodium selenite to dissolve gallium and magnesium at lower temperature in presence of selenium.
- The composition of mixture is shown in Table 1.
- Source materials were listed for 99.99+% purity. We did not perform any further purification of parent components.
- The particle sizes varied but these were in the range of 100 nm size.
- Powders of the parent components were mixed and crushed repeatedly and pressed to make pellets of cm sizes, using a pressure of 6500 to 8000 lb./inch².
- We used a temperature range of 650 °C for sintering and grain growth.

We synthesized compounds in-house

Experimental Method and plan

- We tried to evaluate effects of chemicals on polarity (dielectric constant) of this distorted perovskite also by using acetone and naphthalene

Table. Actual weight of materials in mixture

Parent chemical	Actual weight (g)
Calcium Carbonate	2.14
Sodium phosphate	0.61
Silicon Oxide	2.44
Potassium Hydroxide	1.29
Magnesium Oxide	0.42
Gallium Oxide	0.28
Titanium Oxide	0.85
Sodium Selenite	0.67

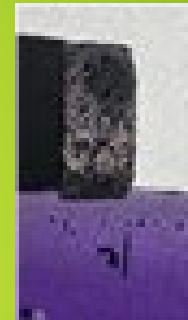


Making the pellets – Pressing powder for pellet press

We synthesized compounds in-house

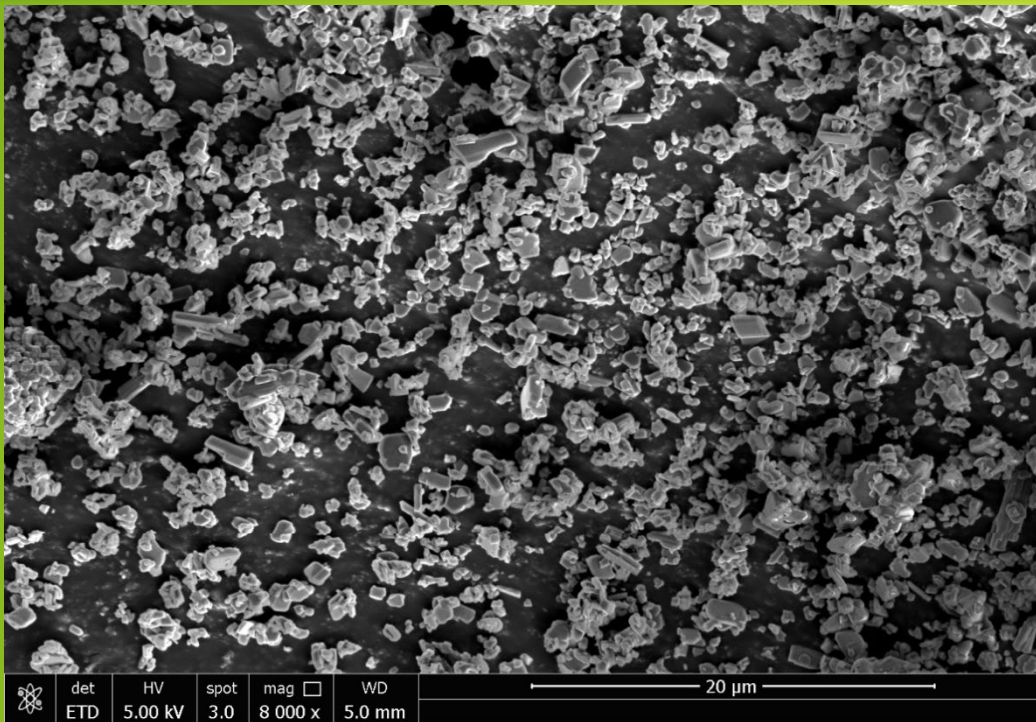
Method of synthesis

- Source materials were listed for 99.99+% purity.
- We used in some cases Wig-L-bug to prepare the particles of uniform sizes.
- The particle sizes varied but these were in the range of 100nm size.
- Powder was pressed to make pellets of cm sizes, using a pressure of 7000 to 8000 lb/inch².
- Samples were initially annealed for about 100 hours at 650 °C and some samples were annealed for an additional 95 hours followed by at 750°C for additional 75
- The morphology of material was studied by optical microscope and scanning electron microscope.



Mixed parent components
Diameter and thickness of
sample of annealed at 650 °C
sample.

NCTO was a light gray powder that was uniform in its color and composition

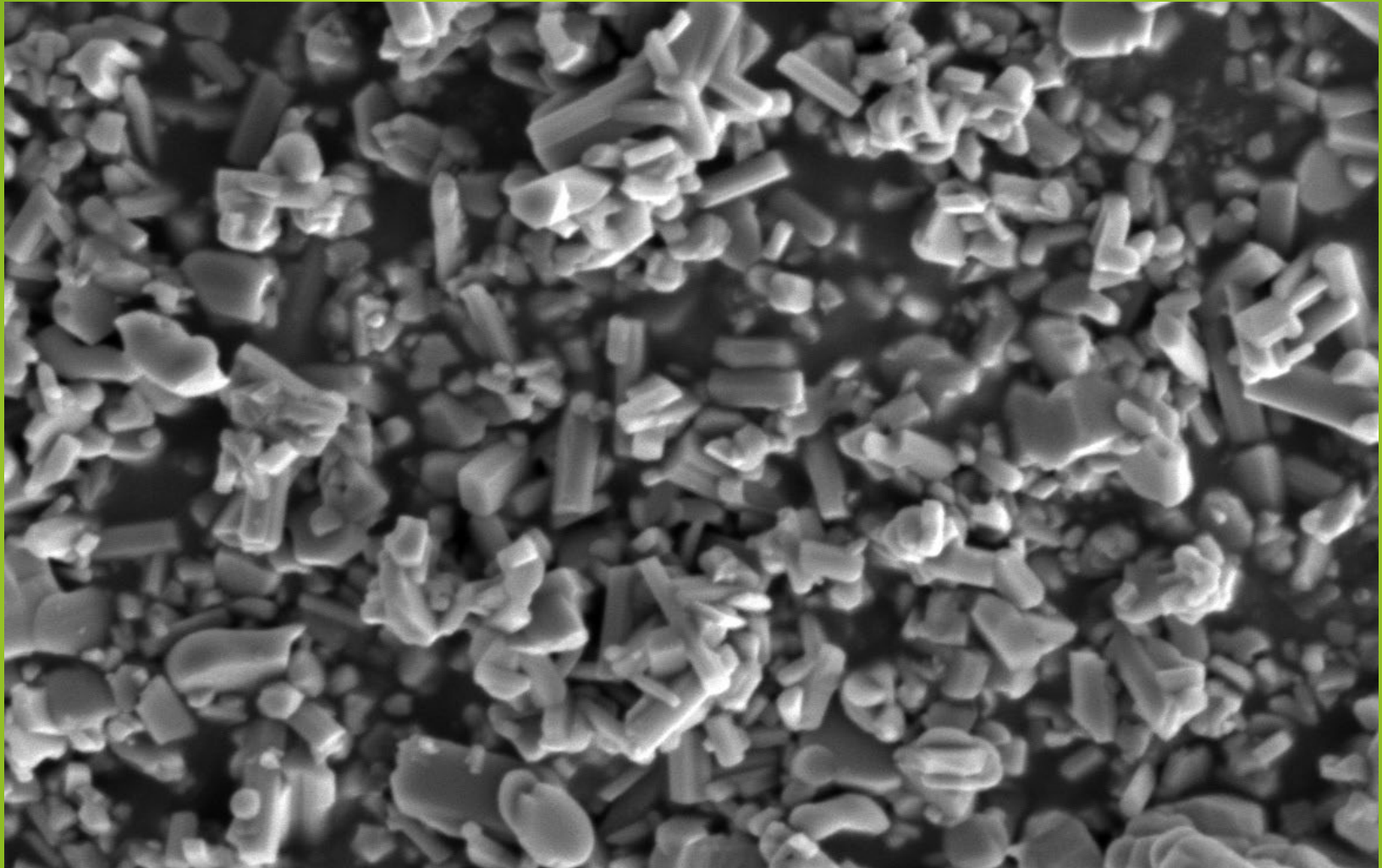


Morphology of annealed material for 95 hours. SEM shows irregular crystal growth at 20 μm scale



Nano rods (2 micrometers) and aggregates of nanoparticles (less than 1 micrometer) were observed

SEM Microstructure at higher magnification



	det	HV	spot	mag	WD	 5 μ m
	ETD	5.00 kV	3.0	35 000 x	4.9 mm	

Nano rods (2 micrometers) and aggregates of nanoparticles (less than 1 micrometer) were observed

Fabrication and measurements of dielectric constant, capacitance and resistance

- Agilent/HP 4284A LCR meter was used for electrical measurements
- Good quality polished surfaces achieved with sand papers/pads and using several solvents.
- For the measurements we used silver paste as the electrode source. Parallel-plate capacitors were fabricated from pressed and sintered pellets with thickness from 3 to 4 mm.
- Dielectric capacitance of bulk samples was inferred from measurement of complex impedance as a function of frequency from 100 Hz to 100 kHz
- Resistivity can be inferred from two measurements:
 - (a) using a parallel-resistance model of complex-impedance measurements
 - (b) measuring current from a dc voltage bias.

Mixture was a light gray powder that was uniform in its color and composition

Furnace and LCR meter

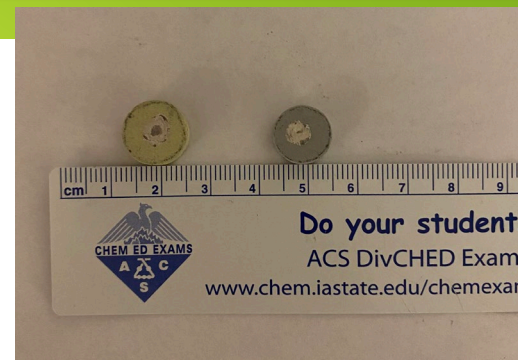


Annealing furnace and LCR Meter for testing

Silver was used on the pellets to help ensure strong circuit was made while testing

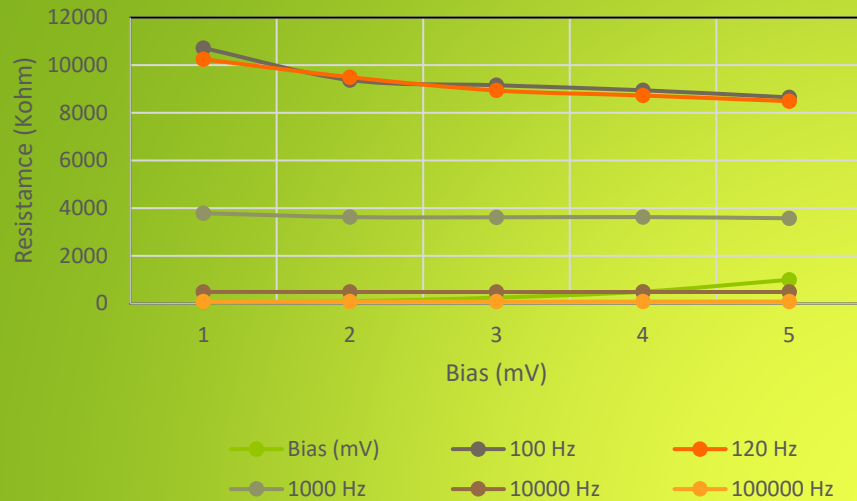
Dimension used for calculation

- A silver dot was placed on both sides of each pellet.
- Dimension:
- Sample A: $D = 5.75$ mm,
- Thickness $d = 4.5$ mm
- Sample B: Diameter = 4.7 mm,
- thickness $d = 5.0$ mm
- The diameter of the silver dot for pellet A was 0.5 cm and 0.4 cm for pellet B.

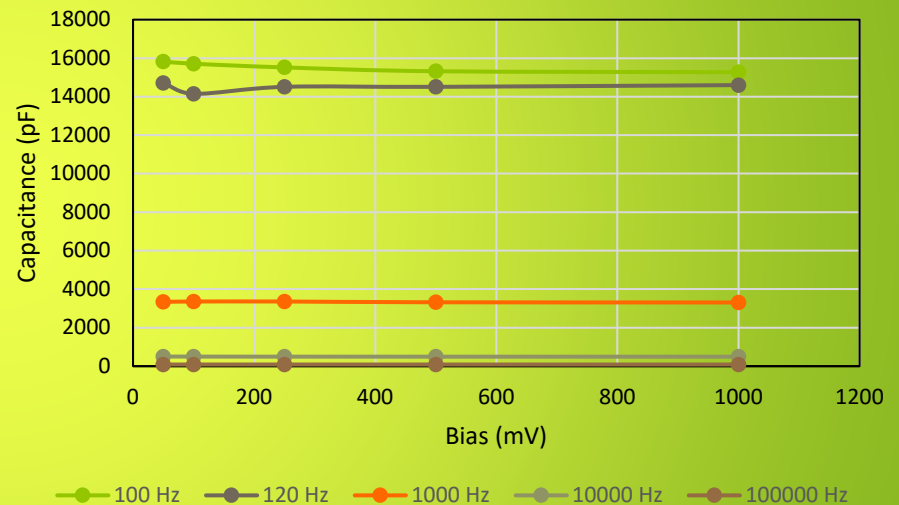


- Typical dimension
- **Sample A:** $D = 4.8$ mm, $r = 2.4$ mm,
- Thickness $d = 4.3$ mm
- **Sample B:** Diameter = 4.75 mm, $r = 2.37$
- thickness $d = 5.1$ mm
- The diameter of the silver dot for pellet A was 0.5 cm and 0.4 cm for pellet B.

Resistance of materials before and after treatment of chemicals

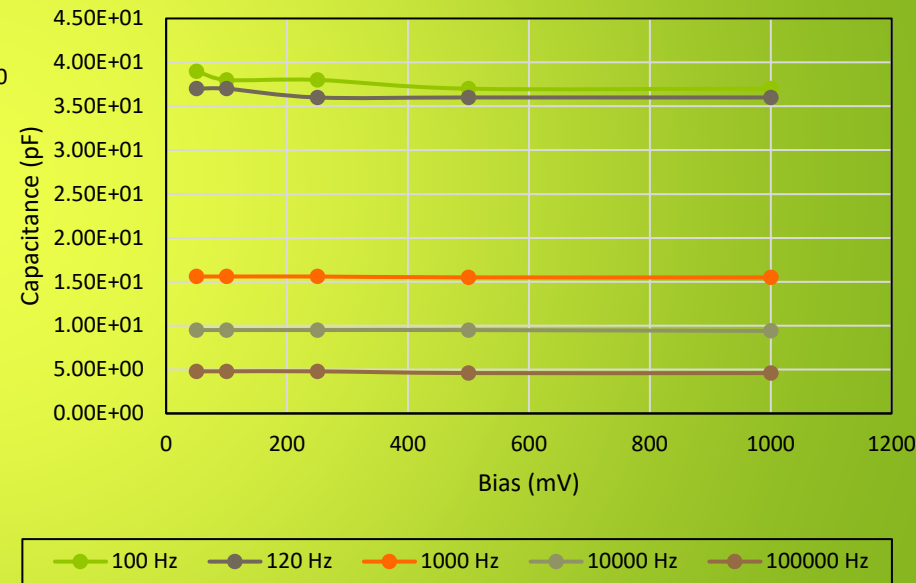
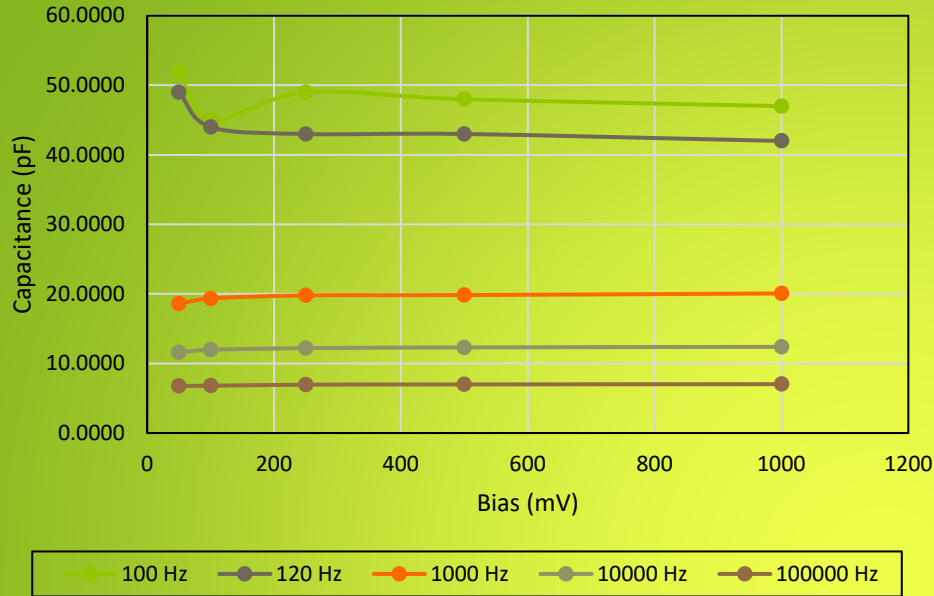


Resistance of pellet (a) before and
(b) after chemical exposure



There is no linear relationship between Bias and Resistance or Resistivity

capacitance of materials before and after treatment of chemicals



Capacitance of pellet (a) before and
(b) after chemical exposure

There is no linear relationship between Bias and Resistance or Resistivity

Summary

- We have studied oxide bone material system extensively for developing sensors
- Capacitance were measured from 100 KHZ to 100000 KHz at different bias voltage
- The capacitance and resistance are significantly affected by presence of chemicals and this is basis for sensing of chemicals
- We investigated effect of acetone and on the dielectric constant and resistivity.
- There was significant changes in both values due to exposure chemicals.
- There was no effect of bias up to 1000mV indicating that material did not breakdown
- Experiments to study effect of methanol is continuing
- It is inferred from data that chemicals affect the polarity of bone materials
- We are determining dielectric constant and resistivity based on the diameter and thickness of samples
- The results of methanol and dielectric constant will be reported in future.

Measurements on resistivity and dielectric constant are still underway

Thank you very much for your time