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RESEARCH ARTICLE

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Effect of high energy radiation on electrical properties of synthetic bone materials

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Abstract

Hydroxyapatites have been investigated since past six decades as laser host materials. Because of their important roles in bone and teeth, these have been subjects of recent investigations. Gallium and titanium have great potential for decreasing the depletion of calcium and reducing osteoporosis. The electrical properties and polarity play important roles in regeneration of the bones. We observed growth of grains in selenium-doped gallium and titanium containing silicate hydroxyapatites. Observed morphology showed non-facetted microstructures and it helped in achieving larger grains. For the material processed for the period of longer than 70 h, we did not observe any difference in the dielectric constant and resistivity of the selenium-doped materials. For irradiating the materials, a Cs-137 γ-radiation with 5 μm curie dose was used up to 100 h. We observed that the dielectric constant and resistivity at different frequencies ranging from 100 to 100 000 Hz were affected by the high energy radiation. However, bias voltage in the range of 50–1 000 mV did no alter the dielectric constant or resistivity. This indicated that the breakdown of the material did not occur for this bias range.

KEYWORDS

bone material, dielectric, electrical resistivity, grain, hydroxyapatite, microstructure, silicates, γ-ray

1 | INTRODUCTION

High energy radiations such as X-ray, γ-ray, and neutron rays affect the bone and blood cells negatively. Studies indicate that extremely high energy radiations cause diseases such as cancer. With increasing interest to travel to space, it is extremely important to be aware of the effect of radiation. The high energy radiation affects the polarity and hence ionic characteristics affecting the electrical properties which are important for the bone materials (hydroxyapatite). Mazelsky and Hopkins had pioneered the growth[1,2] and performed extensive research on the single crystal of hydroxyapatite for a variety of applications including for the laser host material. They indicated that the mineral fluorapatite (FAP), which has the composition $Ca_5(PO_4)_3F$, provided the lowest thresholds and highest efficiency of many known laser hosts. Another class silicate oxyapatites (known as SOAP) were also studied by

them and had the general chemical formula $MR_4(SiO_4)_3O$, where M is a divalent ion such as Ca or Sr, and R is a trivalent rare earth. They used very high temperatures > 2 100°C for growing pure and doped for silicates and phosphates materials. Since then, a variety of dopants have been used in apatite's[2–5] and ZnSe[6] for laser developments. The calcium-based hydroxyapatites both silicates and phosphates constitute almost 55%–70% of the bone materials.[7–9] The discovery of bioactive glasses (BGs) in the late 1960s by Hench et al. was driven by the need for implant materials with an ability to bond to living tissues, which were intended to replace inert metal and plastic implants that were not well tolerated by the body. Among a number of tested compositions, the one that later became designated by the well-known trademark of 45S5 Bioglass excelled in its ability to bond to bone and soft tissues.[9] This is the reason that hydroxyapatites are considered very important materials in the bone and teeth of human and animals. It plays a role in the structural strength of bone and in bone regeneration. This class of compounds naturally occurs in bone but attempts to repair damaged bones by synthetic and natural hydroxyapatites and is a key for the recent progress in the health care industries. The importance of the growth and adherence of synthetic bone materials with natural bone is very complex and extremely important to control bone diseases. Another factor in the aging population is the depletion of calcium ion in the bone. This depletion has been identified as the main cause of osteoporosis. For the regeneration and addition of synthetic bones, electrochemical properties (polarity) have been identified as an especially important factor. Because of this reason we have studied electrical characteristics of synthetic materials. Since calcium depletion causes problems in aging population, the body tries to compensate the calcium loss by regeneration. The calcium-based hydroxyapatites play a particularly important role. In this process, ionic properties and polarity are especially important factors. Also, it has been suggested that elements such as titanium and gallium may decrease the osteoporosis since these may be less prone to depletion compared to calcium. To investigate electrical properties of hydroxyapatite materials, resistivity and dielectric constant of titanium, gallium, and magnesium containing materials were determined. From the doping of alloys, it is well proven that magnesium and titanium can also increase the strength significantly.

2 | EXPERIMENTAL METHODS

2.1 | Materials synthesis

A typical silicate-based material was prepared using sodium bicarbonate, calcium carbonate, potassium carbonate, and silicon oxide. The listed purity for these chemicals was listed as >99.99%. No further purification was used before mixing. Repeated mixing was used to ensure complete mixing. In some cases, uniform size particles were prepared by using a wig-L-bug in a closed quartz ampoule. The particle sizes of the source materials were in the range of 50–100 μm. Pellets of the stoichiometric mixture were prepared using a pressure in the range of 7 000–8 000 lb/inch^2. In few runs, we used selenium to enhance the grain growth and its effect on the properties. For the dopants, we used titanium oxide and magnesium oxide also to enhance the thermal stability in the low depletion rate compared to calcium depletion. Table 1 shows the summary of the composition of the synthesized materials. Mixtures were prepared for silicate-based apatites. These mixtures did not have phosphate compounds to ensure that material was crystalline silicate hydroxyapatite. The as-prepared size of pellets was 12 mm in diameter and thickness was 1–2 mm. The pellets were placed in a boat in the furnace. In the beginning, we kept furnace at 250°C for 2 h followed by 750°C. The temperature for the sintering and grain growth was maintained in one set of experiment for 30 h and in the second set of experiment for 70 h. The temperature range of 750°C was observed to be suitable for the grain growth. We observed melting of mixture above 750°C temperature. Figure 1 and 2 shows typical material before and after annealing and grain growth. The morphology of material was studied by optical microscope and scanning electron microscope. The stability of final samples was studied and determined by using thermogravimetric measurements.

TABLE 1 Compositions of two runs for grain growth by annealing and grain growth processes.

Source materials	Mixture I (g)	Mixture II (g)
Sodium bicarbonate	0.60	0.61
Calcium carbonate	2.0	2.05
Silicon oxide	5.303	5.305
Potassium sulfate	1.21	1.207
Magnesium nitrate	0.20	0.201
Gallium oxide	0.396	0.407
Titanium oxide	0.11	0.105
Selenium	0.0	1.088

2.2 | Microstructural studies

Microstructure of the synthesized and annealed pellets was determined by the scanning electron microscope NOVA NANOSEM 450. A typical voltage used in the study was in the range of 2–20 kV energy.

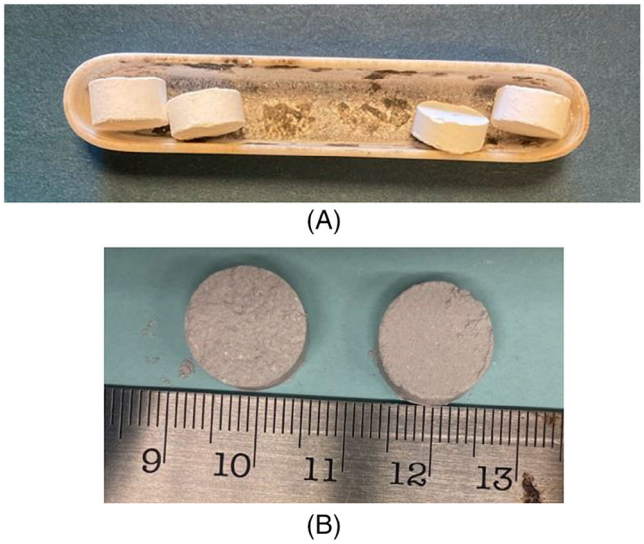

FIGURE 1 (A) Synthesized and compacted samples placed in boats for annealing and grain growth and (B) processed samples after grain growth.

FIGURE 2 Samples of 2 mm thickness and 12 mm diameter were placed closed to the radiation source in a plastic box for exposing γ-ray radiation.

2.3 | Electrical characterization

Parallel polished surfaces of pellets were prepared for electrode bonding. For the electrode, we tested silver and gold. We observed that both gold and silver were stable on the prepared pellets. The surfaces of the pellets were polished to achieve good quality surfaces on polishers with fine sandpapers followed by cloth-based pads and cleaned using several solvents. Silver paste was used as electrode to determine the resistance and capacitance. Resistance and capacitance were measured by Hewlett Packard 4263A LCR meter. For the determination of the dielectric constant, we used the equation; $C = \varepsilon\varepsilon_0 A/d$, where ε is the dielectric constant of the material, $\varepsilon_0 = 8.854 \times 10^{-12}$, C is the measured capacitance, A is the overlapping surface area of the plates, and d is the thickness of the pellet. Dielectric capacitance of bulk samples was inferred from the measurement of complex impedance as a function of frequency from 100 Hz to 100000 kHz at the bias voltage of 50–1 000 mV. Resistivity was inferred from two measurements: (A) using a parallel-resistance model of complex-impedance measurements and (b) measuring current from a dc voltage bias.

2.4 | Evaluation of γ-ray response of the materials

A commercially supplied Cs-137 γ-radiation source [Figure 2] was used to evaluate γ-ray response. The γ-radiation source Cs-137 was listed for 5 µCi, 30.2 year half-life, β and γ-radiation. The current voltage responses of composites were measured at different voltages, ranging from 50–1 000 mV and frequencies ranging from 100– 100 000 Hz for the non-irradiated and irradiated samples.

3 | RESULTS AND DISCUSSION

The silicate material was prepared by milling and mixing the powder of the parent components listed in Table 1. The typical size of powder ranged between 50 and 100 nm. 3B Previously several processes to achieve large grains of this type of materials were explored by using semiwet techniques.[10–13] This study focused on the effect of the addition of gallium, titanium, and magnesium elements. It is well proven that the addition of gallium will decrease the depletion compared to calcium ion in addition to increase the radiation resistance. The addition of magnesium and titanium will increase the mechanical strength. However, there is no data on polarity as well as resistivity of materials. The addition of selenium had two objectives; first objective was to evaluate its effects on properties and second selenium helps in grain growth acting as a flux material. Figure 3 shows the microstructures of materials at the initial stage (30 h) and after few hours for the sample without selenium. We observed that after sintering grains started growing slowly and bunching together. Larger grains in the form of faceted particles are formed after 30 h. The microstructure is shown for the material grown at 750°C and time period of 70 h.

As shown in Figure 3B, we observed that facetted particles are formed and do not merge easily with other grains. However, there is greater tendency to form larger bundles of these grains. In most of the cases, complex structures are formed. The formation of shaped and facetted grains is favored due to strong anisotropy and interface energy. The coarsening mechanism and facetted growth in anisotropic materials have been shown by Singh et al.[10–13] during grain growth complex oxide materials. The addition of

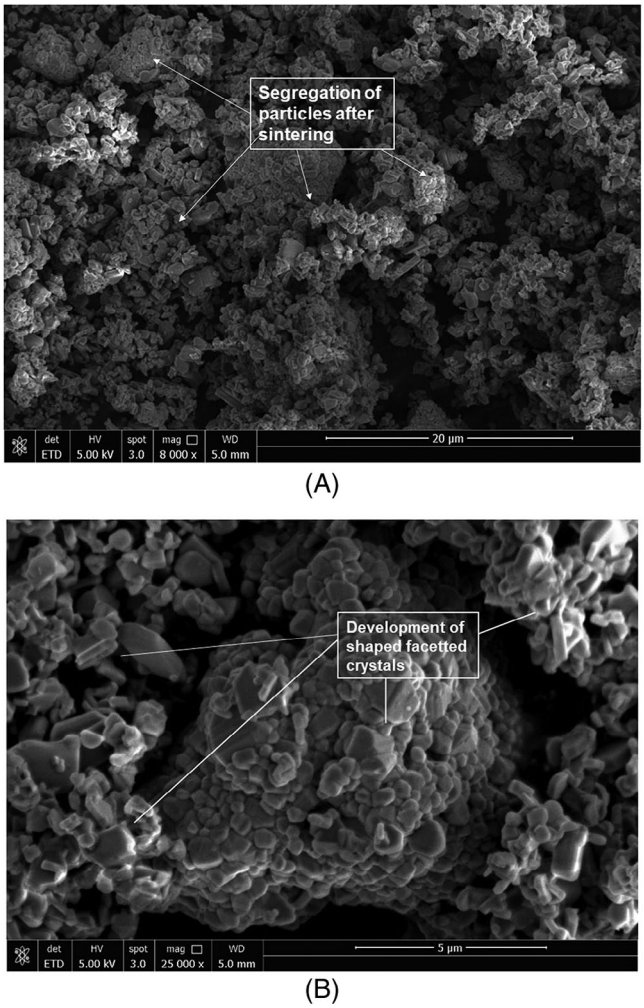

FIGURE 3 Microstructures of material sintered at 750°C for a period of (A) 30 and (B) 70 h.

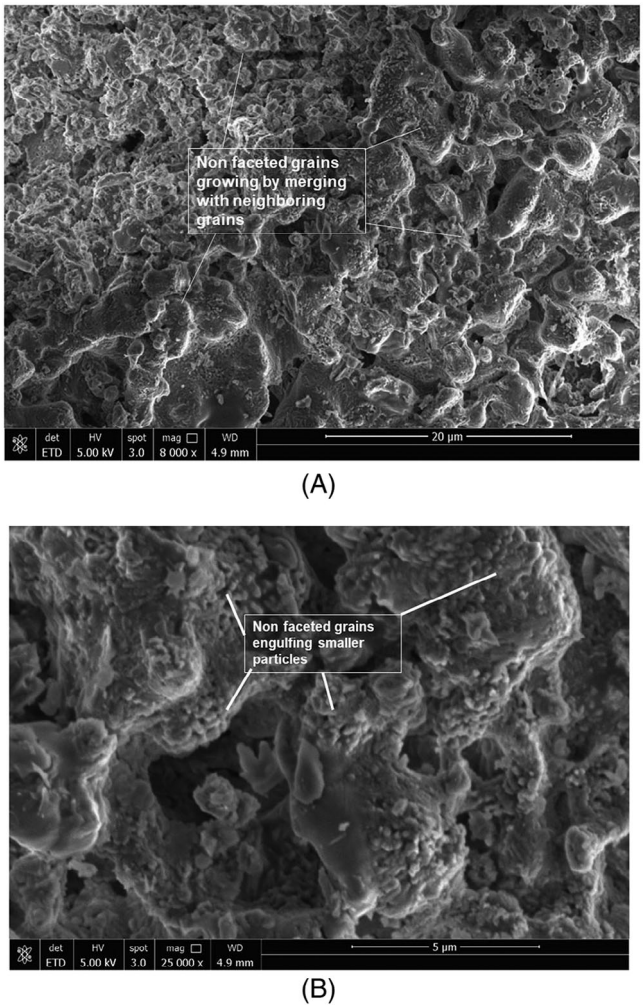

FIGURE 4 Microstructure of selenium compound (A) nonfacetted grains growing at the expense of smaller grains and (B) growing grains and expanding in sizes larger than 5 µm.

impurity[10] showed large changes in anisotropy and nonfacetted to faceted grains. At some places, we observed micrometer size grains with plane surfaces. The grain growth and mechanism in the selenium containing samples were different than samples without selenium. Grains were nonfacetted and grew into very large grains without visible gaps. Figure 4B shows a larger magnification of this phenomenon. It was clear that smaller grains easily got engulfed into larger grains and no sign of facets was observed. Also, during this process there were gaps which got filled with larger grains together by the channeling mechanism.[10,11] The grains grow by the channeling mechanism and by merging grains together. In the case of selenium-doped material, the channeling mechanism was observed, and larger grains were observed. The faceting as shown in Figure 3 was not observed in microstructures shown in Figure 4 due to changes in interface energy and changes in anisotropy as discussed in refs. 11, 12 This may be an important reason for the role of selenium in growth of bone materials.

TABLE 2 Source materials used in phophosilicate material.

Source material	Amount (g)
Sodium carbonate	0.6
Silicon 0xide	5.3
Potassium carbonate/phosphate	1.2
Titanium oxide	0.1
Gallium oxide	0.4
Magnesium oxide	0.2

For the comparision with silicate material (without phosphate), we prepared a phophosilicate hydroxyapatite material by the solution method also. In this case, the composition of the materials used is listed in Table 2. The microstructure of this material for a period of 30 h at 700°C (slightly lower since showed low melting temperature) is shown in Figure 5. The microstructure showed mixture of crystallites and glossy materials indicating that higher

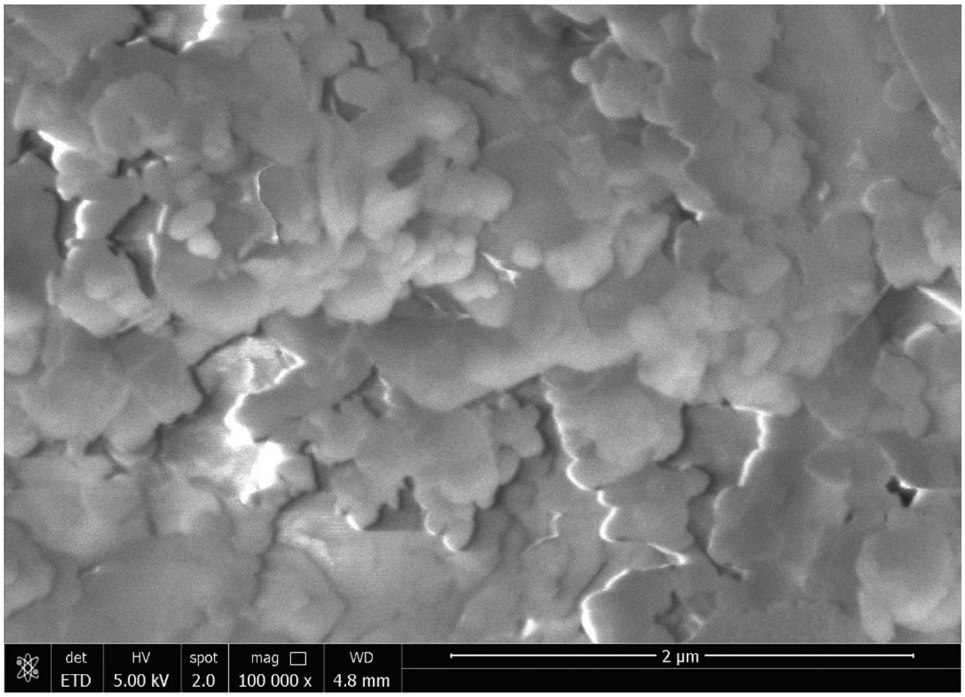

FIGURE 5 Microstructure of doped phophosilicate after grain growth of 30 h at 700°C. It shows mixture of crystallites and glossy materials.

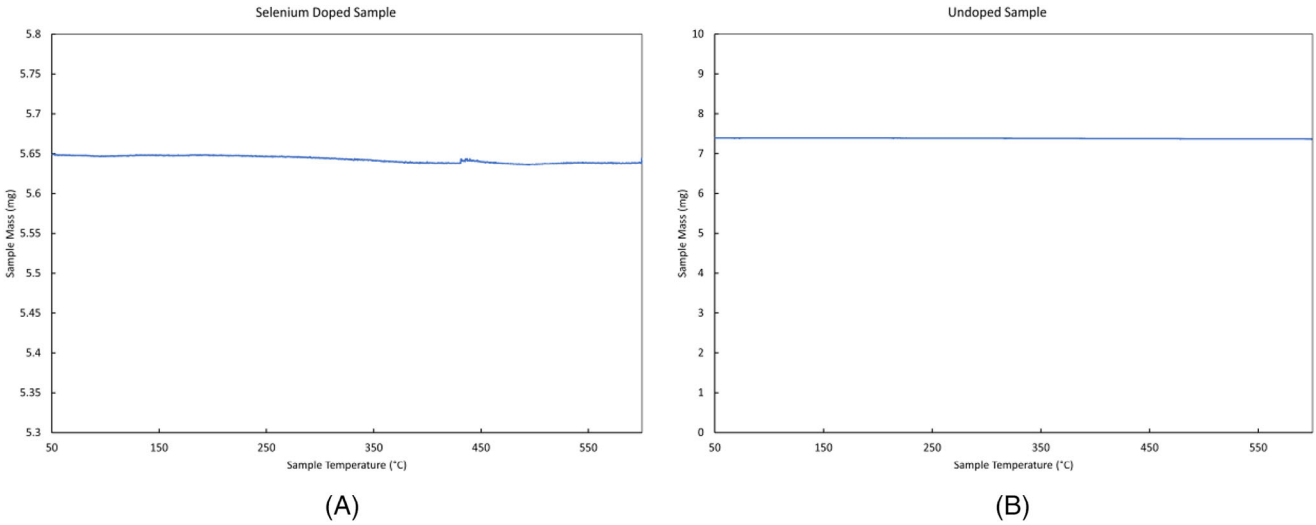

FIGURE 6 The thermogravimetric analysis (TGA) data for the sample I with magnesium, titanium, and gallium without selenium and (B) data for the sample II with magnesium, titanium, and gallium with selenium.

temperature and longer time of grain growth may reveal clear indication of its behavior. The details of this class of materials are under study.[14]

The thermal stability of the silicate materials of the compositions in Table 1 was studied by thermogravimetric method up to 800°C and the results are shown in Figure 6. The thermogravimetric analysis (TGA) showed that for the sample II with the selenium loss was 0.32%, while as for the material without material the loss was 0.11%. Both samples contained magnesium, titanium, and gallium. The TGA was performed by raising the temperature of the samples up to 800°C. The total weight loss was very insignificant for both mixtures compared to total weight used for analysis.

The reactivity of pure and selenium-doped material was performed by using both materials in a small diameter (5 mm diameter) tube from two sides. Figure 7 shows the schematics of the reaction tube. The reactivity was evaluated by placing the tube at 150°C, 200°C, and 300°C. The movement of color change of the mixture as a function of time was observed for determining the reaction

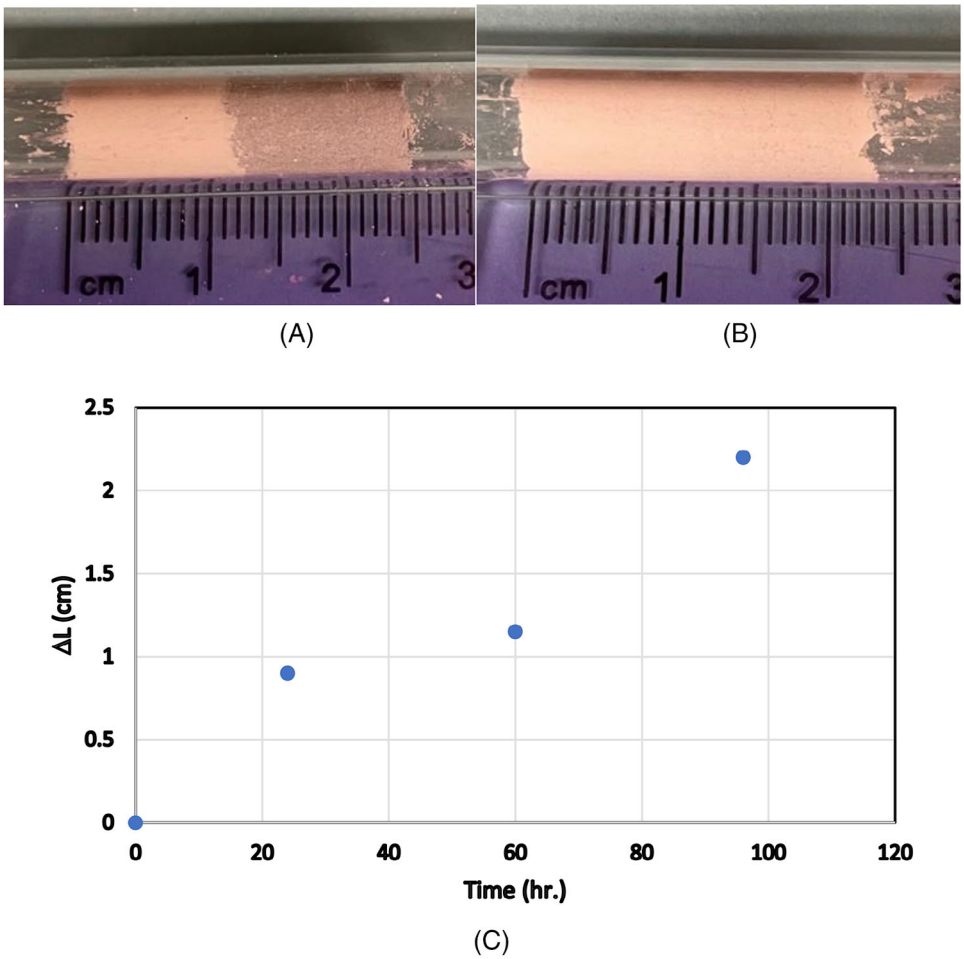

FIGURE 7 Both mixtures showing reaction at (A) 0 h and (B) 100 h after treatment at 300°C. (C) The reaction rate of selenium-doped mixture with undoped material.

rate. A typical reactivity plot is shown in Figure 7c for the temperature of 150°C. Further refinement and rate determination at lower temperature are continuing. The reaction at higher temperatures was not determined since within few hours color completely changed at 300°C as shown in Figure 7b.

The electrical characteristics of the synthesized material were studied by measuring the capacitance and resistance of the material. The dielectric constant was determined from the capacitance data and resistivity was determined from the resistance measurements. These data were determined at room temperature. As mentioned in Section 2, we used the equation; $C = \varepsilon\varepsilon_0 A/d$ for the dielectric constant, where ε is the dielectric constant and $\varepsilon_0 = 8.854 \times 10^{-12}$, C is the measured capacitance, A is the surface area of the plates, and d is the thickness of the pellet. The resistivity was determined by using equation $\Omega = \rho d/A$, where Ω is the resistivity, ρ is the resistance, d is the thickness, and A is the area. Figure 8 shows values of the dielectric constant at different frequencies ranging from 100 to 100000 Hz. The data showed that as we increased the frequency, the dielectric constant decreased significantly. In addition to the frequency, we used different bias voltages to determine the breakdown of bone materials as a function of applied bias. The bias voltage used in this study was 50– 1 000 mV. Unlike several oxide materials, the dielectric constant was constant for the bias applied. It is very important that there was no degradation in the material as the function of the applied bias voltage. Similarly, the resistance for different bias voltage and frequencies were measured. The data are shown in Figure 9.

Since long it has been reported by the literature that high energy radiation affects the bone material significantly. However, quantitative data on this subject are very limited. Because of this reason, we irradiated the material for 20 and 100 h by using a γ-ray source. For exposure, we used a source of Cs-137 which has dose of 5 μm curie. We could not expose with higher dose since this was only allowable dose for our laboratories. The dielectric constant for 20- and 100-h exposed sample is shown in Figure 10. A comparison of the Figures 8 and 10 showed that the dielectric constant increased significantly due to the exposure of the radiation.

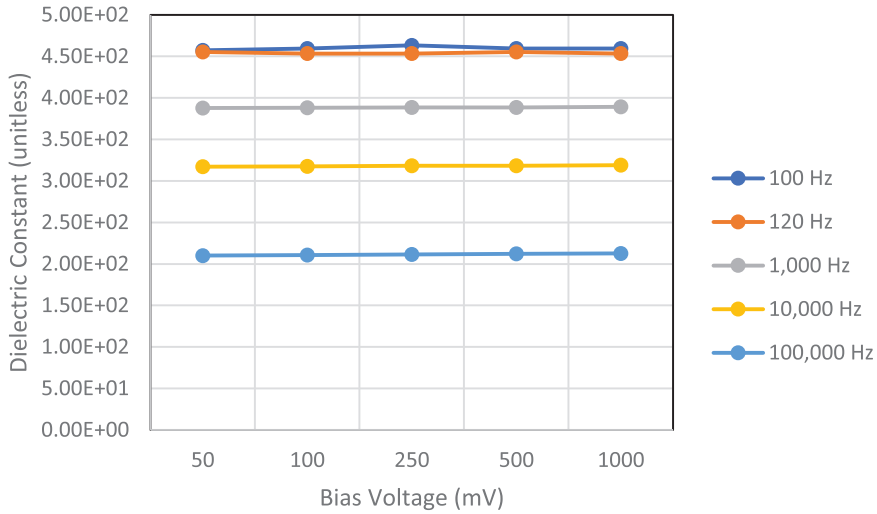

FIGURE 8 The dielectric constant of the non-irradated sample at frequencies 100–100 000 Hz range at bias voltage of 50–1 000 mV.

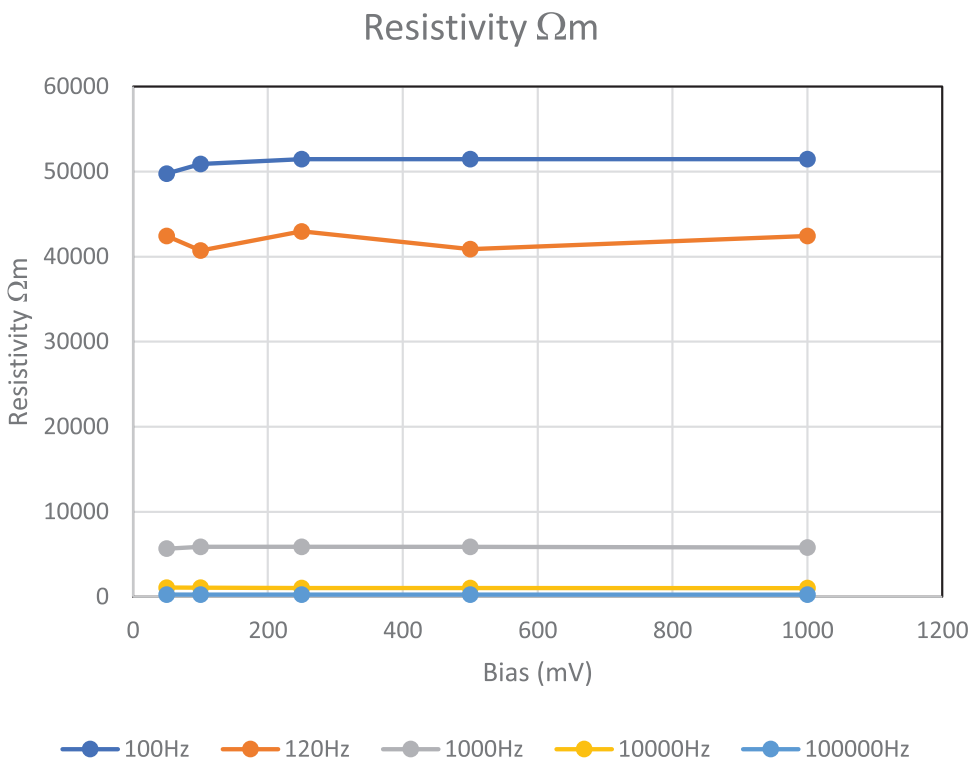

FIGURE 9 Resistivity of the non-irradiated sample at frequencies 100–100 000 Hz range at bias voltage of 50–1 000 mV.

The data for the resistivity are shown in Figure 11 for 20 and 100 h. The maximum change was observed within 20 h. Extended exposure did not change the dielectric constant significantly.

The comparison of data for irradiated and non-radiated material shows that resistivity was significantly decreased for the irradiated material. These data are very significant for many reasons. The dielectric constant and resistivity changes due to radiation are very large indication that these parameters can be used as radiation sensing for oxide materials. However, it was observed that values were constant for a particular frequency as the function of the bias voltage. This is a very good characteristic indicating that bone materials do not breakdown in the bias range of 50–1 000 mV.

Figure 12 shows a direct comparison of the dielectric constant and resistivity at several frequencies for a bias voltage of 50 mV. Unlike several perovskite materials, dielectric constant did not decrease[13] with increasing bias voltage. However, in both irradiated and non-irradiated materials dielectric constant and resistivity decreased as function of increasing frequency. These values were almost

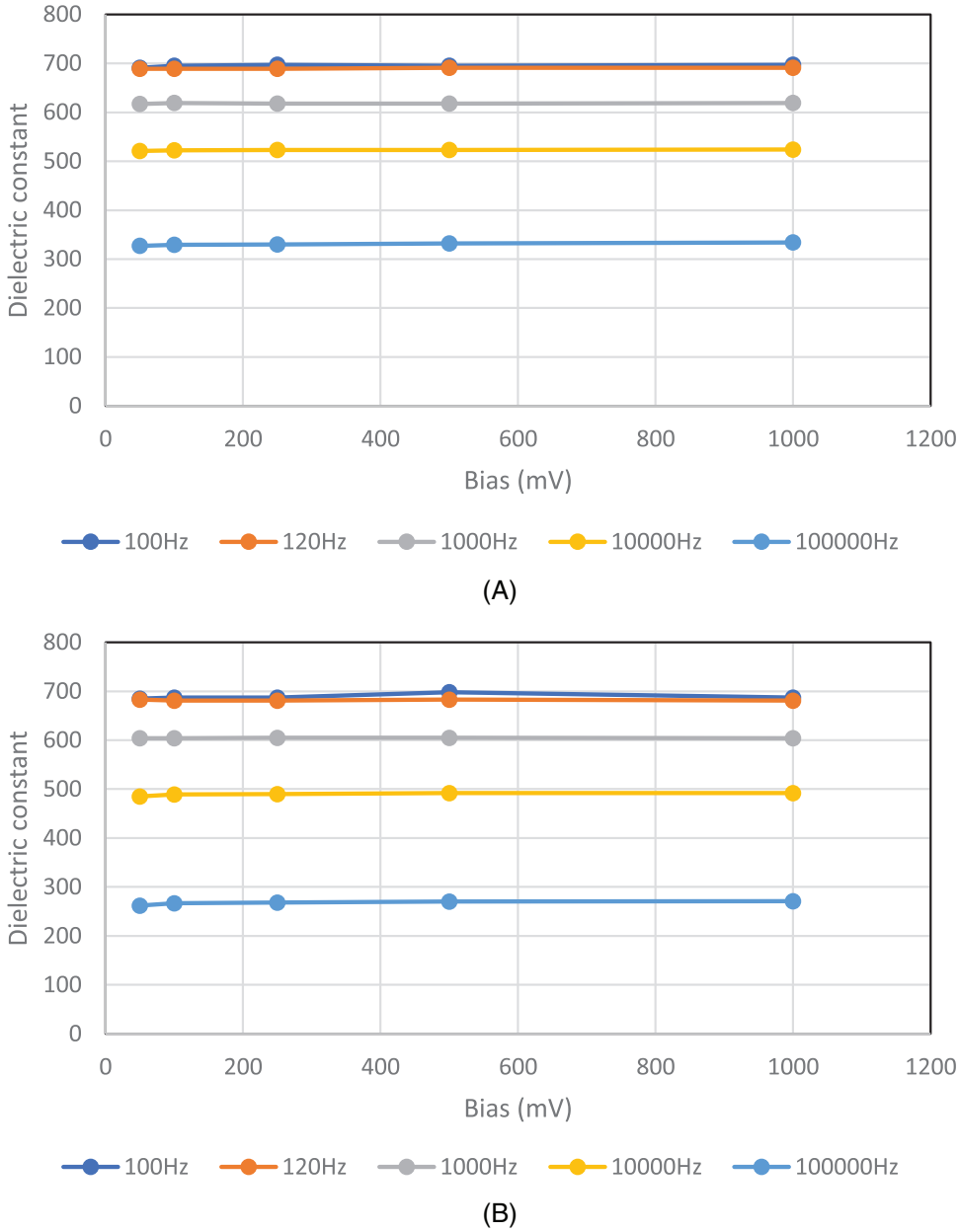

FIGURE 10 Dielectric constant (A) after 20 h and (B) 100 h of the irradiated sample at frequencies 100–100 000 Hz range at bias voltage of 50–1000 mV. There was no significant change in dielectric constant due to long exposure of gamma radiation.

identical for both mixtures listed in Table 1. As discussed in refs., 10–13 dielectric constant and resistivity depend on the oxidation and grain boundaries. The processing temperature and time may affect the grain sizes and hence values may change slightly. To resolve this issue in complex materials, grain growth for longer than 200 h processing may be required.

4 | SUMMARY

The detailed experiments were performed on the silicate hydroxy appetites' mixtures containing magnesium, titanium, and gallium to determine the electrical characteristics of as synthesized and irradiated materials to evaluate the effect of high energy radiation. We observed that the addition of small amount of selenium produced non-faceted morphology and it helped in achieving larger grains. For the material processed for the period of longer than 70 h, we did not observe any difference in the dielectric constant and resistivity due to the addition of the small amount of selenium. The gallium and titanium added silicate material was stable up to 800°C. There were two advantages of the materials prepared in the present study. The effect of magnesium, titanium, and gallium was studied on the thermal stability

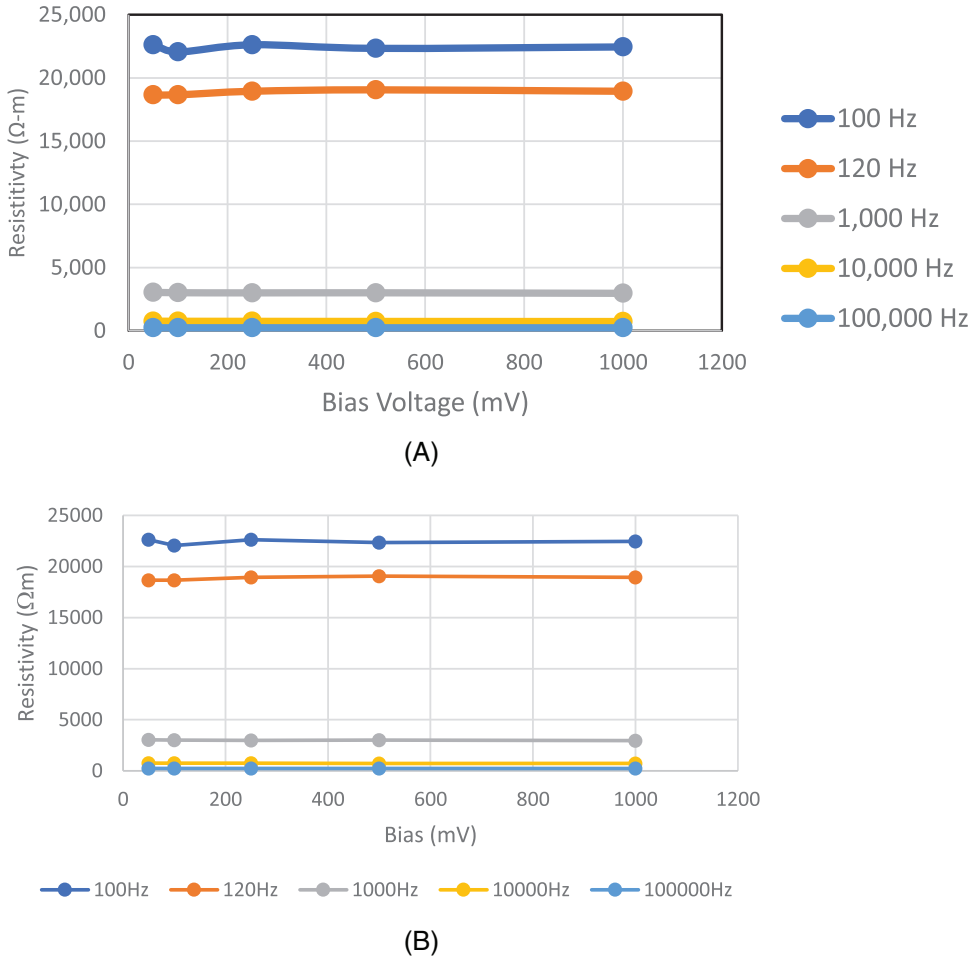

FIGURE 11 Resistivity of material (A) after 20 h and (B) 100 h of radiation at frequency of 100–100 000 Hz for the bias voltage of 50–1 000 mV range. The data show that there was no significant change in resistivity at a frequency due to long exposure of gamma radiation.

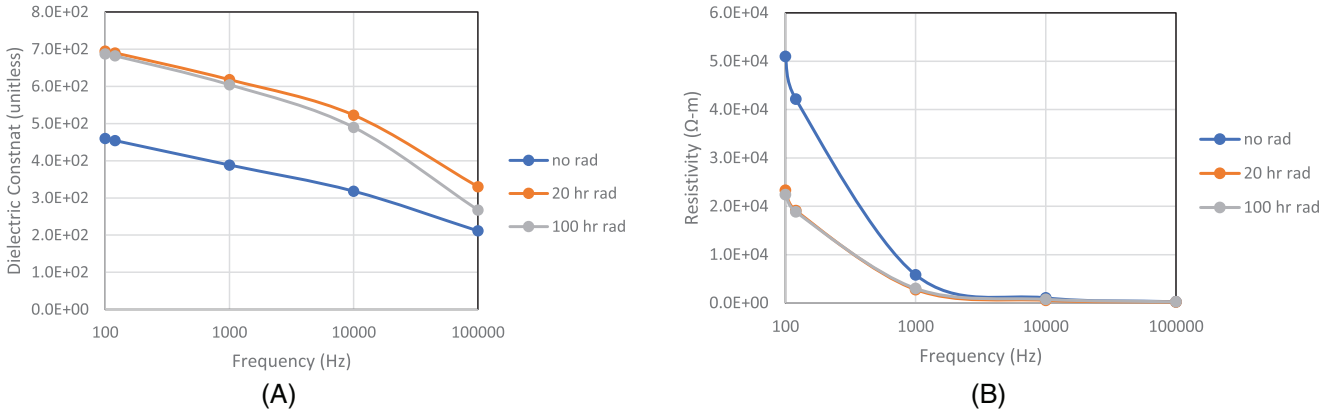

FIGURE 12 A comparison of the (A) dielectric constant and (B) resistivity of non-radiated and radiated materials at different frequency at bias voltage of 50 mV.

and electrical characteristics. The synthesized silicate materials were stable up to 800°C. The addition of Ti, Mg, and Ga may require higher temperature for the grain growth. But the addition of selenium helps in achieving grain growth at 700°C–750°C. The dielectric constant and resistivity changed significantly indicating that Cs-137 source with a 5 μm curie affects the silicate bone material significantly. The values of the dielectric

constant and resistivity were observed to be higher than values available in the literature for some mixtures prepared for bones.

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