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Effect of the Ca/P ratio on the dielectric properties of nanoscaled substoichiometric hydroxyapatite

Mario Quilitz · Klaus Steingröver · Michael Veith

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Abstract Nanoscaled hydroxyapatite (n-HAp) was prepared by a wet chemical precipitation method, pressed to pellets and sintered at various temperatures between 900 and 1200°C. With input stoichiometries of Ca/P ratios between 1.4 and 2.0, compositions in the substoichiometric range of Ca/P between 1.45(1) and 1.62(3) were determined after preparation. After sintering, final values of the Ca/P ratio between 1.45(8) and 1.66(4) were found. Capacitances and dielectric losses were determined in the frequency range between 20 Hz and 1 MHz and dielectric constants calculated from the capacitances. Dependencies of the dielectric properties on the composition, as well as on sintering temperature and frequencies were investigated. The dielectric constants generally tend to increase with increasing Ca-content. Different behaviour was observed for low frequencies (below 10^3 Hz) and for compositions far from the stoichiometric point of hydroxyapatite (Ca/P: 1.67). Comparable results were found for dielectric losses.

1 Introduction

Hydroxyapatite is the major inorganic component of bones and teeth [1, 2]. Due to its excellent biocompatibility [3] it is used for a broad range of biological and medical applications [4–6]. Hydroxyapatite finds its most extended area of use as an implant material for reconstructive orthopaedic and dental surgery, where it is taken either as a massive filling for bone gaps or as a surface coating [7, 8] of implanted bodies.

Besides this field, in which extended work was devoted to research on synthesis, mechanical properties and mechanical enforcement in various forms of composite materials, hydroxyapatite has been used for other applications such as chemical sensors—especially for alcohol and gases [9, 10]—for liquid chromatography columns in order to separate proteins and nucleic acids, for catalysts, for dehydration and dehydrogenation of some alcohols, and as a migration barrier for radioactive waste disposal in geological sites [11]. Last but not least, more recently hydroxyapatite is used for electric applications, i.e. as an electrolyte for high-temperature fuel cells [12], an electrical insulating coating for electronic devices including—but not limited to—implantable devices [13] and dielectric coatings [14].

An investigation of the dielectric properties however is not only of interest for the latter case but also for biomaterial applications. This has several causes. First, the application of electrical fields can accelerate the healing of fractures in bones [15–17]. Furthermore, an electrical stimulation enhances the rate of bone growth for bone grafts in spinal fusion [18, 19] and is also used to treat osteoarthritis and osteonecrosis [20]. Finally, the electric poling of hydroxyapatite enhances its bioactivity [21]. For all these reasons and because bone is a composite of fluids, collagen and the hydroxyapatite matrix, especially the electric and dielectric properties of hydroxyapatite are very important.

Some data were available reporting on dielectric properties of hydroxyapatite. Fanovich et al. [22] report a dielectric constant of 12.61 for a sample sintered at 1200°C and a dielectric loss of around 0.3 at a frequency of 10^2 Hz. Ikoma et al. [23] found a dielectric constant of 20 (at

M. Quilitz (✉) · M. Veith
INM—Leibniz-Institute for New Materials, Campus D2 2, 66123 Saarbrücken, Germany
e-mail: mario.quilitz@inm-gmbh.de

K. Steingröver
Bühler PARTEC GmbH, Saarbrücken, Germany

10^2 Hz) and 15.4 (at 10^5 Hz) both at T = 18°C. The loss values were rather high for these measurements. Khalil et al. [24] in addition give data on the dependence on sintering temperature. In this reference sintering was performed at 1250 and 1000°C. Dielectric constants of 6–7 at 1250°C were found at 10^2 Hz decreasing to about 4 at 10^4–10^5 Hz. On samples sintered at 1000°C dielectric constants up to about 350 were observed at 10^2 Hz decreasing to below 50 at 10^3 Hz while the losses determined for these samples were extremely high. Hoepfner et al. [25] collected data on the porosity dependence of the dielectric constant of hydroxyapatite. In the porosity area of $P = 0$–0.1, they reported dielectric constants of around 12–14. Furthermore, some references provide data on dielectric properties of thin or thick films [13, 26]. In these films lower dielectric constants compared to bulk material are found.

Mainly in recent years the role of the Ca/P ratio—especially with regard to the preparation of hydroxyapatite—has been investigated. Several references mentioned the influence of processing parameters on the ratio of hydroxyapatite [27–35]. Especially Mahabole et al. [34] reported the influence of various methods of preparation. While a near-to-stoichiometric-composition of Ca/P of 1.63 is achieved with a chemical preparation, hydrothermal method leads to Ca-deficient and microwave processing to Ca-rich samples. Dielectric constants are reported to vary between 9 and 13 in these samples. Salas et al. [35] very recently presented results on the Ca/P dependence of the preparation of hydroxyapatite via a top–down synthesis method. Unfortunately they did not report any data on dielectric properties.

Finally, Silva et al. [36] provided data on the influence of Ca/P ratio on the dielectric constants and losses. The reported dielectric constants vary between 14.50 and 16.07. Though these data give useful hints, there are several reasons for an extended analysis of the influence of Ca/P ratio on the dielectric properties of hydroxyapatite:

- The analysis of Silva et al. only covers compositions in the range between 1.43 and 1.56 (atomic ratio) but it is highly desirable to have data up to the ideal stoichiometry at a value of Ca/P = 1.66.
- The dielectric losses are comparably high also in the medium frequency range (1 kHz data are given). This can be due to a poor sample quality.
- Silva et al. provide data on a rather narrow range of frequencies.

In this work, we present measurements of dielectric constants and losses and their dependence mainly on the composition which is represented by the Ca/P ratio. Dependencies of the dielectric properties on frequency of measurement and temperature of sintering are also briefly reported.

2 Experimental section

The wet chemical synthesis of hydroxyapatite was generally performed in the following way: In a 10 l mantle reactor, tempered to 45°C, H_2O (6 l) and $Ca(NO_3)_2{\cdot}4H_2O$ (291 g) were given into a solution and charged with a solution of H_2O (1.5 l) and NH_3 (75 ml, 25%). Subsequently, the mixture was rinsed 20 min with N_2. Under continuous stirring, a solution of $(NH_4)_2HPO_4$ (97.6 g), NH_3-solution (175 ml, 25%) and H_2O (1.5 l) was added dropwise. During the operation, a white precipitate was formed After 3 h a pH-value of 9.5 was measured and set with NH_3-solution (60 ml, 25%) to pH = 10. Stirring was performed for 24 h at a mantle temperature of 45°C. Then the precipitate was sedimented, the surmounting solution removed and the precipitate was washed with deionised water. The process was repeated until the conductivity of the washing water attained 50 μS/cm. Afterwards, the residue was washed with ethanol. The white residue was dried over night at 70°C in a drying cupboard. Final yield of the synthesis was 116.9 g $Ca_5(PO_4)_3OH$, which corresponds to 94% of the theoretical value. For the variation of the stoichiometry, the Ca/P ratio of the input compositions was varied in the range between 1.4 and 2.0. In the following the examples for the methods of characterization relate to samples with a final composition of Ca/P of 1.54.

The sizes of the primary particles were determined by signal measurements of XRD patterns to be typically around 10 nm. With the BET method, the surface area of the powders was found to be typically about 117.6 $m^2\ g^{-1}$ measured with an outgas temperature of 120°C and an outgas time of 23 h. The weight of the sample was typically around 0.7849 g. The temperature was 77.4 K. The calcium- and phosphorus-contents in the hydroxyapatite were determined by ICP/AES. For this analysis, typically about 30 mg of the material were charged with 2 ml concentrated HCl (37%) and filled up to 100 ml with double deionised water. Afterwards, samples were diluted to 1/10. To avoid matrix effects the standards were adapted to the acid contents of the samples. The weight content of Ca was determined to be 35.54 ± 0.27 corresponding to 8.87 mmol/g, while the weight content of P was found to be 17.87 ± 0.15 corresponding to 5.57 mmol/g. From that measurement, in this case a Ca/P ratio of 1.54 according to ICP/AES (Ca: $\lambda = 393.366$ nm, P: $\lambda = 213.618$ nm) was calculated.

The powders prepared as above were densified to pellets in two steps. First the powder was uniaxially predensified at 100 MPa. This procedure was followed by a cold isostatic pressing (CIP) at 800 MPa. For the sintering, the pellets were heated for example to 1200°C with a heating rate of 5°C/min. At 1200°C the temperature was kept constant for 2 h. Afterwards, the samples were

furnace-cooled. For the investigation of the effects of sintering temperature, several other sintering temperatures between 900 and 1200°C have been used while the other conditions remained constant.

After sintering, the density of the pellets was determined by the Archimedes method. The phase content of the pellets was characterized via XRD. Electrical measurements were performed at sintered pellets of hydroxyapatite. The pellets were approximately 10 mm in diameter and about 1 mm thick. For the measurements, a precision LCR meter, type 4285 A (Agilent Technologies) was used. Capacitances of the pellets were measured in the frequency range between 20 Hz and 1 MHz. The relative dielectric constants were calculated from the capacitances obtained in the experiment according to Eq. 1

$$C = (\varepsilon_0 \varepsilon_r A)/t \quad (1)$$

in which C is the capacitance, ε_0 the dielectric constant of the free space (8.854×10^{-12} F/m), A the area of the dielectric, t its thickness and ε_r the dielectric constant of the sample. Dielectric losses (tan δ) could be measured directly by using the LCR meter.

3 Results and discussion

The atomic Ca/P ratio of ideal stoichiometric hydroxyapatite—$Ca_5(PO_4)_3(OH)$—is 1.667. As already mentioned, the Ca/P ratio was varied in the input mixtures to get hydroxyapatite with different stoichiometries in the range between 1.4 and 2.0. A survey of the resulting compositions after the wet chemical synthesis showed that the Ca/P ratio obtained varied only in the range between 1.45(1) and 1.62(3). This result thus indicated that by the application of wet chemical processing only substoichiometric or Ca-deficient hydroxyapatite could be obtained.

Sintering of the pellets at 1100°C for 2 h resulted only in a small change of Ca/P ratio in the samples. The Ca/P ratio in the samples varied in the range between 1.45(8) and 1.66(4). Figure 1 illustrates these findings. It shows clearly that the substoichiometric compositions of hydroxyapatite are set by the wet chemical synthesis. The subsequent sintering process obviously did not affect the samples with an initial Ca/P ratio below 1.8. For the samples with a Ca/P ratio of 1.8 and above, the sintering at 1100°C for 2 h resulted in a minor enhancement of the Ca/P ratio. Only the sample with the highest input ratio of Ca/P = 2.0 nearly reached the ideal stoichiometric composition of hydroxyapatite (Ca/P = 1.667) after sintering.

After sintering the nanoscaled hydroxyapatite pellets at temperatures between 900 and 1200°C the densities of the pellets were determined. The dependence of the densities on the sintering temperature in relation to the theoretical

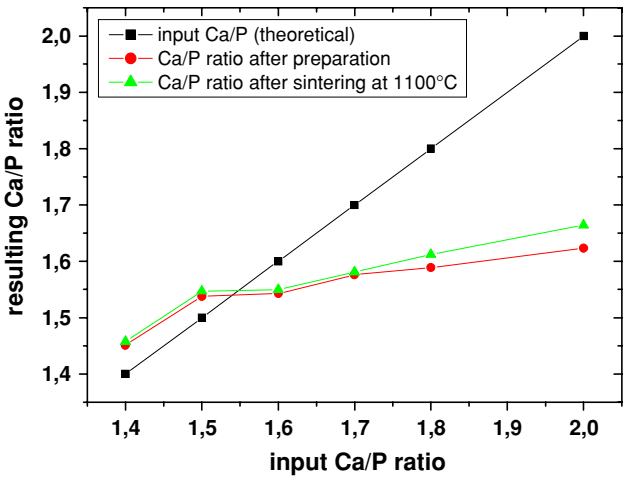

Fig. 1 Ca/P ratio of various hydroxyapatite samples: **a** theoretical (input) Ca/P ratio, **b** measured Ca/P ratio after wet chemical preparation and **c** measured Ca/P ratio after sintering at 1100°C for 2 h

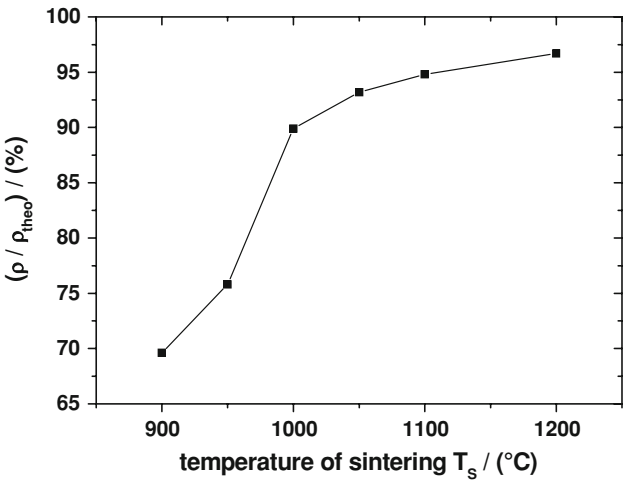

Fig. 2 Densities of hydroxyapatite ceramics versus temperature of sintering

density of hydroxyapatite is depicted in Fig. 2. As can be seen, the main densification takes place at rather low temperatures between 900 and 1000°C. At higher temperatures, the densities of the sintered pellets show saturation at a high level. Finally, by sintering at 1200°C, maximum density values of about 97% of the theoretical density are achieved. Trials to further enhance densities by adding up to 3% PEG as a densifying additive did not result in remarkable improvements of this value.

For all samples, capacitances were determined between 20 Hz and 1 MHz. According to Eq. 1, dielectric constants were calculated on that basis. Figure 3 shows the dielectric constants over the whole range of frequencies for the various Ca/P ratios obtained after wet chemical processing and sintering at 1100°C for 2 h.

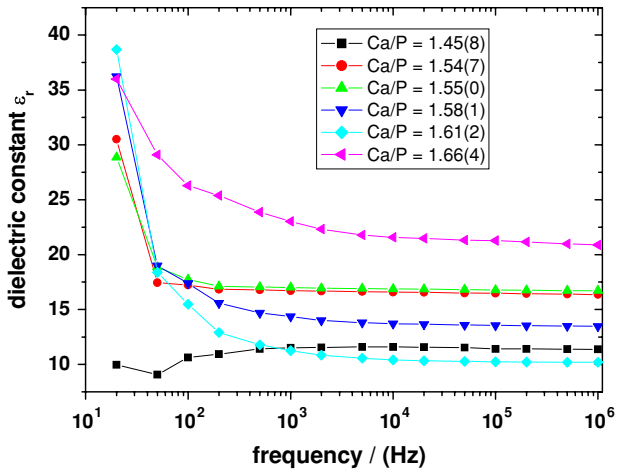

Fig. 3 Dielectric constant of hydroxyapatite ceramics with various Ca/P ratios depending on frequency in the range 20 Hz to 1 MHz

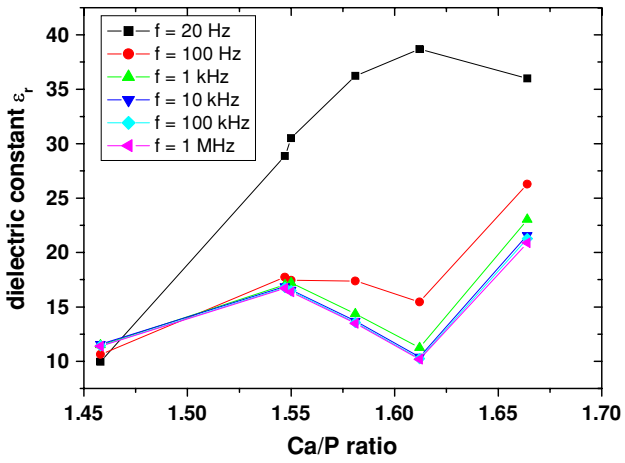

Fig. 4 Dielectric constants of hydroxyapatite ceramics depending on Ca/P ratio for various frequencies sintered at 1100°C for 2 h

The dielectric constants obviously depend on frequency and Ca/P ratio. With one exception, for all samples the dielectric constant decreases with increasing frequencies. This decrease becomes less important towards high and very high frequencies. The frequency dependence can be divided roughly in the frequency region above 1 kHz, where the samples show a "plateau region", in which the dielectric constant only has a small decrease towards higher frequencies and a low frequency region below 1 kHz exhibiting a steep increase of dielectric constant towards low and especially very low frequencies (20 Hz). The only exception from this is the sample with the lowest Ca/P ratio (Ca/P = 1.45(8)) which shows a small decrease of dielectric constant below 100 Hz.

For a broad range of compositions it can be observed that the dielectric constant decreases with an increase of Ca-content. This holds for all Ca/P ratios between 1.54(7) and 1.61(2). Only the two compositions Ca/P = 1.45(8) being the most Ca-deficient sample and Ca/P = 1.66(4) being the Ca-richest sample very near to the ideal stoichiometry of hydroxyapatite behave differently. For the most Ca-deficient sample with Ca/P = 1.45(8), a much higher dielectric constant between 20 and 22 was found. On the other hand, the increase of dielectric constant towards low frequencies was not that distinct as found for the other samples. The Ca-richest sample very near to the ideal stoichiometry of hydroxyapatite with Ca/P = 1.66(4) shows, as already mentioned, a different low frequency behaviour. Also at higher frequencies the dielectric constants are higher compared to the other samples with values around 11.

The findings seem to indicate therefore a Vegard-like behaviour for the range of compositions between Ca/P = 1.54(7) and Ca/P = 1.61(2). The boundaries of this "phase region" are probably located between 1.45(8) and 1.54(7) on one hand and 1.61(2) and 1.66(4) on the other hand. This becomes more obvious if the dielectric constants are plotted against the Ca/P ratio as shown in Fig. 4. The different behaviour at low frequencies (i.e. 20 Hz) is clearly visible. At this frequency the dependency of the dielectric constant on the Ca/P ratio shows only a broad peak with a weak maximum at Ca/P = 1.61(2). The Vegard-like dependence becomes more distinct if the frequency increases. This remains rather unchanged over three orders of magnitude.

Though Silva et al. [36] only report compositions in the range between 1.43 and 1.56, a hint of a Vegard behaviour seems to be present in their findings too. However, their "phase region" is shifted towards slightly lower Ca-contents. The overall dielectric constants they report are between 14.50 and 16.07 compared to values between 10 and 21 obtained in this work. However, data are in good accordance with Fanovich et al. [22] reporting a dielectric constant of 12.61 for a sample sintered at 1200°C, Ikoma et al. [23] reporting a dielectric constant of 20 (at 100 Hz) and 15.4 (at 100 kHz) and Hoepfner et al. [25] reporting dielectric constants of around 12–14.

The dielectric losses of the samples reflecting the chemical and microstructural quality of the samples are comparably low in our work indicating a superior quality of the ceramic samples. We obtained values as low as 10^{-3} in some cases. Figure 5 depicts the dielectric losses of hydroxyapatite ceramics. To work with more comfortable numbers, the losses are given in percent. Differences due to the composition are not so distinct for the losses. Still the samples with the most Ca-deficient and the most Ca-rich stoichiometry behave differently. While the first exhibits lowest losses in the high frequency region and the highest increase of losses towards low frequencies, the latter shows the highest losses at high frequencies. Figure 6 shows

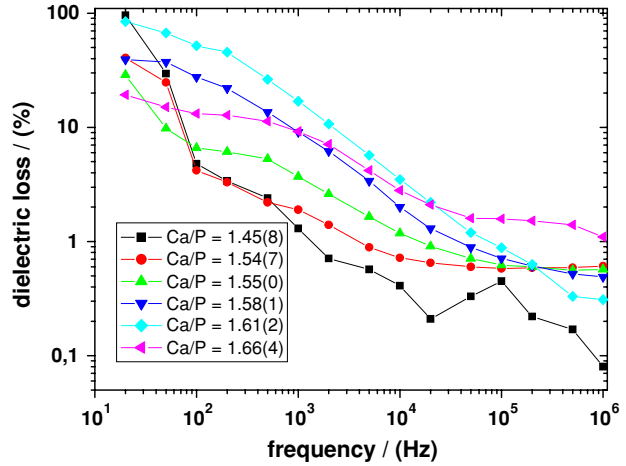

Fig. 5 Dielectric losses of hydroxyapatite ceramics multiplied with a factor of 100 depending on frequency of measurement for samples with various Ca/P ratios sintered at 1100°C for 2 h

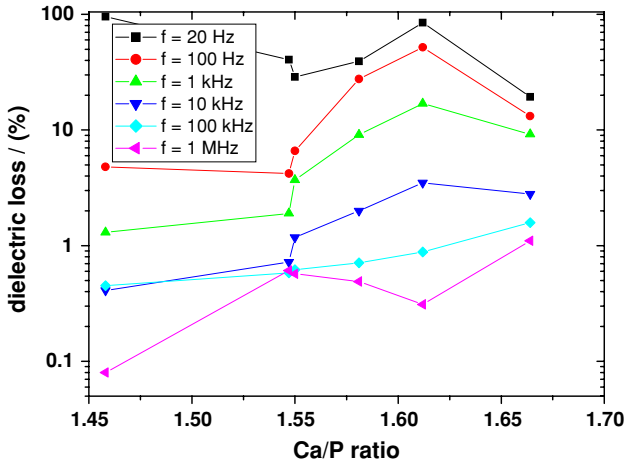

Fig. 6 Dielectric losses of hydroxyapatite ceramics multiplied with a factor of 100 depending on Ca/P ratio for various frequencies sintered at 1100°C for 2 h

again some Vegard-like behaviour for the losses. The difference between the low and the high frequency values is rather small for the Ca-richest composition but very large for the most Ca-deficient one. The dependence of the dielectric loss on the Ca/P ratio is poor. Taking the frequencies above 1 kHz as a rough indicator, the Ca-content seems to have a slightly negative effect i.e., leads to slightly increasing loss values. Though Silva et al. [36] only give loss values for 1 kHz, their dielectric losses are comparably higher in the Ca/P range between 1.46 and 1.56 with values between 9 and 15%.

The dielectric properties were investigated also on samples with a composition of 1.55 sintered at 900 and 1200°C, respectively. The results are illustrated in Figs. 7

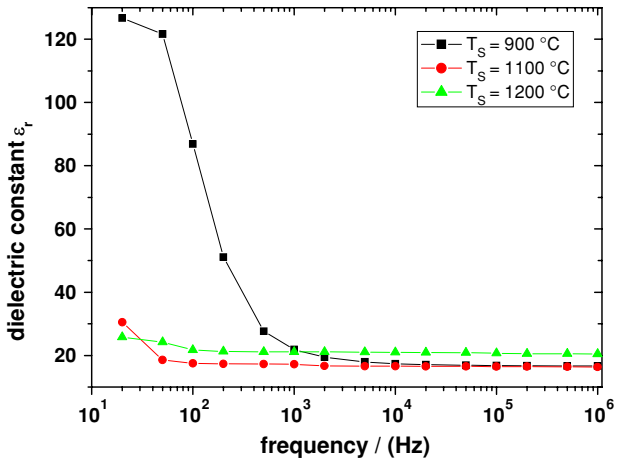

Fig. 7 Dielectric constants of hydroxyapatite ceramics depending on frequency for various temperatures of sintering for Ca/P ratio of 1.55

and 8. While the sample sintered at 1200°C shows higher dielectric constants above 1 kHz, it has only a small increase of dielectric constant at very low frequencies. The lower the temperature of sintering, the more distinct the increase of the dielectric constant is at very low frequencies. If the samples are sintered at 900°C, the increase of the dielectric constant sets on at a frequency as high as 500 Hz. At 20 Hz the sample exhibits a dielectric constant of more than 120. Figure 8 shows that the dielectric loss reflects the quality of microstructure and, in this case, the quality of densification. Therefore, the samples sintered at 1200°C have the lowest loss values and the samples sintered at 900°C have the highest values. The shift of the loss maximum towards higher frequencies for the sample sintered at 900°C is also interesting. Here the loss maximum is between 200 and 500 Hz.

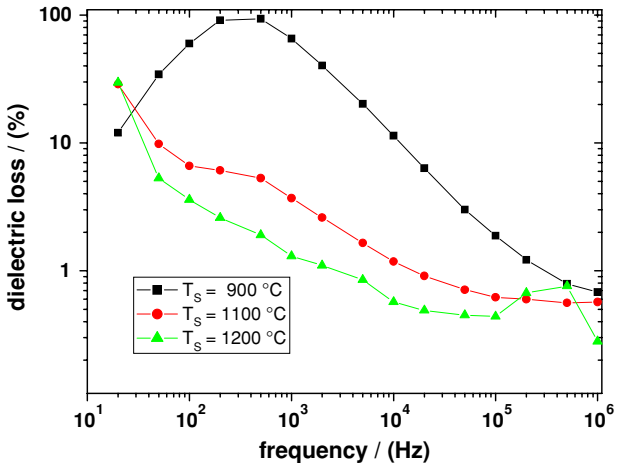

Fig. 8 Dielectric losses of hydroxyapatite ceramics depending on frequency for various temperatures of sintering for Ca/P ratio of 1.55

4 Conclusions

We prepared nanoscaled hydroxyapatite (n-HAp) by a wet chemical precipitation method. The samples with the different stoichiometries were pressed to pellets and sintered at various temperatures between 900 and 1200°C, followed by a characterization of the dielectric properties. With input stoichiometries comprising Ca/P ratios from 1.4 to 2.0, compositions in the substoichiometric range of Ca/P between 1.45(1) and 1.62(3) were obtained after preparation. Sintering at 1100°C for 2 h leads to final values of Ca/P ratio between 1.45(8) and 1.66(4), which means that it leaves the Ca/P values set by the chemical processing rather unchanged. The dielectric constant generally tends to increase with an increasing Ca-content. Different behaviour was observed for low frequencies (below 10^3 Hz) and for Ca-deficient (Ca/P = 1.45(8)) as well as for very Ca-rich (Ca/P = 1.66(4)) compositions. Values of the dielectric constants are mainly between 10 and 20 between 1 kHz and 1 MHz. A Vegard-like behaviour is indicated for the dependence of the dielectric constant from the Ca/P ratio. Samples with rather low dielectric losses were obtained. A slight increase of loss values with increasing Ca-content was observed for frequencies above 1 kHz. A higher or lower temperature of sintering (900 or 1200°C instead of 1100°C) enhances the dielectric constants especially at low frequencies. The higher the temperature of sintering, the lower the dielectric losses are.

The reasons for the observed complex behaviour with regard to the influence of the Ca/P composition remain still unclear. Further investigations of the dielectric properties in relation to the Ca/P ratio and the correlation of these data with structural and microstructural data could bring more insight into the complex theme.

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