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ELECTRICAL PROPERTIES OF BIOACTIVE CERAMICS IN A BROAD FREQUENCY AND TEMPERATURE RANGE

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Abstract. Measurements of the complex ac conductivity at frequencies $0.1\text{Hz} \leq \nu \leq 500\text{MHz}$ and temperatures $10\text{K} \leq T \leq 600\text{K}$ are reported for a bioactive glass ceramic which contains tridymite, fluoro apatite and crystallites exhibiting NASICON structures. The data show a low frequency dispersion which for high frequencies turns into a power law behaviour $\sigma' \propto \nu^s$ with $s = 0.7$, characteristic for hopping conductivity. In addition, two relaxation processes have been detected. The relaxation dynamics of one of these processes obeys an Arrhenius law. The other process exhibits significant deviations from Arrhenius behaviour. Both relaxation processes can be assigned to distinct crystalline phases of the glass ceramic.

1. Introduction

Recent advances in the preparation of glass ceramics have led to the development of numerous applications of these materials. One example is the use of phosphate based glass ceramics as hard tissue replacement [1]. These ceramics are bioactive, i.e. a linkage of natural and artificial bone is achieved by exchange of ions. Therefore it is of vital importance to obtain knowledge about the nature of the ionic transport processes in these materials. For this purpose measurements of the complex ac-conductivity in a broad frequency and temperature range are an ideal tool. Here we present the results of measurements of the ac-conductivity of an alkali-phosphate based bioactive glass ceramic in a temperature range $10\text{K} \leq T \leq 600\text{K}$ and a frequency range of $0.1\text{Hz} \leq \nu \leq 500\text{MHz}$.

2. Experimental Details

The glasses were prepared by melting at 1100°C and quenching. Devitrification is achieved by a subsequent heat treatment at temperatures well above 500°C . To obtain homogeneous bulk crystallization, a nucleation agent (FeO) was added. Apart from AlPO_4 , apatite $[\text{Ca}_5(\text{PO}_4)_3\text{X}]$, $\text{X}=\text{F,H}$ and an iron containing orthophosphate with $\text{NaZr}_2(\text{PO}_4)_3$ structure (NASICON-type), x-ray diffraction, electron microscopy and nuclear magnetic resonance have revealed the appearance of three structurally unknown pyrophosphates [2]. Sample A, crystallized at 700°C , contains all phases mentioned above. A glass ceramic with apatite as main crystalline phase can be obtained if the glass is heated at 520°C (Sample B). For comparison, a glass ceramic with ZrO_2 as nucleation agent was prepared (Sample C). It contains $\text{NaZr}_2(\text{PO}_4)_3$ as the primary crystalline phase.

Platelets of typical dimensions $5 \times 10 \times 0.5 \text{ mm}^3$ have been covered on opposite sides by silver paint or gold electrodes to form electrical contacts.

Measurements of the complex conductivity $\sigma = \sigma' + i \sigma''$ were carried out in a broad frequency and temperature range using different experimental setups. For frequencies $0.1 \text{ Hz} \leq \nu \leq 100 \text{ Hz}$ a frequency response analyser supplemented with a high impedance preamplifier has been used (Schlumberger 1260 and Chelsea dielectric interface). The frequency range $20 \text{ Hz} \leq \nu \leq 1 \text{ MHz}$ was covered using the autobalance bridge HP4284. The high frequency data ($\nu \geq 1 \text{ MHz}$) were recorded using an HP4191 impedance analyser connected to the cooling/heating device via an air line [3]. In addition, time domain measurements were obtained by recording the time dependent current after the application of a constant voltage on the sample.

Most of the measurements were performed in a nitrogen gas heating system covering a temperature range $10 \text{ K} \leq T \leq 600 \text{ K}$. In addition, a closed cycle refrigerator and various ovens have been used.

3. Results and discussion

Fig. 1 shows the temperature dependence of the real part of the conductivity σ' of the glass ceramic A for various frequencies. Obviously, different processes contribute to the conductivity and give rise to a rather complicated behaviour:

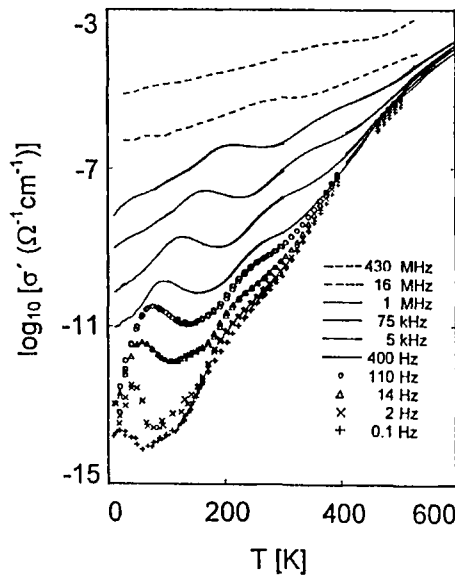


Fig. 1. Temperature dependence of the real part of the conductivity σ' of sample A for various frequencies.

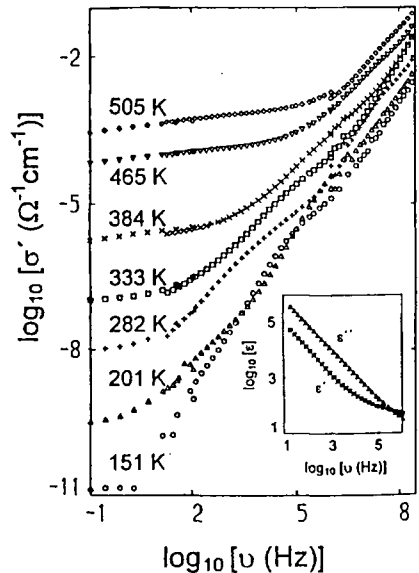


Fig. 2. Frequency dependence of the real part of the conductivity σ' of sample A for various temperatures. The inset shows the frequency dependence of the complex dielectric constant for $T=505 \text{ K}$.

i.) At high temperatures and low frequencies all $\sigma'(T)$ curves approach the one obtained at 0.1 Hz which therefore could be interpreted as dc-limit, at least above approximately 350K. For $T > 350$ K $\sigma'(T)$ can be fitted by an Arrhenius law, $\sigma' = \sigma_0 \exp(-E_{dc}/k_B T)$. This finding implies a thermally activated process. An energy barrier of 0.71 eV can be deduced.

ii.) Ac-conductivity is the dominant process in this material, especially at frequencies $\nu > 1$ MHz.

iii.) In addition to these global transport processes there are at least two local relaxation processes which most probably are due to single particle hops of ions in local double well potentials.

Additional information on the ac-conductivity can be obtained from Fig. 2 where we have plotted the frequency dependence of σ' for various temperatures in a double logarithmic representation. At high frequencies and low temperatures the overall behaviour is governed by a power law, $\sigma' \propto \nu^s$, with $s \approx 0.7$ which is typical for hopping conductivity [4]. Superimposed on this power law are two peaks which are caused by the same processes as the peaks in Fig. 1. At low frequencies and high temperatures $\sigma'(\nu)$ changes to a very weak frequency dependence, $\sigma' \propto \nu^{0.07}$. In this range the real and the imaginary parts of the dielectric constant ϵ decrease with the same power law which is demonstrated for 505 K in the inset of Fig. 2. Such a behaviour, called Low Frequency Dispersion (LFD) is often explained in terms of electrochemical processes [5].

At the highest temperatures and for very low frequencies the slope of $\sigma'(\nu \rightarrow 0)$ becomes steeper again which indicates the onset of blocking electrode effects. The blocking of the electrodes has been confirmed by time domain measurements and measurements at very high temperatures ($600 \text{ K} < T < 1000 \text{ K}$) which corroborates the assumption that ions are the dominant charge carriers in this material.

To gain closer insight into the relaxation dynamics we have plotted in Fig. 3 the frequency of the peak maximum (determined after subtraction of the conductivity background) vs. temperature in an Arrhenius representation. The high temperature peak (+) exhibits thermally activated behaviour, $\nu_p = \nu_0 \exp(-E_1/k_B T)$ with $E_1 = 0.52$ eV and $\nu_0 = 10^{13}$ Hz. The temperature dependence of the low temperature relaxation (x) can be described by an Arrhenius type of behaviour for temperatures $T > 150$ K with parameters $E_2 = 0.21$ eV and $\nu_0 = 10^{11}$ Hz. However, there are clear deviations from the thermally activated behaviour at lower temperatures.

To find out which local environments within the glass ceramic give rise to each of the two relaxation peaks, we have performed comparative measurements in the glass ceramics B and C which have fluoro apatite or $\text{NaZr}_2(\text{PO}_4)_3$ (NASICON-structure) as primary crystalline phases, respectively. Both samples exhibit a single relaxation process. The peak found in glass ceramic B (Δ) follows an Arrhenius behaviour with $E = 0.6$ eV and $\nu_0 = 10^{15}$ Hz. The temperature dependence of the relaxation peak of sample C (L) shows very good agreement with the temperature dependence of the high temperature process in sample A. Therefore in glass ceramic A this process can be attributed to the crystallites with NASICON-structure.

For the low temperature relaxation in sample A an equivalent peak has been found neither in sample B nor in sample C. The deviation from Arrhenius behaviour of the low temperature process can be ascribed to quantum mechanical tunneling or to two different energy barriers for high and low temperatures. Both phenomena appear possible in hydroxy apatite because (i) the proton of the OH^- ion has a high tunneling probability due to its low mass and (ii) two energy barriers could arise from the motion of the whole OH^- ion at high temperatures and a hopping of the proton between two positions on either side of the oxygen at low temperatures. Indeed two energy barriers of 0.2 eV and 0.02 eV have been found in hydroxy apatite crystals by dielectric measurements [6].

In order to discuss the relevance of our results in relation to the biochemically important electrolyte transport it is pointed out that the mobile ions most likely are Na^+ , Ca^{2+} , and OH^- . The multitude of relaxational processes in the bioactive material points to the existence of different pathways which may be adapted to the various charge carriers. The ion transport across the interface connecting artificial and natural tissue appears to be of particular importance for the understanding and optimising of the surgical application. In order to address these questions further electrochemical studies would certainly be most helpful.

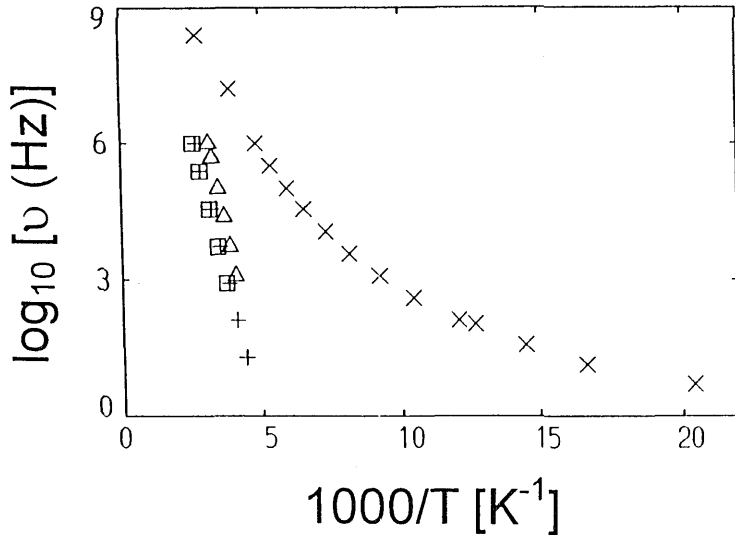


Fig. 3. Logarithm of the frequency of the relaxation peak maximum versus inverse temperature for samples A (x, +), B (Δ) and C (□).

4. Summary

The complex ac-conductivity of a bioactive alkali-phosphate glass ceramic has been measured in a broad frequency and temperature range. At high frequencies and low temperatures hopping conductivity is the dominant charge transport process. In addition, at low frequencies and high temperatures LFD and blocking electrode effects have been found which deserve further attention in connection with the surgical application of this material. The blocking of the electrodes gives evidence for ions as dominant charge carriers. In addition, there are two relaxation processes superimposed on the conductivity. The high temperature process has been found to arise from the NASICON structured crystalline component of the sample. Most probably, the low temperature process is associated with motions of OH^- ions in the hydroxy apatite phase of the ceramic.

Acknowledgements

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