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Bioactivity characterization of 45S5 bioglass using TL, OSL and EPR: Comparison with the case of 58S sol-gel bioactive glass

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ABSTRACT

The current work exploits the effective application of thermoluminescence (TL), optically stimulated luminescence (OSL) and the possibility of applying Electron Paramagnetic Resonance (EPR) for the discrimination between different bioactive responses in the case of the 45S5 bioactive glass (SiO_2 45, Na_2O 24.5, CaO 24.5, P_2O_5 6 in wt%), which was synthesized through melting process. These techniques are suggested mainly due to their low spectroscopic detection thresholds. The original 45S5 in grain size range of 20–40 μm was immersed in the Simulated Body Fluid (SBF) for various different immersion times ranging over one week. In this work the 110 °C TL peak, a specific OSL component and the EPR signal at $g = 2.013$ ascribed to oxygen hole center (OHC) are used due to their sensitivity to the different bioactive responses. For all luminescence and EPR components, the intensity plot versus immersion time yields sharp discontinuities, resulting in effective probes regarding the timescale for both the beginning as well as the end of the procedure of the crystalline HCAp formation respectively. On the contrary to the smooth decreasing pattern of both luminescence entities, the peak to peak amplitude of the EPR signal indicates an initial increase for the initial 16 min of immersion, followed by a further decrease throughout the immersion time duration. The discontinuities monitored for both sensitivity of TL, OSL and EPR, in conjunction with the discontinuities monitored for the sensitization of TL and OSL, when plotted versus immersion time, provide an individual time scale for each one of the chemical reactions involved in the five steps of the aforementioned procedure. According to the authors' best knowledge, scarce characterization techniques could provide this time scale frame, while it is the first time that such an application of OSL and EPR is attempted. Finally, the bioactive response of the 45S5 bioglass was compared with that of the 58S sol-gel bioactive glass, in terms of the timescale of these five stages required for the final formation of the HCAp. The techniques of luminescence and EPR which take advantage of trapped charges are proposed as alternative cheap and prompt effective techniques towards discrimination between different bioactive responses in bioactive glasses.

1. Introduction

Bioactive glasses consist a specific group of synthetic, surface reactive, amorphous silica-based, glass-ceramic biomaterials with high biocompatibility [1]. The first bioactive glass manufactured ever was the bioglass 45S5 [2], also known as the Hench bioglass, a melt derived, quaternary glass-ceramic constituting of SiO_2, Na_2O, CaO and P_2O_5 in specific proportions. The basic feature of this latter material includes the weight percentage of SiO_2 in the glass matrix, being <60%, in conjunction to its increased content of Na_2O and CaO and the appropriate corresponding value of the ratio CaO/P_2O_5. Of course, binary and ternary bioglasses and even bioglasses with much more complex formulations have been synthesized; for an extended review the readers could refer to [3].

Two basic characteristics are correlated with bioactivity; the value of the ratio $SiO_2/[CaO + Na_2O + P_2O_5]$ [4] and the material porosity [5] related to amorphous phase. According to the essential requirement for a bioactive material [6], the formation of bone-like apatite on its surface when implanted in the living body indicates that the material bonds with bone rapidly; stimulating bone growth away from the bone–implant interface is also very much welcome [7].

Since the discovery of bioglass [2,8], much research has been devoted to the synthesis and characterization of novel biomedical materials with advanced osteoinductive and osteoconductive properties, mostly glasses and glass-based materials, as these are reported to be able to

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stimulate more bone regeneration than other bioactive ceramics [7]; these materials have assumed substantial interest and importance because they can be used in repairing damaged living tissues and organs by interacting with biological systems. For an overview regarding emerging applications of bioglasses in contact with soft tissues please refer to [5,9,10]. The cornerstone of the bone-bonding of any bioactive glass is the ability of the implant-glass to chemically react with the living tissue in the presence of body fluids, through a number of sequential chemical surface reactions, the final product of which is a carbonated hydroxyapatite (hereafter HCAp) layer. Hench and West [11] proposed a complex process for the formation of apatite layer involving five main reaction stages [2,12] including: step 1) Dealkalization of the surface by exchange of cations (Na^+ or Ca^{2+}) with H^+ or H_3O^+; step 2) Loss of soluble silica in form of $Si(OH)_4$; step 3) Repolymerization of $Si(OH)_4$ leading to condensation of a SiO_2-rich layer on the glass surface; step 4) Migration of Ca^{2+} and PO_4^{-3} groups to the surface forming CaO—PO_4^{-3} clusters on the top of the SiO_2-rich layer, followed by growth of the amorphous CaP (CaO-P_2O_5) film; step 5) Crystallization of the amorphous CaP by incorporation of OH^-, CO_3^{-2} anions from the solution to form a hydroxylcarbonate ($Ca_5(PO_4)_3(OH)$, HCAp) apatite layer. Recently, the opportunity for in vivo apatite formation was elucidated, using the so-called simulated body fluid (hereafter SBF), including ion concentrations nearly equal to those of human blood plasma [6]. Therefore, in vivo bone bioactivity of various types of materials, which can be predicted through the apatite formation on its surface in SBF, can be tested in vitro, by the apatite formation in SBF, as the latter simulates the blood plasma.

Among the extended literature related to the study on the various properties of several types of bioglasses, two major groups of publications could be easily resolved, based on the main research topic. In the framework of the first group, studies aim at the overall characterization of the bioactive material/glass response, by monitoring the gradual crystallization of an initially amorphous HCAp phase, emphasizing thus to the apatite identification. To date, among the available techniques used for structural characterization of several biomaterials, Scanning Electron Microscopy (SEM), X-Ray Diffraction (XRD), Differential Thermal Analysis (DTA) and Fourier Transformed Infrared Spectroscopy (FTIR) stand as the most widely applied structural characterization techniques; for examples, the readers could refer to [5,13–16,17,18–20]. Nevertheless, as it was also recently pointed out [21], all these aforementioned techniques bear certain deficiencies, are time consuming and not well suited to detailed and rapid monitoring of changes regarding the bioactive behaviour of the biomaterials [21–23]. Another topic of great interest is the identification, characterization and study of each one of these aforementioned chemical steps/stages of the glass dissolution mechanism and the apatite formation. Regarding stages 1 and 2, the literature is quite extensive [24–26] whereas the study of stages 3 to 5 is limited but conclusive. Nevertheless, a big lack in the literature deals with the identification of the time scale over which each one of these aforementioned steps are taking place [27].

Consequently, the need for a more reliable and more accurate technique towards bioactivity characterization becomes of great interest, in the framework of the requirement for high sensitivity and discrimination associated with identifying the presence and behaviour of both host and precipitate phase transitions. Thermoluminescence (hereafter TL) has been increasingly used for dosimetric purposes that presently constitute an important part of solid-state dosimetry [28,29]. However, besides dosimetry and dating, several alternative and, at first sight, unlikely applications have either been reported or just attempted. A full list of these applications would, undoubtedly, include solid state crystal and defect structure analysis [30]. Recently, the usefulness of TL was investigated as an alternative experimental technique towards the effective discrimination between different bioactive responses for the case of the irradiated 58S bioactive glass [21,31]. The 58S bioactive glass stands as the most characteristic sol-gel derived, silica based ternary glass ceramic, containing SiO_2, CaO and P_2O_5. Results presented in the aforementioned citations strongly support the usefulness of the 110 °C TL peak as a bioactivity probe. For a review on the reasons supporting this latter conclusion the reader could refer to [21]; nevertheless, in a nutshell, the most important are the following: (a) the intensity of the 110 °C TL peak was proven to be very sensitive to the different bioactive responses, indicating a strongly decreasing pattern with increasing time immersion in SBF and (b) the ability of this latter TL peak shape, intensity and discontinuities in yielding a timescale regarding the immersion period for the beginning of some among the initial stages included in the bioactivity sequence, the beginning of amorphous CaP formation as well as the end of crystalline hydroxyl-apatite formation respectively.

The present study follows on directly from this latter aforementioned citation [21], which ends by questioning whether the same technique, namely TL, could be effectively used for the case of 45S5 bioactive glass as well. The aim of the present paper is threefold: (a) to examine whether TL could provide, for the case of 45S5, bioactivity probes as effective as for the case of the 58S, (b) to study the feasibility of both optically stimulated luminescence (hereafter OSL) as well as electron paramagnetic resonance (hereafter EPR) as a bioactivity marker and (c) to compare the bioactive response that was monitored by TL for both cases of 58S as well as 45S5, in terms of the timescale of each chemical stage. While luminescence offers detection of phase inclusions or surface defects even below the ppm levels [22,30], for the case of EPR the detection threshold could be even better, since 10^9–10^{10} spins could be easily detected [32]. The low detection threshold of both luminescence and EPR, in combination with the chemical composition of the 45S5 bioactive glass, consisting of 45% silica, constitute two powerful motivations for further investigation of these techniques towards their viable use as proxies for bioactivity studies.

2. Experimental

2.1. Materials: synthesis and handling

The material subjected to the present study was the melt-derived Bioglass® 45S5, also known as the Hench bioglass, with composition (in weight %): 45% SiO_2, 24.5%Na_2O, 24.5% CaO and 6% P_2O_5 [33]. The production of 45S5 bioactive glass has been carried out through the melting process, in which precursors are mixed homogeneously and melted at a high temperature (>1300 °C). The product is subsequently quenched in order to form amorphous glass [16].

Handling of the material was similar to that previously reported by [21] for the case of 58S. The samples subjected to the present study include grains in the dimension range between 20 and 40 μm, which were initially crushed and subsequently immersed in the SBF for 16 different durations ranging between 0 and 6 days. All experiments were carried out under solution renewal conditions [6]. After immersion, grains of the reacted powders were selected and deposited on stainless steel discs of 1 cm^2 area. For all subsamples corresponding to different immersion times, three aliquots were prepared. Reproducibility in masses of all subsamples throughout the entire range of the immersion time intervals was better than 5%.

2.2. Apparatus

All TL measurements were performed at the nuclear physics laboratory of the Physics Department, Aristotle University of Thessaloniki, Greece, using a Littlemore type 711 setup, with a P/M tube: EMI 9635QA bialkali (Sb K–Cs) and a thermo couple type: 90/10 Ni/Cr and 97/03 Ni/Al, filter transmitting in the 320–440 nm range. In all cases, a beta-test dose was provided by a $^{90}Sr/^{90}Y$ beta source delivering 1.72 Gy/min. All TL measurements were performed in a nitrogen atmosphere with a constant heating rate of 2 °C/s in order to avoid significant temperature lag, up to a maximum temperature of 500 °C.

All OSL measurements were performed at the Institute of Nuclear Sciences, Ankara University, Turkey, using a RISØ TL/OSL reader