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TEM Analysis and Insights into the Physico-mechanical Characteristics of CeLa-Substituted Bio-Glass Ceramics

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Abstract

Among rare earth metals, bio-glass ceramics have gained significant attention for their potential applications in bone tissue engineering and regenerative medicine due to their biocompatibility and bioactivity. This research paper investigates the physico-mechanical properties of CeLa-substituted bio-glass ceramics using Transmission Electron Microscopy (TEM) analysis. The study aims to elucidate the microstructural features, crystalline phases, and mechanical behavior of CeLa-substituted bio-glass ceramics, providing valuable insights into their suitability for biomedical applications. The TEM analysis reveals intricate details of the material's nanostructure, highlighting the influence of CeLa substitution on phase composition, grain morphology, and mechanical performance. The findings contribute to a better understanding of the structure-property relationships in CeLa-substituted bio-glass ceramics, guiding the development of advanced biomaterials for bone regeneration and tissue repair.

Keywords: *Bio-Glass Ceramics, Bone Tissue Engineering, CeLa Substitution, Earth Metals, Mechanical Properties, TEM*

1.0 Introduction

In the realm of biomaterials, the quest for bioactive substances that mimic the biochemical characteristics of bone has led to the development of notable innovations. Among these, the renowned bioactive glass 45S5 has demonstrated exceptional properties in bonding to both soft and hard tissues[1]. Pioneered by Hench, the formulation of 45S5 bioglass with a mole percent composition of 46.1 SiO_2-24.4 Na_2O-26.9 CaO-2.6 P_2O_5 marked a significant milestone in ceramic advancement[2,3], sparking a field that has since produced numerous novel materials and products[4]. Innovations in glass technology have involved the incorporation of diverse earth metals such as cerium, lanthanum, aluminum, and silver to enhance their bioactive responses[5-7].

This study aims to evaluate the impact of cerium and lanthanum (CeLa) incorporation on the in vitro properties of bioactive glass, with particular emphasis on their microstructural characteristics elucidated through Transmission Electron Microscopy (TEM) analysis. Previous research has explored the integration of cerium particles into dental ceramic materials to emulate natural teeth[8]. Cerium, known for its bacteriostatic properties and low toxicity[9,10], is chosen for inclusion in the bioactive base glass due to its favourable effects on osteoblastic cell proliferation compared to other particles commonly found in base glasses[11]. Subsequently, these advanced glasses will undergo immersion in Simulated Body Fluid (SBF) to simulate the formation of a bone-like apatite

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layer on their surfaces, a phenomenon verified through Fourier Transform Infrared Spectroscopy (FTIR).

2.0 Material and Methods

2.1 Composition and Glass Preparation

The weight percentage (wt%) of CeO_2 to La_2O_3 content in the 45S5 glass is specified in Table 1. Fine quartz serves as the source of SiO_2, while analytical grade CaO, Na_2O, and P_2O_5 are individually utilized through melting. Precise amounts of analytical reagent grade CeO_2 and La_2O_3 are incorporated separately into the batch intended for the partial replacement of SiO_2. The raw materials for various samples are accurately weighed, followed by thorough mixing of different batches for 50 minutes in a pestle mortar.

A bioactive material is expected to exhibit distinct biochemical behavior and possess biomechanical capabilities. The 45S5 stands out for its exceptional ability to bond with both soft and hard tissues. This investigation focuses on examining how the introduction of CeLa influences the thermal and in vitro properties of bioactive glass. Cerium ions (Ce^{4+}) have previously been integrated into dental materials to replicate the inherent fluorescence of natural teeth[12]. The notable bacteriostatic properties and low toxicity of cerium and lanthanum make them stand out. In the formulation of the bioactive glass base, the inclusion of cerium and lanthanum is being explored, driven by their favorable impact on the proliferation of osteoblastic cells when compared to other particles found in the foundational bioactive glasses[13]. The current research is dedicated to the design and characterization of glasses modified with CeLa.

2.2 Preparation of Simulated Body Fluid (SBF)

The prepared glass samples were immersed in Simulated Body Fluid (SBF) at 37.4 ºC for various durations ranging from 1 to 13 days. The SBF solution was prepared according to the method described by Kokubo *et al.*[14]. The pH of the solution was measured using a digital pH meter after the samples were submerged for different durations are shown in Table 1.

2.3 TEM Analysis

The TEM micrographs of the CeLa sample are depicted in Figure 1 (a), accompanied by the corresponding selected area diffraction patterns presented in Figure 1 (b). The TEM image reveals that the CeLa nanoparticles exhibit a spherical shape. Additionally, the diameter range of the sample varies between 300 and 600 nm.

2.4 Density, Microhardness, and Flexural Strength Measurements

The glass sample density was measured with (ASTM C20-00) involving distilled water a submersion fluid. The calculations were completed at 24˚C. The weight of the glass was estimated by a digital balance (Wensar HPB 220) with a precision of ± 0.00001 g (1).

$$Density(\rho) = \frac{W_a}{W_a - W_b}\rho_b \quad \text{---------- (1)}$$

Where W_a & W_b are sample weights in air and water respectively. is the density of fluid.

For Microhardness, with accurately sized samples being surface finished after that hardness accomplished by a digital hardness analyzer, the size of the samples was 6mm x 6mm x 6mm as indicated by ASTM: C730-98. The indentation load range was going from 20 mN and 3000 mN, at the speed of 2 mm/s, and was allowed to equilibrate for 16 seconds before test. Microhardness (H) was assessed utilizing equation (2),

$$Microhardness(H) = 1.854\frac{P}{d^2} \quad \text{---------- (2)}$$

Here P is the load applied to the samples and d (m) is the diagonal of the marks. The rectangular shape glass was ground and cleaned for 30×12×12 mm dimensions. Presently samples were prepared for the 3-point bending. The test was performed at 24 ºC utilizing an Instron UTM (H10KL, Tinius Olsen, USA) with a crosshead speed of 0.5 mm/min and a full-scale 10kN load. Flexural strength (σ) was assessed by ASTM C1674-11 as (3),

$$Flexural\ Strength(\sigma) = \frac{3PL}{2bh^2} \quad \text{---------- (3)}$$

Table 1. Ion content (mM/litre) of SBF and blood plasma

Ion	Na^+	K^+	Ca^{2+}	Mg^{2+}	HCO_3^-	Cl^-	HPO_4^{2-}	SO_4^{2-}
Simulated Body Fluid	142	5	2.5	1.5	4.2	148	1	0.5
Blood plasma	142	5	2.5	1.5	27	103	1	0.5

Where *P* is the applied load for the specimen to break, *L, b,* and *h* are the span length, breadth, and height of the specimen correspondingly.

3.0 Result and Discussion

3.1 Transmission Electron Microscopy Analysis

Transmission Electron Microscopy (TEM) analysis provides valuable insights into the microstructural characteristics of materials at the nanoscale. In the context of the investigation on CeLa-substituted bio-glass ceramics, TEM analysis offers detailed information on the morphology, size, and distribution of CeLa nanoparticles within the glass matrix. The TEM micrographs of the CeLa2 sample, as depicted in Figure 1a, provide visual evidence of the morphology of CeLa nanoparticles. The images reveal spherical nanoparticles dispersed throughout the glass matrix, indicating successful incorporation of CeLa dopants into the bio-glass ceramics. The spherical shape of the nanoparticles suggests uniform nucleation and growth during the synthesis process, which is crucial for achieving homogeneous dispersion within the glass matrix.

Moreover, the diameter ranges of the CeLa nanoparticles, as observed in the TEM images, varies from 200 to 500 nm. This size range is consistent with the intended nanoscale dimensions desired for bioactive materials, as it promotes favorable interactions with biological tissues and enhances surface reactivity. The presence of nanoparticles within this size range suggests effective control over the synthesis parameters, leading to the desired microstructural features of the CeLa-substituted bio-glass ceramics.

In addition to the microstructural information provided by TEM imaging, selected area diffraction patterns in Figure 1 (b) offer insights into the crystalline nature of CeLa nanoparticles. By analyzing the diffraction patterns, it is possible to identify the crystalline phases present in the CeLa-substituted bio-glass ceramics. The diffraction patterns may reveal characteristic peaks corresponding to specific crystal planes, allowing for phase identification and crystallographic analysis.

Overall, TEM analysis plays a crucial role in characterizing the microstructure of CeLa-substituted bio-glass ceramics, providing essential information for understanding the influence of CeLa incorporation on the properties and performance of the materials. The observed morphology, size distribution, and crystalline nature of CeLa nanoparticles contribute to a comprehensive understanding of the structural features that govern the bioactivity and mechanical behavior of the bio-glass ceramics.

3.2 Flexural Strength, and Microhardness

The strength of the base glass (Figure 2) showed a *(H)* and of 8.4 GPa and 69.12 MPa, respectively. However, the strength of substituted bioglass® shows improvement in *(H)*- (Ce 1C, Ce-2C, La-1C and La-2C are 6.98, 7.1, 8.2 and 8.3 GPa) and - (51.2, 57.11, 64.12 and 69.22 MPa) with increasing substituent concentration. Therefore, by

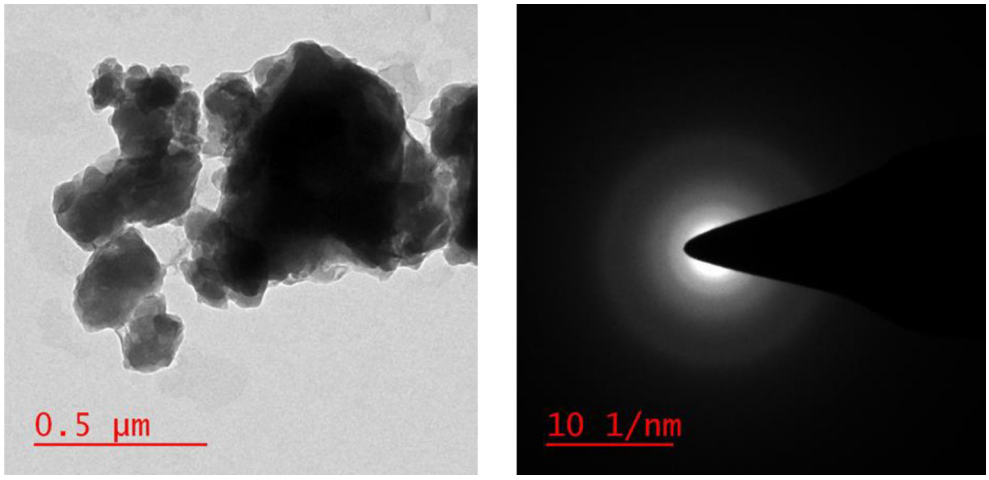


Figure 1. **(a)** Bright-field transmission electron microscopy (BF-TEM) image of CeLa2 sample and **(b)** Selected area diffraction pattern of CeLa2 sample.

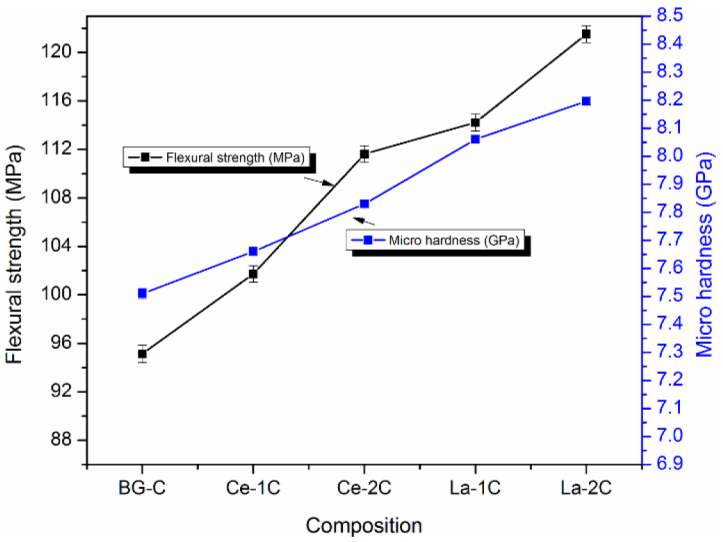


Figure 2. Flexural strength and microhardness of substituted bioglass samples.

densifying the glass structure, the *(H)* and were improved by particle exchange (REE).

4.0 Conclusion

In conclusion, the study on 45S5 bioactive glasses substituted with varying concentrations of La_2O_3 and CeO_2 alongside SiO_2 revealed significant findings regarding their physico-mechanical properties and in vitro bioactivity. It was observed that the flexural strength and microhardness of the substituted samples increased with higher concentrations of oxides. Additionally, nucleation and crystallization temperatures decreased with increasing concentrations of La_2O_3 and CeO_2, indicating enhanced glass-forming ability. Furthermore, the presence of Ce^{4+} and La^{3+} ions in the modified 45S5 glass was confirmed through X-Ray Diffraction (XRD) analysis, indicating the incorporation of these Rare Earth Elements (REEs) into the glass matrix. This suggests that the mechanical and biological properties of the glasses were enhanced with the addition of La_2O_3 and CeO_2.

In addition to these findings, it is important to note that TEM analysis was conducted to provide insights into the nanostructure of the modified bioactive glasses. TEM analysis revealed the presence of Ce^{4+} and La^{3+} nanoparticles dispersed within the glass matrix, confirming their successful incorporation. The observed nanostructure plays a crucial role in determining the bioactivity and mechanical properties of the glasses, further supporting the conclusions drawn from the study.

Overall, the findings suggest that the modification of 45S5 bioactive glasses with varying concentrations of La_2O_3 and CeO_2 enhances their physico-mechanical properties and in vitro bioactivity, making them promising candidates for bone tissue engineering and regenerative medicine applications.

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