J Nanostruct 15(4): 1718-1723, Autumn 2025

RESEARCH PAPER

Modification of Bioactive Glass-Ceramic by ZrO_2/Ag_2O Micro/Nanocomposite for Biomedical Applications

Hadeer Sadeq Abd Ali *, Ali Güngör

Karabuk University, Turkey

ARTICLE INFO

Article History:
Received 07 June 2025
Accepted 19 August 2025
Published 01 October 2025

Keywords:
Bioactive glass-ceramic
Biomedical applications
Micro/nanocomposite
ZrO_2/Ag_2O

ABSTRACT

Bioactive glass-ceramics are utilized as bone tissue replacements due to their bioactivity, compatibility, and their capacity to form a crystallized hydroxyapatite (HA) bonding layer, which closely mimics the composition and structure of the inorganic component of bone minerals. The main objective of this research is to assess the effect of adding ZrO_2 and Ag_2O on the properties of bioactive glass-ceramics based on a composition of 45 wt.% SiO_2, 24.5 wt.% Na_2O, 24.5 wt.% CaO, and 6 wt.% P_2O_5. The bioactive glass-ceramics were synthesized using traditional glass-melting techniques at 1200°C for 2 hours, followed by compression and sintering at 950°C. X-ray diffraction analysis confirmed the formation of $Na_2CaSi_3O_8$ and $Na_2Ca_2Si_3O_9$ phases in the bioactive glass-ceramic structure. Mechanical and physical testing revealed that increasing the ZrO_2 and Ag_2O content improved bending strength, compressive strength, microhardness, and density, while reducing porosity. FTIR spectroscopy confirmed the presence of Si-O-Ag and Zr-O-Si bonds in the material. The biological testing involved immersing the samples in simulated body fluid (SBF) for 21 days. Scanning electron microscopy (SEM) analysis showed the formation of apatite layers on the surface of the samples, providing evidence of their bioactivity. Overall, the results of this study indicate that partial replacement of CaO with ZrO_2 and Ag_2O in the 45S5 glass-ceramic enhances both mechanical and biological properties, suggesting that the modified glass-ceramic is well-suited for biomedical applications.

How to cite this article
Ali H., Güngör A. Modification of Bioactive Glass-Ceramic by ZrO_2/Ag_2O Micro/Nanocomposite for Biomedical Applications. J Nanostruct, 2025; 15(4):1718-1723. DOI: 10.22052/JNS.2025.04.020

INTRODUCTION

Hench and his colleagues pioneered the development of bioactive glasses, most notably the 45S5 Bioglass[1]. Both glasses and glass-ceramics are biocompatible and bioactive materials capable of bonding directly to bone tissue through the formation of biologically active hydroxyapatite (HA) layers. These HA layers form an interfacial bond and are structurally and chemically similar to the mineral phases found in bone [2]. However, the low hardness of bioactive glass has restricted its use to non-load-bearing applications [3]. It has been demonstrated that the mechanical properties of bioactive glasses can be enhanced by incorporating oxides such as alumina, magnesia, titania, or zirconia. Additionally, crystallizing bioactive glasses to form glass-ceramics can also improve their mechanical characteristics [4]. Glass ceramics in the $CaO\text{-}SiO_2\text{-}P_2O_5\text{-}Na_2O$ system, when processed through sintering and subsequent

* *Corresponding Author Email: hadeersadeqz@gmail.com*

crystallization, exhibit excellent mechanical properties and can form a chemical bond with living bones. These bioactive glass ceramics, which fall under the category of osteoconductive biomaterials, are ideally suited for medical applications. They are particularly effective in orthopedic and dental implants due to their strong bioactivity and established biocompatibilit. [5]. Generally, these bioactive glass ceramics form hydroxyapatite layers when exposed to simulated body fluids (SBF), which are buffered salt solutions that mimic the ionic concentrations of bodily fluids. This hydroxyapatite layer enhances their ability to bond with bone and supports tissue regeneration [6]. From a clinical perspective, one of the primary challenges surgeons face is the risk of post-implantation infections. Silver (Ag) has been shown to have significant antibacterial properties, which can help mitigate the risk of infections and combat bacterial growth around implants [7,8]. Over the past few years, biologists have extensively studied the biological properties of silver (Ag). These investigations have focused on its antibacterial effects, mechanisms of action, and potential benefits in medical applications, such as infection control in implants [9]. Therefore, incorporating silver oxide into biological implants is a reliable approach. Studies have shown that bacteria generally cannot develop resistance to silver (Ag) incorporated into biomaterials, making it an effective option for reducing the risk of infection [10,11]. Thus, numerous studies on silver-containing bioactive glasses (Ag-BGs) have been conducted to determine the optimal amount of silver needed in the glass structure for various applications. These investigations aim to balance the antimicrobial benefits with other desired properties of the bioactive glass. [12,13]. Zirconia was first used about 20 years ago to address the problem of ceramic brittleness and reduce the risk of implant failure. Its introduction significantly improved the mechanical strength and durability of ceramic implants [14], this is because zirconia provides an oxide ceramic with superior mechanical properties due to phase transformation toughening, which enhances its resistance to crack propagation and significantly improves its overall strength [15]. The utilization of composites made from zirconia (ZrO_2) and bioactive glass in the $Na_2O–CaO–SiO_2–P_2O_5$ system offers significant potential, particularly in applications like bone regeneration and implants [16], Combining the high strength provided by zirconia reinforcement with the excellent compatibility and bioactivity of bioactive glass presents a promising approach for creating durable, bioactive materials [17]. The high bending strength of the zirconia-toughened glass-ceramic composite was validated, with no signs of degradation noted after 12 weeks of in vivo implantation. The optimal zirconia content for achieving both high strength and bioactivity was found to be 30 vol% [18]. A composite coating layer of bioactive glass-ceramic with varying zirconia concentrations was utilized, and hardness tests indicated that increasing the zirconia content resulted in enhanced coating hardness. The incorporation of zirconia was aimed at mitigating ceramic brittleness and minimizing the risk of implant failure[14]. The objective of this study is to synthesize bioactive glass-ceramic with enhanced mechanical properties and antibacterial activity using the melting technique, aimed at applications in biomedical fields.

MATERIALS AND METHODS

The materials used in this study include Sodium oxide (Na_2O, 98%, India), Silica foam (SiO_2, 99.9%, India), Phosphorus pentoxide (P_2O_5, 98%, China), Calcium oxide (CaO, 98%, India), Zirconia (ZrO_2, 98%, China), and Silver oxide (Ag_2O, 98%, China).

Glass-ceramic preparation

The synthesis of 45S5 bioactive glass was carried out using the conventional melting technique, comprising 45 wt% SiO_2, 24.5 wt% Na_2O, 6 wt% P_2O_5, and CaO (24.5 - X) with X wt% of ZrO_2/Ag_2O (where X = 0, 1, 3, or 5). For each variant of bioactive glass, a 10 g batch was created by thoroughly blending analytical reagents in a planetary ball mill (SFM-1, QM-3SP2) at 300 rpm for 6 hours. The resulting mixture was then melted in an alumina crucible using an electric furnace set to 1200 ± 10 °C for 2 hours to ensure complete melting. After this process, the molten glass was gradually cooled in the oven. The produced glass-ceramic was crushed in a mortar to obtain a semi-finished powder, which was subsequently milled in a planetary ball mill (SFM-1, QM-3SP2) at 300 rpm for 12 hours. The composition of each batch is detailed in Table 1. Compacted samples, measuring 10 mm in diameter and 30 mm in length, were sintered at 1200 °C with a heating rate of 5 °C/min. X-ray diffraction (XRD) analysis of the powder samples was carried out at room temperature

using a Shimadzu 6000 with CuKα radiation (λ = 1.5405 Å). The scan range was from 10° to 80° (2θ) at a speed of 5°/min, with an applied power of 40 kV/30 mA to analyze the structure and phases.

The XRD peaks were compared with standard JCPDS files: NO. 00-022-1455 for sodium calcium silicate ($Na_2Ca_2Si_3O_9$) and NO. 00-012-0671 for sodium calcium silicate ($Na_2CaSi_3O_8$(. This study examines the impact of ZrO_2/Ag_2O weight percentage on the structure, mechanical properties, and biological behavior of bioactive glass-ceramics within the SiO_2, Na_2O, CaO, P_2O_5, ZrO_2/Ag_2O system. It explores how different concentrations of ZrO_2 and Ag_2O affect the material's structural integrity, mechanical performance, and bioactivity.

FTIR was employed to verify the presence of ZrO_2/Ag_2O within the glass-ceramic matrix. The apparent porosity of the samples was determined using the Archimedes method, in accordance with ASTM C373-88 (1988). Compressive strength testing was conducted following ASTM C773-88 (1999). Vickers microhardness was measured in line with ASTM C1327-99, applying a 9.8 N indentation load and using the designated equation for calculation.

$$Hv=1.854(p/d^2)$$

Hv: Vickers hardness (Mpa), p: Loads (N), D: Diagonal lengths of the indentations impressions (µm).

The bending test was performed in accordance with the ASTM C1161 standard, utilizing a computerized universal testing machine set to a testing speed of 0.5 mm/min. The three-point bending strength was determined using the equations outlined below.

$$Q_b=3\,p_f\,L/2wt^2$$

Where: Qb: Bending strengths (MPa), Pf: Fractures loads (N), w: Samples width (mm), t: Samples thickness (mm).

In order to investigate samples bioactivity, (SBF) the simulated body fluid was prepared

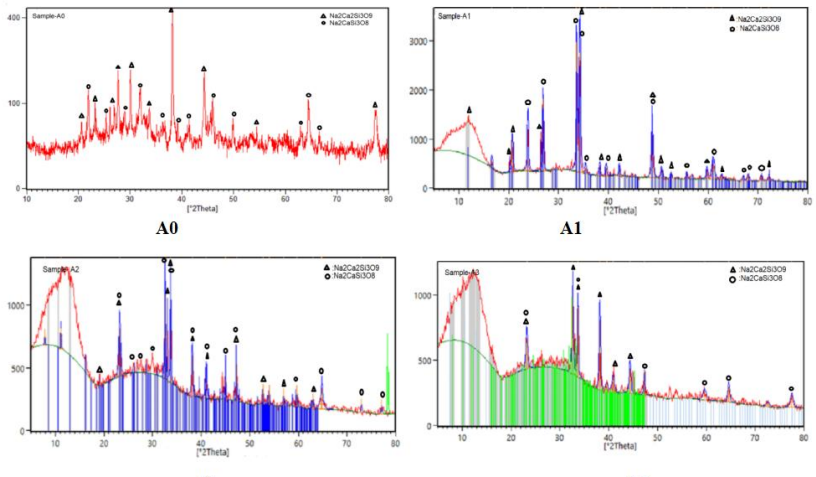

Fig. 1. XRD patterns for bioactive glass ceramic powder.

Table 1. The composition of each prepared sample.

Samples	SiO_2%	CaO%	Na_2O%	P_2O_5%	ZrO_2%	Ag_2O%
A0	45	24.5	24.5	6	0	0
A1	45	22.5	24.5	6	1	1
A2	45	18.5	24.5	6	3	3
A3	45	14.5	24.5	6	5	5

according to[19]. The sample was immersed in Simulated Body Fluid (SBF) at 37 ºC for 21 days. At the end of the immersion period, scanning electron microscopy (SEM) was performed on the sample surfaces to examine the formation of hydroxyapatite (HA) on the surfaces.

RESULTS AND DISCUSSION

X-Rays Diffractions (XRD) Analysis

The phases of the prepared powders were obtained using XRD. Fig. 1 shows XRD patterns of glass-ceramic powders with different of ZrO_2 and Ag2O that melted in 1200 °C, two types of sodium calcium silicat that obtained in each sample which is ($Na_2CaSi_3O_8$) ($Na_2Ca_2Si_3O_9$) that scanned in a diffraction angle ranging from 10º to 80º and agree with (JCPDS, card NO.12-0671) and (JCPDS, card NO. 22-1455) respectively.

The various added dopants did not produce significant changes in the types of crystalline phases; rather, they resulted in only minor variations in the percentages of the main crystalline phases.

In general, XRD results shows that the intensity of crystal phases and its quantity changed with the addition of ZrO_2 and Ag_2O for all samples [20].

For compact bioglass-ceramic samples sintered at 950 ºC, Fig. 1 presents the XRD results. The samples exhibit two types of sodium calcium phosphate: $Na_2Ca_2Si_3O_9$, which corresponds to JCPDS card No. 22-1455, and $Na_2CaSi_3O_8$, which is commonly associated with combeite in certain peaks. These findings are consistent with results reported by various researchers [21-23].

Results of FTIR analysis

FTIR spectra of bioglass-ceramic doped with different amount of ZrO_2 and Ag_2O samples melted at 1200 °C are shown in Fig. 2. According to previous FTIR studies on bioglasses-ceramic [24], it's clear that bands in the wavenumber 625, 1120, 1050 cm^{-1} corresponds to rocking

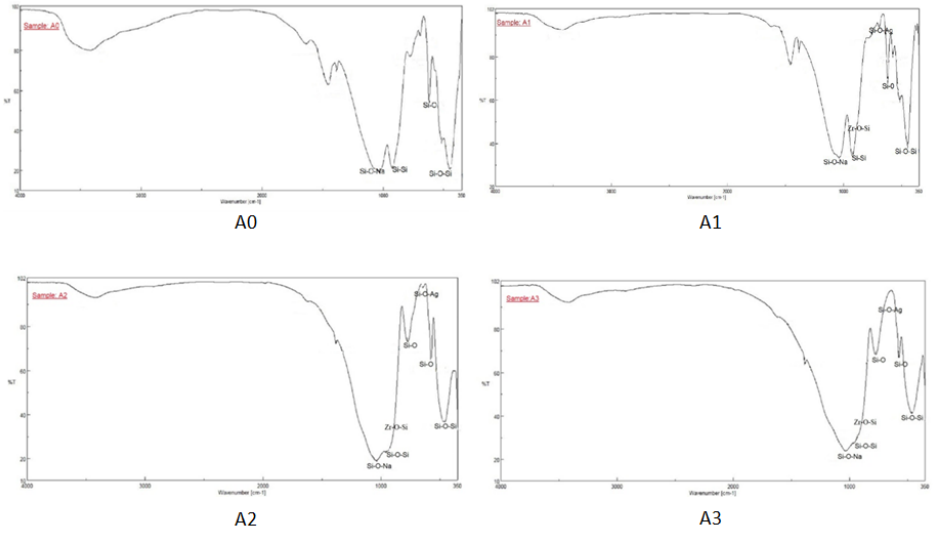

Fig. 2. (FTIR) spectra results.

Table 2. physical properties of compact samples sintered at 950 °C.

Samples	Density (g/cm³)	Porosity (wt.%)
A0	1.98	32.4
A1	2.02	30.88
A2	3.18	18.43
A3	3.32	11.43

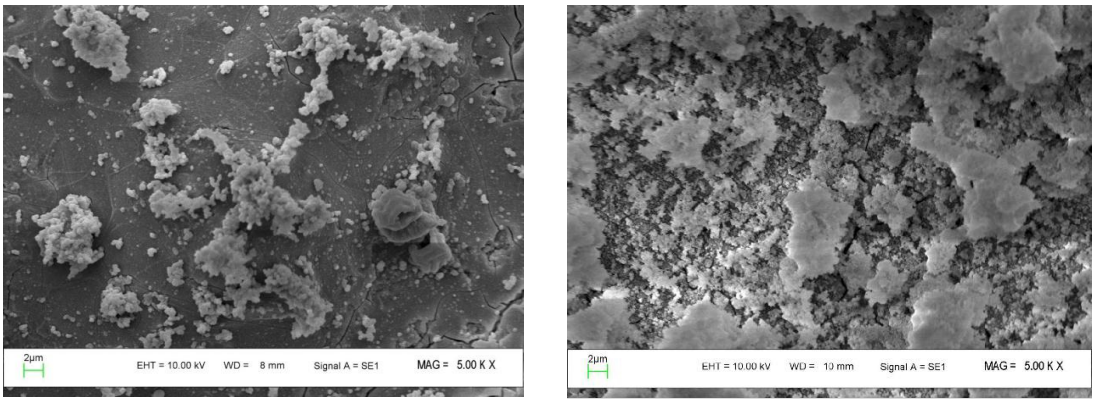

Fig. 3. A) SEM images of (A0) sample after soaking in SBF for 21 days at 2Mm of magnification. B) SEM images of (A9) sample after soaking in SBF for 21 days at 2Mm of magnification.

Table 3. Mechanical properties of compact samples sintered at 950 °C.

Samples	Compressive strength (Mpa)	Bending strength (Mpa)	Vickers hardness (HV)
A0	48.7	23.6	155.8
A1	54.3	25.7	183.2
A2	78.3	37.9	245.6
A3	108.8	53.3	356.4

vibrations of Si-O-Si bridges, Zr-O-Si and Si-O-Na bridges respectively. As well as characteristic wavenumbers 932 cm^{-1} related to Si-Si bridge [25]. The improvement in mechanical properties of bioglass-ceramic samples is attributed to the formation of Zr-O-Si and Si-O-Ag bonds. Because zirconium ions was occupied interstitial sites within the bioglass network [26].

Density and Mechanical Properties Measurement

Table 2 presents the bulk density and apparent porosity of the bioglass-ceramic samples as a function of ZrO_2/Ag_2O weight percentage. It is evident that as the ZrO_2/Ag_2O wt.% increases in the glass-ceramic, the density rises from 1.98 to 3.32 g/cm^3. This increase is attributed to the substitution of the lighter element Ca (density = 1.55 g/cm^3) with the heavier elements Zr (density = 6.52 g/cm^3) and Ag (density = 10.49 g/cm^3). Additionally, structural changes occur due to the addition of modifying metal oxides (ZrO_2), which coordinate the NBOs (Zr-O-Si) and (Si-O-Ag), forming links between atoms. This leads to improved network connectivity and dimensionality, resulting in greater compactness and packing efficiency within the bioglass-ceramic structure. The increase in density is also linked to a reduction in average interatomic spacing during sintering, which in turn decreases the porosity from 32.4% to 11.43%.

Table 3 shows that increasing the ZrO_2/Ag_2O content from 1 to 5 wt% results in a substantial improvement in compressive strength, bending strength, and Vickers microhardness. This enhancement is attributed to the formation of new strong bonds, such as Zr-O-Si and Si-O-Ag, as confirmed by FTIR analysis. Additionally, the incorporation of Zr and Mg ions into interstitial sites within the bioglass-ceramic network contributes to increased density and improved mechanical properties, reinforcing the glass-ceramic structure.

In Vitro Bioactivity Tests

SEM Results of Bioglass-ceramic after Immersing in SBF Solutions

Significant changes were observed in the bioglass-ceramic samples after 21 days of immersion in SBF, as shown in Fig.3. Agglomerations of HA were visible on the surfaces of both the (A0) and (A3) samples, consistent with the findings reported in [28,29].

CONCLUSION

A 45S5 bioactive glass-ceramic can be toughened by ZrO_2/Ag_2O particles as reinforcing phase. The experimental results showed the positive effect of ZrO_2 and Ag_2O introducing to bioactive glass-ceramic which was 1, 3 and 5 wt% of ZrO_2/Ag_2O together. The bending strength improved from 23.6 to 53.3 MPa while the compresive strength improved from 48.7 Mpa for the pure glass-ceramic to 108.8 Mpa for glass-ceramic sample involves 5wt% ZrO_2 and Ag_2O. The formation of a hydroxyapatite layer on the bioglass surface after immersion in simulated body fluid (SBF) was investigated using scanning electron microscopy (SEM). This in vitro study analyzed the behavior of the bioglass-ceramic sample in SBF. It can be seen increasing in the hydroxyapatite value with ZrO_2/Ag_2O addition. This indicates that with increasing the immersion period and ZrO_2/Ag_2O addition, the bioactivity of the samples had increased.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

REFERENCES

1. Brink M, Turunen T, Happonen RP, Yli-Urpo A. Compositional dependence of bioactivity of glasses in the system Na_2O-K_2O-MgO-CaO-B_2O_3-P_2O_5-SiO_2. J Biomed Mater Res. 1997;37(1):114-121.
2. De Aza PN, De Aza AH, Pena P, De Aza S. Vidrios y Vitrocerámicos Bioactivos. Boletín de la Sociedad Española de Cerámica y Vidrio. 2007;46(2):45-55.
3. Thompson ID, Hench LL. Mechanical properties of bioactive glasses, glass-ceramics and composites. Proceedings of the Institution of Mechanical Engineers, Part H: Journal of Engineering in Medicine. 1998;212(2):127-136.
4. El-Ghannam A, Hamazawy E, Yehia A. Effect of thermal treatment on bioactive glass microstructure, corrosion behavior, ? potential, and protein adsorption. J Biomed Mater Res. 2001;55(3):387-395.
5. Hoppe A, Güldal NS, Boccaccini AR. A review of the biological response to ionic dissolution products from bioactive glasses and glass-ceramics. Biomaterials. 2011;32(11):2757-2774.
6. Huygh A, Schepers EJG, Barbier L, Ducheyne P. Microchemical transformation of bioactive glass particles of narrow size range, a 0–24 months study. J Mater Sci Mater Med. 2002;13(3):315-320.
7. Baker C, Pradhan A, Pakstis L, Pochan D, Shah SI. Synthesis and Antibacterial Properties of Silver Nanoparticles. Journal of Nanoscience and Nanotechnology. 2005;5(2):244-249.
8. Clement JL, Jarrett PS. Antibacterial Silver. Met-Based Drugs. 1994;1(5-6):467-482.
9. Alexander JW. History of the Medical Use of Silver. Surg Infect (Larchmt). 2009;10(3):289-292.
10. Ciołek L, Karaś J, Olszyna AR, Zaczyńska E, Czarny A, Żywicka B, et al. In Vitro Studies of Antibacterial Activity of Bioglasses Releasing Ag. Key Eng Mater. 2011;493-494:108-113.
11. Bellantone M, Williams HD, Hench LL. Broad-Spectrum Bactericidal Activity of Ag_2O-Doped Bioactive Glass. Antimicrobial Agents and Chemotherapy. 2002;46(6):1940-1945.
12. Delben JRJ, Pimentel OM, Coelho MB, Candelorio PD, Furini LN, Alencar dos Santos F, et al. Synthesis and thermal properties of nanoparticles of bioactive glasses containing silver. J Therm Anal Calorim. 2009;97(2):433-436.
13. Kargozar S, Baino F, Banijamali S, Mozafari M. Synthesis and physico-chemical characterization of fluoride (F)- and silver (Ag)-substituted sol-gel mesoporous bioactive glasses. Biomedical Glasses. 2019;5(1):185-192.
14. Christel P, Meunier A, Dorlot JM, Crolet JM, Witvoet J, Sedel L, et al. Biomechanical Compatibility and Design of Ceramic Implants for Orthopedic Surgery. Annals of the New York Academy of Sciences. 1988;523(1):234-256.
15. Chevalier J. What future for zirconia as a biomaterial? Biomaterials. 2006;27(4):535-543.
16. Trang GTT, Linh NH, Linh NTT, Kien PH. The Study of Dynamics Heterogeneity in SiO_2 Liquid. HighTech and Innovation Journal. 2020;1(1):1-7.
17. Elgayar I, Aliev AE, Boccaccini AR, Hill RG. Structural analysis of bioactive glasses. Journal of Non-Crystalline Solids. 2005;351(2):173-183.
18. Rabiee SM, Azizian M. Effect of Zirconia Concentration on the Growth of Nanowires in Bioactive Glass–Ceramic Coatings. International Journal of Applied Ceramic Technology. 2012;10(1):33-39.
19. Kokubo T, Kushitani H, Sakka S, Kitsugi T, Yamamuro T. Solutions able to reproduce in vivo surface-structure changes in bioactive glass-ceramic A-W3. J Biomed Mater Res. 1990;24(6):721-734.
20. Hashmi MU, Shah SA. Dissolution behavior of bioactive glass ceramics with different CaO/MgO ratios in SBF-K9 and r-SBF. Progress in Natural Science: Materials International. 2014;24(4):354-363.
21. Brentrup GJ, Moawad HMM, Santos LF, Almeida RM, Jain H. Structure of Na_2O–CaO–P_2O_5–SiO_2 Glass–Ceramics with Multimodal Porosity. J Am Ceram Soc. 2009;92(1):249-252.
22. Kim CY, Lim HB. Hardening and Hydroxyapatite Formation of Bioactive Glass and Glass-Ceramic Cement. Key Eng Mater. 2003;254-256:305-310.
23. Lin F-H, Hon M-H. A study on bioglass ceramics in the Na2O-CaO-SiO2-P2O5 system. Journal of Materials Science. 1988;23(12):4295-4299.
24. Oliveira JM, Correia RN, Fernandes MH. Effects of Si speciation on the in vitro bioactivity of glasses. Biomaterials. 2002;23(2):371-379.
25. Souza MT, Crovace MC, Schröder C, Eckert H, Peitl O, Zanotto ED. Effect of magnesium ion incorporation on the thermal stability, dissolution behavior and bioactivity in Bioglass-derived glasses. Journal of Non-Crystalline Solids. 2013;382:57-65.
26. Jha P, Singh K. Effect of MgO on bioactivity, hardness, structural and optical properties of SiO_2–K_2O–CaO–MgO glasses. Ceram Int. 2016;42(1):436-444.
27. Newby PJ, El-Gendy R, Kirkham J, Yang XB, Thompson ID, Boccaccini AR. Ag-doped 45S5 Bioglass®-based bone scaffolds by molten salt ion exchange: processing and characterisation. J Mater Sci Mater Med. 2011;22(3):557-569.
28. Sharifianjazi F, Parvin N, Tahriri M. Synthesis and characteristics of sol-gel bioactive SiO_2-P_2O_5-CaO-Ag_2O glasses. Journal of Non-Crystalline Solids. 2017;476:108-113.
29. Zohourfazeli M, Mahdi Tajer MH, Moghanian A. Comprehensive investigation on multifunctional properties of zirconium and silver co-substituted 58S bioactive glass. Ceram Int. 2021;47(2):2499-2507.