Research Article

In Vitro Evaluation of Some Types of Ferrimagnetic Glass Ceramics

S. A. M. Abdel-Hameed, M. A. Marzouk, and R. L. Elwan

Glass Research Department, National Research Center, Dokki, Cairo 12311, Egypt

Correspondence should be addressed to M. A. Marzouk; marzouk.nrc@yahoo.com

Received 26 December 2013; Revised 19 March 2014; Accepted 23 March 2014; Published 8 May 2014

Academic Editor: Claudio Migliaresi

Copyright © 2014 S. A. M. Abdel-Hameed et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

The present study aimed at studying the acceleration of the bioactive layer on the surface of ferrimagnetic glass ceramic with a basic composition $40\text{Fe}_2\text{O}_3\text{-}15\text{P}_2\text{O}_5\text{-}20\text{SiO}_2\text{-}5\text{TiO}_2$ through the addition of 20% of different types of metal oxides like MgO or CaO or MnO or CuO or ZnO or CeO_2 . SEM, EDAX, and ICP were applied to present the results of the study. SEM and EDAX measurements indicated the presence of apatite layer formed on the surface of the prepared glass ceramics after immersion in SBF within 7 to 30 days. The investigation of the results clarified that the addition of CaO or ZnO accelerated the formation of apatite on the surfaces of the samples in the simulated body fluid faster than other metal oxides. Inductive coupled plasma (ICP) analysis shows the evolution of ion extraction by the simulated body fluid solution (SBF) with time in relation to the elemental composition.

1. Introduction

Bioactive materials [1, 2] are known to bond to living bone in the body through formation of an apatite layer on their surface [3]. Bioactive glasses and glass ceramics find a variety of biological applications such as in cell separation, drug delivery, and magnetic intracellular hyperthermia treatment of cancer [4–6]. The success of bioglass [7], ceravital [8], A-W glass ceramic [9], and dense hydroxyapatite ceramic [10] materials in clinical applications [11] has propelled the search for bioactive glasses and glass ceramics with enhanced properties. Recently, development of bioglass ceramics containing a magnetic phase has received attention for application as thermoseed in hyperthermia treatment of cancer [9–11]. The interest in these materials started when $\text{SiO}_2\text{-CaO-P}_2\text{O}_5$ glasses containing iron oxide were found to yield ferrimagnetic glass ceramics upon heat treatment at elevated temperatures [10]. The magnetic properties of this bioceramic arise from magnetite (Fe_3O_4) crystallized from hematite present in the glass during heat treatment. When this bioceramic is placed in the region of the tumor and is subjected to an alternating magnetic field, heat is generated by magnetic hysteresis loss [11]. The tumor is effectively heated

and selectively destroyed when local temperatures of $42\text{--}45^\circ\text{C}$ are attained by this process [12–14]. Magnetic glass ceramics with zinc ferrite in a CaO-SiO_2 glass matrix [12], Fe_3O_4 in $\text{Na}_2\text{O-CaO-SiO}_2\text{-P}_2\text{O}_5$ glass matrix [13–16], and Fe_3O_4 in a CaO-SiO_2 glass matrix [17] have also been developed for this purpose. Thus, the ferromagnetic bioactive glass ceramics can be used not only for the hyperthermia treatment of cancer but also as a substitute for a cancerous/damaged bone. A number of ferromagnetic glass ceramic systems have been developed for this purpose like $\text{FeO-Fe}_2\text{O}_3\text{-CaO-SiO}_2$ [18], $\text{ZnO-Fe}_2\text{O}_3\text{-CaO-SiO}_2$ [19], $\text{SiO}_2\text{-Na}_2\text{O-CaO-P}_2\text{O}_5\text{-FeO-Fe}_2\text{O}_3$ [20], $\text{Li}_2\text{O-MnO}_2\text{-CaO-P}_2\text{O}_5\text{-SiO}_2$ [21], $\text{Fe}_2\text{O}_3\text{-CaO-ZnO-SiO}_2\text{-B}_2\text{O}_3$ [22], magnetite/hydroxyl apatite composite [23], and $\text{CaO-SiO}_2\text{-P}_2\text{O}_5\text{-Na}_2\text{O-Fe}_2\text{O}_3$ [9, 10]. Bioactivity tests have shown that apatite forming ability increases in $\text{CaO-SiO}_2\text{-P}_2\text{O}_5\text{-Na}_2\text{O}$ glasses with an increase in Fe_2O_3 content with proper choice of constituent compositions [24].

In previous work [25], we applied heat treatment to study the crystallization behavior and magnetic properties of ferromagnetic glass ceramics in the system $\text{Fe}_2\text{O}_3\text{-CaO-ZnO-SiO}_2$. Another systematic study was applied to investigate the phase formation, microstructure, and both the amount and grain size of the crystallized magnetite after gradual addition of

different types of nucleating agents to ferromagnetic glass ceramics [26].

The aim of this work was to evaluate the bioactivity of ferrimagnetic glass ceramics in the system Fe_2O_3 - TiO_2 - P_2O_5 - SiO_2 with the addition of different types of metal oxides (MgO - CaO - MnO - ZnO - CeO_2 - CuO). The bioactivity was evaluated in vitro by examining the formation of bone-like apatite layer on their surfaces when treated in simulated body fluid (SBF).

2. Experimental Procedures

2.1. Glass Composition and Preparation. The glass ceramics were prepared from dry mixtures of reagent grade SiO_2 , Fe_2O_3 , TiO_2 , and P_2O_5 with the batch composition $40\text{Fe}_2\text{O}_3$ - $15\text{P}_2\text{O}_5$ - 20SiO_2 - 5TiO_2 in addition to 20% changeable metal oxides (CaO as CaCO_3 , MnO , MgO , CeO_2 , CuO , and ZnO). Our target was to obtain a glass ceramic, not a ceramic material, so a melting step was necessary to achieve the nucleation of magnetite in a liquid-derived amorphous phase. The batches were placed in a platinum crucible and melted in an electric furnace at 1450°C for 2 h. The melts were poured onto a stainless steel plate at room temperature and pressed into a plate 1-2 mm thick by another cold steel plate.

2.2. Soaking in the Simulated Body Fluid (SBF). Each sample was soaked in a cellular simulated body fluid (SBF, 50 mL), with ion concentrations and pH nearly equal to those of human blood plasma [17] as shown in Table 1. The SBF was prepared according to Kokubo [1] by dissolving reagent grade NaCl , NaHCO_3 , KCl , $\text{K}_2\text{HPO}_4 \cdot 3\text{H}_2\text{O}$, $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, CaCl_2 , and Na_2SO_4 in an ion exchanged water contained in a polystyrene bottle. These reagents were added in the order listed. The solution was buffered at pH value ≈ 7.25 with 50 mM of Tris-(hydroxymethyl)-amino methane ($(\text{CH}_2\text{OH})_3\text{CNH}_2$, hereafter as TRIS) and 45 mM hydrogen chloride and its temperature was kept at $\pm 37^\circ\text{C}$. The soaking was carried out at 37°C , under continuous stirring and for various times (0, 15, and 30 days).

2.3. Measurement of Element Concentrations. After the specimens were removed from the soaking solutions, changes in the concentrations of calcium and phosphorous of these solutions were measured by inductively coupled plasma (ICP) spectrometer, equipped with ultrasonic useful for trace elements.

2.4. Surface Structure Analysis and Characterization. Scanning electron microscopy (SEM) and EDAX techniques were performed on the glasses before and after soaking in SBF solution. The samples were removed from this solution, washed with pure acetone, and dried at room temperature.

The morphological analyses were carried out by means of SEM technique: the microscope was equipped with an energy dispersive X-ray analyser for compositional study. The samples were mounted on a stainless steel stub using double stick tape and then coated with a thin layer of Au.

3. Results and Discussion

3.1. Morphological and Spectra Properties. Figures 1(a)–6(a) show the SEM micrographs of the present series of glass ceramic of the system Fe_2O_3 - TiO_2 - P_2O_5 - SiO_2 after immersion in SBF for 0, 1, 2, and 4 weeks. Increase in bioactivity with increasing zinc oxide content was observed. The results have been used to understand the evolution of the apatite surface layer as a function of glass composition and immersion time in SBF as follows.

- (1) It can be seen from Figures 1(a)–6(a) that combination of metal oxides (Mg, Ca, Cu, Mn, Zn, and Ce) with the basic composition produces no apatite formation on the surface before the immersion in the simulated body fluid (0 week). On the other hand, within 1–4 weeks of immersion, the apatite layer was clearly observed.
- (2) It was observed that the acceleration of forming the apatite layer within the early period depends on the type of the metal ion. Figures 1(a), 2(a), 5(a), and 6(a) show that Ca, Mg, Zn, and Ce accelerate the formation of apatite layer within one week while both Mn- and Cu-doped samples (Figures 3(a) and 4(a)) accelerate the formation of apatite layer within 2–4 weeks.
- (3) Ca- and Zn-doped glass ceramic exhibit the best results among the glasses tested in vitro in the SBF solution.
- (4) The EDAX analysis confirmed the formation of apatite (Figures 1(b)–6(b)).

These results might be interpreted as follows: apatite formation on the surfaces of the heat-treated glasses in the simulated body fluid is governed by the chemical reaction of the surface of the matrix with the fluid [17]. In the present series of glass ceramics, the major constituent is Fe_2O_3 and the addition of SiO_2 and P_2O_5 in the matrix allows the formation of bioactive ferrimagnetic bioglass ceramics [17–24]. The previous assumption is confirmed by Singh and Srinivasan [27]; in their study, they assumed that the addition of metal ions to ferrimagnetic bioglass ceramics (weight ratio) accelerated the formation of apatite on the surfaces of the glasses in the simulated body fluid by increasing the pH of the surrounding fluid due to the dissolution of M^{n+} ions.

In the present case, apatite formation on the surface of the glass ceramics was accelerated by the addition of both CaO and ZnO . Ebisawa et al. [17] postulated the formation mechanism of an apatite-like layer on materials and assumed that this might be due to the release of Ca^{2+} ions, which results in the rapid increase in the pH of the solution. In such materials, an exchange of ions Ca^{2+} of material with H_3O^+ of the SBF is produced. The Ca^{2+} dissolved from the glass ceramics increases the Ca^{2+} concentration in the SBF, and the consumption of H_3O^+ results in the increase of pH value [27]. Similarly, the addition of ZnO to the present basic composition is also assumed to accelerate the formation of apatite on the glass ceramics. Zinc ions migrate into the fluid as $\text{Zn}(\text{OH})_2$ contributes more OH^- ions required for the

TABLE 1: Ion concentrations of simulated body fluid and human blood plasma [17].

	Na ⁺	K ⁺	Mg ²⁺	Concentration (mM)				
				Ca ²⁺	Cl	HCO ₄ ²	HPO ₄ ²	SO ₄ ²
Simulated body fluid	142.0	5.0	1.5	2.5	147.0	4.2	1.0	0.5
Human blood plasma	142.0	5.0	1.5	2.5	103.0	27.0	1.0	0.5

FIGURE 1: (a) SEM micrograph of Mg-doped glass ceramics (A) before, (B) after 1 week, (C) after 2 weeks, and (D) after 4-week immersion in SBF. (b) EDAX of Mg-doped glass ceramics after 4-week immersion in SBF.

(a)

(b)

FIGURE 2: (a) SEM micrograph of Ca-doped glass ceramics (A) before, (B) after 1 week, (C) after 2 weeks, and (D) after 4 weeks of immersion in SBF. (b) EDAX of Ca-doped glass ceramics after 4-week immersion in SBF.

crystallization of the amorphous Ca-P from the solution to form the apatite layer [27].

3.2. Corrosion of Biosamples in SBF (Solution Analysis). ICP analysis shows the evolution of ion extraction by the simulated body fluid solution (SBF) with time in relation to the initial elemental composition in the prepared samples. It was observed that a marked release of Ca and P ions takes place,

which governs, by the bioactivity behavior of the glass, the effect of ions releasing on pH value of the solution and the composition of the bioactive glass.

The corrosion behavior data of the studied samples are exhibited in Table 2, which shows the concentrations of calcium and phosphorous species presented in the SBF solution. From Table 2, one can deduce that by soaking the samples separately in SBF, the concentrations of both Ca and P

FIGURE 3: (a) SEM micrograph of Mn-doped glass ceramics (A) before, (B) after 1 week, (C) after 2 weeks, and (D) after 4 weeks of immersion in SBF. (b) EDAX of Mn-doped glass ceramics after 4-week immersion in SBF.

increase as they dissolve rapidly from the bulk glass samples; then, they were consumed for HCA layer formation on the glasses surfaces; by continuous immersion in the solution, all the samples dissolved and lead to higher concentrations of both Ca and P in the solution; also Table 2 shows the effect of adding different metal ions on the HCA layer formation through the difference in Ca and P concentrations in the SBF solution.

Table 2 exhibits the concentration values of Ca and P in SBF solution after soaking the samples which contain one of

the following metal oxides: CaO, MnO, MgO, CeO₂, CuO, and ZnO for 7, 14, and 30 days; from that table, we can find that by adding CaO or ZnO to sample the bioactivity of samples is increased and it accelerates HCA layer formation through the fast consuming of Ca and P ions.

The quantitative analysis of the Ca and P ions during and after SBF immersion tests is important to understand the kinetics of surface reaction in bioactive materials. The decrease or increase in Ca and P concentrations with glass soaking in SBF solution is consistent with the formation

FIGURE 4: (a) SEM micrograph of Cu-doped glass ceramics (A) before, (B) after 1 week, (C) after 2 weeks, and (D) after 4 weeks of immersion in SBF. (b) EDAX of Cu-doped glass ceramics after 4-week immersion in SBF.

and growth or inhibition of $\text{Ca-P}_2\text{O}_5$ layer on the glass surface.

A quantitative analysis of the ions in the solution after in vitro tests is very useful to complement the understanding of surface kinetic reactions in bioactive materials [28]. The data recorded in Table 2 revealed that the concentrations of calcium and phosphorous elements in SBF solutions of glass samples decreased or increased with the ability of the glass samples to form HCA layer on their surfaces and that

consequently affects their bioactive behavior. In the early stage of immersion (2 days), the concentrations of Ca, P, and Si ions were increased in the SBF solution. These results suggested that a relative interaction between SBF solution and the glass samples occurred. This may be due to the release of alkali and alkaline earth ions, loss of soluble SiO_2 from the surface of the glass specimens to the SBF solution, condensation, and repolymerization of SiO_2 -rich layer [29]. Calcium and phosphorous concentrations then fell in the SBF

FIGURE 5: (a) SEM micrograph of Zn-doped glass ceramics (A) before, (B) after 1 week, (C) after 2 weeks, and (D) after 4 weeks of immersion in SBF. (b) EDAX of Zn-doped glass ceramics after 4-week immersion in SBF.

solution with increasing the silicon ion concentration after 7-day duration, and this may be due to the formation of amorphous $\text{CaO-P}_2\text{O}_5$ layer on the surface of the glass sample. With increasing the silicon, the subsequent rapid decrease in phosphorous and calcium ion concentrations in SBF solution after 14-day immersion indicated that crystallization and growth of the $\text{CaO-P}_2\text{O}_5$ rich layer occurred [30]. Studies of carbonate containing hydroxy-carbonate apatite (HCA) layer formed on the surface of bioactive glasses have shown

that the reactions occur on the material side in five stages. These stages are faster for the highest level of bioactivity [29].

4. Conclusion

Homogeneous glass ceramics of the chemical composition $40\text{Fe}_2\text{O}_3\text{-}15\text{P}_2\text{O}_5\text{-}20\text{SiO}_2\text{-}5\text{TiO}_2$ doped with 20 mol% of varieties of metal ions like MgO , CaO , MnO , CuO , ZnO , and

FIGURE 6: (a) SEM micrograph of Ce-doped glass ceramics (A) before, (B) after 1 week, (C) after 2 weeks, and (D) after 4 weeks of immersion in SBF. (b) EDAX of Ce-doped glass ceramics after 4-week immersion in SBF.

CeO_2 were obtained. In vitro analysis was applied to show the bioactivity of the samples after immersion in the simulated body fluid. SEM and EDAX studies show that the prepared glass ceramics behave as a bioactive material and the formed apatite-like layer on the surface accelerated depending on the type of the metal oxide. Inductive coupled plasma (ICP) analysis shows the evolution of ion extraction by the simulated body fluid solution (SBF) with time in relation to the elemental composition. The combination of metal oxides (Mg, Ca, Cu, Mn, Zn, and Ce) with the basic composition

produces no apatite formation on the surface before the immersion in the simulated body fluid (0 week), while within 1–4-week immersion the apatite layer was clearly observed. The formation of the apatite layer depends on both time of immersion and type of the metal ion. Ca-, Mg-, Zn-, and Ce-doped samples accelerate the formation of apatite layer within one week, while Mn- and Cu-doped samples accelerate the formation of apatite layer within 2–4 weeks. Ca- and Zn-doped glass ceramics exhibit the best results among the glasses tested in vitro in the SBF.

TABLE 2: ICP results.

Sample	Time/weeks	Si	Ca	P	Fe
Mg	1	0.129	44.74	2.08	—
	2	—	0.310	0.032	0.21
	4	1.080	103.99	0.014	0.01
Ca	1	0.137	48.430	2.05	—
	2	—	45.97	0.023	0.03
	4	0.010	60.64	0.07	0.08
Mn	1	0.131	49.66	2.88	—
	2	—	57.54	3.455	0.11
	4	0.770	—	0.66	0.02
Cu	1	0.157	56.52	6.08	—
	2	—	35.93	0.015	0.09
	4	0.610	89.31	0.002	0.05
Zn	1	0.124	54.16	2.17	—
	2	—	33.65	1.68	0.01
	4	3.310	51.621	0.010	0.02
Ce	1	0.322	45.02	1.39	—
	2	—	66.40	4.76	2.29
	4	0.120	78.03	0.09	0.04

Conflict of Interests

The authors declare that there is no personal or financial conflict of interests in the current paper.

Acknowledgment

This work was supported financially by the Science and Technology Development Fund (STDF), Egypt, Grant no. 1044.

References

- [1] T. Kokubo, "Bioactive glass ceramics: properties and applications," *Biomaterials*, vol. 12, no. 2, pp. 155–163, 1991.
- [2] L. L. Hench, "Bioactive materials: the potential for tissue regeneration," *Journal of Biomedical Materials Research A*, vol. 41, no. 4, pp. 511–518, 1998.
- [3] M. Neo, S. Kotani, T. Nakamura et al., "A comparative study of ultrastructures of the interfaces between four kinds of surface-active ceramic and bone," *Journal of Biomedical Materials Research*, vol. 26, no. 11, pp. 1419–1432, 1992.
- [4] M. Ikenaga, K. Ohura, T. Nakamura et al., "Hyperthermic treatment of experimental bone tumours with a bioactive ferromagnetic glass-ceramic," *Bioceramics*, vol. 4, pp. 255–262, 1991.
- [5] Y. Ebisawa, F. Miyaji, T. Kokubo, K. Ohura, and T. Nakamura, "Bioactivity of ferrimagnetic glass-ceramics in the system $\text{FeO}-\text{Fe}_2\text{O}_3-\text{CaO}-\text{SiO}_2$," *Biomaterials*, vol. 18, no. 19, pp. 1277–1284, 1997.
- [6] R. K. Singh, G. P. Kothiyal, and A. Srinivasan, "Magnetic and structural properties of $\text{CaO}-\text{SiO}_2-\text{P}_2\text{O}_5-\text{Na}_2\text{O}-\text{Fe}_2\text{O}_3$ glass ceramics," *Journal of Magnetism and Magnetic Materials*, vol. 320, no. 7, pp. 1352–1356, 2008.
- [7] L. L. Hench, R. J. Splinter, W. C. Allen, and T. K. Greenlee, "Bonding mechanisms at the interface of ceramic prosthetic materials," *Journal of Biomedical Materials Research*, vol. 5, no. 6, pp. 117–141, 1972.
- [8] H. Bromer, E. Pfeil, and H. H. Kos, Ger. Patent no. 2,326,100, 1973.
- [9] T. Kokubo, S. Ito, M. Shigematsu, S. Sakka, and T. Yamamuro, "Mechanical properties of a new type of apatite-containing glass-ceramic for prosthetic application," *Journal of Materials Science*, vol. 20, no. 6, pp. 2001–2004, 1985.
- [10] M. Akao, H. Aoki, and K. Kato, "Mechanical properties of sintered hydroxyapatite for prosthetic applications," *Journal of Materials Science*, vol. 16, no. 3, pp. 809–812, 1981.
- [11] P. Vincenzini, Ed., *Ceramics in Clinical Applications*, Elsevier, Amsterdam, The Netherlands, 1987.
- [12] M. Kawashita, Y. Iwahashi, T. Kokubo, T. Yao, S. Hamada, and T. Shinjo, "Preparation of glass-ceramics containing ferrimagnetic zinc-iron ferrite for the hyperthermal treatment of cancer," *Journal of the Ceramic Society of Japan*, vol. 112, no. 1307, pp. 373–379, 2004.
- [13] T. Leventouri, A. C. Kis, J. R. Thompson, and I. M. Anderson, "Structure, microstructure, and magnetism in ferrimagnetic bioceramics," *Biomaterials*, vol. 26, no. 24, pp. 4924–4931, 2005.
- [14] O. Bretcanu, S. Spriano, E. Verné, M. Cöisson, P. Tiberto, and P. Allia, "The influence of crystallised Fe_3O_4 on the magnetic properties of coprecipitation-derived ferrimagnetic glass-ceramics," *Acta Biomaterialia*, vol. 1, no. 4, pp. 421–429, 2005.
- [15] R. K. Singh, G. P. Kothiyal, and A. Srinivasan, "Magnetic and structural properties of $\text{CaO}-\text{SiO}_2-\text{P}_2\text{O}_5-\text{Na}_2\text{O}-\text{Fe}_2\text{O}_3$ glass ceramics," *Journal of Magnetism and Magnetic Materials*, vol. 320, no. 7, pp. 1352–1356, 2008.
- [16] M. Kawashita, H. Takaoka, T. Kokubo, T. Yao, S. Hamada, and T. Shinjo, "Preparation of magnetite-containing glass-ceramics in controlled atmosphere for hyperthermia of cancer," *Journal of the Ceramic Society of Japan*, vol. 109, no. 1265, pp. 39–44, 2001.

- [17] W. Leenakul, P. Intawin, J. Ruangsuriya, P. Jantaratana, and K. Pengpat, "Magnetic bioactive $\text{SrFe}_{12}\text{O}_{19}$ - SiO_2 - CaO - Na_2O - P_2O_5 glass-ceramics for hyperthermia treatment of bone cancer," *Integrated Ferroelectrics*, vol. 148, no. 1, pp. 81–89, 2013.
- [18] A. Karamanov, G. Taglieri, and M. Pelino, "Iron-rich sintered glass-ceramics from industrial wastes," *Journal of the American Ceramic Society*, vol. 82, no. 11, pp. 3012–3016, 1999.
- [19] M. Kawashita, Y. Iwahashi, T. Kokubo, T. Yao, S. Hamada, and T. Shinjo, "Preparation of glass-ceramics containing ferrimagnetic zinc-iron ferrite for the hyperthermal treatment of cancer," *Journal of the Ceramic Society of Japan*, vol. 112, no. 1307, pp. 373–379, 2004.
- [20] O. Bretcanu, E. Verne, M. Coisson, P. Tiberto, and P. Allia, "Magnetic properties of the ferrimagnetic glass-ceramics for hyperthermia," *Journal of Magnetism and Magnetic Materials*, vol. 305, pp. 529–533, 2006.
- [21] C. S. Hsi, H. Z. Cheng, H. J. Hsu, Y. S. Chen, and M. C. Wang, "Crystallization kinetics and magnetic properties of iron oxide contained $25\text{Li}_2\text{O}$ - 8MnO_2 - 20CaO - $2\text{P}_2\text{O}_5$ - 45SiO_2 glasses," *Journal of the European Ceramic Society*, vol. 27, pp. 3171–3176, 2007.
- [22] S. A. M. Abdel-Hameed, M. M. Hessien, and M. A. Azooz, "Preparation and characterization of some ferromagnetic glass-ceramics contains high quantity of magnetite," *Ceramics International*, vol. 35, no. 4, pp. 1539–1544, 2009.
- [23] S. Murakami, T. Hosono, B. Jeyadevan, M. Kamitakahara, and K. Ioku, "Hydrothermal synthesis of magnetite/hydroxyapatite composite material for hyperthermia therapy for bone cancer," *Journal of the Ceramic Society of Japan*, vol. 116, no. 1357, pp. 950–954, 2008.
- [24] R. K. Singh, G. P. Kothiyal, and A. Srinivasan, "In vitro evaluation of bioactivity of CaO - SiO_2 - P_2O_5 - Na_2O - Fe_2O_3 glasses," *Applied Surface Science*, vol. 255, no. 15, pp. 6827–6831, 2009.
- [25] S. A. M. Abdel-Hameed, M. A. Marzouk, and A. E. Abdel-Ghany, "Magnetic properties of nanoparticles glass-ceramic rich with copper ions," *Journal of Non-Crystalline Solids*, vol. 357, no. 24, pp. 3888–3896, 2011.
- [26] S. A. M. Abdel-Hameed, M. A. Marzouk, and M. M. Farag, "Effect of P_2O_5 and MnO_2 on crystallization of magnetic glass ceramics," *Journal of Advanced Research*, 2013.
- [27] R. K. Singh and A. Srinivasan, "Bioactivity of SiO_2 - CaO - P_2O_5 - Na_2O glasses containing zinc-iron oxide," *Applied Surface Science*, vol. 256, no. 6, pp. 1725–1730, 2010.
- [28] L. L. Hench and J. K. West, "Biological applications of bioactive glasses," *Life Chemistry Reports*, vol. 13, pp. 187–241, 1996.
- [29] L. L. Hench and G. La Torre, "Reaction kinetics of bioactive ceramics, part IV: effect of glass and solution composition," in *Bioceramics*, T. Yamamuro, T. Kokubo, and T. Nakamura, Eds., vol. 5, pp. 67–74, Kobonshikankokai, Kyoto, Japan, 1992.
- [30] J. M. Oliveira, R. N. Correia, and M. H. Fernandes, "Effects of Si speciation on the in vitro bioactivity of glasses," *Biomaterials*, vol. 23, no. 2, pp. 371–379, 2002.