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The Structural Characterization of Ga_2O_3-Na_2O-CaO-ZnO-SiO_2 Bioactive Glasses

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***Abstract*—The characterization of bioactive glasses in which zinc (Zn) has been incrementally replaced by gallium (Ga).**

I. Introduction

Bioactive glasses are glasses which contain ions that are analogous to those found in bones and tissue fluids, and upon implantation, dissolution of the glass occurs, ultimately resulting in the formation of a chemical bond between the implanted material and the surrounding tissue [1]. An important feature of bioactive glasses is the chemical composition. These glasses stimulate different therapeutic effects within the body depending on the ions that are released. Currently, bioactive glasses play a larger role than ever in developing implantable materials, with applications ranging from use as bone void fillers, as glass/ceramic scaffolds, to coatings on metallic implants that are used in total joint replacements [2]. The increased demand for bioactive glasses has led to diversification in their design and purpose. Since these glasses are extremely dependent on their chemical compositions, as well as their ability to consistently dissolve while still maintaining sufficient structural integrity upon implantation, it is important to thoroughly understand the specific structural role of each of the compositional elements before proceeding to biological testing. This study focuses on the structural characterization of a series of bioactive glasses in which zinc (Zn) has been incrementally replaced by gallium (Ga). Gallium was chosen because it has exhibited properties such as the ability to lower blood-calcium levels [3], inhibit bacterial growth [4], and also because it has exhibited anti-cancer abilities [5].

II. Experimental Methods

A. Synthesis

Three glasses were designed for this study including one Ga-free glass (*Control)*, and two Ga-containing glasses (*TGa-1, TGa-2).*In the Ga-containing glasses, Ga_2O_3 is included at the expense of ZnO. Glass compositions can be found in (Table I).

TABLE I

Glass Compositions (mol fraction)

	Control	*TGa-1*	*TGa-2*
SiO_2	0.42	0.42	0.42
Ga_2O_3	0.00	0.08	0.16
ZnO	0.40	0.32	0.24
Na_2O	0.10	0.10	0.10
CaO	0.08	0.08	0.08

B. Sample Preparation

To obtain glass frit samples, the powdered mixes of analytical grade reagents (Sigma-Aldrich, Dublin, Ireland) were oven dried (100°C, 1h) and fired (1500°C, 1h) in platinum crucibles and shock quenched into water. The resulting frits were dried, ground, and sieved to obtain glass powders with a maximum particle size of either 90 µm or 425 µm.

C. Glass Characterization

X-ray diffraction (XRD) was first carried out in order to confirm that the glasses were maintaining an amorphous structure upon addition of gallium. The network connectivity of the glasses was calculated using the molar compositions of the glass, and assuming that Ga performs as both a network former and a network modifier in (1):

$$NC = \frac{\text{No. BOs} - \text{No. NBOs}}{\text{Total No. Bridging Species}} \quad (1)$$

Where:

NC= Network Connectivity

BO= Bridging Oxygens

NBO= Non-Bridging Oxygens

Differential thermal analysis (DTA) was performed in order to determine the glass transition temperature (Tg) for each glass (Fig. II). Inductively coupled plasma (ICP) spectroscopy was then performed in order to determine the rate at which ions

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were being released from the glasses upon submersion in double distilled water (Table II), and in particular, to confirm that Ga ions were being released. Raman spectroscopy was performed on glass frit samples in order to determine structural characteristics of each glass composition (Fig. III).

III. RESULTS

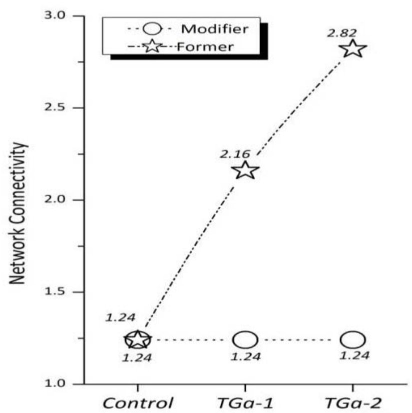

Fig. I. Network connectivity of glass series.

The XRD patterns confirmed the amorphous nature of all three glasses, while the network connectivity calculations suggest that the gallium ion acts predominantly as a network modifying oxide.

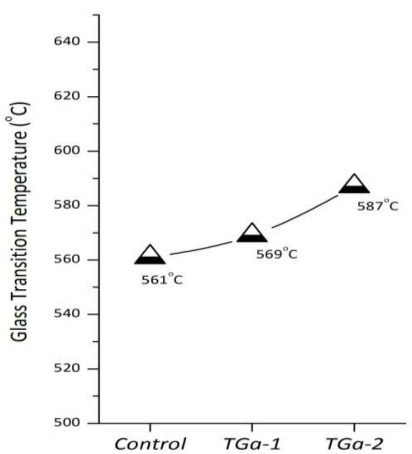

Fig. II. Glass transition temperatures (T_g) of the glasses.

The glass transition temperatures of the glasses increase from 561°C - 587°C as the gallium concentration increases from 0 – 0.16 mol fraction.

TABLE II

ION RELEASE CONCENTRATIONS

	<90 um Samples						<425 um samples				
	Ca (ug/ml)	Ga (ug/ml)	Na (ug/ml)	Si (ug/ml)	Zn (ug/ml)		Ca (ug/ml)	Ga (ug/ml)	Na (ug/ml)	Si (ug/ml)	Zn (ug/ml)
Control (1D)	1.18	0	11.4	3.51	0		0.48	0	1.44	0.68	0.16
Control (14D)	1.47	0	13.09	4.31	0		0.51	0	1.81	1.05	0.94
TGa-1 (1D)	2.6	6.3	11.05	6.35	0		0.53	0.46	0.88	0.83	0.5
TGa-1 (14D)	3.99	11.32	14.51	8.17	0		0.64	0.7	1.39	1.75	1.61
TGa-2 (1D)	6.89	19.55	14.45	12.3	0		1.6	2.06	2.7	2.54	0.08
TGa-2 (14D)	10.1	37.43	23.05	18.86	0		3.78	17.54	7.43	10.24	0.15

The table shows that ions are being released from each of the glasses, and that higher concentrations are being released from the samples with smaller particle size. Table II also shows that higher concentrations of ions are released from the glasses as their incubation time in water increases, and that higher concentrations of gallium ions are being released as gallium content increases.

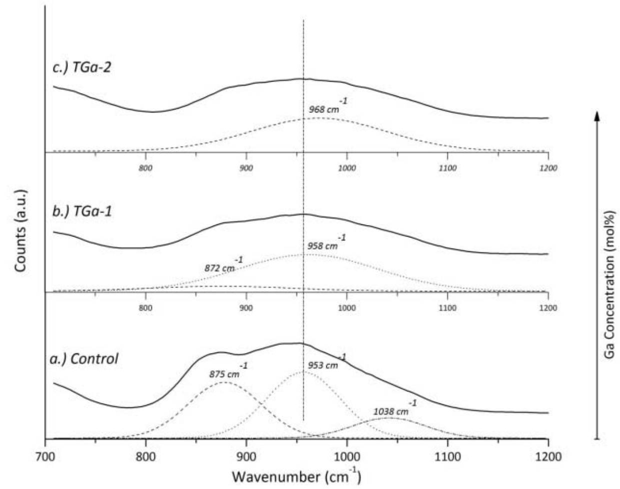

Fig. III. Raman Spectroscopy of Ga Glass series.

The Raman spectra exhibit the difference in connectivity within each glass. The shift in the spectra from the control glass to the TGa-1 glass, and then again from TGa-1 to TGa-2, indicates an incremental increase in the number of bridging oxygens present in the glasses.

IV. CONCLUSION

From this study we can conclude that although the inclusion of gallium (Ga) does increase the network connectivity of bioactive glasses, glasses containing Ga still maintain their amorphous nature and possess the ability to release ions when submerged in water.

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