



Contents lists available at ScienceDirect

Journal of the European Ceramic Society

journal homepage: www.elsevier.com/locate/jeurceramsoc

Original Article

Structure, energetics and bioactivity of silicon oxycarbide-based amorphous ceramics with highly connected networks

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ARTICLE INFO

Keywords:

Bioactive glasses
 Polymer-derived ceramics
 Silicon oxycarbides
 Network architecture
 Network connectivity

ABSTRACT

Mg and Ca substituted silicon oxycarbides are investigated with respect to their network architecture, enthalpy of formation and bioactivity. The synthesized materials have highly connected structural network with an open architecture and a minor but critical fraction of depolymerized Q-species. This combination of structural features allows for providing bioactivity at the same time with enhanced thermo-mechanical robustness and crystallization resistance. It is argued that silicon oxycarbide amorphous ceramics may consequently serve as model compounds for developing rational design concepts for advanced bioactive glasses.

1. Introduction

Bioactive glasses have been developed within the last five decades and are typically based on variations of a soda-lime phospho-silicate composition [1–5]. Thus, numerous melt-derived glasses with compositions in the system Na₂O-CaO-SiO₂-P₂O₅ as well as variations thereof containing additional cations and anions (e.g., Mg²⁺, Sr²⁺, Zn²⁺, F⁻ etc.) were reported in the last decades to exhibit bioactivity, i.e. being able to provide spontaneous integration with hard and soft tissue upon biomineralization of hydroxyapatite on their surface when exposed to (simulated) body fluids [6–10]. The biomineralization of hydroxyapatite on the surface of bioactive glasses has been related to a multi-step process involving the release of cations such as Na⁺ as well as soluble silica-based species from the glass, the formation of a hydrated scale, which is depleted of modifier cations, enriched in silica, and contains Ca²⁺ and PO₄³⁻ and CO₃²⁻ anions [11–15]. Incorporation of collagen macromolecules within the hydroxyapatite layer and subsequent interactions with body fluids and cells lead to the formation of new bone tissue. Obviously, there is an intimate interplay between the partial dissolution of the glass network in contact with body fluids and the reactivity/evolution of the glass surface which dictates the bioactivity of melt-derived glasses [16].

It was shown that melt-derived silicate glasses exhibit bioactivity within a rather narrow compositional range [5]. Efforts in improving their behavior relate mainly on empirical assessments involving compositional variations of the bioactive glasses and correlations with their bioactivity. Recently, several studies discussed the potential of

rationally designing and improving bioactive glasses and defined relevant structural parameters of the glass which are believed to determine its bioactivity [17–20]. One structural parameter of the glass, which was recognized by Strnad [21] and by Rawlings [22] to determine the bioactivity, was the connectivity of the silicate network (NC). Typically, NC correlates with the number of bridging oxygens per SiO₄ tetrahedron in the glass network – here, the tetrahedra are conventionally described with Qⁿ symbols, *n* indicating the number of bridging oxygens in the SiO₄ unit.

The correlation between the Qⁿ(Si) and Qⁿ(P) speciations of numerous compositions in the Na₂O-CaO-SiO₂-P₂O₅ system and their bioactivity were studied recently by Mathew et al. [20]; they identified an upper limit for the NC values of glasses exhibiting bioactivity to be ca. 2.7; beyond that value the bioactivity was shown to strongly decrease or disappear [20]. The most suitable NC range for bioactivity was found to be between 2.1 and 2.6, with an optimum at 2.55 [20].

In addition to melt quenched bioactive glasses, sol-gel-derived amorphous silicates of specific compositions were found to be bioactive [23–26]. Interestingly, the sol-gel silicate glasses combine a significantly higher NC (as compared to the Na₂O-CaO-SiO₂-P₂O₅ systems discussed above) with a much larger specific surface area (compare a few m²/g for melt quenched glasses with ~10² m²/g for sol-gel-derived materials) [27,28]. For instance, bioactive glass materials in the system SiO₂-CaO were synthesized via the sol-gel process and exhibited NC values between 2.62 and 3.6 which are significantly higher than those reported for bioactive melt-quenched glasses [29].

Recently, we have reported the synthesis of a Mg and Ca containing

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silicon oxycarbide amorphous material which was prepared from a polysiloxane-based single-source precursor and exhibited bioactivity [30]. Polymer-derived amorphous ceramics such as silicon oxycarbides are typically made upon thermal conversion (pyrolysis) of silicon-containing preceramic polymers. Their structure is composed of a network of corner-shared silicon-centered tetrahedra incorporating both Si–C and Si–O but no C–O bonds. The network is distinct from a mixture of separate, intergrown silicon carbide and silicon oxide nanophases and exhibits the full range of mixed bonded $\text{SiO}_x\text{C}_{4-x}$ tetrahedra (SiO_4 , SiO_3C , SiO_2C_2 , SiOC_3 , and SiC_4) [31]. The presence of carbon within the amorphous network indicates that the Si tetrahedra are corner-shared not only via oxygens (i.e., 2 tetrahedra corner-sharing an oxygen) but also by carbons (i.e., four tetrahedra corner-shared by one carbon); this leads formally to a clearly higher degree of cross-linking of the network as compared to that of fully-connected SiO_2 glass (consisting of corner-shared Q^4 tetrahedra via bridging oxygens; i.e. with $\text{NC} = 4$). Thus, the presence of carbon within the network of silicon oxycarbide provides a fully connected network by corner sharing and a different local structure than that of silica/or silicate networks. Extensive studies based on magic-angle-spinning nuclear magnetic resonance (MAS NMR) spectroscopy, small-angle x-ray scattering (SAXS), high-temperature creep and transmission electron microscopy (TEM) data indicate that the SiOC amorphous network has a nano-heterogeneous and fractal nature (mass fractal dimension of 2.4–2.5) [31–36].

There has also been success in incorporating different metal cations into the silicon oxycarbide glassy network, including alkali metals [37], alkaline earth metals [30], and transition metals [38–41], as well as main group metals [41–43]. The incorporation of metals into SiOC was shown to affect the high temperature evolution of its phase composition as well as the network architecture [39,40,44]. In a case study related to the synthesis of a lithium-substituted silicon oxycarbide [37], it has been shown that mixed bonding Si coordination tetrahedra (SiO_4 , SiO_3C , SiO_2C_2 , SiOC_3 , SiC_4) exist in less polymerized configurations (e.g., SiO_3C tetrahedra bearing one non-bridging oxygen, i.e. $\text{SiO}_2^{\text{b}}\text{O}^{\text{nb}}\text{C}$) as well as in fully connected networks. In this context, it was proposed that carbon may substitute for oxygen in silicon-centered tetrahedra in geologic systems based on analogy with these polymer derived ceramics [37].

In conclusion, structural studies related to silicon oxycarbide amorphous ceramics and the corresponding metal modified systems reveal two main features: (i) The incorporation of carbon within the silica network induces a significant increase of cross-linking degree (formally, $\text{NC} > 4$). The immediate consequence has been demonstrated in the improved thermomechanical properties of the SiOC glass as well as in its outstanding crystallization resistance; (ii) The incorporation of metal into the SiOC glass seems to remove some of the carbon from the network. Moreover, for specific metals (e.g., Li) the network connectivity is reduced (e.g., SiLiOC [37]).

Obviously, there are two “knobs” which can be turned to adjust the degree of cross-linking of the silicon oxycarbide network (as compared to that of silica and silicate glasses): carbon incorporation to increase it and metal cation incorporation to decrease it. The main challenge in making a potentially bioactive material is to find an optimum carbon and metal cation content, to provide an amorphous network with high crystallization resistance and, at the same time, with the ability to eventually dissolve in simulated body fluids. In the present study, the network architecture of the recently reported bioactive Mg and Ca substituted silicon oxycarbide amorphous materials [30] are characterized by means of ^{29}Si MAS NMR. Exposure to simulated body fluid (SBF) is performed in order to demonstrate the bioactivity of the prepared glasses. High temperature oxide melt solution calorimetric studies are performed to determine the enthalpy of formation of these bioactive materials. We discuss here the bioactivity of the prepared Mg and Ca containing silicon oxycarbide materials within the context of their network architecture as well as their thermodynamic stability. The results presented here may help to design thermo-mechanically robust

Table 1
Samples prepared in the present study and their elemental compositions.

Sample	Amount of PMS [g]	Amount of $\text{M}(\text{acac})_2$ (M = Mg, Ca) [g]	Composition
SiOC	5	–	$\text{Si}_1\text{O}_{1.51}\text{C}_{0.68}$
M1	5	0.30 $\text{Mg}(\text{acac})_2$	$\text{Mg}_{0.012}\text{Si}_1\text{O}_{1.52}\text{C}_{0.62}$
M2	5	2.89 $\text{Mg}(\text{acac})_2$	$\text{Mg}_{0.16}\text{Si}_1\text{O}_{1.86}\text{C}_{1.16}$
MC1	5	0.12 $\text{Mg}(\text{acac})_2$ 0.09 $\text{Ca}(\text{acac})_2$	$\text{Mg}_{0.008}\text{Ca}_{0.006}\text{Si}_1\text{O}_{1.52}\text{C}_{0.64}$
MC2	5	1.25 $\text{Mg}(\text{acac})_2$ 0.90 $\text{Ca}(\text{acac})_2$	$\text{Mg}_{0.07}\text{Ca}_{0.05}\text{Si}_1\text{O}_{1.73}\text{C}_{0.96}$

amorphous materials (i.e. having highly connected architectures) which exhibit bioactivity. Because of their superior mechanical properties and stability, these materials might offer exciting opportunities when envisaging load-bearing applications as well as high temperature fabrication and densification of bioactive coatings, fibers, fiber mats, complex scaffolds etc.

2. Materials and methods

SiOC and MgCaSiOC samples were synthesized using a commercial polysilsesquioxane precursor (Wacker-Belsil PMS MK powder, Wacker, Burghausen, Germany), which was chemically modified with magnesium and calcium acetylacetonate ($\text{Mg}(\text{acac})_2$ and $\text{Ca}(\text{acac})_2$, Sigma Aldrich, Germany). The polysilsesquioxane precursor contains cross-linkable hydroxy and ethoxy groups which can further react with metal alkoxides, acetylacetonates, or acetates. The polysilsesquioxane was reacted in isopropanol with the corresponding amount of metal acetylacetonate(s) at room temperature to prepare the single-source precursor for the SiOC-based glasses modified with earth-alkali metals (see Table 1). The reaction solution was stirred overnight at room temperature and subsequently the solvent was removed in vacuum (10^{-2} mbar). The resulting single-source precursors were cross-linked at 250 °C and converted upon pyrolysis in argon at 1100 °C to SiOC, MgSiOC and MgCaSiOC glasses. The elemental composition of the prepared glass powders was measured by Mikroanalytisches Labor Pascher (Remagen, Germany). Beside the ternary silicon oxycarbide glass sample (referred as to SiOC), four samples were synthesized for this study. Two samples contained low amounts of earth-alkali metals (i.e., M1 for the Mg-modified and MC1 for the Mg + Ca-modified SiOC glass) and two samples were prepared to contain higher amount of Mg and Mg + Ca (M2 and MC2, respectively). The experimentally determined elemental compositions of these samples are listed in Table 1.

High temperature oxidative solution calorimetry in a molten oxide solvent was used to measure the enthalpies of formation of each sample. Pellets of ca. ~1 mg were dropped from room temperature into molten sodium molybdate ($3\text{Na}_2\text{O}\cdot 4\text{MoO}_3$) at 802 °C in either a custom-built Tian-Calvet twin microcalorimeter or a commercially-built Setaram AlexSYS twin microcalorimeter, having a very similar design. Oxygen gas was bubbled into the solvent at 4.95–10.90 ml/min to maintain an oxidizing environment and assist pellet dissolution by stirring the melt. Evolved gases were removed and an oxidizing atmosphere was maintained by flushing the headspace above the solvent with oxygen gas at 70.80 ml/min. Between 8 and 13 drops were conducted for each sample to get appropriate statistics. The thermal effect of the drops was calibrated against a platinum standard as in [45,46].

Fourier Transformed Infrared (FTIR) spectra were collected using a Bruker Vertex 70 FT-IR instrument (Bruker, USA) in attenuated total reflectance geometry (ATR). X-ray diffraction (XRD) measurements were performed at a STOE X-ray diffractometer (Stoe & Cie GmbH, Germany) in transmission geometry (Mo K_α radiation).

^{29}Si magic angle spinning nuclear magnetic resonance (MAS NMR) spectra and ^{13}C (^1H) cross-polarization (CP) MAS NMR spectra were collected using either a 4 or 7 mm Bruker CPMAS probe and a Bruker

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