Na$_2$CaSi$_2$O$_6$–P$_2$O$_5$ based bioactive glasses. 
Part 1: Elasticity and structure

Chung-Cherng Lin $^{a,*}$, Li-Chen Huang $^{b}$, Pouyan Shen $^{b}$

$^{a}$ Institute of Earth Sciences, Academia Sinica, Taipei 115, Taiwan, ROC
$^{b}$ Institute of Materials Science and Engineering, National Sun Yat-Sen University, Kaohsiung 804, Taiwan, ROC

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Abstract

The glass structure and elastic properties of two bioglasses having bulk compositions near Na$_2$CaSi$_2$O$_6$ (45S5.2) and Na$_2$CaSi$_3$O$_8$ (55S4.1) were studied using both Raman and Brillouin scattering techniques. The annealed 45S5.2 glass has more Q$^2$ and Q$^0$ but less Q$^3$ species than 55S4.1 glass due to lower (Si$^{4+}$ + P$^{5+}$)/(Na$^+$ + Ca$^{2+}$) ratio. Brillouin scattering measurements of the as-annealed glasses indicated that 45S5.2 glass is ca. 2% and 9% higher in Young/C$^{213}$s and bulk moduli than 55S4.1 glass due to more modifiers in the 45S5.2 glass. Nearly full crystallization of 45S5.2 glass was observed after treating it at 715°C for ca. 30 min. Devitrification of the 45S5.2 glass caused an increase in the elastic moduli up to ca. 30% (fully crystallized) but a negligible change in density. This 45S5.2-derived crystalline phase displayed at least 17 Raman bands, and has the average elastic moduli of 72.4 (bulk), 41.6 (shear), and 104.7 (Young’s) GPa.

Na$_2$O is an effective flux in the glass melting process, making it easier to homogenize, cast and flame spray the glasses. Second, dissolution of Na$^+$ and Ca$^{2+}$ from the glass will result in the formation of a silica-rich and CaO–P$_2$O$_5$-rich bilayer and finally the formation of hydroxycarbonate apatite (HCA), which is necessary for the tissues to bond to the implant as of concern to the bone-bonding ratio [2,4]. The leached Na$^+$ and Ca$^{2+}$ also affect the physiological balance of solution at the glass–ceramic interface and modify the local pH [1]. In fact, the alkalinization may promote synthesis and cross-linking of collagen and the formation of hydroxyapatite – a beneficial effect for in vivo bone growth and repair [5]. The network former (i.e., SiO$_2$) in the bioactive glass holds the three-dimensional non-periodic glass structure during selective dissolution of cations (e.g., Na$^+$) by suppressing the detachment of some other ions [1]. The presence of SiO$_2$ also helps the precipitation or surface reconstruction of the loose silica-rich layer, and hence enhances the formation of HCA.

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1. Introduction

Most of the bioactive materials developed for applications in prosthesis or bone implantation are the (Ca, P)-bearing silicate glasses and ceramics. Hench and co-workers had developed a series of Na$_2$O–CaO–P$_2$O$_5$–SiO$_2$ bioactive glasses (the so-called Bioglass®) with acceptable in vivo bioactivity index [1,2]. This type of bioactive materials is attractive because of no elicitation of foreign body response and strong bonding to bone tissue. The bioactivity and biocompatibility of a bioactive glass are due to the presence of phosphorus and calcium – the typical surface active sites in a bioglass [3]. Sodium ions in the bioglass composition can also contribute to two effects. First, Na$_2$O is an effective flux in the glass melting process, making it easier to homogenize, cast and flame spray the glasses. Second, dissolution of Na$^+$ and Ca$^{2+}$ from the glass will result in the formation of a silica-rich and CaO–P$_2$O$_5$-rich bilayer and finally the formation of hydroxycarbonate apatite (HCA), which is necessary for the tissues to bond to the implant as of concern to the bone-bonding ratio [2,4]. The leached Na$^+$ and Ca$^{2+}$ also affect the physiological balance of solution at the glass–ceramic interface and modify the local pH [1]. In fact, the alkalinization may promote synthesis and cross-linking of collagen and the formation of hydroxyapatite – a beneficial effect for in vivo bone growth and repair [5]. The network former (i.e., SiO$_2$) in the bioactive glass holds the three-dimensional non-periodic glass structure during selective dissolution of cations (e.g., Na$^+$) by suppressing the detachment of some other ions [1]. The presence of SiO$_2$ also helps the precipitation or surface reconstruction of the loose silica-rich layer, and hence enhances the formation of HCA.
of hydroxyapatite layer [2,6,7]. The interactions of bone tissues and the Na$_2$O–CaO–SiO$_2$–P$_2$O$_5$ bioactive implants, in particular the interfacial reaction kinetics and the sequence of reactions, have been critically reviewed by Hench [2,8].

An ideal biomaterial requires both good biochemical and biomechanical compatibility. A particular advantage of bioglass is the ability to bond to both hard and soft tissues. However, a disadvantage of bioglass is its brittleness. As a consequence, its handling and mechanical properties are not adequate for significant load bearing applications. The monophase bioactive glass, with low strength, was generally restricted to clinical non-load bearing situation. On the other hand, the glass–ceramics, derived from bio-glasses by devitrification or combination with other materials (e.g., polymers, inert alloys and ceramics), have offered a better mechanical/biological performance [9,10]. It is also noteworthy that bone must be loaded in order to remain healthy. The implant with too much higher Young’s modulus than bone tends to carry the load. The resultant stress shielding of bone would induce biological change and even bone resorption. The interface between a stress shielded bone and the implant would then deteriorate as the bone structure is weakened [9]. Thus, elastic properties should not be neglected while searching biological implant materials based on chemical criterion.

The intrinsic strength of a bioglass can be used as a reference for development of new bioactive materials, e.g., a bioactive glass–ceramic with a specified crystallinity or a composite with specified mechanical strength based on that glass. The mechanical strength of a glass product depends on its elastic constant, shape/architecture, surface/internal defects (e.g., scratches, flaws, and bubbles) and the character of the force to which it is subjected. These factors inevitably degrade the mechanical strength of a material to 1/10 or lower of its intrinsic (theoretical) strength. Thus, one cannot obtain the intrinsic strength by using conventional and destructive mechanical test on a big specimen. Brillouin spectroscopy is a powerful alternative for elasticity measurement of transparent materials without a second phase [11–13]. The surface defects of a small and bubble-free glass specimen causes only a slightly higher background but no frequency shift for the Brillouin signals. Therefore, the elastic constants/moduli determined by Brillouin spectroscopy represent the intrinsic and highest strength of the glass.

Raman spectroscopy has been widely used to study the structure of glasses and supercooled melts. Recently, Raman spectroscopy was used to study the structure in several bioglasses [14] and to detect the formation of HCA on bioactive materials after exposure to simulated body fluid (SBF) [15]. A combination of Raman and Brillouin scattering methods allows researchers to investigate the detailed relations among composition, elastic properties, and glass structure of a bioactive glass. This information may be applied to screen the optimal biomaterial from a series of candidates.

Among the Na$_2$O–CaO–P$_2$O$_5$–SiO$_2$ glasses, 45S5 material (a composition 24.5Na$_2$O·24.5CaO·6P$_2$O$_5$·45SiO$_2$ (in wt%), where S denotes the network former SiO$_2$ in 45% followed by a specific Ca/P molar ratio 5.2) has been the most popular one and its properties and applications widely studied. The 45S5 glass is non-toxic and biocompatible [16], and in fact clinically used for middle ear prostheses and as endosseous ridge implants [9]. Nevertheless, the intrinsic strength of this glass or its glass–ceramics counterpart was not explored till now.

Here, we report the anionic structure and elastic properties of the as-annealed 45S5.2 glass and its thermal evolution using both Raman and Brillouin spectroscopic methods. Another bioglass, 55S4.1, which has an in vivo bioactivity index lower than that of 45S5.2 glass but close to that of Ceravital® glasses [2] was also characterized in order to study the effect of composition on the structure and elastic properties of this popular bioglass system. The results of specific devitrification treatments to form glass–ceramics with crystals dispersed in the glass matrix are reported in the interrelated paper [17].

2. Experimental

2.1. Fabrication of glasses

Bioactive glasses 45S5.2 with SiO$_2$ 45, Na$_2$O 24.5, CaO 24.5 and P$_2$O$_5$ 6 wt% (Ca/P molar ratio = 5.2) and 55S4.1 with SiO$_2$ 55, Na$_2$O 19.5, CaO 19.5 and P$_2$O$_5$ 6 wt% (Ca/P molar ratio = 4.1) were prepared in this study. The notation of the bioactive glasses followed Hench et al. [1] with the first digit representing SiO$_2$ content in wt% and the second the Ca/P molar ratio. Note that symbols 45S5 and 55S4.3 have been used in Hench’s work for the same glasses [1,2]. The powders of Ca$_3$(PO$_4$)$_2$ (Merck, Ca = 35–40%), CaCO$_3$ (99.95%, Cerac, 325 mesh), Na$_2$CO$_3$ (GR grade, Hanawa), and SiO$_2$ (99.99%, Cerac, 100 mesh) based on the above specified ratios were mixed and ground using an alumina mortar and pestle for 25 min at least.

The sample charges of mixed reagents were calcined twice before firing at high temperature – the first calcination was conducted at 750 °C×6 h for combustion of oxalate, the second was carried out at 1300 °C×2 h for decarbonation and vitrifying the sample charges. The melts were then quenched from 1000 °C. All sample charges were pulverized after each calcination treatment. Finally, the sample charges were melted at 1420 °C for 2 h and then quenched together with their containers on a brass plate. Pt containers were used throughout the heat treatments. The two as-quenched glasses are both colorless and transparent. According to DSC analysis (Netzsch DSC404, 10 °C/min in air), the glass transition temperatures ($T_g$) of 45S5.2 and 55S4.1 are ~540 °C and ~580 °C, respectively (Fig. 1). Thus, the two as-quenched glasses were annealed at 5 °C below their $T_g$ for one hour to remove residual stress and prevent glass from devitrification, which
Archimedes the calculation of elastic modulus, was measured using evolution after thermal treatment at 715°C. The resolution and confocal length of the spectrometer are 1 cm⁻¹/pixel and 80 cm, respectively. The frequencies and number of Raman bands reported in this study were obtained by considering the possible vibrational groups and the equilibrium between Q species in the samples and the assumption of Gaussian peak profile.

2.3. Measurements of elasticity

For Brillouin scattering experiments, the glass plates with size of ca. 2 x 2 mm² and a thickness of ~140 μm were used. The polished opposite faces of the glass plates are parallel to each other within 0.3°. Specimens thus prepared were mounted on a goniometer head of an Eulerian cradle, and then aligned for a symmetric scattering geometry with an external angle of 90° between the incident and scattered beams. With this geometry, the refractive index can be cancelled out in the calculation of acoustic velocity. A 514.5 nm Ar⁺ laser with a temperature-controlled étalon and a six-passes tandem Fabry–Pérot interferometer (JRS Scientific Instruments) were used for the Brillouin experiments at 22 °C. A photomultiplier tube was used as the detector. The free spectral range (FSR) and finesse were 29.9792 GHz and 120, respectively. The laser power on the specimen was about 70 mW. For a 90° symmetric geometry, the acoustic velocity (V) can be calculated by the following formula [18]:

\[ V = \Delta \omega \lambda / 2^{1/2}, \]

where \( \Delta \omega \) is the Brillouin shift, and \( \lambda \) the wavelength of the incident laser. Each Brillouin frequency shift was estimated by assuming the Gaussian peak profiles. In order to obtain better signals, a Glan–Taylor prism was used to rotate the polarization of the incident laser beam to 45°. The bulk (\( K \)), shear (\( G \)), and Young’s (\( E \)) moduli and Poisson’s ratio (\( \nu \)) were then calculated according to the following formulae for elastically isotropic materials:

\[ V_T = (C_{44} / \rho)^{1/2} = (G / \rho)^{1/2}, \]

\[ V_L = (C_{11} / \rho)^{1/2} = [(K + 4G/3) / \rho]^{1/2}, \]

\[ E = 9K / (1 + 3K / G), \]

\[ \nu = (1 - 2G/3K) / (2 + 2G/3K), \]

where \( \rho \) is the density of sample, and \( V_T \) and \( V_L \) denoting the transverse and longitudinal acoustic velocities, respectively. For Brillouin scattering method, the transit time of the waves is too short to allow exchange of heat. Thus, the entropy is regarded to be constant during measurement and the moduli obtained from a Brillouin spectrum are all adiabatic.

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Fig. 1. DSC traces of the as-quenched bioactive glasses (a) 45S5.2 and (b) 55S4.1.
3. Results

3.1. XRD and Raman spectroscopy

The XRD patterns of the two annealed bioglasses show three broad peaks (diffuse rings). The 2θ values for the first (the strongest) and the third (the weakest) peaks are near the same for the two glasses (Fig. 2). The first strong band would be the leakage of the incident X-ray beam due to scattering by sample chamber and/or dusts. For the medium peak, the two glasses are different – maximum at 32° and 29.8° for 45S5.2 and 55S4.1 glasses, respectively. From Fig. 2, the relative peak area (intensity) of the second peak in the XRD pattern of 45S5.2 glass is slightly larger than that of 55S4.1 glass. These results indicate that the amorphous nature (i.e., the type and extent of short and/or medium range ordering) for the two glasses are different only in the secondly nearest neighbor. A larger 2θ for a glass means a shorter distance from any central atom, while a larger relative peak area means more atoms in the secondly nearest neighbor. The slight difference in the second peak therefore implies a slightly higher density for 45S5.2 glass than the 55S4.1 glass, in consistent with the densities measured at 22°C, i.e., 2.702 and 2.655 g/cm³ for the annealed 45S5.2 and 55S4.1 glasses, respectively. The higher density for the 45S5.2 glass can be attributed to more modifiers, Na⁺ and Ca²⁺, inside the empty polyhedra of the loose silicate network.

Fig. 3 shows the Raman spectra of the annealed bioactive glasses 45S5.2 and 55S4.1. The basic anionic structure of silicate melts and glasses has been widely studied by ²⁹Si nuclear magnetic resonance (²⁹Si NMR) and Raman spectroscopies two decades ago [19–22]. Both methods have revealed that the major structure of silicate glasses and melts at one atmosphere can be described by five anionic units, i.e., the so-called Q species used in NMR studies: SiO₄⁴⁻ (Q⁰, monomer, orthosilicates), Si₂O₆⁴⁻ (Q¹, dimmer, disilicates), Si₂O₄⁶⁻ (Q², chain and ring, metasilicates), Si₂O₃⁵⁻ (Q³, sheet, phyllosilicates), and SiO₂ (fully polymerized SiO₄ network, Q⁴, tectosilicates). The examination of the Raman spectra based on the literature indicated that the 45S5.2 glass should have Q⁰, Q², and Q³ species at least, while Q², Q³, and Q⁴ for the 55S4.1 glass. Thus, the equilibrium between Q³ and (Q² + Q⁴) has to exist in the two glasses at their Tg. For the 45S5.2 glass, the presence of Q⁰ may imply the presence of the equilibrium between Q¹ and (Q² + Q³), though Q¹ is usually rare in silicate melts [23]. A deconvolution of the 800–1200 cm⁻¹ envelope has shown that the presence of Q¹ is acceptable for obtaining a better fitting (the correlation coefficient R² > 0.998). On the other hand, the representative bands for Q³ species are at ~430, 1060, and 1190 cm⁻¹, and the latter two are rather weak in amorphous silica [24]. In Fig. 3, we cannot find any signal in the spectrum of 45S5.2 glass above 1150 cm⁻¹. Therefore, we neglected the intensity contribution from the two weak bands in the fitting process of 45S5.2 glass. Finally, there was certainly the contribution from phosphorus-related vibrations due to its role of network former and its considerable amount (6 wt% of P₂O₅) in the two glasses. All the described factors have been considered in the deconvolution of a Raman spectrum. The results were listed in Table 1 by assuming that Q¹ is existent in both glasses. However,
Table 1
Frequencies and assignments for Raman bands of the bioactive glasses 45S5.2 and 55S4.1

<table>
<thead>
<tr>
<th>45S5.2a</th>
<th>55S4.1b</th>
<th>Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>344</td>
<td>346</td>
<td>(I) Modifying cation–oxygen cage stretching⁵ or (II) coupling of modifying cation deformation of SiO₄ network⁶</td>
</tr>
<tr>
<td>347</td>
<td>345</td>
<td>(I) Symmetric oxygen stretching of Si–O–Si⁵e or (II) symmetric O–Si–O angular deformation of the coupled SiO₄ group⁶</td>
</tr>
<tr>
<td>605</td>
<td>791</td>
<td>Symmetric Si-O-Si bending of three-membered siloxane ring of SiO₄⁴</td>
</tr>
<tr>
<td>632</td>
<td>626</td>
<td>Rocking motion of bridging oxygen in structural units that contain non-bridging oxygen⁴</td>
</tr>
<tr>
<td>674</td>
<td>773</td>
<td>Oxygen-bending motion⁶(c)</td>
</tr>
<tr>
<td>864 (0.10/0.13)</td>
<td>–</td>
<td>Symmetric stretching of Q⁡⁴a,⁹</td>
</tr>
<tr>
<td>906 (0.08/0.10)</td>
<td>906 (0.04/0.03)</td>
<td>(I) Symmetric stretching of Q⁡⁴e,⁹ and/or (II) “O–P–O” stretching of PO₃ chain unit³</td>
</tr>
<tr>
<td>944 (0.58/0.22)</td>
<td>945 (0.40/0.11)</td>
<td>Symmetric stretching of Q⁡⁴a,⁹</td>
</tr>
<tr>
<td>974</td>
<td>970</td>
<td>P–O–P stretching⁴f</td>
</tr>
<tr>
<td>1008</td>
<td>999</td>
<td>⁴O–P–O˚ stretching of P₂O₅ sheet unit³</td>
</tr>
<tr>
<td>1044</td>
<td>1035</td>
<td>Asymmetric stretching of bridging oxygen in all Q species⁴b</td>
</tr>
<tr>
<td>–</td>
<td>1064</td>
<td>Asymmetric stretching of Q⁡⁴, Si–O–Si = 120°k,c</td>
</tr>
<tr>
<td>1086 (0.24/0.55)</td>
<td>1093 (0.56/0.86)</td>
<td>Symmetric stretching of Q⁡⁴a,⁹</td>
</tr>
<tr>
<td>–</td>
<td>1160</td>
<td>Asymmetric stretching of Q⁡⁴, Si–O–Si = 160°k,c</td>
</tr>
</tbody>
</table>

References: (a) McMillan and Wolf [22], (b) Mysen et al. [27], (c) Mysen et al. [21], (d) Konijnendijk and Stevelts [19], (e) Mysen et al. [28], (f) Wong [29]

Values inside the parentheses are the estimated relative abundance (fractions) among Q⁰, Q¹, Q², and Q³: the left data were based on the fitted peak areas (intensities) of the bands, while both fitted intensity and the normalized cross-sections suggested by Mysen et al. [25] were adopted for the calculation of the right values. The uncertainties for band frequency and the relative abundance of Q species are estimated to be ±5 cm⁻¹ and ±5%, respectively.

The basis for determination of the so-called normalized cross-sections proposed in [25] was not clear. Hence, we also included the fitted peak areas (relative intensities) for these Q species in Table 1 as references. Lockyer et al. [26] used NMR to study the structure of some bioactive glasses. In their results, the relative abundance of Q² and Q³ in the glass BG6 (containing (wt%) 18.8 Na₂O, 28.2 CaO, 47 SiO₂, and 6 P₂O₅) were estimated to be 0.70 and 0.30, respectively, which are close to the data of the 45S5.2 glass based on only peak areas (see Table 1). From Table 1, we know that the most abundant species in 45S5.2 and 55S4.1 glasses are Q² and Q³, respectively. The presence of Q¹ and its amount is uncertain although the band at 900–910 cm⁻¹ is required for a better fitting. A candidate responsible for the ~906-cm⁻¹ band may be the “O–P–O” stretching of PO₃ chain unit. The assignments for other bands can be found in Table 1.

When the annealed 45S5.2 glass was subjected to thermal treatment at 715 °C, devitrification took place quickly. An observation for glass heat treated at 715 °C for 15 min has revealed that the crystallization involved bulk nucleation (refer to [17]). The crystal form seems to be cube but with curved faces. Raman spectrum collected from the cube crystals is shown in Fig. 4. The signals from crystal are at 337, 591, and 986 cm⁻¹. The blending of the spectrum of crystal with that of glass is attributed to the small size (~12 μm) of the crystals, which are smaller than the spatial resolution of Raman spectrometer. Nearly full crystallization took place in the 45S5.2 sample after dwelling at 715 °C for 30 min. Fig. 5 shows the typical Raman spectrum of the crystalline phase derived from 45S5.2 glass. 17 bands have been recognized for this crystal: 292 (w), 341 (w), 395 (w, sh), 416 (mw), 453 (w), 500 (vw, sh), 517 (w), 531 (mw), 592 (s), 608 (vw, sh), 622 (w, sh), 697 (vw), 909 (mw), 944 (mw), 988 (vs), 1021 (mw, sh), and 1062 (mw, sh) cm⁻¹, where vw denotes very weak, w: weak, mw: medium to weak, s: strong, vs: very strong, and sh: shoulder. The X-ray diffraction pattern of this crystalline phase appeared to be identical to that observed in the 45S5 glass–ceramics reported by Hench and his co-workers [1,30,31]. In the interrelated paper [17], we pointed out that this crystal in fully crystallized 45S5 glass–ceramics reported by Hench and his co-workers [30,31]. The name ‘45S5.2-derived phase’ is therefore used throughout the text for this crystalline phase. To our knowledge, Raman spectrum of the 45S5.2-derived phase has not been reported.
3.2. Brillouin scattering

Table 2 lists the elastic constants of the annealed 45S5.2 and 55S4.1 glasses at 22 °C. For the sake of comparison, the data of two apatites and the 45S5.2-derived phase are also included. It is found that all the elastic moduli of the 55S4.1 glass are lower than those of the 45S5.2 glass: from 1.1% for shear modulus to 8.6% for bulk modulus. It is known that an elastic modulus can be represented as a function of density of material (see Eqs. (2)–(5)). However, the lowering in density is only 1.7% from 45S5.2 to 55S4.1 glasses. Other factors should contribute to the large difference in moduli.

The typical Brillouin spectra of the annealed 45S5.2 glass after devitrification at 715 °C for various periods are shown in Fig. 6. It should be reminded that the 45S5.2 glass was almost fully crystallized (>98%) after devitrifying at 715 °C for 30 min. The elastic data in Table 2 for the 45S5.2-derived phase are the average of a total of 19 data from samples after 30, 45, and 60 min of devitrification. Except for a special crystallographic plane, an anisotropic single-crystal specimen should display two signals from the interaction of incident laser beam and the transverse phonons. The Brillouin spectra of the 45S5.2-derived phase (collected at any position of specimens, thus with arbitrary crystal orientation) turned out to have single-like peaks for the signals from the interaction of incident beam with transverse phonons (the symbol T in Fig. 6). Apparently, the crystalline phase is elastically isotropic, and the formulae used for glasses can be applied to calculate the elastic constants of this crystal. However, an analysis about the full width at half maximum (FWHM) of peaks has revealed that the average FWHMs of transverse and longitudinal Brillouin signals of the 45S5.2-derived phase are about 32% and 47%, respectively, wider than those of the 45S5.2 and 55S5.2 glasses (cf. the spectra of 0, 30 and 60 min in Fig. 6). This result indicates that the 45S5.2-derived phase is slightly elastically anisotropic rather than a truly isotropic crystal. It is known that elastic isotropy can occur only for amorphous materials and some cubic crystals. The X-ray diffraction also confirmed that this

### Table 2

<table>
<thead>
<tr>
<th>Materials</th>
<th>Density (g/cm³)</th>
<th>C₁₁ (GPa)</th>
<th>C₁₂ (GPa)</th>
<th>Shear modulus (GPa)</th>
<th>Young's modulus (GPa)</th>
<th>Bulk modulus (GPa)</th>
<th>Poisson's ratio (v)</th>
</tr>
</thead>
<tbody>
<tr>
<td>45S5.2 Glass</td>
<td>2.702 (0.006)</td>
<td>96.6 (0.5)</td>
<td>35.2 (0.7)</td>
<td>30.7 (0.2)</td>
<td>77.9 (0.3)</td>
<td>55.6 (0.7)</td>
<td>0.267 (0.003)</td>
</tr>
<tr>
<td>55S4.1 Glass</td>
<td>2.655 (0.005)</td>
<td>91.3 (0.8)</td>
<td>30.6 (0.8)</td>
<td>30.4 (0.2)</td>
<td>75.9 (0.5)</td>
<td>50.8 (0.8)</td>
<td>0.251 (0.004)</td>
</tr>
<tr>
<td>45S5.2-Derived phase b</td>
<td>2.700 (0.009)</td>
<td>127.9 (1.8)</td>
<td>44.6 (2.0)</td>
<td>41.6 (0.5)</td>
<td>104.7 (1.0)</td>
<td>72.4 (1.8)</td>
<td>0.259 (0.006)</td>
</tr>
<tr>
<td>Hydroxyapatite c</td>
<td>3.146</td>
<td>140</td>
<td>13</td>
<td>45.6</td>
<td>115.0</td>
<td>80.4</td>
<td>0.262</td>
</tr>
<tr>
<td>Fluorapatite c</td>
<td>3.200</td>
<td>141</td>
<td>46</td>
<td>101.8</td>
<td>263.3</td>
<td>212.3</td>
<td>0.293</td>
</tr>
</tbody>
</table>

a The data of glasses and the 45S5.2-derived crystal were collected at 22 °C. The values inside the parentheses are standard deviation based on 3–4 measurements for density and 6–7 measurements for elastic moduli.

b According to Huang et al. [17], the 45S5.2-derived phase is (Na,Ca)₂Ca(Si,PO)₄; i.e., the Na₂CaSi₄O₉ phase.

c The data of hydroxyapatite and fluorapatite are from Bass [40].
crystal is not a cubic phase although it can be regarded as a pseudocubic or pseudohexagonal crystal [17]. Nevertheless, the narrow distribution of Brillouin shifts for signals from different orientations has enabled us to assume that any peak in the Brillouin spectrum of the 45S5.2-derived phase (e.g., Fig. 6) is the average from all crystal orientations. Thus, the formulae used for glasses (see Section 2.2) can be applied to the present case, and the data listed in Table 2 for the 45S5.2-derived phase are actually the average of all orientation. Besides, both $C_{11}$ and $C_{12}$ are not exactly but very close to the true $C_{ijkl}$ values of the crystal. Similar consideration for estimation of the elastic moduli of polycrystalline materials was also found elsewhere [32].

4. Discussion

4.1. Glass structure of the bioactive glasses and its evolution

Besides NMR, Raman spectroscopy has been widely used to study the anionic structure of silicate glasses/melts and the effect of phosphorus on the structure [19,21,28]. The presence of Q species in a glass is related to the bulk number of non-bridging oxygen per each tetrahedral cation (NBO/T, $T$ = tetrahedral-coordinated cations) and the deviation from its equilibrium at $T_g$. It has been pointed out that the phosphorus in pure silica tends to depolymerize the silicate network by entering the network as a fourfold coordinated cation [33]. On the other hand, phosphorus may polymerize the silicate network by forming cation phosphate complexes if other modifying cations exist in glasses or melts [23,28,33]. In such a case, the cation phosphate complexes occur as discrete units as suggested for silicate melt [28]. The bulk NBO/T ($T$ = Si, P) is 1.693 and 1.071 for the 45S5.2 and 55S4.1 glasses, respectively, if phosphorus acts as a network former; whereas 1.884 and 1.170, respectively, if all phosphorus ions are associated with modifying cations. In any case, the 55S4.1 glass is more polymerized than the 45S5.2 glass. This result was confirmed by Raman spectroscopy.

In Table 1, the relative abundance of $Q^3$ unit in 45S5.2 glass is less than that in 55S4.1 glass, while the inverse holds for $Q^2$. By considering the uncertainty of $\sim$5% (based on $\sum A_{Q^i} = 100$, where $A_{Q^i}$ is the percentage of $Q^i$ peak area, $i = 0–3$), $Q^1$, if any, may be of nearly the same amount for the two glasses. $Q^0$ was found only in 45S5.2 glass. We cannot estimate directly the abundance of $Q^4$ using the method suggested in [25]. However, $Q^4$ in 45S5.2 glass may be nil or less than that in 55S4.1 glass due to the presence of the $\sim$1060/1160 cm$^{-1}$ pair and stronger 435 cm$^{-1}$ band in the latter. The difference in glass structure between the 45S5.2 and 55S4.1 glasses is attributed to different ($Si^{4+} + P^{5+})/(Na^+ + Ca^{2+})$ ratio. The assignment for the $\sim$906 cm$^{-1}$ band is twofold: it may be caused by symmetric stretching of $Q^4$ and/or the $O\cdot P\cdot O$ stretching of PO$_4$ chain unit. In the NMR study of Lockyer et al. [26], $Q^4$ was not detected in all the glasses they studied. $Q^1$ was not found either in several binary and ternary silicate melts having a NBO/T between 1 and 2, and the equilibrium was suggested to be between $Q^2$ and $(Q^0 + Q^3)$ [34,35]. The relative abundance of $Q$ species for the present glasses would increase (e.g., by $\sim$8.5% for 45S5.2 glass) if $Q^1$ is indeed absent in our glasses. It is noteworthy that Raman signal of $Q^1$ was also observed in a Na$_2$O–MgO–SiO$_2$ glass with NBO/Si of 1.5 [36]. The cause of $Q^1$ in these studied glasses is unclear, perhaps due to different extent of deviation from the equilibrium at $T_g$ of the supercooled melts.

On the basis of polymerization sequence, the disproportion reaction for $Q^3$ and $Q^2$ would be

\[
2Si_2O_7^{4-} \rightleftharpoons 2SiO_4^{4-} + Si_2O_6^{2-},
\]

\[
2Si_1O_6^{2-} \rightleftharpoons Si_2O_5^{2-} + Si_1O_5^{2-}.\]

In other words, the Eq. (6) represents $2Q^3 \leftrightarrow 2Q^0 + Q^2$, and Eq. (7) denotes $2Q^2 \leftrightarrow Q^1 + Q^3$. (Note that the values of NBO/Si are 1, 2, 3, and 4 for Si$_2O_5^{2-}$ ($Q^3$), Si$_2O_6^{4-}$ ($Q^2$), Si$_2O_7^{6-}$ ($Q^1$), and SiO$_4^{2-}$ ($Q^0$) units, respectively.) As shown in Fig. 3 and Table 1, our 45S5.2 glass has a depolymerized species, $Q^0$ (i.e., the 864 cm$^{-1}$ band). If $Q^1$ is unstable at a given NBO/Si and temperature, then the reaction (6) trends toward the right, and the resultant of reactions (6) and (7) may be reduced to $3Q^2 \leftrightarrow 2Q^0 + 2Q^3$ as suggested by Virgo et al. [34] and Mysen et al. [35] for $1 < $NBO/Si$ < 2$. However, if the $Q^1$ content is not truly nil or the reactions are not at equilibrium, the system should involve both reactions (6) and (7), which may be the case of 45S5.2 glass. Furthermore, $Q^4$ seems to exist in the 55S4.1 glass (NBO/T = 1.071). In such a case, an extra reaction between $Q^3$ and $(Q^2 + Q^0 + Q^4)$ should be involved in 55S4.1 glass. The work of Mysen et al. [35] has implied that both equilibria between $Q^2$ and $(Q^0 + Q^3)$ and between $Q^3$ and $(Q^2 + Q^0)$ coexist in a silicate melt at NBO/T = 1. Nevertheless, $Q^0$ was not found in 55S4.1 glass as manifested by the absence of the band at 850–880 cm$^{-1}$ (see Fig. 3 and Table 1). Therefore, the $Q^0$ in our 55S4.1 glass has to be produced only from the disproportional decomposition of $Q^3$.

According to the in vitro immersion of bioactive glasses in SBF, Oliveira et al. [4] concluded that $Q^0$-rich glasses are easily leached to form a silica gel layer. It is known that the presence of a silica-rich layer is the requirement for the formation of the CaO–P$_2$O$_5$-rich layer and finally the formation of HCA layer between bone and the bioglass [2]. Thus, a higher in vivo bioactivity index for 45S5.2 glass than that of 55S4.1 can be partly attributed to the presence of $Q^0$ in the former (cf. Fig. 3). To interpret the difference in Raman intensity of silicate glasses, McMillan [37] assumed that a single site $\equiv$SiO (i.e., $Q^1$) defines a site for one $M^+$ cation, while the double-charged site $\equiv$SiO$_2$ (i.e., $Q^2$) may be associated with one $M^{2+}$ or two $M^{4+}$ cations. Similarly, to interpret the changes in NMR chemical shifts of Q species, Lockyer et al. [26] also considered that $Q^2$ and $Q^3$ species in the Na$_2$O–CaO–SiO$_2$ (6 wt% P$_2$O$_5$) glasses may prefer to associate with Ca$^{2+}$ and Na$^+$, respectively.
On the other hand, it has been postulated that the beneficial effect of 45S5 glass on in vivo bone growth and repair may be due to some extent of alkalization, which in turn increases the synthesis and cross-linking of collagen and hydroxyapatite formation [5]. If these arguments are correct, then we can say that the contribution of leaching out of Q^3 species to bioactivity of the Na_2O–CaO–SiO_2–P_2O_5 glasses may exceed that of Q^2 due to more Na^+ being associated with Q^3 and thus a higher alkalinity for the local solution.

By comparing the Raman spectra collected from the 45S5.2 samples after thermal treatment at 715 °C for 15 and 60 min (see Figs. 4 and 5, respectively), we concluded that the crystals appeared after firing for 15 min are also the Na_2CaSi_2O_6 phase; that is, only one crystalline phase was formed during devitrification of the 45S5.2 bioglass. The relative abundance of Q^3 species in the 45S5.2 sample did not show appreciable change after devitrification for 15 min due to only little amount of crystals in the devitrified sample. The crystalline phase derived from the 45S5.2 glass displayed 17 Raman bands at least (Fig. 5). An assignment for this crystal is beyond the scope of this study. However, according to the assignments for glasses, the two bands (292 and 341 cm⁻¹) with lowest frequency may be the lattice vibrational modes. The FWHMs of the 292 and 341 cm⁻¹ bands are 2–3 times that of other bands.

It has been pointed out that crystal defects may cause significant broadening in some Raman bands [38]. The 45S5.2-derived phase is a non-stoichiometric compound, and can be described as (Na,Ca)_2Ca(Si,P)_2O_6 [17]. The broadening of the two low-frequency bands implies the presence of considerable amount of defects (e.g., the Schottky pair V_{Na}^s and Ca_{Na}^s) in the crystal assuming no overlap of the bands.

4.2. Elastic properties – bioactive glasses and its derived crystal

The elastic constants of both 45S5.2 and 55S4.1 glasses are listed in Table 2. For applications in implants, Young’s modulus would be the most important parameter. It is found that Young’s, shear, and bulk moduli of the 55S4.1 glass are only 2 (2.6%), 0.3 (1.1%), and 4.8 (8.6%) GPa, respectively, lower than those of the 45S5.2 glass. The Poisson’s ratio shows that the 55S4.1 glass is a perfect (elastically) isotropic material. It is known that the elastic moduli of an isotropic material are proportional to its density (see Eqs. (2)–(5)). The densities of the annealed 45S5.2 and 55S4.1 glasses (2.702 and 2.655 g/cm³, respectively) are close to that of (2.9–3.0 g/cm³) of teeth enamel with 92–97% hydroxyapatite [39]. The difference in densities of the two glasses is only 1.7%. Thus, density should not be the only factor of the large difference in bulk modulus between the two glasses.

The elastic modulus of alkali silicate glasses commonly increases with increasing amount of modifier above a critical concentration, as a result of increasing contribution of cohesion [13]. Thus, a higher bulk modulus in the 45S5.2 than 55S4.1 glass can be partly attributed to more modifiers, Na_2O and CaO. The effect of P_2O_5 on the elasticity of the present glasses is unclear, though phosphorus has caused a more polymerized silicate network. Note that the Young’s modulus of the 45S5.2 bioglass reported in previous literature lies in the range of 30–50 GPa [8,9], which is much lower than that measured in this work (cf. Table 2). The inconsistency is chiefly attributed to different methods adopted for elasticity measurements and a minor difference in thermal histories of the samples.

All moduli of the 45S5.2 sample increased with the increase of time period for devitrification at 715 °C. The 45S5.2-derived phase has composition and density nearly identical to the parent glass. However, all elastic moduli of the 45S5.2-derived phase are about 30% higher than those of its parent glass. The elasticity of devitrified 55S4.1 samples was not measured. However, the elastic moduli of the 55S4.1 glass–ceramics should increase with increasing time for devitrification because the crystalline phase in the devitrified 55S4.1 sample is also the Na_2CaSi_2O_6 phase [17]. It is noteworthy that the crystal derived from the present glass has elastic moduli comparable to those of hydroxyapatite (cf. Table 2) and therefore may have potential applications as implant materials as addressed below.

Matching the stiffness of the implant material to bone allows stress transfer from the implant to the surrounding bone under loading, known as Wolff’s law [41]. This effect stimulates the surrounding bone for continued bone remodeling, a part of which includes bone deposition onto the biomaterial’s surface. The Young’s modulus of cortical bone is about 7–30 GPa that is far below most ceramic-based implants [8]. Hence, from the viewpoint of biomechanical compatibility, the 55S4.1 bioglass is slightly better than the 45S5.2 glass, though the latter shows higher bioactivity. Fluorapatite may be combined in the formation of HCA layer if F-bearing bioactive materials are used as an implant [2,8]. In Table 2, it is found that all Young’s, bulk, and shear moduli of fluorapatite are more than twice of those of hydroxyapatite. Thus, a pure fluorapatite implant may lead to stress shielding of bone when it is implanted in body. It is also known that the glasses and ceramics are brittle solids, as a consequence, their handling and mechanical properties are not adequate for significant load bearing applications due to lower toughness. Therefore, a bioglass having elastic modulus higher than that of bone (i.e., higher resilience) is required for clinical applications.

It has been pointed out that a HCA layer can be formed on the crystals derived from 45S5.2 and Na_2O–CaO–SiO_2–P_2O_5 glasses after exposure to SBF [30,31]. In such a case, the 45S5.2-derived phase (i.e., 100% crystallized 45S5.2 sample) would be better than its parent glass for using as a substitute of bone due to its comparable elastic moduli with hydroxyapatite, though a longer time (ca. 1 d [30]) is needed for initiating the crystallization of HCA. Of course, the effect of grain boundary on the mechanical properties
of the 45S5.2-derived polycrystals needs to be evaluated in the future before clinical applications.

5. Conclusions

The glass structure and elastic properties of two annealed Na2O–CaO–SiO2–P2O5 glasses having bulk compositions near Na2CaSi2O6 (45S5.2) and Na2CaSi3O8 (55S4.1) have been studied using both Raman and Brillouin scattering techniques. Raman spectroscopic study indicates that the relative abundance of Q3 unit in 45S5.2 glass is less than that in 55S4.1 glass, while the inverse holds for Q2. The presence of Q0 in the two glasses is uncertain. Q0 was found only in 45S5.2 glass. Q4 in 45S5.2 glass may be nil or less than in 55S4.1 glass due to the presence of the ~1060/1160-cm−1 pair and stronger intensity in the ~435-cm−1 band for the latter. The difference in glass structure between the two glasses is attributed to different (Si4+ + P5+)/([Na+ + Ca2+]) ratio. Based on the Brillouin scattering data, it was found that Young's, shear, and bulk moduli of 55S4.1 glass are 2 (2.6%), 0.3 (1.1%), and 4.8 (8.6%) GPa, respectively, lower than those of 45S5.2 glass. The higher elastic moduli can be partly attributed to more modifiers, Na2O and CaO, in 45S5.2 glass. A higher in vivo bioactivity index for 45S5.2 glass than that of 55S4.1 glass, while the inverse holds for Q2. The higher elastic moduli can be partly attributed to more Na+ being associated with Q3. The bioactivity index of leaching out of Q3 species to bioactivity of the Na2O–CaO–SiO2–P2O5 glasses may exceed that of Q2 due to more Na+ being associated with Q3. The elastic moduli of the devitrified 45S5.2 glass increase with increasing time for devitrification at 715°C. Only one crystalline phase was formed during devitrification of the 45S5.2 bioglass. The fully crystallized 45S5.2 sample displays 17 Raman bands and elastic moduli about 30% higher than those of its parent glass. If the effect of grain boundary is minor, the present result implied that the 45S5.2-derived phase would be a better candidate than its parent glass as a bone implant, though a longer time is needed for initiating the crystallization of HCA.

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