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Non-random bonding of mono/divalent cations in mixed phosphate glasses

José F. Schneider^{a,*}, Gabriel Barroco Zinn Fontes^b^a Instituto de Física de São Carlos, Universidade de São Paulo – CERTEV, Brazil^b Escola de Engenharia de São Carlos, Universidade de São Paulo, Brazil

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ABSTRACT

Incorporation of Sr to biocompatible Ca-phosphate glasses opened many possibilities for clinical applications. Transport properties relevant to the cation release in physiological conditions depend, among other factors, on the interaction with the PO₄ forming groups. To understand these issues, three series of mixed glasses with mono (Na⁺) and divalent (Ca²⁺/Sr²⁺) cations were considered here: polyphosphates (0.57 – x) Na₂O·x MO·0.43 P₂O₅ (M=Ca, Sr; 0 ≤ x ≤ 0.57), and metaphosphate (0.50 – x) Na₂O·x SrO·0.50 P₂O₅ (0 ≤ x ≤ 0.50). Molar volumes and glass transition temperatures were analyzed as a function of the concentration of the alkaline earth. ³¹P and ²³Na nuclear magnetic resonance techniques were applied to analyze local structure around phosphate groups and Na sites. As a function of the alkaline earth content, transitions in the evolution of properties (molar volume, glass transition temperature and ³¹P resonance of Q¹ chain-end tetrahedra) were detected in the polyphosphate series. This behavior can be interpreted in terms of preferential bonding of the divalent cation to the oxygens in (PO_{3.5})²⁻ anions (Q¹), instead of (PO₃)⁻ (Q²). This non-statistical bonding to the available O is only possible up to a maximum concentration of the alkaline earth oxide (x = 0.28), in good agreement with the observed break in properties of Na–Sr polyphosphate (x = 0.30). A similar behavior seems plausible for Ca²⁺ in Na–Ca polyphosphate, but changes in the medium range order and progressive structural distortions induced by the stronger ion cause smooth variations of the molar volume. These findings may be relevant to understand the ion dissolution rates in biocompatible glasses, as the more hydrolysable Q² groups concentrate the weaker cations, while the stronger Sr²⁺ or Ca²⁺ are located near chain-end Q¹ groups.

1. Introduction

Several promising therapeutic applications of strontium have been demonstrated. The administration of strontium ranelate has been indicated to treat postmenopausal osteoporosis, obtaining significant increases in lumbar spine bone mineral density [1–6]. The addition of Sr to bioglasses seeks to produce materials exploiting the therapeutic effects associated to the release of this species. Besides the promotion of bone regeneration by the formation of apatite [7–10], strontium shows other useful applications such as antibacterial agent in bone or dental bioglass [11], reducing the risk of infections after implant, and also as inhibitor of dental caries [12–15]. The incorporation of strontium in glass and glass-ceramic dental implants increases the X-ray opacity, improving imaging contrast in post-treatment radiological analysis [16]. The viability of many of these applications is based on the similar structural chemistry of Ca²⁺ and Sr²⁺, which allow the replacement of Ca²⁺ in bioglasses and in hydroxyapatite, despite both ions having sizable differences in ionic radii (Ca²⁺: 1.00 Å, Sr²⁺: 1.16 Å) and electrostatic potential (Ca²⁺: 2.00 e Å⁻¹, Sr²⁺: 1.72 e Å⁻¹) [17]. An

extensive experimental study of Sr incorporation in the bioglass 49.46 SiO₂·26.38 Na₂O·1.07 P₂O₅·(23.08 – x) CaO·x SrO with 0 ≤ x ≤ 23.08 supports the assumption of isomorphic substitution of Sr by Ca [18]. Molecular dynamics simulations in the system 46.1 SiO₂·24.4 Na₂O·(26.9 – x) CaO·2.6 P₂O₅·x SrO with x = 0, 1, 5, 10, 15 indicate similar replacement of Sr by Ca, and revealed that glass formers (SiO₄ and PO₄) interact with the modifier species Sr, Ca and Na, in decreasing order of preference [19]. A recent study analyzed the incorporation of alkali and alkaline earths to a base S53P4 bioglass to adjust the solubility, demonstrating the role of Sr in increasing the dissolution rate when replacing Ca [20]. Biocompatible glasses without silica are also being considered as matrices to deliver ions of therapeutic interest in biological systems. For instance, quaternary phosphate glasses in the system P₂O₅–Na₂O–CaO–TiO₂ are being considered to deliver strontium, showing good compatibility with MG63 cells and the possibility to control the high dissolution rate of phosphates in physiological conditions through the incorporation of Ti and Sr [21,22].

The replacement of modifier species and/or the incorporation of other former species to the base bioglass are strategies used to tailor the

* Corresponding author.

E-mail address: schnei@ifsc.usp.br (J.F. Schneider).<http://dx.doi.org/10.1016/j.jnoncrysol.2017.04.045>Received 18 February 2017; Received in revised form 4 April 2017; Accepted 30 April 2017
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properties relevant to bioactivity, such as optimum ion dissolution rates [4,20,23]. The mixed ion effect and the mixed former effect are two well known examples of how transport properties of ions can be controlled by adequate choice of the glass composition allowing, for instance, the optimization of the chemical durability of the glass [24]. The distribution of ions in the glass matrix and their interaction with the forming groups, defining specific sites for each cation, are factors that determine the mechanisms of diffusion and the behavior of transport properties. Understanding the fundamentals of the bonding behavior of cations, such as Na^+ , Ca^{2+} and Sr^{2+} , in model phosphate glasses may help to design more complex bioactive phosphates. In this context, one particular question concerns the interaction of two cations species, one monovalent and one divalent, with the oxygens from the network forming PO_4 groups. In phosphate glasses, PO_4 units are classified according to the number n of bridging oxygens (BO) per tetrahedron involved in P–O–P bonds between neighbor tetrahedra, identified with the notation Q^n with $n = 0, 1, 2, 3$ [25]. The preferential, non-statistical, bonding of certain cation species to the oxygens from certain Q^n groups have been proposed to explain the behavior of properties and spectroscopic parameters in some glass systems. Montagne et al. concluded, based on electronegativity arguments, that Zn^{2+} interacts preferentially to oxygens from Q^1 groups in glasses $(1-x)\text{NaPO}_3 \cdot x\text{ZnO}$ with $0 \leq x \leq 1$ [26]. Two kinds of phosphate species, Q^1 and Q^2 , are present in these glasses, having formal charges of -1.5 and -1 respectively. As Zn^{2+} is more electronegative than Na^+ , it was proposed that it should preferentially bind to Q^1 groups, since the oxygen atoms of this species carry a larger partial charge than Q^2 . Preferential bonding of Sr^{2+} to Q^1 forming groups has also been proposed to explain anomalies observed in the properties of the system $(0.55-x)\text{Na}_2\text{O} \cdot x\text{SrO} \cdot 0.45\text{P}_2\text{O}_5$ with $0 \leq x \leq 0.55$, as a function of the Sr incorporation [27]. Breaks in the behavior of the glass transition temperature and ^{31}P nuclear magnetic resonance frequencies for Q^1 species were interpreted in terms of a preferential bonding of Sr^{2+} to the oxygens of the more charged Q^1 anions, instead of an equal probability bonding to O in Q^1 and Q^2 . Above a certain critical concentration of SrO, calculated as 0.20 mol fraction, all O from Q^1 are involved in Sr^{2+} bonds and bonding to O from Q^2 is required for glasses with higher SrO concentrations. This behavior determines a non-random distribution of Sr in the network at low concentrations, directly dependent on the population and spatial distribution of Q^1 groups.

In order to test the generality of this type of preferential bonding in alkali-alkaline earth mixed glasses, two systems were analyzed in this study: $(0.57-x)\text{Na}_2\text{O} \cdot x\text{MO} \cdot 0.43\text{P}_2\text{O}_5$ with $\text{M}=\text{Ca}, \text{Sr}$ and $0 \leq x \leq 0.57$. The composition of these series, with $[\text{O}]/[\text{P}] = 3.16$, corresponds to the polyphosphate range, with phosphate fractions of 0.33 for Q^1 and 0.67 for Q^2 within the model of binary speciation for Q^n [25,28]. The concentration of Q^1 species is higher than in the series studied in Ref. [27] (0.22). If Q^1 sites determine the non-random mixing of cations, the changes in the behavior of properties in this new series should occur at higher SrO concentrations. The Na–Ca polyphosphates were analyzed to test the possible influence of the cation potential on the proposed non-random mixing, and to evaluate to which extent the glasses resulting from the full replacement of Ca by Sr can be considered as structurally homologue systems, an assumption frequently invoked in the design of Sr-containing bioglasses. The molar volume and glass transition temperature of these systems were analyzed as a function of the alkaline earth concentration. ^{31}P and ^{23}Na nuclear magnetic resonance (NMR) techniques were applied to analyze the local structure around phosphate groups and Na sites. The metaphosphate series of glasses $(0.50-x)\text{Na}_2\text{O} \cdot x\text{SrO} \cdot 0.50\text{P}_2\text{O}_5$ was considered here as a standard system to check the behavior of properties in a glass with no Q^1 tetrahedra, where Na^+ and Sr^{2+} interact only with oxygens from Q^2 .

2. Experimental

Metaphosphate glasses in the system $(0.50-x)\text{Na}_2\text{O} \cdot x\text{SrO} \cdot 0.40\text{P}_2\text{O}_5$ with $0 \leq x \leq 1$ were prepared from crystalline Na and Sr metaphosphate powders mixed in the desired ratios. Commercial sodium trimetaphosphate $(\text{NaPO}_3)_3$ (Alfa Aesar 99%) was used as received without further purification. Crystalline strontium metaphosphate, $\text{Sr}(\text{PO}_3)_2$, was prepared from SrCO_3 (Alfa Aesar 95%) and $\text{NH}_4\text{H}_2\text{PO}_4$ (Alfa Aesar 98%), mixing the powders as a slurry in ethanol in porcelain crucibles. The mixture was subjected to a three step thermal treatment with ramps of $5^\circ\text{C}/\text{min}$: 2 h at 80°C to evaporate ethanol, 2 h at 350°C to evaporate NH_3 and H_2O , and 12 h at 700°C to evaporate CO_2 . The material obtained through this solid-state reaction was cooled down slowly to room temperature. Samples of this powder were analyzed with X-ray diffraction and ^{31}P NMR. The glasses were prepared by mixing both metaphosphate powders as a slurry in ethanol, dried at 80°C for 2 h to evaporate ethanol and then heated to the melting temperature, between 900°C and 1100°C , at a rate of $10^\circ\text{C}/\text{min}$. Polyphosphates glasses in the system $(0.57-x)\text{Na}_2\text{O} \cdot x\text{MO} \cdot 0.43\text{P}_2\text{O}_5$ with $\text{M}=\text{Ca}, \text{Sr}$ and $0 \leq x \leq 0.57$ were prepared mixing the corresponding carbonates (Na_2CO_3 Sigma-Aldrich 99.6%, CaCO_3 J.T. Baker 99.6%) and $\text{NH}_4\text{H}_2\text{PO}_4$ in porcelain crucibles. The powders were ground and mechanically mixed as slurry with ethanol. The three step thermal treatment in the solid state was also applied with a ramp of $5^\circ\text{C}/\text{min}$: 2 h at 80°C , 2 h at 350°C , and 12 h at a temperature between 550°C and 800°C , depending on the MO content. This mixture was immediately heated up to melting temperatures between 900°C and 1100°C . The liquids were poured and pressed between two brass blocks previously heated at 20°C below the glass transition temperature. The vitrified samples were annealed for 8 h at the same temperature and slowly cooled down to room temperature. In the Na–Sr metaphosphate system, it was possible to vitrify the melts in the entire composition range. In contrast, partial crystallization was detected in Na–Ca and Na–Sr polyphosphates glasses for samples with alkaline earth oxide contents above 0.47 CaO and 0.37 SrO mole fractions, respectively. Table 1 shows the compositions of the glasses obtained in the three series. The glass transition temperature T_g was determined as the extrapolated onset temperature from Differential Scanning Calorimetry (DSC) curves, using a TA Instruments DSC-2910 calorimeter operating with a heating rate of $10^\circ\text{C}/\text{min}$ under nitrogen flux. The mass density ρ of glass pieces was measured with the Archimedes method using ethanol as immersion fluid in a Shimadzu analytical balance kit. From these values, the molar volume was calculated as $V_{mol} = M/\rho$, where M is the molecular weight of the glass.

^{31}P MAS-NMR experiments were carried out at a magnetic field strength of 8.2 T in a Varian UNITY Inova spectrometer using a 4 mm probe. Samples were packed inside silicon nitride rotors, which were spun at a frequency of 11 kHz. For ^{31}P NMR in glass samples, $\pi/2$ pulses of 3 μs and recycle delays up to 150 s were used. In crystalline $\text{Sr}(\text{PO}_3)_2$, a relaxation delay of 10 h was required in a single acquisition ^{31}P experiment. ^{31}P chemical shifts are relative to an 85% H_3PO_4 solution. ^{23}Na -Triple Quantum MAS experiments (3Q-MAS) were carried out to determine the values of the ^{23}Na isotropic chemical shift δ_{CS} and the second-order quadrupolar coupling parameter $P_Q = e^2qQ/(1 + \eta^2/3)^{1/2}$. Here eq and η represent the principal value and the asymmetry parameter of the electric field gradient tensor (efg) at the position of the nucleus, and eQ is the electric quadrupole moment of the nucleus. The 3Q-MAS z-filtered pulse sequence was used [29], applying pulses with 120 kHz nutation frequency for excitation and reconversion of 3-quantum coherences, followed by a soft detection pulse with nutation frequency of 10 kHz. Conventional ^{23}Na -MAS experiments were carried out with a single $\pi/16$ pulse and 2000 scans. The recycle delay used in these experiments was 1 s and the spinning frequency was 11 kHz. ^{23}Na chemical shifts are relative to a 1 M NaCl solution. From the two-dimensional 3Q-MAS spectra, the average values of δ_{CS} and P_Q were calculated according to a standard procedure using the values of the

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