Structural characterization of some sol–gel derived phosphosilicate glasses

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HIGHLIGHTS

- Triethyl-phosphite/phosphate (TEP) and H_3PO_4 were P-sources to obtain $10P_2O_5$–$90SiO_2$.
- Spectral data by NMR, Raman, XPS and XRF was obtained for these gels and glasses.
- Un-hydrolyzed TEP in gel underwent partial vaporization and degradation by annealing.
- A 1.84 higher P_2O_5/SiO_2 ratio was found for the H_3PO_4 derived glass than TEP one.

GRAPHICAL ABSTRACT
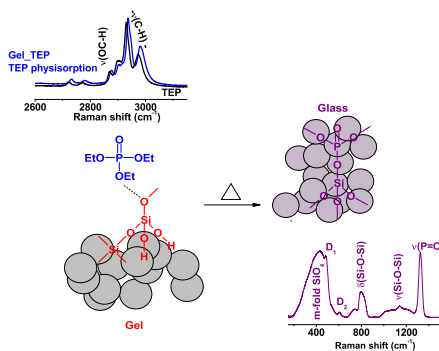
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ABSTRACT

A comparative study of three phosphosilicate gels of the $90SiO_2$–$10P_2O_5$ composition obtained from tetraethoxysilane and three phosphorous precursors: triethylphosphate (TEP), triethylphosphite (TEPI) and H_3PO_4 is performed. ^{29}Si and ^{31}P Magic Angle Spining NMR, X-ray Photoelectron, X-ray Fluorescence and Raman spectroscopies as well as TG analysis are used in order to establish phosphorous precursors and annealing influence on composition and structure of the outcome materials. Unlike the three dimensional silicate network made of $Si(OSi)_x(OH)_{4-x}$ species, unreacted TEP (100% Q_1 condensed phosphorous units) from TEP derived gel and a large amount of isolated phosphorous species (39.7% Q_0) in the H_3PO_4 derived gel are identified. Annealing at 700 °C of the three gels give similar structure with the $90SiO_2$–$10P_2O_5$ glass, excepting the triethylphosphate derived glass that has a much lower P content. Thus, the H_3PO_4 derived glass at 700 and 1000 °C shows 1.89 and 1.94 times higher P_2O_5/SiO_2 ratios than in the case of the TEP derived one.

Introduction

Phosphate glass-containing materials have numerous technological uses (rare-earth ion hosts for solid-state lasers, planar waveguides, biomaterials, proton-conducting glass-based composite membranes for fuel cell, low-temperature sealing glasses etc.) due to their low melting temperature, high dimensional stability, ionic exchange and electrical conductivities [1–3].

Although, phosphosilicate glasses can be obtained by classical methods, their sol–gel synthesis offers the advantages of a lower cost process and advanced mixing of the starting materials up to molecular scale [4]. Various phosphorous precursors were employed along with tetraethoxysilane (TEOS) for sol–gel synthesis of the phosphosilicate gels. The mostly used phosphorous precursors in the sol–gel method were H_3PO_4, $OP(OC_2H_5)_3$ (TEP) and

P(OC$_2$H$_5$)$_3$ or TEPI, although they presented some disadvantages. Different reactivity of the metal alkoxides towards hydrolysis and condensation was governed by electronegativity and coordination of the metal atom as well as steric factor of the alkoxide group [5]. Thus, Si- and P-alkoxides were found to react slowly in the sol–gel conditions [5,6]. Due to the lack of the TEP reactivity probed by ^{31}P NMR, Fernando-Lorenzo et al. [6] used H$_3$PO$_4$ as phosphorous source and the obtained materials by heat treatment of the gels at 300, 500 and 800 °C were highly non-homogeneous. Among the three phosphorous alkoxides used by Scrotter et al. [7], OP(OC$_2$H$_5$)$_3$ (TEP), P(OC$_2$H$_5$)$_3$ (TEPI) and (OC$_2$H$_5$)$_2$–O–P(OC$_2$H$_5$)$_2$, TEP was little reacted in sol after ten months while system with TEPI gave P—O—P and P—O—Si in the corresponding gel. Hydrolysis of TEOS was proven to be faster then the phosphorous alkoxides. Higher proton-conductive solid electrolyte was prepared from the TEOS and H$_3$PO$_4$ or TEP precursors [8]. Developing the water/vapor managed sol–gel processes [9] enabled faster obtaining of the high-proton conductive SiO$_2$–P$_2$O$_5$ electrolytes.

Despite the similar structure of silicates and phosphates consisting in corners sharing SiO$_4$ and PO$_4$, their solution chemistry depends on type and sensitivity of the alkoxides toward hydrolysis, i.e. type of the metallic atom and its ability to enhance the coordination number [10]. Extensive NMR investigations [4,10–13] of the phosphosilicate gels and corresponding glasses were carried out while Raman approach of their structure draws less attention [14,15]. Both Raman and NMR spectroscopies are versatile tools to monitor various stages of the whole sol–gel to glass preparation process [7,16,17]. Analogous to gels, the final glass structure is highly dependent on the synthesis parameters [18]. Thus, the four-coordinated silicon atoms (Q_n) in m-fold ring units [18] coexist with smaller amounts of six-coordinated silicon atoms in the gel-derived phosphosilicate glasses with 30 mol% P$_2$O$_5$ [11]. Instead, phosphorus atoms have always tetrahedral coordination in the phosphate glasses [19]. Connectivity and identification of the m-membered ring structure (where m represents the Q_n units forming a ring) of both silicate and phosphate glasses were considered according to the interconnected tetrahedral units, Q_n (where n stands for bridging oxygens, BOs, per tetrahedron unit) [14,19].

Our earlier studies concerning the sol–gel preparation of phosphosilicate gels underlined that type of the phosphorous reagents (TEP, TEPI and H$_3$PO$_4$) highly influences their composition and thermal behavior [20–24]. It is well known that H$_3$PO$_4$ reacts strongly with (TEOS) leading to the formation of Si—O—P bonds [20], while TEP does not hydrolyze or condense in the presence of TEOS [21]. In this way, the gelation in the latter system is assigned only to the TEOS whereas TEP is embedded in the Si—O—Si network [22–24]. The reaction mixture containing TEPI has an intermediate behavior due to its partial hydrolysis generating HOP(OC$_2$H$_5$)$_2$ [21] that could allow formation of hydrogen bonds between the OH of phosphorous compound and the OH of the silica network.

Hence, comparative structural investigations by Raman, NMR, XRF and XPS spectroscopies are carried out in this work to clear up stages of transformation of the liquid precursors (TEP, TEPI, H$_3$PO$_4$ and TEOS) into the resulted gels, as well as structural modifications underwent by these gels to glassy state as a result of the thermal treatment applied. Quantitative approach of the P$_2$O$_5$/SiO$_2$ ratio in the bulk of the obtained phosphosilicate glasses was attained from Raman and XRF spectroscopies.

Experimental procedure

Materials

Tetraethoxysilane, Si(OC$_2$H$_5$)$_4$ (TEOS) as silica precursor and three different types of phosphorous oxide precursors, namely: triethylphosphate OP(OC$_2$H$_5$)$_3$, triethylphosphite P(OC$_2$H$_5$)$_3$ and phosphoric acid, H$_3$PO$_4$ were used as starting materials in the sol–gel preparation. Ethanol was used as solvent, hydrochloric acid as catalyst and water for hydrolysis. The molar ratio of the reagents and preparation procedure of the phosphosilicate gels (10P$_2$O$_5$–90SiO$_2$), here named Gel_(TEP/TEPI/H$_3$PO$_4$), are presented in Table 1 as being selected based on the previous work [19]. Due to the high gelation tendency of the solution containing H$_3$PO$_4$ [23], its molar ratio of ethanol/precursors of silicon and phosphorous, i.e. Et(OH)/$\sum$precursors in Table 1, was raised to 10 instead of 4 as used for the other two solutions. Further, these gels were dried at room temperature, ground and thermally treated at: (a) 300 °C and 700 °C with 1 h plateau in both cases (named (TEP/TEPI/H$_3$PO$_4$)_700); and (b) at 1000 °C for an hour (called (TEP/TEPI/H$_3$PO$_4$)_1000).

Methods

Thermal analysis of the gels

The thermogravimetric analysis (TGA) was carried out by using a Mettler Toledo TGA/SDTA 851e equipment on ~25 mg of the Gel_(TEP/TEPI/H$_3$PO$_4$) samples in alumina crucibles, with a heating rate of 10 °C/min, in air, within 20–1000 °C temperature range.

Raman spectroscopy

The three gels and corresponding calcined samples at 700 and 1000 °C were analyzed by a LabRam HR spectrometer (Jobin–Yvon–Horiba) over 50–4050 cm^{-1} range. The 514 nm line of an Ar$^+$ laser at an incident power of 50 mW was used as exciting radiation through a 100 × objective of an Olympus microscope in a backscattering geometry and at a confocal hole of 200 μm. The spectral resolution was better than 2 cm^{-1}. A multipass cell holder was used to record Raman spectra of the TEOS, TEP and TEPI liquid precursors. The resulted spectra were background corrected and curves fitted by using the Igor 6.20 software.

NMR spectroscopy

The ^{31}P and ^{29}Si MAS NMR spectra of the as-prepared gels and phosphosilicate glasses thermally treated at 1000 °C were collected by using a Bruker AVANCE 400 spectrometer at a spinning frequency of 8 and 10 kHz for ^{29}Si and ^{31}P, respectively. The ^{29}Si and ^{31}P MAS NMR chemical shifts are expressed in ppm relative to 1% Si(CH$_3$)$_4$/CDCl$_3$ and H$_3$PO$_4$ water solution, respectively. All the spectra were processed using Bruker NMR programs and then they were deconvoluted using Dmfit program [25].

XPS measurements

Surface analysis performed by X-ray Photoelectron Spectroscopy (XPS) was carried out on a Quantera SXM equipment with a base pressure in the analysis chamber of 10^{-9} Torr. The X-ray source was Al Kα radiation (1486.6 eV, monochromatized) and overall energy resolution is estimated at 0.65 eV by the full width at half maximum (FWHM) of the Au4f$_{7/2}$ line. In order to take into account the charging effect on the measured Binding Energies (BEs) the spectra were calibrated using the C1s line (BE = 284.8 eV, C—C (CH)$_n$ bondings) of the adsorbed hydrocarbon on the sample surface. After recording the survey XPS spectra, the high resolution photoelectron spectra of the most prominent XPS transitions (C 1s, O 1s, Si2p and P2p) were collected for the Gel_(TEP/TEPI/H$_3$PO$_4$) and (TEP/TEPI/H$_3$PO$_4$)_700 samples. The estimated errors in quantification were hold in the range of ±10% for the relative concentrations and within ±0.2 eV for the Binding Energies (BEs) assignments.