

# Investigation of sol-gel derived silicate glasses loaded with vitamin C

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This study is focused on entrapping the vitamin C (ascorbate) into silicate matrices prepared via sol-gel method, and on evaluation of ascorbate influence on the glass matrices and conversely. Silicate glasses of  $\text{SiO}_2$  and  $56\text{SiO}_2\text{-}40\text{CaO-}4\text{P}_2\text{O}_5$  compositions were loaded with vitamin C for potential application as biomaterials in tissue regeneration. The changes induced in vitamin C and in glass matrices by loading with vitamin C were analyzed using DTA, XRD, BET methods, and FTIR spectroscopy. Surface area and pore volume diminish in both samples as loaded with vitamin C, while the thermal stability of vitamin C is increased by entrapment in sol-gel derived silicate.

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## 1. Introduction

The results reported on silica-based bioactive glasses [1] followed by that on ordered mesoporous silica materials [2] triggered the research and development of these materials to a large scale in order to obtain new silica-based bioactive materials for biomedical applications [3].

Nowadays the incorporation of vitamins into these systems provides a simple way to develop novel functional glasses with better properties to reduce the risk due to other diseases, after implantation [4].

L-ascorbic acid, or rather the anion of ascorbic acid, named ascorbate, also known as vitamin C, is a representative water soluble vitamin and has a variety of biological and pharmaceutical functions [5]. Most animals and plants are able to synthesize the necessary amount of vitamin C from D-glucose, but the humans do not possess this ability because of the absence of the necessary enzyme – gulonolactone oxidase – and require dietary intake of ascorbic acid [6, 7].

Vitamin C helps in the metabolism of tyrosine, folic acid and tryptophan, and contributes to the synthesis of the amino acids carnitine and catecholamine that regulate nervous system. It enhances the absorption of iron in the gut, is needed for tissue growth and wound healing, and is important in the formation of neurotransmitters. Being an antioxidant, it protects the body from the harmful effects of free radicals and pollutants [8, 9].

This study is focused on entrapping the vitamin C into silicate matrices prepared via sol-gel method, and on evaluation of ascorbate influence on the glass matrices and conversely.

## 2. Experimental

Vitamin C was incorporated into  $\text{SiO}_2$  and silicate gels during sol-gel synthesis. The composition of the chosen glasses was  $100\text{SiO}_2$  and  $56\text{SiO}_2\text{-}40\text{CaO-}4\text{P}_2\text{O}_5$  (mol %) (named further BG). The precursor for  $\text{SiO}_2$  was tetraethoxysilan  $\text{SiC}_8\text{H}_{20}\text{O}_4$  (TEOS), for CaO was calcium nitrate tetrahydrate  $\text{Ca}(\text{NO}_3)_2\cdot 4\text{H}_2\text{O}$ , and for  $\text{P}_2\text{O}_5$  was triethyl phosphate  $(\text{C}_2\text{H}_5)_3\text{PO}_4$  (TEP). The corresponding amount of tetraethoxysilan was mixed with ethanol and distilled water in a 1: 0.5: 2 molar ratios, and stirred for one hour at room temperature on a magnetic stirrer. The precursor for CaO was dissolved in distilled water at saturation point. The compounds were mixed together at room temperature. The final pH of solutions were adjusted at 2 with nitric acid. Pharmaceutically pure vitamin C was dissolved in distilled water at saturation point and then added to the previously obtained sols in the molar ratio: 1 mol vitamin C : 2 moles  $\text{SiO}_2$  or BG. The resulting solutions were gelled and aged at  $36^\circ\text{C}$  for 30 days.

The thermal analysis was performed using Shimadzu analyser DTG-60H, in air, in alumina crucibles, with heating rate of  $10^\circ\text{C}/\text{min}$ , from room temperature to  $300^\circ\text{C}$  for vitamin C, to  $600^\circ\text{C}$  for  $\text{SiO}_2$  sample, and to  $1000^\circ\text{C}$  for BG sample.

The structure of the samples was analyzed by X-ray diffraction with a Shimadzu XRD-6000 diffractometer, using Cu K $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ), with Ni-filter. The diffractograms were recorded between  $10$  and  $80^\circ$  in  $2\theta$  continuous scanning mode.

The specific surface area and pore volume of the samples were obtained from  $\text{N}_2$ -adsorption-desorption isotherms, using a Qsurf Surface Analyser. The Brunauer-Emmett-Teller (BET) method was used for specific surface area, and the Barret-Joyner-Halenda (BJH) method for pore volume analysis.

Fourier transform infrared (FTIR) spectroscopic analyses were performed in absorption configuration with a JASCO 6200 FTIR spectrometer in the 4500 to 400  $\text{cm}^{-1}$  spectral range with a spectral resolution of 4  $\text{cm}^{-1}$  using KBr pellet technique.

### 3. Results and discussion

The solutions resulting after addition of vitamin C to  $\text{SiO}_2$  and BG soles are colourless and transparent at the beginning, but over time their colour is changed to pale yellowish. As has been reported in the literature [10], the density of the yellow coloration gradually increases over time and also with concentration of vitamin C, and for high concentration of vitamin C the colour becomes completely dark yellow. The color change of the samples entrapping vitamin C is related to oxidation without a significant decrease in the ascorbate activity [11].

The DTA/TG measurements were made for the reason to study the thermal stability of the vitamin C and to follow its presence and thermal behavior in the glass samples. The DTA results on the used vitamin C are in agreement with the literature data and point out a thermal stability until around 200°C (Fig. 1) when the vitamin C starts to decompose. Two additional decomposition steps were reported in the 250–500 °C temperature range, while at 500 °C was appreciated that about 11% of the initial sample remains as charred residue [12].

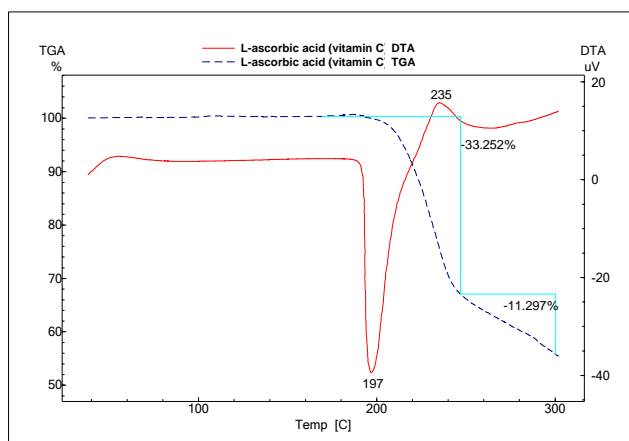


Fig. 1. DTA and TGA curves of pure vitamin C.

The DTA curve recorded for pure  $\text{SiO}_2$  bioactive glass (Fig. 2) shows an endothermic peak around 100°C that is accompanied with a weight loss observed on the TGA curve, attributed to the elimination of residual water and ethanol used in preparation process.

The decomposition of vitamin C is recorded about 260 °C. In case of BG sample (Fig. 3.) the first two endothermic peaks at 88°C and 138.5°C are attributed to ethanol and water removal. As observed on TGA curve, a total weight loss of 22.67% accompanies these endothermic events. The decomposition of vitamin C is recorded about 250 °C. The next two exothermic events at 271 and 308 °C are related to the loss of alkoxy groups remained from synthesis reagents. The events noticed between 562°C and 683°C, with a corresponding total weight loss about 18%, are attributed to the loss of hydroxyls and nitrates (in the form of  $\text{CaNO}_3 \cdot 4\text{H}_2\text{O}$  and  $\text{HNO}_3$ ) used in the sol preparation [13, 14].

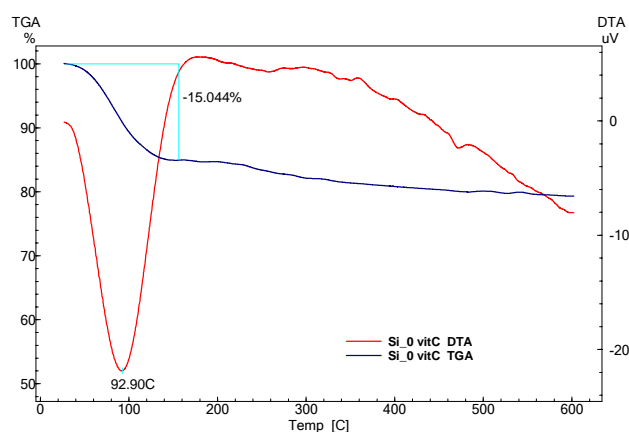


Fig. 2. DTA and TGA curves of  $\text{SiO}_2$  matrix.

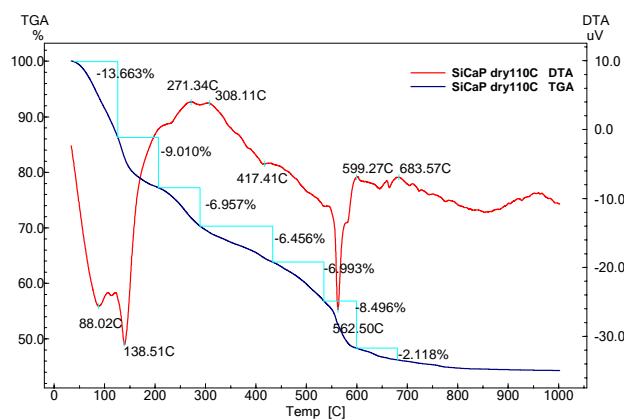


Fig. 3. DTA and TGA curves of BG sample.

The DTA runs of both vitamin C loaded samples (Fig. 4) present an endothermic event at 71.70 °C respectively at 72.70 °C assigned to the elimination of water and ethanol. The  $\text{SiO}_2$  glass loaded with vitamin C compared with unloaded  $\text{SiO}_2$  matrix, present an exothermic peak at 366.74°C associated with the burning out of vitamin C [12]. The assignments of all other thermal events are similar to the ones mentioned above.

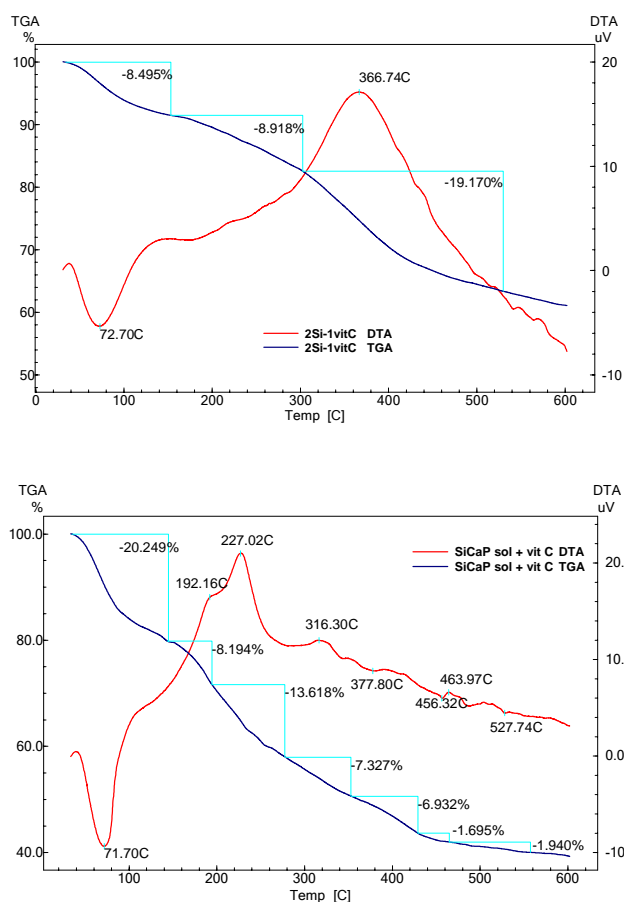


Fig. 4. DTA of  $\text{SiO}_2$  and BG loaded with vitamin C.

The X-ray diffraction patterns of vitamin C and glass samples free of vitamin C and loaded with vitamin C are presented in Fig. 5. Pure vitamin C has a crystalline structure denoted by six intense peaks at  $2\theta = 10.60, 17.54, 19.98, 25.40, 28.16, 30.10$  [10] confirmed by XRD pattern of the vitamin C powder used in the synthesis of the investigated sample. The X-ray diffractograms recorded from glass samples loaded with vitamin C do not show any crystalline phases, i.e. they further present only amorphous structure. But for all that, comparing the XRD patterns of the loaded and unloaded samples, it is noticed that the amorphous halo slightly shifts to lower angles. This shift indicates that the microstructure was expanded when vitamin C was incorporated. This kind of shift is usually recorded at the intercalation of ascorbic acid into the layered structures [15].

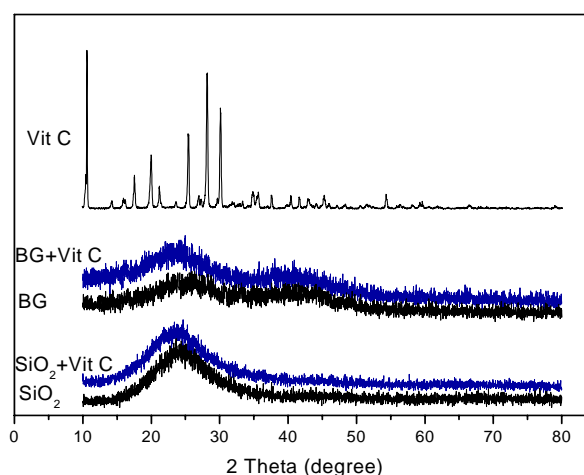


Fig. 5. X ray diffraction patterns of pure vitamin C and of glass samples before and after entrapment of vitamin C.

Surface area and pore size measurements were performed in order to evidence the influence of vitamin C on textural properties of the host glasses. The results are presented in Table 1.

Table 1. Specific surface area and pore volume of the vitamin C loaded and unloaded samples

Sample	Specific surface area ( $\text{m}^2/\text{g}$ )	Pore volume ( $\text{ml/g}$ )
$\text{SiO}_2$	416.5	0.3565
$\text{SiO}_2 + \text{Vit C}$	1.4286	0.0136
BG	28.135	0.0764
BG+Vit C	0.8185	0.0045

The pure  $\text{SiO}_2$  samples surface area of  $416.5 \text{ m}^2/\text{g}$  decreases in the presence of vitamin C to  $1.43 \text{ m}^2/\text{g}$ , also the pore volume from  $0.3565$  to  $0.0136 \text{ m}^2/\text{g}$ . In the case of BG without vitamin C the surface area is smaller than that of pure  $\text{SiO}_2$  matrix,  $28.135 \text{ m}^2/\text{g}$ , while after loading with vitamin C the surface area and pore volume decrease but less pronouncedly than in case of  $\text{SiO}_2$  sample.

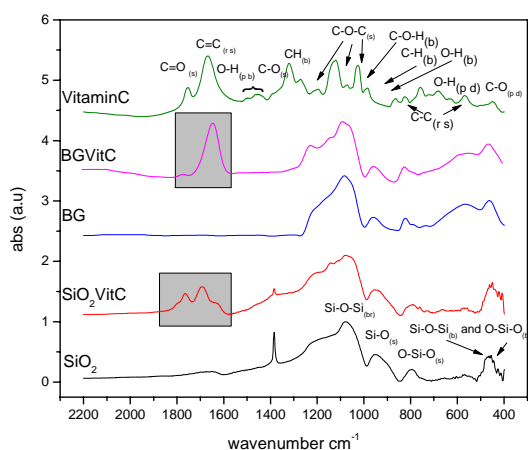


Fig. 6. FTIR spectra of pure vitamin C and of glass samples before and after entrapment of vitamin C.

The absorption bands occurring in FTIR spectra (Fig. 6) were assigned to the corresponding modes of vibrations of different functional groups. The assignment of IR bands recorded in 400 - 2200  $\text{cm}^{-1}$  spectral range from vitamin C is given in Table 2 [10, 16].

Table 2. Assignment of infrared absorption bands recorded from vitamin C.

Wavenumbers ( $\text{cm}^{-1}$ )	Assignment
1755	C=O stretching
1669	C=C ring stretching
1496	CH bending
1454	CH bending, CH <sub>2</sub> scissoring
1320	CH bending (wagging)
1270	C-O-C stretching
1195	C-C(=O)-O stretching
1120	C-O-C stretching
1072	C-O-C Stretching and C-O-H bending
1024	C-O-H bending
984, 955	C-H and O-H bending
863, 826	C-C ring stretching
758, 723	OH out-of-plane deformation
679, 635, 568	OH out-of-plane deformation / C-C ring stretching
451	C-O in plane deformation

The FTIR spectra of samples without vitamin C are showing the characteristic vibrational peaks of  $\text{SiO}_4$  structural units. The peak at 467  $\text{cm}^{-1}$  is assigned to the bending vibration modes of the Si-O-Si and O-Si-O bonds and the peak at 819  $\text{cm}^{-1}$  corresponds to the stretching mode of the O-Si-O bond [17-20]. The 1200–1080  $\text{cm}^{-1}$  range brings information about the degree of condensation

(Si-O-Si bridges) and the presence of sylanol groups (-SiOH) on the surface [17, 18, 20]. The absorption band at 1384  $\text{cm}^{-1}$  is attributed to some carbon impurity atoms [18, 20, 21]. After entrapment of vitamin C in BG and  $\text{SiO}_2$  glass matrices, the 1669  $\text{cm}^{-1}$  absorption band arising from C=C ring stretching vibration is shifted to lower wavenumbers in BG matrix, and to higher wavenumbers in  $\text{SiO}_2$  glass matrix. In both matrices the 1755  $\text{cm}^{-1}$  absorption band assigned to C=O stretching vibration is slightly shifted to higher wavenumbers, and is strongly attenuated in BG matrix. This result denotes that the two host matrices have different influence on the bonds of the embedded vitamin C.

#### 4. Conclusions

The embedding of vitamin C in sol-gel derived  $\text{SiO}_2$  and  $\text{SiO}_2$ -CaO- $\text{P}_2\text{O}_5$  glasses imparts to the hosting glass matrices a yellow colour. BET measurements point out that after vitamin C addition the specific surface area and pore volume diminished much more in  $\text{SiO}_2$  sample than in  $\text{SiO}_2$ -CaO- $\text{P}_2\text{O}_5$  sample. The thermal stability of vitamin C entrapped in sol-gel derived silicate matrices is enhanced, as denoted by the increase of its decomposition temperature from about 200 °C to 260 °C and 250 °C in  $\text{SiO}_2$  and  $\text{SiO}_2$ -CaO- $\text{P}_2\text{O}_5$  glasses, respectively. The XRD results support the expansion of matrix microstructure after the vitamin C entrapment. The FTIR data indicate that the two glass matrices differently influence the bonds of vitamin C entrapped therein, and the absorption band corresponding to C=O stretching vibration is notably diminished in  $\text{SiO}_2$ -CaO- $\text{P}_2\text{O}_5$  sample.

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