The Formation of Black Glass with Ladder-like Silsequioxanes

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Abstract **- The main objective of this paper is to determine the process of formation of black glasses from ladder-like silsesquioxane precursors. Well-defined polysilsesquioxanes with ladder-like structure obtained via the sol-gel process allowed to control the amount of introduced carbon which allows us to control the properties of received glasses. Raman and middle infrared (MIR) spectroscopy research allowed to determine the structure of obtained materials and thus, to describe the process of formation of black glasses.**

Keywords- silsesquioxanes; black glasess; SiOC.

I. INTRODUCTION

Black glasses (SiOC glasses) are materials of amorphous silica structure, in which two O^{2-} ions are substituted by one C^{4-} anion (Figure 1). That type of substitution leads to a local increase in the density of bonds and therefore to a significant strengthening of the network. The ideal structure of black glasses contains only Si-O and Si-C bonds.

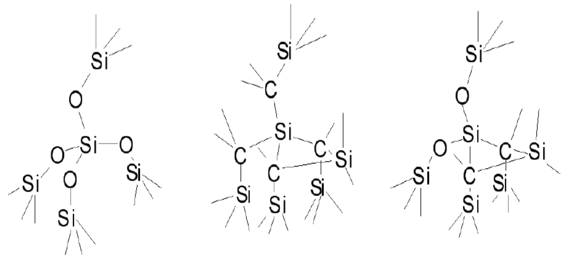

Figure 1. The structural formula of: silica SiO_2 (left), SiC (center), silicon oxycarbide (right) [1].

Unfortunately, the silica glass structure can accept only a limited amount of carbon ions. Therefore, black glasses usually also contain so called free carbon (phase separation) - that is responsible for their black color.

The presence of free carbon and its structure has a tremendous impact on the thermal stability and mechanical properties of the glasses. Analysis of the literature shows that functional parameters of black glasses may vary within very wide limits, depending on the amount of free carbon and isomorphous substitution in the glass structure [2]-[9].

II. EXPERIMENTAL

As it was mentioned, the main reason for the use of ladder-like polysilsesquioxanes as precursors of black glass was the need to ensure the stoichiometry of the glass. This allows to control the amount of Si-C bonds. The $CH_3Si(OCH_3)_3$ (T units) and $((CH_2Si(OC_2H_5)_2)$ (D units) were used as a silsesquioxane precursors. A mixture of T/D=2/1 was hydrolyzed using water and HCl catalyst to obtain ladder-like structures (P0). To obtain glassy SiCxOy, dried samples were subsequently heat-treated in a tube furnace at 200, 400, 600 and 800 ^oC temperature ranges.

III. RESULTS AND DISCUSSION

The temperatures for further studies were selected based on thermogravimetric analysis (Figure 2). The first weight loss was observed around 200^{o}C (P1), the second at about 400^{o}C (P2), the third at 600^{o}C (P3) and the end at about 800^{o}C (P4).

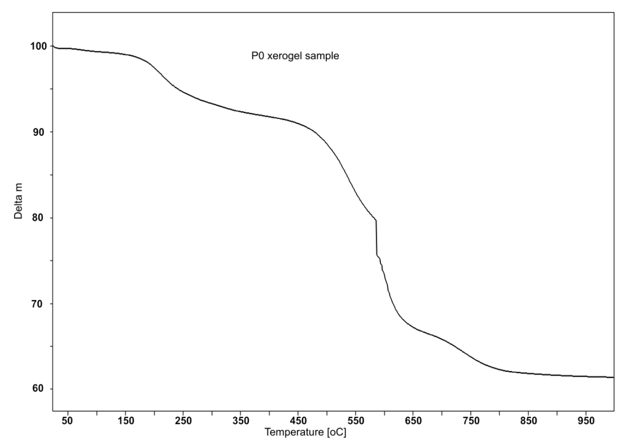

Figure. 2. Thermogravimetric (TG) curve of P0 sample

Spectroscopic studies (MIR and Raman) of samples (P0-P4) show that the transition from xerogel into black glasses (Figures 3 and 4). On MIR spectrum of P1, an increase in intensity of bands responsible for C-H vibrations (857, 1270, 1409, 2910, 2969 cm^{-1}) and the appearance of additional bands in the range of approx. 3055 cm-1 (vibration CH sp^2) and OH at 3693, 3756 cm^{-1} is observed. This is most probably due to formation of D-oligomers [1]. As temperature increases (P2 - P4) a decrease in the intensity of the bands associated with the CH groups can be observed [10].

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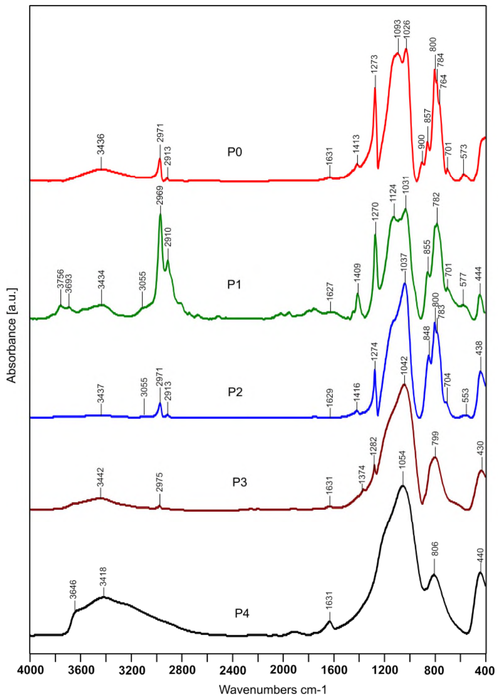

Figure 3. MIR spectra of xerogel and pyrolised samples

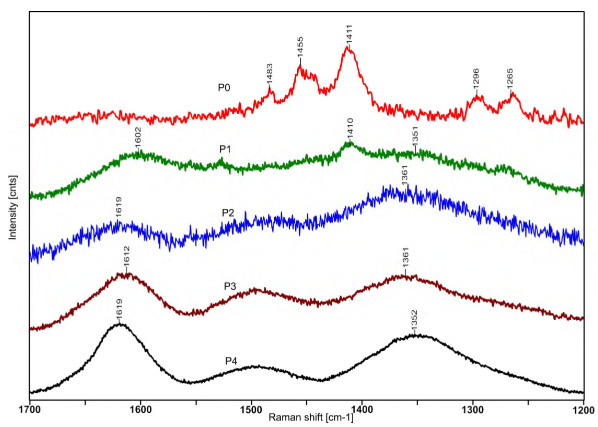

Figure 4. Raman spectra of xelogel (P0) and pyrolised samples (P0 - P4)

On Raman spectra (Figure 4), the so called G (at about 1615 cm^{-1}) and D bands (P1-P4) characteristic for sp^2 hybridized carbon pairs and breathing of hexagonal carbon rings respectively are visible. As temperature rises, an increase in the intensity of the G band is observed. This is especially visible for P3 (600 ^oC) and P4 (800 ^oC) samples.

IV. CONCLUSION

In this paper, it has been shown that using ladder-like silsesquioxanes, black glasses with different amount of free carbon can be obtained. Spectroscopic studies showed that, with the increase of temperature, free carbon phase starts to form. Raman studies have shown that the process of forming the carbon phase begins at about 600 °C.

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