CHARACTERIZATION OF SELENIUM DOPED SILICA GLASSES SYNTHESIZED BY SOL-GEL METHOD

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ABSTRACT

Selenium is a rare element in nature. It is used in the food, pharmaceutical, and glass industries. In commercial glasses, selenium is the element responsible for most of the pink or light red color, but its effect is primarily dependent on the oxidation state of the element in the glassy matrix. Besides, selenium is highly volatile, and as high as 80 wt% may be lost in the furnace during the industrial glass elaboration. The sol–gel method yields synthesized materials of high purity and homogeneity, and uses low processing temperatures. Samples of silica glass were obtained by sol-gel method, incorporating precursors of selenium, with the main objective of reducing selenium losses during its heating. The results of optical absorption, XRD and thermal analysis (TGA, DSC) of the glasses are presented and discussed.

Keywords: sol gel process, selenium, silica glasses.

INTRODUCTION

The commercial glass is an amorphous solid constituted of about 70% silica (SiO_2) and other oxides that change the properties of silica making the fusion easier. By the addition of colorant oxides in the glass composition, it is possible obtain several colors: iron provides mainly the green color; cobalt is the blue, and selenium the pink/red color.

Pink color is hard to be reproduced due to some factors such as: poor reproducibility, high volatilization and low intensity of the pink color. Selenium is found in nature in small quantities, which makes it high cost. In large industrial furnaces, from the selenium placed into the initial composition of the glass almost 80% are vaporize or reacts forming colorless selenium. Currently, metallic selenium is added to form pink color. As the glass is comprised of oxides, in the fusion,

reactions of oxi-reduction change the valence of metallic selenium, which difficult the coloration control in the final glass.

Sol-gel process consists in a preparation route of inorganic materials from reactions of molecular precursors [1] in solution, which through the manipulation of their properties allow to control the production of monoliths , fibers, films or particles extremely small, and obtain materials with new characteristics [2].These materials are obtained with high purity, homogeneity and temperatures lower than the traditional methods employed , besides it does not need the utilization of high sophistication equipments and technologies [2,3]. It is possible obtain amorphous or crystalline materials depending of the composition, precursors, handling and thermal treatment used [4].The disadvantage of the technique is in the need of utilization of toxic reagents. Besides, the high cost of reagents and the difficult of obtain materials with high thick – due to the high contraction of the material during the drying and sinterization – are also pointed as inconvenient of the technique.

Samples of silica glass were obtained by the sol-gel method, incorporating selenium precursors in the attempt to reduce the lost of selenium during its heating. To do so, characterization of these samples were performed about their thermal properties.

EXPERIMENTAL

A first solution containing HCl (eletrolite) and destilated water were prepared for the dissolution of the precursors of selenium - $ZnSeO_3$ and Na_2SeO_3, in proportions of 0.5 g and 2.0 g, which represents 0.43 wt% and 1.67 wt% of Se at the preparation. After completely solubilization of the precursor of selenium this solution was mixed to a second solution where TEOS (tetraethilorthosilicate) was used as source of silica and methanol was used as the solvent. Constant agitation was performed in magnetic agitator with heating up to 50ºC for 20 minutes. Then, solution was transferred to a porcelain crucible, remaining in ambient temperature up to completely drying.

Due to the high intern tension generated during the solution drying, the samples cracked, as shows Figure 1. But, some pieces could be analyzed by optical

absorption. Thermogravimetric Analysis (TGA) and Differential Sccaning Calorimetry (DSC) were performed in order to observe the behavior of the samples during their heating. X-Ray Diffraction (XRD) was performed in order to observe if the obtained samples are amorphous or presents crystalline phases.

Figure 1 - Sample containing 2.0 g $ZnSO_3$.

RESULTS AND DISCUSSION

The samples obtained are almost colorless, with a very smooth pink color, as showed in Figure 2. A first observation is about the hygroscopic characteristic of the sample containing 2.0 g Na_2SeO_3. Some days after preparation, the sample present itself wet as a thick paste, making impossible performing the characterization tests.

Figure 2 - Samples produced with precursors of selenium.

Semi quantitative chemical analysis was performed by X-Ray Fluorescence (XRF) spectrometry for the sample containing 2.0 g $ZnSeO_3$ and the result is shown in Table 1. Almost 50 wt% of the sample is composed of silica (SiO_2). SeO_2 amount in the sample reaches 24.6 wt%. ZnO is present in the sample with 18.3 wt%, and Cl 8.67 wt%.

Table 1 – Semi quantitative chemical analysis by XRF of sample containing 2.0 g $ZnSeO_3$.

Components	wt %
MgO	0,25
Al_2O_3	0,09
SiO_2	48,0
SO_3	0,02
Cl	8,67
NiO	0,01
ZnO	18,3
SeO_2	24,6

The XRD analysis demonstrated that the samples are amorphous, as showed in Figure 3.

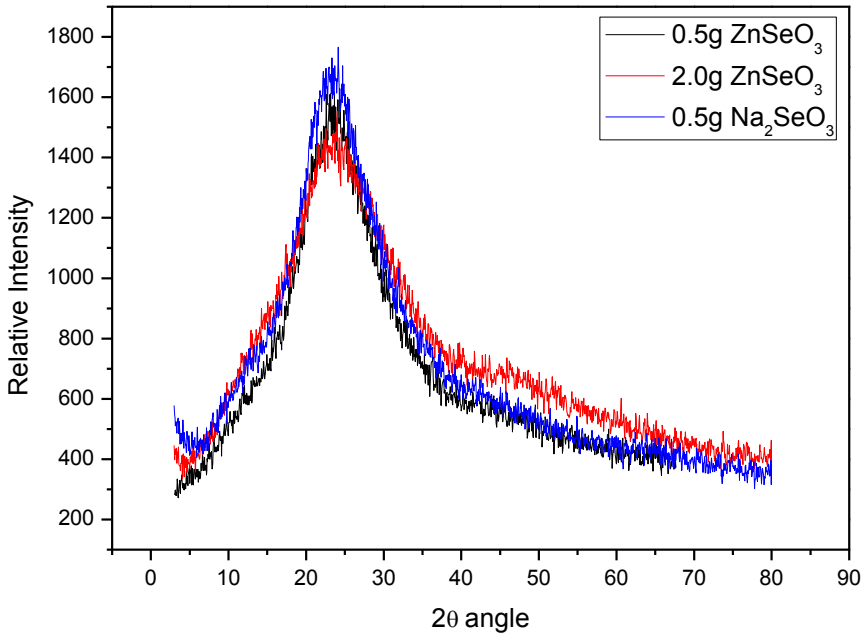

Figure 3 - XRD of the samples.

For the samples containing $ZnSeO_3$, optical absorption analysis was performed Figure 4 shows. An absorption band is observed at 500 nm, which indicates the incorporation of the selenium into the glass. The intensity of this band increases with the concentration of the precursor of selenium. The transmission window starts around 400 nm.

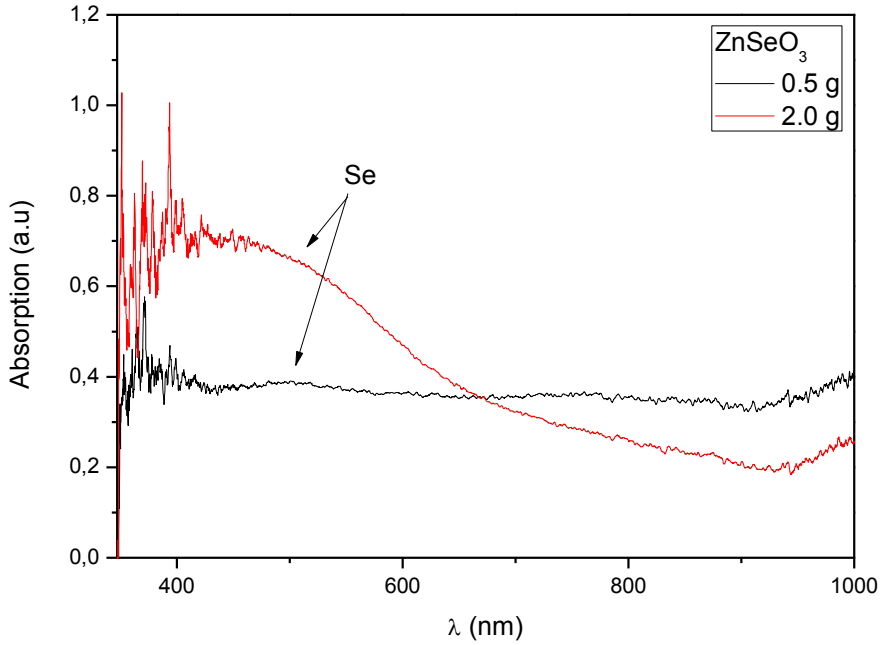

Figure 4 - Optical absorption spectrum for samples containing $ZnSeO_3$.

TGA and dTG (Figure 5) were performed up to 1300ºC and shows that the major weight loss occurs around 100ºC due to water and solvent molecules. The peaks between 200°C and 650°C were possibly due to the decomposition of residual organic groups. But also might be related to the selenium loss. Selenium begins to volatilize at 200°C and its melting point is 217°C. Significant volatilization happens above 300°C. According to Volf [5], at 600°C, that is below the boiling point, 688°C, all selenium will volatilize in 5 minutes. Samples containing 0.5 g of the precursors of selenium had a maximum loss of 40 wt% and for the sample containing 2.0 g the lost reached 60 wt%. The sample containing 2.0 g $ZnSeO_3$ presents a peak at 630ºC; this might be related to the melting of the stable form β-$ZnSeO_3$ obtained with heating. For the sample containing 0.5 g of Na_2SeO_3, a peak at 368ºC might be related to the melting of the compound $Na_2Se_2O_5$ [6]. That compound could be formed during the preparation of the sample. DSC presents transition glass temperature (*Tg*) of the samples, in Figure 6.

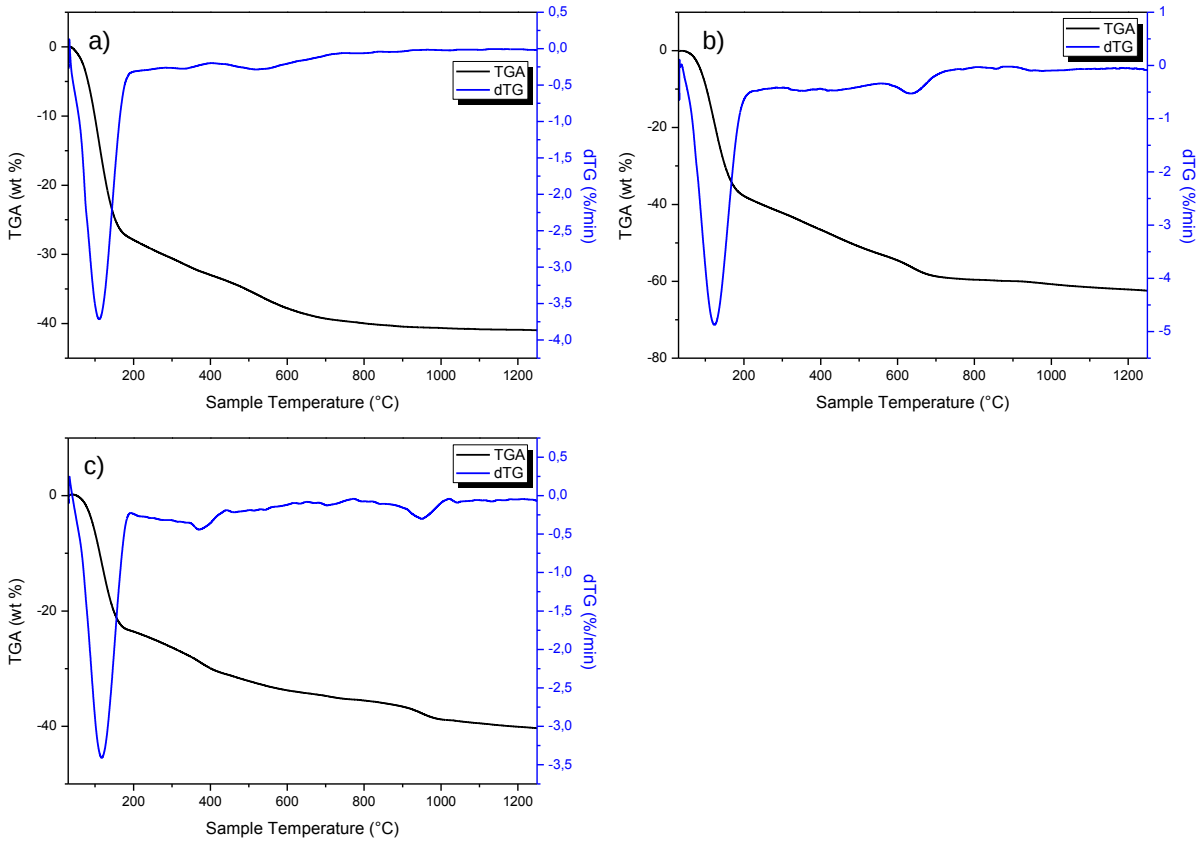

Figure 5 - TGA and dTG of the samples containing a) 0.5g $ZnSeO_3$, b) 2.0g $ZnSeO_3$, c) 0.5g Na_2SeO_3.

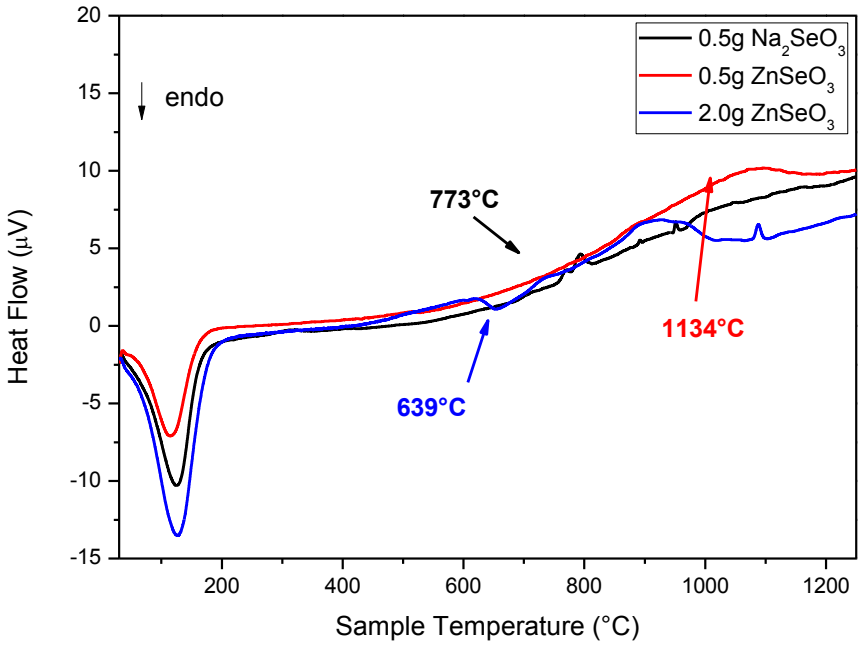

Figure 6 - DSC of the samples containing selenium precursors.

Another interesting observation is about the spontaneous changing of coloration from the samples. These were kept into plastic bags and after almost six months, the pink color had intensified. Figure 7 shows an example of this phenomenon with the sample containing 2.0g $ZnSeO_3$. This fact might be related to a characteristic of the material being photosensitive, but this observation still needs to be confirmed.

Figure 7 - Coloration changing of sample containing 2.0g $ZnSeO_3$.

CONCLUSIONS

Sol-gel process is a very interesting way to synthesize glass material with high purity and homogeneity. The samples doped with selenium precursors are amorphous and incorporation of selenium could be seen by optical absorption test. The sample with 2.0 g Na_2SeO_3 did not show chemical stability, so it was not possible to perform the tests for its characterization. That might be related to the excess of sodium into the glass matrix. FRX of sample containing 2.0 g $ZnSeO_3$ showed that it is composed of almost 50 wt% of silica and 25 wt% of SeO_2. Thermal analysis, TGA and DSC, were performed and allowed to understand the behavior of the samples during heating. The loss mass of the samples is between 40 wt% and 60 wt%. The photosensitive phenomenon must be studied for a complete understanding.

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