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Dedicated to Dr. Maria Zaharescu
on the occasion of her 80th anniversary

STRUCTURAL AND PHYSICO-CHEMICAL CHARACTERIZATION OF Zn-DOPED SiO_2 GLASSES OBTAINED BY SOL-GEL ROUTE

Oana Cătălina MOCIOIU,[a*] Irina ATKINSON,[a] Jeanina PANDELE-CUSU,[a] Veronica BRĂTAN,[a] Simona PETRESCU,[a] Diana Irinel BĂILĂ[b] and Ana-Maria MOCIOIU[c]

[a] "Ilie Murgulescu" Institute of Physical Chemistry of Roumanian Academy, 202 Splaiul Independenței, Bucharest 060021, Roumania
[b] "POLITEHNICA" University of Bucharest, 313 Splaiul Independenței, district 6, 060042, Bucharest, Roumania
[c] National R&D Institute for Non-ferrous and Rare Metals,102 Biruinței Blvd, Pantelimon, Ilfov 077145, Roumania

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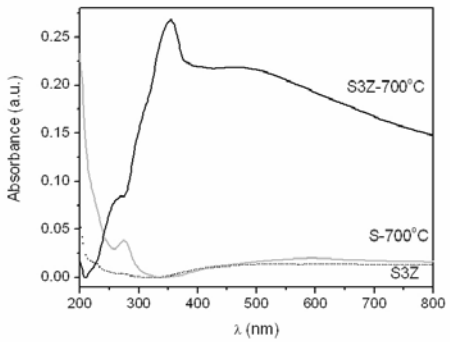
The small quantities (≤ 5 %wt) of transitional elements added in glass composition have good influence on the properties. Zn-doped silica glasses were obtained by sol-gel method. The gels were investigated by FT-IR and DTA/TG methods. In the FT-IR spectra were identified the characteristic bands of Si-O and Zn-O in silicate glasses. The vitreous transition temperatures were highlighted on the DTA/TG curves. Based on DTA results, gels were thermally treated at 700°C for 3 hours in order to obtain glasses. By XRD and FTIR methods the vitreous state was revealed. The absorption in UV-VIS was influenced by zinc addition and thermal treatment.



INTRODUCTION

SiO_2-ZnO based glasses obtained on classical route of melt-quenching were studied previously due to their good properties. The classical route involves high melting temperatures (>1400 °C) which can lead to high prices and the obtained films have micrometer dimensions. According to the phase diagram the compositional domain for glass obtaining is between 0-35% mol ZnO.[1,2] In the SiO_2–ZnO–BaO system were obtained glasses at 1500°C and they shown photoluminescent properties.[3] Glasses doped with Mn have luminescent properties, also.[4] Glasses in the SiO_2–ZnO–PbO-B_2O_2 system were used as varistors.[5] Glasses in SiO_2-ZnO-BaO system, with ZnO concentration higher then 30 mol% were studied and a significant red-shift of both absorption edge and emission band was observed with the increasing of ZnO content.[6] Researchers reported an improved luminescence efficiency of ZnO embedded in glass compared to that of bulk ZnO.[7,8] Excellent nonlinear optical properties, saturable absorption and optical bi-stability have also been reported for these composites.[7] Glasses in ZnO–SiO_2–B_2O_3 ternary system with different ZnO/B_2O_3 ratios were studied as scintillating materials. In case of zinc borosilicate glasses the photoluminescence spectra showed the elimination of the visible

* Corresponding author: omocioiu@icf.ro

emission band which is favorable in scintillating glasses.[8]

In order to develop glasses with same properties for miniaturized devices, other synthesis must be studied. One of them is the sol-gel route that will be used also, in the present article. In the literature data, few studies of SiO_2-ZnO nanomaterials obtained by sol-gel route were reported.[9-12] Thin films with composition of 5 wt % ZnO and 95wt % SiO_2 on Si substrate were reported as sensors for phenyl hydrazine.[10] Films with 25% ZnO that have optical or electrical properties were reported.[11] Optical and photoluminiscent nanocomposite materials with 20% ZnO, obtained by sol-gel method, were studied.[12]

In this paper we studied Zn-doped silica glasses obtained by sol-gel method, in order to develop new compositions with different properties.

EXPERIMENTAL

In order to obtain glasses by sol-gel method solutions were prepared starting to TEOS (tetraethyl ortosilicate) [$Si(OC_2H_5)_4$] and zinc acetate dehydrate as sol-gel precursors, ethanol as solvent, distillated water for hydrolysis and HCl as a catalyst. The solution for silica glass with molar ratio: C_2H_5OH: TEOS: H_2O: HCl = 10: 1: 3: 0.03 was used previously by authors for anticorrosion thin films .[9] The doped solutions with 1%, 3% and 5% Zn were obtained by adding zinc acetate dehydrate at silica solution. The gels obtained were noted S1Z, S3Z and S5Z. The gels were thermally treated at 700°C in order to obtain glasses.

The structure of obtained gels and glasses was investigated by FT-IR Spectroscopy with a 6700 Nicolet FTIR Spectrometer in 400-4000 cm^{-1} domain; with sensibility of 4 cm^{-1}. The finely ground glasses (1 mg) were mixed with 200 mg KBr and pressed in transparent pellets.

The XRD patterns of finely ground glasses were recorded of a Rigaku diffractometer type Ultima IV in parallel-beam geometry. The X-ray comes from a Cu tube (λ=0.15418 nm) operating at 40 kV and 30 mA. Counts were collected from 10 to 70 degree with a step size of 0.02 degree and a speed of 5 degree/min.

The morphology of the samples was investigated by scanning electron microscopy (SEM) using a microscope Quanta FEI model, at an accelerating voltage of 10 kV. Sample preparation was minimal and consisted in immobilizing the samples on a double-sided carbon tape, with no coating.

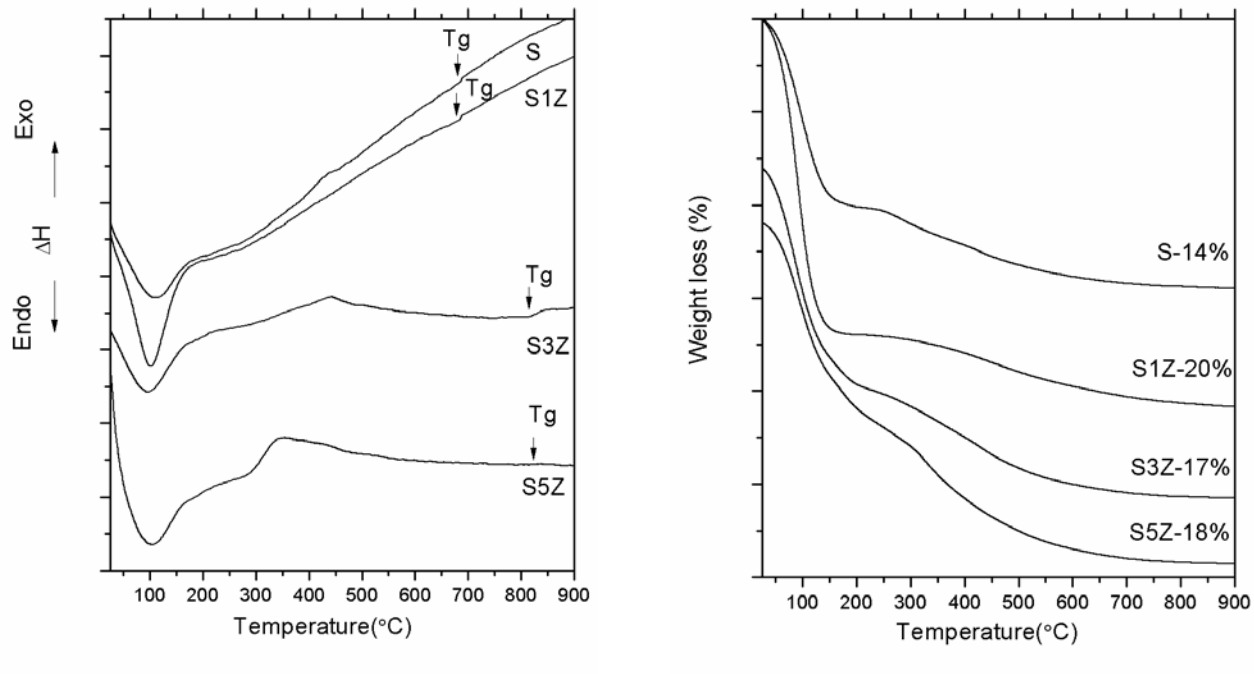
DTA/TG measurements on gels were made with a Mettler-Toledo apparatus with 10 degree/minute between 20-900°C.

Diffuse reflectance UV-Vis spectra were obtained using a spectrophotometer Perkin Elmer Lambda 35, equipped with an integrating sphere. The measurements were carried out on gels and glasses, in the range 800-200 nm, using spectralon as a reference. The reflectance measurements were converted to absorption spectra using the Kubelka-Munk function, $F(R_\infty)$.

RESULTS

1. Thermal characterization of glasses

In the Figure 1 and table 1 the thermal effects and weight losses of gels are presented.



a) DTA b) TG

Fig. 1 – DTA/TG curves of initial gels.

Table 1

Thermal effects and weight loss of the gels obtained by sol-gel in range 20-900°C

Glass	Endothermic effect (°C)	Weight loss (%)	Assignment
S	25-170	10	water and ethanol elimination
	218-360	2	organic residues combustion
	390-500	2	hydroxyl evolution
	650	-	glass transition temperature
		total loss is 14%	
S1Z	25-170	17	water and ethanol elimination
	243-550	3	organic residues combustion and hydroxyl evolution
	687	-	glass transition temperature
		total loss is 20%	
S3Z	25-180	12	water and ethanol elimination
	230-560	5	organic residues combustion and hydroxyl evolution
	790	-	glass transition temperature
		total loss is 17%	
S5Z	25-200	12	water and ethanol elimination
	280-500	6	organic residues combustion and hydroxyl evolution
	813	-	glass transition temperature
		total loss is *18%*	

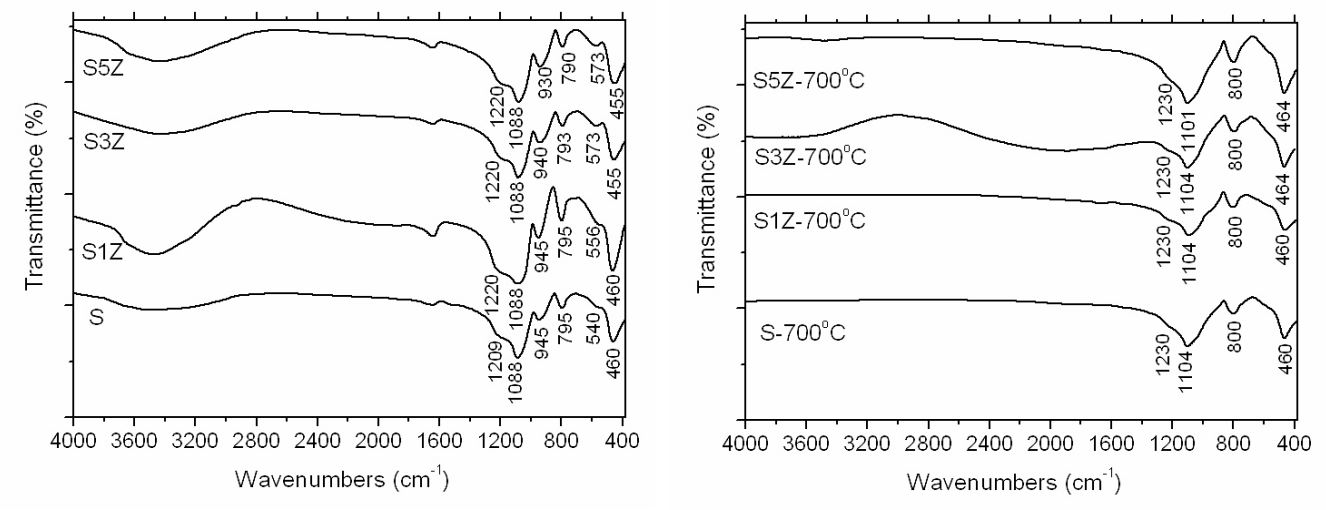
All curves shows two endothermic effects between 25-200°C and 218-560°C as well as a change of the slope line after 600°C. First endothermic effect in the 25-180°C range was assigned to elimination of water and ethanol adsorbed. The second endothermic effect between 190- 445°C was assigned to the evolution of the hydroxyls groups and combustion of un-reacted organic groups from matrix. Similar endothermic effects in gels were reported previously for other silica based compounds obtained by sol-gel method.[13] The glass transition is a temperature characteristic of glasses and it is highlighted in Figure (1a) in DTA curves as a change of the slope line (Figure 1a). The temperature of glass transition increased from 687°C to 813°C with increasing of zinc addition from 1 to 5 wt% in composition.

2. Structural characterization of glasses

The structure of prepared glasses was investigated by X-ray diffraction and infrared spectroscopy.

In the Figure 2 the curves of initial gels and of thermally treated glasses at 700°C are presented. The spectra of initial S glass (Fig 2a) show the vibration bands at 460 cm^{-1}, 540 cm^{-1}, 795 cm^{-1}, 945 cm^{-1} and 1088 cm^{-1} (with shoulder at 1220 cm^{-1}). Infrared spectroscopy is a technique that can evidence the structural groups such as SiO_4 due to characteristic vibrations that appear in spectra at different wavenumbers.[14-20] The band at 1088 cm^{-1} is characteristic to structural units bonded as chains; the shoulder at 1220 cm^{-1} represent double chains and the band at 945 cm^{-1} is characteristic to isolated SiO_4[16] or to Si-OH stretching vibration.[21, 22, 23] The presence of one band in the domain 650-800 cm^{-1} evidences the vitreous structure of initial gels. It is well known that crystalline silicates have 5-7 bands in this domain.[16, 18] The strong band at 460 cm^{-1} is also characteristic of Si-O-Si bonds. The band at 540 cm^{-1} can be assigned to Si-O vibration from cyclic tetramers.[22, 23] The bands were reported in literature for silica glasses.[15-19] The addition of zinc in the glasses shift the bands positions in 455-950 cm^{-1} domain. The bands at 573 cm^{-1} and 790 cm^{-1} can be assigned to Si-O-Zn or O-Zn-O bonds, in agreement to literature data.[24] In the spectra of glasses treated at 700°C, few bands near 540 and 945 cm^{-1} disappeared, due to relaxation of structure and formation of chains of tetrahedra.

Figure 3 show the X-ray diffraction patterns recorded on glasses treated at 700°C for 3 hours. The measurements were made on powder obtained by grinding of glasses, up to a grain size below 0.3 μ. The shape of XRD patterns was characteristic to vitreous state. Absence of peaks demonstrates that glasses are homogeneous, without micro-crystallites that prove a good quality.



a) initial gels b) glasses thermally treated at 700°C for 3 h

Fig. 2 – FTIR spectra of initial gels and thermally treated glasses.

3. Optical characterization of glasses

In the Figure 4 are presented the UV-VIS spectra of the glasses noted S3Z, S3Z-700°C and S-700°C. There is no absorption in the wavelength range 200-800 nm for initial gels as can be seen for S3Z in figure 3. UV absorption of oxide glasses is predominantly attributed to the excitation of electrons of oxygens bonded with glass formers.[7, 25] The electrons of weakly bonded nonbridging oxygens (NBOs) are excited more easily compared to those of strongly bonded oxygens (BOs) and thus they are more prone to absorb the energy generated from UV emission after excitation.[7, 25] The studied glasses show absorption bands at 256 nm related to three oxygen-excess defects or non-bridging oxygen hole center, NBOHC, reported by other researchers in silicate glasses.[25-27] In the spectra of S3Z-700°C glass an additional peak at 354 nm is present, which could be assigned to the bonding of zinc in silica glass and to ordering of structural units at small distance. The peak at 354 nm was reported by others authors related with presence of ZnO in glasses.[25, 26]

4. Morphological characterization of glasses

Figure 5 show the SEM images of glasses. The SEM images present the typically morphologies of glass matrix (grey background) and white dots. The dots dimensions decreased in doped glasses. In order to identify the dots compositions, EDAX analysis were performed. In the figure 6 the EDAX results are presented. EDAX analysis of white dots on the surface of S glass shows the composition 73.17 at% Si and 26.83 at% O. EDAX analysis of white dots on the surface S3Z glass shows the composition 72.05 at % Si, 27.45 at% O and 0.5 at% Zn.

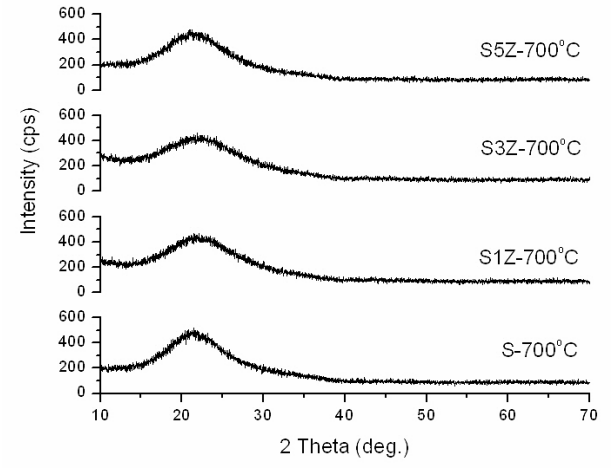


Fig. 3 –XRD patterns of the glasses treated at 700°C for 3h.

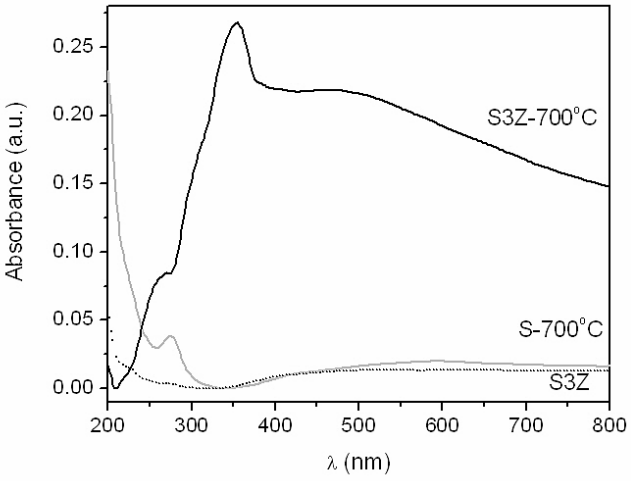
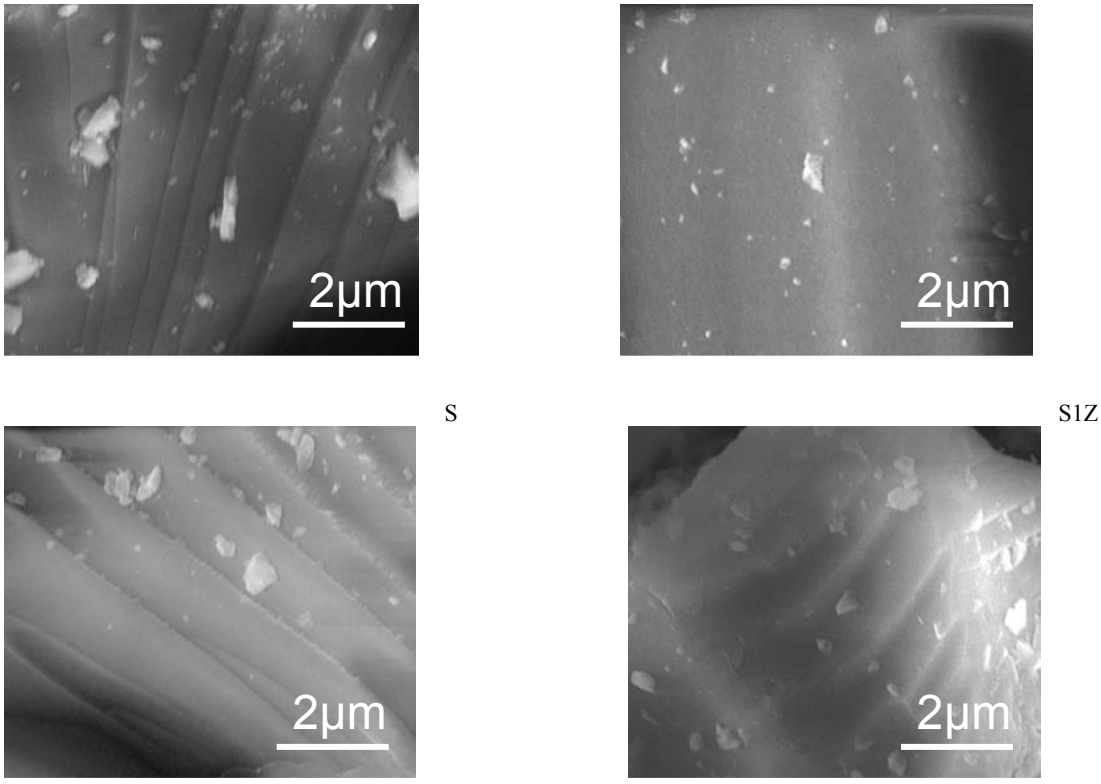


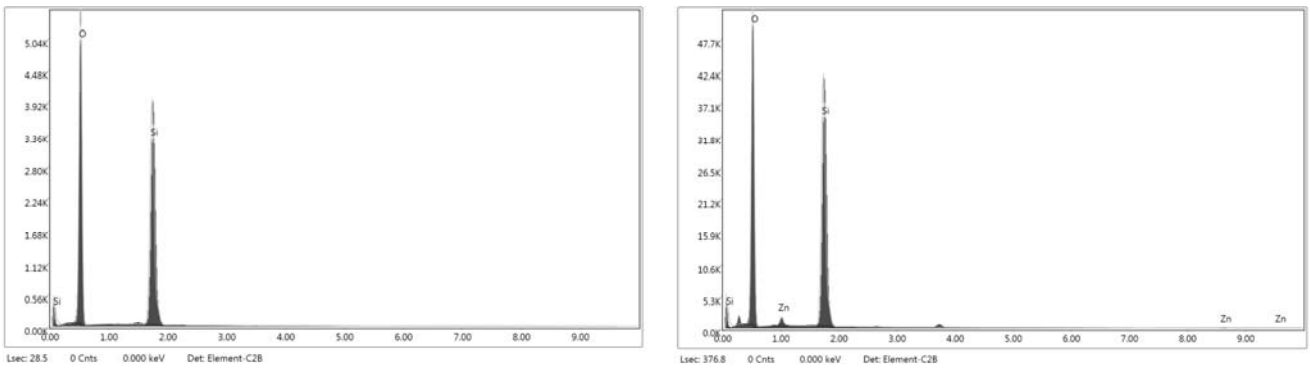
Fig. 4 – UV-VIS absorption spectra of the S3Z gel and S-700°C and S3Z-700°C glasses.



S S1Z

S3Z S5Z

Fig. 5 – SEM images of obtained glasses.



S S3Z

Fig. 6 – EDAX of glasses.

CONCLUSIONS

Zn-doped silica glasses were obtained by sol-gel route. All glasses exhibit vitreous state as can be seen from XRD and FT-IR spectra. DTA/TG measurements have been highlighted the vitreous transition temperatures. The glass transition temperature and weight loss increased with increase of zinc addition. SEM images show glass matrix as morphology with small white dots that were identified by EDAX analysis. The gels have not exhibit absorption in UV-VIS. The absorption in UV-VIS spectra was observed in case of glasses obtained after thermal treatment at 700°C for 3 hours. The absorption in UV-VIS was influenced by zinc addition and thermal treatment.

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