

## THERMAL AND STRUCTURAL CHARACTERIZATION OF THE VITREOUS SAMPLES IN THE $\text{SiO}_2 - \text{PbO} - \text{Na}_2\text{O}$ SYSTEM

*Oana Cătălina Mocioiu, Georgeta Jitianu and Maria Zaharescu*

*Lead-containing glasses have been used from the ancient time. Recently, due to the possible application in optics, electronics, nuclear techniques, wastes inactivation, the interest in these types of glasses has been renewed. For lead waste inactivation, glasses with high amount of PbO in the composition are required, those exhibiting at the same time a high chemical and thermal stability. Thermal behaviour of lead-silicate glasses was examined by differential thermal analysis (DTA). Infrared spectroscopy was used to investigate the structure of the glasses. The spectra were interpreted in terms of the structures of silicate group by comparison with the spectra of other silicate crystals. The DTA and infrared data were correlated with the chemical stability tests.*

KEYWORDS: Lead-silicate glasses; DTA and IR analysis

### INTRODUCTION

Lead glasses are both important materials from both scientific and technological point of view, since they have very interesting structure and offer properties such as high value of the refractive index, low absorption in the visible region of the spectrum, an improved chemical stability and brightness (1, 2). The lead containing glasses, such as crystal glass, have been used from the ancient time. Recently, due to the possible application in optics, electronics, nuclear techniques, and wastes inactivation, the interest in these types of glasses has been renewed.

In the binary  $\text{SiO}_2$ -PbO system, when the PbO content is low, the  $\text{Pb}^{2+}$  ion is distinctly framework modifier, but at PbO content higher than 15 to 20% it is framework former, i.e.,  $[\text{PbO}_4]$  coordination groups are present. In the intermediate concentration range up to 15%, this increase in tetrahedral  $[\text{PbO}_4]$  can be systematically observed. Above 30%

PbO a distinct change in the bonding mechanism develops, most probably by a change in the electron distribution (3, 4). Raman and infrared investigations of the binary glasses confirm that the silicate network is only gradually depolymerised with increasing PbO concentration (2).

Generally, when glasses are heated (the thermal treatment depends on the chemical composition), they may undergo crystallization and oxide compounds are formed, which is on the DTA curves registered as an exothermic effect. The glass crystallization can occur either in the presence of nucleation agents (method used for the glass ceramics production) (5) or in their absence. In the absence of the nucleation agents the crystallization starts from the surface and only some systems can crystallize in the volume (6).

The purpose of the present work was thermal, structural and chemical characterization of glasses in the  $\text{SiO}_2 - \text{PbO} - \text{Na}_2\text{O}$  ternary system. The lead oxide role in the studied glasses was investigated by infrared spectroscopy. The spectra were interpreted in terms of the structures of silicate groups. The correlation of differential thermal analysis and infrared spectroscopy data with the results of chemical stability tests helped to establish the compositions, which have a high PbO content and good chemical stability.

## EXPERIMENTAL

### *Glass preparation*

Lead silicate glasses were prepared from PbO,  $\text{SiO}_2$ ,  $\text{Na}_2\text{CO}_3$  (analytical grade reagents). Batches (100 g) were melted in alumina crucibles in an electrical oven at 1200-1400 °C. Melting times were minimized in order to reduce the volatilisation of PbO, without influencing homogeneous composition of glasses. Glass frits were obtained by fast quenching in cold water.

### *Structural investigations*

**Infrared spectra** between 200 and 2000  $\text{cm}^{-1}$  were recorded on a M80 Carl Zeiss Jena Specord. Fine powder (1 mg) was mixed with KBr (200 mg) and vacuum-pressed into a transparent pellet suitable for measurement.

**X-ray analysis** of the glasses was performed on a DRON 3 equipment using  $\text{CuK}_\alpha$  radiation

### *Thermal investigations*

DTA curves of powder samples with the size between 0.3-0.5 mm were recorded on a Q-1500D (MOM, Budapest) Paulik-Paulik-Erdey derivatograph in static air atmosphere in the temperature range of 20-1000°C, using powdered alumina as a reference.

### *Chemical resistance tests*

Chemical resistance tests in water were realized according to ISO 598/1-71, method A. The conductivity of the extraction solutions after boiling for 1 hour at 98°C was measured.

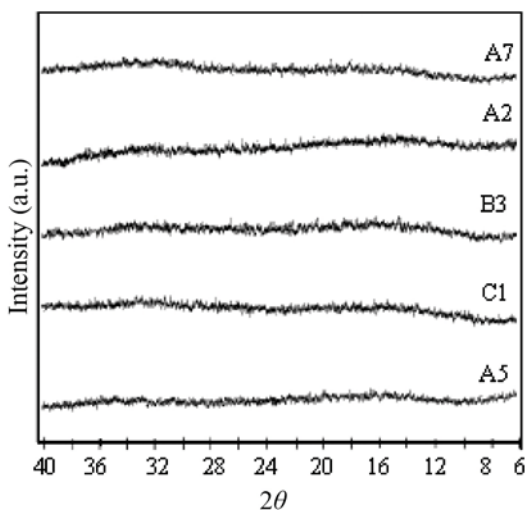
## RESULTS AND DISCUSSION

The compositions of glasses are presented in Table 1. In the first series, which contains the A7, A2, B3, C1, D3 glasses, % wt SiO<sub>2</sub> increases and % wt PbO decreases. In the second series, which contains the A2 and A5 glasses % wt, SiO<sub>2</sub> is same and % wt PbO increases.

**Table 1.** Glass composition in the ternary system SiO<sub>2</sub> – PbO – Na<sub>2</sub>O

No.	Glass	Chemical Composition					
		SiO <sub>2</sub>		PbO		Na <sub>2</sub> O	
		% wt	% mol	% wt	% mol	% wt	% mol
Series 1	A7	<b>32.0</b>	53.5	<b>55.0</b>	25.3	<b>13.0</b>	21.2
	A2	<b>35.0</b>	50.0	<b>40.0</b>	15.4	<b>25.0</b>	34.6
	B3	<b>44.0</b>	59.3	<b>35.0</b>	13.0	<b>21.0</b>	27.7
	C1	<b>45.0</b>	63.0	<b>38.3</b>	14.3	<b>16.7</b>	22.7
	D3	<b>50.0</b>	61.9	<b>25.0</b>	8.2	<b>25.0</b>	29.9
Series 2	A2	<b>35.0</b>	50.0	<b>40.0</b>	15.4	<b>25.0</b>	34.6
	A5	<b>35.0</b>	54.2	<b>48.0</b>	20.6	<b>17.0</b>	25.2

The results of the XRD measurements of the prepared glasses are presented in Figure 1, underlying their vitreous character.



**Fig. 1.** XRD pattern of some glasses in the SiO<sub>2</sub> – PbO – Na<sub>2</sub>O system

Infrared spectra of the studied glasses are presented in Figure 2. All the spectra of the obtained glasses contain broad absorption bands in the following ranges: 400-550, 600-800, 800-1300, 1400-1500, 1550-1700  $\text{cm}^{-1}$ . The vibration bands assigned to the Pb-O bonds are located below 400  $\text{cm}^{-1}$  and are not evident in our spectra.

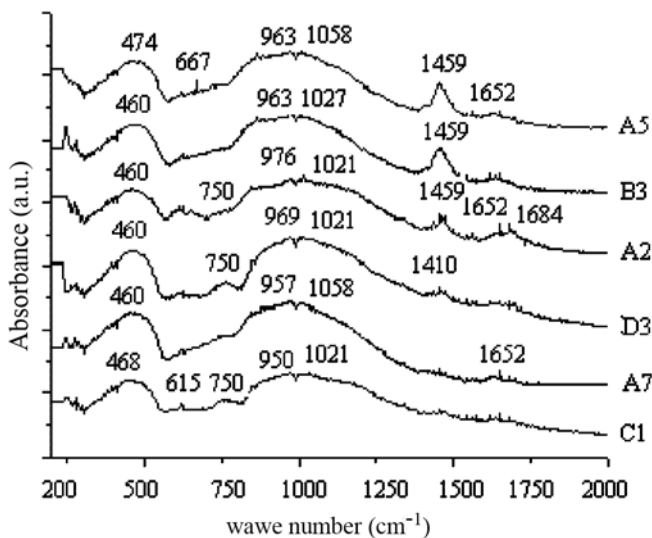


Fig. 2. Infrared spectra of some glasses in the  $\text{SiO}_2 - \text{PbO} - \text{Na}_2\text{O}$  system

In our case the bands between 400-550  $\text{cm}^{-1}$  with the maximum at about 460  $\text{cm}^{-1}$  are assigned to the deformation ( $\delta$ ) vibrations of the bonds in silicon-oxygen groups. They are not significantly different for the different studied glasses.

The weak infrared bands in the range of 600 to 750  $\text{cm}^{-1}$  in chain silicates have been assigned to the stretching vibrations of Si-O-Si bridging bonds. The number of the bands in this range is then correlated with the number of distinct repeating units in the silicate chain (8). The infrared spectra of hexagonal  $\text{PbSiO}_3$  contain five or more bands in this region indicating more  $\text{SiO}_4$  units in the chain (9).

The symmetric ( $\nu_s$ ) valence vibrations of the bonds in the  $[\text{SiO}_4]$  tetrahedra are located in the 700-800  $\text{cm}^{-1}$ . In the case of our glasses, these bands are active in the IR spectrum at about 750  $\text{cm}^{-1}$  for the glasses C1 and D3, showing that the symmetry of the  $[\text{SiO}_4]$  tetrahedra is due to the fact that the silicon-oxygen network is predominately composed of tetrahedra with non-bridging oxygen ions and structural network is significantly depolymerised.

The broad band in the range of 800-1300  $\text{cm}^{-1}$  is assigned to the asymmetric ( $\nu_{as}$ ) valence vibrations of the bridging Si-O-Si bonds. The  $[\text{SiO}_4]$  tetrahedron can be bonded with variable non-bridging oxygen ions (maximum at 1106 and 1027  $\text{cm}^{-1}$ ) and non-bridging Si-O bonds (maximum 893  $\text{cm}^{-1}$ ) (7). Zarzycki also noted that the characteristic frequency range for  $\text{SiO}_4$  group in the oxide glasses is 1050-800  $\text{cm}^{-1}$  (3). In the case of the studied glasses the band assigned to the bonding of the  $[\text{SiO}_4]$  network tetrahedra to the non-bridging oxygen is located between 1020 and 1058  $\text{cm}^{-1}$ , while the bonding to the Si-O bonds are significantly shifted, being located in the range of 950-975  $\text{cm}^{-1}$ . The differences no-

ticed in the IR spectra of the synthesized glasses in the 800-1300  $\text{cm}^{-1}$  range indicate different structural ordering of the glass network that can be correlated to the different amount of  $\text{PbO}$  and  $\text{Na}_2\text{O}$  in the glass composition.

In the literature, the bands within the ranges 1550-1650 and about 1400-1450 are assigned to deformation vibration of the H-O-H groups in the structure of glass or surface adsorbed water (7). The bands have fine structure due to different character of interaction between structurally bonded water with silicon-oxygen network. The band about 1410  $\text{cm}^{-1}$  is assigned to the presence of  $\text{Na}_2\text{O}$  acting as network modifier (10). In the case of our glasses, the bands in the 1400-1450  $\text{cm}^{-1}$  range are shifted to the higher wavenumber, probably, due to the interaction with both the tetrahedral  $\text{SiO}_4$  and pyramidal  $\text{PbO}_3$ . The intensity of the band at 1460  $\text{cm}^{-1}$  increases in the order: C1, A7, D3, A2, A5, B3. The C1 and A7 glasses contain bands with lower intensity in this wavenumber range. That is in correlation with the smaller content of  $\text{Na}_2\text{O}$  in the oxide composition.

Figure 3 shows DTA curves of the glasses. The only sample that exhibits a clear exothermic effect with an associate shoulder is sample A5. The B3 glass has a broad band appearing in a large range of temperatures, between 550°C and 735°C. This behaviour can be assigned to the successive crystallization of several phases, accompanied by the corresponding exothermic effects that overlap. In the case of A2 glass, three very small effects could be observed. The A2 glass contains high amount of  $\text{Na}_2\text{O}$ , about 25%. The D3 glass shows an exothermic effect at 657°C. The sample A7 seems to have the lowest crystallization tendency, so the highest thermal stability, while sample A5 exhibits an opposite behaviour and the highest crystallization tendency.

In the  $\text{Pb}_2\text{SiO}_4 - \text{PbSiO}_3$  system, the DTA pattern obtained from  $\text{Pb}_2\text{SiO}_4$  shows an endothermic peak at 615°C on heating and exothermic peak at 525°C on cooling (8). In the glasses that exhibits exothermic peaks at about 600°C, they can be assigned to the crystallization of the  $\text{Pb}_2\text{SiO}_4$  phase.

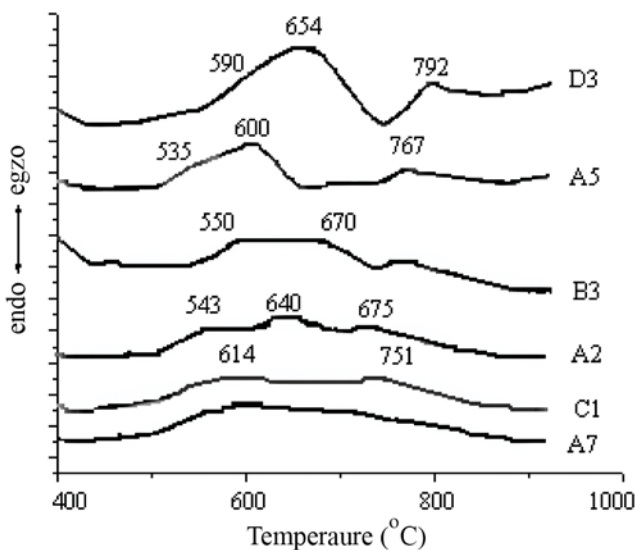


Fig. 3. DTA curves of the glasses in the  $\text{SiO}_2 - \text{PbO} - \text{Na}_2\text{O}$  system

Data of chemical resistance in water (cf. ISO 598/1-71, method A) of the glasses and the electrical conductivity of the solutions after boiling for 1 hour at 98°C are presented in the Table 2. The reference glass was window glass, whose conductivity determined by the sodium ions dissolved from the glass. In the studied glasses, the conductivity is determined both by the sodium ions and the lead ions release form the glass composition.

Comparing the results of chemical resistance with the structural ordering of the glasses, as determined by infrared spectroscopy and their thermal behaviour, we may notice that the samples with the highest tendency of crystallization have the lowest chemical stability. Among all studied samples, the A7 glass exhibits a good hydrolytic resistance (class 1) and it also showed a very good thermal stability.

**Table 2.** Chemical resistance of the glasses obtained by ISO 598/1-71 and conductivity measurements

Glass	Chemical Resistance Class	Conductivity ( $\mu\text{S}/\text{cm}$ )
A7	1	63
C1	1-2	137
A2	2	836
B3	2	1046
A5	2	1470
D3	3	1930
window glass	3	31

\*Conductivity of the solutions after boiling for 1 hour.

## CONCLUSIONS

The glasses in the  $\text{SiO}_2 - \text{PbO} - \text{Na}_2\text{O}$  system were studied in order to establish the conditions to include high amount of the PbO in the compositions and at the same time obtain a good chemical and thermal stability. The glasses were characterized from the point of view of the thermal stability by differential thermal analysis. The structure was established by infrared spectroscopy. The chemical stability was determined by standard tests and conductivity measurements. The results lead to the conclusions that is possible to obtain glasses with rather high amount of PbO and with satisfactory thermal and chemical properties. The correlation between thermal and chemical stability and the structure of the glasses was established.

## REFERENCES

1. Komatsu, T., H. Mohri: Raman Scattering Spectra and Optical Properties of Telluride glasses and Crystalline Phases Containing PbO and CdO, *Phys. Chem. Glasses* **40**, 5 (1999) 257-266.

2. Zahra, A. M., C.Y. Zahra, B. Piriou: DSC and Raman Studies of Lead Borate and Lead Silicate Glasses, *J. Non-Crystalline Solids* **155** (1993) 45-55.
3. Zarzycki, J.: Glasses and the vitreous state, Cambridge University Press (1991) p.122.
4. Bray, P., G., M. Leventhal, H.O. Cooper: Nuclear Magnetic Resonance Investigations of the Structure of Lead Borate Glasses, *Phys. Chem. Glasses* **4**, 2 (1963) 47-52.
5. McMillan, P.W.: Glass Ceramics, Academic Press, (1979) p.285.
6. Zanotto, E.D.: Isothermal and Adiabatic Nucleation in Glass, *J. Non-Cryst. Solids*, **89** (1987) 361-365.
7. Tolstova, O., S. Stefanovsky, T.Lashtchenova: Structure of Sodium-Lead-Silicate Glasses for Conditioning of High Level Waste, *Proceedings of the Second Balkan Conference on Glass Science and Technology. 14th Conference of Glass and Ceramics, Varna, 24-28 September 2002*. Editors: B.Samuneva, S.Bachvarov, I.Gutzov, Y. Dimitriev: Publishing House Science Invest Sofia, 2004, Vol.1- Glass (CD-ROM).
8. Furukawa, T., S. Brawer, W. White: Raman and Infrared Spectroscopic Studies of the Crystalline Phases in the System  $Pb_2SiO_4 - PbSiO_3$ , *J. Am. Ceram. Soc.*, **62** (1979) 351-355.
9. Ryall, W.R. and IM Threadgold: Evidence for  $[(SiO_3)_5]_x$  Chains in Inside as Shown by X-ray and Infrared Absorption Studies, *Am. Mineral.*, **51** (1966) 754.
10. D. Becherescu: Metode de analiză în chimia silicaților, ed. Tehnică București (1975).

## ТЕРМИЧКА И СТРУКТУРНА КАРАКТЕРИЗАЦИЈА СТАКЛА ИЗ СИСТЕМА $SiO_2 - PbO - Na_2O$

*Oana Cătălina Mocioiu, Georgeta Jitianu and Maria Zaharescu*

Оловна стакла се користе од давнина. У новије време, због могуће примене у оптици, електроници, нуклеарној техници, декативацији отпада, појавио се поново интерес за та стакла. Оловна стакла за инертизацију отпада су стакла са високим уделом  $PbO$ , што им обезбеђује и добру хемијски и термичку стабилност. Термичко понашање узорака олово-силикатног стакла је одређено диференцијално термијском анализом (ДТА). Инфрацрвена спектроскопија је коришћена за анализу структуре стакла. За интерпретацију спектра коришћено је поређење спектра који одговарају структури силикатне групе са спектрима других силикатних кристала. Резултати ДТА и инфрацрвене спектроскопије су повезани са тестовима хемијске стабилности тих стакала.

Received 22 May 2006

Accepted 20 July 2006