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Influence of CaO addition on the structure and properties of the glasses in the SiO_2-PbO-Na_2O system

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The lead silicate glasses are interesting for their potential use in optics, electronics, waste inertization, etc. The present work, studies the influence of CaO addition to glasses in the ternary SiO_2-PbO-Na_2O. The melting behaviour of the selected glasses was determined by high temperature microscopy. The structure of glasses was examined by X-ray diffraction and IR spectroscopy. X-ray patterns show that all samples are in vitreous states and the IR spectroscopy puts in evidence different structural ordering depending on the composition of the glasses. In order to establish their thermal behaviour and hydrolytic stability the DTA measurements and ISO 719/1996 tests were performed. The thermal properties of glasses have shown the vitreous transitions and glass crystallization tendency depending on the amount of CaO in the composition. All quaternary glasses show good chemical stabilities. The results of the mentioned investigations were correlated in order to establish the influence of the CaO addition on the structure, thermal behaviour and hydrolytic stability of the glasses.

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1. Introduction

The lead silicate glasses were used for long time as so called "crystal glasses". The interest to lead silicate glasses increased due to the possibility of application in new domains as soldering and sealing glasses for electronic devices, and optical glasses, because of their excellent stability against devitrification, high refractive index, and low melting temperature [1, 2].

Previous studies on the binary glasses have shown their local structure as determined by nuclear magnetic resonance (NMR) [3-7], Raman [2,8], infrared spectroscopy [2,8], and X-ray photoemission spectroscopy (XPS) [5].

The structure of silicate glass is dominated by discrete silicate units with short-to-medium range order, and the physical and chemical properties are controlled by the relative percentage of these silicate units [8]. The structural units in silicate glasses are commonly modelled using the silicate units found in crystals. The silicate units in crystals are grouped according to their ratio of non-bridging oxygen per network forming tetrahedral configurations (NBO/T) to provide a measure of their polymerisation [8].

In case of glasses soda–lime-silica glass the eutectics have been founded at the percentage of 2 and 5.2 % CaO [9]. When the amount of CaO increases the melting temperature increases and the crystallization tendency increases [9]. The quantity that is recommended to be added in the composition is 5.2% CaO [9].

In case of silicate glasses the increases of the amount of divalent oxide (PbO) improves the chemical stability and decreases the crystallization tendency [9].

Our previous studies on the glasses synthesized in the ternary SiO_2-PbO-Na_2O system [10, 11] allowed to establish the compositions with different amount of PbO that present suitable thermal and chemical stability. In the present work, 5% and 10% CaO were added to the ternary glass with the best chemical stability. CaO replaces SiO_2, PbO and Na_2O, respectively. The influence of CaO addition on the structure, thermal and chemical stability of the glasses was studied.

2. Experimental

2.1. Glasses preparation

The glasses were prepared from PbO, SiO_2, Na_2CO_3 and CaO (analytical grade reagents from Merck). Batches (100 g) were melted in alumina crucibles in an electrical oven in 1000-1400 ˚C range temperature using a heating rate of 10 degree/min. The melts were cooled in water and on metallic plates. The oxide compositions of the elaborated glasses are presented in Table 1.

2.2. Characterization of samples

The high temperature microscopy was performed with a Carl Zeiss Jena microscope between 20 and 900 ^oC, with a heating rate to 10 deg/min.

X-ray analysis of the glasses was performed with DRON 3 equipment using CuK_α radiation.

FT-IR spectra were recorded using a spectrophotometer model Nicolet, at a resolution of 4 cm^{-1}, over the frequency range from 2000 to 400 cm^{-1}. The spectra were taken from thin transparent KBr pellets. The pellets were prepared by compacting and vacuum-pressing an intimate mixture obtained by grinding 1 mg of substance in 200 mg KBr.

The positions of deconvoluted spectra were established using the Omnic software.

The thermal behaviour of the glasses was determined by DTA measurements, using a Mettler Differential Thermal Analyser (20-1000 ^{0}C, rate 10 ^{o}C/ min).

The chemical stability was determined by standard tests in water according to the standard ISO 719/1996.

The conductivity measurements for all the solutions obtained after boiling in water at 98^0 C were performed with Jenway conductivity & pH meter 4330.

3. Results

Homogeneous glasses were obtained and the compositions are presented in Table 1.

Table 1. The oxide compositions of samples.

Glass	Chemical composition (% mol)			
	SiO_2	PbO	Na_2O	CaO
E1	55.0	25.0	20.0	-
E2	50.0	25.0	20.0	5.0
E3	45.0	25.0	20.0	10.0
E4	55.0	20.0	20.0	5.0
E5	55.0	15.0	20.0	10.0
E6	55.0	25.0	15.0	5.0
E7	55.0	25.0	10.0	10.0

The influence of the CaO addition on the melting properties of the glasses is determined by high temperature microscopy and the results are presented in Table 2.

Table 2. The characteristic temperatures of the melting process.

Glass	Staining temperature	Half-ball temperature	Flow temperature
E1	480	580	700
E2	500	580	680
E3	680	740	820
E4	520	680	730
E5	560	860	920
E6	540	650	700
E7	480	620	680

The structure of the samples was investigated by X-ray diffraction and infrared spectroscopy. The vitreous state of samples is confirmed by the absence of the diffraction peaks in the X-ray patterns.

Figs. 1 presents the infrared spectra of the ternary glass noted E1. The principal band presents a maximum at the 980cm^{-1}, characteristic for ν_{as} Si-O-Si vibration in the chains of tetrahedra in silicate glasses.

In Fig. 2 the infrared spectra of the studied glasses in the quaternary system are shown: when CaO replaces Na_2O (Fig 2a); when CaO replaces PbO (fig 2b); when CaO replaces SiO_2 (Fig. 2c).

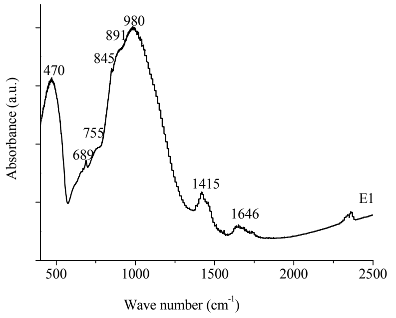
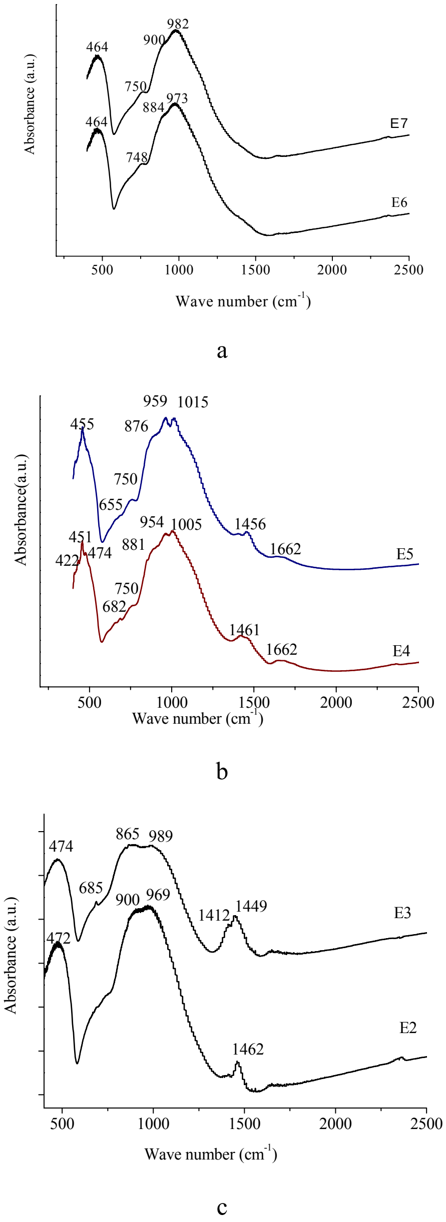


Fig. 1. IR spectra of ternary glass.



a

b

c

Fig. 2. IR spectra of glasses in the quaternary systems: a) glasses that CaO replaced Na_2O, b) glasses that CaO replaced PbO, c) glasses that CaO replaced SiO_2.

All the spectra contain bands in the ranges: 400-550 cm^{-1}, 600-700 cm^{-1}, 750-1200 cm^{-1} and 1400-1600 cm^{-1}. It can be observed that the shape of curves changes as a function of the oxide that was replaced.

Due to the overlaps bands in the range 750-1200 cm^{-1} in the infrared spectra of quaternary glasses we performed the deconvolution of some samples. The scope of deconvolution was to identify what kind of structural groups are presented in our glasses and to correlate the groups in the structure with the properties of the glass samples. Table 3 presents the position of the bands obtained by deconvolution of spectra with the Omnic software. The attribution of groups is made according to the literature data [8, 9, 12, 13, 14].

Table 3. Position of vibration bands (cm^{-1}) of the investigated glasses.

Glass	Isolated groups SiO_4^{4-}	Pairs of tetrahedra	Chains of tetrahedra	Chains of tetrahedra	Network
E1	859	-	965	1044	1084
E2	884	900	-	996	1089
E3	813	901	-	1034	1132
E4	852	917	955	1000	1122
E5	876	-	961	1020	1100
E6	862	-	951,971	1055	-
E7	865	-	957	1055	1136

The thermal behaviour of the quaternary glasses is determined by differential thermal analysis, in non-isothermal condition.

Fig. 3 shows the differential thermal analysis (DTA) curves of ternary glass and glasses in the quaternary systems.

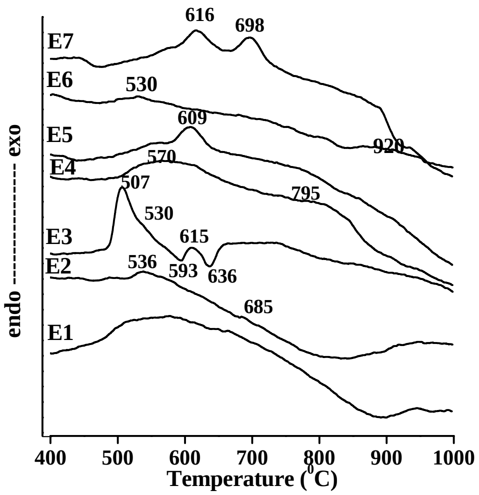


Fig. 3. DTA curves of studied glasses: E1 is the ternary glass and E2-E7 glasses are the quaternary.

In order to determine the crystalline phases that crystallized in quaternary glasses, thermal treatments at the temperatures corresponding to the maxima of exothermal peaks are performed. According with the DTA curves two thermal treatment temperatures were selected, namely, 530 and 615 ^{0}C, (duration: 24 hours). The treated samples were investigated by X-ray diffraction. The obtained XRD patterns are presented in Figs. 4 and 5.

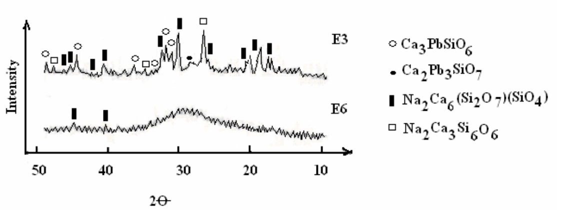


Fig. 4. X-ray patterns of samples treated at 530 ºC for 24 h.

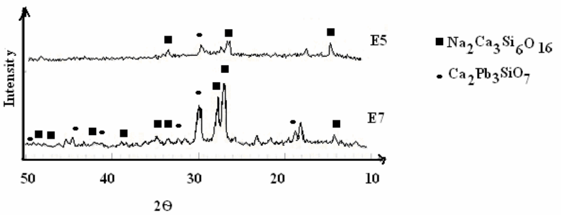


Fig. 5. X-ray patterns of samples treated at 615 ºC for 24 h.

All glasses are analysed to point out their chemical properties. Table 4 shows the results for the chemical stability tests according to the standard ISO 719/1996.

The conductivity measurement of the extraction solution after 1 hours boiling at 98 ^oC evidenced small values of the electrical conductivity.

Table 4. Results of the chemical resistance and conductivity measurement.

Glass	Chemical Resistance Class (ISO719/96)	Conductivity (µS/cm)
E1	1	186.4
E2	2	395
E3	2	324
E4	2	270
E5	1	266
E6	1	315
E7	1	310

4. Discussion

Homogeneous glasses are obtained in the studied oxide systems. The ternary glass was selected based on the previous works [10, 11] in which 19 compositions were prepared and investigated. The ternary glass similar with E1 has the best chemical stability and the lowest crystallization tendency.

In the ternary system the SiO_2, PbO and Na_2O are partially replaced by CaO. Table 1 shows the composition of the samples.

The high temperature microscopy offers the information about the melting process. In the case of the studied quaternary glasses the melting temperature interval increase. The addition of CaO in the composition "lengthens" the glasses and could improve their quality.

The high temperature microscopy offers information about the melting process. The addition of CaO in the ternary composition extends the melting interval.

The X-ray diffraction patterns, of the prepared glasses, confirm the vitreous character of all samples.

The structural data are completed by the infrared spectroscopy measurements. All the spectra of glasses contain absorption bands in the ranges: 400-550 cm^{-1}, 600-700 cm^{-1}, 750-1200 cm^{-1} and 1400-1600 cm^{-1}.

The absorption curves change in dependence on the oxide that was replaced. When the 5% molar CaO replaced SiO_2, the IR spectra is not significantly change. In case of glasses E4, E5 when CaO replaced PbO the order in the network Si-O-Si is enhanced. At low frequencies appear the bands characteristic to the bonds Pb-O.

The shape of the IR curves of the glasses E6 and E7 where the CaO replaced partially Na_2O leads to the conclusion that Si-O-Si network is better polymerised than in other cases.

The presence of the bands at 1460 cm^{-1} and 1600 cm^{-1} are assigned to the vibration of adsorbed CO_2 and H_2O during the preparation of the transparent pellet by mixing and vacuum pressing.

All the samples in the quaternary system show a wide band in the range 750-1200 cm^{-1} that is due to the overlapping of the bands due to vibration and translation motions of the groups of SiO_4. This kind of band overlapping is characteristic to the vitreous state.

The low intensity bands in the 600-750 cm^{-1} range could be assigned to bending motions of the Si-O-Si bonds.

The band at 460 cm^{-1} can be ascribed to deformation vibrations (δ) of the Si-O bonds in the tetrahedra. This band exhibits a shoulder at 430 cm^{-1} that is assigned to the symmetric vibration of the Pb-O bond. All glasses show an asymmetry in the range of small wave number.

The overlapping bands between 750 and 1200 cm^{-1} are deconvoluted in order to identify the frequencies characteristic to groups. In the case of glasses E1, E5, E6, E7 the structure is formed mainly by chains of tetrahedra. In the case of E2 and E3 higher number of isolated and pairs of tetrahedral exists.

The DTA curves of the glasses in the ternary and quaternary systems are show in the Fig. 3 and the temperatures of crystallization peak are noted.

The glass transition temperatures (T_g values) obtained by DTA and high temperature microscopy ranged in 450-550 ^{0}C domain and are of very low intensity.

In the case of the ternary E1 glass a rather small crystallization tendency is observed, due to the fact that the recorded curve does not present specific exothermal effects, but just a broad band with lowest intensity in the 500-870 °C range.

In the case of glasses in the SiO_2-PbO-Na_2O-CaO system the presence of exothermal peaks assigned to their crystallization could be observed. The glasses with 5% CaO content exhibit low crystallization tendencies. The glasses which have 10%CaO in compositions present higher crystallization tendency than the glasses with 5% CaO, but their crystallization tendency can be considered well balanced for technical applications.

In the literature data no specific information on the crystallization of the glasses in the studied quaternary system is given.

All thermally treated samples, in the conditions presented above, present two or three crystalline phases corresponding to double silicates of lead and calcium and the silicates of sodium and calcium as shown Figs. 4 and 5. One may notice that all crystallized phases contain Ca, indicating the influence of the CaO on the glass crystallization.

All quaternary glasses have good chemical stabilities, ranging in the 1-2 class according ISO 719/1996. In ISO 719/1996 the best class is considered class 1 and the worst is the class 5. The substitution of SiO_2 and PbO by CaO leads to lower chemical stability, as compared with the ternary glass. The substitution of the Na_2O by CaO does not change the chemical stability.

The conductivity of quaternary glasses is higher than that of ternary glass. The increase of the conductivity could be correlated to the contribution of the other ions (Pb, Ca), beside Na, to the total conductivity.

5. Conclusions

The glasses with CaO content were synthesized and their structure, thermal behaviour and chemical properties were investigated.

The crystallization tendency and structure depend on the CaO content.

The structures consisting of chains of tetrahedra correspond to the most resistant glasses.

Glasses with 10%mol CaO present higher tendency of crystallization, than glasses with 5%CaO, but they are acceptable for applications.

All quaternary glasses present good chemical stability. The good chemical stability of the ternary glass is maintained in the SiO_2-PbO-Na_2O-CaO system even up to 10%CaO content.

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