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Synthesis, structural and thermal characterization of silica glasses containing BaO, SrO and ZnO oxides.

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Abstract

Alternatives to lead crystal glass were initially selected from CD-ROM "interglad" data, and then elaborated. These samples have properties closer to those of conventional lead crystal, are completely lead free. In this study, vitrifiable mixtures based on silicon, barium, strontium and zinc oxides were melted at 1450°C, annealed at 580°C, and characterized by X-ray diffraction, infrared spectroscopy, Raman spectroscopy and Calorimetric Thermal Analysis (DSC). X-ray diffraction confirms the amorphous character of all investigated glasses. The vibration bands are identified by infrared and Raman spectroscopy. These results highlight the influence of glass composition on structural properties. The glass transition temperatures (T_g) were determined by differential scanning calorimetric analysis (DSC). The obtained results vary from 546.8 to 632.6°C, confirming the effect of the composition on the thermal properties.

Key words: Glass, glass transition temperatures (T_g), network modifier oxides, differential scanning calorimetric analysis (DSC).

1. Introduction

Crystal glass is made up mainly of lead and silica. The insertion of lead in crystal glass composition poses many problems related to public health and respect for the environment [1]. To overcome this inconvenience, alternatives to lead crystal have been proposed [2,3, 4].

Based on the CD-rom "interglad" data [5]; compositions contain barium, strontium and zinc oxides were chosen. The samples were developed in a previous work [3], in which showed properties close to those of traditional lead crystal (refractive index, density, microhardness, thermal expansion and viscosity) have been taken up and studied in this present work.

The introduction of these oxides into crystal glass composition makes understanding their effects necessary to develop an alternative to lead crystal.

An industrial silica glass consists of three types of oxides: network formers, network modifiers and intermediates [6]. The last category can behave as a network former or a network modifier. In soda-lime glasses, it is commonly understood that alkaline earths M^{2+} and alkaline M^+ metal ions modify the silicate glass network by introducing non-bridging oxygens (NBO). The intermediate oxides include Al_2O_3 [7]. To understand the exact role of such oxide on the structural and thermal properties of a glass, it is necessary to consider all the constituting oxides present in the vitrifiable mixture. Thus, when adding Al_2O_3 in a glass containing M^{2+} or M^+ ions, the Al^{3+} ions mainly forms $[AlO_4]^{5-}$ tetrahedrons if $(M^{2+}+M^+)/Al_2O_3$ ratio is much greater than 1 [8]. Under these conditions, Al_2O_3 is a network former. Conversely, for lower ratios, Al_2O_3 behave as a network modifier.

The three oxides investigated in the present work (i.e. BaO, SrO and ZnO) are classified as intermediate and network modifiers [9].

ZnO acts in the same way than Al_2O_3 [10]. When associated to low alkaline ions fractions in the vitrifiable mixture, Zn^{2+} is a modifying ion by creating two non-bridging oxygens.

On the other hand, if there are enough of alkaline ions, Zn^{2+} can be placed in tetrahedral position and then acts as a network former [11, 12]. Valences equilibriums is provided by two neighboring alkaline ions. In high silica and alumina content glasses, some authors report that zinc oxide acts as a network former from an amount of 10% by mass [13].

BaO [14] and SrO [15, 16] are alkaline earths modifier oxides. In the presence of alkaline oxides, BaO as a strong melting effect and promotes the formation of a liquid phase below 1000°C [17]. At high content (14% by weight), it causes anomalies in glass viscosity as well as in the temperature of dilatometric softening [18]. This oxide improves the ability of glass formation and gives good optical properties [19]. The corrosion of glasses (expressed as weight loss) is increased by SrO content [20].

The objective of this work is to synthesis new silica glasses containing BaO, SrO and ZnO oxides and highlight the effects of these oxides on the structural and thermal properties of these materials. This work aims at completing previous study on this family of glasses [21].

2. Materials and experimental methods

Glass samples were prepared from chemically pure grade reagents. The chemicals included SrO, BaO, K_2O and Na_2O were introduced in the form of their respective anhydrous carbonates, while SiO_2 , Al_2O_3 , ZnO and As_2O_3 were introduced under oxide form. All raw materials were purchased from Aldrich and used without further purification.

Vitrifiables mixtures were melted in platinum crucibles at 1450°C for 4 hours, then resulting glasses are annealed at 580°C for 2 hours, after that the furnace was cooled down to room temperature. Two series of fusion A and B were realized. Five (05) compositions were retained for each fusion A (A_1 , A_2 , A_3 , A_4 and A_5), B (B_1 , B_2 , B_3 , B_4 and B_5) as shown in tables 1 and 2.

Table 1: Series A: Composition (Wt %)

Serie n°	SiO ₂	Al ₂ O ₃	Na ₂ O	K ₂ O	BaO	SrO	ZnO	As ₂ O ₃	Total (%)
A ₁	52,00	4,00	6,40	7,00	30,00	00,00	00,00	0,60	100
A ₂	57,00	4,00	6,40	7,00	25,00	00,00	00,00	0,60	100
A ₃	56,80	5,00	5,00	5,00	25,00	00,00	2,60	0,60	100
A ₄	50,80	3,00	10,00	8,00	00,00	25,00	2,60	0,60	100
A ₅	50,00	3,00	8,00	7,00	00,00	29,00	2,40	0,60	100

Table2: Series B:Composition(Wt %)

Verre n°	SiO ₂	Al ₂ O ₃	Na ₂ O	K ₂ O	BaO	SrO	ZnO	As ₂ O ₃	Total (%)
B ₁	51,40	5,00	5,00	8,00	6,00	00,00	24,00	0,60	100
B ₂	51,40	4,00	4,00	7,00	29,00	00,00	4,00	0,60	100
B ₃	55,40	5,00	5,00	8,00	0,00	8,00	18,00	0,60	100
B ₄	55,40	5,00	5,00	8,00	8,00	8,00	10,00	0,60	100
B ₅	55,40	5,00	5,00	8,00	11,00	11,00	4,00	0,60	100

3. Experimental methods

X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and Raman spectroscopy were used for the structural characterization. The differential scanning calorimetric (DSC) was applied for thermal characterization.

4. Results and discussions

4. 1 X-ray diffraction

The X-ray analyses of the samples after melting at 1450°C were realized on a Bruker type diffractometer ($\lambda_{Cu\ K\alpha}=1.5418\text{\AA}$, 40 KV, 30 mA, 2 θ from 10 to 70° with a rate of two (2°) degrees per minute).

The X-ray diffraction patterns are presented in Figures 1 and 2. None of those patterns show diffraction peaks that could be associated to any crystalline phase. The wide bumps centered at $2\theta\approx 27-29^\circ$ highlight the amorphous nature of all the samples.

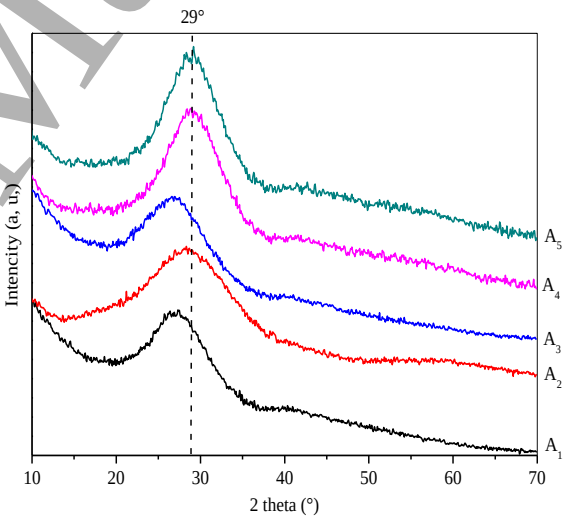


Figure 1. X-ray diffraction patterns of series A

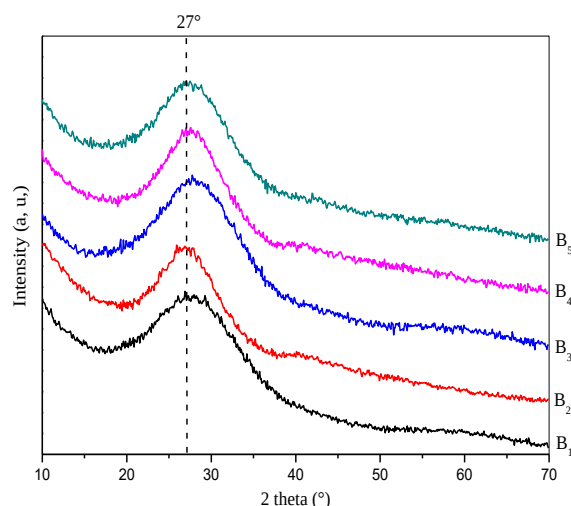


Figure 2. X-ray diffraction patterns of series B

4. 2. Infrared Spectroscopy

Fourier Transform Infrared Spectrometry (FTIR) was operated thanks to a SHIMADZU IR Affinity Spectrophotometer. Figures 3 and 4 show the IR spectra collected on series A and B respectively.

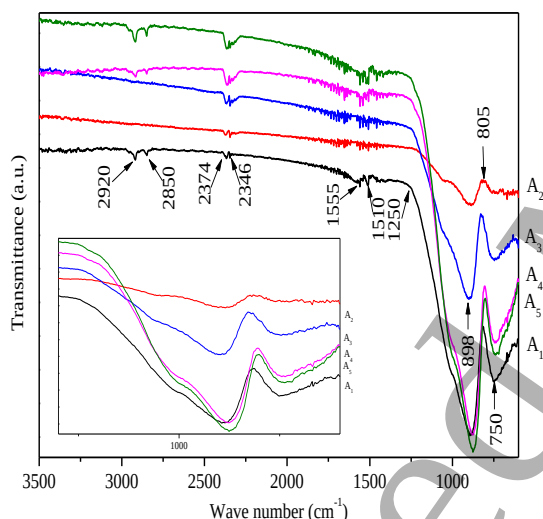


Figure 3. IR spectra (Transmittance) of series A.

The infrared spectra of synthesized glasses are mainly similar. The most important changes are in the 600-1300 cm⁻¹ frequency range (see the insets in figures 3 and 4).

Two absorption bands of low intensity situated at about 2850 and 2920 cm⁻¹ are attributed to the hydrogen bonds in the glass network; some authors think that these bands are characteristic of soda-lime glasses, although they do not exist in all of our samples [22].

The two doublets observed in the neighborhood of 2346-2374 cm⁻¹ and 1510-1555 cm⁻¹ are associated to the hydroxyl (OH) bonds formed on the non-bridging oxygen sites [23, 24]. Vibration frequencies in the 750-770 cm⁻¹ region may be due

to the presence of Si-O-Zn bonds [25]. The band between 1030-1050 cm⁻¹ is attributed to Si-O-Na⁺ (NBO) bond stretching vibrations [26]. The bands at about 600-850 cm⁻¹ and 950-1200 cm⁻¹ are attributed to the symmetric and asymmetric stretching vibrations of Si-O-(Si, Al) bonds respectively [27].

In barium strontium titanate borosilicate glasses doped with La₂O₃, the authors remark the effect of BaO/SrO ratio in bands position and intensity. The bands situated in 2853-2924 and 2340-2365 cm⁻¹ remain unaffected. Absorption band at around 983 cm⁻¹ is attributed to a stretching vibration of B-O-Si [28].

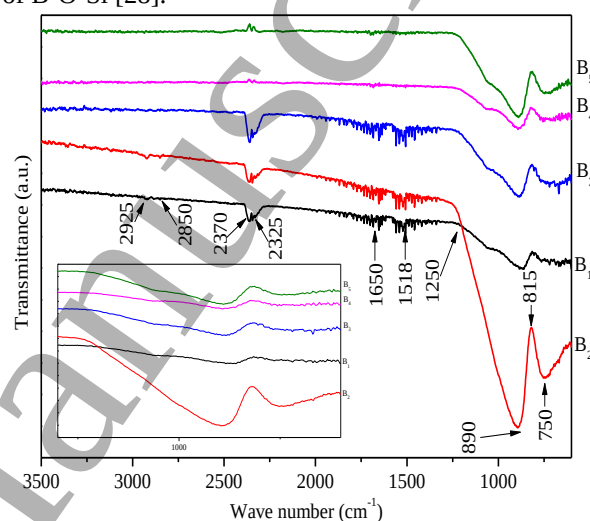


Figure 4. IR spectra (Transmittance) of series B.

4. 3. Raman Spectroscopy

The Raman spectra were obtained on a Jobin Yvon T64000 spectrophotometer coupled with an Olympus confocal microscope. The excitation source is a laser ionized by argon (principal ray equal 514.5 nm, power 400 mW), equipped by CCD detector and refrigerated with liquid nitrogen.

The spectra are shown in figures 5 and 6. The band at 470 cm⁻¹ is attributed to the symmetric stretching vibration of bridging oxygens in the glass network (Q⁴); this band corresponds to high SiO₂/(Na₂O+K₂O) molar ratio [29]. The bands at about 330 and 580 cm⁻¹ persist for a moderate SiO₂/(Na₂O+K₂O) molar ratio. The last band corresponds to Q³ and Q² structure of alkaline silicates in ordinary glass [30].

The peak at about 780 cm⁻¹ is due to the presence of BaO [31], it becomes less important with the decrease of this oxide (A₄, A₅).

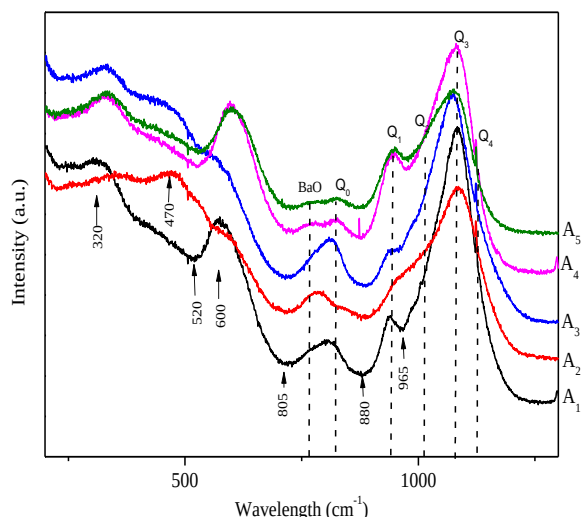


Figure 5. Raman spectra of series A

The band between 1150 and 1200 cm^{-1} is due to the Q^4 species of vitreous silica [32]. The peak at 1100 cm^{-1} is attributed to the stretching modes of Si-O bond in Q^3 species of silica glass [33]. The interval between 980-1000 cm^{-1} is attributed to the stretching vibrations of the Si-O bond in Q^2 species [34]. The band between 900-950 cm^{-1} is due to the symmetrical stretching vibrations of Q^1 species [35]. The band at 800-880 cm^{-1} is due to the symmetrical stretching vibrations of Q^0 species (monomers) [36].

In barium strontium titanate borosilicate glasses doped with ferric oxide, A. K. Yadava & C. R. Gautam find the symmetric stretching vibrations of Si-O in Q^2 in the range 988-998 cm^{-1} . The band between 1006 and 1037 cm^{-1} is attributed to Q^3 units, while the peak in range 1207-1212 cm^{-1} has been attributed to stretching vibrations of Q^4 group [37].

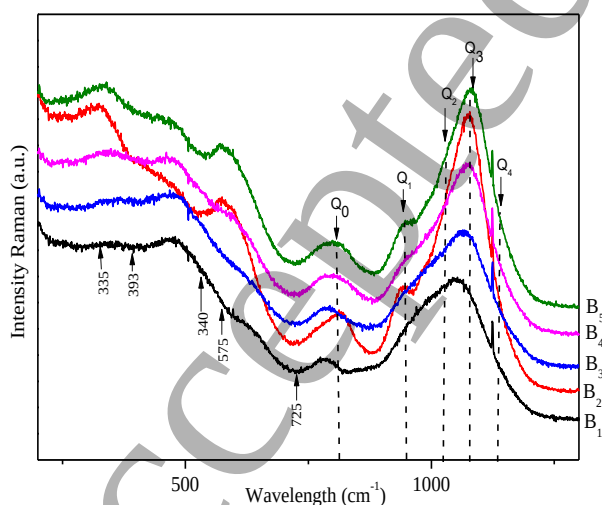


Figure 6. Raman spectra of series B

4. 4. Differential scanning calorimetry(D.S.C).

Glass transition temperature (T_g) was measured by differential scanning calorimetry (DSC) method combined with thermogravimetry (TG) at the heating rate 10°C/min. Figures 7 and 8 show the curves obtained by DSC type NETZSCH STA 449 F3 Jupiter. Glass powder samples weighing 240 mg. The results are presented in Tables 3 and 4 [38, 39].

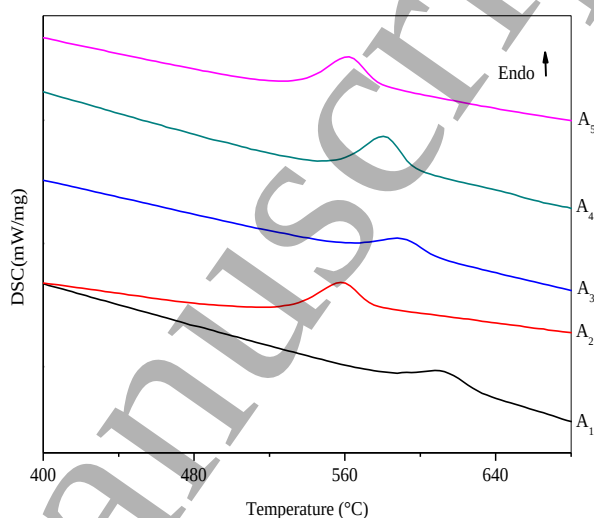


Figure 7. DSC curves of Series A

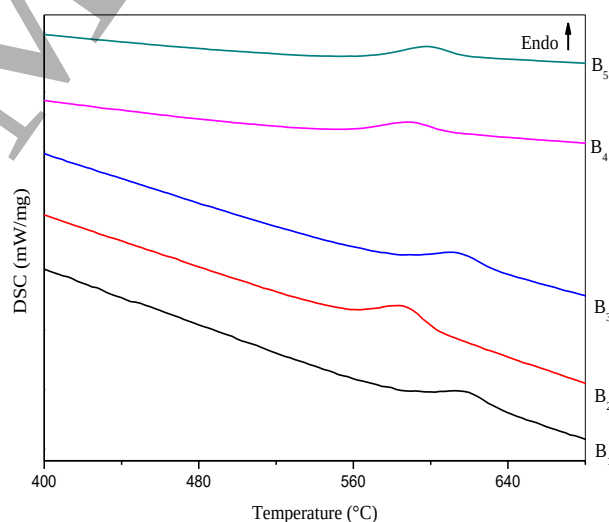


Figure 8. DSC curves of Series B

In general, the glass transition temperature (T_g) is variable for each series. It extends in temperature range named transition interval; it mainly depends on heating rate and chemical composition of glass. This parameter corresponds to viscosity value of approximately 10^{13} poise. In pure silica glasses, the glass transition temperature (T_g) is around 1100°C [40]. For the studied compositions, this parameter is

much smaller; because these materials contain significant quantities of melting oxides. The transition interval varies from 546.8 to 632.6°C like as shown in Tables 3 and 4. We will have two remarks to mention.

Remark 1:

The samples (B₃, A₄ and A₅) show a decrease in (T_g) temperature with increasing of SrO content. The evolution of glass transition temperature (T_g) is inversely proportional with fluxing oxides quantities (A₃, A₄, A₅). When the fluxing oxides content is practically stable (A₄ and A₅); the subtraction even a small amount of ZnO decreases rapidly (T_g). The insertion of a small quantity of ZnO into the vitrifiable mixtures (A₂, A₃ and A₄) increases rapidly (T_g).

Remark 2:

The molar ratio: C=ZnO/BaO is the mainly parameter that influences the transition temperatures of the elaborated glasses [41]; If C > 1, the evolution is proportional with T_g (B₁, B₄). However, when C < 1; the variation is inversely proportional to T_g (A₃, B₂ and B₅).

In small quantities in front of ZnO, barium oxide has the property to create non-bridging oxygens [42]. It can then play the role of a network modifier.

Table 3: Glass transition temperature (T_g) of series A.

Glass n°	T _g (°C)
A ₁	588.6
A ₂	546.8
A ₃	598.4
A ₄	590.6
A ₅	552.8

Table 4: The glass transition temperature (T_g) of series B.

Glass n°	T _g (°C)
B ₁	632.6
B ₂	595.5
B ₃	622.0
B ₄	606.1
B ₅	569.3

5. Conclusion

A dozen of lead free crystal glass compositions containing BaO, SrO and ZnO oxides were successfully synthesized by conventional melting

method in platinum crucibles at 1450°C, then annealed at 580°C for 2 hours in electric furnaces.

The influence of composition on structural and thermal properties of glasses was implemented by various characterization techniques.

Indeed, X-ray diffraction, infrared and Raman spectroscopies showed the amorphous nature of all glasses, thus the structural evolution as a function of the content of these oxides.

The glass transition temperatures were calculated from calorimetric thermal analysis curves (DSC) confirm the influence of composition on thermal properties of glasses ranging from 546.8 to 632.6°C.

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