

Article

Crystallization of Glasses Containing K_2O , PbO , BaO , Al_2O_3 , B_2O_3 , and TiO_2

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Abstract: The objective of this work was to obtain glass-ceramics from stable glasses, with a composition of barium, lead, and potassium titanate phases, for use as semiconductors. For this purpose, the glass-ceramic technique was used to control crystal growth and obtain a fine-grained microstructure. Various glasses containing K_2O , PbO , BaO , Al_2O_3 , B_2O_3 , and TiO_2 were prepared using a melt-quenching method. X-ray diffraction (XRD) and scanning electron microscopy (SEM) showed a single amorphous phase of all samples. Infrared spectra confirmed the presence of B-O bonds stretching vibrations of $(B_3O_6)^{3-}$ boroxol rings and BO_3 triangles, as well as Ti-O stretching vibrations of $(TiO_6)_2$ and $(AlO_6)_2$ octahedral units. Thermal analyses confirmed the presence of one or more crystallization peaks in the range of 700 to 744 °C. On this base, they were heat-treated to promote crystal growth. XRD and SEM detected $Ba_4Ti_{12}O_{27}$, Ti_7O_{13} , and $BaTiO_3$ phases, homogeneously distributed throughout the material with fine crystallite size. In addition, crystallized glasses' (glass-ceramics) properties were determined; the density values were 2.8–3.55 g/cm³; the chemical resistance to acidic and basic media was low; and the band-gap values were in the range of 2.88 to 3.05 eV. These results suggest that crystallized glasses may have application in photocatalysis.

Keywords: titanate glasses; glass-ceramics; band-gap; photocatalytic properties



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1. Introduction

The crystallization of glasses is a process by which polycrystalline solids (glass-ceramic, GC) can be obtained, and they have advantages on precursor glasses such as higher mechanical and chemical resistance. Moreover, during processing, it can control the growth of crystalline phases, resulting in fine-sized microstructure materials with specific properties for varied applications. In this sense, for many years, TiO_2 glasses and glass-ceramics have had a great interest in fundamental and technologic research due to their optical and chemical properties [1]. However, the main problem reported is obtaining stable glasses (without superficial or volume crystallization) since it is well-known that TiO_2 increases spontaneous crystallization tendency during cooling. Despite this, several researchers have obtained stable glasses in oxide systems such as BaO - TiO_2 - B_2O_3 , K_2O - Al_2O_3 - TiO_2 , BaO - PbO - B_2O_3 - Al_2O_3 - TiO_2 , K_2O - BaO - B_2O_3 - Al_2O_3 - TiO_2 , PbO - TiO_2 - Al_2O_3 - SiO_2 , BaO - PbO - TiO_2 - B_2O_3 - SiO_2 , $55[(Pb_xBi_{1-x})TiO_3]-44[2SiO_2 \cdot B_2O_3]-1CeO_2$, and others [2–9]. In these systems, the introduction of fluxes and modifier oxides was necessary to obtain a stable glassy structure. Furthermore, the controlled crystallization of glasses was reported to

obtain glass-ceramics with titanate phases, such as BaTiO_3 , PbTiO_3 ($\text{K}_{0.58}\text{Ba}_{0.36}$) $_2\text{Ti}_6\text{O}_{13}$, BaTi_2O_5 , and $\text{Bi}_2\text{Ti}_2\text{O}_7$, among others.

There is extensive research on titanate-type materials, with sufficient information concerning barium, bismuth, strontium, lead, copper, lanthanum, and lithium titanates, among others. For example, BaTiO_3 is the most widely investigated ferroelectric material, and it possesses very stable chemical and mechanical behavior. Additionally, it presents dielectric, ferroelectric, and piezoelectric properties [3,4,10]. It can also act as a semiconductor by adding specific doping [10] and together with PbTiO_3 are two of the most relevant ferroelectric ceramics useful in many technologic applications [11,12]. Another titanate reported in the literature is $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$, which exhibits the highest dielectric constant (>105) but a considerably high dielectric loss [13]. In addition, SrTiO_3 is used to fabricate capacitive sensors at cryogenic temperatures. On the other hand, $\text{Li}_2\text{O} \cdot \text{La}_2\text{O}_3 \cdot 4\text{TiO}_2$ is useful in sensors and solid-state batteries because of Li^+ 's high ionic conductivity [14–19]. Likewise, $\beta\text{-Al}_2\text{TiO}_5$ or tialite present high mechanical and thermal shock resistance, which allows its use in applications where these properties are required [20]. One more of the titanates is $\text{K}_2\text{Ti}_6\text{O}_{13}$, fibrous material, considered a lower bandgap semiconductor, photo-catalytic, and reinforcing agent used to produce hydrogen from water-splitting reaction [21–23].

In previous work, we reported several stable one-phase glasses in the K_2O - BaO - B_2O_3 - Al_2O_3 - TiO_2 system; however, a high quantity of K_2O (20–25 mol%) and a relatively low amount of BaO (3–12 mol%) were used [9]. On the other hand, Ruiz-Valdez et al. [3] reported stable titanate glasses with a composition containing BaO (18–22 mol%) and PbO (4–9 mol%), successfully crystallized. The results showed a mixture of barium and lead titanate polymorphs with crystal sizes between 90 and 200 nm. Considering the mentioned works, in this study, we proposed the following mixture (mol%): (9) K_2O , (23.5) BaO , (0.5) PbO , (13) B_2O_3 , (16) Al_2O_3 , and (38) TiO_2 as base composition, varying only in the BaO and PbO content. The objective was to obtain stable one-phase glasses and glass-ceramics, including crystalline phases such as barium, lead, and potassium titanates, with homogeneous fine grain structure, as promising materials for optical and electronic applications. In addition, taking into account that most of the research is focused on the study of ferroelectric properties (dielectric constant and losses) [2,3,24–28], another aim of this work was to obtain glass-ceramics materials with a mixture of crystalline titanate phases to understand their structural, chemical, and optical properties in detail. The above is to discover the great variety of technological applications, principally, semiconductors.

2. Materials and Methods

2.1. Glass Synthesis

The reagents ($>99\%$ purity) used for the synthesis of the glasses were: TiO_2 , K_2CO_3 , $\text{Ba}(\text{NO}_3)_2$, PbO , Al_2O_3 , and H_3BO_3 ; stoichiometric amounts of each reagent, according to Table 1, were weighed, homogenized in an agate mortar, and deposited in a platinum crucible and introduced in a furnace (Lindberg blue M, BF51433PC-1). The furnace program included heating up to 400°C and maintained for 1 h (to decompose boric acid and avoid losses due to volatilization [29]), followed by heating up to 1350°C and maintained for 1 h; the heating rate used in both stages was $10^\circ\text{C}/\text{min}$. The molten glass was poured onto a stainless-steel plate at room temperature.

Table 1. Samples identification, composition, T_g , and T_c .

Sample Code	Glass Composition (Mole %)						Glass-Ceramics Code	Glass Transition temperature T_g ($^\circ\text{C}$)	Crystallization Temperature T_c ($^\circ\text{C}$)
	TiO_2	K_2O	BaO	PbO	Al_2O_3	B_2O_3			
G1	38	9	23.5	0.5	16	13	GC1	715	723
G2	38	9	22.5	1.5	16	13	GC2	710	718
G3	38	9	21.5	2.5	16	13	GC3	708	716
G4	38	9	20.5	3.5	16	13	GC4	692	700
G5	38	9	19.5	4.5	16	13	GC5	690	700

2.2. Glass Characterization

A piece of each glass was ground in an agate mortar, so the powder was characterized by differential thermal analysis (DTA, Netzsch STA 449 F1 Jupiter). The studies were performed from room temperature up to 1000 °C in the N₂ atmosphere and using a heating rate of 10 °C/min. The glass transition temperature (T_g) was determined by the inflection point method, and the crystallization temperature (T_c) was taken as the higher point of each peak. In addition, the structure was studied by X-ray diffraction (XRD, Philips X'pert, Cu K α radiation) using pulverized samples with particle size less than 212 μ m (mesh 70). The infrared analyses (FTIR, ABB MB3000) were performed using a mixture of KBr and glass powder, pressed into a disk form, and carried out from 500 to 3500 cm⁻¹. The microstructure was investigated by scanning electron microscopy (SEM, Jeol microscope JSM-6610, equipped with an EDS detector), a piece of glass was mounted into quick-setting resin, then sanded with silicon carbide paper of different grain, subsequently were diamond-paste polished, and, finally, were carbon-coated to make them conductive.

2.3. Glass Crystallization

Based on the DTA results, the glasses were heat-treated to crystallize at the temperature of the first crystallization peak. The resulting materials were designated as GC1 to GC5, Table 1. The heat treatment was carried out in an electric furnace (Kodiak) from room temperature to the desired temperature using a heating rate of 10 °C/min for 2 h; a new piece of parent glass was used for each treatment.

2.4. Glass-Ceramic Characterization

The glass-ceramics obtained were characterized by XRD and SEM. The preparation of the samples was performed in the same way described for glasses characterization. The glassy and crystalline phases were calculated from the XRD patterns; first, a baseline was drawn where the diffractogram begin and end, then the area of each peak was delimited and calculated using the number of counts multiplied by the angle two theta (°). The % area gives us an estimated content of each phase. In addition, samples were analyzed using the Scherrer equation to estimate the average size of the crystals. For the calculation the first four peaks of each diffractogram, Equation (1) was used:

$$L = \frac{Kl}{B\theta} \quad (1)$$

where: L = Crystallite size (nm); K = Scherrer constant; l = wavelength; B = FWHM (full width at half maximum); and θ = diffraction angle.

The chemical resistance in acid and basic media was measured by the Russian standard GOST 10134-82, using HCl and NaOH 1N solutions, respectively [30]. For the analyses, powder samples were deposited in PE containers with the corresponding solution with a ratio of 1:10 (glass:water) and then introduced in a stove (Lab-Line, Imperial V) at 96 °C for 3 h. Then, the solutions were filtered and dried, and the losses (in weight %) were calculated using Equation (2):

$$\% \text{ of losses} = \frac{m_i - m_f}{m_i} \times 100 \quad (2)$$

where: m_i = initial mass, and m_f = final mass.

Density was measured by the pycnometer method using a calibrated 25 mL glass pycnometer, 5 g of sample powder, and toluene as the immersion liquid. Density was calculated using Equation (3) [31]:

$$d = \frac{(m_1 - m)(d_1)}{(m_3 + m_1 - m - m_2)} \quad (3)$$

where: d = density; d_1 = immersion liquid density (toluene = 0.8623 g/cm³ at 25 °C); m = pycnometer mass; m_1 = pycnometer mass plus sample mass; m_2 = pycnometer plus sample plus liquid mass; and m_3 = pycnometer plus liquid mass.

For both chemical resistance and density, each sample was measured in triplicate, and the values obtained were averaged.

On the other hand, band-gap energy was measured using a UV-Vis spectrophotometer (Perkin Elmer LAMBDA-10) equipped with an integration sphere for diffuse reflectance studies. The results were converted to Kubelka–Munk units [22] through Equation (4):

$$F(R) = (1 - R)^2 / 2R \quad (4)$$

where: R is the diffuse reflectance, and $F(R)$ is the Kubelka–Munk function.

To determine the direct bandgap energy of the samples, it was extrapolated the linear region from the inflection point of the diffuse reflectance spectrum to the intersection of the photon energy axis (X -axis). This point gives the value of the material bandgap.

3. Results and Discussion

3.1. Glass Characterization

All selected compositions fused and formed yellowish stable glass. Figure 1 presents XRD patterns and can be appreciated the absence of diffraction peaks which indicated that materials were fully amorphous. The microstructure of glasses showed unique homogeneous phase free pores and cracks, Figure 2. These glasses had similar microstructure to those reported in previous work [9], but different from the microstructure reported by Ruiz-Valdes et al. [5]. Although the EDS results are semi-quantitative, since no boron can be detected, the increase in PbO in the compositions can be seen.

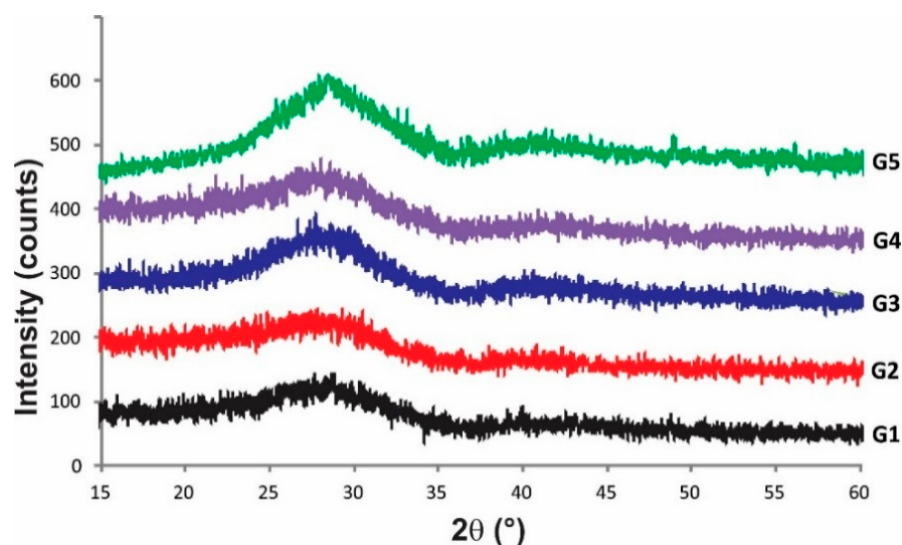


Figure 1. The XRD patterns of synthesized glasses G1–G5 show their amorphous nature.

Glass characterization by FTIR, Figure 3, showed the presence of two absorption bands: the first at wave number range 1100–1500 cm^{−1}, which is associated with the B–O bond stretching vibrations and B–O bridging between (B₃O₆)^{3−} boroxol rings and BO₃ triangles [32,33]. The second band appeared at wave number range 500–900 cm^{−1}, attributed to the Ti–O stretching vibrations of the octahedral [TiO_{6/2}] and [AlO_{6/2}] units [4,20,29,34].

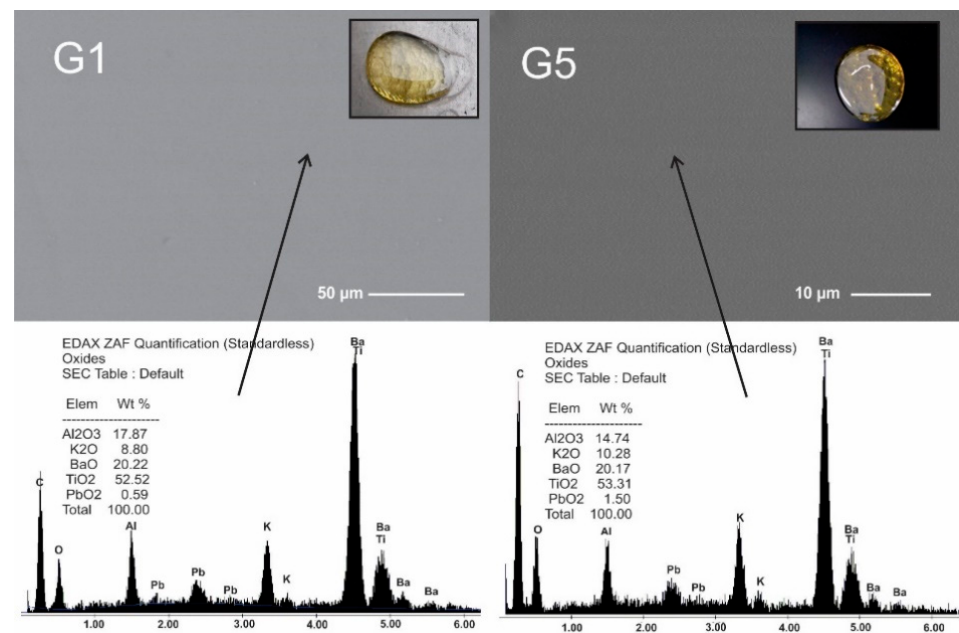


Figure 2. SEM Micrographs and EDS quantification of G1 and G5 glasses. The arrows indicate the point where EDS was performed. The image of each micrograph shows the glass obtained.

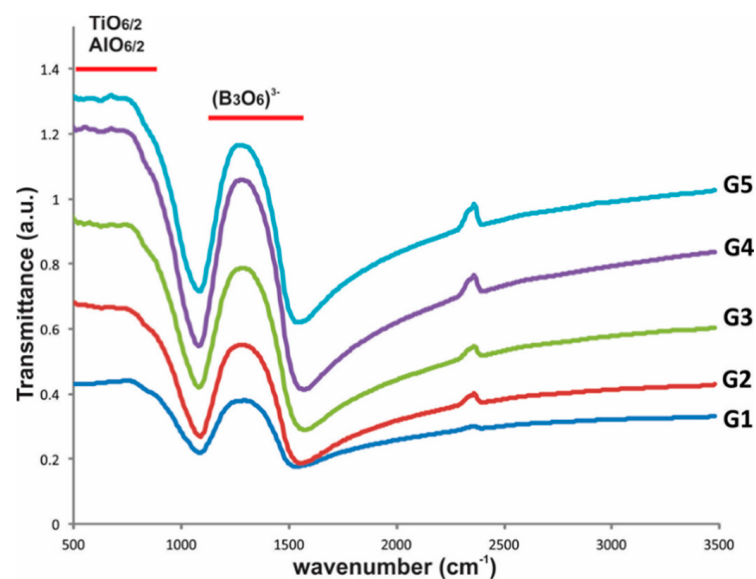


Figure 3. FTIR results of the glasses.

On the other hand, Figure 4 shows the DTA curves of glass samples. The curves observed one or two exothermic peaks at temperatures between 700 and 744 °C, attributed to crystallization events, indicating that all samples can crystallize to obtain glass-ceramics materials with at least one crystalline phase. Likewise, it can be appreciated that an increasing PbO content in starting compositions from 0.5% (G1) to 4.5% (G5) diminished T_g and T_c temperatures, which is essential for economic reasons related to energetic costs.

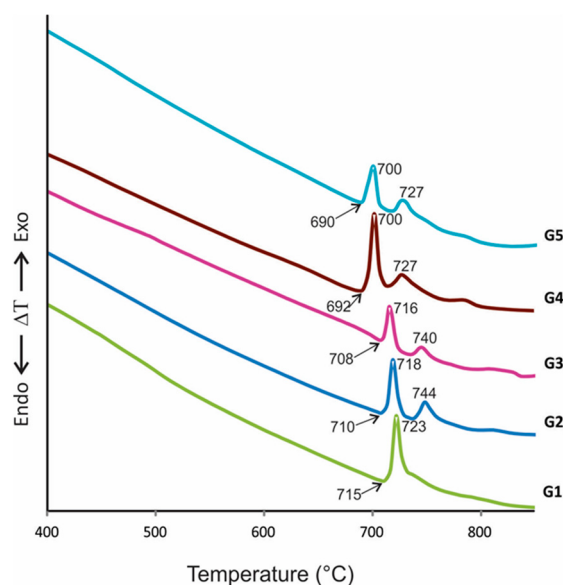


Figure 4. DTA curves of the glasses show T_g (value marked whit arrow) and T_c temperatures.

3.2. Glass-Ceramic Characterization

According to the DTA results, the glassy samples that were heat-treated at the first exothermic peak temperature were crystallized. Figure 5 and Table 2 show the XRD results and crystallite size of the obtained glass-ceramics, which are partially crystallized; the XRD patterns are also strongly distorted due to the materials' poor crystallinity, which means they have disordered atoms in crystalline phases and there is a significant quantity of amorphous phase. The samples presented $\text{Ba}_4\text{Ti}_{12}\text{O}_{27}$ (ICDD 00-044-0013) and Ti_7O_{13} (ICDD 00-050-0789) as principal phases. In addition, BaTiO_3 (ICDD 96-210-0859) was a minor phase, considering the intensities of diffraction peaks. Likewise, the increasing PbO concentration and decrease in BaO did not make a difference in the obtained crystalline phases since no phases of lead or potassium titanates were detected. The above suggests that these elements could join the residual vitreous matrix or substitute barium atoms in the crystalline phases to form solid solutions. In Figure 6a, the idealized structure of the glasses, formed by boroxol rings and octahedral Ti groups, can be principally appreciated; however, there is the possibility that the glassy network contains other minor functional groups such as the tetrahedral species ^4Ti and ^4Al , reported for similar glasses but with higher B_2O_3 content [4]. Figure 6b presents the glass with a small area with ordered atoms, which can act as a nucleus for the crystalline growth of BaTiO_3 with perovskite structure, which is the simplest phase in the obtain glass-ceramics. In the same way, the octahedral units of $[\text{TiO}_{6/2}]$ become bonded by Ba ions to form more complex structures such as $\text{Ba}_4\text{Ti}_{12}\text{O}_{27}$, as described by others researchers [35,36]. Additionally, according to the XRD patterns, there is a considerable quantity of remaining vitreous phase, which was calculated taking into consideration the areas under the curve of the diffraction peaks. The amount (Area %) of each sample's crystalline and vitreous phase is shown in Table 2, and these results suggested that heat treatment time can be increased to obtain a significant amount of crystalline phase.

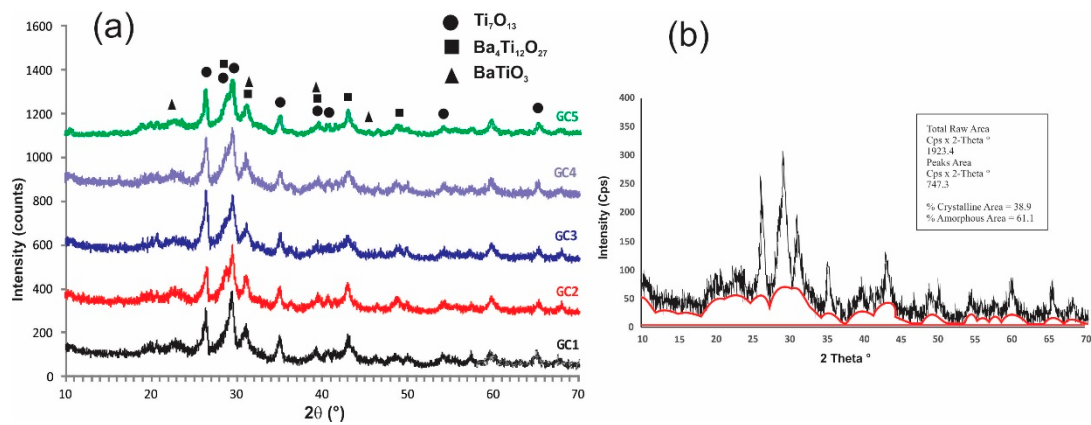


Figure 5. XRD results: (a) X-ray patterns showing crystalline phases present in the glass-ceramics, (b) Glassy and crystalline phases calculated from XRD pattern of the GC5.

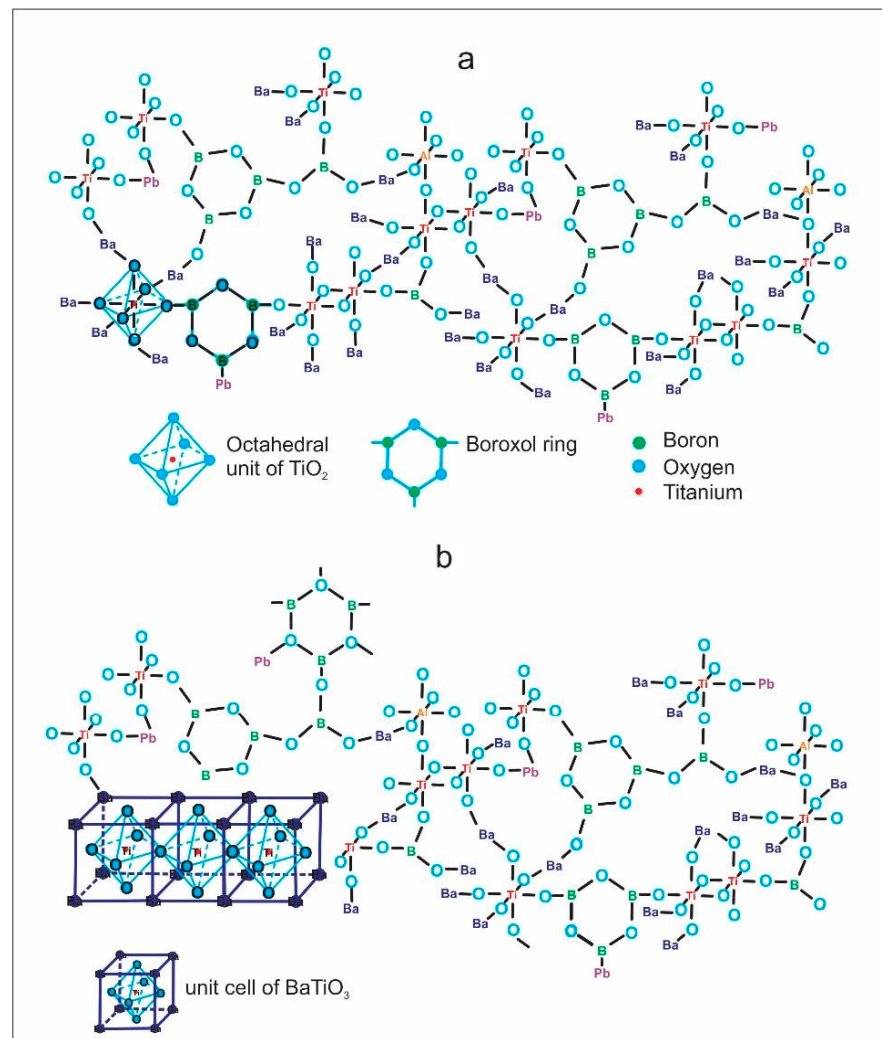


Figure 6. (a) Idealized structure of the obtained glasses and (b) glass with a small area with ordered atoms forming BaTiO₃ phase.

Table 2. Results: % of glassy and crystalline phases, crystallite size, density, chemical resistance, and band-gap of glass-ceramics materials.

Sample	Glassy Phase (Area %)	Crystalline Phase (Area %)	Crystallite Size (nm)	Density (g/cm ³)	Chemical Resistance (Losses, wt.%)		Band-Gap (eV)
					Acid	Basic	
GC1	60.9	39.1	22.35	2.80	29.99	12.95	3.01
GC2	60.0	40.0	10.14	3.08	30.48	16.30	3.02
GC3	64.4	35.6	14.03	3.28	25.80	10.70	3.05
GC4	65.5	35.5	13.24	3.53	22.83	12.45	2.90
GC5	61.1	38.9	15.74	3.55	26.52	15.94	2.88

Figure 7 shows the micrographs of samples GC1 and GC5. All glass-ceramics presented a uniform microstructure without pores and cracks. The microstructure is proposed to be formed by crystals with a fine grain size embedded in the abundant residual vitreous phase and homogeneously distributed throughout the material. The above is confirmed by the XRD results showing the presence of crystalline phases with nanometric size in the range of 10.14 to 22.35 nm, as well as a uniform elemental distribution according to the EDS mapping, as seen in Figure 8.

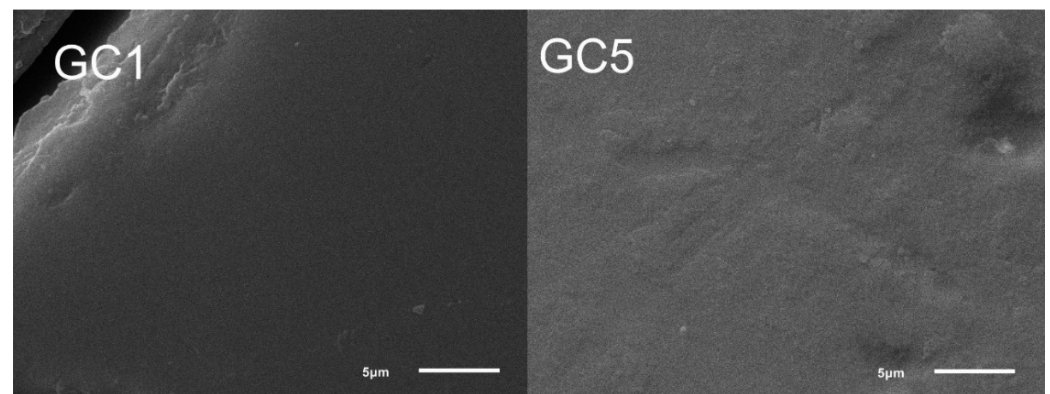


Figure 7. SEM micrographs of the samples GC1 and GC5.

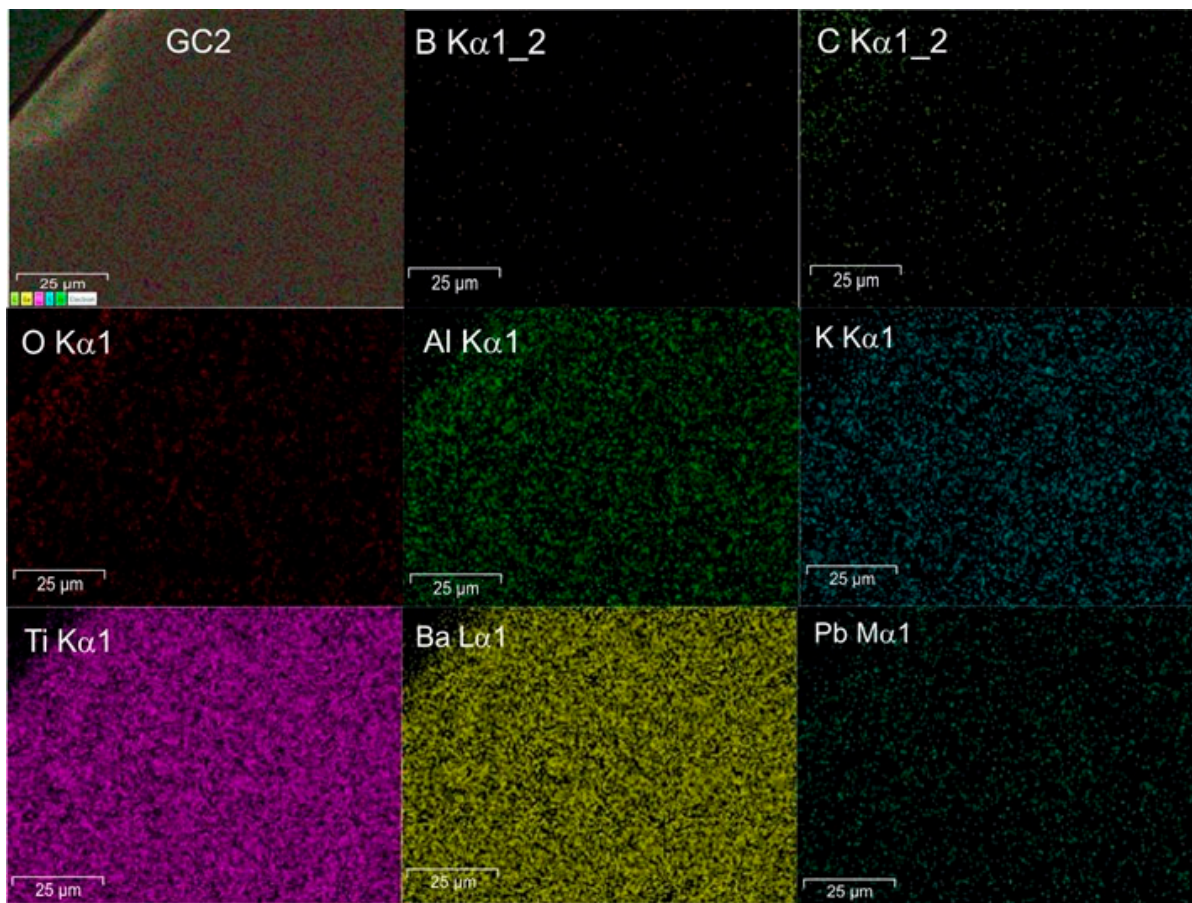


Figure 8. EDS mapping of the sample GC2.

3.3. Evaluation of Properties

Table 2 presents the results of properties evaluated for the glass-ceramics composites. The density values were between 2.80 and 3.55 g/cm³, which increased with the PbO content in the initial batch; this agrees with Fernandez Navarro's statement that this oxide increases glass density [37].

In addition, the chemical durability of glass-ceramics was determined to estimate the chemical resistance in acid and alkaline environments, respectively. The chemical resistance (% weight losses) was 22.83 to 30.48 in the acid medium and 10.7 to 16.3 in the basic medium, Table 2. In this context, the chemical attack can be attributed mainly to the composition stability of crystalline and vitreous phases, each phase's amount in the material, and the attack media. According to the standard, samples with values higher than 5% should not be used in humid atmospheres.

The DRUV-Vis results of samples GC1–GC5 are shown in Figure 9 and listed in Table 2. The values were in the range of 2.88 to 3.05 eV, and it can be seen that lower values correspond to the compositions GC4 and GC5, which have the higher contents of PbO (3.5 and 4.5%, respectively).

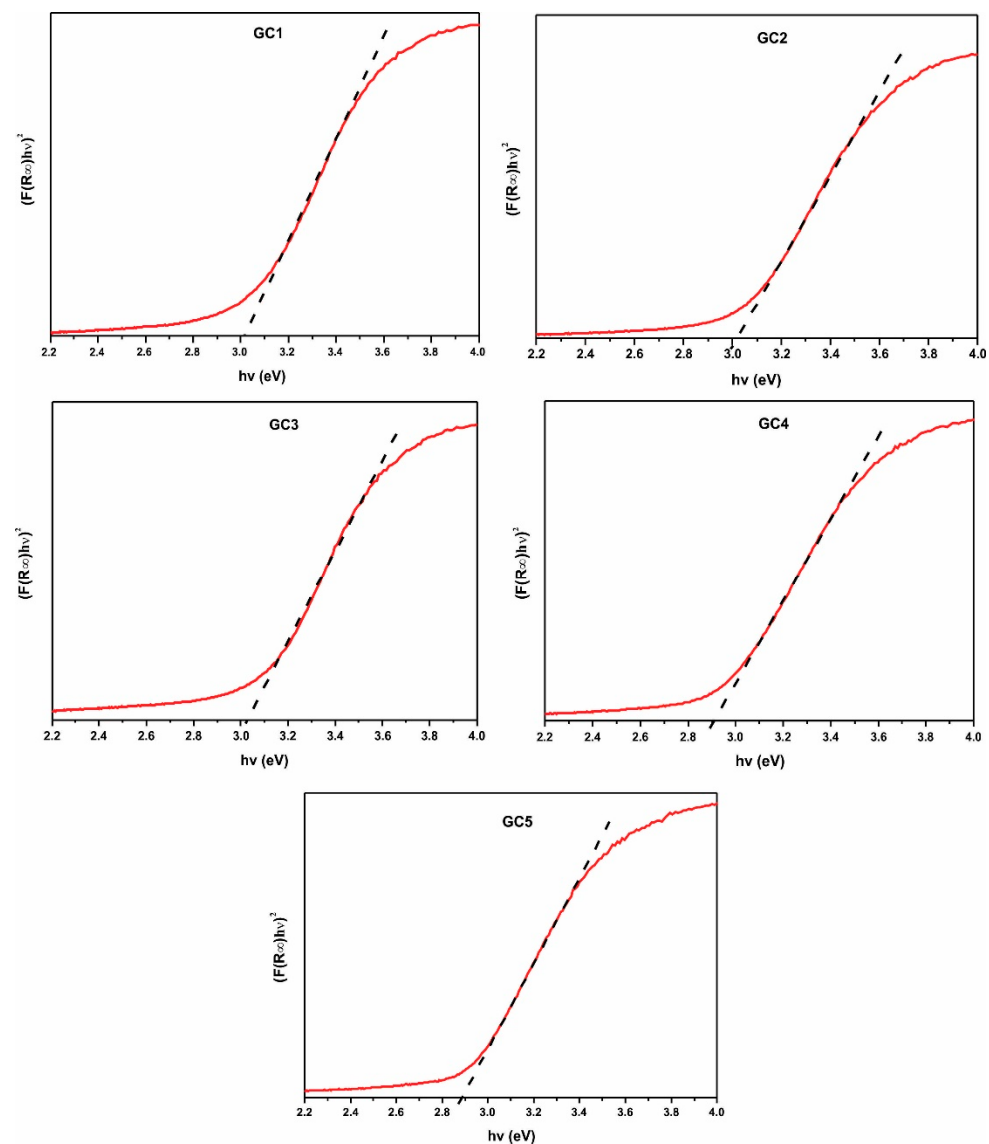


Figure 9. UV-Vis spectra of the synthesized glass-ceramics.

4. Discussion

The melting technique obtained the free pore or cracked stable glasses. From DTA curves, it is observed that the glass transition (T_g) and the crystallization peak onset temperature (T_x) are very close, which means that the glasses contain structural units with high crystallization tendency [38,39], which is necessary for glass-ceramics obtaining. It is clear that both T_c and T_g decreased with increasing PbO content (comparing G1 and G5, T_c diminished 23 °C, approximately); this can be attributed to the flux effect of PbO and is related to the decrease in glass viscosity, which facilitated the pouring of glasses [37] and implies the reduction in the manufacturing cost of glass-ceramics.

On the other hand, the FTIR gives us information about the short-range ordering of the glasses. In this case, it can be deduced that boroxol rings (B_3O_6)^{3−} were incorporated into the titanate glassy phase by Ba^{2+} and Pb^{2+} ions, giving rise to a single glassy phase (Figure 2), and EDS did not detect the presence of B_2O_3 , but FTIR did. In addition, the principal identified Ba ions could link units $[TiO_6/2]$ to form crystalline structures such as $Ba_4Ti_{12}O_{27}$ and $BaTiO_3$, present in glass-ceramics after heat treatment, as a consequence of the rearrangement of these octahedral groups, which are essential in both structures [25,40,41].

Concerning the low chemical resistance in glass-ceramics (high weight losses), according to Barbieri et al., acid attack occurs by ionic diffusion due to proton domain H^+ and is closely related to the ionic exchange with alkaline ions [40]. This medium is attributed principally to the dissolution of the glassy matrix, composed of boron, aluminum, and potassium oxides; therefore, ions are easily interchangeable as K^+ can be responsible for the low resistance in acid solutions. It is reported in the literature that the incorporation of heavy metals can improve the chemical stability of borate glasses. This work observed no effect on the glass-ceramic behavior for the five compositions investigated [41,42].

On the other hand, the band-gap results of obtaining glass-ceramics are directly related to crystalline phases. Still, principally with $Ba_4Ti_{12}O_{27}$ (the main phase detected), these results are in accordance with Kataoka K. et al., who established that this compound presents a conductivity at 300 K and behavior as a type-n semiconductor [36]. Glass-ceramics band-gaps are similar to those reported by Madheshiya et al. for glass-ceramics containing $Bi_2Ti_2O_7$ as the principal crystalline phase [32]. Moreover, it can also appreciate that all samples presented values lower than TiO_2 anatase (3–3.38 eV), the $BaTiO_3$ (3.2 eV), and the Bismuth Barium titanates (2.94–2.99), which have been reported as photocatalyst [43–47]. The results show that glass-ceramics produced could be promissory as photocatalytic materials. Several applications such as hydrogen production or organic compounds degradation by heterogeneous photocatalysts using UV-Vis irradiation, especially GC4 and GC5 (with 3.5 and 4.5 PbO percent, respectively). The glass-ceramics mentioned above presented lower band-gap values than other similar materials and crystallite sizes of nanometers.

Finally, it can conclude that the introduction of (9) K_2O and (0.5–4.5) PbO in glasses does not affect the composition of crystalline phases in glass-ceramics since potassium or lead titanates were obtained. However, glass-ceramics with higher content of PbO (GC4 and GC5) showed the lowest values of band-gap and T_c , making them more attractive for production.

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