Structural, Thermal and Physical Properties of the Calcium Borovanadate Glasses Belonging to the 40CaO-(60-x)B_2O_3-xV_2O_5 System

Ayoub Kaouass 1, Abdelkader Ben Ali 1, Fouad Alloun 1, Abdelkader Zarrouk 2,*, Mohamed Saadi 1

1 Laboratoire de Chimie Appliquée Des Matériaux (LCAM), Faculty of Science, Mohammed V University in Rabat, P.O. Box. 1014 Agdal-Rabat, Morocco;
2 Laboratory of Materials, Nanotechnology and Environment, Faculty of Sciences, Mohammed V University in Rabat, P.O. Box. 1014 Agdal-Rabat, Morocco;
* Correspondence: azarrouk@gmail.com (A.Z.);

Abstract: The calcium borovanadate glasses within the system 40CaO-(60-x)B_2O_3-xV_2O_5 with x= 0, 5, 10, 15, 20, 30, 40 mol% was studied. The glass samples were elaborated via melting, followed by quenching. Its structural, thermal, and physical properties were explored. Powder X-ray diffraction was used to demonstrate that the developed glasses were amorphous. The influence of vanadium, a 3d transition element, on physical characteristics such as density and molar volume was investigated. The variation of density and molar volume has been discussed in terms of the structural changes in the vitreous matrix with adding the V_2O_5. Infrared (FTIR) and Raman spectroscopies were done to check the group constitution of the glass. This analysis shows that the vitreous materials are mainly established from BO_4 and BO_3 units with four and five coordinated vanadium in all glasses containing V_2O_5, confirmed with the density results. Moreover, it is found from the infrared spectra the existence of diborovanadate [B_2V_2O_9]^2- in glass samples with composition x =15, 20, 30, 40.

Keywords: borovanadate; glass; vanadium oxide; transition temperature; spectroscopic studies.

1. Introduction

Borates are well-known as one of the greatest materials for creating glass. Furthermore, because boron atoms may be accommodated in both trigonal and tetrahedral settings, anionic sites can be created to accommodate various modified metal cations [1,2].

XRD, FTIR, Raman, and UV-visible spectroscopies have all been used to investigate the structural, optical, and physical properties of borovanadate glasses [1,3–6].

Furthermore, the addition of oxide-based transition elements such as V_2O_5, MoO_3, TiO_2, Fe_2O_3, WO_3, ZnO, etc., to oxide glasses are known to exhibit semiconducting behavior. Transition-element glasses have been extensively studied due to their numerous applications, including optical and electrical memory switching, active cathode material for solid-state device construction, and optical fiber assembly [4,7–10].

Vanadium is a significant semiconductor among transition metals because of the electron hopping between V^{5+} and V^{4+} ions [7]. Vanadium ions are suggested to exist in the glass materials in three possible oxidation states: tri-, tetra-, and pentavalent states [7,9,11,12].
Glass is not formed by transition metal oxides (Bi$_2$O$_3$, TeO$_2$, MoO$_3$, V$_2$O$_5$, WO$_3$, etc.). They can easily create a glass when combined with a second glass-forming oxide. A stronger glass network could be achieved by combining different glass-forming techniques. When a modifier oxide like B$_2$O$_3$ or V$_2$O$_5$ is added to glasses with two formers, the environment and connection of the borate and vanadate species might vary dramatically [5,13].

Considerable work has been done on the borate glasses holding V$_2$O$_5$ [1,3–7,11]; nonetheless, the glasses containing CaO, B$_2$O$_3$, and V$_2$O$_5$ together are found very few. Divalent cations like Ca$^{2+}$, Zn$^{2+}$, Pb$^{2+}$, Ba$^{2+}$, etc., play a significant key in both formation and modification of local structure [5]. CaO was chosen to be used in glass materials in some previous studies for their bioglass properties. Bioactive glass is composed of many elements of the human body, which Ca is one of them; for that reason, it has an interesting role in bioglasses [14–16].

Recent studies on borovanadate glasses show that in binary vanadium borate glasses [11], the vanadium adopts tetrahedral or penta-hededral environments while boron is mainly in diborate pyroborate groups using spectroscopy technics. In their unique vibrational modes, the bands of all generated glasses exhibit both triangular BO$_3$ groups and tetrahedral BO$_4$ groups; however, transition metal ions have a limited impact due to the low doping concentration (0, 2 percent). In the infrared spectra of lead borovanadate glass [5], the characteristic band corresponding to B–O–B, V–O–V, B–O–V, and B–O–V vibrations can be seen, indicating the creation of advanced structural groups such as diborovanadate [B$_2$V$_2$O$_9$]$^{2-}$ and four coordinated boron atoms.

X-Ray Diffraction (XRD), Density Measurement, Differential Scanning Calorimetry (DSC), Scanning Electron Microscopy (SEM), Fourier Transform Infrared (FT-IR), and Raman Spectroscopy have been used in this work to study the structural, thermal, and physical properties as a function of V$_2$O$_5$ concentration 40CaO–(60-x)B$_2$O$_3$ -xV$_2$O$_5$ (0 ≤ x ≤ 40) glasses.

2. Materials and Methods

2.1. Sample preparation.

40CaO–(60-x)B$_2$O$_3$ -xV$_2$O$_5$ (with x = 0, 5, 10, 15, 20, 30, 40 mol %) are prepared by melt quench method. Vanadium oxide (V$_2$O$_5$), boric acid (H$_3$BO$_3$), and calcium carbonate (CaCO$_3$) were used as raw materials. These reagent masses are accurately weighed, then mixed, and thoroughly ground to homogenize the mixture before being gradually heated in a crucible at 400 °C. Depending on the composition, the mixtures were melted at 900–950 °C for about 60 min before being quenched into a preheated steel mold. The composition of the seven elaborated glasses in this study is summarized in Table 1.

<table>
<thead>
<tr>
<th>Glass</th>
<th>CaO</th>
<th>B$_2$O$_3$</th>
<th>V$_2$O$_5$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CBV0</td>
<td>40</td>
<td>60</td>
<td>0</td>
</tr>
<tr>
<td>CBV1</td>
<td>40</td>
<td>55</td>
<td>5</td>
</tr>
<tr>
<td>CBV2</td>
<td>40</td>
<td>50</td>
<td>10</td>
</tr>
<tr>
<td>CBV3</td>
<td>40</td>
<td>45</td>
<td>15</td>
</tr>
<tr>
<td>CBV4</td>
<td>40</td>
<td>40</td>
<td>20</td>
</tr>
<tr>
<td>CBV5</td>
<td>40</td>
<td>30</td>
<td>30</td>
</tr>
<tr>
<td>CBV6</td>
<td>40</td>
<td>20</td>
<td>40</td>
</tr>
</tbody>
</table>

Table 1. Glass composition (molar %) with sample labels.
2.2. X-ray diffraction analysis.

The amorphous/crystalline condition of the produced samples was determined by powder X-ray diffraction (XRD) using a LabXRD-6100 Shimadzu diffractometer at a scanning rate of 2 degrees/min and 2 varied between 10–70° with a CuKα radiation source.

2.3. Physical parameters measurement.

The Archimedes principle was used to compute the density of glasses using Diethyl phthalate (C_{12}H_{14}O_4) as an immersion liquid, in which sample weights are assessed in both air and Diethyl phthalate. The density of the glass (ρ) is determined by using the following formula:

$$\rho = \frac{W_A}{W_A-W_B} \times \rho_{\text{liquid}} \quad \text{Eq (1)}$$

$W_A$ is the weight of the sample in air, $W_B$ is the immersed weight of the sample in Diethyl phthalate, and $\rho_{\text{liquid}}$ is the density of the Diethyl phthalate (1.120 g/cm$^3$).

The molar volume ($V_M$) of each glass was then calculated using the equation and the density of the glass.

$$V_M = \frac{M}{\rho_{\text{glass}}} \quad \text{Eq (2)}$$

where $M$ denotes the molecular weight of glass and $\rho_{\text{glass}}$ glass denotes its density.

2.4. Thermal behavior of prepared glasses.

The glass transition temperature (T$_g$) was determined in an argon environment using a Setaram121 equipment and differential scanning calorimetry at a heating rate of 10 °C/min (DSC).

2.5. Structural investigation.

The local environment of the boron and vanadium atoms in elaborated glasses has been studied using infrared and Raman spectroscopies. The infrared transmission spectra of the glasses were measured at room temperature in the wavenumber range 4000–400 cm$^{-1}$ with a Bruker Platinium-ATR apparatus.

The samples Raman spectra were obtained at room temperature using a DXR2 Smart Raman Spectrometer and a laser source (633nm) as the excitation light; the laser power at the sample surface was 6.1 mW. The spectra were recorded between 100 and 3500 cm$^{-1}$.

2.6. Microstructural characterization.

The microstructure of glasses has been explored via A QUANTA scanning electron microscope (SEM). The solid pieces were studied on carbon substrates.

3. Results and Discussion

3.1. X-ray diffraction.

The X-ray diffraction pattern of the studied glasses inside the 40CaO–(60-x)B$_2$O$_3$ - xV$_2$O$_5$ (0 ≤ x ≤ 40) system is given in Figure 1. This analysis reveals that all the prepared samples are completely amorphous due to the absence of peaks where the spectra reveal the
only hump around 2θ ~ 28–29. The absence of sharp and strongly diffracted beams in the X-ray diffraction diagrams clearly indicates the amorphous nature [7,17].

![Figure 1. XRD of the obtained glasses in the 40CaO-(60-x)B₂O₃-xV₂O₅ (0 ≤ x ≤ 40) system.](https://doi.org/10.33263/BRIAC131.048)

3.2. Glass transition temperature, density, & molar volume.

Density of the 40CaO-xV₂O₅-(60-x)B₂O₃ (0 ≤ x ≤ 40) glasses (Table 2 and Figure 2), depends strongly on the content of highest mass substance. The molecular weight of V₂O₅ (181.88 g/mol) is higher than that of B₂O₃ (69.62 g/mol); thus, the density of V₂O₅ (3.36 g/cm³) is also higher than that of B₂O₃ (1.82 g/cm³) [11]. Therefore, the density of the prepared glasses increases from 2.60 to 2.91 g/cm³ with increasing of the V₂O₅ content from 0 to 40 mol%, which are in good agreement with the previously reported results [11,18].

Additional oxygen is available from V₂O₅, which causes the coordination of BO₃ to BO₄ to shift [19]. Can explain why the presence of V₂O₅ increases the density of glass. Because the tetrahedral BO₄ units are more tightly coupled than the triangular BO₃ units, a compact structure with a higher density is expected [7,20,21]. Furthermore, increasing density with the addition of V₂O₅ could be attributed to the formation of VO₄ and VO₅ groups. Thus, the incorporation of V₂O₅ has adjusted the borate glass structure by creating more BO₄, VO₄, and VO₅ groups.

However, as the V₂O₅ content climbed from 0 to 40 mol percent, the developed glasses’ molar volume increased from 24.66 to 37.44 cm³/mol (Table 2 and Figure 2). Generally, density and molar volume are usually expected to present opposite behavior, but this is not the case in these investigated glasses. Nonetheless, several other investigations [11,22–26] have demonstrated this strange relationship between density and molar volume.

The variation of density and molar volume with V₂O₅ mol% was presented in Figure 2.

<table>
<thead>
<tr>
<th>Glass</th>
<th>ρ (gm/cm³)</th>
<th>Vₘ (cm³/mol)</th>
<th>Tg (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CBV0</td>
<td>2.603</td>
<td>24.664</td>
<td>650.95</td>
</tr>
<tr>
<td>CBV1</td>
<td>2.637</td>
<td>26.481</td>
<td>610.28</td>
</tr>
<tr>
<td>CBV2</td>
<td>2.669</td>
<td>28.264</td>
<td>570.31</td>
</tr>
<tr>
<td>CBV3</td>
<td>2.716</td>
<td>29.841</td>
<td>530.20</td>
</tr>
<tr>
<td>CBV4</td>
<td>2.749</td>
<td>31.524</td>
<td>480.81</td>
</tr>
<tr>
<td>CBV5</td>
<td>2.853</td>
<td>34.313</td>
<td>430.95</td>
</tr>
<tr>
<td>CBV6</td>
<td>2.914</td>
<td>37.438</td>
<td>381.12</td>
</tr>
</tbody>
</table>

Table 2. Density (ρ), molar volume (Vₘ), and glass transition temperature (Tg) for all elaborated glasses.
The glass structural adjustment (Tg) affects the glass transition temperature, and the construction of thermally stable glasses is dense [22]. Figure 3 shows the DSC curves of several glass samples 40CaO–(60-x)B2O3 xV2O5 with x=5, 10, 15, 30.

![Figure 2](https://doi.org/10.33263/BRIAC131.048)

**Figure 2.** Variation of density and molar volume with V2O5 mol%.

![Figure 3](https://biointerfaceresearch.com/)

**Figure 3.** Differential scanning calorimetric curves of the glass samples.

![Figure 4](https://biointerfaceresearch.com/)

**Figure 4.** Variation of glass transition temperature with V2O5 content.
The evolution of Tg in the function of V_2O_5 concentration is illustrated in Figure 4; the values of the glass transition temperatures are listed in Table 2. As can be depicted from this variation, the Tg temperature decreases from 650.95 to 381.12 °C with increase in the concentration of vanadium oxide V_2O_5. The increase in V_2O_5 content causes a decrease in Tg and an increase in molar volume. As a result, the Tg values vary, indicating that an increase in V_2O_5 content weakens the network structure by causing more voids in the glass matrix [22]. According to Roy, the molar volume impacts Tg more than the binding strength [22]. Reddy _et al._ [5] observed the same behavior when they added PbO to borovanadate glasses. The Tg increases straightly with the percentage of PbO and decreases with increasing V_2O_5 demonstrating that the conversion of three coordinated boron atoms into four coordinated boron atoms affects the Tg [5].

### 3.3. FTIR spectra analysis.

Figure 5 shows the infrared transmittance spectra for different compositions of calcium borovanadate glasses recorded in the 4000-400 cm\(^{-1}\) region.

According to the literature, the vibrational modes of the borate network are located in three regions of the infrared spectrum [6,7,27–29]. Due to the bending of B-O-B links in borate networks, the first is positioned at approximately 700 cm\(^{-1}\) [5,28,29]. The second area, roughly 800-1200 cm\(^{-1}\), corresponds to the tetrahedral BO4 units B-O bond stretching [1,4,11,30,31]. The stretching relaxation of the trigonal BO\(_3\) units B-O band [27,28,32] and stretching of trigonal boron found in [B\(_2\)V\(_2\)O\(_9\)]\(^2-\) [5,12,13,33] is responsible for the third area, which lies between 1200 and 1600 cm\(^{-1}\).

![Figure 5. Infrared spectrum for all the prepared glasses.](image-url)

The observed IR bands for the 40CaO–(60-x)B\(_2\)O\(_3\) -xV\(_2\)O\(_5\) (0 ≤ x ≤ 40) glass are presented in Table 3.

No peak has been observed in the 4000–1500cm\(^{-1}\) region. All elaborated glasses exhibit bands in the 1200-1600 region, the peak with maxima situated at 1350 cm\(^{-1}\) is assigned to the
B–O vibration in [BO$_3$] [32,34–38], the second band in the 1200-1600 region with the maxima at 1230 cm$^{-1}$ begins to appear when the molar content of V$_2$O$_5$ exceeds 15%. This could be explained by the trigonal boron bending in [B$_2$V$_2$O$_8$]$^2-$ [5,13,33]. The presence of B-O vibrations (band situated at 1230) in the glasses containing more than 15 mol% of V$_2$O$_5$, indicate the occurrence of the diborovanadate groups [B$_2$V$_2$O$_9$]$^{2-}$, the formation of diborovanadate groups is elucidated by supposing that in glasses containing more than 15 mol% of V$_2$O$_5$, a continuous random network is formed of either two BO$_4$ units and two VO$_4$ units (type 1) or two BO$_3$ units and two VO$_5$ units (type 2), the same building was proposed by Reddy and his collaborators for diborovanadate [B$_2$V$_2$O$_9$]$^{2-}$ [5,13,33].

![Type 1 and Type 2](https://example.com/)

**Figure 6.** Diborovanadates groupements [B$_2$V$_2$O$_9$]$^{2-}$ (according to reddy et al. [5]).

The band situated from 848 to 890 cm$^{-1}$ can be assigned to the vibration B-O in BO$_4$ unit [38–42]. Its corresponding intensity decreases with increasing of V$_2$O$_5$ percentage. When the concentration of V$_2$O$_5$ increases from 15% to 40%, the observed peak shifts from 848 to 882 cm$^{-1}$, which is probably related to the V-O stretching of the VO$_4$ group [7]. According to Arya et al.[3], the movement of bands may be caused by the structural changes related to the variation of bond angles.

A very weak peak at around 680 cm$^{-1}$ was presented in all the elaborated glasses accorded to B–O–B linkage in the borate networks [40,43,44]. This peak shifts to 622 cm$^{-1}$ with increasing vanadium oxide concentration in the glass. This behavior may be related to grouping the vibration bands of the B-O-V and B-O-B bonds present respectively in vanadate and borate glasses [5,13].

### Table 3. Observed IR and Raman bands in 40CaO–(60-x)B$_2$O$_3$-xV$_2$O$_5$ (0 ≤ x ≤ 40) glasses.

<table>
<thead>
<tr>
<th>Glass</th>
<th>Peaks positions (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>IR</td>
</tr>
<tr>
<td>CBV0</td>
<td>680</td>
</tr>
<tr>
<td>CBV1</td>
<td>680</td>
</tr>
<tr>
<td>CBV2</td>
<td>675</td>
</tr>
<tr>
<td>CBV3</td>
<td>667</td>
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<tr>
<td>CBV4</td>
<td>661</td>
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<tr>
<td>CBV5</td>
<td>656</td>
</tr>
<tr>
<td>CBV6</td>
<td>626</td>
</tr>
</tbody>
</table>

### 3.4. RAMAN spectroscopy analysis.

Figure 7 and Table 4 presents the Raman spectrum of all elaborated glass samples in the region of 100-2000 cm$^{-1}$ and the Raman shift of the observed bands, respectively.
the sample without vanadium CBV0, the major Raman bands are observed at 555 cm\(^{-1}\), 786 cm\(^{-1}\) and 1280 cm\(^{-1}\). When adding the V\(_2\)O\(_5\), two-band at 930 cm\(^{-1}\) and 1104 cm\(^{-1}\) appear; the band at 930 cm\(^{-1}\) shifts up to 947 cm\(^{-1}\) and becomes even stronger as V\(_2\)O\(_5\) content rises. A band at 1280 cm\(^{-1}\) disappeared when V\(_2\)O\(_5\) was added.

From Raman spectra of borate calcium glass CBV0, a strong peak observed at 1286 cm\(^{-1}\) result from the contribution of B–O stretching vibrations in trigonal arrangements such pyroborate composed by boroxol [45–48].

The absence of a peak in the range of 930-947 cm\(^{-1}\) for the CBV0 glass is ordinary in that there is no V = O bond, whereas when we add the V\(_2\)O\(_5\) this peak begins to appear, which is attributed to the V=O vibrations of tetrahedral VO\(_4\) or VO\(_5\) units [49,50].

It is known from many studies [45,47,48] that the bands at around 1075-1150 cm\(^{-1}\) consist of diborate groups. Consequently, in this work, the observed band at 1104 cm\(^{-1}\) was attributed to the diborate groups [45–47,51].

In addition, all the synthesized glass samples exhibit bands around 555 and 775 cm\(^{-1}\), these peaks attest to the presence of the B-O-B stretching in the BO\(_4\) units (pentaborate) [42,46,48,51]. The band present at 775 cm\(^{-1}\) is characteristic of six-member rings with one or two BO\(_3\) triangles replaced by BO\(_4\) tetrahedra [47,49,51,52].

![Raman spectrum for all the glass samples.](https://biointerfaceresearch.com/)

**Figure 7.** Raman spectrum for all the glass samples.

3.5. *Scanning electron microscopy (SEM).*

The morphology of the prepared glass samples is performed by scanning electron microscopy (SEM). Figure 8 illustrates the SEM images of the 40CaO–(60-x)B\(_2\)O\(_3\) -xV\(_2\)O\(_5\) samples with x=0 and 10%. As shown, the samples under investigation CBV0 and CBV2 indicate good homogeneity and smooth surface in sheets.

4. **Conclusions**

The physical, thermal and structural properties have been investigated for the 40CaO-xV\(_2\)O\(_5\)–(60-x)B\(_2\)O\(_3\) (0 ≤ x ≤ 40) glasses. The X-ray diffraction method confirmed the amorphous state of the elaborated glasses.

The density values and molar volume of glasses rise as V\(_2\)O\(_5\) content increases, implying the existence of more oxygen from V\(_2\)O\(_5\) that moves the coordination of BO\(_3\) to BO\(_4\);
adding the $\text{V}_2\text{O}_5$ more groups of $\text{BO}_4$, $\text{VO}_4$, and $\text{VO}_5$ are created. It is observed from DSC studies that $T_g$ decreases with increasing $\text{V}_2\text{O}_5$, which can be attributed to a transformation of $\text{BO}_3$ to $\text{BO}_4$.

![SEM Micrographs of CBV0 and CBV2 glass samples.](image)

From the FT-IR results, it is clear for calcium and borate binary glass that we have the existence of the $\text{BO}_3$ and $\text{BO}_4$ groups. When $\text{V}_2\text{O}_5$ with different percentages is added, $\text{BO}_3$ group starts converting into $\text{BO}_4$ groups, and $\text{VO}_4$ groups start to appear, thereby the presence of diborovanadate units. This shows that $\text{V}_2\text{O}_5$ is present in the glass structure as a network former and a modifier. Raman spectroscopy confirms the conversion of $\text{BO}_3$ to $\text{BO}_4$, and the presence of $\text{VO}_4$ or $\text{VO}_5$ in glasses containing $\text{V}_2\text{O}_5$, diborate, pyroborate, and pyroborate are observed from Raman spectra.

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Conflicts of Interest

The authors declare no conflict of interest.

References


