The Investigation of xCaO - (50-x)SrO – 50B₂O₃ Glass Systems Added with CaO from Aassava Rhizome on Elastic and Structural Properties

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Abstract

The purpose of this work was to study the elastic moduli and structural properties of xCaO - (50-x)SrO – 50B₂O₃ glass system (where x was 0, 10, 20, 30, 40 and 50 wt.% of CaO) prepared by rapid quenching technique. In this work, the cassava rhizomes were source of calcium oxide in this glass system. All of glass samples were melted at the temperature 1250 °C for 2 hr and annealed at the temperature 450 °C for 2 hr. The ultrasonic velocities were measured by pulse echo technique at 4 MHz at room temperature. Then, the elastic moduli (longitudinal modulus, shear modulus, bulk modulus, Young’s modulus Poisson’s ratio and micro-hardness) and other physical properties such as softening temperature and Debye temperature were calculated. The results showed that the elastic moduli and the physical properties depended on mass percentage of CaO in glass system. This related to the number of bridging oxygen (BO) and non-bridging oxygen (NBO), which could be confirmed by the results of IR spectra.

Keywords: Glass; Cassava rhizome; Pulse echo technique; Elastic moduli; FTIR spectroscopy
Introduction

In Thailand, there are many types of agricultural products. Some products can be used in the energy sector such as biomass. The agricultural production from sugar cane, cassava, maize and paddy leave considerable amount of agricultural wastes such as bagasse, cassava rhizome, corn stalk and rice husk, respectively. The planted area of the cassava in Thailand is about 11,840 km² in year 2000 and Thailand is the world’s largest exporter of dried cassava, with a total of 77% of world export in 2005 [1-2]. The cassava is important source of food in tropical countries. Normally, cassava is the third largest source of carbohydrates in the tropics, after rice and maize. Furthermore, cassava is also biofuel, animal feed, etc. Annually, Thailand has a large amount of the agricultural waste from cassava plantation such as cassava stalk and cassava rhizome [3-5]. The cassava rhizomes can be a good source of calcium oxide. Therefore the calcium oxide from cassava rhizomes can be used to modify a glass network of glass materials to improve glass structure, hardness, strength and decrease the viscosity at high temperature.

The present study aims to investigate the density, ultrasonic velocities, elastic moduli and other physical properties such as softening temperature and Debye temperature of \(x\text{CaO} - (50-x)\text{SrO} - 50\text{B}_2\text{O}_3\) glass system with CaO from cassava rhizomes. In addition, infrared absorption measurement is conducted for confirmation.

Experimental and theoretical techniques

1. Preparation of the glass samples

Appropriate amounts of SrO, \(\text{B}_2\text{O}_3\) and cassava rhizome were weighed using an digital balance with 0.0001 g accuracy and put into ceramic crucible. Then, they were melted using electric furnace at temperature of 1250°C for 2 hr. After that, the melt was poured into a preheated stainless steel mold, slowly cooled to room temperature and annealed at 450°C for 2 hr. The element analyses of the glass system were carried out by using the EDXRF technique as shown in Table 1. The glass samples were cut and polished using different silicon carbide grades for ultrasonic measurement which were repeated three times to check the reproducibility of the data.

Table 1 The result of analyzed by EDXRF technique of cassava rhizome

<table>
<thead>
<tr>
<th>Element</th>
<th>Concentration (Wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>3.51</td>
</tr>
<tr>
<td>O</td>
<td>33.32</td>
</tr>
<tr>
<td>Mg</td>
<td>12.70</td>
</tr>
<tr>
<td>Al</td>
<td>0.63</td>
</tr>
<tr>
<td>Si</td>
<td>6.06</td>
</tr>
<tr>
<td>P</td>
<td>6.35</td>
</tr>
<tr>
<td>S</td>
<td>1.92</td>
</tr>
<tr>
<td>Cl</td>
<td>0.91</td>
</tr>
<tr>
<td>K</td>
<td>4.00</td>
</tr>
<tr>
<td>Ca</td>
<td>28.05</td>
</tr>
<tr>
<td>Mn</td>
<td>0.55</td>
</tr>
</tbody>
</table>

2. Density and molar volume measurements

The weights of the glass samples were measured in air and in n-hexane as immersion liquid by using a digital balance with 0.0001 g accuracy. Then, the density was determined from the relation [6].

\[
p = \rho_b \left( \frac{W_a}{W_a - W_b} \right)
\]
where \( \rho_i \) is the density of n-hexane, \( W_a \) and \( W_b \) are the glass sample weights in air and in n-hexane, respectively. The estimated error of three experiments was \( \pm \) 0.0016 g/cm\(^3\). The molar volume \( (V_m) \) was calculated using the relation [7].

\[
V_m = \frac{M}{\rho}
\]

(2)

where \( M_i \) is the molecular weight of the glass samples, \( x_i \) is the mole fraction of the component oxide \( i \) and can be calculated according to the relation [8].

\[
M = \sum x_i M_i
\]

(3)

3. Ultrasonic velocity measurement

The longitudinal and shear velocities at room temperature were measured using pulse echo technique. The Ultrasonic flaw detector (SONATEST, Sitescan 230) was used to measure ultrasonic wave velocity. The probe models SLG4-10 for longitudinal velocity and SA04-45 for shear velocity were used in this study. The ultrasonic velocity can be calculated by the relation [9].

\[
V = \frac{2x}{\Delta t}
\]

(4)

Where \( x \) is the glass sample thickness and \( \Delta t \) is the time interval. The longitudinal and shear velocities were measured three times to check the reproducibility of the data. The estimated error of longitudinal and shear velocities measurement were \( \pm \) 10 m.s\(^{-1}\) and \( \pm \) 3 m.s\(^{-1}\), respectively.

4. Determination of elastic moduli

The elastic moduli include longitudinal modulus \( (L) \), Shear modulus \( (G) \), bulk modulus \( (K) \), Young’s modulus \( (E) \), Poisson’s ratio \( (\sigma) \) and micro-hardness \( (H) \) as well as other physical properties such as softening temperature \( (T_s) \) and Debye temperature \( (\theta_D) \) of the glass samples have been determined from the value of ultrasonic velocities and density using the relations [10].

Longitudinal modulus:

\[
L = \rho V_L^2
\]

(5)

Shear modulus:

\[
G = \rho V_S^2
\]

(6)

Bulk modulus:

\[
K = L - \frac{4}{3} G
\]

(7)

Young’s modulus:

\[
E = (1 + \sigma)2G
\]

(8)

Poisson’s ratio:

\[
\sigma = \frac{L-2G}{2(L-G)}
\]

(9)

Micro-hardness:

\[
H = \frac{(1-2\sigma)E}{6(1+\sigma)}
\]

(10)

Softening temperature:

\[
T_s = \frac{V_m}{\sigma^2}
\]

(11)

Debye temperature:

\[
\theta_D = \left( \frac{h}{k_B} \right) \left( \frac{3\pi N_a}{4\pi V_m} \right)^{1/3}
\]

(12)

where \( h \) is Planck’s constant, \( k_B \) is Boltzmann’s constant, \( N_a \) is Avogadro’s number, \( \sigma \) is the number of atoms in the chemical formula, \( C \) is the constant of proportionality (equals 507.4 m.s\(^{-1}\) K\(^{1/2}\)) and \( V_m \) is the mean ultrasonic velocity defined by the relationship [11].

\[
V_m = \left( \frac{3\pi^2 n_2}{10^2 + n_2} \right)^{1/3}
\]

(13)

2.5 Infrared absorption measurements

The Infrared spectra of glass samples were measured at room temperature in the wavelength range of 400–2000 cm\(^{-1}\) by a
Fourier Transform Infrared spectrometer using a KBr disc technique. The powdered glass samples were mixed with KBr in the ratio of 1:100. The mixture was then subjected to a pressure to make a homogeneous disk. After that, infrared absorption measurement was carried out immediately.

Results and Discussion

1. Density and molar volume

The chemical composition, density and molar volume for the prepared glass samples as a function of weight percentage of CaO in glass system are given in Table 2 and shown in Figure 1. It can be seen that with increasing weight percentage of CaO from 0 to 50 wt%, the density of glass samples decreases from 3.02 to 2.60 g/cm³ and the molar volume of glass samples decreases from 28.5 to 23.6 cm³/mol. The decreasing of molar volume can be attributed to the ionic radius of the modifier. Since the ionic radius of Ca²⁺ (1.0 Å) is smaller than that of Sr²⁺ (1.18 Å), the insertion of Ca²⁺ ions lead to the decrease in the molar volume. Moreover, the decrease in molar volume may be also due to the decrease in the formation of number of non-bridging oxygens (NBOs) [12].

![Figure 1](image-url)  
*Figure 1* Density and molar volume of glass samples as a function of weight percentage of CaO in glass system

**Table 2** Chemical composition, density and molar volume of glass system

<table>
<thead>
<tr>
<th>Chemical composition (wt.%)</th>
<th>( \rho ) (g/cm³)</th>
<th>( V ) (cm³/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO 50 SrO 50 B₂O₃ 50</td>
<td>3.032</td>
<td>28.568</td>
</tr>
<tr>
<td>CaO 40 SrO 30 B₂O₃ 50</td>
<td>3.003</td>
<td>28.300</td>
</tr>
<tr>
<td>CaO 30 SrO 20 B₂O₃ 50</td>
<td>2.974</td>
<td>27.527</td>
</tr>
<tr>
<td>CaO 20 SrO 10 B₂O₃ 50</td>
<td>2.948</td>
<td>26.905</td>
</tr>
<tr>
<td>CaO 10 SrO 0 B₂O₃ 50</td>
<td>2.919</td>
<td>25.814</td>
</tr>
<tr>
<td>CaO 0 SrO 0 B₂O₃ 50</td>
<td>2.662</td>
<td>23.609</td>
</tr>
</tbody>
</table>
2. Ultrasonic velocities and elastic moduli

Figure 2 shows the longitudinal and shear velocities as a function of weight percentage of CaO in glass system. It can be seen that the shear velocity increases from 3336 m.s\(^{-1}\) to 3493 m.s\(^{-1}\) with increasing weight percentage of CaO. This may be attributed to the increased bridging oxygens (BOs) in the glass networks. However, trend for longitudinal velocities is different, its value fluctuate when the weight percentage of CaO increase. It was mentioned that normally, the increase in longitudinal and shear velocities is related to the decrease in the number of non-bridging oxygens and connectivity of glass network [7]. The value of elastic moduli such as longitudinal modulus (L), shear modulus (G), bulk modulus (K), Young’s modulus (E) and Poisson’s ratio (ν) are given in Table 3. Bulk modulus and Young’s modulus as a function of weight percentage of CaO in glass are shown in Figure 3. The figure indicates that the Young’s modulus decreases from 86.6 to 80.5 GPa and bulk modulus decreases from 66.7 to 51.3 GPa. It was mentioned that the change in Young’s modulus can be accounted to the change in rigidity of glass system which is related to the change in the number of non-bridging oxygen (NBO) in the glass network, and the change of bulk modulus can be ascribed to the change in the cross-linkage coordination of glass network [13,14]. Therefore, the decrease in Young’s modulus and bulk modulus with increase weight percentage of CaO in glass system indicate the decreasing of the rigidity of glass system and decrease in cross-linkage coordination of glass network, respectively.

![Figure 2 Variation of longitudinal and shear velocities with weight percentage of CaO in glass system.](image)
Figure 3 Variation of Young’s modulus and bulk modulus with weight percentage of CaO in glass system

Figure 4 shows the variation of Poisson’s ratio with weight percentage of CaO in glass system. Mainly, the value of Poisson’s ratio decrease from 0.28 to 0.238 with increasing weight percentage of CaO in glass system, except for 30 wt.%. This Poisson’s ratio relates to the cross-link density which is defined as the number of bridging bonds per cation. The range of Poisson’s ratio 0.1 to 0.2 indicates a high cross-link density while 0.3 to 0.5 indicates a low cross-link density [15, 16]. Thus, the decrease of Poisson’s ratio shows the increasing of cross-link density, which indicates the decrease in number of non-bridging oxygen

Figure 5 shows the result of micro-hardness. Micro-hardness value increase from 4.8 to 5.2 GPa with increasing weight percentage of CaO from 0 to 10 wt.%. Then, it decrease from 5.0 to 4.7 GPa with increasing weight percentage of CaO from 20 to 30 wt.%. After that, the value of micro-hardness increase again when weight percentage of CaO increase to 40 wt.% and decrease when the weight percentage of CaO increase further to 50 wt.%. The micro-hardness reveal the rigidity of glass network structure and related to Poisson’s ratio and Young’s modulus.
Figure 5 Variation of micro-hardness with weight percentage of CaO in the glass system

The Variation of softening temperature and Debye temperature with weight percentage of CaO shows in Figure 6. The value of softening temperature indicates the maximum temperature of glass before it permanently deforms. Softening temperature decreases from 935 to 744 K with increasing weight percentage of CaO. The Debye temperature is one of important parameter of solids. The value of Debye temperature represents the temperature at which nearly all the vibration modes are excited [17]. The Debye temperature increases from 596 to 659 K with increase weight percentage of CaO. This increase in Debye temperature indicates the decrease in number of non-bridging oxygen as a direct effect of insertion of CaO to the glass network structure [18].

Figure 6 Variation of softening temperature and Debye temperature with weight percentage of CaO in glass system
Table 3 Longitudinal modulus (\(L\)), Shear modulus (\(G\)), Young’s modulus (\(E\)) bulk modulus (\(K\)) and Poisson’s ratio (\(\sigma\)) of all glass samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>(L) (GPa)</th>
<th>(G) (GPa)</th>
<th>(E) (GPa)</th>
<th>(K) (GPa)</th>
<th>(\sigma)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>± 0.0001</td>
<td>± 0.0002</td>
<td>± 0.0005</td>
<td>± 0.0001</td>
<td>± 0.0005</td>
</tr>
<tr>
<td>S1</td>
<td>111.69</td>
<td>33.74</td>
<td>86.62</td>
<td>66.70</td>
<td>0.283</td>
</tr>
<tr>
<td>S2</td>
<td>103.82</td>
<td>33.19</td>
<td>83.98</td>
<td>59.56</td>
<td>0.264</td>
</tr>
<tr>
<td>S3</td>
<td>101.12</td>
<td>32.37</td>
<td>81.87</td>
<td>57.95</td>
<td>0.264</td>
</tr>
<tr>
<td>S4</td>
<td>104.09</td>
<td>31.94</td>
<td>81.69</td>
<td>61.49</td>
<td>0.278</td>
</tr>
<tr>
<td>S5</td>
<td>97.23</td>
<td>33.27</td>
<td>82.51</td>
<td>52.87</td>
<td>0.239</td>
</tr>
<tr>
<td>S6</td>
<td>94.71</td>
<td>33.48</td>
<td>80.50</td>
<td>51.39</td>
<td>0.238</td>
</tr>
</tbody>
</table>

3. Fourier transforms infrared absorption

The FTIR absorption spectral curves of \(x\)CaO - (50-x) SrO - 50B\(_2\)O\(_3\) glasses with different weight percentage of dopant shows in Figure 7. The frequency bands from the glasses network vibrations appear in the range 400 – 1500 cm\(^{-1}\). The first vibration signals at around 455- 490 cm\(^{-1}\) is assigned to bending vibration of B-O linkage in the borate network. The peak at around 700 cm\(^{-1}\) is related to bending vibration of B-O linkage. The peak in the region range of 870 – 1080 cm\(^{-1}\) represents the B-O stretching vibrations of BO\(_4\) tetrahedral. The peak at around 1219 – 1233 cm\(^{-1}\) is associated the stretching vibrations of the B–O bonds of BO\(_3\)\(^3-\) unit involving mainly the linkage oxygen connecting different groups. The absorption band between 1380 – 1411 cm\(^{-1}\) is due to the antisymmetrical stretching vibrations with three (NBOs) of B–O–B groups. The band at 1450 cm\(^{-1}\) is attributed to vibrations of the Ca-O bonds and indicates that BO\(_4\) changes to BO\(_3\)\(^3-\) [19-21]. The FTIR spectra in Figure 7 show that with increasing weight percentage of CaO, the absorption of function group increases. This result from infrared spectra confirms our conclusion from molar volume and ultrasonic studies.

![Figure 7](image-url)

Figure 7 The IR spectra of the glass samples with different weight percentage of CaO in the glass system
Table 4 Depicts the detailed assignments of IR bands

<table>
<thead>
<tr>
<th>Bond peak</th>
<th>Peak position (cm⁻¹)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>455-490</td>
<td>Assigned to bending the vibratio of B-O linkage in the boratenetwork [19,20]</td>
</tr>
<tr>
<td>2</td>
<td>700</td>
<td>Assigned to bending vibration of linkage [19,20]</td>
</tr>
<tr>
<td>3</td>
<td>870-1080</td>
<td>Assigned to B-O stretching vibrations of BO₄ tetrahedral [19,20]</td>
</tr>
<tr>
<td>4</td>
<td>1219-1233</td>
<td>Assigned to the stretching vibrations of the B–O bonds of BO₃⁺ [19-21]</td>
</tr>
<tr>
<td>5</td>
<td>1271–1316</td>
<td>Assigned to the stretching vibrations of the B–O of trigonal BO₃⁻ [19-21]</td>
</tr>
<tr>
<td>6</td>
<td>1380-1411</td>
<td>Assigned to the antisymmetrical stretching vibrations with three (NBOs) of B–O–B groups [20-21]</td>
</tr>
<tr>
<td>7</td>
<td>1460-1480</td>
<td>Assigned to vibrations of the Ca-O bonds and indicates that BO₄ changes to BO₃ [19-21]</td>
</tr>
<tr>
<td>8</td>
<td>1600</td>
<td>Assigned to vibrations of the H-O-H bond</td>
</tr>
</tbody>
</table>

Conclusions

The ultrasonic velocities of xCaO - (50-x) SrO – 50B₂O₃ glasses change due to the increasing in weight percentage of CaO dopant in glass system from 0 to 50 wt.%. The increasing in weight percentage of CaO dopant in glass system also affect to the elastic moduli and other physical properties of the glass samples due to the change in number of non-bridging oxygens (NBOs) in glass network. This numbers of non-bridging oxygens relates to the rigidity of glass structure. The change in value of bulk modulus, Young’s modulus, micro hardness and Poisson’s ratio with increasing weight percentage of CaO dopant in glass system from 0 to 50 wt.% indicates the increase in numbers of non-bridging oxygens and this implies the increasing of rigidity of glass network. The results of FTIR spectra also support the result of the pulse echo technique. Therefore this research shows that CaO from cassava rhizomes can be substituted for the pure CaO and can be used as modifier in the glass system.

Acknowledgments

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Reference


