Structural studies of transition metal ions doped in biomass ash as silica source for glass production in Thailand

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Abstract. (55-x)SiO2-13B2O3-1.0Al2O3-4.5BaO-6.3CaO-0.2Sb2O3-20Na2O-XMO (X=0.0, 0.1, 0.2, 0.4, 0.6, 0.8, 1.0 and M= NiO, CoO, CuO and Fe2O3) were prepared by conventional melt quenching technique. In this research, glass productions from rice husk ash (RHA) and the effect of CoO, CuO, NiO, and Fe2O3 on structural properties were investigated. The local RHA in Nakhon Pathom Province, Thailand was used as a silica source for glass matrices. FTIR and RAMAN analysis were performed. FTIR revealed Si–O–Si antisymmetric vibrations of bridging oxygens for all transition ion doped glasses. Vibrations of transitional metal ions were observed in the lower wavenumber (<1000cm⁻¹) region in RAMAN spectra.

1 Introduction

Vast amounts of food waste around the world cause significant health and environmental problems that ultimately lead to direct economic costs. However, most food wastes contain valuable minerals that could serve as raw materials for the production of glass, ceramics, and glass-ceramics. Agricultural wastes are also used as resource materials in many engineering applications. In general, silica is a major constituent of the agricultural / food waste ash. It varies from 98–36wt% in ash of rice husk, sugarcane leaves and corn husk etc [1]. In addition to silica, other metal oxides like CaO, MgO and K2O are also present along with some trace elements [2]. Rice husk after burning in air, produces highly reactive silica particles (usually nanosized) [3]. Container glass is ~70 wt% silica, and, thus, consumed ~36.4 million tons of silica raw material [1]. Since RHA contains a large amount of SiO2, which is a main glass network former and a little contaminate of transition component, it is feasible to use RHA as a raw material to develop glass matrices [4]. In the present work we focus on biomass ash as silica as raw material for preparing glasses doped with metal transition ions (CoO, CuO, Fe2O3, NiO) to understand their structural modifications observed in these glasses.
2 Experimental:

The local RHA in Nakhon Pathom Province, Thailand was sintered at 1050 °C and used as a silica source in glass matrices. The color glass samples were prepared by using high purity Na$_2$CO$_3$, Al$_2$O$_3$, B$_2$O$_3$, CaO, Sb$_2$O$_3$, BaCO$_3$, SiO$_2$ (use RHA as SiO$_2$) in formula (55-x)SiO$_2$-13B$_2$O$_3$-1.0Al$_2$O$_3$-4.5BaO-6.3CaO-0.2Sb$_2$O$_3$-20Na$_2$O-XMO (RHA Glass) (X=0.0, 0.1, 0.2, 0.4, 0.6, 0.8, 1.0 and M=CoO, CuO, Fe$_2$O$_3$, MnO). The detailed experimental procedure for glass making is given elsewhere [4].

2.1 FTIR Analysis: MO (M = CuO, Fe$_2$O$_3$, CoO, NiO) Doped RHA Glass

Analysis of the IR vibrational spectra however can provide structural information when a thorough analysis of the data is carried out [5]. In addition, vibrational spectra can be readily used to identify the presence of defect groups or radiation-induced defects [6] within a glass. Infrared spectroscopy has also been used to identify low concentration impurities such as water, hydroxyl ions, etc in glass [5]. Furthermore, infrared spectroscopy has been used to confirm corrosion behaviour [7, 8] and crystallization process [9] in some glasses. The experimentally observed IR absorption spectra shown in Fig. 1 are familiar and evident to be characteristic of the silicate chains which are active in the mid region of the spectrum (600–1800 cm$^{-1}$). The spectrum of the base RHA silicate glass resembles to a great extent. The IR spectrum of all metal transition doped in RHA glass is presented in Fig.1 (i-v), it can be realized and interpreted as follows: (a) A small band at 745–800 cm$^{-1}$ is identified which is due to symmetric stretching vibration of O–Si–O bonds [5-12]. (b) A shoulder at about 920–970 cm$^{-1}$ can be related to vibrations of non-bridging oxygens [1-6]. (c) A shoulder at 1100 cm$^{-1}$ to 1270 cm$^{-1}$ is identified and related to Si–O–Si antisymmetric vibrations of bridging oxygens [5-10]. (d) A small band at about 1520–1650 cm$^{-1}$ is related to molecular water [5].
Figure 1 FTIR Spectra of d-transition metal ions doped RHA glass (i) Fe$_2$O$_3$ (ii) CuO (iii) NiO (iv) CoO

2.2 RAMAN Analysis: MO (M = CuO, Fe$_2$O$_3$, CoO, NiO) Doped RHA Glass

To analyze the effect of the changing Fe$_2$O$_3$ content on each alkali-RHA silicate network, special interest was given to lower-wavenumber envelope in Raman spectrum. According to space group symmetry and factor group analysis, the optical Fe$_2$O$_3$ normal modes are distributed over the symmetry species of the D$^{6}_{3d}$ group as $\Gamma = 2A_{1g} + 3A_{2g} + 2E_g + 5E_u$. Among these, six are IR-active vibrations (2A$_{2u}$ + 4E$_u$ modes) and seven are Raman-active vibrations (2A$_1g$ + 5E$_g$ modes) [13]. Low intensity bands observed around 625 cm$^{-1}$ (E$_g$ mode) are associated with Fe–O bending modes in different boro-silicate units in the glass and/or iron silicate content [14]. The most intense band is at approximately 900–1100 cm$^{-1}$ and is related to stretching vibrations of Fe–O polyhedra [15]. Copper(II) oxide (CuO) belongs to the C$^{6}_{2h}$ space group with two molecules per primitive cell. There are nine zone-center optical phonon modes with symmetries 4A$_{u}$+5B$_{u}$+A$_{g}$+2B$_{g}$; only three A$_{g}$ + 2B$_{g}$ modes are Raman active [16-17]. We can assign the peak at 332 and 628 cm$^{-1}$ to the B$_{g}$ modes. We note that these wave numbers are lower than those reported in the literature (345 and 632 cm$^{-1}$) due to size effects [4]. The Raman band in the region around 540–560 cm$^{-1}$ range one phonon LO mode of CoO. The second-order two-phonon longitudinal optical (LO) Raman scattering should appear in the 1000–1100 cm$^{-1}$ range [18]. On the other hand, Dietz et al. [19] observed that a broad Raman peak around 600–400 cm$^{-1}$ appears more remarkably in black (oxygen rich) NiO, this peak is also composed of impurity-activated LO and TO one phonon peaks. The shoulders at around 540-565 cm$^{-1}$ can be attributed to Si–O bond stretching and bending in SiO$_4$ tetrahedra [20]. Vibration of B–O–B, B–O–Si and Si–O–Si bending [21] and Diborate structures [22].

Fig. 1(i-iv) shows the typical Raman spectra of RHA glasses where the following vibrational modes can be identified: (i) Si–O–Si asymmetric stretching at 1000–1100 cm$^{-1}$ related to Q$^1$ groups (structural units Q$n$ in Si, where n means the number of bridging oxygen's), composed of sites with three- and four-fold rings [23-26], Boron is always four-coordinated and silica is either Q$^2$ or Q$^3$. Four coordinated boron is present in excess of what is expected which may be explained by considering the possibility of oxygen coordinated to more than two atoms due less availability of boron, silicate structural units dominate over four coordinated structures in these glasses. (ii) a prominent Si–O–NBO stretching at 900–970 cm$^{-1}$ [24-25] also this region corresponds to Q$^2$ terminology of Silicate structure [26]. Around 935 - 945 cm$^{-1}$ refers to B–O–Si stretching vibration [21]. The distinct peak around 625 -
630 cm\(^{-1}\) observed in all glasses are attributed to danburite-like units \([\text{B}_2\text{Si}_2\text{O}_3]^{2-}\), four-membered rings having two adjacent \(\text{SiO}_4\) and two \(\text{BO}_4\) tetrahedra [27-30].

**Figure.2** RAMAN Spectra of d-transition metal ions doped RHA glass.

(i) \(\text{Fe}_2\text{O}_3\) (ii) \(\text{CuO}\) (iii) \(\text{CoO}\) (iv) \(\text{NiO}\)

Raman band about 750 - 760 cm\(^{-1}\) occurs because of metaborate groups and symmetric breathing vibrations of \(\text{BO}_3\) triangles replaced by boron tetrahedral (\(\text{BO}_4\)) [21, 31]. The bands in the 1300–1500 cm\(^{-1}\) range in the spectra are ascribed to the terminal vibration of oxygen atoms in \(\text{Si-O}^\text{\%}\) [32] and stretching vibrations of \(\text{B-O}^\text{-}\) bonds and stretching vibrations of \(\text{O}_2\text{B-O-BO}_4\) bonds in \(\text{BO}_3\) pyramidal units, stretching vibrations of \(\text{B-O-B}\) bonds in pyramidal \(\text{BO}_3\) units [33-36].

**2.3 Raman Intensity:**

The Raman bands centered at 900–970 cm\(^{-1}\) that appears in this case is assigned to \(\text{Si-O-NBO (Non-Bridging Oxygen's)}\) stretching vibrations and \(\text{Q}^2\) units. Addition of \(\text{MO}\) determines a change in their vibration intensity due to presence of \(\text{NBO's available. From Fig.3 (i-iv)}\) one can observe that the addition of \(\text{MO}\) where \(\text{M} = \text{Fe}_2\text{O}_3, \text{CuO}, \text{CoO}, \text{NiO}\) in RHA glasses shows decrease in its intensity with addition of d-transition metal ions. This suggests that the available \(\text{NBO's in these glasses are being converted to BO's (Bridging Oxygen's)}\) with addition of metal ions [37]. In the case of RHA glasses, the observable increase in intensity at ~1070 cm\(^{-1}\) can be straightforwardly described.
by the additional conversion of $Q^3$ species to $Q^2 / Q^4$, due to the high NBO content of the glass. Given the slight increase of the intensity around 935 - 945 cm$^{-1}$ and 1070 cm$^{-1}$ related to $Q^2$ and $Q^4$ species, the conversion mechanism proposed for degradation of network of rice ash silicate glass are given as follows:

$$2 \times Q^3 \rightarrow Q^2 + Q^4$$ as described in Fig.4.

![Figure 3](image_url)

**Figure 3** RAMAN Intensity of d-transition metal ions. (i) $Q^3$ units in Fe$_2$O$_3$ and CuO doped RHA glass (ii) $Q^2$ units in Fe$_2$O$_3$ and CuO doped RHA glass (iii) $Q^3$ and $Q^2$ units in CoO doped RHA glass (iv) $Q^3$ and $Q^2$ units in NiO doped RHA glass.

![Figure 4](image_url)

**Figure 4** $Q^0$ Structural Units of Si with addition of MO (M=Fe/Cu/Co/Ni).
2.4 $Q^3$ & $Q^2$ Units in MO (M=Fe, Co, Ni, Cu) doped RHA glasses:

Fig.5 shows that addition of transition metal oxides could lead to structural changes in their glass network. Structural changes observed in these glasses were quite interesting for CoO case, from fig.5 it is clear that CoO doped glasses shows less Raman intensity of $Q^3$ and pronounced intensity in $Q^2$ units than compared to other dopants which could be due to degradation in the network as discussed in the above mechanism.

![Figure 5](image_url)

**Figure 5**: $Q^3$ and $Q^2$ units in 1mol% of MO (M=Fe, Co, Ni, Cu) doped RHA glass.

The confirmation of such structural degradation is been analysed their area under the peak, full width half maximum (FWHM) around 900–970 cm$^{-1}$ ($Q^2$ units) and ~1070 cm$^{-1}$ ($Q^3$ units) as displayed in Fig.6(a-d). These regions were deconvoluted to calculate the area under the curve and FWHM, which provide differences in their $Q^2$ and $Q^3$ structural units observed as presented in Table.1. The effective electronegativity charges of [SiO$_{3/2}$O$^-$], [SiO$_{2/2}$O]$^{2-}$ were calculated using Sanderson procedure, the partial charge of Si in $Q^2$ and $Q^3$ structural units works out to be 0.11 and -0.36 whereas for oxygen partial charges are -0.44 and -0.81 respectively. Hence the partial charge could play vital role in forming the bridging and non bridging oxygen's in glasses. Table.1 shows the number of $Q^2$ or $Q^3$ units available, number of bridging oxygen's (BO's) and non bridging oxygen's (NBO's) available in these glasses. It shows that the non-bridging oxygen's available in CoO doped RHA glasses shows very less in $Q^3$ units and more in $Q^2$ units that could confirm the changes observed in fig.5. Fig.7 shows that $Q^2$ structural units in CoO doped RHA glasses shows increase in area (%) whereas decrease in $Q^3$ structural units confirming that these glasses shows less degradation than any other dopants. Whereas CuO doped RHA glasses shows higher degradation in silicate network forming more number of $Q^3$ units and less in $Q^2$ units.

**Table 1**: $Q^3$ $Q^2$ units of silica in 1mol% of MO (M = Fe, Co, Ni, Cu) doped RHA glass.

| Glass Sample | $Q^2$ units (in %) | NBO's (in $Q^2$) | BO's (in $Q^2$) | $Q^3$ units (in %) | NBO's (in $Q^3$) | BO's (in $Q^3$) | $Q^2$ FWHM | $Q^3$ FWHM |
|--------------|---------------------|-----------------|----------------|---------------------|-----------------|----------------|-------------|-------------|
| Fe$_2$O$_3$: RHA | 44.289 | 22.14 | 77.86 | 55.71 | 18.5 | 81.5 | 0.563 | 0.436 |
| CoO: RHA | 61.122 | 30.56 | 69.44 | 38.87 | 12.94 | 87.06 | 0.639 | 0.360 |
| NiO: RHA | 21.324 | 10.66 | 89.34 | 78.67 | 26.91 | 73.09 | 0.504 | 0.4959 |
| CuO: RHA | 14.129 | 7.064 | 92.93 | 85.87 | 28.59 | 71.41 | 0.432 | 0.567 |
Figure 6 (a) Deconvoluted Raman Peaks of Q\textsuperscript{3} and Q\textsuperscript{2} units in CuO doped RHA glass (b) Deconvoluted Raman Peaks of Q\textsuperscript{3} and Q\textsuperscript{2} units in Fe\textsubscript{2}O\textsubscript{3} doped RHA glass (c) Deconvoluted Raman Peaks of Q\textsuperscript{3} and Q\textsuperscript{2} units in CoO doped RHA glass (d) Deconvoluted Raman Peaks of Q\textsuperscript{3} and Q\textsuperscript{2} units in NiO doped RHA glass.
Figure 7. Area under the curve of $Q^2$ and $Q^3$ structural units in 1mol% of MO (M=Fe, Co, Ni, Cu) doped RHA glass

Conclusions

Rice husk ash (RHA) silica glasses were prepared by conventional melt quenching technique. FTIR spectrum shows a shoulder at 1100 cm$^{-1}$ to 1270 cm$^{-1}$ which is identified and related to Si–O–Si antisymmetric vibrations of bridging oxygens. Si–O–Si asymmetric stretching at 1000–1200 cm$^{-1}$ related to $Q^4$ groups, composed of sites with three- and four-fold rings. The Raman intensity at ~1070 cm$^{-1}$ can be described by the $Q^3$ species of silicate structures in RHA glass. Prominent Si–O–NBO stretching and $Q^2$ terminology of Silicate structure corresponds to 900-970 cm$^{-1}$ in RHA glass. Addition of transition metal oxides could lead to structural changes in these glass network where CoO doped RHA glass show less degradation than any other transition metal doped oxides, while CuO doped RHA glass show maximum degradation than other dopants. Addition of metal transition oxides in RHA glass show $Q^3$ and $Q^2$ terminology depicting that these glasses reduces their NBO's to form BO's.

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