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Influence of Montmorillonite Clay on Structure and Properties of Sodium Borate Glasses

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Abstract. In the light of environmental perspective, clay minerals attract special interest because of their capability to absorb and chemically stabilize heavy metals in their structure [1, 2]. The absolute suppression of heavy element leakage from clay structures to the environment, which is obviously a strict demand, can be achieved with clay vitrification. This work is related to the influence of the addition of (0-50 wt%) of montmorillonite to a borate glass with composition of $0.33Na_2O$-$0.67B_2O_3$ on its structure. This influence has been studied with Raman and FT-IR spectroscopies, Archimedean density measurements, chemical durability in 90°C water and finally by studying of the ultrasonically measured elastic properties, such as Young's and shear modulus and Poisson's ratio, of the resultant glasses. The experimental results showed that the glass structure is predominantly comprised from tetrahedral and trigonal borate units and silicon and/or aluminium tetrahedral units. The results of density and chemical durability are fairly well correlated with structure. Higher amounts of montmorillonite lead to glasses of higher mechanical strength and chemical durability.

Experimental procedure

Glass preparation. The precursor boric glass with the composition (in mol%): $0.33Na_2O$-$0.67B_2O_3$ was prepared by mixing appropriate amounts of powder raw materials. Reagent grade H_3BO_3 and Na_2CO_3 were used to obtain the starting composition. Stoichiometric powder mixture was heated in Ni-crucible at 1000°C for 30min and then the melt was quenched between two copper plates. The obtained glass was mill grinded and mixed with appropriate amounts of montmorillonite clay. The used clays were unpurified, i.e. were used as the companies ship it. As the impurities comprise a very small fraction of the clay, these do not have any significant effect on the final result (glass forming region and properties). The choice to use the clay as received has also been selected to avoid the multiple purification stages which complicates the large scale preparation of such glasses. More specifically, six new glasses were prepared by the addition of 9, 17, 23, 29, 33 and 50% SWy-2 montmorillonite. All glasses were prepared at 1000°C for 30min.
X-ray powder diffraction. XRD patterns were recorded at the X-ray diffractometer Siemens Diffract 500 system (Cu Ka) to investigate the amorphous nature of the samples.
Chemical durability. The chemical durability of the bulk glasses was evaluated from the dissolution rate (D_R) of samples immersed in deionized water at 90°C for 1, 3, 7 hours and 1, 3, 7 days. The dissolution rate was calculated from the measured weight loss (ΔW) using the equation (1)

$$D_R = \frac{\Delta W(g)}{A(cm^2) \times t(\min)} \qquad (1),$$

where A is the surface area of the specimen, ΔW is the weight loss W_i-W_t (W_i is the initial weight and W_t is the weight of the same specimen after a time t).
Mechanical properties and density. Young's modulus (E), shear modulus (G) and Poisson ratio (v) were obtained by measuring the longitudinal (C_L) and shear (C_s) sound velocities in the glass disks with an ultrasonic device and substituting the velocities into a set of formulas that are given further down.

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$$E = d \times C_L^2 \quad (2), \quad G = d \times C_S^2 \quad (3), \quad \text{and} \quad v = \frac{d \times C_L^2 - 2 \times G}{2 \times d \times C_L^2 - 2 \times G} \quad (4),$$

where d is the mass density of the glasses. The density of each glass was measured by Archimedes method.

Infrared and Raman spectroscopy. The infrared (IR) spectrum for each glass was measured between 400 and 1800 cm^{-1} using an FT-IR Perkin-Elmer GX spectrometer. Samples were prepared as pellets by pressing a mixture of about 5 mg of glass and 100 mg of anhydrous KBr. Raman spectra were collected with a micro Raman system Renishaw 1000 using a solid state laser with a wavelength of 532nm.

Results

X-ray powder diffraction. X-ray powder diffraction showed that none of the final compositions did not show any signs of crystallization. This leads to the conclusion that the clay added in the glass has been decomposed and all its elements have been incorporated in the new glass network.

Chemical durability. The results of chemical durability tests are presented in Fig. 1. It is obvious that the chemical durability of the glasses is increased upon increased addition of montmorillonite. The precursor borate glass shows a fairly poor chemical durability ($logD_R$=-2.9) in contrast with the glass that contains 50% clay which has an increased chemical durability ($logD_R$= -4.3). The very important fact is that all glasses have been prepared at the same temperature.

Mechanical properties and density. Young's modulus (E), shear modulus (G), Poisson ratio (v) and density (d) are given in Table 1.

Table 1: Density, longitudinal (C_L) and shear (C_s) velocity and calculated elastic properties (E,G,v)

Glass	d [g/cm^3]	C_L [m/sec]	C_S [m/sec]	E [GPa]	G [GPa]	v
Noclay	2.363	5211	3149	64.2	23.4	0.21
9%clay	2.376	5315	3167	67.1	23.8	0.22
17%clay	2.399	5758	3234	79.5	25.1	0.27
23%clay	2.407	5937	3304	84.8	26.3	0.28
29%clay	2.413	6259	3417	94.5	28.2	0.29
33%clay	2.417	6612	3333	105.6	26.8	0.33

Density of the glass is increased with the addition of clay, as a consequence of the heavier elements (Si, Al) which originate from the clay structure and take part in the new glass network. Also, probably the structural modifications originating from the new element additions lead to the density

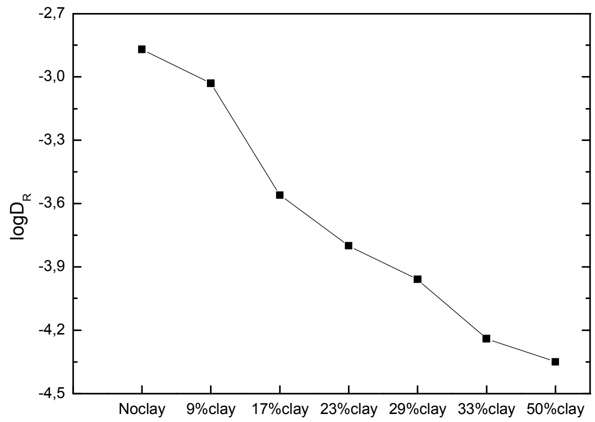

Figure 1: Chemical durability as measured for 3 hours in 90°C H_2O versus the clay % addition.

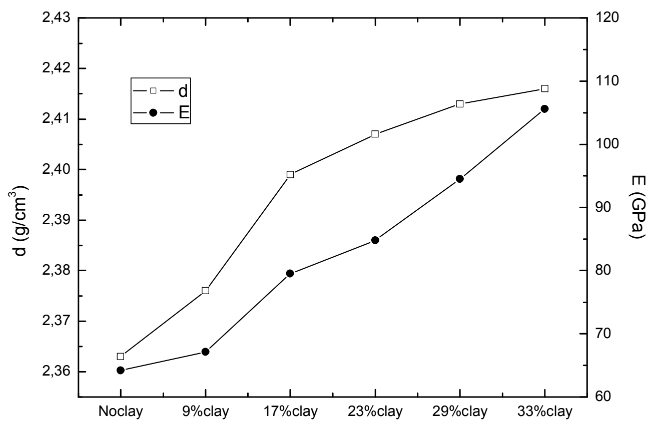

Figure 2: Density (d) and Young modulus (E) versus the clay % addition.

increase. The addition of clay increases not only the chemical durability but the mechanical properties as well, as it can be seen from the calculated elastic constants. Fig. 2 shows the glass density in g/cm^3 and Young modulus in GPa as function of the clay addition percentage .

Infrared and Raman spectroscopy. Normalized infrared spectra of the studied glasses are presented in Fig.3. The precursor glass (0.33Na_2O-0.67B_2O_3), ie containing no clay, has a typical alkali borate glass spectrum with three basic absorption regions as they are given by Kamitsos et al. [3]: 600-850cm^{-1} is attributed to the bending vibrations of borate segments, 850-1200cm^{-1} is attributed to stretching vibration of structural groups containing BO_4 tetrahedra and 1200-1500 arises from B-O stretching vibrations of BO_3 units. With the gradual addition of clay three new bands appear in the IR spectra which are connected with the increasing amount of Si and Al in the glass structure, which are the 1265, 1008 and 455cm^{-1} . The last two bands are attributed to the creation of $Si(OAl)_m$ tetrahedral [4] which are part of the borate glass network, while the first may be probably to the trigonal borate units, which appear after the rearrangement of the network.

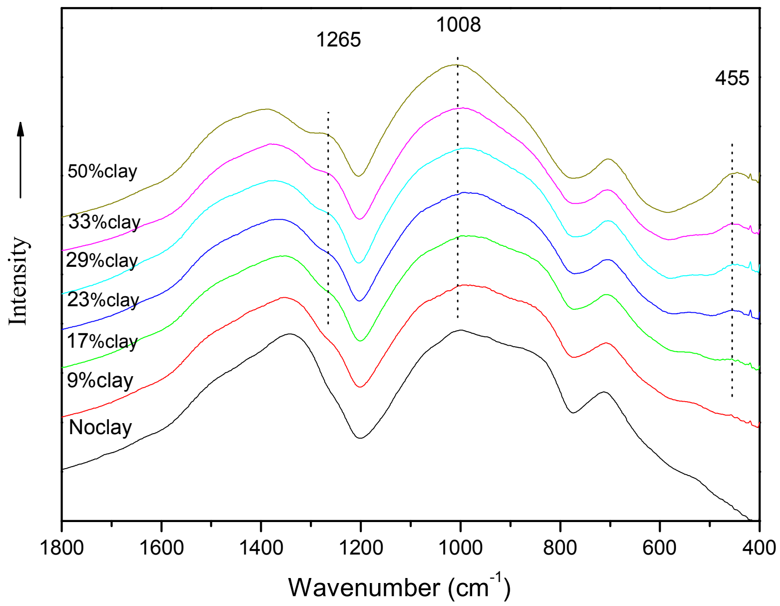

Figure 3: Infrared spectra of the various glasses prepared using various clay additions.

Raman spectra (Fig. 4) are in good agreement with infrared spectra. The 770cm^{-1} peak reveals the existence of boroxol rings bearing BO_4 tetrahedra, the 1490cm^{-1} peak reveals the existence of BO_2O^{-} trigonal units, and the 503cm^{-1} peak reveals the existence of B-O-B bridges [5]. As the amount of clay is increased two new bands can be detected. The 800-1220cm^{-1} band can be attributed to the formation of $Si(OAl)_m$ units and the 431cm^{-1} shoulder can be attributed to B-O-Si bridges [6]. As it has been observed from the spectra the borate network is not modified by the addition of the clay content, by creating of higher charged units (pyro/ortho). This is a consequence of the modifier cations to prefer the cations of Al and Si to equilibrate the network charges.

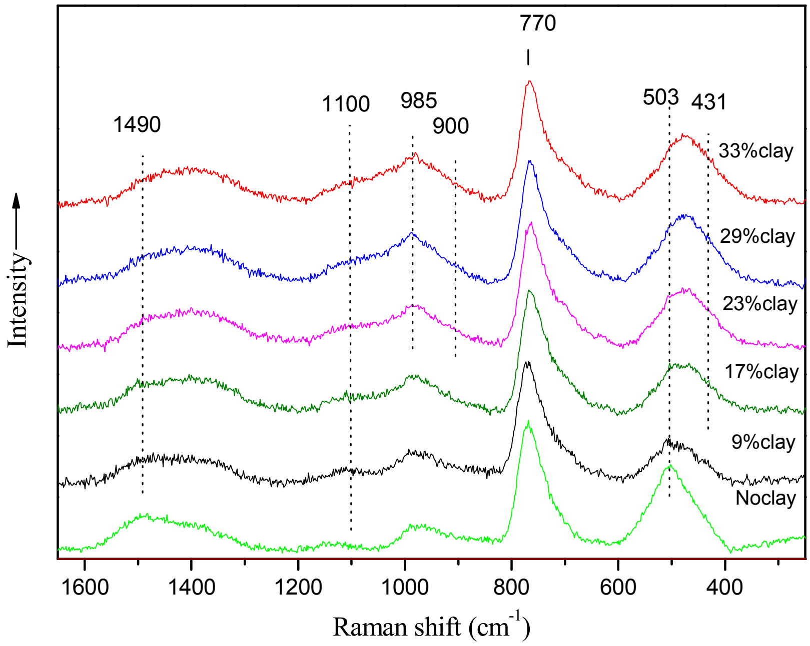

Figure 4: Raman spectra of the various glasses prepared using various clay additions.

Conclusions

Sodium borate glasses with the addition of montmorillonite have been prepared and characterized. The addition of montmorillonite increased the chemical durability of the glasses as well as the elastic properties also. From the structural characterization of the new glasses it can be concluded that the new superior properties are due to the decomposition of the clay and the creation of B-O-Si and Si-O-Al bonds in the glass network.

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