Effect of annealing on structure and properties of borates borosilicates glasses

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Glasses constitute a multivarious set of products whose properties are numerous. These properties depending strongly on the glass composition and treatments involved, specially thermal.

In our research work, we have prepared glasses within the sodo – borates systems " $Na_2O – B_2O$" and borosilicates" $Na_2O –B_2O_3 –SiO_2$".

In the framework of the first system, we have studied the effect of annealing on certain properties knowing that the use of transition metals ions constitutes one of the methods implemented in the structural studies.

Introduction :

The soda - borate glasses of a 15-30 mol % in alkalis oxides show certain anomalies with regard to their physical properties[1]. The structural changes that appear in boric glasses with the addition of alkaline oxides.

B_2O_3 network might be modified additions in two ways[2]**:**

- Non bridging oxygen's formation or
- Tetrahedral boron formation.

Different structures should lead to different trends in properties.

The annealing of glasses and the addition of B_2O_3 cause to the increase the structural network's rigidity by thus enhancing several properties, in particular the chemical and thermal durability.

Experimental part :

Glasses from chemical composition in the system $Na_2O – B_2O_3$ were prepared from mixing Na_2CO_3 soda ash with HBO_3 boric acid. Five different batches were chosen: the first being pure (20 mol. % of Na_2O 80 mol. % of B_2O_3) while we have added for the others small quantities of oxides (CaO) respectively in the order: 0.75, 0.77 , 1.55 and 3.90mol% designed as NB1.....NB5.The melting temperature being 1000°C, half of the simples obtained from each of the batch which has annealed at 250°C during one hour. The determination of bulk density , index refractive, Vickers Hardness (H_v) and chemical durability were made before and after annealing.

In the ternary system $Na_2O –B_2O_3 –SiO_2$, we have prepared five batches of chemical compositions following table N°1.

We have used a local sand (sand from the Chlef region - ALGERIA) as the source of SiO_2 at a granulometry of 0.1mm.

Melting temperatures range from 1550 to 1560°C.

In order to observe the influence of boric oxide. we have determined some properties through theoretical calculations on the basis of additivity formulas [3] and others through practical tests.

Table 1. Chemical compositions (mol. %) borate glasses **(NB)** elaborated**.**

Composition(%) / Variant	Na_2O	B_2O_3	CuO
NB1	20.00	80.00	-
NB2	19.97	79.95	0.075
NB3	19.84	79.38	0.77
NB4	19.68	78.77	1.55
NB5	19.21	76.88	3.90

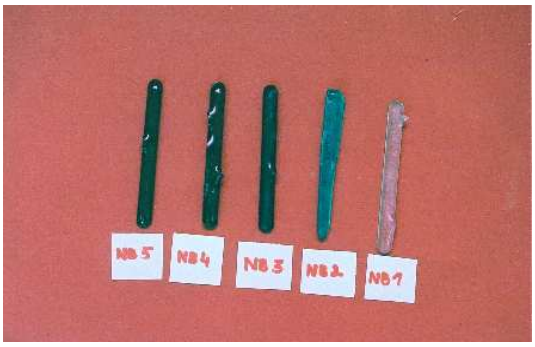


Figure 1. Aspect of samples glasses (NB) elaborated

Colours observed on NB samples, copper dumped (fig. 1) depend primarily on the electronic configuration of ions colouring elements (Cu) and consequently on the nature of element as well as on environment (oxygen's ions). [2,4]

system's Na_2O –$4B_2O_3$

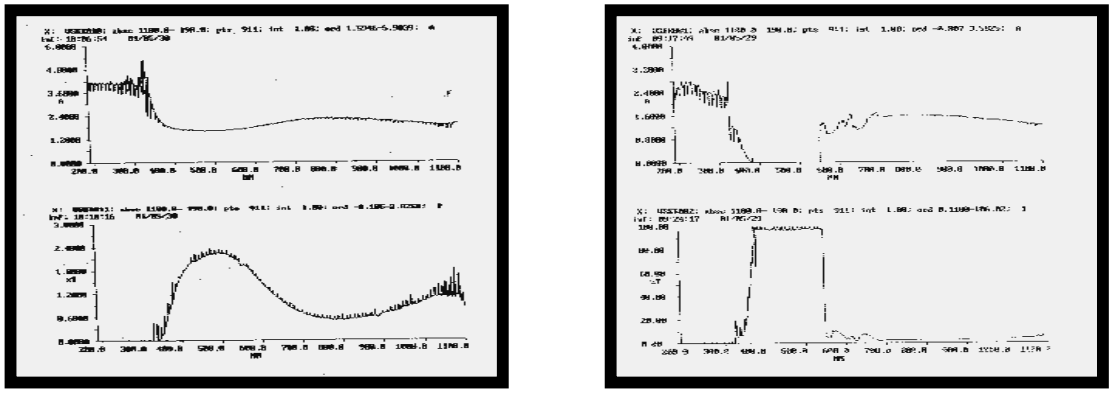
Diffraction RX

Two spectrums RX of sample NB1 before and after annealing have almost shape (with the existence of a few picks due probably to bad cooling and impurities) , but the spectrum after heating holds to a lesses position and intensity than that before heating. The annealing thermal treatment has affected the structure of a soda borate glass by the redistribution of structural units hence partial alteration of defaults and the reinforcement of structure.

Optical spectroscopy:

The absorption spectrum s of NB2 sample after annealing show some absorption bands between 300 and 400nm characteristics of tetrahedral coordination of ion Cu^{2+} while after annealing the absorption band displayed to 400 and 600nm with an decrease in intensity.

The absorption band positions due to octahedral coordination of ion Cu^{2+}in the ligand $[Cu(H_2O)]^{2+}$ [4]**.** Thus , the annealing thermal treatment has affected the coordination of ion Cu^{2+} to which it was converted from tetrahedral to octahedral coordination.



a) b)

Figure 3.Absorption spectrums of NB2 ; (6mm thick.)

a) without annealing

b) after annealing

Properties of glasses** (NB) **elaborated

Figures 4,5, 6 and 7 illustrate measured results before and after annealing of (NB) samples.

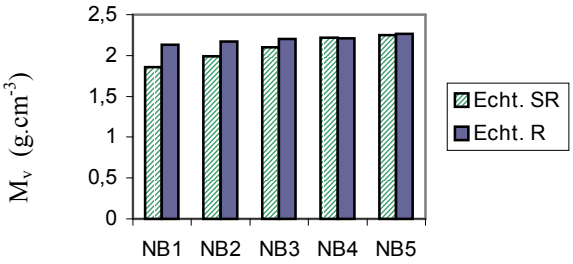


Figure 4. Bulk density (NB)

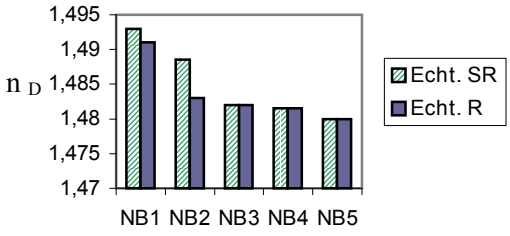


Figure 5. Refractive Index (NB)

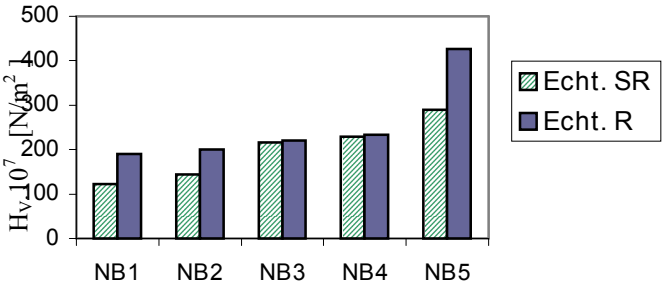
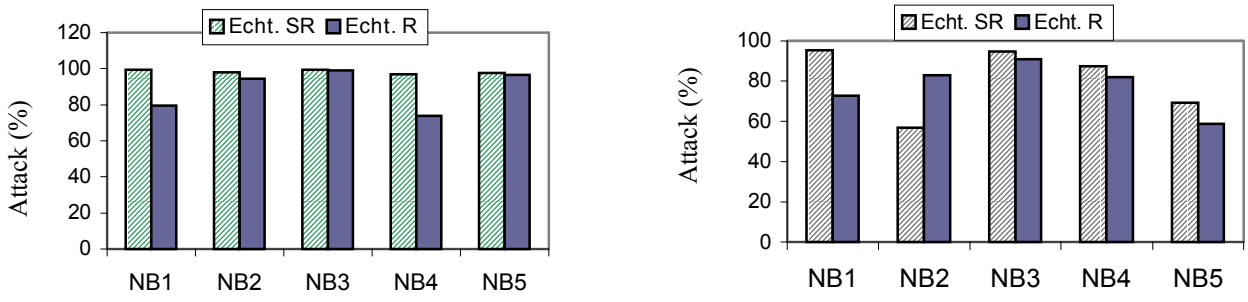


Figure 6. Microhardness " H_V" (NB)



a) b)

Figure 7. Chemical durability during 3h ;

a- acid medium

b- alkaline medium

Experiment results of thermal expansion

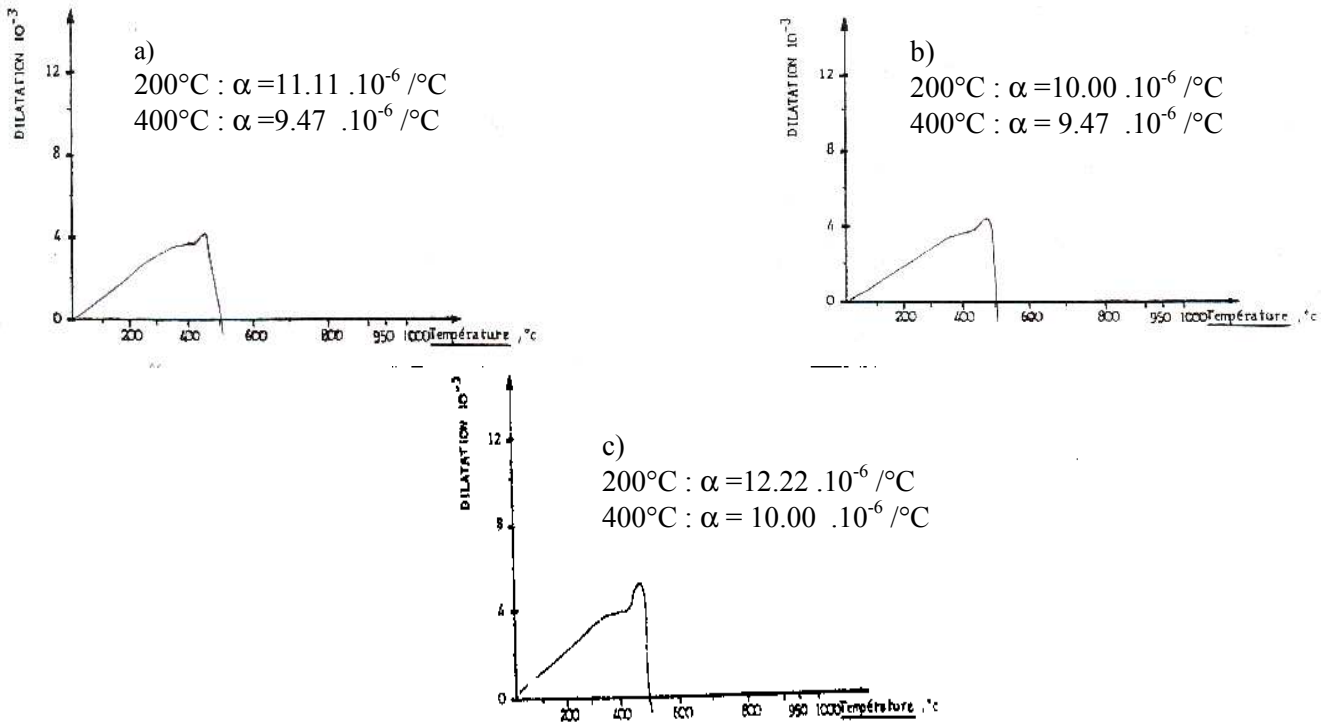


Figure 7: Curves of de thermal expansion coefficient of annealed samples (NB)

a- sample NB1 b- sample NB2
c-sample NB3

Interpretation :

system's Na_2O –$4B_2O_3$ doped with copper

Following tests results; the properties of samples are better after annealing.
The density of samples after annealing increases, the structure being more compact, a fact which affects also the refractive index through the diminution of structural imperfections generating the diminution of the refractive index .
Annealed samples present high microhardness due to structural reinforcement of defects constraints.
The chemical reaction was less intense for annealed samples but remains, whatsoever, important given the nature of the bonds of soda – borate glasses elaborated.[5]
(Fig.7).The reaction through acid was very high, so there was a substitution of ions H^+ of acid by modifiers ions, then reaction through water and finally by a basic is not a strong as the first reaction(OH^-).
The consolidation of the structure after annealing has increased the chemical durability.
The thermal expansion's coefficient "α" decrease of $11.11.10^{-6}$/ °C to $10.00.10^{-6}$/ °C in the intervalle of temperature [0 – 200°C] for the sample SN3. I contrast,the supplementaly addition of CuO to the system leads increasing of "α" in the range [0 – 400°C] due to formation of no bridging oxygens.

System's Na_2O –B_2O_3 –SiO_2

Table 2. Chemical compositions (mol. %) borosilicate glasses elaborated**.**

composition % / Variants	SiO_2	Na_2O	B_2O_3
SNB1	82.76	17.24	-
SNB2	82.76	13.80	3.44
SNB3	82.76	12.93	4.31
SNB4	82.76	11.50	5.74
SNB5	82.76	3.44	13.80

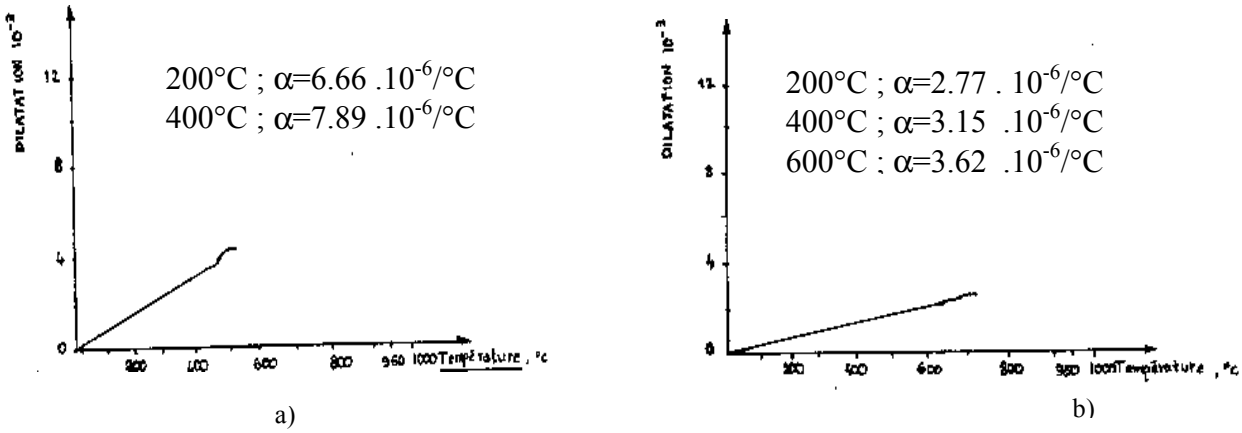


Figure 9. Thermal expansion: a) sample SN1, b) sample SN5

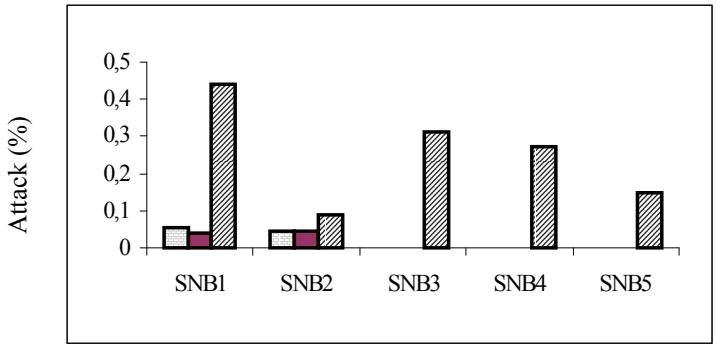


Figure 10. Chemical durability (SNB) after 3 h

Intepretation:

System's Na_2O –B_2O_3 –SiO_2

For samples elaborated in ternary system Na_2O –B_2O_3 –SiO_2, we have noticed that with the substitution of Na_2O by B_2O_3, some properties have been enhanced.
The thermal expansion resistance coefficient has decreased while increasing thermal shock.
Densities, indices refractive and averages dispersions have diminished.

The thermal conductivity has increased. In contrast calorific capacity has decreased.

The introduction of B_2O_3 to Na_2O – SiO_2 glasses(table 2) leads to the formation of bridging oxygen's and of $[BO_3]$ triangles and $[BO_4]$ tetrahedral.
As a results, the connectivity of structural network of borosilicate glass increases and implies:

- the diminution of linear thermal expansion coefficient (see Fig. 9 b)
- the index refractive, electrical permittivity and ion polarisibility Na^+ decrease.

The increase of structure's rigidity with the addition of B_2O_3 enhanced the mechanical strength and elastic properties as well as microhardness (Fig.6).
In spite of existence of $[BO_4]$ tetrahedral in the network vitreous, the superficial stress decrease due to the presence of $[BO_3]$groups on the surface**.**
The water and acid attack is weak , and can be observed only for samples (SNB1) and (SNB5) (see Fig.10), the reaction between ion H^+ and the 'acid' network can be negliged because the components are so strongly inserted that practically no possibility of migration in the network could exist.
The substitution of Na_2O by B_2O_3 leads augmentation of chemical durability , but the attack by alkalis solutions is determined by another behaviour, OH^+ ion reveals to be determinant and the disrupt of bond's network is noticed.

Conclusion :

Annealing effect on soda- borate glass doped with copper under softening point consists in the partial removing of structural defects and the of redistribution of groups in away that BO_3 decrease favour of BO_4 and the Cu^{2+} ions to octahedral coordination [6]**.**
In the composition of borosilicate glass, the substitution of Na_2O by B_2O_3 leads to the structural reinforcement and thus to enhancing of mechanical, thermal properties and chemical durability.

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Keys words
Alkaline - borate, alkaline - silica- borate, annealing, boric oxide, glass