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ANNEALING EFFECT ON COPPER-DOPED SODIUM BORATE GLASSES ($Na_2O.4B_2O_3$)

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The annealing effect of an alkali borate type glass below its softening point was investigated according to the Na_2O-B_2O_3 binary system. The samples were doped by introducing different amounts of copper oxide (CuO). The properties of elaborate glasses before and after annealing were studied. X-ray diffraction (XRD) as well as optical and infrared spectroscopy were used in this study. The results obtained show that annealing, that is, a heat treatment process, affects the structure of this type of glass by redistributing its structural units and partially correcting any defects, thereby reinforcing the structure. It was noticed that the BO_3 units were reformed while the number of BO_4 ones decreased, leading to an increase in the coefficient of thermal expansion, a decrease in both the refractive index and optical dispersion, the weakening of mechanical properties as well as a reduction in thermal conductivity and electric permittivity.

Keywords: alkali borate glass; sodium borate glass; annealing heat treatment; copper oxide; X-ray diffraction (XRD); optical spectroscopy and infrared spectroscopy

1. Introduction

Although types of glass containing the usual network modifiers are usually completely colorless in the visible region of the spectrum, this is not the case if they also contain elements from the transition metals; Cu, Ti, V, Cr, Mn, Fe, Co and Ni being the most important [1]-[3]. Regarding these elements, the excited state of electrons changes as a result of the absorption of electromagnetic radiation, even when exposed to low-energy light, so coloration of the glass in the visible range occurs. The observed color depends firstly on the electronic configuration and, therefore, on the nature of the element as well as its environment, that is, the proximity of oxygen ions.

Among the theories that explain this phenomenon of staining, the Ligand Field Theory by Hartmann predicts that the coloring of glass by the "3d" transition metals is due to electronic transitions between the degenerate energy levels of the electrons orbiting free ions in the absence of an electromagnetic field. The "3d" electronic levels are identical in energy, but when a transition metal ion is surrounded by a few anions called "ligands", the interaction between the electric fields causes some perturbations in the energy levels whose amplitudes are a function of the electromagnetic fields as well as the number and geometric arrangement of the neighboring anions [4]. The number of different levels formed is a function of the electronic configuration and coordination number of the cation.

The absorption of photons as a result of electronic transitions between the "3d" levels gives rise to coloration of the glass in the visible spectrum. Given that most metal ions of "3d" electronic transitions occur as a result of tetrahedral or octahedral coordination in the oxide glass, the coordination number will change as a result of differences in energy, depending on the number of "3d" electrons present. It is also evident that the color is affected by the concentration of the colored cation: as absorption by the coloring species increases, the effects of changes in the network of ions that are formed or modified are due to alterations to the distance between the bands as well as the electrostatic attraction between the coloring ions and the ligands surrounding them [5]-[12].

Industrially, glass is always manufactured by annealing glasses, which is important and necessary to eliminate thermal stress. In this work, the annealing effect of an alkali borate type glass below its softening point was studied according to the Na_2O-B_2O_3 binary system [1, 10-16]. Doping of the samples was achieved by introducing different amounts of copper oxide (CuO). The properties of elaborate types of glass before and after annealing were studied. X-ray diffraction (XRD) as well as optical and infrared spectroscopy were used in this study.

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Table 1. Chemical compositions of the variants

Samples	Composition [mol%]		
	Na_2O	B_2O_3	CuO
NB1	20.00	80.00	-
NB2	19.97	79.95	0.075
NB3	19.84	79.38	0.770
NB4	19.68	78.77	1.550
NB5	19.21	76.88	3.900

2. Experimental

2.1. Preparation of the studied samples of glass

A mixture of sodium carbonate (Na_2CO_3), boric acid (H_3BO_3) and pure copper oxide (CuO) was used. Five variants (NB1 to NB5) were selected according to *Table 1*. Well-homogenized mixtures of raw materials were slowly heated to 675 °C for three hours, before increasing the temperature to and maintaining it at 1000 °C for one hour [17]-[19]. The fusions were made in air in stainless steel molds heated to 250 °C.

2.2. Test methods

Differential thermal analysis (DTA) and thermogravimetric analysis

The piece of apparatus used was a NETZSCH STA 449C Jupiter simultaneous thermal analyzer, which can measure the differential variations in temperatures as well as changes in weight and enthalpy. It works in a high-temperature furnace with protective tubing and in the presence of Al_2O_3 within the temperature range of 25 to 1550 °C. A Pt:Pt-Rh thermocouple was used. The glass transition (*Tg*) and crystallization temperatures (*Tc*) were determined from the second endothermic peak and first exothermic peak of the DTA curve.

Dilatometric analysis

The expansion curves of the samples were determined using a NETZSCH DIL 402C dilatometer (URMPE - University of Boumerdes, Algeria) at an average heating rate of 5 $Kmin^{-1}$. The samples were rectangular in shape, 8 mm wide and 20-25 mm long. *Tg* was determined from the expansion curve by calculating the intercept, whereas the softening points (*Ts*) were determined to be the maximum temperature of the expansion curve.

Density and molar volume measurements

The densities were determined using the Archimedes' method by immersing the samples in liquid xylene. The relative error in these measurements was about ± 0.03 gcm^{-3} and the molar volume (*Vm*) was calculated from the molecular weight (*M*) and density (δ) according to the following equation:

$$V_m = M/\delta \qquad (1)$$

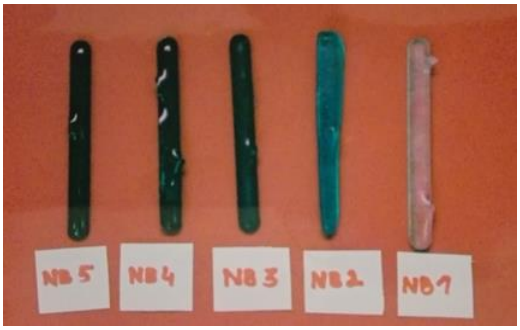

Figure 1. Appearance of the elaborate samples

3. Results and discussion

3.1. Appearance of the samples

The elaborate types of glass are shown in *Figure 1*, where their blue color becomes darker and darker each time CuO is added.

3.2. Theoretical calculations of properties

The different components make a definite contribution to the effect of certain properties and the structure of types of glass. Therefore, from their composition, these properties can be calculated by using additive formulae. However, this conclusion is only valid within a restricted range of compositions because how the ions interact with each other must be taken into account [18]-[21].

According to Appen [18], within the temperature range of 20 - 400 °C between the NB1 and NB2 variants, a decrease in the coefficient of expansion (α) was observed, probably due to the increase in BO_4 following the addition of small quantities of CuO; the non-bridging oxygen atoms of B_2O_3 in the binary glass Na_2O-B_2O_3 binded with those reintroduced by CuO to form bridging oxygen atoms (BO_4), hence the strengthening of the structure (conversion of BO_3 units into BO_4). However, regarding the NB3 variant, since α increases in a progressive manner, it is assumed that the introduction of more CuO (greater than 0.77 mol%) increases the coefficient between 20 and 400 °C, leading to the reformation of non-bridging oxygen atoms.

The densities of silica glass and boric glass measured show that the [SiO_4] tetrahedra bonded to each other or the [BO_3] trihedra predominantly contain large voids, which influence the density of binary glasses of alkali silicates. If an alkali oxide is introduced into silica glass, the added oxygen ion contributes to the stacking of the oxygen ions, while the cations fill the empty spaces. As a result, the total space filled becomes larger and the density increases [1]-[3] as opposed to alkali borate types of glass where their density decreases as modifiers are added [22]-[23].

However, in our case, an increase in density is observed as the Na_2O content decreases as a result of the increase in the CuO content. The Cu^{2+} ion, which has a relatively large atomic mass, was inserted between boron tetrahedra or trihedra by filling progressively more voids,

Table 2. Calculated properties of elaborate types of glass

Samples	α (10^{-6}/K)	δ (g/cm^3)	n_D	d	E (kbar)	G (kbar)	μ	σ_t (MN/m^2)	σ_c (MN/m^2)	λ_c (W/mK)	ε
NB1	6.336	1.998	1.4940	0.00812	331.90	155.00	0.3107	56.81	739.84	0.8778	7.92
NB2	6.335	2.000	1.4928	0.00810	331.58	154.39	0.3104	56.76	739.20	0.8780	7.91
NB3	6.346	2.016	1.4823	0.00800	328.93	153.32	0.3079	56.29	733.14	0.8779	7.85
NB4	6.353	2.035	1.4708	0.00790	325.89	152.12	0.3051	55.78	726.45	0.8778	7.79
NB5	6.381	2.092	1.4356	0.00770	316.91	148.48	0.2967	54.24	706.37	0.8778	7.61

thereby increasing the mass per unit volume of the samples. The properties of the studied types of glass are summarized in *Table 2*.

The refractive index (n_D) increases in proportion to the content of alkali oxides because of the polarizability of the ions, namely as the polarizability increases, so does the refractive index. In our case, a remarkable decrease in the refractive index as the Na_2O content reduced and the CuO content increased was observed. The addition of Cu^{2+} ions contributes significantly to the decrease in the refractive index, because it becomes less polarizable and allows the glass to be colored by the effect of ligand fields.

The average degree of dispersion (d) also decreases as CuO is added for the same reasons that resulted in the refractive index decreasing.

The relatively open structure of B_2O_3 glass explains its low modulus of elasticity (E) of only 175 kbar. As the Na_2O content in binary borate glasses increases, their structure becomes more rigid and the modulus of elasticity increases rapidly. According to Narsimha [5], at 28.5 mol% of Na_2O, the modulus of elasticity has already risen to 565 kbar. As the Na_2O content decreases, a reduction in the modulus of elasticity is observed. In terms of the shear modulus (G), changes in this parameter as a function of its composition are similar to those of the modulus of elasticity albeit smaller.

Since the values of Poisson's ration (μ) measured are relatively high, a large transverse contraction occurred, however, by adding CuO, the values gradually decreased.

Given that the mechanical strength of the samples was low, their structures are not sufficiently rigid. As non-bridging oxygen atoms were added, both the mechanical tensile and compressive strengths (σ_t and σ_c) decreased.

The thermal conductivity (λ_c) was calculated, the values of which did not change much according to the variants studied ($\lambda_c \approx 0.877$ W/mK). This value is larger than that for silicate glasses ($\lambda_c = 0.850$ W/mK) [22]-[24]. By adding CuO, the thermal conductivity progressively decreased as Cu^{2+} ions impede the transfer of heat inside the glass.

This permittivity effect is caused by the fact that shifts in charge occur in the presence of an electric field. The electronic envelope in an ion may be deformed, the ions themselves may move slightly or they may change sites. The first possibility is all the more important as the polarizability of the ion under consideration is greater. Therefore, the permittivity depends on the refractive index, which is also significantly influenced by the polarizability. At very high frequencies in glass, the oxygen ion is most easily polarized [7]. As has been seen with the reduction in the refractive index as a function of a decrease in the Na_2O content, the same phenomenon is observed by decreasing the electric permittivity (ε).

3.3. Annealing effect

Certain properties of the samples were determined before and after annealing. Annealed samples were marked as NB1-A, NB2-A, NB3-A, NB4-A, NB5-A; their non-annealed counterparts were marked as NB1-NA, NB2-NA, NB3-NA, NB4-NA, NB5-NA.

a) Practical determination of density

The measured densities are given in *Table 3*. The densities of the samples that were and were not annealed are different, namely annealed samples were denser than non-annealed ones. Since annealing influenced the structure of the types of glasses, the change in their densities was due to structural changes [25]-[28].

It has been shown that the structure of glass after annealing is more compact than beforehand. To confirm this observation, it is necessary to structurally analyze

Table 3. The measured densities of glass samples

Samples	δ (g/cm^3)
NB1-NA	1.857
NB2-NA	1.988
NB3-NA	2.100
NB4-NA	2.219
NB5-NA	2.250
NB1-A	2.134
NB2-A	2.170
NB3-A	2.200
NB4-A	2.220
NB5-A	2.261

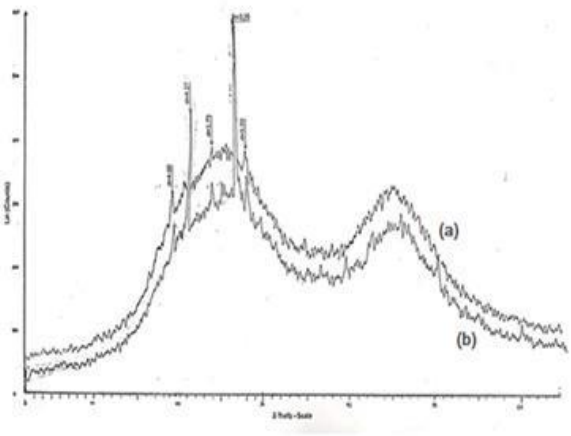

Figure 2. Diffraction spectra (XRD) of the NB1 samples (a): before annealing and (b): after annealing

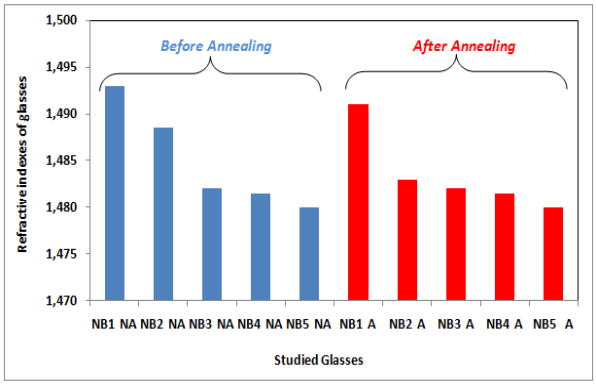

Figure 3. Refractive indices of the studied samples of glass before and after annealing

their structures before and after annealing by, for example, XRD (*Figure 2*). As defects in their structure before annealing were corrected, the densities of the annealed samples increased [27].

b) Structural diffraction analysis (XRD)

The diffraction of sample NB1 before annealing (*Figure 2a*) suggests an amorphous structure, while that after annealing (*Figure 2b*) exhibits some peaks (impurities) but the structure remains unchanged.

If the spectra of NB1 samples before annealing (a) and after annealing (b) are compared, it is observed that the last diffraction pattern, which can almost be superimposed on the first one, is less intense.

Therefore, annealing affects the structure of sodium borate glass by redistributing its structural units, partially correcting any defects and reinforcing its structure.

c) Practical determination of the refractive index

The refractive indices measured for the different types of glass are presented in *Table 4*. The refractive index always reduces as the amount of alkali oxides decreases and CuO is added. Although the refractive indices of samples NB1 and NB2 decrease after annealing, those of NB3 remain the same before and after annealing. As a result, the structure influences the refractive index of the NB2 sample which contains little CuO and variant NB1 which does not contain any CuO because annealing decreases the number of defects in their structures (*Figure 3*).

For samples containing high levels of CuO (0.77, 1.55 and 3.90 mol%), annealing has no influence on n_D, which remains constant for each variant.

d) Practical determination of Vickers microhardness (HV)

Hardness is a property that characterizes the strength of the glass surface vis-à-vis its concentrated mechanical load, which is referred to as microhardness. The microhardnesses of the samples were measured using an Equotip durometer. According to our results (*Table 5*), it was observed that the microhardness increased as the Na_2O content (network modifiers) decreased and CuO was added. The annealed samples represent a strong degree of pickup, which is explained by the reinforcement of their structures and the release of structural stress.

e) Determination of chemical attack

The etching test is based on the determination of the mass loss of the glass samples before and after three hours of chemical attack in chemical solutions (acids, bases and

Table 4. Measured refractive indices of the samples of glass

Samples	n_D
NB1-NA	1.4930
NB2-NA	1.4885
NB3-NA	1.4820
NB4-NA	1.4815
NB5-NA	1.4800
NB1-A	1.4910
NB2-A	1.4830
NB3-A	1.4820
NB4-A	1.4815
NB5-A	1.4800

Table 5. Vickers microhardness of the measured samples

Samples	$HV.10^7$ (N/m^2)
NB1-NA	122.2
NB2-NA	144.0
NB3-NA	216.0
NB4-NA	229.0
NB5-NA	289.6
NB1-A	190.0
NB2-A	200.0
NB3-A	221.0
NB4-A	233.0
NB5-A	426.2

Table 6. The results of samples in different chemical environments

Samples	neutral solution (distilled water)			acid solution (HCl)			basic solution ($NaOH+Na_2CO_3$)		
	M0 (g)	*M1* (g)	$\frac{M1-M0}{M0}$ (%)	*M0* (g)	*M1* (g)	$\frac{M1-M0}{M0}$ (%)	*M0* (g)	*M1* (g)	$\frac{M1-M0}{M0}$ (%)
NB1-NA	2.583	0.010	99.61	1.808	0.01	99.44	2.076	0.102	95.08
NB2-NA	2.593	0.254	90.20	0.536	0.01	98.13	4.313	1.861	56.85
NB3-NA	3.680	0.549	85.08	1.670	0.01	99.40	3.592	0.199	94.45
NB4-NA	4.429	1.246	71.86	3.090	0.009	96.99	3.172	0.402	87.32
NB5-NA	2.553	0.965	62.20	4.138	0.009	97.70	1.243	0.382	69.26
NB1-A	3.649	0.481	86.81	1.117	0.229	79.49	2.040	0.558	72.64
NB2-A	1.908	0.450	76.41	3.273	0.179	94.53	1.586	0.272	82.84
NB3-A	3.259	0.819	74.86	1.222	0.01	99.18	3.772	0.350	90.72
NB4-A	3.345	1.078	67.77	6.334	1.657	73.83	1.348	0.242	82.04
NB5-A	2.150	1.118	48.00	1.567	0.053	96.61	3.240	1.337	58.73

neutral ones). In the three environments, since it was initially observed that the chemical attack was less severe for the annealed samples, annealing also improved their chemical resistance. In light of the values recorded (*Table 6*), these samples of glass are unstable in the aqueous solutions used; the reactions that take place are complex and depend on the nature (composition) of the glass studied. Investigation of the IR bands leads to an explanation for this phenomenon. Generally, borate glasses are soluble in chemical solutions because of their weak structure composed of borate units. The chemical resistance of these samples of glass and the density of their structure increase by adding CuO compared to their basic chemical compositions without CuO [25]-[26].

f) Optical spectroscopy of the samples (NB)

The absorption spectra of samples NB1 and NB2 were recorded before and after annealing (*Figure 4*).

Regarding sample NB1-NA, some absorption bands of low intensity were observed and after sample NB1-A had been annealed, their intensities became even lower. Annealing is believed to have reduced structural defects within the glass, thereby increasing transmission and decreasing the absorption of light.

For sample NB2, to which CuO was added, the sample turned light blue in color due to the existence of divalent Cu^{2+} ions resulting from the effect of ligand fields.

By adding CuO, its color became even darker (*Figure 1*). In the absorption spectrum of the NB2-NA sample, absorption bands between 300 and 400 nm were observed, which are characteristic of the tetrahedral coordination of Cu^2. However, after annealing (NB2-A), the absorption band was observed between 600 and 700 nm, moreover, its intensity decreased [27]. The positions of this band are characteristic of Cu^{2+} ions with octahedral coordination in the complex $[Cu(H_2O)]^{2+}$ [22]. Therefore, annealing influences the coordination of Cu^{2+} ions which are transformed from tetrahedral to octahedral coordination.

Formation of the octahedral complex is indicated by the polarization of the transition metal ion bonded to the oxygen atom. This effect is weak for BO_3 (due to the counter-polar effect of the two bridging atoms bound to bridging oxygen atoms) and strong for BO_4 (or the bridging oxygen atoms are more weakly counter-polarized), the latter favors octahedral coordination.

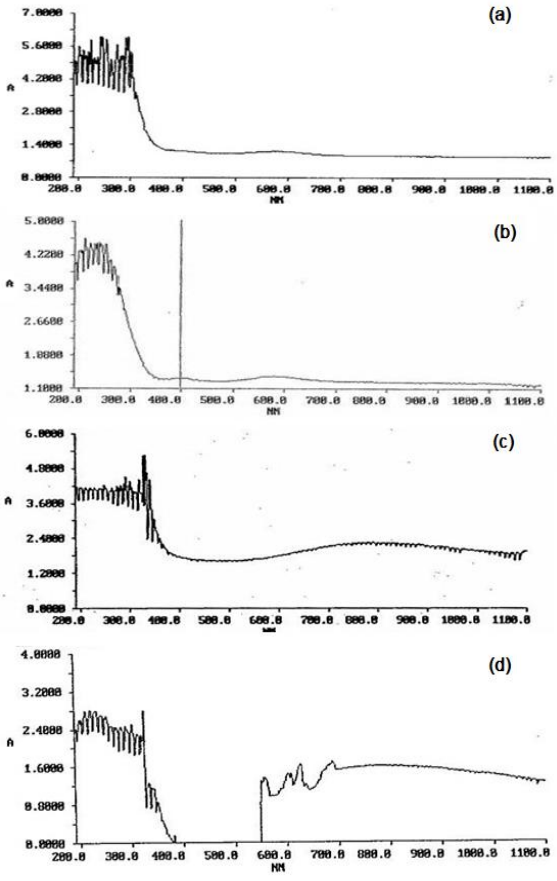

Figure 4. Absorption spectra of 6mm-thick samples
(a) NB1-NA, (b) NB1-A,
(c) NB2-NA, (d) NB2-A

g) Infrared transmission

The absorption of light in the ultraviolet and visible regions of the spectrum is due to electronic transitions, while some low-energy electronic transitions are observed in the infrared region of the spectrum due to vibrational transitions. The frequency (ν) of a vibrational absorption in a diatomic molecule is given by the following formula [16-17,28]:

$$\nu = \left(\frac{1}{2\pi}\right)\sqrt{\frac{F}{\mu}} \qquad (2)$$

where F denotes the binding constant and μ the reduced mass of the molecule, which is calculated by the formula below:

$$\mu = \frac{m1 \cdot m2}{m1 + m2} \qquad (3)$$

where m_1 and m_2 denote the atomic masses of the two atoms which form the molecule.

Due to the complexity of the infrared spectra, which is related to the great diversity of structural groupings present in the borate glasses, their interpretation is difficult.

The IR spectra of samples NB1 and NB2 (without annealing) are shown in *Figure 5*, the interpretations of which are based on data from the literature of some types of glass and borate phases [19-20,28]. It is known that the absorption bands in the vibrational spectrum of boric glass fall between 1270 and 700 cm^{-1} due to the BO_3 groups which form the boroxol groups. The vibrational modes of the borate network in binary M_2O (MO) - B_2O glasses are mainly active in the following three regions of the infrared spectrum:

- 1500-1200 cm^{-1} (B-O vibrational band of trihedral BO_3 units)
- 1200-850 cm^{-1} (B-O vibrational band of tetrahedral BO_4 units)
- 800-600 cm^{-1} (asymmetric vibrational band of borates)

BO_3 and BO_4 form structural units such as diborate, triborate and pentaborate, in which the ratio of B3 to B4 varies.

Absorption in the high frequency regions of the spectrum is given by the vibrational band of the hydroxyl groups forming the hydrogen bonds. The bands between 3700 and 3200 cm^{-1} are attributed to the vibrations of the O-H linking groups which prove the presence of dissolved water in these glasses. According to the IR transmittance curves of the samples, almost the same band at about 3443.09 cm^{-1} was observed, which is characteristic of the O-H bond. When CuO was introduced, a change in intensity was observed. It can be concluded that the addition of CuO to the network seems to progressively transform rigid tetrahedra (BO_4) into more flexible trihedra (BO_2O-) [27]-[28].

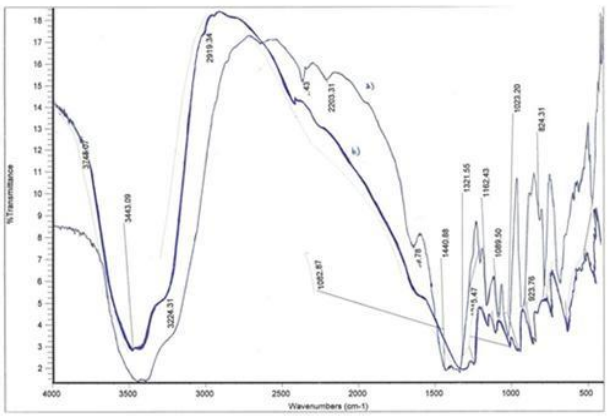

Figure 5. IR transmission spectrum of (a) NB1-NA and (b) NB2-NA

4. Conclusion

By adding small amounts of CuO (0.075 mol%) to a sodium borate glass, the BO_3 units were transformed into BO_4 ones. However, following the addition of 0.770 mol% of CuO, it was noticed that the BO_3 units reformed and the quantity of BO_4 ones decreased, leading to an increase in the coefficient of thermal expansion, a decrease in the refractive index and optical dispersion as well as a reduction in the mechanical properties, thermal conductivity and electric permittivity. In contrast, an increase in density, microhardness and chemical resistance was observed by adding CuO. The oxygen added following the addition of CuO became a non-bridging oxygen atom and created trihedral BO_3 units, which released its glassy structure. However, the insertion of Cu atoms in the structure increased the density, microhardness and resistance to chemical attack of the glasses. It can be concluded that the addition of CuO to the network seems to progressively transform rigid tetrahedra (BO_4) into more flexible trihedra (BO_2O-) with non-bridging oxygen atoms. This local structural rearrangement favors the insertion of copper atoms.

The annealing effect of-these copper-doped alkali-borate glasses was also studied and it was found that annealing affects their structure by redistributing the structural units, partially correcting the defects and reinforcing it.

Nomenclature

α (10^{-6}/K)	coefficient of thermal expansion
δ (g/cm^3)	density
n_D	refractive index
d	optical dispersion
E (kbar)	modulus of longitudinal elasticity
G (kbar)	Shear modulus
μ	Poisson's ratio
σ_t (MN/m^2)	tensile strength
σ_c (MN/m^2)	compressive strength
λ_c (W/mK)	thermal conductivity
ε	electric permittivity

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