COLOR AND OPTICAL PROPERTIES OF CaO-Na_2O-SiO_2 GLASSES CONTAINING LOW AMOUNTS OF TRANSITION METAL OXIDES

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Abstract

The aim of this work is to study the color and optical properties of CaO-Na_2O-SiO_2glasses containing low amounts of transition metal oxides as TiO_2 and Cr_2O_3.Several compositions were prepared based on Algerian sand (S_T). A decrease of thermal expansion coefficients and an increase of glass transition temperatures as TiO_2 and Cr_2O_3content increase were noticed. Optical properties determined by UV-Visible spectroscopy reveal that the glass absorptions decrease with increasing TiO_2. Three new absorption bands around 350, 445 and 650 nm characteristic of Cr^{3+} and Cr^{6+} ions were also appeared on the spectra of the samples containing Cr_2O_3. The color parameters (L * a * b *) showed that the samples with TiO_2 were colorless and an improved of clarity was detected. A greenish color and a significant increase in Cr_2O_3 doped glasses b * parameter values is noticed.

Résumé

L'objectif de ce travail porte sur l'étude des propriétés optiques et colorimétriques des verres sodo-calciques renfermant des teneurs minimes en oxydes métalliques de transition tels que le TiO2 et le Cr_2O3. Plusieurs compositions ont été élaborées à base de sable quartzeux algérien (S_T). Les coefficients de l'expansion thermique diminuent au fur et à mesure que les quantités de TiO2 et le Cr_2O3 augmentent alors que les températures de transition vitreuses augmentent. Les propriétés optiques des verres déterminées par la spectroscopie optique montrent que l'absorption diminue à mesure que la quantité de TiO_2 augmente. Trois nouvelles bandes d'absorption sont apparues sur le spectre aux environs de 350, 445 et 650 nm caractéristiques des ions of Cr^{3+} et Cr^{6+} dans les verres renfermant Cr_2O3. Les paramètres de couleur (L*,a*,b*) des différents verres déterminés par spectrocolorométrie (CIE L*a*b*) montrent que les échantillons à base de TiO_2sont moins colorés ce qui conduit à l'augmentation du paramètre de clarté (L*> 88,7 %) alors que ceux contenant du Cr_2O3 sont teintés en vert et accusent une augmentation du paramètre b*.

Keywords: Color and optical properties, Soda-lime-silica glass, Sand, Thermal expansion, Transition metal oxides.

1- INTRODUCTION

Soda-lime-silica glasses are easily synthesizable, very homogeneous and the most important oxide glasses with a wide range of applications as flat glass, new electrical devices or biomaterials. This importance result from the material properties such as high stability towards crystallization, high potential for fiber drawing, refractive index and thermal expansion coefficient control by composition variation [1]. The addition of transition metal oxides even in small amounts plays an important role in improving the silicate glass properties such as optical absorption and fluorescence [2]. Therefore, great importance was devoted to these transition metal ions glass, in the last decades [3], giving birth to several applications in various areas such as in the field of optical and colored glasses [4, 5] as well as in advanced technologies such as lasers, solar energy converters and a number of electronic devices [6]. One of the most known transition metal oxides affecting the glasses properties is TiO_2. It is also one of the most encountered impurities in the glass raw materials. Usually, colorless soda-lime glasses are obtained with TiO_2 content lower than 0.05% in weight percent, while higher content generates yellowish colored glasses**.** TiO_2 addition oxide glasses, generally contributes to their structure stabilization and their properties improvement [7], for example, chemical durability, mechanical properties, electrical conductivity, etc. Even small amount of TiO_2 additions in the glass composition produce an increase in the refractive index and the density of the obtained glasses **[**7-10]. According to Gwinn et al. and Alberto et al. [9,10], the iron red-ox equilibrium is also affected by the titanium oxide presence, a phenomenon which also influence the glass coloration. Regarding the thermal behavior, a decrease of the thermal expansion coefficient is observed with increasing TiO_2 concentration [8, 11]. Several other properties such as softening temperature, Elastic modulus, Vickers hardness and viscosity depend on the TiO_2 content [12].

Chromium is also a major example of the transition metals that confers interesting optical and electrical properties to the glasses, making them thus intended for various applications [13]. Chromium ions dissolved even in small amounts colored glasses. They have a strong influence on optical transmission andon insulation degree of glasses [14]. Beyond the green coloration that it permits to bring to the industrial glasses (under Cr^{III} state), chromium offers important perspectives in the domain of the telecommunications (materials for amplification) and lasers, consequences of its luminescence properties [15].Chromium doped glasses properties are the result of the multiplicity of its red-ox states. Chromium with its electronic configuration $3d^5 4S^1$, on its external layer, has anoxidization degree capable to go from 0 to + VI. Nearly all degrees of oxidization are present in the glasses. Nevertheless, the III degrees and VI are the most current in silicate glasses [15]. Chromium ions in their oxidation state Cr^{3+} act as network modifier ions with CrO_6 as a structural unit. While under their Cr^{6+} form, they act as network former ions with their structural units CrO_4^{2-} [14].

In this study, five soda-lime silica glasses V_T, V_{T1}, V_{T2}, V_{C1} and V_{C2} were elaborated. V_{T0} corresponds to the glass obtained without $TiO_2$and Cr_2O_3 addition, $V_{T1}$and V_{C1} correspond to the glasses doped with 0.1 wt % of $TiO_2$and Cr_2O_3 respectively and V_{T2} and V_{C2} correspond to the glasses doped with 0.2 wt % of TiO_2 and Cr_2O_3 respectively.The silica source was Algerian sand (S_T) from Tebessa (East Algeria). The color and optical properties of the different composition of glasses were studied.

2- MATERIALS AND METHODS

2.1- Materials

The basic glasses composition is summarized in table 1.Mixture of 100 g of raw materials (Algerian sand, Na_2CO_3, $CaCO_3$, Na_2SO_4, dolomite and TiO_2) is placed in a platinum crucible in an electric furnace for a step of melting-refining at 1560 °C for 2 hours.

Table1: Sample raw materials (wt %)

Raw materials	Wt (%)
Sand	61.29-x
$CaCO_3$	14.36
Na_2CO_3	19.85
Na_2SO_4	0.5
$MgCa(CO_3)_2$	4
TiO_2 or Cr_2O_3	x = 0, 0.1 , 0.2

The experimental procedure of the obtained materials is presented in fig 1.

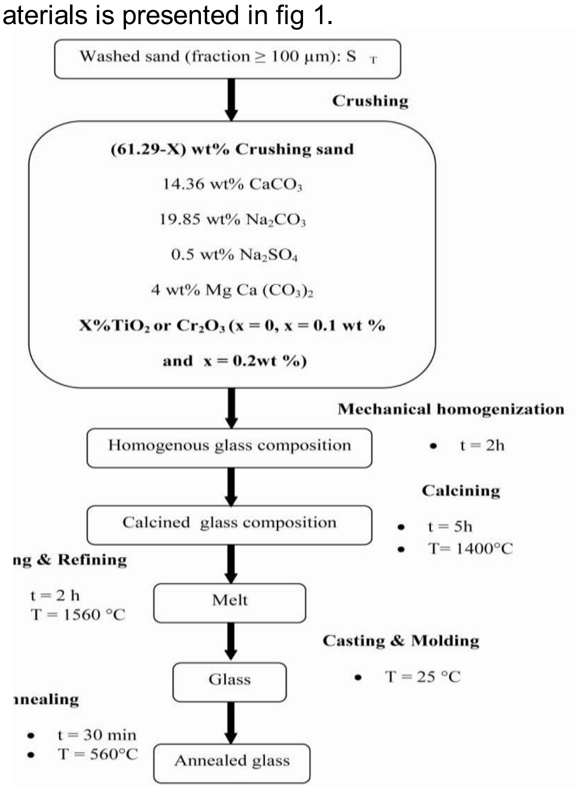

Fig.1: Diagram of the experimental procedure of the obtained glasses

The liquid is then poured in a stainless steel mold at ambient temperature, allowing a rapid cooling to room temperature and finally annealed at 560 °C for a period of 30 min. After glass elaboration, a mechanical preparation step is performed: cutting into test tubes, polishing (P400, P600, P1200, P2500, P40000 and with cerium oxide) and grinding until obtaining a powder with a fineness ≤ 0.63 mm.

2.2- Sand and glasses characterization

S_T Sand mineralogical composition was determined used an X-ray Panalytical X' Pert PRO diffractometer (Cu Kα, λ = 1,540598 Å, 2θ range 0-80°, 0.025 2θ step). The collected data are processed by Panalytical X' Pert Highscore software. The chemical composition of S_T Sand (Table 2) was carried out by X-ray fluorescence (PanalyticalPerl'X 3). The samples were prepared in the pellets form: 8 g of crushed sand with 4.5 ml of a compacted Elvacite resin. The dilatometric measurements were made by a horizontal dilatometer dual road model DIL402, Netzsch with a heating rate of 1 °C/min. The samples were in a prism form.The glass optical absorption spectra were realized with a double beam Perkin-Elmer 1050 spectrometer in transmission mode. It scans a range of wavelengths between 300 and 4000 nm. The samples were previously polished with Cerium oxide. The glass color analysis was carried out by an X-Rite spectrometer, model 962 S / N 000967 (USA), X-Rite ink formulation software Pinter Pro 5.11 working light D65.10°: White daylight, camera viewing angle 10°. The measurements were repeated three times for each composition and an average value was taken.

3- RESULTS AND DISCUSSION

3.1- Sand characterization

3.1.1- Mineralogical analysis

According to the fig 2, the quartz is the main mineralogical phase encountered. This confirms the siliceous nature of the sand.

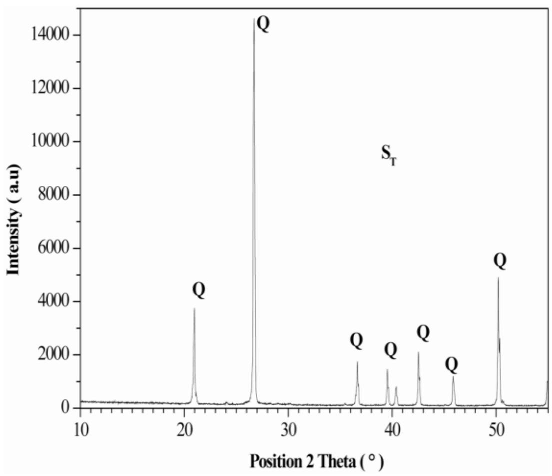

Fig.2: Diagram of X-Ray of the sand ST (Q: quartz)

3.1.2- Chemical composition

As summarized on Table 2, S_T is mostly composed by 98 wt % of SiO_2. However, TiO_2 is present in very low amount (0.07 wt %). S_T does not contains clay fractions since its loss on infusion is very low (L.O.I = 0.022wt %).

Table 2: Chemical composition of the raw material (Sand S_T)

Oxides	Wt (%)
SiO_2	98
Al_2O_3	0.88
K_2O	0.34
CaO	0.20
Fe_2O_3	0.12
TiO_2	0.07
Na_2O	0.05
MgO	0.05
P_2O_5	0.038
L.O.I	0.022

3.2- Properties of the obtained glasses

3.2.1- Dilatometric analysis

The curves representing the expansion behavior of the glasses V_{T0}, V_{T1}, V_{T2}, V_{C1} and V_{C2} are shown in Fig 3 The inflexion point of these curves corresponds to the glass transition temperature Tg, the maximum point is the dilatometric point Td while the thermal expansion coefficient α is also determined from these experimental curves.

A decrease of thermal expansion coefficient according to the TiO_2 and Cr_2O_3 addition is noticed (Table 3). This decrease is also proportional to the added amount and it is more observed with TiO_2 addition (8.2± 0.2 and 8.8± 0.2 10^{-6} $°C^{-1}$ for V_{T1} and V_{C1} respectively). Proportionality between the glass transition temperature and the TiO_2 and Cr_2O_3 amount is also found. This Tg increase is more noticed with Cr_2O_3 addition (574±2 and 580±2°C for V_{T1} and V_{C1} respectively). This proportionality suggests glass network reinforcing therefore its polymerization. A reduction followed by an increase of the dilatometric softening temperature is noted with the addition of 0.1 wt% and 0.2 wt% of TiO_2 or Cr_2O_3 respectively.

The thermal expansion coefficient decreases (Table 3) with TiO_2 and Cr_2O_3 addition due to the fact that the glass thermal expansion is controlled by the thermal vibrations amplitude asymmetry of the bonds in the glass.This vibration asymmetry decreases as the rigidity of the glass network increases [5, 14].Similar results concerning TiO_2 doped glasses were found by Meechoowas et al. [9],in their work devoted to the study of the soda-lime glasses with properties for possible use in glass-ceramics development.

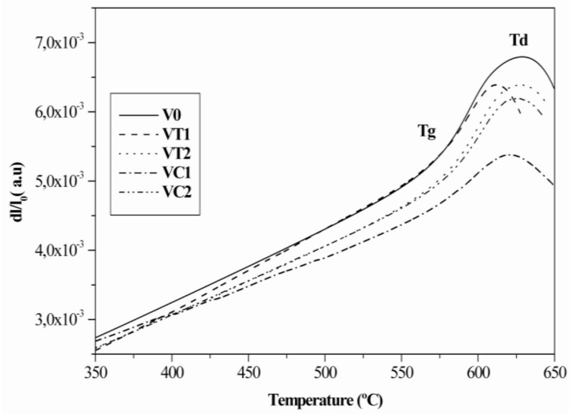

Fig.3: Dilatometric behavior of V0, VT1, VT2, VC1 and VC2 glasses

Table 3: Thermal expansion coefficients, Tg, Td V_0, V_{T1}, V_{T2}, V_{C1} and V_{C2} samples

Glasses	T_g(°C)	T_d (°C)	α (50-350°C) (10^{-6} °C^{-1})
V_0	573 ±2	629 ±2	8.9 ±0.2
V_{T1}	574 ±2	612 ±2	8.2 ±0.2
V_{T2}	585 ±2	628 ±2	8.3 ±0.2
V_{C1}	580±2	621±2	8.8±0.2
V_{C2}	587±2	625±2	8.5±0.2

Glass transition temperaturesincrease with TiO_2 addition, suggesting also some structural changes in the glass network. Hence the idea that increasing Tg glasses doped with titanium oxide can also be attributed to the strengthening of the glass network by titanium addition[16].Similar results were also observed by Meechoowas et al.[9].The strengthening of the glass network after adding small Cr_2O_3 amount is also to consider. Chromium ion can act as network former ion,under its Cr^{6+} form with CrO_4^{2-} as structural units [14].

3.2.2. UV-visible – IR studies

As it is shownin fig4, the three samples exhibitordinary glasses absorbance values.There is also evidence that the TiO_2addition decreases slightly this absorption. However V_{T1}absorption is the most decreased compared to V_{T0} and V_{T2} absorptions. The glasses containing titanium dioxide optical absorption spectra show strong ultraviolet cutoff at approximately 310 nm, thus showing an infinite ultraviolet absorption and a zero emission. Similar results were obtained by Kumar[16] in his study. The characteristic absorption bands of the Ti^{3+} ions at 480-510 nm, 570 and 680 nm are not detected.This result is expected as under ordinary melting conditions, it is difficult to obtain reduced Ti^{3+}ions in soda-lime silicate glasses[3].However the appearance of a small peak around 380 nm, characteristic of Fe^{3+} ions, following the TiO_2 addition is noticed. According to the studies of the iron doped glasses by Rus et al.[17] and Kukkadapu et al.[18], ferric ions present absorption bands in the range 325-450 nm and 350-500 nm respectively.

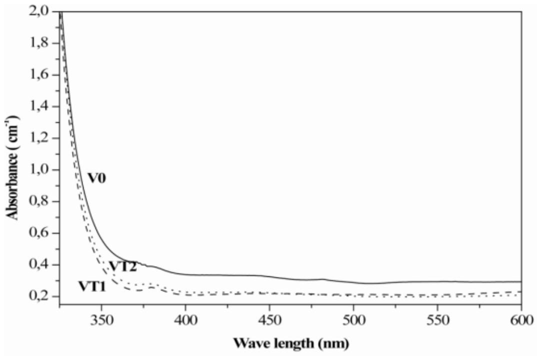

Fig. 4: UV-Visible spectra of V0, VT1 and VT2 glasses.

According to the fig5, Chromium oxide addition causes the appearance of three new absorption bands around 350, 445 and 650 nm in V_{C1} and V_{C2} compositions spectra. The two bands observed at 445 and 630 nm are characteristic of Cr^{3+} ions present especially in a distorted octahedral coordination. While the band centered at 350 nm is characteristic of Cr^{6+} ions [19].

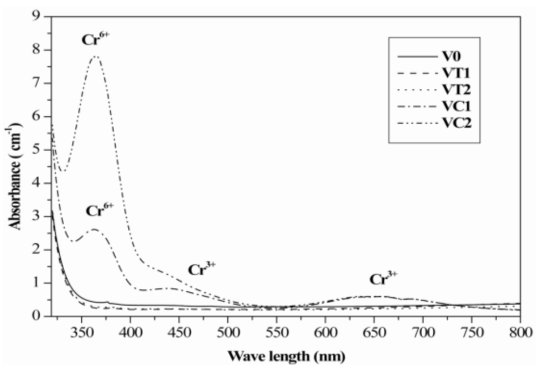

Fig.5: UV-Visible spectra of V0, VT1, VT2, VC1 and VC2 glasses.

The two bands located at 350 and 445 nm in the spectrum of the V_{C2} composition with 0.2 wt % Cr_2O_3 are more intense in comparison with that of the V_{C1} composition with 0.1 wt % Cr_2O_3, while one located at 650 nm has the same intensity in the spectra of the two compositions.

The intensity of Cr^{6+} ions characteristic band is greater compared with those characteristic of Cr^{3+} ions. In alkali silicate glasses, Cr^{6+} ions proportion is predominantly that of Cr^{3+} ion [19, 20].

3.2.3- Colorimetric properties

The basic glass $V_{T0}$is the most chromatic (C* = 2.59) (Table 4), comparatively with V_{T1} and V_{T2}. By adding small amount of TiO_2 (0.1 wt %), chromaticity decreases to become 2.51. By increasing the TiO_2content up 0.2wt %, the glass becomes more chromatic. The TiO_2 addition increases the b * parameter to the yellow color. However,a* parameter values are very influenced by the interference between Fe^{2+} / Fe^{3+} and Ti^{3+} / Ti^{4+} [21]. Its negative values indicate a slight green color which is attributed to the ferric ions.TiO_2 addition brings a slight improvement in the glasses clarity represented by the L * parameter, from 88.4 then 89.4 and 88.7 for V_{T0}, V_{T1} and V_{T2} respectively.

*Table 4: L *, a*, b * and C* color parameters of V_0, V_{T1}, V_{T2}, V_{C1} and V_{C2} glasses*

Samples	V_0	V_{T1}	V_{T2}	V_{C1}	V_{C2}
L*	88.4	89.4	88.7	76.1	73.2
a*	-2.5	-2.3	-2.6	-18.1	-18.3
b*	0.7	1	1.1	25.3	32.5
$C^* = \sqrt{a^{*2} + b^{*2}}$	2.59	2.51	2.82	31.31	37.30

Improvements in glasses color, clarity, and light transmissionbyTiO_2 addition are probably due to its influence on Fe^{3+}/ Fe^{2+} ions equilibrium in the glass. Alberto et al. [10] has confirmed the existence of interaction between titanium and the melt which favors oxidation of Fe^{2+} to Fe^{3+}. According to this investigation, the oxidation phenomenon can be explained by considering the presence of direct structural interactions between Fe and Ti: possibility of Iron-Titanium complex formation in analogy to that of Aluminum-Titanium. The effect of Ti on the molten silicate mixture anionic structure is also envisaged.Based on the Mossbauer analysis results, Alberto et al.[10] proposed formationof Fe^{2+}-O-Ti bonds with Ti in tetrahedral coordination and no bridging oxygen linked with ferrous iron. Knowing that Ti^{4+} is substantially larger than Si^{4+}, ferrous-oxygen polyhedra have a greater tendency to distortion when bonded to tetrahedral titanium rather than to silicon. This distortion destabilizes the Fe^{2+}-O polyhedral and favors ferrous ion oxidation.

In regards to Cr_2O_3 addition effect on the glass color (table 4), glass chromaticity increased significantly with small amount addition (2.59 and 37.30 for V0 and V_{C2} respectively). This increase is also observed in the clarity decrease of the compositions which become colored.

a* and b* parameters values are very influenced by the added chromium oxide amount and thus by the proportions of Cr^{3+} and Cr^{6+} contained in the glasses. Cr_2O_3 addition increases the value of a* parameter from -2.6 (without addition) to -18.1 and -18.3 for compositions V_0, V_{C1} and V_{C2} respectively. These negative values are relative to the green color due to Cr^{3+} ions presence in the two last compositions[13]. On the other hand, the presence and the amount of Cr^{6+} ions in the glass influence the b* parameter. Positive values of the latter are the result of a yellowish coloration characteristic of the Cr^{6+} ions [15, 20].

Color measurements come support those of the optical absorption. Increasing Cr_2O_3 added amount induces the predominant formation of Cr^{6+} ions which increases their characteristic absorption band intensity namely 350 nm[19]. This predominance is also notice able in the variation observed in the parameters b* values compared with those of a*[20].

4. CONCLUSION

Addition of small amounts of TiO_2 in soda-lime-silica glasses led to an improved transparency; light transmission, and thermal shock resistance. While Cr_2O_3 addition induced their green coloring (a* increases from 2.5 to -18.1 and b* from0.7 to 32.5 for V_0 and V_{C2} respectively) and also lowering their thermal expansion coefficients:α (50-350°C) is decreased from 8.9 10^{-6} to 8.3 10^{-6} and 8.5 10^{-6} $°C^{-1}$ for V_{T0}, V_{T2} and V_{C2} respectively.

The melt physical characteristics as transition temperature which are also important in an industrial setting (refining, glass forming) are influenced by the addition of TiO_2 and Cr_2O_3 even at low contents. However, glass transition temperature is increased from 573 to 585°C and to 587°C with addition of 0.2 wt % of $TiO_2$and of Cr_2O_3 respectively.

Improvements noticed with low TiO_2 addition are the result of some structural changes. These later are attributed to the oxidation of Fe^{2+} to Fe^{3+} ions and Fe^{3+} clusters formation promoted by titanium oxide addition according to the UV-Visible Spectroscopy.

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