

# The effect of chromium oxide on optical spectroscopy of sodium silicate glasses

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The crystallization of  $Na_2O.3SiO_2$  glasses doped with  $Cr_2O_3$  (0-0.12-0.16-0.2-0.8-2-3-7mol%) has been investigated by UV-Vis-FTIR spectroscopy, XRD and SEM microscopy. The results showed that, By increasing content of chromium oxide, Transmission of light through sodium silicate glasses reduced due to ligand field and charge transfer mechanisms. Transmission of light through sodium silicate glasses with the presence of chromium oxide change and, also lead to formation of crystalline phases. More increasing of chromium oxide caused that light transmission in spectrum of these glasses being reduced, so that increasing chromium oxide up to 3% molar case that light absorbed, in which, by investigation chromium oxide effect on constituent units of glass lattice by means of infrared spectrum at  $400-4000cm^{-1}$  region, it was identified that new peak at  $640cm^{-1}$  has been appeared.

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## 1. Introduction

Chromium is largely used in glasses for a broad range of applications. The redox state of Cr provides glasses specific light transmission properties, which are used, e.g. in packaging technology. Cr(III) gives a green coloration in silicate glasses, whereas Cr(VI) imparts a yellow color and provides interesting thermochromic properties. Cr(III) is also an efficient nucleating agent in oxide glasses and the redox state controls Cr solubility in glasses and melts. Glass melting conditions are then adjusted to control Cr redox state, through an adequate choice of melting atmosphere or refining agents. During the last years, many efforts for studying the effect of transition metals on glasses have been conducted. One of most important transition metals is chromium oxide. Chromium has many applications in wide range of glasses[1-4]. Transition metal ions as active ions are used in tunnel solid-state lasers in infrared region. Glasses that are used as laser bed due to low cost in mass production and fiber forming in which are synthesized more easily than mono-crystals has been developed[5]. Moreover, recently some published papers are referring to  $Cr_2O_3$  crystal and its role on nano-composite application[6]. Selective absorption in visible wavelengths leads to coloring of glasses. Colors are related to electromagnetic energy and have a wavelength in 380-770 nm, also measurement of transmitted light should be done in this wavelength. But, color development in wavelengths out of this region can impressed by absorption effects direct or indirectly. Thus, for ensuring about nature of color development mechanism, measuring intensity of transmitted light in 200-1100 nm has been done. Fundamental of color development is transmission of electrons between 3d electronic energy levels. 3d energy levels have same energy level for free ions. However, when a transition metal ion surrounded by some anions in crystal or glass structure (which are called

ligand), electric field interactions leads to decomposition of energy levels (i.e. conversion of one level into several levels with different energy). Intensity of this decomposition (i.e. amount of energy difference) is a function of field power, number and adjacent anions configuration. Number of produced levels is a function of electronic configuration and coordination number of related cation. Optical absorption spectrum of  $Cr^{3+}$  in solarium silicate, borosilicate potassium and borosilicate sodium glasses in visible – ultraviolet region has been investigated[7]. Chromium in borate and silicate glasses exist as trivalent and hexavalent ions in air atmosphere. Doglass et. al. had studied  $Cr^{3+}$  and  $Cr^{6+}$  equilibrium in silicate[8-9] and borate glasses [10-11] with chemical analysis and ultraviolet absorption. They argue that in silicate glasses hexavalent chromium is similar to aqueous chromium. Trivalent chromium in silicate glasses produces green color, while hexavalent chromium gives yellow color [1] and provides thermo-chromic characteristics [2]. Direct determination of stabilization energy of crystal field  $Cr^{3+}$  in minerals and glasses by visible – ultraviolet spectroscopy creates a link between crystal chemistry of  $Cr^{3+}$  and glass mixture [12]. Also, chromium present as an effective nucleation agent in glasses. Significance of transparent ceramics that are doped with trivalent chromium has been considered as potential material for tunnel lasers, recently [13]. The aim of the present work, which is part of the wider study on glassy and glass-ceramic from sodium silicate, is to study the effect of  $Cr_2O_3$  on crystallization behaviour of a “sodium silicate glasses.

## 2. Materials and methods

For the investigations, glasses were prepared with the base composition  $3SiO_2.Na_2O.Cr_2O_3$ . The batches were mixed from reagent grade raw materials:  $SiO_2$ ,  $Na_2CO_3$

and  $\text{Cr}_2\text{O}_3$ . Raw material of glass component listed in Table 1. The batch was calculated for either 100g of glass. Glasses were melted in alumina crucible and VECSTAR kiln with air atmosphere. Rate of heating for all of samples by this kiln was  $5^\circ\text{C}/\text{min}$  from room temperature. The loading of the batch into the crucible was done at temperatures between 900 and  $950^\circ\text{C}$ . These temperatures should not be higher because then it causes a substantial volatilization of reagents. After the entire batch was pre-melted in the crucible, the temperature was increased stepwise to the melting temperature of around  $1450^\circ\text{C}$  and kept for 2 – 2½ h. During this period of time, the glass was homogenised by stirring. The lasting period is very important because:

- i). the melting temperature (also marked as the equilibrium temperature) is later taken as temperature for the thermodynamic calculations;
- ii). bubbles must be removed from the glass which could disturb the optical absorption measurements;
- iii). the glass is homogenized in the whole crucible.

After this period, the glass was cast at the same temperature into a preheated ( $T=450^\circ\text{C}$ ) stainless steel mold with  $2\text{cm}\times 2\text{cm}\times 2.2\text{mm}$  dimension mould in a quick way in order to avoid temperature-caused inhomogeneities, and cooled in a preheated furnace to ambient temperature using a cooling rate  $30\text{ K.h}^{-1}$ . After grinding and polishing the absorption spectra of glass samples were recorded on Camspec Double (Beam UV-VIS 350m) spectrophotometer in optical range 200–1100nm. For infrared spectroscopy, glass samples were pulverized and were mixed by a given amount of KBr and pressed as very thin tablet and their infrared spectra has been performed by FTIR Bomem(Quebec,Canada) MB100 model in  $400 - 4000\text{ cm}^{-1}$  wavenumber region. For heat treatment, some samples were held in  $900^\circ\text{C}$  24 hours in kiln. At final stage, sample was studied by XRD and for investigating microstructure of formed crystals in samples SEM microscopy VEGA\\TESCAN model has been used.

Table 1. composition of  $3\text{SiO}_2.\text{Na}_2\text{O}.x\text{Cr}_2\text{O}_3$  glasses.

Samples	$\text{SiO}_2$	$\text{Na}_2\text{O}$	$\text{Cr}_2\text{O}_3$
$\text{C}_0$	75	25	0
$\text{C}_{0.12}$	74.90	24.97	0.12
$\text{C}_{0.16}$	74.88	24.96	0.16
$\text{C}_{0.2}$	74.85	24.95	0.2
$\text{C}_{0.8}$	74.40	24.80	0.8
$\text{C}_2$	73.50	24.50	2
$\text{C}_3$	72.75	24.25	3
$\text{C}_7$	69.75	23.25	7

### 3. Results and discussion

The results presented in figure 1 show the effect of chromium oxide on the optical absorption sodium silicate glass. In samples without chromium additive, no absorption peaks detected, and glass is colorless. Enhancement of chromium in glass leads to formation of two absorption bands in 470 and 640nm wavelengths that

indicating optical peak of  $\text{Cr}^{3+}$  ion in glass. Dominant absorption wavelength is 545 nm that results in emerald green development. Comparisons of figure 1 spectra indicate that with enhancement of chromium in sodium silicate glass, amount of transmitted light decreases. Increasing chromium amount results in increase of colored center and absorption increases.

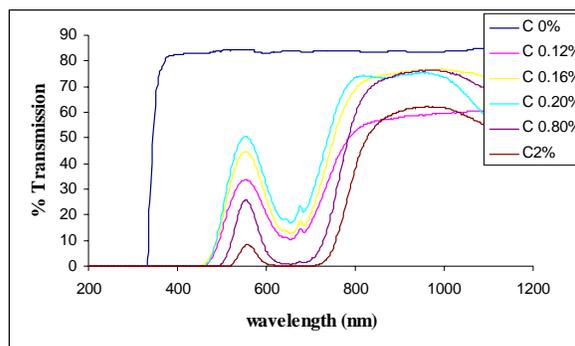


Fig. 1. UV-Vis spectroscopy of glasses contained  $\text{Cr}_2\text{O}_3$ .

With increasing to 3%mol of chromium oxide, absorption peaks go stronger and are not distinguishable easily. Glass sample contained chromium oxide more than (3%mol) shows no light transmission at 200–1100nm wavelength region. For investigation samples at higher wavelength regions, infrared spectrum was taken. In Fig. 2, FTIR spectrum for sodium silicate glasses that have chromium oxide in ranged  $400 - 4000\text{ cm}^{-1}$  wavenumber are reported.

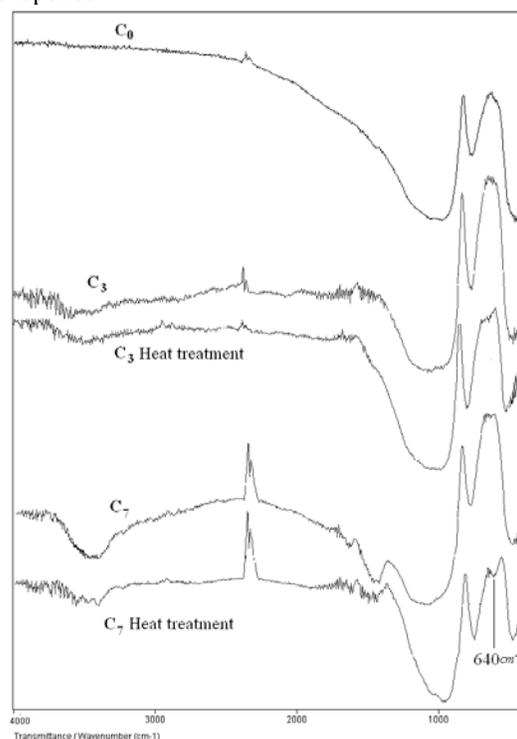


Fig. 2. FTIR spectroscopy of glasses contained  $\text{Cr}_2\text{O}_3$  samples  $\text{C}_3$ ,  $\text{C}_7$  before and after heat treatment.

According to the figure, increasing chromium oxide leads to some changes in these spectra. In fact, spectrum has two parts: the first part consist of specified absorption peaks and distinguishable main sharp peak that ranged in the middle of FTIR region from 400 to 1400  $\text{cm}^{-1}$ , second part has two small peaks around 1450 and 1640  $\text{cm}^{-1}$  and another small peak around 2440  $\text{cm}^{-1}$ . Spectrum that ranged from 400 to 1400  $\text{cm}^{-1}$  has absorption for the sake of main silicate groups of the network and different bounding configuration. remain of the spectrum from 1400 to 4000  $\text{cm}^{-1}$  consist of vibration of water's atomic bond, hydroxyl (Si-OH) or other similar groups[8]. Peak of 1400  $\text{cm}^{-1}$  is due to carbonate group and peak of 1640  $\text{cm}^{-1}$  could be attributed to molecular water or related hydroxyl band. In these spectra, absorption peak at 1050  $\text{cm}^{-1}$  is due to nonsymmetrical expansion of bridged oxygen of Si-O-Si and peak of 950  $\text{cm}^{-1}$  is associated with expansion of non-bridged oxygen that when  $\text{Na}_2\text{O}$  increase, strength of this peak also will increase.

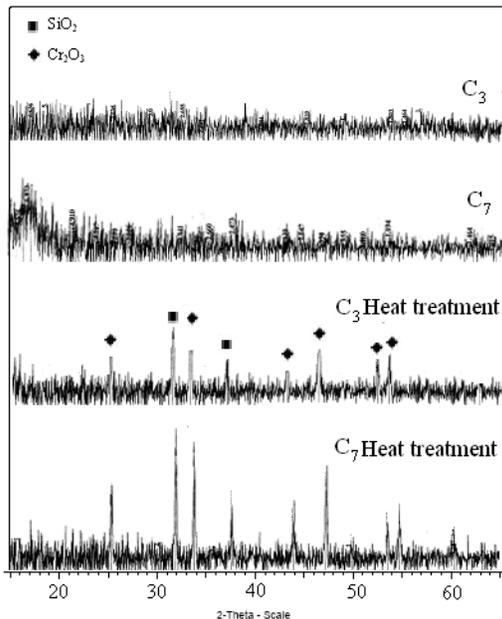


Fig. 3. XRD results of samples  $C_3$ ,  $C_7$ , sodium silicate glasses contained 3, 7%mol chromium oxide.

Also, another peak occurs at 760  $\text{cm}^{-1}$  that is related to symmetrical expansion of Si-O-Si. Two peaks 600 and 470  $\text{cm}^{-1}$  are be attributed to removing the bending of bridged oxygen. Obtained results are consistent with other researches[16–17]. With increase of chromium oxide, absorption peaks of infrared spectrum shift toward lower wavenumber region. Peak of 640  $\text{cm}^{-1}$  is related to glass without chromium oxide that has a strong absorption. Conducting heat treatment samples  $C_3$  and  $C_7$  causing some changes in FTIR spectrum. By conducting heat treatment, amount of oxygen ions have been increased in structure that these ions are separated from silicon and due to increase crystalline phase in glasses. In order to understand the most probable cause, XRD have been collected and analysed. Fig. 3 shows the XRD patterns for  $C_3$  and  $C_7$  specimens before and after heat treatment at

800 °C temperature with increase of chromium oxide in base glass, crystalline phase has been formed but  $C_3$  sample shown a weak crystallisation (figure 3-a). However, electronic microscopy images show SEM of formed crystals due to increasing chromium oxide (figure 4). With increasing amount of chromium oxide ( $C_7$ ) and without heat treatment, The XRD pattern of samples had been changed (figure 3-b). However, obtained peaks were weak and were not identified. The microstructure of  $C_7$  sample is presented in Fig. 5.

This technique gives moreover a qualitative indication about the amorphous phase present in the samples. The relative abundance of these crystalline and glassy phases, varies depending both on the compositions of the parent glass and the devitrification temperature. With performing appropriate heat treatment, one could increase more crystalline phase in glass. With increasing crystalline phases in sample, new crystalline phases produce that shows its X-ray scattering pattern.

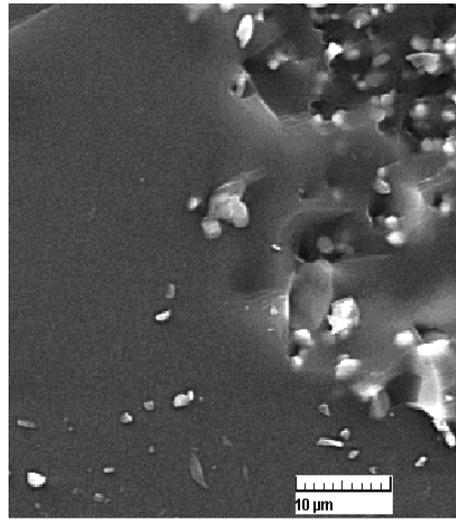


Fig. 4. SEM image of sample  $C_3$ , sodium silicate glass with 3%mol chromium oxide.

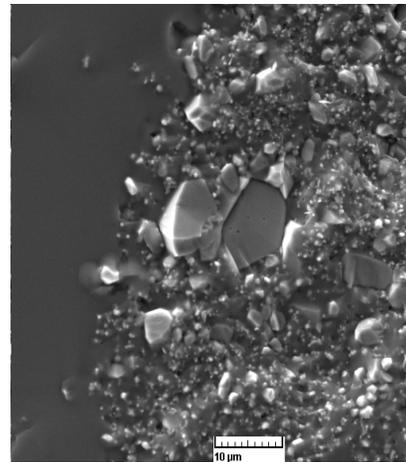


Fig. 5. SEM image of sam ple  $C_7$ , sodium silicate glass with 7% mol chromium oxide.

By conducting heat treatment of samples  $C_3$ ,  $C_7$ , 3h at  $800^\circ C$ , The XRD pattern shows strong crystallization peak which could be attributed to chromium oxide in glass (figure 3-c, 3-d). The microstructure of  $C_3$ ,  $C_7$  samples is presented in Figs. 6,7.

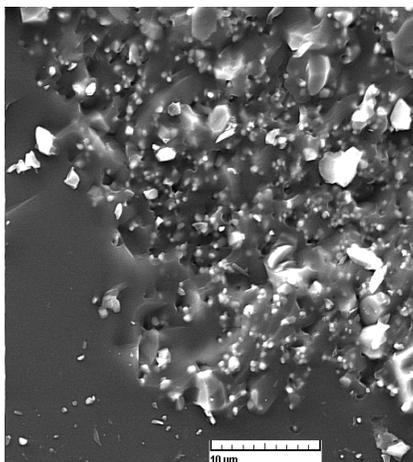


Fig. 6. SEM image of  $C_3$ . heat treatment at  $800^\circ C$ .

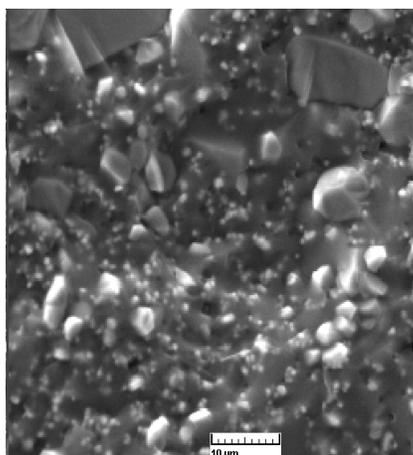


Fig. 7. SEM image of  $C_7$ . heat treatment at  $800^\circ C$ .

#### 4. Conclusion

Sodium silicate glasses has a great capability in solving chromium oxide and as an effect of increase of chromium oxide, UV-Vis spectrum exhibit several absorption peaks that some of them could develop colour in glass. Investigating infrared spectrum of these glasses shows that with increase of chromium percent a new absorption peak forms at  $640\text{ cm}^{-1}$  and also location of each absorption band with respect to transmission one for a sample free of chromium shifts toward smaller wavenumber. Increasing chromium oxide up to 3% mol, resulted in weak crystalline phase formation in glass. Increasing chromium oxide 7%mol and conducting heat treatment 3h at  $800^\circ C$  cause that crystalline phase increasing and formation glass-ceramic.

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