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Investigation of optical absorbance and crystallization of vanadium oxide in glasses

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The crystallization of sodium silicate glasses doped with vanadium oxide (0-3-5-7–11 molar percent) has been investigated by ultraviolet-visible(UV-Vis) and fourier transform infrared(FTIR**)** spectroscopy, X-Ray diffraction(XRD) and scanning electron microscopy(SEM). The results showed that, By increasing content of vanadium oxide, Transmission of light through sodium silicate glasses reduced due to ligand field and charge transfer mechanisms, colored glass was developed in some special wavelengths. Transmission of light through sodium silicate glasses with the presence of vanadium oxide change and, also lead to formation of crystalline phases. More increasing of vanadium oxide caused that light transmission in spectrum of these glasses being reduced, so that increasing vanadium oxide up to 11%mol case that light absorbed, in which, by investigation vanadium oxide effect on constituent units of glass network by means of infrared spectrum at 400-4000 cm^{-1} region, it was identified that new peak at 610 cm^{-1} has been appeared that this peak has been shifted to 615 cm^{-1} by heat treatment. XRD investigation showed that by increasing heat treatment temperature of sample up to 900°C strong peaks appeared.

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1. Introduction

During the past decades, significant considerations have been given to glasses contain transition metal ions. More recently, mechanical, optical, electrical and physical properties of glasses with different transition metal ions are studying by many researchers due to their technological applications in laser, solar cells, plasma monitoring panels and some electronic devices[1-6]. Also developing colors by vanadium oxide in glasses lead to application of this oxide as glaze in tiles and ceramics[7]. Vanadium is the strongest absorbent in critical range for optical wavelengths in communicating systems (800 – 1000 nm), and so many attention is toward studying possible valences of vanadium in different glasses[8-10]. Presence of vanadium results in emergence of semi-conducting characteristics in these glasses, that stem from happing unpaired electrons [11–10]. In studying transition metal ions in glasses encounter several problems because some of these ions have more than one oxidation states. Presence of vanadium in glass with four oxidation states V^{2+}, V^{3+}, V^{4+} and V^{5+} depends upon glass composition and melting conditions[12] that V^{2+} ions is less in glasses. Glasses containing vanadium can exhibit a range of colors from green to yellow to almost colorless as the alkali oxide content is increased. Different valences of vanadium develop various colors. V^{5+} ions develop yellow to colorless, V^{4+} blue color and V^{3+} ions create green to yellow color in glass. Each of these valences has a special electronic configuration. Pentavalent vanadium is of the (A) ($3d^0$) configuration, and as such it will not give rise to d-transitions, since it contains no d-electrons, however it displays a charge transfer band in the UV region. The high raised-end in the UV region for borate and silicate glasses may thus be attributed to the presence of VO^{5+} and can be assigned to be a charge transfer band. Tetra-valence vanadium has (A)($3d^1$) configuration and exist like VO^{2+} ions in glass, and therefore d-d transitions (related to ligand field transitions) reach absorption bands[8,12]. Tri-valence vanadium has (A)($3d^2$) configuration that leads to d-d transitions. One could be attributed 380 and 430 nm bands in silicate glasses to presence of V^{3+} ions. Thus, one could consider each of these two band (430 and 630 nm) as a combined band that one of them is due to V^{3+} and the other to V^{4+} ion[8-13]. Based on investigated researches, most amounts of electron transitions and conduction occurs between V^{5+} and V^{4+} ions and this is a proper condition for construction of semiconducting glasses[14-15]. In this study, for considering absorption position of resulted peaks from vanadium ions in glass, UV-Vis spectroscopy and for considering building units of glass network, Fourier transform infrared (FTIR) spectroscopy will be used. Also, crystals formation has been investigated by XRD and SEM microscopy.

2. Empirical methods

For the investigations, glasses were prepared with the base composition $3SiO_2.Na_2O.xV_2O_5$. The batches were mixed from reagent grade raw materials: SiO_2, Na_2CO_3 and V_2O_5. Raw material of glass component listed in table 1.

Table 1: Composition of the nominally prepared and analyzed sodium vanadium silicate glasses(%mol). The relative uncertainty in the ICP results is +5%.

sample no	Nominal			Analysed		
	SiO_2	Na_2O	V_2O_5	SiO_2	Na_2O	V_2O_5
1	75	25	0	74.834	24.230	0
2	72.25	24.5	3	72.118	24.105	2.67
3	71.25	23.75	5	70.850	23.352	4.56
4	69.75	23.25	7	69.11	22.71	6.87
5	66.75	22.25	11	66.367	21.654	10.11

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 $5^{\circ}C/\min$ from room temperature. The loading of the batch into the crucible was done at temperatures between 900 and 950°C. These temperatures should not be higher because then it causes a substantial volatilization of reagents. The chemical compositions of the glasses were determined by a combination of inductively coupled plasma (ICP, JY124 model) emission spectroscopy and the results of the analysis are shown in Table 1. After the entire batch was pre-melted and sintered in the crucible, the temperature was increased stepwise to the melting temperature of around 1450°C and kept for 2 – 2½ h. During this period of time, the glass was homogenised by stirring. Than the glass melt was cast at the same temperature into a preheated (T= 450°C) stainless steel mold with $2cm \times 2cm \times 2.2mm$ 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 $K.h^{-1}$. After grinding and polishing the absorption spectra of glass samples were recorded on Camspec Double (Beam UV-VIS 350m) spectrophotometer in optical range 200-1100 nm. 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 cm^{-1} wavenumber region. For heat treatment, some samples were held in 800 and 900 $^{\circ}C$ for 24 hours in kiln. At final stage, sample was studied by XRD(Siemens, D-500, using Cu $K\alpha$ radiation at 40 kV and 20mA setting and in 2θ range from 5° to 70°) and for investigating microstructure of formed crystals in samples SEM microscopy VEGA\\TESCAN model has been used.

3. Results and discussion

The results presented in Fig. 1 show the effect of vanadium oxide on the optical absorption sodium silicate glass. In samples without vanadium additive, no absorption peaks detected, and glass is colorless. With increasing of vanadium oxide to 3%mol several absorption peaks appears. A peak that is associated to charge transfer is located in ultraviolet range that it's transmission amount reached zero. Overlapping of charge transfer peak related to V^{5+} ions and ligand field peak related to V^{3+} ions in 380 and 420 nm cause that a specified peak appears in this region. Presented peak of 630 nm is due to V^{3+} ions. A broad absorption peak at 1000 nm is observed that is associated to V^{4+} ions and could be attributed it to distortional tetrahedral of V^{4+} ions[8]. With increasing amount of vanadium oxide, light transmission decreases.

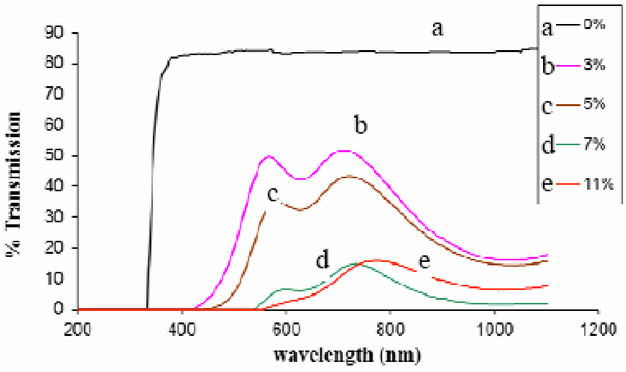

Fig. 1. UV-Vis spectrum in sodium silicate glasses containing vanadium oxide.

This phenomenon is due to enhancement of colored centers because of increasing vanadium oxide in glass. With increasing to 11%mol of vanadium oxide, absorption peaks go stronger and are not distinguishable easily. Glass sample contain vanadium oxide up to 11%mol shows no light transmission at 200-1100 nm wavelength region. For investigation samples at higher wavelength regions, infrared spectrum was taken. In figure.2, FTIR spectrum for sodium silicate glasses in 400–4000cm^{-1} are reported. Increasing vanadium 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 cm^{-1}, second part has two small peaks around 1450 and 1640 cm^{-1} and another small peak around 2440 cm^{-1}. Spectrum that ranged from 400 to 1400 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 4000cm^{-1} consist of vibration of water's atomic bond, hydroxyl (Si-OH) or other similar groups[8].

Peak of 1400cm^{-1} is due to carbonate group and peak of 1640cm^{-1} could be attributed to molecular water or related hydroxyl band. In these spectra, absorption peak at 1050cm^{-1} is due to nonsymmetrical expansion of bridged oxygen of Si–O–Si and peak of 950cm^{-1} is associated with expansion of non-bridged oxygen that when Na_2O increase, strength of this peak also will increase. Also, another peak occurs at 760 cm^{-1} that is related to symmetrical expansion of Si–O–Si. Two peaks 600 and 470cm^{-1} are be attributed to removing the bending of bridged oxygen. Obtained results are consistent with other researches[16–17].

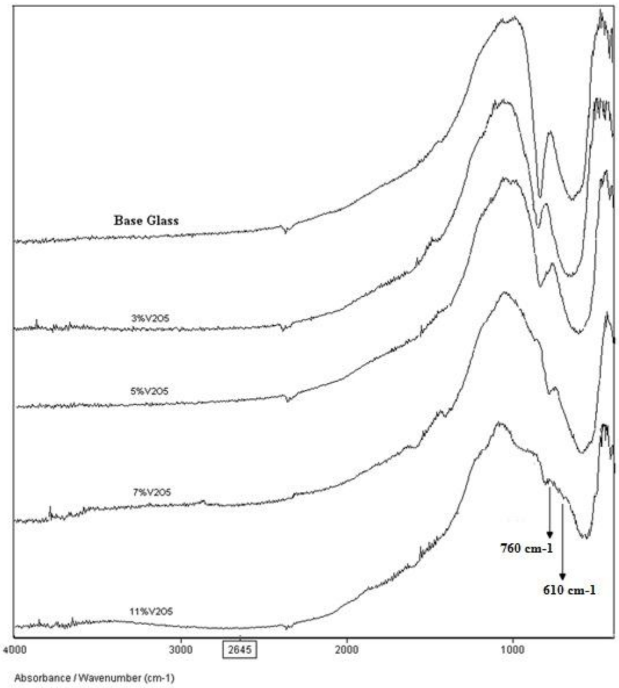

Fig. 2. FTIR spectrum of sodium silicate glasses containing vanadium oxide.

With increase of vanadium oxide, absorption peaks of infrared spectrum shift toward smaller wavenumber region. Peak of 760cm^{-1} is related to glass with no vanadium oxide that has a strong absorption. In which, with increase of vanadium oxide this peak is weakened and its absorption will decrease. This peak is be attributed to vibrations of Si–O–Si bonding. With enhancement of vanadium oxide because of strong vanadium bonds, oxygen apart from silicones and attach to vanadium and form V–O–V bindings. According to scientist researches, vanadium vibration peak will appear at 1005-1025 cm^{-1} region if present ions of composition be V^{5+} completely [13]. New absorption peak at 610 cm^{-1} in glass contain 11%mol is be attributed V^{5+} ions. Conducting heat treatment this sample cause that new peak shift to 615 cm^{-1}(not shown). It is probable that the 615cm^{-1} band in the glass is a result of this phenomenon, i.e. some of the vanadium is present as V^{5+} and the rest is present as V^{4+}. Results of crystalline phase formation in this study due to increasing amount of vanadium oxide by XRD have been shown in Fig. 3. X-ray diffraction pattern of sodium silicate glass due to amorphous state shows no crystalline peak (figure 3-a).

Also, with increasing amount of vanadium oxide, at low level, amount of crystalline phase is very low and were not identified by XRD. With increasing amount of vanadium oxide to 11%mol and without heat treatment, sample's XRD had been changed (figure 3-b). However, obtained peaks were weak and were not identified.

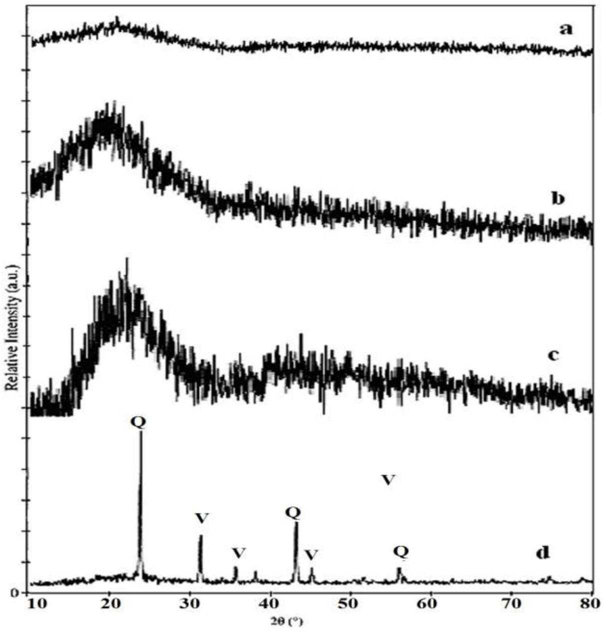

Fig. 3. XRD results of sodium silicate glasses contain vanadium oxide. a)glass without additive. b) 11%mol vanadium oxide without heat treatment. c) 11%mol vanadium oxide with heat treatment at 800 ^{o}C. d)11%mol vanadium oxide with heat treatment at 900 ^{o}C.

Fig. 4-a show the micrograph of this specimen containing low amount crystalline phase. By conducting heat treatment of samples at $800^{\circ}C$, XRD of this sample has been changed and peaks are forming (figure 3-c). Crystalline phase of this sample is needle-like shaped that has been shown in figure 4-b. Heat treatment at $900^{\circ}C$ leads to formation of considerable crystalline phase, quartz and vanadium, at sample that has shown in (figure 3-d). Increasing heat treatment temperature leads to change of ceramic glass microstructure. As confirmed by SEM observation, the crystallization process starts from the glass surface and continue inwards the glassy matrix. Microstructure of glass sample after heat treatment at $900^{\circ}C$ is tree-like shaped that has been shown in Fig. 4-c. Fig. 4-d depict EDS microanalysis of the glass-ceramic sodium silicate vanadium.

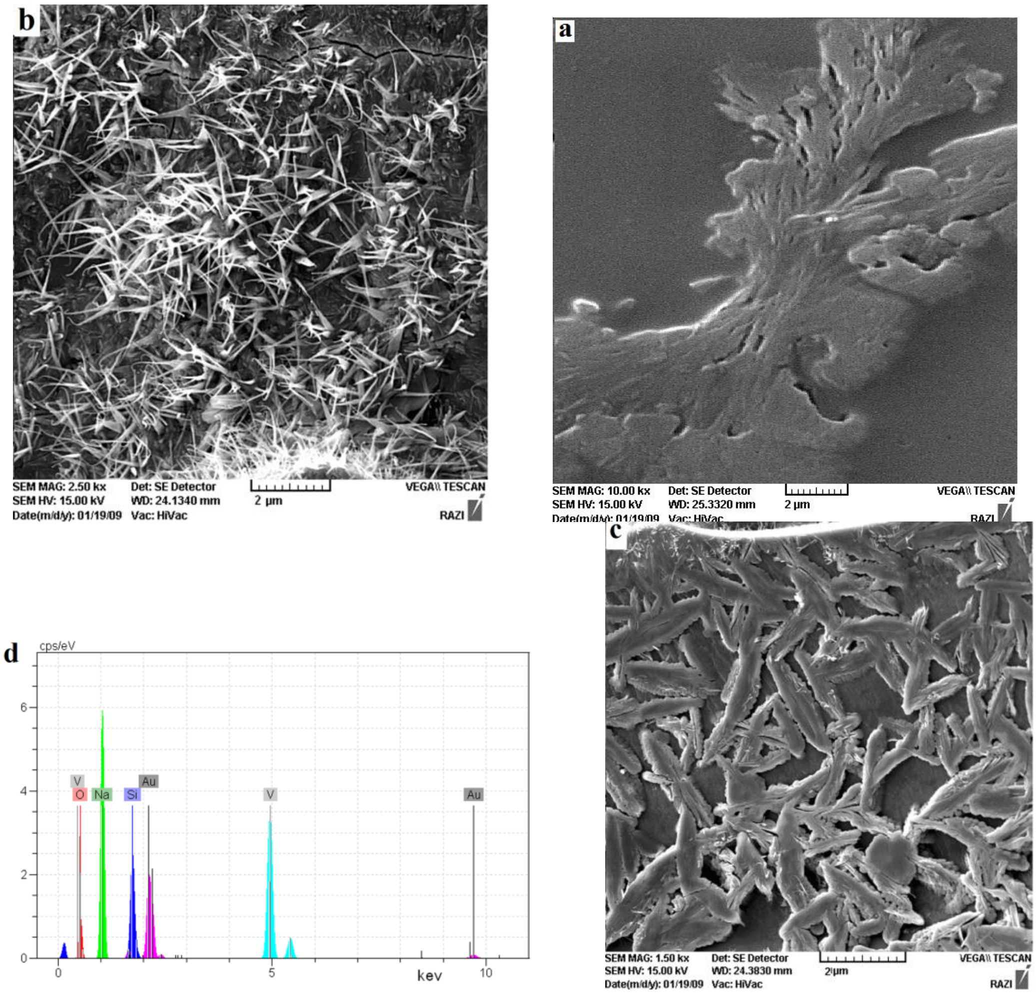

Fig. (4-a). SEM image of sample with 11%mol vanadium oxide without heat treatment. Figure (4-b) SEM of sample with 11%mol vanadium oxide after heat treatment at 800 $^{\circ}C$ *.Figure(4-c): SEM of sample with 11%mol vanadium oxides after heat treatment at 900* ^{o} *C. Figure(4-d): EDS microanalysis of sodium silicate contained 11% vanadium oxide.*

4. Conclusion

Sodium silicate glass has a great capability in solving vanadium oxide and as an effect of increase of vanadium oxide, UV-Vis spectrum exhibit several absorption peaks that some of them could develop color in glass. Investigating infrared spectrum of these glasses shows that with increase of vanadium percent a new absorption peak forms at 610 cm^{-1} and also location of each absorption band with respect to transmission one for a sample free of vanadium shifts toward smaller wave number. Increasing vanadium oxide up to 11%mol, resulted in crystalline phase formation in glass. Due to heat treatment at 800 $^{\circ}C$, microstructure of formed crystalline phase was needle-shaped and more increasing of heat treatment temperature leads to tree microstructure. Heat treatment at 900 $^{\circ}C$ leads to formation of considerable crystalline phase, quartz and vanadium.

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