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Morphogenesis of Sodium Silicate Glass and Glass Ceramics with High Amounts of Vanadium Pentoxide

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Abstract

Glass sample of compositions $xNa_2O_2xSiO_2zV_2O_5$ for z=20 to 60 mole fraction are prepared by melt quench method. The structural analysis of glasses is carried out by Fourier transform infrared spectrophotometer (FTIR) and X-ray diffractometer (XRD) and interpreted structurally in terms of chemical bonding. The spectra of V_2O_5 containing glasses show an increased number of distinct peaks in the low frequency region (400 - 1200 cm^{-1}) with a convolution of broad Gaussians in the high frequency region (1200 - 4000 cm^{-1}). NS25V, NS30V, NS40V glass compositions are infrared inactive. All the spectra are base line corrected and Overlapped Gaussians are deconvoluted to appropriate number of Gaussians using computer program. The distinct peaks and peak positions of the deconvoluted Gaussians are assigned to Si-O-Si, O-Si-O, V-O-V, V-O, V=O, VO_2, Si-O, O-H and H-O-H bands. The compositional dependence of the band positions show a positive correlation with V_2O_5 content. The base and heat treated samples are X-ray diffracted to examine either they are amorphous or crystalline. By increasing content of V_2O_5, transmission of light through sodium silicate glasses reduced due to ligand field and charge transfer mechanisms.

Keywords

XRD, IR Spectroscopy, Deconvolution, Gaussians, V_2O_5

1. Introduction

Glass is an amorphous solid. A material is amorphous when it has no long range order. Chemically glass materials are mixture of organic oxides, which have cooled to a rigid condition without crystallizing. The atoms or molecules in the glass structure must be linked in the form of three dimensional network of a variety of species. Normally in silicate glasses the network former is SiO_4. Like univalent modifier oxide e.g. Na_2O, it helps network formers to melt at lower temperature, to achieve more practical temperature due to the addition of V_2O_5, modifies the silicon environment [1] and produces different types of colorful glass without addition of coloring reagent. Presence of vanadium in the glass with oxidation states V^{2+}, V^{3+}, V^{4+} and V^{5+} depends upon glass composition and melting conditions but V^{2+} ions are less in vanadate glasses. Different valences of vanadium develop various colors. The glasses containing vanadium are highly conductive which makes them more suitable for applications in electrical switching devices. Presence of vanadium results in emergence of semiconducting characteristics in these glasses that stem from hopping unpaired electrons [2]. Conduction in glasses is explained by the phonon assisted hopping of electrons (small polaron hopping) between the low and high valence states of TM (transition metal) ions [3].

2. Experimental Details

To investigate the structural analysis of vanadium doped sodium silicate glasses and the effect of vanadium pentoxide in it, simple $xNa_2O_2xSiO_2zV_2O_5$base glass samples were prepared and characterized. In this work, mainly IR spectroscopy and XRD of the base and heat treated sample are used to characterize the materials. The infrared spectroscopy provides absorption spectra, which gives information about the strength and stiffness of chemical bonds; binding of atoms in compound and characterize the vibrational motion of atom-atom bonds. The qualitative and quantitative analysis of the infrared absorption spectra is employed with the deconvolution to several Gaussians to characterize the materials. According to the National Research Council, "characterization means the description of those feature of the composition and structure of a material which are significant for a particular preparation, study of

various properties and suffice for the reproduction of the materials". In X-ray diffraction techniques the measured pair distribution functions are compared to the distribution functions that are calculated from various models of glass structures and the best fit is taken. The glass compositions chosen for present study are listed in Table 1.

Table 1: Nominal composition, melting temperature and optical quality of glasses of various compositions

Title of the samples	Nominal composition in mol %			Melting temperature in ^{O}C	Optical quality	XRD
	Na_2CO_3	SiO_2	V_2O_5			
NS20V	26.67	53.33	20	1300	Milky	Partially crystallized
NS25V	25	50	25	ND*	Not form glass	NI**
NS30V	23.33	46.67	30	ND*	Not form glass	NI**
NS40V	20	40	40	ND*	Not form glass	NI**
NS50V	16.67	33.33	50	1300	opaque	Amorphous
NS60V	13.33	26.67	60	1350	opaque	Amorphous

N for Na_2O, S for SiO_2, V for V_2O_5, ND*= Not determined. (Glass was not formed)
NI**= Not investigated.

3. Results and Discussion

3.1. The Results of IR Spectra

The infrared spectra are recorded between 400 and 4000 cm^{-1} at room temperature. The typical infrared spectra of $xNa_2O_2xSiO_2zV_2O_5$ of base and heat treated glasses with different concentration of V_2O_5 are shown in Figure 1 and Figure 2. From these figures one can obtain only qualitative information. The plots have been positioned in such a way to compare the modifications accompanying for the replacement of both Na_2O and SiO_2 by V_2O_5. The spectra of the above samples are divided into two regions; one is the lower wavenumber in the frequency range 400 - 1200 cm^{-1} and the other in the higher wavenumber in the frequency range 1200 - 4000 cm^{-1}. The absorption intensity of the former region and later region are absolutely different. These absorption spectra exhibit some structural changes that occur in the various matrix of the studied samples with increasing their V_2O_5 content up to 60 mol%. In 20 mol% V_2O_5 (NS_20V) base glass, two shoulder peaks appear at 510 cm^{-1} and 1440 cm^{-1} and it becomes weaker in 50 mol% V_2O_5 (NS50V) base glass and almost

disappears in the 60 mol% V_2O_5 (NS60V) base glass. It is also found that the band positions shifted towards high frequency because of increasing V_2O_5. In NS20V base glass, two distinct strong broad peaks appear but in NS50V glass, only one strong broad peak exists and it becomes sharper than NS20Vglass system. The noisy peak appears in the NS60V glass system because of more hygroscopic nature. And it is found that the absorption of water of our prepared samples increases with increasing V_2O_5 concentration. The IR spectra of NS25V, NS30V and NS40V compositions do not show peak because they do not form glass. The band positions of NS20V, NS50V and NS60V heat treated samples are more distinct than the base samples. The band positions of the heat treated samples are shifted. The positions of the prominent absorption peaks associated with shoulder of each base and heat treated samples are summarized in table 2 and table 3. All the prominent peaks of base and heat treated glasses are identified as strong, weak, very weak, medium and strong broad. The peaks of the heat treated glasses are shifted more with increasing V_2O_5. IR spectra seem to consist of relatively broad absorption bands and it is very difficult to identify the exact position of the absorption band. For this reason, deconvolution of these bands is considered as a useful tool to obtain the exact position of the absorption band. The band positions and widths obtained from the deconvolution are thus considered to be true representation of the spectra. Here the bands observed in the 400 - 1800 cm^{-1} region is deconvoluted to several Gaussians depending on the basis of spectral shape using computer program to estimate the band position and relative amounts of various bonding mechanisms.

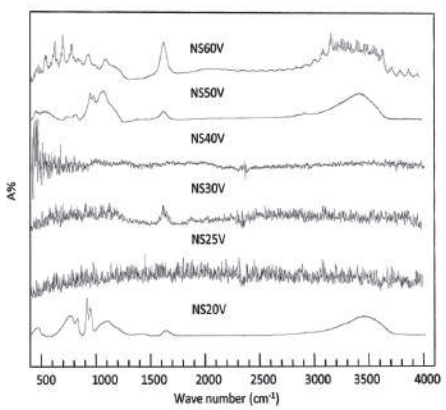


Figure 1: Infrared Spectra of $xNa_2O_2xSiO_2zV_2O_5$ Base Glasses (z=20-60 mol %)

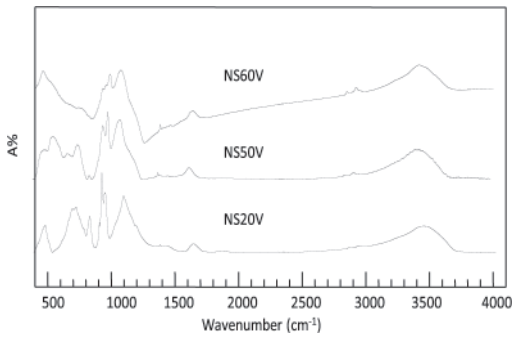


Figure 2 : Infrared Spectra of $xNa_2O_2xSiO_2zV_2O_5$ Heat-treated Glasses (z=20, 50, 60 mol %)

Table 2 : The prominent band positions in the spectra of$xNa_2O_2xSiO_2zV_2O_5$ base glasses.

Specimens	Position of prominent absorption maxima (cm^{-1})									
NS20V	493m	510sh	650m	788vs	843vw	912s	1143sb	1440sh	1655m	3466sb
NS25V*	-	-	-	-	-	-	-	-	-	-
NS30V*	-	-	-	-	-	-	-	-	-	-
NS40V*	-	-	-	-	-	-	-	-	-	-
NS50V	480vw	585w	666sh	777w	846vw	961w	1107s	1477sb	1663m	3485sb
NS60V	476vw	544w	632m	710m	812w	950m	1109w	-	1643vs	3336n

where s = strong, vs = very strong, m = medium, w- weak, vw = very weak, sh = shoulder, n=noisy, sb=strong broad

NS25V*,NS30V* and NS40V* did not form glass.

Table 3 : The position and nature of characteristics IR bands of the $xNa_2O_2xSiO_2zV_2O_5$ heat-treated glasses

Specimens	Position of prominent absorption maxima (cm^{-1})									
NS20V	490m	522w	610sh	739s	835m	920vw	1109vs	1490sh	1676m	3499sb
NS25V*	-	-	-	-	-	-	-	-	-	-
NS30V*	-	-	-	-	-	-	-	-	-	-
NS40V*	-	-	-	-	-	-	-	-	-	-
NS50V	498w	581s	632w	770m	840w	996w	1100s	1513sh	1657sh	3481sb
NS60V	491s	-	650sh	710sh	854sh	960w	1110w	1518sh	1664w	3482sb

Where s=strong, m=medium, sb=strong broad, sh=shoulder, w=weak, vw=very weak, vs=very strong

The deconvoluted spectra for samples NS20V, NS50V and NS60V are shown in Figure 3. The assignments of the chemical bonds are carried out by comparing its

position with the related glasses and crystalline phases. The assignments of these chemical bonds are summarized in table 4. Some of these bonds are attributed to vibrations of silicate, the rest are attributed to vibrations of vanadate bonds. Each component band is related to some type of vibration in a specific structural group.

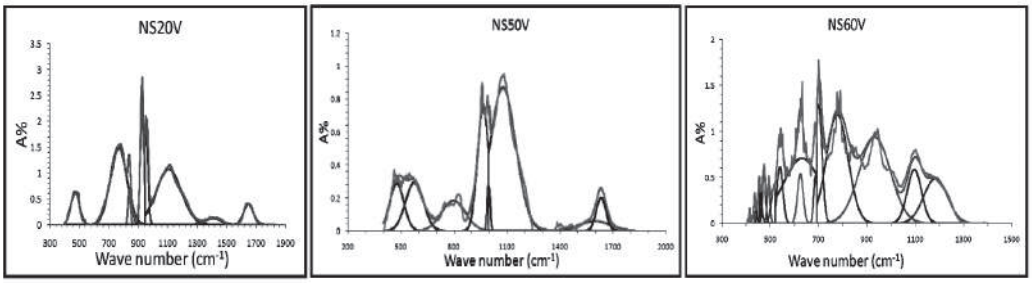


Figure 3: Deconvoluted spectra of $xNa_2O_2xSiO_2zV_2O_5$ (z = 20, 50, 60 mol %)

3.2. X-ray Diffraction of Base and Heat-treated Samples

The X-ray diffraction for NS20V, NS50V and NS60V base and heat- treated samples are shown in Fig.4.The X-ray diffraction patterns did not show any peaks and there was a broad haloes between 2θ=12 to 33(deg.).

The sample NS20V is partially crystallized. But NS50V and NS60V samples do not show any crystallinity except amorphous haloes. The samples were heated at 475˚C for 6 hours. The heat treated samples show the crystallinity in the material. From Figure 4 it is cleared that the heat treated glasses are not devitrified fully at 475˚C/6 hours. So we can conclude that the crystallization rate is slow and crystallization is not complete at 475˚C for 6 hours heat treatment

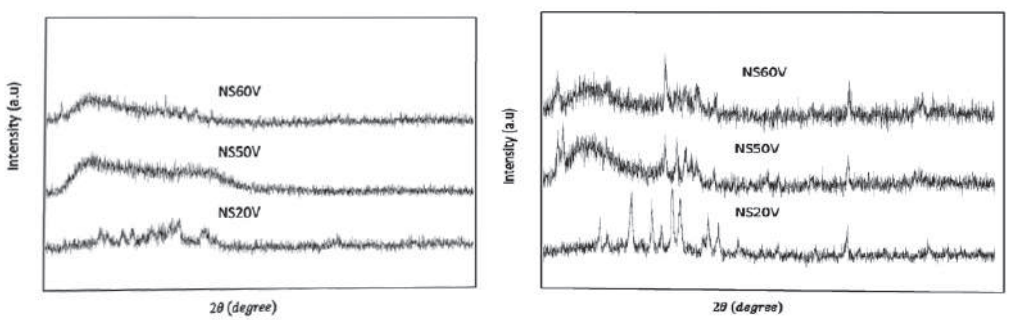


Figure 4 : XRD Pattern of $xNa_2O_2xSiO_2zV_2O_5$ bases and heat-treated glasses.

3.3 Discussion

The infrared spectra of our prepared glasses mainly consist of bridging, non-bridging oxygen bonds and vanadyle groups. K. El-Egili [4] observed a band for vitreous SiO_2 in IR spectraat 450 cm^{-1}. This band is attributed to the bending vibrational mode of Si-O-Si. The band at 490 cm^{-1} [6]is attributed to O-Si-O bending vibration. The IR band situated at 510-561 cm^{-1}, is attributed to the overlapping of the angular deformation vibration of the V-O-V chains. The intensity of these bands increases with increasing the V_2O_5 content up to 60 mol%. These bands can be assigned to low energy vibration of the V-O-V chains [7-8]. With enhancement of vanadium bonds, oxygen apart from silicones and attach to vanadium and form V-O-V bindings. It is clear from the IR spectra of NS20V, NS50V, NS60V glasses that the bands are slightly shifted towards the higher wave numbers. The symmetric stretching V-O-V ring frequency of V_2O_5 at 650-740 cm^{-1} [9] agree with our results 618 - 696 cm^{-1}. In the 761-774 cm^{-1} of the IR spectra there are higher absorption band characteristics of motions of the vanadate network, more precisely of stretching vibrations of V-O bonds in pyrovanadate structural units. Our result agrees with [10] and [11,12]. A second component of enhancement of vanadium bonds for NS20V, NS50V, NS60V glasses is situated at about 801-835 cm^{-1} and is assigned to the asymmetric stretching vibrations of the V-O-V bridges according to [13]. The band situated at 925-990 cm^{-1},assigned to the symmetric vibration of VO_2 in the [VO_4] structural units [9,14] and the other bands created at 1065-1086 cm^{-1}, due to the vibration of the isolated V=O non bridge bonds in the [VO_5] trigonal bipyramids. This observation agrees with [15] and [16]. The shifting of the high frequency band of the V=O bond towards higher wave number can be attributed to the changes in the structure of V_2O_5 produced by the reduction of Na_2O. The bands at 1102 cm^{-1} and 1178 cm^{-1} may be assigned to Si-O asymmetric stretching vibration. This frequency of Si-O band is observed by [17] within the range 1100-1210 cm^{-1}. The hygroscopic nature of the $xNa_2O_2xSiO_2zV_2O_5$ glass system should permit one to refer as $xNa_2O_2xSiO_2zV_2O5.H_2O$ compositions. In this work, the vibrational band for O-H bending mode lies between 1622-1643 cm^{-1}. This variation indicates that the water seems to be nearly free or loosely held by the glass network. It is very much clear from table 1 and table 2 that the peaks of the heat treated samples have been shifted which is the precondition of crystallization. The reason behind this phenomenon is that some of the vanadium is present as V^{5+} and the rest is present as V^{4+}.

NS25V, NS30V and NS40V did not melt in our laboratory furnace because of high

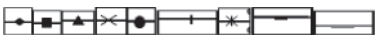
melting temperature and the limitation of temperature of our laboratory furnace. An oxyacetylene flame was applied on these samples but these compositions were burnt out without melting. The IR spectra of these samples were taken but we do not find any peaks because the vibrational motion of NS25V, NS30V and NS40V compositions may be infrared inactive. The heat treatments of these samples (NS25V, NS30V, and NS40V) were not performed. The comparison of the deconvoluted and observed chemical bonds with related glasses and crystalline phases are arranged in table 4. For each band attributed to a given vibrational mode, Figure 5 shows the compositional dependence of the band position with V_2O_5 concentration for $xNa_2O_2xSiO_2zV_2O_5$ glass system(a) without error bars (b) with error bars.The solid lines with  indicate infrared active compositions while the dashed lines with filled circles  represent the infrared inactive compositions. The variation in band positions for all concentration of V_2O_5 (20, 50, 60 mol%) justify the phase transformations of vanadate species, i.e. ortho, pyro, metavanadate.

Table 4 : Comparison of the main IR absorption bands observed in base glasses with related glasses and crystalline phases

Remarks	Structural groups	Absorption band (cm^{-1})	Corresponding references
Bending vibration	Si-O-Si	450 470 [428-471]	[4] [5] Present work
Bending vibration	O-Si-O	490 [490]	[6] Present work
Chain	V-O-V	400-570 [510-561]	[7,8] Present work
Symmetric stretching vibration	V-O-V	650-740 [618-696]	[9] Present work
Stretching vibration in the pyro vanadate structure unit	V-O	700 820 [761-774]	[10] [11,12] Present work
Asymmetric stretching vibration	V-O-V	820-830 [801-835]	[13] Present work
Symmetric stretching vibration	VO_2	966 [925-990]	[9,14] Present work
Non-bridging	V=O	1020 1100 [1065-1086]	[16] [17] Present work
stretching vibration	Si-O	1100-1210 [1178]	[18] Present work
Bending	O-H	1600-1660 [1622-1643]	[19] Present work
Symmetric stretching vibration	H-O-H	3420-3437 [3336-3485]	[6] Present work

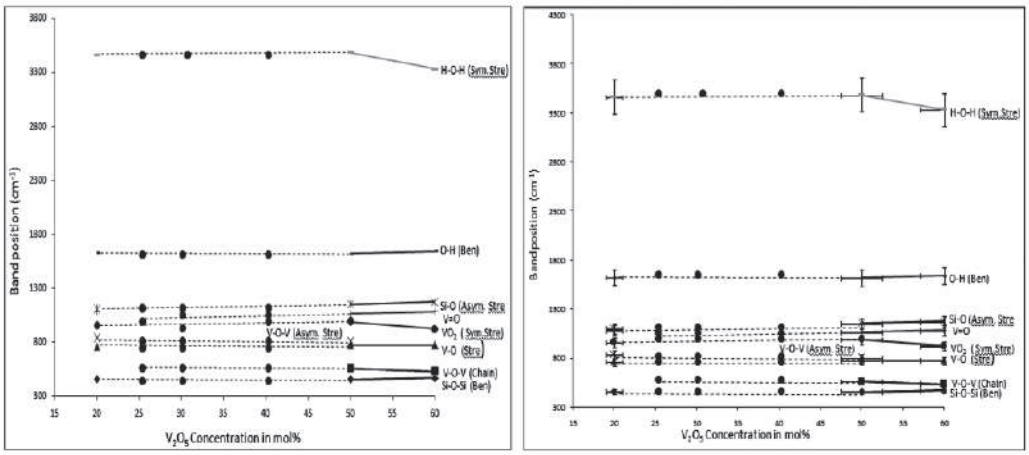


Figure 5 : The composition dependence of the band position with V_2O_5 concentration (a) without error bars (b) with error bars

4. Conclusion

The ratio of Na_2O/SiO_2 was always kept constant in $xNa_2O_2xSiO_2zV_2O_5$ glass system. It was found that the melting temperature of the glass samples depended on the amount of V_2O_5. The peaks and peak positions were assigned to Si-O-Si, O-Si-O, Si-O, V-O-V, V=O, VO_2 and V-O bonds. The IR band positions in these glasses changed with the increasing of V_2O_5. The formation of O-H bond around 1643 cm^{-1} and 3485 cm^{-1} expresses the hygroscopic nature of the glass and provides wealth information about the structural units. In the case of vanadium doped glasses, at high concentration the bands belonging to the vibration in V_2O_5 groups dominated the spectra. It can be said that vanadium prefers to bridge with the oxygen that did not take part in the SiO_4 units making new structures and in consequence it acted as a network former. This indicates the reduction of transmission of light. X-ray diffraction pattern of the NS20V, NS50V and NS60V base sample shows amorphous haloes. The X-ray diffraction pattern of the heat treated NS20V, NS50V and NS60V samples show the crystallinity in the material which indicates that when heat treatment is performed the glass may show glass ceramic properties.

References

1. S. Mandal and S. Hazra, J. Mater. Res., Vol. 15, No.1, Jan 2000

2. Bahman and Mirhadiet al., *Journal of Optoelectronics and Advance Materials,* Vol.13 No.6, June 2011, pp. 679-683

3. Md. R. Ahsan. M.G. Mortuza, *Journal of Non- Crystalline Solids,* pp. 351
4. K. El-Egili. Infrared Studies of Na_2O-B_2O_3-SiO_3 and $A1_2O_3$- Na_2O-B_2O-SiO_3 Glasses, J. Physica B 325(2003) pp. 340-348
5. F.A. Khalifa, F.A. Mustafa et al., *India, Journal of Pure & App. Phys,* 34, 207(1995)
6. S Thirumaran& N Prokash, *Indian Journal of pure and Applied Physics,* Vol. 53, February 2015, pp. 82-92
7. M. Rada, L. Rus et al., *Journal of Non-Crystalline Solids* 414 (2015) 59-65
8. S. Rada, T. Ristoiu, M. Rada et al., Mater. Res. Bull. 45 (2010) 1598
9. Poonam Sharma et al., *New Journal of Glass and Ceramics,* 2011, 1, 112-118
10. M. Rada, S. Rada et al., *Journal of Non-Crystalline Solids* 4414 (2015) 59-65
11. I.Ardelean, C. Andronache, C. Campean, P. Pascuta, Structural investigation of $xFe_2O_3 \cdot (100\text{-}x)[P_2O_5{\cdot}CaO]$ and $x(Fe_2O_3{\cdot}V_2O_5){\cdot}(100\text{-}x)[P_2O_5{\cdot}CaO]$ glass systems by IR spectroscopy, Mod. Phys. Lett. B 45 (2004) 1811-1816.
12. L.Stanescu, E. Indrea et al., Some contributions to the investigation of V_2O_5-MoO_2 system, Rev. Roum. Phys. 21 (9) (1976) 939-951
13. Vassalin Dimitrov et al., *Journal of Non- Crystalline Solids,* 180 (1994) 51-57
14. Poonam Sharma et al., *Indian Journal of Pure & Applied physics,* Vol.48, January 2010, pp. 39-46
15. Padmasree K P, Kanchan D K et al., Solid State Commun 136 (2005) 102
16. D.A. Magdas et al., *Journal of Non-Crystalline Solids* 428 (2015) 151-155
17. King, P.L., Ramsey, M.S., & Swayze, G.A., 2004. Infrared Spectroscopy in Geochemistry, Exploration Geochemistry and Remote Sensing. Mineral. Assoc. Canada, Short Course Series, vol. 33, 93-133
18. J. Wong, J. Non-Cryst. Solids, 20 (1976), pp. 83
19. C. Dayanan et al., J. Mater. Sci.31, (1996), pp. 123