Turk J Phys
26 (2002) , 441 – 447.
© TÜBİTAK

Effect of the Oxygen/Halogen Ratio on the Physical Properties of Some Sodium-Boro-Vanadate Glasses

Ahmed Gamal El-Din MOSTAFA
Phys. Dept., Faculty of Science, Al-Azhar Univ. (11884),
Nasr City, Cairo-EGYPT
e-mail: dr_ahmedgamal@hotmail.com

Received 28.12.2001

Abstract

Four different glass systems of the sodium boro-vanadate type containing halogen ions, were prepared by melting at 1000°C for three hours and annealed at 300°C. These glasses were investigated using dc conductivity, density, molar volume and magnetic susceptibility measurements.

It was found that the activation energy shows a decrease as the halogen ions were increased, which was attributed to the increase in the mobility of sodium ions and the gradual formation of some terminal non-bridging halogens, in addition to the electron hopping between the different oxidation states of vanadium. The activation energy values for glasses containing iodine ions was less then the activation energy for glasses containing fluorine ions, a function that can be ascribed to the ionic radii of the respective halogen ions. The decrease in activation energy in turn is due to the increase in the interstitial vacancies in the same sequence. This was confirmed by the density and the molar volume results.

It was supposed that the decrease in the paramagenetic properties of these glasses with the increase of the halogen ions content may be due to the formation of VXO_3 groups. Also, the magnetic properties was found to decrease as the ionic radius of the introduced halogen ions increased, which was attributed to the increase in the internal vacancies inside the network.

An attempt is made to correlate the experimentally obtained values of both the activation energy and the. magnetic susceptibility with the calculated molar volume values of these glasses.

Key Words: Physical Properties of glass, Glass containing halogen ions, Glass structure.

1. Introduction

Vanadium pentoxide containing glasses have now many important applications in the field of solid state electronics [1]. Such glasses have attracted the attention of many workers and thus many articles have been published dealing with the study of their structure as well as their electronic transport properties [2-6].

It was previously found that vanadium ions can exist as V^{5+}, V^{4+} and/or V^{3+} in different oxide glasses [7]. Mott had concluded that the electronic conduction in vanadium oxide containing glass may be caused by the phonon assistance of electron hopping between the different present localized states (small polaron hopping) [8,9]. If a sufficient quantity of an alkali oxide is introduced into a glass, ionic conduction is present, and the electrical conductivity of the glass is markedly increased [10]. It is also found that the diffusion coefficient of the alkali ions in a glass network increases as the alkali oxide content is increased [11].

From another point of view, many studies on the structure and the properties of oxide glasses containing halogen ions have been performed [12-15]. From these studies, it was found that the addition of halogen ions increases the electrical conductivity of such glasses.

In spite of the many published articles in this field, the problem still needs more study. Therefore, in this work the effect of oxygen/halogen ratio on the physical properties of some alkali-boro-vanadate glasses containing halogens was studied. An attemp is made to correlate the experimentally obtained values of both the activation energy and the magnetic susceptibility with the calculated molar values of these glasses.

2. Experimental Work

The glass samples were prepared by using pure grade chemicals and the batches were melted in porcelain crucibles in an electrically heated furnace at 1000°C for three hours. The melts were then cast on a warmed stainless steel plate and after just sitting, they were directly transfered to an annealing furnace at 300°C and were then left to cool to room temperature (RT) at a cooling rate of about 1°C/5 minutes.

For the dc electrical conductivity measurements, the glasses were polished to obtain disks of 10 mm diameter and 2 mm thickness, and both sides were painted by an air drying silver paste to ensure complete electrical contact. A 610C keithley electrometer with DTC2 Oxford temperature stabilizer were used to measure the electrical current throughout these glasses. The measurements were carried out in the temperature range from 300 up to 600 K. The electrical activation energies were then calculated using the Arrhenious equation:

$\sigma = \sigma_o$ exp (-E_a/kT),

where σ is the electrical conductivity of a sample,

σ_o is constant,

E_a is the electrical activation energy,

k is the Boltzmann constant and

T is the absolute temperature.

For magnetic susceptibility measurements, powder glasses with particle size less than 200 mesh were used applying the Gouy method using a one tesla electromagnet.

Archimedes technique was applied to obtain the density values of these glasses using xylene as an immersing liquid of constant density value [0.86 gm/cm^3 at RT]. The molar volumes of these glasses were then calculated [16].

3. Results and Discussion

Four different glass systems were prepared, differing from one another only by the type of the introduced halogen ions. These glasses contain constant amount of 50 mol % $B_2O_3$and 25 mol % V_2O_5, but Na_2O was gradually replaced by NaX (mol/mol) in proportions of 2.5 mol, (where X represents F, Cl, Br, or I, and Table (1) shows the compositions of the prepared glasses).

Table 1. The composition of the studied glasses.

Sample no*	1	2	3	4	5	6	7	8	9	10	11
Na_2O	25	22.5	20	17.5	15	12.5	10	7.5	5	2.5	0
NaX**	0	2.5	5	7.5	10	12.5	15	17.5	20	22.5	25

(*)Each glass sample contains constant 50 mol % B_2O_3 and 25 mol % V_2O_5.

(**) X represents F, Cl, Br or I.

The electrical conductivity values of all these glases were obtained at different steady temperatures. All the calculated values of log conductivity (log σ) were plotted as a function of the reciprocal of the absolute temperatures. Figure 1 presents the obtained straight lines for the glass samples which contain 12.5 mol % NaX of the four glass systems. The electrical conductivities of all glasses show an increase as the reciprocal of the temperature was gradually elevated.

The activation energy of conduction for the investigated glasses show a decrease as the alkali halide content is gradually increased as shown in Figure 2.

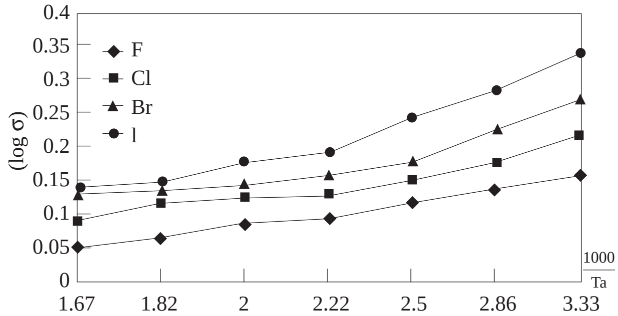

Figure 1. Representative (log σ) versus $\frac{1000}{Ta}$ relationships of the glass containing 12.5 mol % of NaX.

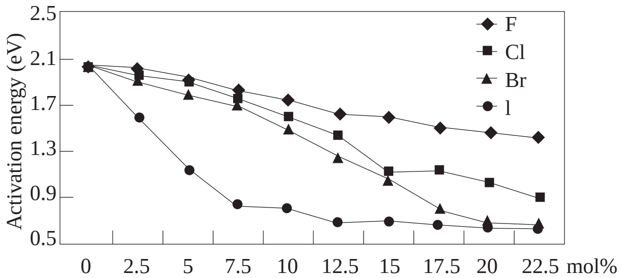

Figure 2. The relation between the activation energy values and the NaX content.

One can also see that the glass system containing sodium iodide represents the lowest activation energy values, while the glass system which contains sodium fluoride represents the highest activation energy values. It is also supposed that the gradual replacement of oxygen ions by the different use of halogen ions in these glasses setup vacancies with different volumes due to the differences of their ionic radii. These halogens may act as substitutional impurities in these glasses. Accordingly, the electrical conduction in these glass systems may be due to the following factors:

(a) The mobility of the positively charged sodium cations throughout the glass network.

(b) The electron hopping between the localized states setforth by the different oxidation states of vanadium cations [17].

(c) The present negatively charged halogens, which act as interstitial impurity and/or as terminal non-bridging halide ions, as well as their effect of changing the volumes of the interstitial vacancies in the glass-network [18].

Since oxygen ions represent the smallest ionic radius in comparison with the different used halogen ions, therefore vacancies of the smallest volume must be formed in the base glass. Hence, the mobility of the positively charged sodium cations appeared in its lowest state [19]. This may be the reason that the base glass shows the highest activation energy value [2.04 eV].

It is known that the ionic radius of fluorine ions is too slight to differ from that of oxygen, therefore the glass samples which contain fluorine ions, show the highest activation energies with respect to the other glass systems. The lowest activation energy values are represented by glasses containing iodine ions because this ion have the largest ionic radius and consequently impose the largest vacancies in the glass netwark.

The addition of halogen ions form the terminal borate and / or the terminal vanadate groups of the form [$VO_3 - X$ and / or $BO_2 - X$]. The presence of such dangling and non-bridging halogen in addition to the larger volume of halogen ions (in comparison to oxygens) produces more open glass structure [18]. This may support the suggestion that the increase of alkali halides increase the ionic conductivity which may be due to the increase of the mobility according to the diffusion path model [20]. Also, the increase in the conductivity with increasing halogen ions may be due to the fact that Na-X bond strength is weaker than the Na-O bond [18].

The calculated activation energies for the glasses containing the same concentrations of the different halogen ions are found to decrease gradually on going from glasses containing fluorine ions to glasses containing iodine ions. Such decrease in the activation energy with the mentioned order is found in correspondance agreement to the increase of the ionic radii of the introduced halogen ions. In addition to this, since the field strength of the halide ions takes the order F > Cl > Br > I, this makes the strength of the bond B-X and / or V-X follow also the same order [18].

The increase in the volume of the individual vacancies on going from glasses contaning fluorine ions into glasses contaning iodine ions can be confirmed by measuring the densities and by calculating the molar valumes of these glasses. Figure 3 shows the change in the obtained density values and Figure 4 represents the variations of the calculated molar volume values as a function of the halogen content. The density value of the base glass (sample free from halogen ions) is found to equal 2.43 gm / cm^3. As the halogen ions begin to enter into the glass network, a considerable decrease is observed. The gradual increase of the halogens replacing oxygen ions makes the density values of all glass systems decrease approximately linearly, and the slop of the decrease of all these systems appears approximately semillar. It is found also that the glasses that contain fluorine ions represent the highest density values, while the glasses that contain iodine ions represent the smallest density values. The molar volume values represent a linear increase with the increase of the introduced amount of halogen ions. It is also shown that the glass system which contains fluorine ions exhibits the smallest molar volume values, but the system which contains iodine ions represents the largest molar volume values. These results are found to be in complete agreement with the change in the obtained activation energy values.

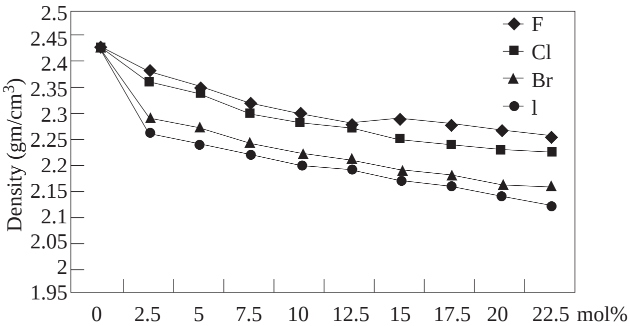

Figure 3. Density values versus NaX content.

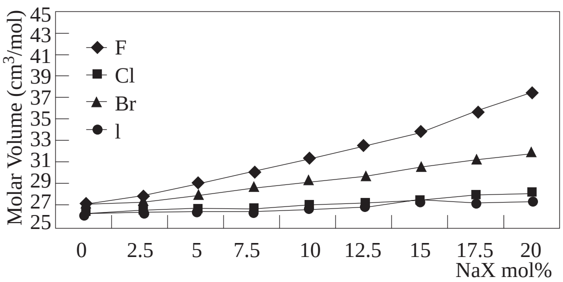

Figure 4. The Molar volume values versus the NaX content.

Nevertheless, the amounts of vanadium and sodium cations are kept constant, the activation energy values show gradual decrease with the increase of the halogen ions. This may be due to the change in the equivalent halogen– oxygen packing density around sodium ions [coordination number of sodium]. This effect may disturb also the electric field gradiant arround sodium ions. All these factors may increase the mobility of the positively charged sodium ions during the network.

Figure 5 shows the change in the volume magnetic susceptibility values as the halogen ions are gradually increased, in all glass systems. It appears that the paramagnetic properties increase gradually as the halogen content is gradually increased and on going from glasses containing fluorine into glasses containing iodine ions.

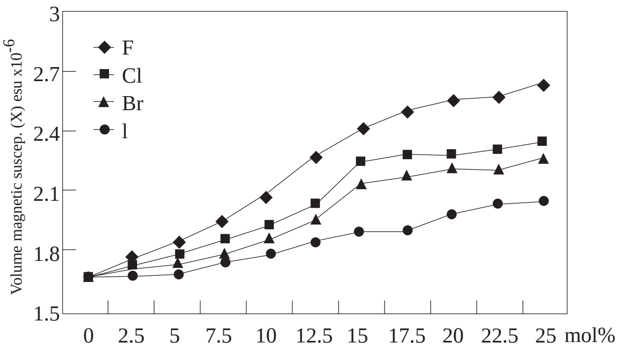

Figure 5. The magnetic susceptibility values versus the NaX content.

Considering the prepared base glass composition, it is supposed that boron cations form BO_3 groups while vanadium cations form VO_3, VO_4 and VO_5 groups, that is, both cations act as network formers in these glasses. The addition, of halogens replacing oxygen ions form some terminated halogen bonds with the presented borate and vanadate groups. A deficiency in the amount of oxygen ions will gradually takes place as the halogen ions increase in the glass network-replacing oxygen ions. So, it is supposed that some VXO_3 groups are formed instead of those VO_4 that formed first. These groups are of lower paramagnetic properties due to the small cooperative interaction between the magnetic moments of the atoms forming such groups [19]. The decrease of the magnetic properties of these glasses when going from glasses containing fluorine ions to glasses containing iodine ions, may be attributed to the decrease in the magnetic interaction between the magnetic moments of the transition metal cations [V] and the surrounding oxygen and halogen ions. This may also be due to the gradual increase in the volumes of the internal vacancies which increase in the same sequence [19].

It is always supposed that the physical proprties of a glass is directly affected by any slight change in its structure, and it is usually stated that the dc conductivity increases when the glass structure becomes open [18], (due to changes in the ionic transport). This supposition is taken in consideration and a relation between the structure of the investigated glasses (represented by their moler volume values) and their electrical conductivity (represented by their activation energy values) are represented in Figure 6. From this figure, it appears that the activation energy values show approximate linear decrease, but at some definite molar volume value-differing from one glass system to the other-the activation energies starts to stabilize. This stabilizations are obtained at molar volumes of approximately equal to 27.4, 28.3, 31.4 and 34.0 cm^3/mole for glasses containing fluorine, chlorine, bromine and iodine, respectively.

From another point of view, no relation is even noticed between the magnetic susceptibility values of any glass system and its molar volume values . An attempt is made here to correlate the magnetic susceptibility and the molar volume values of these glass systems in Figure 7. From this figure, the magnetic susceptibility values, for each glass system, show increasing trends in two different straight lines, intersecting approximately at the same molar volume values at which the activation energy values show their approximate stability.

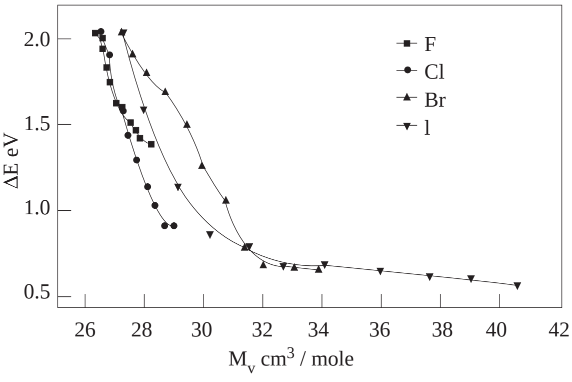

Figure 6. The change of ΔE versus M_v.

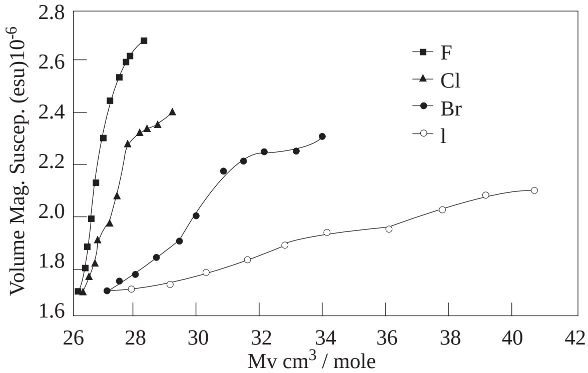

Figure 7. The change of the volume magnetic susceptibility versus M_v.

It is supposed here that these glasses reach their maximum open structure at molar volume values around which the magnetic susceptibilities and the activation energies exhibit their changes (27.4, 28.3, 31.4, and 34.0 for glasses containing flourine, chlorine, bromine and iodine respectively) after which the glass structure may be stabilized.

4. Conclusion

The gradual replacement of oxygen ions by halogen ions leads to a decrease of the activation energy values due to the formation of some VXO_3 groups with a terminal non-bridging halogen. These groups are found to be also of low paramagnetic properties. The decrease of the activation energy values on going from glasses containing fluorine to glasses containing iodine ions may be due to the increase of the volume of the introduced halogen ions which follow the same sequence. This may change the glass structure to become open, and this is shown directly in the density and molar volume values. This change in the glass structure affects directly the internal vacancies which in turn affect the mobility of the ions carrying charges. Two relations are also obtained to correlate both the magnetic susceptibility and the activation energy values with the molar volume values of these glasses. From which it is supposed that, at definite molar volume values the glass structure becomes highly open and then stabilized.

Acknowledgement

The author would like to express his gratitudes to Dr. K. A. Ali, Dr. G. A. Yahya and Dr. F. Abdel-Wahab. Phys. Dept., Faculty of Science in Aswan, South Valley Univ., for their useful help in some measurements.

References

[1] Y. Sakurai and Y. Yamaki, *J. Electrochem. Soc.*, **132**, (1985), 512.

[2] M. Nabavi, C. Sanchez and L.Livage, *J. Philos. Mag.*, **A 40**, (1984), 1081.

[3] B. K. Sharma, D. C. Dube and A.Bbai Mansingh, *J. Non-Cyst. Solids*, **65**, (1984), 39.

[4] S. Prabakar, and K.J. Rao, *London Proc. R. Soc.*, **A 429**, (1990), 1.

[5] Noboru Ichimose and Yuichrio Nakai, *J. Non-Gyst. Solids*, **203**, (1996), 353.

[6] O. Attos, M. Massot, M. Balkanski, E. Haro-Poniatowski and M. Asonoza, *J. Non-Cyst. Solids*, **210**, (1997), 163.

[7] N. A. Ghoneim, *J. Non-Cyst. Solids*, **46**, (1981), 181.

[8] N. F. Mott, *Adv. Phys.*, **16**, (1967), 49.

[9] N. F. Mott, *J. Non-Cyst. Solids*, **1**, (1968), 1.

[10] S. Muthupari, S. Lakshmi Raghavan and K. J. Rao, *J. Phys. Chem.,* **100**, (1996), 4243.

[11] M. D. Ingram, *Phys. Chem. Glasses*, **28**, (1987), 215.

[12] M. Irian, M. Couzi, A. Levasseur, J. M. Reau and J. C. Brethous, *Solid State Chem.*, **31**, (1980), 285.

[13] J. S. Sanghera, J. Heo and J. D. Machenzie, *J. Non-Cyst. Solids*, **104**, (1988), 211.

[14] J. Heo and J. D. Moachenzie, *J. Non-Cyst Solids*, **111,** (1989), 29.

[15] A. A. Soliman, *Al-Azhar Bull. Sci.*, **6 (1),** (1995), 949.

[16] G. Mostafa, *Al-Azhar Bull Sci.*, **11 (2),** (2000), 117.

[17] J. D. Mackenzie, *J. Am. Ceram. Soc.*, **47**, (1964), 211.

[18] A. Abd El-Mongy, *Phys. State Sol.,* **(a) 136**, (1993), Kll.

[19] F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", wiley Eastern, Private limited, New Delhy (1972).

[20] Y. Y. Kim,, K. H. Kim and J. S. Chjoi, *J, Phys. Chem. Solids*, **50**, (1989), 903.