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Infrared Analysis and Physical Properties Studies of B_2O_3·CaO·ZnO·TiO_2 Glass System

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Abstract

The glass system having $(B_2O_3)_{0.60}(CaO)_{0.25}(ZnO)_{0.15-x}(TiO_2)_x$, where $x = 0.0$, 0.025, 0.05,..., 0.15, was investigated using infrared spectroscopy, differential thermal analysis, density, magnetic susceptibility and dc electrical conductivity.

The obtained IR results showed that most titanium ions exist as network former while most zinc ions exist as network modifier but boron ions appeared in different structural groups. As titanium oxide was gradually increased to 10 mol%, the glass stability, density and magnetic susceptibility increased, while the molar volume and dc electrical activation energy decreased. When titanium oxide increased from 10 to 15 mol%, the measured and the calculated properties tend to be stable. It was concluded also that the gradual increase in the molar volume acts to decrease the magnetic susceptibility and to increase the glass transition temperature.

Key Words: Infrared Analysis, Differential Thermal Analysis, Magnetic Susceptibility, DC Electrical Conductivity and Physical Properties of Glass.

1. Introduction

Many studies had been done to study the structural features and the physical properties of glasses doped with transition metal ions (TMIs) [1–3]. Such doping acts to improve the physical properties of these glasses [4–6]. These studies show that the physical properties of these glasses are strongly sensitive to any structural changes [7].

Titanium and zinc are important transition metals in the field of glass science. Glasses containing titanium oxide are of high interest in different scientific and technological fields, such as in the manufacture of compact lenses [8]. Zinc is also of high interest due to its many valuable uses to manufacture different types of soft and soldering glasses [9].

From the structural point of view, it is known that boron forms the main frame of the glass network, but calcium can act either as bridges between any two adjacent polyhedra or it can be enclosed within the interstices of the glass network. Titanium and zinc ions can act either as a glass network former (GNF) or as glass network modifier (GNM), since they can form strong covalent bonds in the glass network [10].

The present work was devoted to investigate selected calcium borate glasses containing different amounts of zinc- and titanium oxides. Infrared (IR) spectroscopy and differential thermal analyses (DTA), as well

as the volume magnetic susceptibility, dc electrical conductivity and density were measured while the molar volume, mass- and molar- magnetic susceptibilities and electrical activation energy were calculated. Both the molar magnetic susceptibility and the glass transition temperature will be correlated to changes in the molar volume of these glasses.

2. Experimental Work

The composition of the prepared glasses was selected via the following molecular formula: $(B_2O_3)_{0.60}(CaO)_{0.25}(ZnO)_{0.15-x}(TiO_2)_x$, where $x = 0.0$, 0.025, 0.05, ... , 0.15. The glass batches were prepared from analytically pure chemicals. The weighted batches were mixed well, and they were then melted in porcelain crucibles in an electric muffle furnace at 1100 °C for two hours under atmospheric air. The melts were poured on a pre-heated stainless-steel plate and after sitting for a short period were directly transferred to the annealing furnace at 350 °C, in which they stayed for twelve hours, in order to obtain strain-free samples.

For IR, DTA and volume magnetic susceptibility measurements, powdered glasses of homogeneous mesh size were prepared. The IR spectra were recorded at room temperature employing the KBr disk method using Fourier Transform intrared spectrometer model Bruker-Vector 22, in the range from 400 to 4000 cm^{-1}. The DTA measurements were carried out up to 700 °C using a Shimadzu DTA-50 analyzer. Gouy technique outfitted with a one tesla Faraday electromagnet was used to obtain the volume magnetic susceptibility values of these glasses at room temperature.

For dc electrical conductivity and density measurements, solid samples were used. Disk shaped samples of two mm thickness, ten mm diameter were used to measure the electrical conductivity between room temperature and 300 °C, using a VA-J-25 electrometer. For good electrical contact, air-drying silver paste was used to paint both faces of the sample. Density values were obtained applying Archimedes liquid displacement technique relative to xylene as an immersing liquid of stable density.

3. Results and Discussion

3.1. Infrared analysis

Figure 1 (a, b and c) shows the IR transmission spectra of the glass samples containing 5, 10 and 15 mol% titanium oxide, respectively. All the obtained IR spectra showed a broad band appeared approximately at 1390 cm^{-1}. This band can be attributed to the stretching vibration of [B–O] bonds in triangle- and meta-borate groups [2, 11]. Another broad band appeared at about 995 cm^{-1} and can be attributed to the stretching vibration of the tetrahedrally coordinated titanium ions [12], as well as the presence of some non-bridging oxygen (NBO) anions [2, 13]. The appearance of titanium oxide in the tetrahedral coordination state indicated that Ti ions occupy GNF positions. In addition, there is a band appeared at 775 cm^{-1}, which can be attributed to the vibration of the linkage between tetrahedral- and triangle-borate groups [4, 5]. This can be attributed to the continuous transformation of the boron cations from triangle to tetrahedral symmetry in the glass network. Another band appeared approximately at 445 cm^{-1}, and can be attributed to the vibration of Zn^{2+} ions in the network vacancies [14]. This band indicated that zinc cations occupy GNM positions [8, 15]. Another band appeared at about 510 cm^{-1}, and can be attributed to the B–O–B bending modes, which usually appeared in high boron content glass [16]. The band that appeared at about 570 cm^{-1} indicated the presence of different deformed borate arrangements, including in plane bending boron oxygen bonds in triangle groups [17]. Some bands are observed between 3400 and 3600 cm^{-1}. These bands can be attributed to water content and some OH groups, which may be due mostly to the used KBr disk technique, since KBr can easily absorb moisture from environmental air.

According to the above IR results, it can be stated generally that, in these glasses, titanium act mainly as GNF, where it forms TiO_4 groups; while zinc acts mostly as GNM, since it occupy only the interstisial vacancies in the glass network. The gradual decrease of zinc oxide decreases the number of the NBO and acts to change the triangle boron to tetrahedral borate groups. It can be concluded also that Ca^{2+} cations occupy only either the modifier positions or can act as bridges between different structural polyhedra in the glass network.

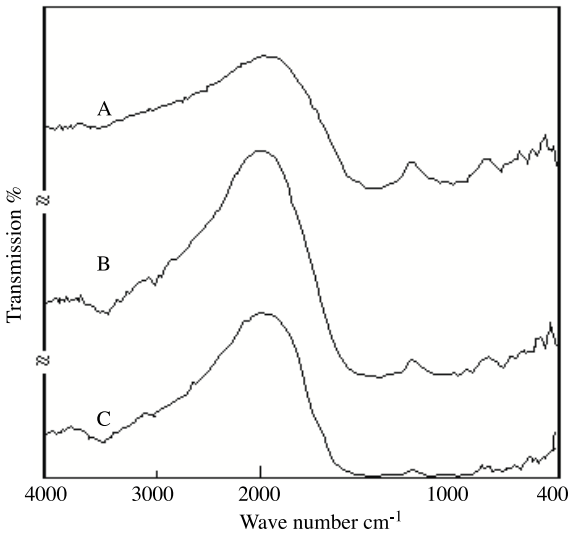

Figure 1. Some representative IR transmission spectra.

3.2. Differential thermal analysis

Figure 2 (a, b and c), shows three representative DTA thermo-grams for the glass samples containing 5, 10 and 15 mol% titanium oxide, respectively. It is seen that all the obtained thermograms show an endothermic peak and an exothermic peak followed by a sharp endothermic peak. It is easy to attribute these peaks to the glass transition temperature T_g, the crystallization temperature T_c and the melting temperature T_m, respectively. Figure 3 shows the change in the characteristic temperatures as titanium oxide was gradually increased. It was observed from this figure that, as titanium oxide gradually increased to 10 mol% in the studied glasses, T_g appears to decrease from 446 to 425 °C, while T_c fluctuates between 484 and 491 °C; but T_m shows slight increase from 552 up to 559 °C. It could be observed also that glasses containing high titanium oxide content (between 10 and 15 mol%) exhibit stable values of all these characteristic temperatures.

The stability of these glasses was calculated as the difference between the crystallization and the glass transition temperatures $(T_c - T_g)$ °C [18, 19], and the calculated values are presented versus titanium oxide content in Figure 4.

Generally speaking, it can be stated that the stability increased linearly as titanium oxide was gradually increased to 10 mole%. Glasses of higher titanium oxide content show approximately constant value. This indicated that Ti^{4+} ions aid the formation of high stable network structure, which in turn may be due to the gradual decrease of the number of the non-bridging oxygen. This means that titanium ions act to increase the homogeneity of the glass and strengthening the glass network. In the same time it acts to increase the relative covalence character and decreases the relative ionicity.

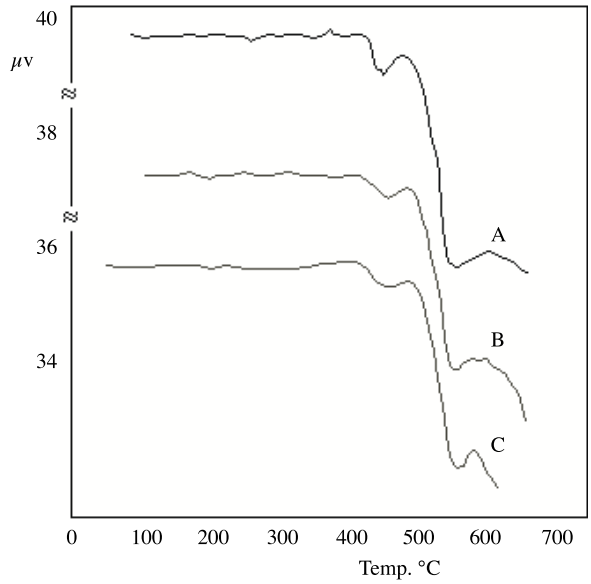

Figure 2. The Differential Thermal Analysis.

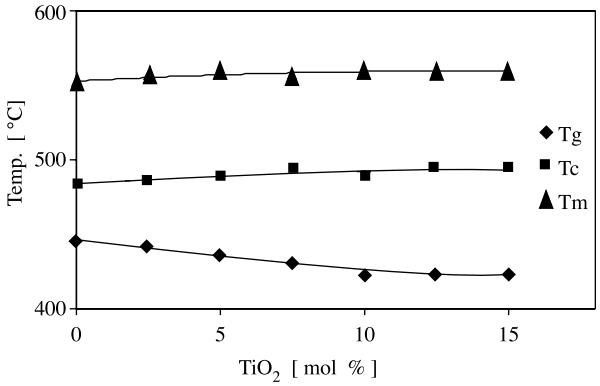

Figure 3. The glass transition T_g, crystallization T_c and melting T_m temperatures versus TiO_2 content.

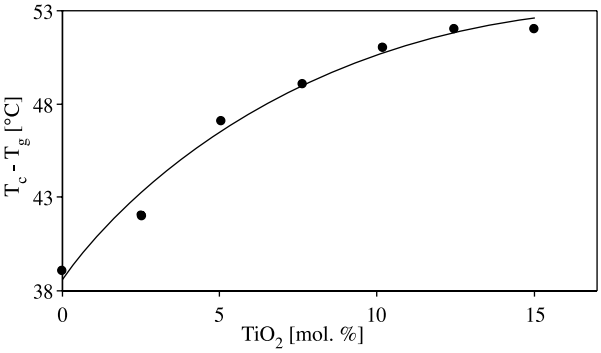

Figure 4. The glass stability versus TiO_2 content.

3.3. Density and molar volume

Density of glass is usually considered as an important property for quality control in glass industry. The observed changes in density reflect-directly the differences in the glass composition and in turn the glass network structure [20]. On the other hand, the molar volume of glass can be preferably used to describe the network structure and the arrangement of the building units, since it deals directly with the spatial structure

of the oxygen network. The behavior of the measured densities and the calculated molar volume values of these glasses were plotted in Figure 5 as a function of titanium oxide content. It appeared from this figure that as titanium oxide was increased, the density increased in an exponential-like curve from 2.85 to 2.98 g·cm^{-3}, while the molar volume decreased exponentially also from 23.86 to 22.72 cm^3·g^{-1}·mol^{-1}. That is, density and molar volume of glasses with higher titanium oxide content show approximately stable values [21].

It was supposed that the first slight increased in density may be due to the gradual increase of TiO_4 groups, together with the gradual decrease in the number of the non-bridging oxygen that accompanied the presence of zinc cations. The approximate stability that appeared with high titanium oxide content reflected that these glasses achieved their maximum homogeneity with 10 mole% titanium oxide. This conclusion is in agreement with the glass stability drawn from DTA measurements.

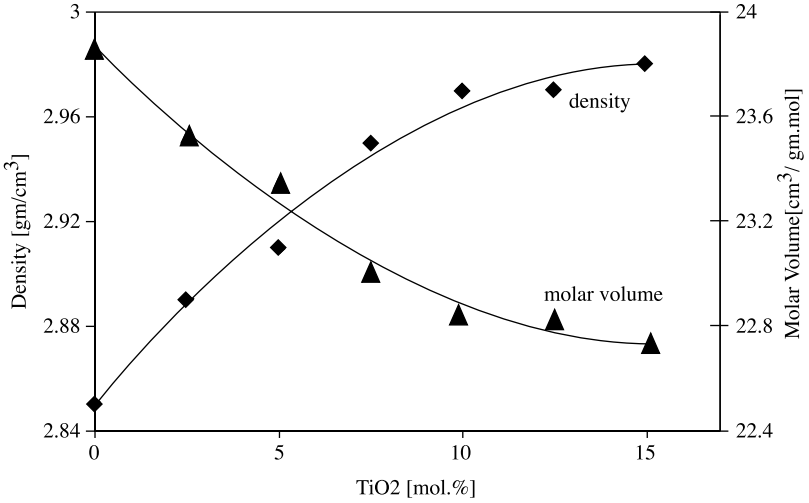

Figure 5. The density and molar volume values versus TiO_2 content.

This behavior may be due to the differences between the roles of both titanium and zinc ions in the glass network, together with the differences in their physical properties. This appeared also in agreement with the IR results, which indicated that titanium occupy GNF positions while zinc act mainly as GNM and occupy the interstitial positions. Hence it is supposed that the main structural forming groups in the high ZnO content glass are the triangle borates, while at high TiO_2 content glasses some triangle borates changes to occupy the tetrahedral borate groups. The number of the present NBO was supposed to decrease gradually with the decrease of zinc oxide content, which aids the increase of the homogeneity of the glass network.

3.4. Magnetic susceptibility

The differences in weight of a sample (dm) due to the change in the intensity of the applied magnetic field H were recorded and plotted as a function of H^2, where straight lines were obtained. The slopes dm/dH^2 were obtained and the volume magnetic susceptibility values k [21] were then calculated employing the equation

$$k = [2g/a][dm/dH^2],$$

where g is the acceleration due to gravity and a is the cross sectional area of the measured sample. The mass magnetic susceptibility values M were then calculated from the equation

$M = k$ / d, where d is the measured density.

Multiplying the mass magnetic susceptibility by the mean molecular weight of each sample w, the molar magnetic susceptibilities Φ were then obtained. The calculated values of the volume-, mass- and molar-

magnetic susceptibilities are listed in Table 1, and the change in the molar-magnetic susceptibility was plotted in Figure 6 as a function of titanium oxide content.

Table1. Magnetic susceptibilities; k in esu $\times 10^{-8}$, M in esu·cm^{-3} gm $\times 10^{-8}$ and Φ in esu·cm^{-3} mol^{-1} $\times 10^{-6}$.

x (TiO_2)♢	0.0	0.025	0.050	0.075	0.100	0.125	0.150
k	14	17	21	29	39	51	66
M	4.912	5.882	7.216	9.831	13.131	17.172	22.142
Φ	0.679	3.974	4.902	6.674	8.911	11.645	15.020

Inspecting the obtained results in this figure, it is easy to observe that the molar magnetic susceptibility increased linearly. This can be reliably attributed to the increase of titanium ions that exhibit high paramagnetic character and the decrease of zinc ions that exhibit diamagnetic character.

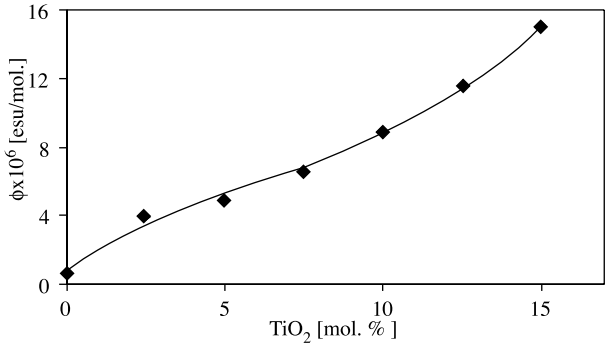

Figure 6. The change in the molar magnetic susceptibility versus TiO_2 content.

This can be attributed to the fact that the d-shell electrons of zinc are all spin-paired while those in titanium are spin-free [22]. Therefore the total magnetic moment of these glasses increased gradually with the increase of titanium oxide.

3.5. DC Electrical Conductivity

The IV characteristic curves were measured between 0 and 100 volts at room temperature to check the ohmic behavior of the contact between the sample and the electrodes. A linear dependence was obtained, which evidenced such behavior. It was supposed generally that both electrons and/or ions can act as charge carriers in these glasses. But it is known that ionic conduction produces polarization at the electrodes, which makes the linear relations look like exponential curves [23]. Such factor was not observed in the obtained results of the studied glasses, and the temperature dependence of log ρ showed linear relations. Therefore it can be supposed that the dominant charge carriers are electrons, and the semi-conduction properties of these glasses may be due to the electron hopping between the different oxidation states of the present transition metal ions (titanium ions) [24].

When the electrical conduction mechanism was considered, and since linear relations between [log (ρ)] and [1/T] were obtained, Arrhenius equation must be applied:

$$\rho = \rho_o \exp .(\Delta E/KT),$$

where ρ_o is constant, ΔE is the electrical activation energy, K is the Boltzmann constant and T is absolute temperature.

It can be stated that when temperature is elevated the conductivity exhibits a thermally activated process. The dc electrical measurements were carried out from room temperature up to 300 °C, where linear plots were obtained between lnρ and the reciprocal of the absolute temperature. The activation energies of the

studied glasses were then calculated and are plotted in Figure 7, as a function of titanium ion concentration. It appeared that the activation energy showed approximately linear decrease until titanium oxide content was increased to 10.0 mol%, above which slight decrease was observed. This is due to the gradual increase of titanium and the gradual decrease of zinc ions, where Ti^{2+} appeared in more than single oxidation state, while Zn^{2+} appears mainly in a single oxidation state. The process of electron hopping between the different valences states of titanium enhances the electronic conductivity and decreases the activation energy in these glasses [23]. The obtained linear relations between the electrical conductivity and the reciprocal of temperature can be taken as evidence for the applicability of Arrhenius-like relationship and therefore it can be supposed that the dominant conduction mechanism in these glasses is the thermally activated electron hopping.

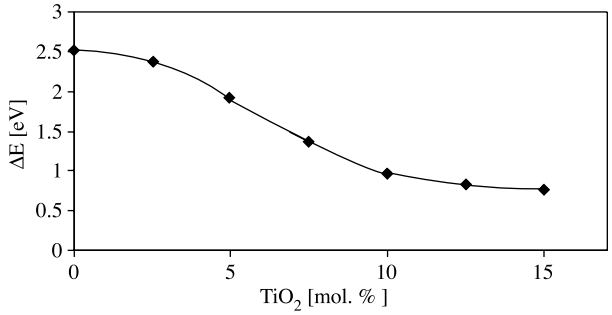

Figure 7. The change in the activation energy ΔE as a function of TiO_2 content.

3.6. The Dependence of Glass Transition Temperature and Molar Susceptibility on the Molar Volume

Since there is a direct correlation between the molar volume and the spatial structures of a glass network, it was therefore expected that any change in physical or chemical property must depend directly on the change in molar volume. As such, we have attempted to correlate the molar volume values of these glasses with some characteristic physical properties [21]. Hence Figure 8 shows the dependence of both the glass transition temperature and the molar magnetic susceptibility of the studied glasses on their molar volume values. As the molar volume increased, the molar magnetic susceptibility exponentially decreased, while the glass transition temperature increased exponentially as well.

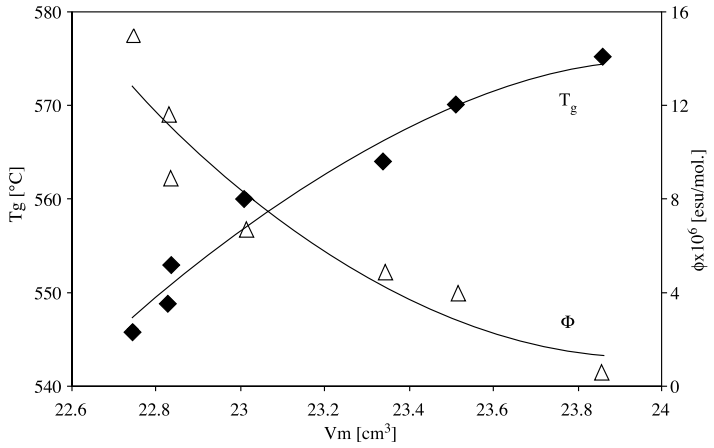

Figure 8. The molar magnetic susceptibility Φ and the glass transition temperature versus molar volume values V_m.

It is supposed that the increase in molar volume can be taken as evidence for decrease of the ionic character and increase of the covalent character of the glass network. It is also observed that slight change in the molar volume values (from 22.84 to 23.86 $cm^3 \cdot g^{-1} \cdot mol^{-1}$) affect rigorously both the glass transition temperature (from 446 to 424 °C) and the molar magnetic susceptibility (from 0.679 to 15.020 $\times$ $10^{-6} esu \cdot cm^{-3} \cdot mol^{-1}$). Such increase in the molar volume reflect the increase of the homogeneity of the network and, in turn, reflect strengthening of the internal chemical bonds. Therefore the glass transition temperature increased. Also the increase in molar volume indicated the opening of the network structure, which in turn decreases the magnetic interaction of the electron spins of the present transition metal ions. This may be the reason for the observed decrease of the molar magnetic susceptibility.

4. Conclusion

According to the presentation of the obtained results, it can be concluded that:

1. In titanium-free glass, only boron ions form the main frame work of the glass matrix, while zinc and calcium act as network modifying cations.

2. Introducing titanium oxide, it enters as GNF and increases the glass stability as well as T_m and T_c but decreases T_g.

3. The magnetic susceptibilities of these glasses increased as titanium oxide content was gradually increased.

4. The thermally activated electron hopping between the different oxidation states of titanium is the supposed conduction mechanism that takes place in these glasses. The observed decrease of the activation energy values can be attributed to the gradual increase of titanium ions.

5. The molar magnetic susceptibility decreases with the increase in the molar volume which may be due to the increase of the internal free volume and the decrease of the interaction between the electronic spins of the present transition metal ions.

6. The exponential increase of the glass transition temperature with the increase of the molar volume may be due to the decrease of the ionic character and the increase of the covalent character of the glass network.

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