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Electrical, IR Spectroscopy, and DTA Studies of Some Sodium Tetraborate Glasses Containing Vanadium Oxide

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The ac electrical conductivity and dielectric constant of semiconductive $(Na_2B_4O_7)_{100-x}(V_2O_5)_x$ glasses with $x = 0.25$, 0.5, 1, 2, 3, and 5 mol% have been measured at a constant frequency of 1 kHz in the temperature range from 293 to 600 K. IR spectra of these samples have been recorded at room temperature in the range between 400 and 4000 cm^{-1}. The results showed a broad absorption band with a peak around 3400 cm^{-1}, indicating the presence of a hydroxyl group and the formation of B–OH within the glass matrix. The addition of V_2O_5 caused new absorption bands in comparison with the absorption bands obtained for the pure $Na_2B_4O_7$ glass between 500 and 1800 cm^{-1}. The differential thermal analysis (DTA) was performed for all samples in the temperature range from room temperature to 600 °C.

1. Introduction

Many transition metal oxides form glasses when melted with $Na_2B_4O_7$. These glasses have been the subject of intensive experimental and theoretical studies [1 to 10].

The loss of oxygen from the melt produces a proportion of lower valency transition metal ions. The general condition for semiconducting behavior is that the transition metal ions (TMI) should be capable of existing in more than one valency state, so that conduction occurs by movement of carriers from the lower valency state to the higher valency state. In the case of vanadium, this has been determined to occur between the V^{4+} and V^{5+} valence states.

In a previous work [10], the effect of adding CuO on the electrical conduction of $Na_2B_4O_7$ was reported. It has been found that the electrical conduction of these samples was electronic rather than ionic. Actually, most investigations of these glasses have attempted to define the properties of a single system, that is, one containing a particular TMI.

The range of parameters which can be obtained by varying the glass composition and the preparation conditions in a single system is limited and it is difficult to distinguish the effects of parameters which may be interrelated.

In the present work, the ac electrical conductivity and dielectric constant of some $Na_2B_4O_7$ semiconducting glasses containing a low concentration of V_2O_5 up to 5 mol%

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have been measured as a function of temperature. Also, IR spectroscopy and DTA analysis of these samples have been studied.

2. Experimental Techniques

Glasses in the system having a composition $(Na_2B_4O_7)_{100-x}(V_2O_5)_x$ where x is varied from 0 to 5 mol% were prepared from chemically pure grade materials, according to their molar composition, in an alumina crucible, as shown in Table 1. In order to reduce the tendency to volatization the crucible was initially heated for 1 h at 300 °C and then transferred to another furnace maintained at 1000 °C. The melt was stirred from time to time using an alumina rod and was finally poured on a clean stainless steel plate and cast into a disc of 2 cm diameter and 2 mm thickness. The samples were introduced to a furnace which was already at 300 °C. The furnace was maintained at this temperature for 1 h and was then switched off to cool down to room temperature. The glass samples were polished using diamond paste. Silver dag was used to make two circular electrodes on both sides of each sample. The sample was placed between two copper electrodes and mounted in a controlled electric furnace with maximum temperature of 1000 °C. The ac electrical conductivity and the dielectric constant were measured as a function of temperature, using an automatic Wyne-Kerr bridge model 900B at a constant frequency of 1 kHz. The temperature of the furnace was controlled by a stabilized variac. The measurements were made in the temperature range from room temperature to 600 K, with a heating rate of 1 K/min. The sample temperature was measured using a copper–chromel–aluminel thermocouple placed at the sample holder.

The infrared spectra of these samples were recorded at room temperature in the range from 400 to 4000 cm^{-1}, using a FT-IR Perking-Elmer spectrometer model 1650 with scanning rate of 4 cm/s.

A Perking-Elmer DTA 1700 system is used for the differential thermal analysis of the samples under investigations. DTA measurements were made at atmospheric pressure in the temperature range from room temperature to 600 °C with a scanning rate of 20 K/min.

3. Results and Discussion

3.1 Electrical conductivity

The inclusion of 0.25 up to 5 mol% of V_2O_5 in the colorless $Na_2B_4O_7$ base glass changed the color to yellowish, it became darker by increasing the V_2O_5 content. This coloration is associated with the presence of valency complexes of vanadium.

In Table 1, the values of the measured electrical conductivity σ at a frequency of 1 kHz at room temperature (293 K) for all samples are given. The logarithm of σ as a function of $1/T$ is illustrated in Fig. 1 and Fig. 2a to f, for pure $Na_2B_4O_7$ glass (sample 1) and samples containing V_2O_5 (samples 2 to 7), respectively. From Fig. 1, it is noticeable that the value of the conductivity increases by increasing the temperature, reaches a maximum value of $1.01 \times 10^{-5}\ \Omega^{-1}\ cm^{-1}$ at $T_1 = 348$ K. Above T_1, the value of σ decreases. It reaches a minimum value of $9.6 \times 10^{-7}\ \Omega^{-1}\ cm^{-1}$ at $T_2 = 438$ K. At $T > T_2$, the value of σ was found to increase with increasing temperature satisfying the formula [11]

$$\sigma = \sigma_0\, e^{-E_a/kT} \tag{1}$$

Table 1
Compositions and values of the ac electrical conductivity (σ) and the dielectric constant at 293 K, T_1 and T_2 (see text) for samples 1 to 7

sample	$(Na_2B_4O_7)_{100-x}(V_2O_5)_x$	ac electrical conductivity σ (Ω^{-1} m^{-1})					dielectric constant				
	x (mol%)	σ_0 (at 293 K)	σ_{max}	T_1 (K)	σ_{min}	T_2 (K)	ε_0 (at 293 K)	ε_{max}	T_1 (K)	ε_{min}	T_2 (K)
1	0	1.21×10^{-7}	1.0×10^{-5}	348	9.6×10^{-7}	438	19	44	368	27	418
2	0.25	3.20×10^{-8}	–	–	–	–	16	–	–	–	–
3	0.50	4.16×10^{-8}	–	–	–	–	24	–	–	–	–
4	1.0	3.95×10^{-7}	4.90×10^{-5}	314	1×10^{-7}	410	24	66	364	32	409
5	2.0	7.44×10^{-7}	1.1×10^{-4}	323	1.57×10^{-6}	408	35	124	397	44	433
6	3.0	3.76×10^{-8}	–	–	–	–	18	–	–	–	–
7	5.0	3.52×10^{-8}	–	–	–	–	17	–	–	–	–

with E_a the activation energy and k the Boltzmann constant. A value of $E_a = 0.74$ eV has been deduced from the slope of the linear relation of Fig. 1 in the temperature range between T_2 and 570 K. This value is compared with the corresponding values of 0.55 and 1.35 eV reported in [7, 8], respectively. In these reports, the dc electrical conductivity of some $Na_2B_4O_7$ containing CuO and Pb_2O_3 as a function of temperature has been measured, respectively. Only experimental data of the dc electrical conductivity of these samples were found at 300 K and in the temperature range between 450 to 573 K. Therefore, the variation of σ with temperature in the range from room temperature to 450 K is missing: For this reason, the measurements presented in [7, 8] should be extended to cover the whole temperature range from room temperature to 600 K for comparison. On the other hand, we found that the theoretical model based on the polaron theory discussed by Mott and Davis [11] does not explain the curve features characterizing the pure $Na_2B_4O_7$ glass sample, (i.e. the plot of ln σT versus $1/T$): From Fig. 1, at least three different conduction mechanisms are observed. These mechanisms are attributed to the moisture present within the glass matrix, leading to the formation of sodium hydroxyl and H_3BO_3 groups [12]. Evidence of the presence of the hydroxyl group within the glass matrix is found from IR spectroscopy and DTA analysis, see Sections 3.4 and 3.5. Here it is believed that the presence of NaOH could be responsible for the conduction mechanism in the temperature range from room temperature to T_1. Above T_1, the H_3BO_3 compound begins to dissociate leading to the increase of BO_3 groups with respect to Na^+ ions, consequently the conductivity is decreased due to the recombination process. Above T_2, the increase of the conductivity is referred to the presence of a high content of BO_4 groups and a low one of BO_3 with respect to Na^+ ions. In this case, the activation energy in the temperature range between 438 and 570 K is the energy needed to activate the ion diffusion and separate one configuration of the borate unit from the other. This conclusion was also discussed in [8].

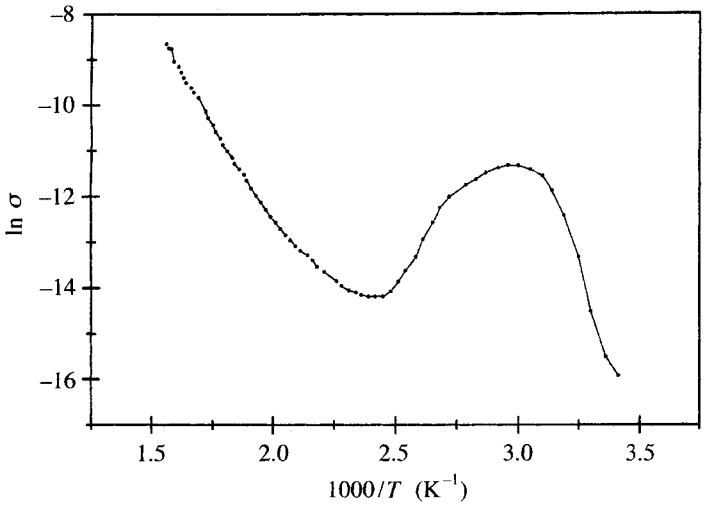

Fig. 1. The logarithm of the ac electrical conductivity of the pure $Na_2B_4O_7$ sample at 1 kHz as a function of $1/T$

From Fig. 2a to f, the behavior of ln σ versus $1/T$ of $(Na_2B_4O_7)_{100-x}(V_2O_5)_x$ glasses shows a strong dependence on the amount of V_2O_5 content within the glass matrix. It is noticed from Fig. 2a and b that the maximum peak of σ at T_1 (characterizing the pure glass sample 1) has disappeared for glass samples 2 and 3 containing 0.25 and 0.5 mol% of V_2O_5, respectively. Here, the possibilities of forming heteropolyanion molecules due to the interaction between NaOH and V_2O [12] leads to different conduction mechanisms characterizing these samples. In this situation the electric conductivity does not satisfy the exponential relation (1). The curves obtained in Fig. 2c and d for samples 4 and 5 containing 1 and 2 mol% of V_2O_5, respectively, show similar features as the curve obtained in Fig. 1 for the pure glass sample 1, except extra structures of σ observed around the maximum value. In these cases, the formation of meta and/or orthovanadate compounds is most probable, especially when the amount of V_2O_5 is increased [12]. These compounds could be responsible for the conduction mechanisms in these samples. On the other hand, condensation of V_2O_5 with the borox could take place by increasing the concentration of vanadium oxide to 3 and 5 mol%. Also, this effect leads to different conduction mechanisms, as shown in Fig. 2e and f, respectively, where two different slopes are found. In Table 1, the maximum and minimum values of σ corresponding to T_1 and T_2 are given for comparison.

3.2 Dielectric constant

The dielectric constants ε for all samples are measured at constant frequency of 1 kHz in the temperature range between 293 and 600 K. The results are illustrated in Fig. 3 and Fig. 4a to f for sample 1 and samples 2 to 7 (see Table 1), respectively. In Table 1, the values of ε at 293 K for all samples are given for comparison. From Fig. 3, it is noticed that the value of $\varepsilon = 19$ at 293 K is obtained for the pure glass sample 1. This value is increased by increasing the temperature, it reaches a maximum value of 44 at 368 K. This value reflects the formation of the $(Na)^+(OH)^-$ compound within the glass matrix

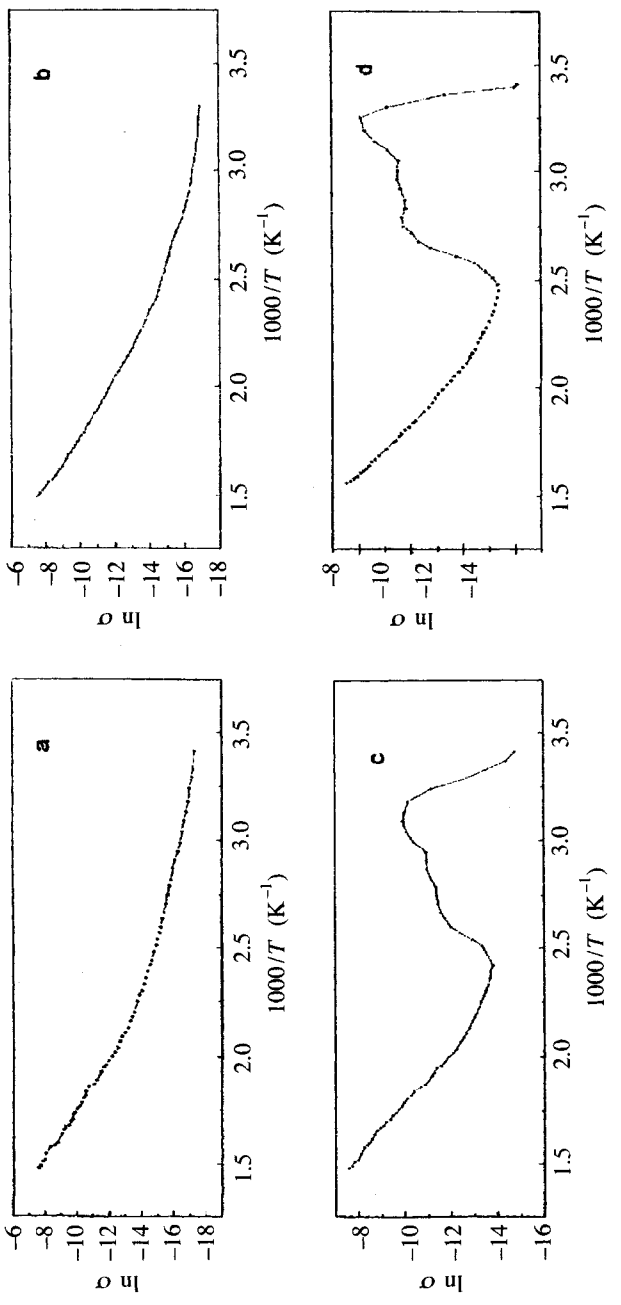

Fig. 2. The logarithm of the ac electrical conductivity of the $(Na_2B_4O_7)_{100-x}(V_2O_5)_x$ glass samples at 1 kHz as a function of $1/T$ (see Table 1). a) Sample 2, b) sample 3, c) sample 4, d) sample 5, e) sample 6, f) sample 7

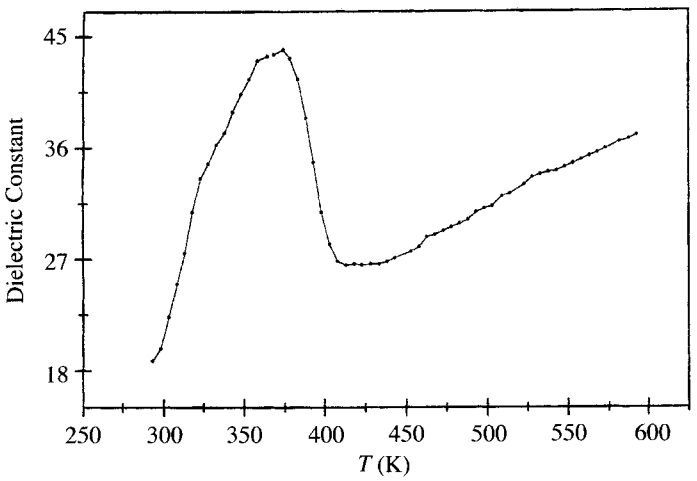

Fig. 3. The value of the dielectric constant ε of the pure $Na_2B_4O_7$ sample at 1 kHz as a function of temperature

which has a high degree of polarization. Above 368 K, the value of ε decreases with increasing temperature. It reaches a minimum value of 27 at 418 K. The dielectric constant was found to be independent of the temperature in the range between 420 to 570 K. The effect of adding V_2O_5 on the value of ε is obvious from the curves shown in Fig. 4a to f. For samples 2 and 3 containing 0.25 and 0.5 mol% of V_2O_5, the value of ε is found to be slightly increasing with increasing temperature in the range between 293 and 570 K (see Fig. 4a and b).

From Fig. 4c and d, for samples 4 and 5 containing 1 and 2 mol% of V_2O_5, respectively, again the value of ε showed a broad peak in the temperature range between 293 and 420 K with some structure. This characteristic is referred to the formation of different chemical compounds within the glass matrix as discussed above. Fig. 4e and f for samples 6 and 7 containing 3 and 5 mol% of V_2O_5, respectively, show similar behavior as observed in samples 2 and 3. In Table 1, the maximum and minimum values of ε corresponding to different values of T_1 and T_2 are given for comparison. From Fig. 4a to f, it is worth noting that above 570 K a fast increase of ε is observed for all samples. This effect is attributed to the charge accumulation in the vicinity of the electrodes, because their neutralization is not comparable with their arrival due to the large increase in the mobility.

3.3 Infrared absorption

The spectral curves for the 400 to 4000 cm^{-1} region for the pure sodium tetraborate glass containing various amounts of V_2O_5 (see Table 1) are shown in Fig. 5. The IR spectrum of V_2O_5 is shown in Fig. 6 for comparison. Fig. 5, curve 1 shows the simple IR spectrum for the pure $Na_2B_4O_7$ due to its symmetry with three main bands at 708, 1019, and 1347 cm^{-1}. This result is in agreement with the spectra obtained for pure sodium tetraborate as thin blown film and as a powder with KBr pellets annealed at 400 °C as reported in [1]. Fig. 5, for samples 2 to 6, respectively, shows a new absorption band in the region between 500 to 1800 cm^{-1}. An absorption band around 3400 cm^{-1}

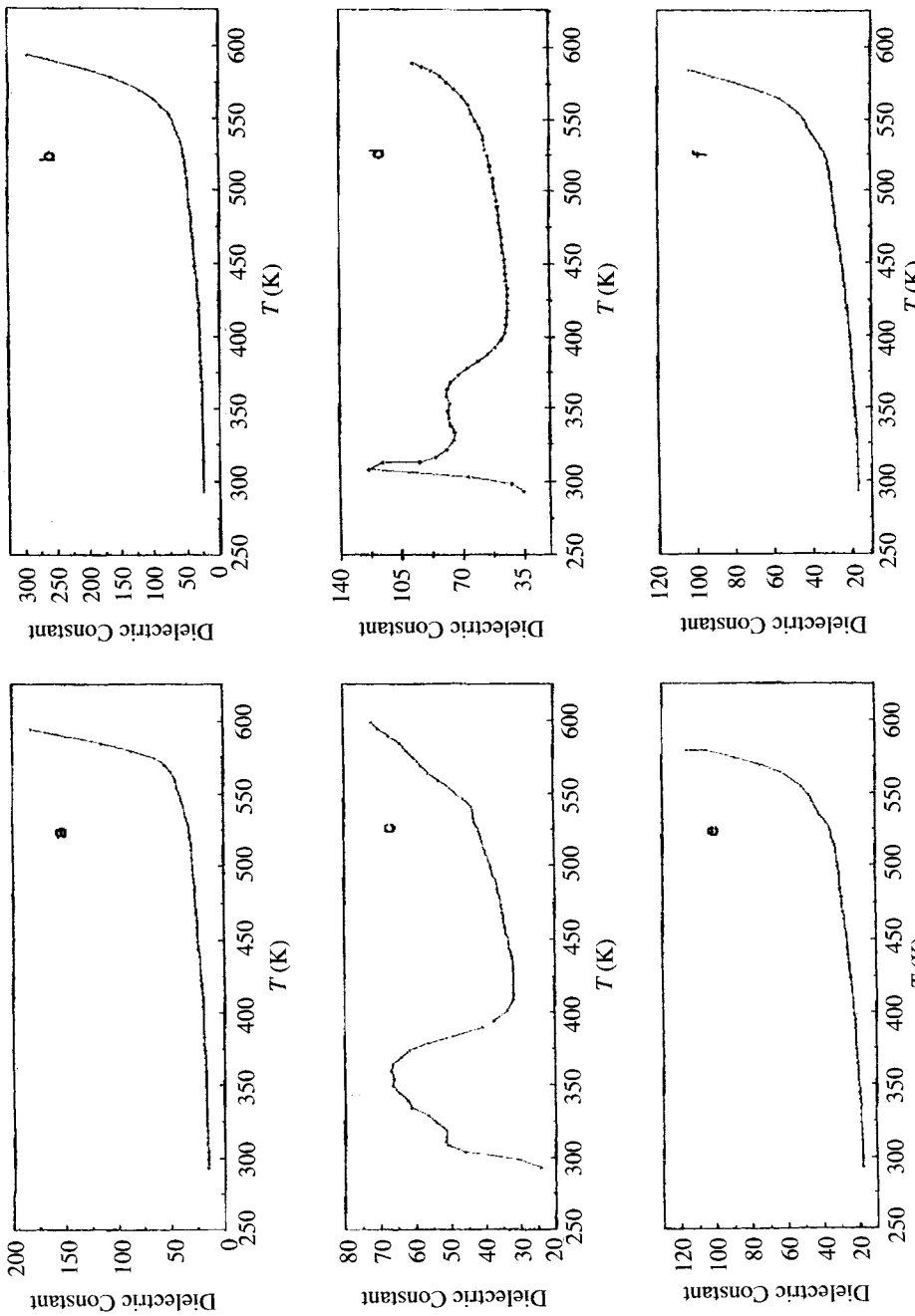

Fig. 4. The value of the dielectric constant ε of the $(Na_2B_4O_7)_{100-x}(V_2O_5)_x$ glass samples at 1 kHz as a function of temperature (see Table 1). a) Sample 2, b) sample 3, c) sample 4, d) samle 5, e) sample 6, f) sample 7

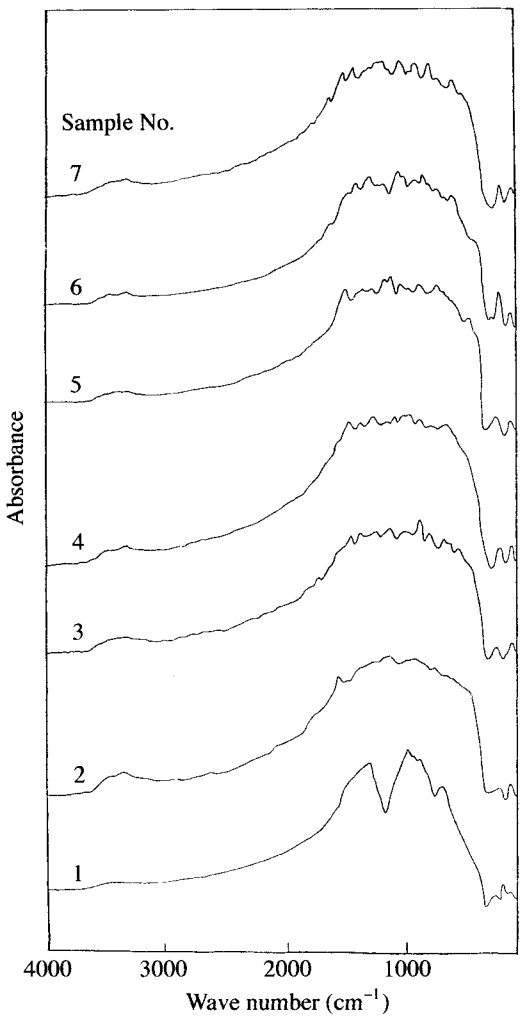

Fig. 5. IR absorption spectra of the $(Na_2B_4O_7)_{100-x}(V_2O_5)_x$ glass samples (see Table 1) at room temperature

with some structures has been observed in all samples, indicating the presence of hydroxyl group and/or B–OH bond within the glass matrix. In Table 2, the identified absorption peaks observed for all samples are listed for comparison. These results are compared with the corresponding data resported for $Na_2B_4O_7$–V_2O_5 thin blown film glasses [1]. In this report, only absorption peaks at 450, 725, 850 to 1200, 1300 to 1500, and 3400 cm^{-1} were observed. On the other hand, Kulieva et al. [14] reported the IR absorption spectrum for pure V_2O_5. They have mentioned that the absorption bands at 1019, 850, and 400 to 650 cm^{-1} are due to the stretching vibrations of V = O double bonds. The other absorption peaks observed in Fig. 6 are attributed to the vibrations of VO_4 tetrahedral and VO_6 octahedral V–O bonds.

In Fig. 5, the appearance of new absorption bands for samples containing various amounts of V_2O_5 is attributed to the formation of different chemical compounds due to the hydrolysis of $Na_2B_4O_7$ and the possible interaction with V_2O_5, such as the formation of $NaVO_3$ compound which has an infinite chain of VO_4 tetrahedra and VO_5 polyhedra linked together. Moreover, the linked BO_3 can interact with V_2O_5 forming what is called a heteropolyanion molecule, which has a complex structure [12]. These chemical processes affected also the conduction mechanisms occurring in these samples as discussed in Sections 3.1 and 3.2.

3.4 DTA measurements

The DTA patterns measured for glass samples 1 to 7 (Table 1) are shown in Fig. 7. All curves have the same curve feature as curve 1 obtained for the pure $Na_2B_4O_7$ glass (sample 1). In curve 1, at least three endothermic reactions can be identified. The first

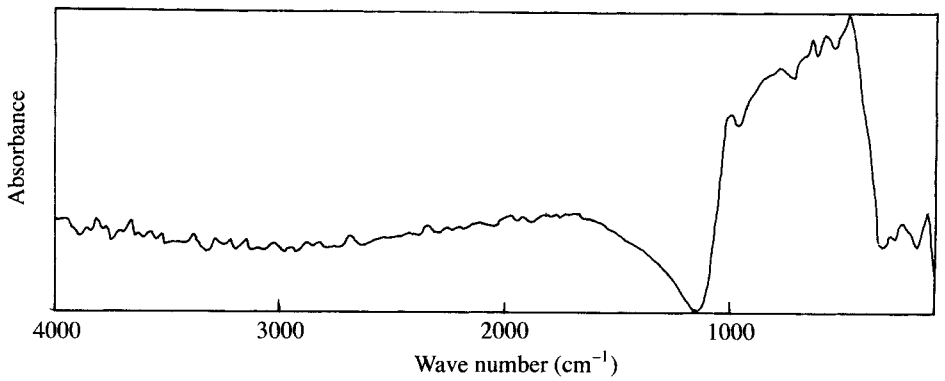

Fig. 6. IR absorption spectra of V_2O_5 at room temperature

reaction is broad with a peak located at 155 °C, while the other two peaks are relatively weak and located at 350 and 460 °C. From curves 2 and 3 for samples 2 and 3 containing 0.25 and 0.5 mol% of V_2O_5 it is noticed that the first peak is shifted towards lower temperature and is located at 120 and 110 °C, respectively. For samples 4 and 5 containing 1 and 2 mol% of V_2O_5 the location of this peak again was found to be at 155 °C, while for samples 5, 6, and 7 containing 2, 3, and 5 mol% of V_2O_5 it is located at 130, 120, and 110 °C, respectively. It is also noticed that, while the second peak at 350 °C is preserved in samples 1, 3, 4 and 7, the peak located at 460 °C is observed in all samples. The location of these peaks was found to be independent of the amount of V_2O_5.

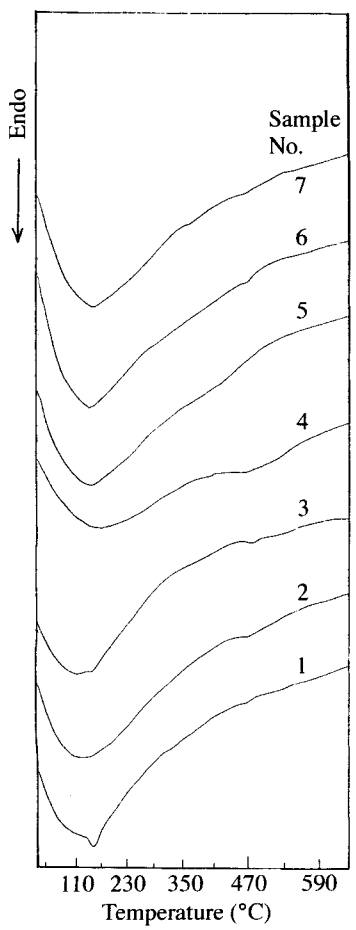

Fig. 7. DTA curves of $(Na_2B_4O_7)_{100-x}(V_2O_5)_x$ (see Table 1)

These results are compared with the data obtained from the differential scanning calorimetry (DSC) measurements reported in [1] for some sodium tetraborate containing 0.5, 2, 5, and 10 mol% of V_2O_5. The following remarks are made:

1. The DSC measurements were made in the temperature range between 200 and 550 °C. Therefore,

Table 2

IR absorption bands, identified in wave number, for samples 1 to 7 (see Table 1) and for V_2O_5

sample	wave number (cm^{-1})												
1	708	1019	1347	3385	–	–	–	–	–	–	–	–	–
2	768	916	1155	1583	3379	–	–	–	–	–	–	–	–
3	578	710	837	919	1057	1178	1290	1420	1497	1772	3378	–	–
4	659	892	976	1100	1167	1290	1391	1479	3367	–	–	–	–
5	516	789	936	1026	1095	1186	1242	1345	1423	1567	3351	–	–
6	639	708	767	852	900	971	1112	1236	1348	1465	1533	3379	–
7	521	613	741	806	930	1059	1149	1202	1318	1455	1544	1663	3374
V_2O_5	477	577	642	680	793	827	999	–	–	–	–	–	–

the first endothermic reaction located at 155 ° was missing. For this reason, the DSC measurements reported in [1, 13] should be extended to cover the whole temperature range from room temperature to 550 °C for comparison.

2. The DSC patterns given in [1] showed an endothermic reaction with a peak located at 519 °C for the pure sodium tetraborate glass. It has been found that this location is shifted towards lower temperature for samples containing V_2O_5.

Therefore, for verification, the DSC measurement of the pure $Na_2B_4O_7$ glass (sample 1) was made using the Mettler TA 3000 thermal analysis system, in the temperature range between room temperature and 550 °C with input power of 20 mW and scanning rate of 20 K/min. The recorded pattern is shown in Fig. 8. It is obviously clear that a strong endothermic peak at 150 °C and two other weak endothermic peaks located at 350 and 480 °C are observed (note: here the broadening of the peaks depends on the input power of the system). This result confirms the DTA measurements shown in Fig. 7 curve 1.

The first endothermic reaction around 150 °C indicates the presence of hydroxyl groups within the glass matrix and the partial hydrolysis of $Na_2B_4O_7$, while the forma-

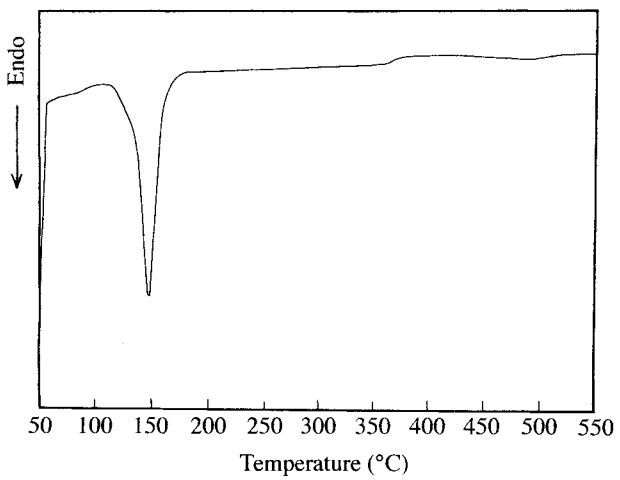

Fig. 8. DSC curve of the pure $Na_2B_4O_7$ glass sample

tion of B–OH could be responsible for the weak phase transitions at 350 and 460 °C which are observed in these samples. These results are consistent with the previous discussion.

In conclusion, the ac electric conductivity and dielectric constant of semiconducting $(Na_2B_4O_7)_{100-x}(V_2O_5)_x$ with $x = 0$ up to 5 mol% have been measured at a frequency of 1 kHz as a function of temperature in the range from 293 to 600 K. From the results, different conduction mechanisms are found. These mechanisms are attributed to the chemical processes occurring within the glass matrix. From the IR spectra and the DTA studies, evidence of the presence of hydroxyl groups and the formation of different chemical compounds are found. At this point, more physical methods including Raman spectroscopy are needed to understand the nature of these samples.

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