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The influence of titanium ions on crystallization, morphological, and structural properties of strontium borate glass

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ABSTRACT

Strontium borate glasses containing different ratios of TiO_2 were prepared. Thermal expansion measurements indicate variable and peculiar data in relation to the role of TiO_2 in host SrO-B_2O_3 acting as both network former and modifier. The prepared glasses were nucleated around 500 °C except the base glass at 520 °C. X-ray diffraction measurements show the formation of strontium triborate as the main phase through all samples. The morphological surface of the glass-ceramics is strongly affected by the TiO_2 ratio and the phase separation in such glasses was observed. Infrared absorption analyses indicate the presence of both triangular and tetrahedral borate groups. Moreover, it shows the formation of B-O-Ti linkage which affected by both of the Ti content and the heat treatment regime. The infrared absorption spectra for the glass-ceramic samples show the resolving band from 1200 to 1600 cm^{-1} into several peaks as the result of the action between the titanium ions and BO_3 units.

1. Introduction

Borate glasses when combined with any alkali, alkaline earth or multivalent oxide (e.g. PbO, Bi_2O_3, Sb_2O_3…) exhibit unique structural network building units consisting of both triangular and tetrahedral coordination's of BO_3 and BO_4 groups. These two specific borate groups exhibit up some interesting properties but in other cases it behaves anomalous [1–3]. The partner oxide reacts with B_2O_3 to modify part of the BO_3 to BO_4 units until certain limit. The excess of more percent of the mentioned oxides leads to create the non-bridging oxygen's (NBOs) as that usually happened in such glasses.

SrO containing glasses and their corresponding glass-ceramics can be applied as gamma ray-shielding candidate [4], bioactive application [5], second harmonic generation, dielectric material and other potential applications [6,7].

TiO_2 is used in many applications in glasses, glass-ceramics and ceramics. It is accepted that titania can be introduced in the doping level to act as a nucleating agent in specific glass-ceramics [8,9]. Also, some authors have investigated the application of low TiO_2 content in the preparation of in-vivo phosphate based bioglasses and bioglass-ceramics [7,10]. The electronic configuration of titanium ions in glasses exhibits two valence states, namely the trivalent (Ti^{3+}) and the tetravalent (Ti^{4+}). Ti^{3+} ions have $3d^1$ configuration and exhibit purple color due to the single visible band at 480–540 nm. In some instances, it shows distortion and the appearance of two further visible peaks at about 680 and 760 nm is observed. Ti^{4+} ions belong to d^0 configuration and reveal no d-d transition but only exhibit an UV band [11–13].

Thakur et al. [14], investigated both of the crystallization behavior and the microstructure of the SrO-TiO_2-B_2O_3-SiO_2 glass-ceramic system containing K_2O. They noticed the formation of $Sr_2B_2O_5$, TiO_2, and $Sr_3Ti_2O_7$ crystalline phases which depend on the potassium ratio. The presence of alkali ion like potassium can control the microstructure of such glasses. Also, the presence of SrO-B_2O_3 in silicate glass network doped with titanium oxide makes these glasses suitable as sealing glass [15]. Moreover TiO_2 facilitates the crystallization of such glasses, improving the sealing properties and their chemical compatibility [16,17]. On the other hand, glass and glass-ceramic system of lead titanium borate containing different ratios of SrO are assumed to be promising for capacitor applications due to their high dielectric constant [18]. Shankar and Deshpande [18] have noticed that the glass transition temperature increases as the SrO increases. These glasses formed ferroelectric lead titanate major phase when transformed into glass-ceramics and specific crystalline phases were detected such as $Sr_2B_2O_5$ and PbB_2O_4.

Hence, this article aims to characterize some prepared glasses and their corresponding glass-ceramics from the system 50 SrO-50 B_2O_3 in

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mole percent ratio containing different added ratios of TiO_2. Also, the present investigations include Fourier transform infrared absorption spectra (FTIR), thermal expansion measurements of the parent glass, X-ray diffraction (XRD) and scanning electron microscopy (SEM) of the crystallized glass-ceramics. The mentioned investigations are expected to give more insight on the relation between the structure of the studied glasses or their glass-ceramics and the collective investigating properties.

2. Experimental details

2.1. Preparation of the glasses

Laboratory chemicals of orthoboric acid (H_3BO_3), strontium carbonate ($SrCO_3$) and titania (TiO_2) were used to prepare the studied glasses and their chemical compositions are presented in Table 1. The accurately weighed batches were melted in platinum crucibles at 1100 ± **5** °C for 90 min in SiC heated furnace (Vecstar, UK). The melts were rotated at equally interval times to achieve mixing and homogeneity. The melts were then cast into preheated stainless steel molds with the required dimensions. The prepared samples were immediately transferred to an annealing muffle regulated at 400 ± 2 °C. The muffle was switched after 1 h and left to cool to room temperatures at a rate of 30 °C with the samples inside it.

2.2. Thermal expansion measurements

The thermal expansion characteristics of the glasses were measured using a recording dilatometer (type NETZCH Dil. 402, Germany) with a heating rate of 10 °C/min up to the dilatometric softening temperature. The data for the transformation and softening temperatures were collected to be utilized for controlling the thermal heat treatment of the parent glasses. All the samples were measured three times to estimate the average values and the errors.

2.3. Preparation of glass-ceramics

The prepared glass samples were subjected to two-step regimes as deduced from thermal expansion measurements. Each sample was heated slowly with a rate of 5 °C/min for the first nucleation temperature for 12 h to produce sufficient nuclei sites. Then, the temperature was raised up to the softening temperature for 6 h to complete specimen crystallization and then it was left inside the muffle to cool to room temperature with a rate of 25 °C/h.

2.4. Fourier transform infrared measurements

Fourier transform infrared absorption spectra of the prepared glasses and their glass-ceramic derivatives were carried out through the KBr disc technique. The measurements were carried out by Fourier transform computerized infrared spectrometer (type Nicolet iS10, USA) within the wavenumber range 400–4000 cm^{-1} for all samples. This technique was used to identify the network structural building units in the studied glasses and glass-ceramics.

2.5. X-ray diffraction analysis

The crystalline phases which were formed within the glasses due to the thermal heat-treatment process were identified by X-ray diffraction technique. The glass-ceramic samples were finely ground and the fine powders were examined using a diffractometer (type Philips PW 1390) adopting Ni-filter and Cu target. Computer software (Materials Studio 4.4 Program) was utilized to identify the crystalline phases and their percents.

2.6. Scanning electron microscopic investigation

The morphological features of the prepared heat-treated samples were examined using an SEM apparatus model Philips XL30 attached with EDAX unit, accelerating voltage 30 kV. All studied samples were broken and coated with gold surface layer for SEM measurements.

3. Results and discussion

3.1. Thermal behavior

Fig. 1 reveals the thermal expansion measurements of the prepared glasses. The studied glasses exhibit negative expansion coefficients within the range from room temperature up to 360 °C. Then the curves reveal positive expansion coefficients reaching to the transformation range followed by a sudden decrease around the dilatometric softening temperature for all samples. Table 1 shows the glass transition temperature and the softening temperature values for the prepared glass samples. It is clearly seen that the glass transition temperature is approximately constant around 500 °C (except the base glass which has only glass transition ~520 °C). Hence it is expected that the parent glass sample can be partially crystallized. The softening temperature is varied with the increase of TiO_2 content and is observed to increase up to 640 °C for 10 TiO_2 glass sample and then slowly decreases as the titanium ion content increases reaching to 630 °C for 20 TiO_2 as clearly observed in Fig. 2.

In general, Glass like most other solids expands on heating except few special cases. The dimensional changes which occur with temperature are very important for sealing purposes and the ability of glass object to survive shock or cycling [19–22]. Normally, expansion is described by the increasing amplitude of atomic vibrations of the constituent ions determined by anharmonic lattice vibrations. So, the specific behavior of the presence of the negative dimensional change in length ($\Delta L/L_o$) in all samples within the range from room temperature up to 360 °C may be related to the lattice or the specific network structure of the strontium borate glasses which can absorb the lattice expansion by the bending of bonds into the empty interstices of structure [23].

On the other hand, the softening temperature, T_d is strongly affected by the addition of TiO_2 content. It increases with increasing the Ti ion content up to 10% TiO_2 and slowly decreases after this ratio. It is suggested that the first introduction of TiO_2 content changes the structural glass network when exceeding 10% by forming structural building units such as TiO_4 groups and thus the thermal expansion measurements reveal the decrease of the softening temperatures. Also, after the process of thermal treatment is completed for converting the glasses into glass-ceramics. Ti ions are assumed to incorporate within the SrO-

Table 1
Thermal expansion data for 50%SrO-50%B_2O_3-xTiO_2 glasses. The glass transition, T_g; The softening temperature, T_d; the temperature difference, ΔT and the negative region in the expansion curves.

x %	Glass symbol	$T_g \pm 5$ [°C]	$T_d \pm 5$ [°C]	$\Delta T = (T_d - T_g) \pm 10$ [°C]	Negative region in the thermal expansion curves [°C]
0	Base	520	–	–	RT-300
5	5 TiO_2	500	601	101	RT-255
10	10 TiO_2	500	640	140	RT-278
15	15 TiO_2	500	637	137	RT-360
20	20 TiO_2	499	630	131	RT-300