



## **Infrared Spectroscopic Study on the Structure of $\text{Ag}_2\text{O} \cdot \text{B}_2\text{O}_3$ Glasses**

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### **Abstract**

Infrared (IR) spectroscopic investigation of binary silver borate glasses in the system  $x\text{Ag}_2\text{O} \cdot (1-x)\text{B}_2\text{O}_3$  for various values of  $x$  ( $0 \leq x \leq 0.77$ ) has been performed in order to understand the glass modifying properties of  $\text{Ag}_2\text{O}$ . The IR spectra show clearly the disappearance of boroxol rings and the formation, in a first step, of tetraborate groups and later of diborate groups as the oxide content increases. For high  $\text{Ag}_2\text{O}$  content, borate groups with non-bridging oxygen atoms are formed.

Keywords: Infrared Spectroscopy, silver borate glass

### **Introduction**

Glasses are amorphous, brittle materials composed of metal oxides and silicates. There is also a group of new materials, termed glass ceramics. The word ceramic conjures up different images with different people. Glass is an amorphous, brittle material obtained by melting together a mixture of various compounds and supercooling the liquid to a temperature where its viscosity exceeds to  $10^{14}$  poise ( $10^{13}$  PaS).

Glass structures have a random network in three dimensions but no unit repeats itself at regular distances. The basic unit is a tetrahedral or triangular co-ordination of a glass former with oxygen. The glass formers are few elements (Si, B, P, Ge and few others). The ionic potential must be seven or more thus indicating a very strong cation–oxygen bond; the oxygen atoms are linked to two glass forming cations (bridging oxygen) or with an ionic bond to modifier cations (non-bridging oxygen).

Due to their structural versatility and well known applications inorganic oxide glasses are of commercial importance and borate glasses have been of particular scientific interest because of the boron anomaly. They have been extensively studied by techniques such as nuclear magnetic resonance and x ray ultraviolet and infrared spectroscopy.

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Infrared spectroscopy which is a powerful tool for investigating structural details has been used in this work. To investigate the effect of  $\text{Ag}_2\text{O}$  concentration in those samples where it is feasible, the series  $x\text{Ag}_2\text{O} \cdot (1-x)\text{B}_2\text{O}_3$  ( $0 \leq x \leq 0.77$ ) was also studied.

The samples are prepared from analytical reagent grade  $\text{AgNO}_3$  and  $\text{H}_3\text{BO}_3$  using the conventional melting and quenching technique. The infrared spectra of freshly prepared samples are obtained using the KBr pellet technique on a spectrophotometer (FT-IR 8400 Shimadzu). The crystallinity of the samples is checked using a Rigaku (Multiflex-2KW) x-ray diffractometer.

In particular for silver borate glasses  $x \text{Ag}_2\text{O} \cdot (1-x)\text{B}_2\text{O}_3$  extensive experimental evidence from IR measurement permitted the following structural model. At low concentration of  $\text{Ag}_2\text{O}$  ( $x \leq 0.25$ ), the trigonal coordination of the boron is partially changed into tetrahedral, giving rise to the formation of  $\text{BO}_4$  groups and to an increase of the network coherence; all the oxygen bridge between two borons. At higher concentration of  $\text{Ag}_2\text{O}$  ( $x \geq 0.25$ ), the relative number of tetrahedrally coordinated boron ions tends to decrease and coherence breakdown commences with the formation of non-bridging oxygen (NBO). With the aim of understanding the influence of  $\text{Ag}_2\text{O}$  content on the network coherence, we report in the present communication, the infrared transmittance measurements on binary silver borate glasses in the system  $x \text{Ag}_2\text{O} \cdot (1-x)\text{B}_2\text{O}_3$  for ( $0 \leq x \leq 0.77$ ).

In this work, structural and crystallization of these glasses system caused by heat treatment are investigated by using Differential Thermal Analysis (DTA). Fourier Transform Infrared (FT-IR) Spectroscopy and X-Ray powder diffraction (XRD) is used in order to determine the crystalline particle precipitate in the glassy matrix.

### Experiment

Analytical grade reagents are used for the preparation of the glass samples in the present study. The samples are prepared in the laboratory by heating the weighted amounts of reagent grade silver nitrate and boric acid in the oven for one and half hour by increasing the temperature from  $45^\circ\text{C}$  to  $300^\circ\text{C}$ . Then they were heated in the electric furnace at  $1100\text{K}$  for an hour. The gravimetric analysis of the molten mass showed that its weight decreased as expected due to the liberation of water from  $\text{H}_3\text{BO}_3$  and nitrogen oxide

from  $\text{AgNO}_3$ . The samples are made by pouring the bubbles free melt in between the copper mold kept at room temperature. Four glass samples are made as in table 1. The samples are transparent, vary from yellow to light brown in colour and darken as the  $\text{AgNO}_3 / \text{H}_3\text{BO}_3$  ratio increases. To avoid the photochemical reaction of  $\text{Ag}^+$  ions, the samples are placed in desiccators, covered with black clothe. For the transmittance experiments between  $300\text{-}1700\text{cm}^{-1}$ , the glasses are powdered, mixed with an appropriate amount of anhydrous KBr powder and then pressed in vacuum at 10 tons load for 2 minutes. This procedure gave transparent pellet with about 2wt% of glass. The instrumental resolution of about  $2\text{cm}^{-1}$  is used for recording the spectra. Only the interesting domain from  $300\text{-}1700\text{ cm}^{-1}$  has been presented the reaction scheme for the formation of borate glass using ceramic method.

Table 1. Chemical composition of the prepare glasses.

Sample number	$\text{AgNO}_3(\text{g})$	$\text{H}_3\text{BO}_3(\text{g})$	Total (g)
1	4.63	9.56	14.19
2	6.23	8.04	14.27
3	9.97	4.62	14.58
4	13.08	1.42	14.50

The amorphous and changes to crystals state of the samples are established by studying its X-ray diffraction Patten (XRD), using a Rigaku (Multiflex-2kW) diffractometer. The XRD pattern is recorded at a scanning rate of  $2\text{ degree min}^{-1}$  with a  $\text{Cu-K}\alpha$  source. The IR transmission spectra are measured on an FT-IR spectrometer (FT-IR 8400 Shimadzu) by the KBr disk method.

Glass transition temperatures ( $T_g$ ) and crystallization peak temperatures ( $T_c$ ) were determined by Differential Thermal Analyzer (DTA) conducted at a heating rate of  $15\text{C min}^{-1}$  using Shimadzu's apparatus DTG 60AH. An aluminum (Al) pan is used as the standard sample. All measurements are carried out by heating run under  $\text{N}_2$  atmosphere  $50\text{ml min}^{-1}$ . The scan speed of heating was chosen the maximum temperature at  $600^\circ\text{C}$  and the rate of  $15^\circ\text{C min}^{-1}$  and kept constant in the respective runs.

## Result and Discussion

The study of glass structure is important because the properties exhibited by the glasses are both composition and structure sensitive. Therefore the XRD, FT-IR, and TGDTA have been employed for the structural characterization of these glasses.

Homogeneous glass samples could be prepared in the  $x \text{Ag}_2\text{O} (1-x) \text{B}_2\text{O}_3$  System when  $\text{B}_2\text{O}_3$  contents ( $x$ ) are  $x = 0, 0.15, 0.22, 0.44$  and  $0.77$ . The XRD pattern is generally observed in several oxide glasses with an "amorphous" structure. The formation of homogeneous glass samples are confirmed by XRD, as illustrated in Fig 1. X-Ray powder diffraction (XRD) is used in order to determine the crystalline particles precipitated in the glassy matrix.

The DTA curve of  $x\text{Ag}_2\text{O} (1-x) \text{B}_2\text{O}_3$  for  $x = 0.44$  glass is shown in Fig 2. The glass transition temperature ( $T_g$ ) and the maximum crystallization temperature ( $(T_c)_{\max}$ ) is observed at the table 2, when heating rate at  $15^\circ\text{C min}^{-1}$ .

Table 2 Glass transition temperature ( $T_g$ ) and the maximum crystallization temperature ( $(T_c)_{\max}$ ) with value of  $x$ .

$x$	$(T_g)^\circ\text{C}$	$(T_c)_{\max}^\circ\text{C}$
0.44	270°C	338°C

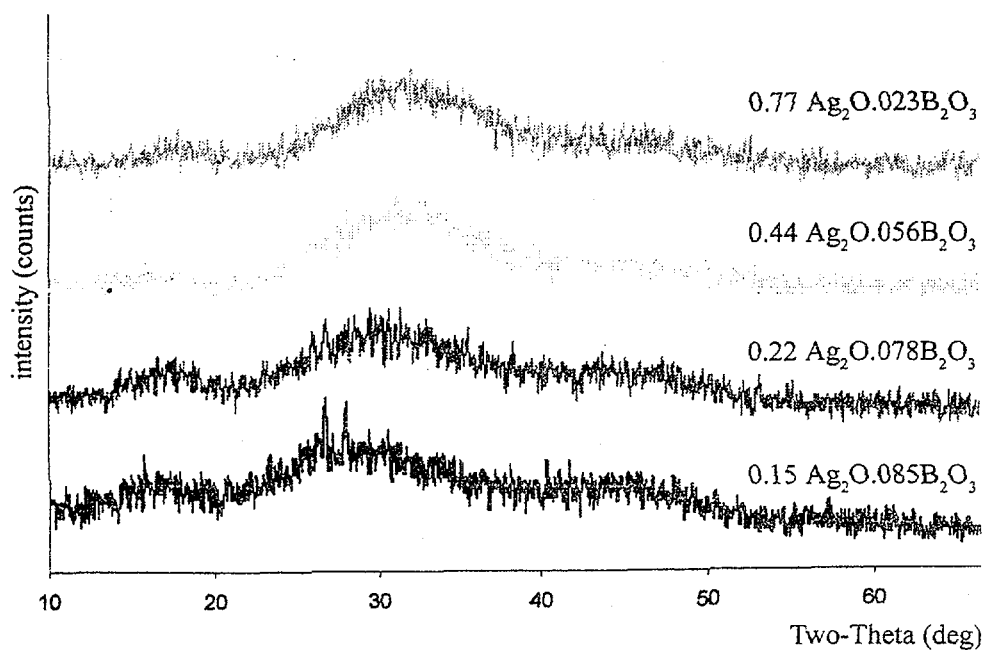


Fig 1. The XRD pattern for  $x \text{ Ag}_2\text{O} (1-x) \text{ B}_2\text{O}_3$

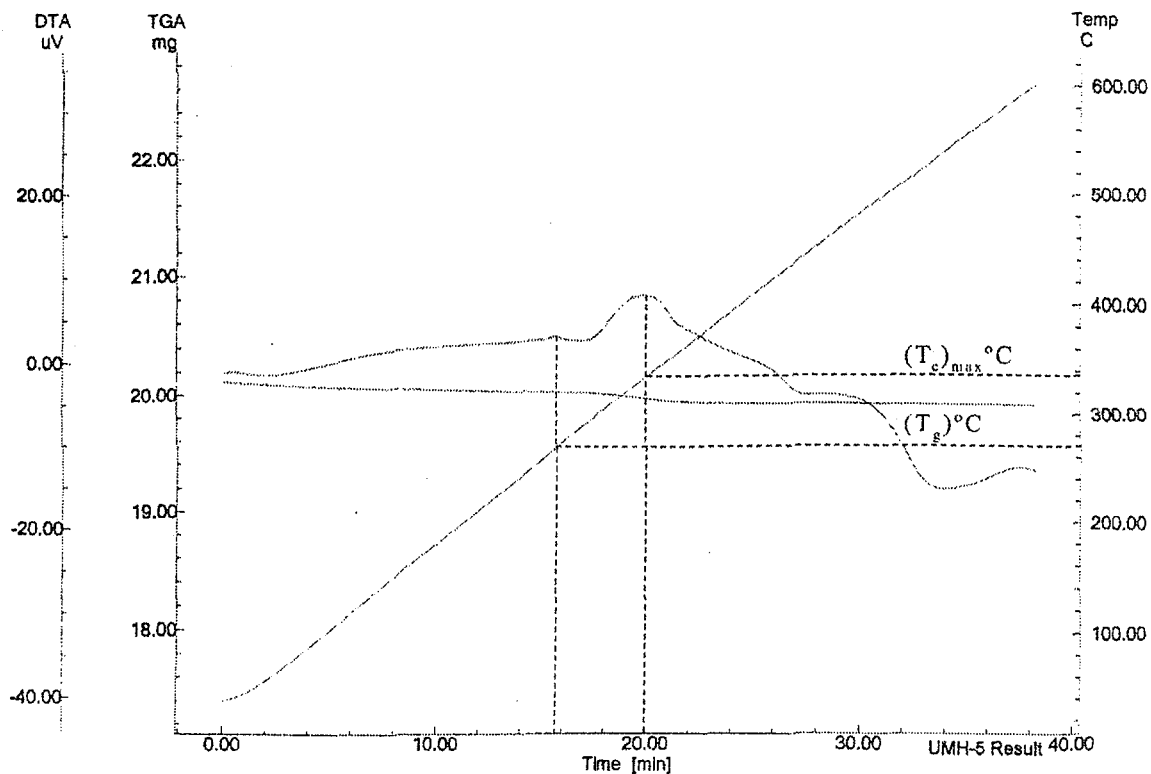


Fig 2. The DTA curve of  $0.44 \text{ Ag}_2\text{O} 0.56 \text{ B}_2\text{O}_3$

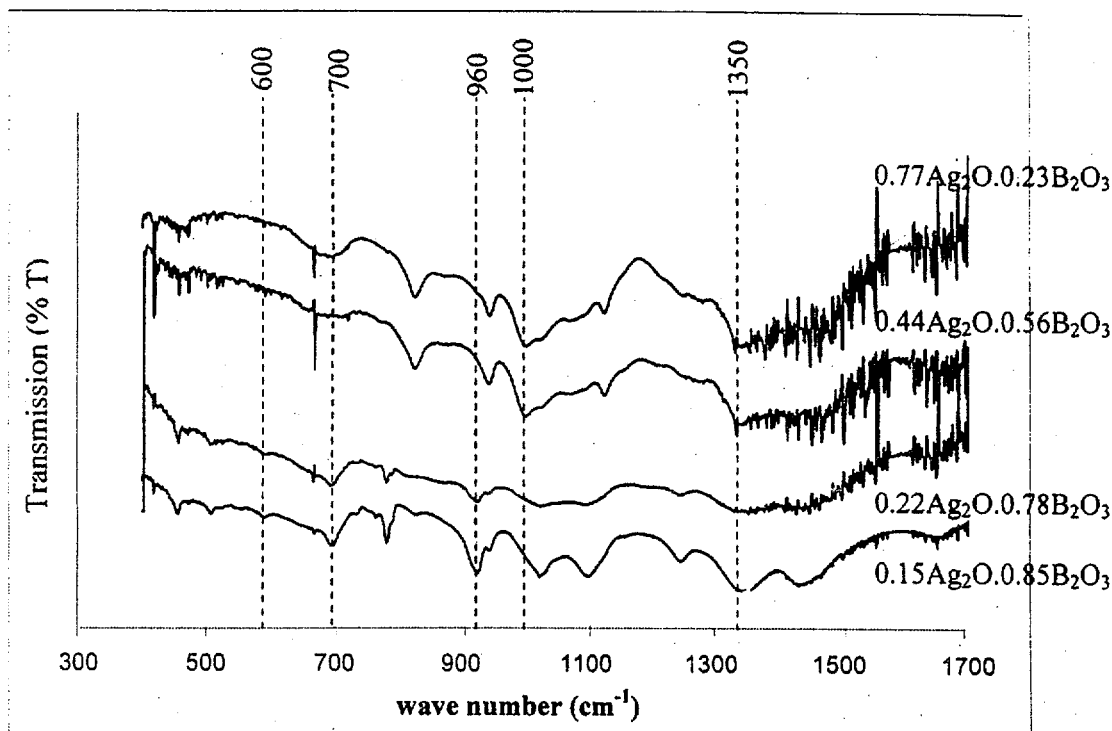


Fig 3. Infrared spectra of  $x\text{Ag}_2\text{O} \cdot (1-x)\text{B}_2\text{O}_3$  glasses for  $x = 0.15, 0.22, 0.44$  and  $0.77$

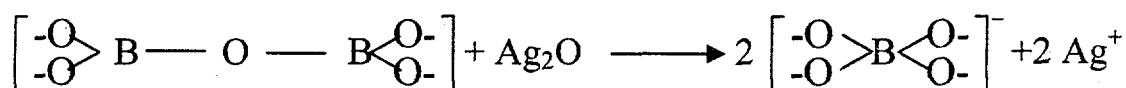
Investigation of the infrared transmittance spectra of the binary silver borate glasses is very helpful in understanding the effect of the dopant ( $\text{Ag}_2\text{O}$ ) on the boron-oxygen network of the system. The mid infrared spectra of binary silver borate glasses in the system  $x\text{Ag}_2\text{O} \cdot (1-x)\text{B}_2\text{O}_3$  for ( $0 \leq x \leq 0.77$ ) in the region  $300\text{-}1700\text{cm}^{-1}$  are shown in Fig 5.3. The transmittance results have been compared with those of the crystalline compounds and discussed in terms of current knowledge of the structure of  $\text{B}_2\text{O}_3$  glass.

IR transmittance spectra of binary silver borate-glasses shown three well distinguished regions:  $1000\text{-}1350\text{ cm}^{-1}$  (B-O stretching of  $\text{BO}_3$  units),  $700\text{-}460\text{ cm}^{-1}$  (B-O stretching of  $\text{BO}_4$  units) and around  $600\text{cm}^{-1}$ , which is attributed to the bending of B-O-B linkages in the borate network.

The effect of  $\text{Ag}_2\text{O}$  can be followed by the systematic change of the IR spectra. The main observations are the growth of new bands in the region between  $720\text{-}850\text{ cm}^{-1}$  upon increasing the concentration of  $\text{Ag}_2\text{O}$  in the  $\text{B}_2\text{O}_3$

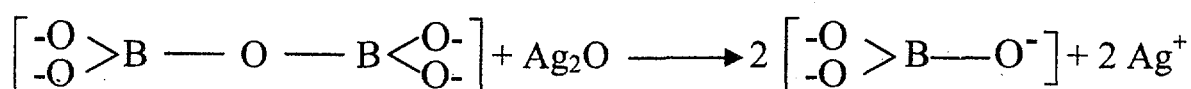
matrix. At the sometime, intensity changes of the 1000 and 1220  $\text{cm}^{-1}$  completely disappears when x reaches 0.15 concentrations with the formation of a new bond at 1020  $\text{cm}^{-1}$ .

By reference to the work of Krogh-Moe<sup>7</sup>, it is widely accepted that the broad band in the region of 1000 $\text{cm}^{-1}$  is attributed to B-O bond stretching of tetrahedral  $\text{BO}_4$  units, while the region 700-900  $\text{cm}^{-1}$  arises from B-O bond stretching of tetrahedral  $\text{BO}_4$  units. The modifying effect of the silver oxide can be described by the equation.



A more precise attribution is possible for the 1000 and 1300  $\text{cm}^{-1}$  bands: they correspond respectively to the  $\nu_1$  and  $\nu_4$  vibration of boroxol ring. The bond at about 600 $\text{cm}^{-1}$  corresponds to the bond bending vibration of B-O-B bridges of the boron oxygen network.

For the value of  $x = 0.15$ , a new band appears a about 1020  $\text{cm}^{-1}$ . This band is assigned to bond stretching of trigonal  $\text{BO}_3$  units with a non-bridging oxygen (NBO) atom. Such as those forming metaborate chain or triborate groups with one NBO atom. This new mechanism which appears during the formation of the oxygen-boron network corresponds to the equation:



The high frequency band envelope 1360  $\text{cm}^{-1}$ ,  $x = 0.15$  which is due to stretching of B-O bonds of rings of various borate groups exhibits a compositional dependence. As the concentration of  $\text{Ag}_2\text{O}$  increased, this band is shifted to higher wave number 1290  $\text{cm}^{-1}$  for  $x = 0.22$  and then start to shift to lower wave number and finally appears at 1362 $\text{cm}^{-1}$  for x 0.44 concentration. The spectrum of crystalline lithium pyroborate shows a bond in this region, originating from asymmetric  $> \text{B}-\text{O}$  stretching of  $\text{B}_2\text{O}_5$  units. On this basic, the 1262  $\text{cm}^{-1}$  band is assigned tentatively with the presence of pyroborate Units in silver borate glasses with high  $\text{Ag}_2\text{O}$  content.

More interesting results on the typical borate units, constituting the glass network have been obtained by analyzing the bands in the region 700-960 $\text{cm}^{-1}$ , which shows a fine structure comprised of four components. By comparison with the spectra of polycrystalline component having the same formular, one component at 840 $\text{cm}^{-1}$  corresponds to B-O bond stretching of

$\text{BO}_4$  units in diborate polycrystals, and the other near  $780, 740$  and  $860\text{cm}^{-1}$  correspond to the same Vibration but in tetraborate units. The observed evolution of the band shape with  $x$  is caused by a change in the relative number of these two different borate groups. At low  $\text{Ag}_2\text{O}$  content,  $\text{BO}_4$  units are preferably contained in tetraborate groups. The Smoothing of the band and the position of its maximum at about  $840\text{cm}^{-1}$  indicates its transformation into diborate rings with an increase in  $x$ .

The region  $500\text{-}600\text{ cm}^{-1}$  decreases in intensity with addition of  $\text{Ag}_2\text{O}$  content and finally disappears at  $x = 0.44$  concentration. Pentaborate groups of crystalline show bands at  $550$  and  $525\text{ cm}^{-1}$  respectively, while tetraborate groups do not show bands in this region. Thus it can be concluded that  $550\text{cm}^{-1}$  band denotes the presence of pentaborate groups.

### Conclusion

X ray powder diffraction (XRD) is used in order to determine the crystalline particles precipitated in the glassy phase. Formation silver-borate is confirmed by XRD. The structure changes of the glass system are observed by FT-IR transmission spectra by KBr disk method.

Analysis of the bands at  $740, 840$  and  $875\text{ cm}^{-1}$  reveals that the four coordinated boron atoms, or a large number of them are grouped as diborate groups rather than tetraborate groups at higher concentration of  $\text{Ag}_2\text{O}$ . A small band located at  $1070\text{ cm}^{-1}$  indicates that some  $\text{BO}_3$  units with a non-bridging oxygen atom exist in the boron-oxygen network.

Thus it can be concluded that with increasing concentration of  $\text{Ag}_2\text{O}$  progressive formation of pentaborate, tetraborate, diborate, metaborate and pyroborate along with the destruction of some of the groups takes place.

Glass transition temperature ( $T_g$ ) and crystallization temperature ( $T_c$ )<sub>max</sub> are determined by DTA conducted at a heating rate of  $15^\circ\text{C min}^{-1}$ , using aluminum pan as the standard.

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