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Preparation and characterization of TiO_2–BaO–ZnO–B_2O_3 glass systems for optical devices

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We study the TiO_2–BaO–ZnO–B_2O_3 glass system, where the ZnO and B_2O_3 compositions were constant and the ratio TiO_2/BaO was varied from 0.87 to 1.76. A super kanthal resistance furnace was used to melt the compounds inside an alumina crucible, at 1200 °C, for 10 min. After melting, the glasses were poured out into steel moulds and rapidly cooled by quenching. The glasses obtained were homogeneous, bubble free and transparent. They were characterized by X-ray diffractometry, Fourier transform infrared spectroscopy (FTIR), UV-VIS spectroscopy, dilatometry, density and linear refractive index. An infrared "cut off" caused by the composition influence was found in both IR and UV-vis spectra. From dilatometry T_d and T_g were verified as being anomalous. The linear thermal expansion coefficient α presented an anomalous behaviour in relation to TiO_2 concentrations. The density and linear refractive index increased with increasing TiO_2/BaO ratio arriving at their peak value of $TiO_2/BaO = 1.5$ and then decreasing. The dependence of softening point T_d on the ratio TiO_2/BaO exhibited the same behaviour. It is suggested that Ti^{4+} plays a dual part in the glass system, assuming a predominantly tetrahedral coordination in the low titania region and a predominantly octahedral coordination in the high titania region. With a heat treatment of the glass around 600 °C, we observed a rapid change of refractive index with increasing temperature.

1. Introduction

Nonlinear optical glasses with fast response times and very low absorption coefficients are promising materials for ultra-fast all-optical switches [1].

The nonlinearities present in glasses under the influence of the high-intensity fields, can also be described as a third order nonlinear susceptibility. In this sense, different glass systems are now under investigation to increase their nonlinearity by introducing a variety of modifiers into the glass network. For example, in oxide glasses, high linear and nonlinear refractive indices are found in systems containing large polarizable cations [2].

Transition metal elements are also known to increase the refractive index. They exhibit high polarizability and form structure units that frequently differ from the silicon tetrahedral structure. They show an increase in nonlinear refractive index n_2 with the linear refractive index n_0. However the variations in n_2 are much larger than those for n_0 [2].

Recently Lines [3] developed a bond-orbital theory for both the linear and nonlinear electronic responses of a number of a transparent transition-metal oxides, which is not strictly valid for studies on glass, but can be used with success. From Lines theory, the dependence of n_2 on n_0 can be written as:

$$n_2 = \frac{(n_0^2 - 1)^3 (n_0 - 1) d^2}{n_0^2 E_s^2} \times 10^{-20} \frac{m^2}{W}$$

where n_2 and n_0 are nonlinear and linear refractive index, respectively, d is the bond length and E_s is the Sellmeier gap [4]. An analysis of the influence of the empty d orbital on n_2 in the transition metal oxides reveals that the most influential ions for the objective of increasing n_2 are Ti^{4+}, Nb^{5+} and W^{6+} and these are the most viable additives in this context.

Glasses with high TiO_2 composition have been described by many works [5]. However, glasses in binary TiO_2–BaO were prepared in an attempt to breed $BaTiO_3$ crystals by melting as close as possible to this composition [6]. Very high TiO_2 glasses are used also in the production of high-refracting glass beads for road signs [7].

The present work deals with the synthesis and characterization of the TiO_2–BaO–ZnO–B_2O_3 glass system, that in this context, presents high potential for nonlinear optical devices. We report the results of

TABLE I Glass compositions (mol %)

Glass	TiO_2	BaO	ZnO	B_2O_3
TBZB-1	35.0	40.0	10.0	15.0
TBZB-2	40.0	35.0	10.0	15.0
TBZB-3	43.5	34.5	12.3	10.2
TBZB-4	45.0	30.0	10.0	15.0
TBZB-5	49.2	28.3	12.3	10.2
TBZB-6	53.0	23.0	10.0	14.0

X-ray diffractometry, infrared and absorption spectroscopy, dilatometry, density and refractive index of some glass compositions.

2. Experimental details

2.1. Glass preparation and their properties

The nominal glass compositions used in this study are presented in Table I. The starting materials were TiO_2 powder (Riedel), BaO powder (Riedel), ZnO powder (Riedel) and $H_3B_2O_3$ (Merck). The appropriate mixture was molten in an alumina crucible at a temperature of 1200 °C for 10 min in a super kanthal resistance furnace. The glass was then rapidly quenched between two steel plates and later annealed at a temperature close to the glass transition temperature T_g. It should be noted that the molten glass was quite fluid and nonviscous. Then, it was desirable that the molten glass was quenched rapidly because of the considerable proportion of TiO_2, which has a tendency to cause devitrification. Thus, the molten glass was poured directly into the two steel plates where it was rapidly cooled.

The following analytical tools were used in this work: (i) the densities were determined by a Micromeritics Multivolume He gases pycnometer model 1305; (ii) linear refractive indexes were measured using a Brewster angle method at 632.8 nm (He–Ne laser) on polished glass sample; (iii) the infrared spectra of glasses were obtained using a Nicolet 60X-B model spectrometer at 400–4000 cm^{-1} for the slab or KBr pellets; (iv) the X-ray diffractograms were performed on a Shimadzu 3X-A Model, with Ni filter and CuK_α at 0.15418 nm, with scanning rate of 2 grades min^{-1}; and (v) the absorption spectra were obtained by a Cary-Varian 2300 model spectrophotometer and dilatometry was carried out on a Harrop dilatometer with 6° C min^{-1} rate.

3. Results and discussions

3.1. Observation about the glass

The glasses obtained were homogeneous, transparent, colourless and bubble free. The thickness is only about 1.5 mm, because of the strong crystallization tendency.

3.2. X-ray diffractometry

The X-ray diffractograms of powder samples are presented in Fig. 1. The halo in the region of $2\theta = 28°$ shows the presence of the vitreous state. Curve 1 of the TBZB-1 glass is similar to the curves for TBZB-2 to TBZB-5 glasses. Curve 6 of TBZB-6 glass shows the presence of peaks on the halo indicating two phases: amorphous and crystalline, which is classified as a vitro-ceramic glass.

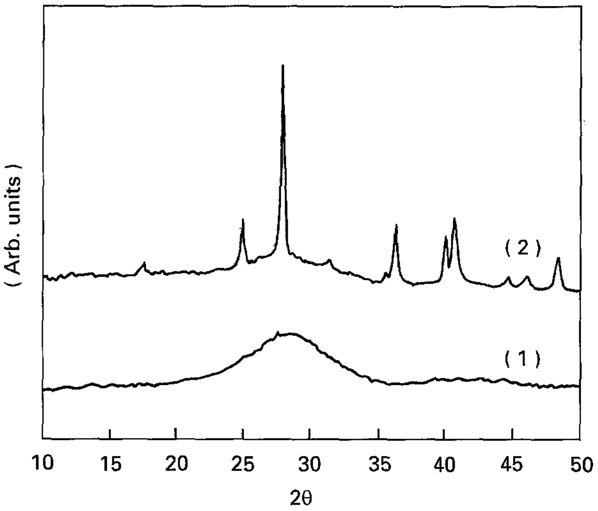

Figure 1 X-ray diffractograms of glasses (1) TBZB1-TBZB5; (2) TBZB6.

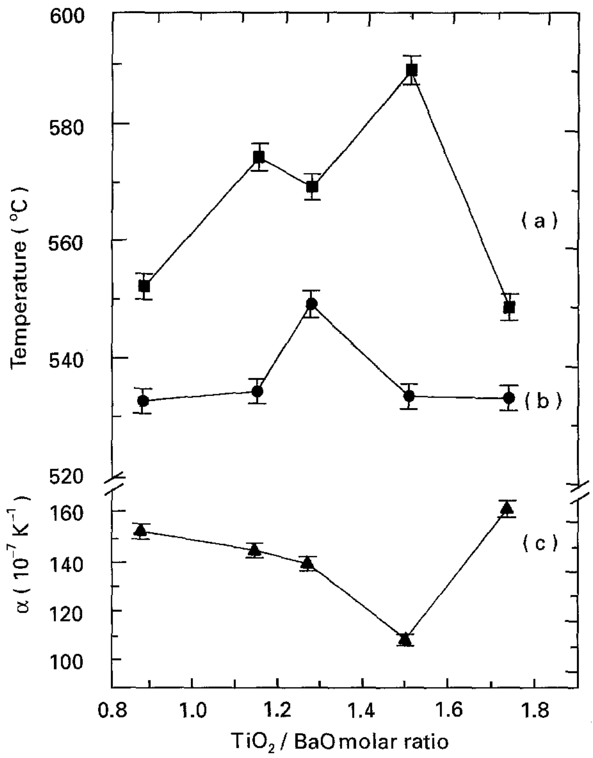

Figure 2 (a) Softening point, (b) transition glass temperature in function of the TiO_2/BaO ratio and (c) thermal expansion coefficient.

3.3. Dilatometry

The properties of dilatometric softening point T_d, glass transition temperature T_g and thermal expansion coefficient α can be extracted from these curves. We can identify in Fig. 2a that the softening temperature of glasses (and hence the viscosity at constant temperature) at first increases with the concentration of TiO_2, reaches a maximum and then decreases with increasing TiO_2 concentration. The glass transition temperature in Fig. 2b presents anomalous behaviour. On the other hand, the thermal expansion coefficient in Fig. 2c at first decreases to a minimum at a critical TiO_2 concentration, and then reverses its trend to increase with further increasing TiO_2 concentration.

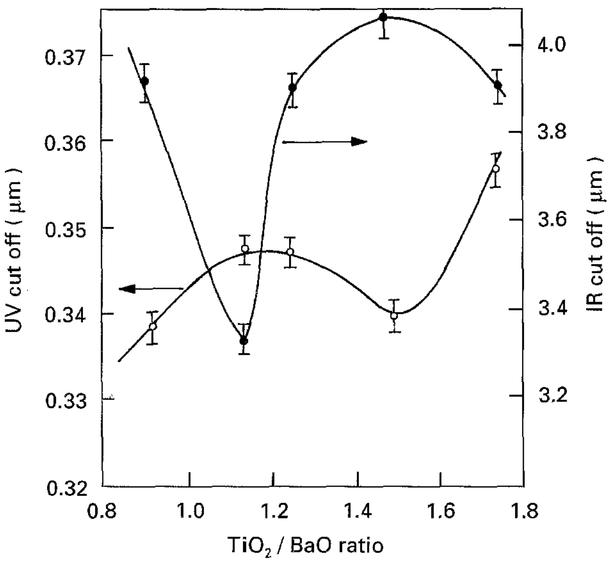

Figure 3 UV and IR "cut off" curves as a function of the TiO_2/BaO ratio.

3.4. Absorption spectra

The UV-VIS "cut off" from the absorption spectra change as a function of TiO_2 concentration, as shown in Fig. 3. The electronic transitions from the valence to the conduction bands are in the range 0.33–0.35 μm, in anomalous forms that depend on the glass composition.

3.5. Infrared spectra

We have observed from infrared spectra an IR "cut off" which depends on TiO_2 concentration, as shown in Fig. 3. The IR "cut off" can be interpreted by a change in structural behaviour in this region, because the IR "cut off" passes through a minimum frequency for a TiO_2/BaO ratio around 1.50 [8].

Infrared absorption spectra of TBZB glasses in powder form are shown in Fig. 4. Bars at the top of figure show the wave number regions where TiO_4 and TiO_6 are reported to give an absorption, respectively. It can be seen that TBZB glasses show the strongest absorption at 550–650 cm^{-1} and 700–750 cm^{-1} in wave number. These wave numbers are located in the region of the absorption ascribed to TiO_4 and TiO_6 [9]. Then it can be speculated that most of the Ti^{4+} ions in the present glasses are tetrahedral and octahedral coordinated with O^{2-}ions, respectively.

The trends of the curves in Figs 2 and 3 indicate that Ti^{4+} displays an anomalous behaviour in this glass system that brings about an overall weakening of the structure at higher concentrations. This apparent anomaly can be explained by the fact that Ti^{4+} can exist in fourfold as well as in sixfold coordination depending on its environment [10].

3.6. Density and refractive index

We have observed a maximum point in both refractive index and density curves around a TiO_2/BaO ratio equal 1.50. From the literature it is ascertained that the maximum points on these curves indicates a change of coordination number from tetrahedral to octahedral [11, 12]. These behaviours are illustrated in Fig. 5a and b, respectively. We have evaluated a very high value of linear refractive index. This means a very high nonlinear refractive index glass, according to Lines theory [3]. The vertical scale is amplified to show the maximum in the linear refractive index (Fig. 5a). Another interesting fact is that we have a very high refractive index glass with a relatively low density. This indicates that the high value of the linear refractive index was caused mainly by the polarizability of Ti^{4+} ions and not by the density.

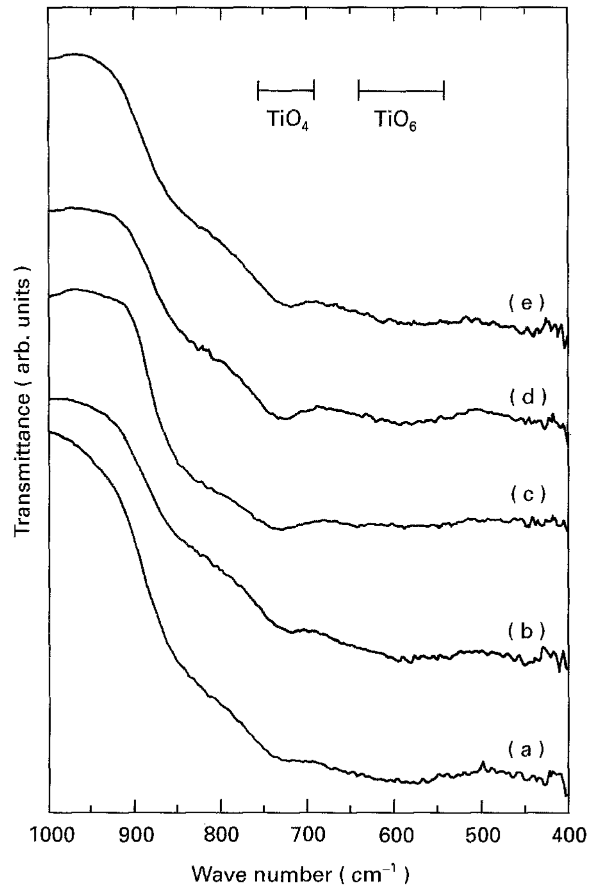

Figure 4 Infrared spectrum of powder samples from TBZB1 to TBZB6 glasses. Arrow indicates absorption bands of the Ti^{4+} and Ti^{6+} ions, respectively.

3.7. Refractive index thermal behaviour

With a heat treatment of the glass at a temperature around 600 °C, we have observed a change of refractive index at a rate that increases rapidly with increasing temperature. This effect is shown in Fig. 6. The explanation for these large increases in refractive index with heat treatment can be related to structural changes within the glass. It has been known that crystalline TiO_2 has a high refractive index up to 2.90. During heat treatment, structural groups may have been formed within the glass that closely resemble some of the crystalline forms or compounds of TiO_2 but without necessarily forming such crystals.

4. Conclusions

In the TiO_2–BaO–ZnO–B_2O_3 glass system, the Ti^{4+} ion is a network-former in its own right and is capable

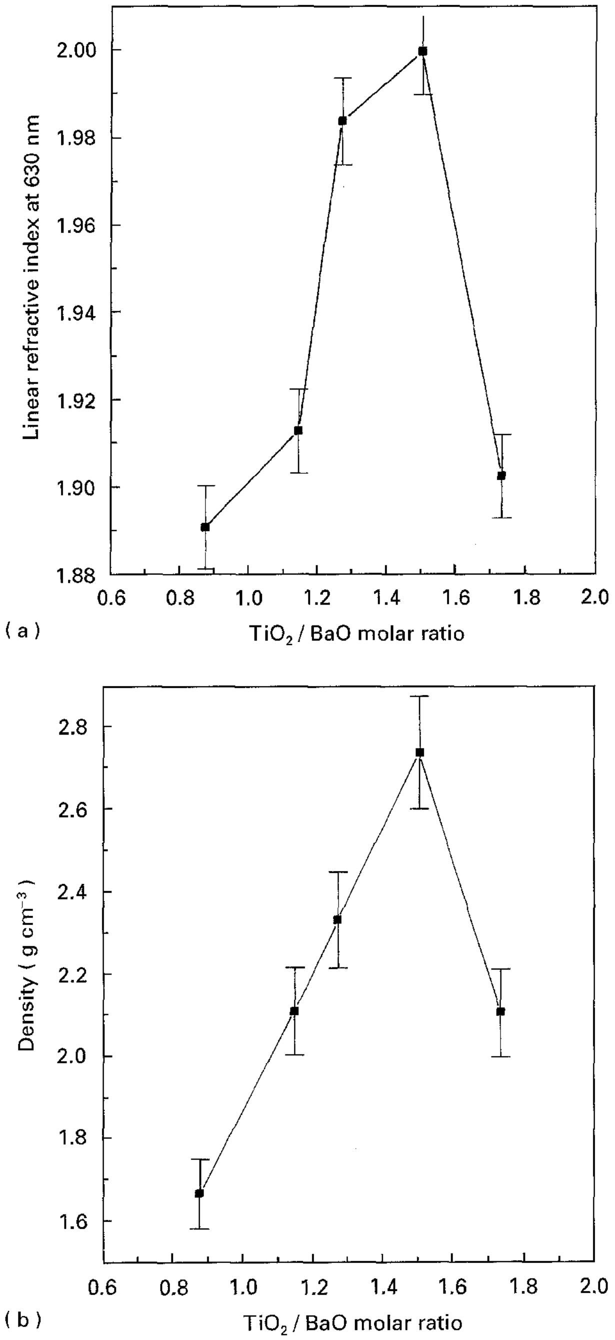

Figure 5 (a) Linear refractive index and (b) density of TBZB glass as a function of the TiO_2/BaO ratio.

of taking part in the network in tetrahedral or octahedral coordination, depending on conditions. It strengthens the structure when in fourfold coordination and weakens it when in sixfold coordination.

We have observed in this work that, a variation in the Ti^{4+} concentration leads to a change in the relative concentrations of the different structural units, such as Ti^{4+}, Ti^{6+} and non-bridging oxygen groups. These results are consistent with Lines theory of effects of ions with an empty *d* orbital on nonlinear properties, such as the Ti^{4+} ions.

It has been found that if this glass system is heat treated at temperatures in and above its annealing range, unusually from a given composition of glass depending on the temperature and time used, an increase of linear refractive index will be produced. These increases in refractive index can be produced without any loss in transparency, visible devitrification or any effect on colouration in the glass.

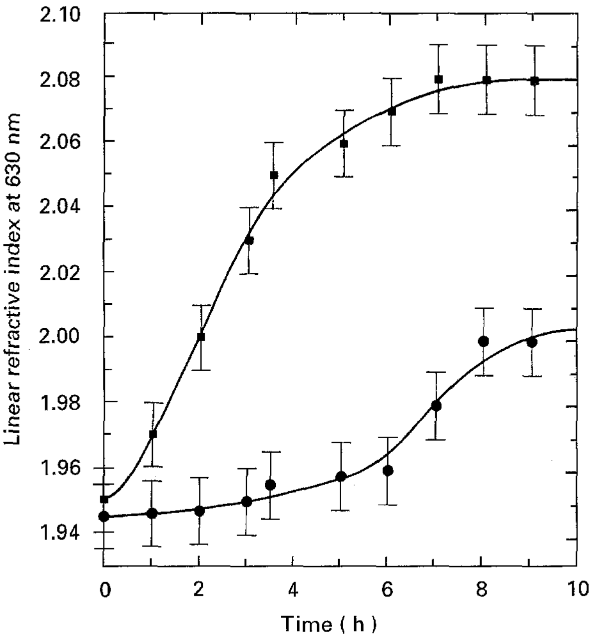

Figure 6 Thermal refractive index behaviour of TBZB2 glass sample as a function of heat treatment time at 600 (●) and 625 °C (■), respectively. Linear refractive index was measured at room temperature.

This glass system will find its application in all types of optical devices requiring a transparent glass component. For example, using a laser scriber to produce the device. Future research will be directed to the study of the nonlinear refractive index n_2 and its relation with the glass composition.

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References

1. E. M. VOGEL, *J. Amer. Cer. Soc.* **72** (1989) 719.
2. N. L. BOLING, A. J. GLASS and A. OWYOUNG, *IEEE J. Quant. Elec.* **14** (1978) 601.
3. M. E. LINES, *J. Appl. Phys.* **69** (1991) 6876.
4. S. H. WEMPLE, *J. Chem. Phys.* **67** (1977) 2151.
5. B. V. RAO, *ibid.* **4** (1963) 22.
6. A. HERCZOG and M. LAYTON, *J. Amer. Cer. Soc.* **50** (1967) 360.
7. C. SEAREIGHT and M. ALEXANDER, US Patent 3198641.
8. J. E. SHELBY, *J. Non-Cryst. Solids* **49** (1982) 287.
9. T. KOKUBO, Y. INAKA and S. SAKKA, *ibid* **95** & **96** (1987) 547.
10. J. L. TRAP and J. M. STEVES, *Phys. Chem. Glass.* **1** (1960) 107.
11. M. K. MURTHY and J. IP, *Nature* **201** (1964) 286.
12. H. J. L. TRAP and J. M. STEVES, *Phys. Chem. Glass.* **1** (1960) 181.

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