



# Structure and mechanical properties of copper–lead and copper–zinc borate glasses



Z.Y. Yao<sup>a,b</sup>, D. Möncke<sup>b</sup>, E.I. Kamitsos<sup>c</sup>, P. Houizot<sup>a</sup>, F. Célarié<sup>a</sup>, T. Rouxel<sup>a</sup>, L. Wondraczek<sup>b,\*</sup>

<sup>a</sup> Glass & Mechanics Department, Institute of Physics, UMR UR1-CNRS 6251, University of Rennes 1, Campus de Beaulieu, 35042 Rennes Cedex, France

<sup>b</sup> Otto Schott Institute of Materials Research, University of Jena, Fraunhoferstrasse 6, 07743 Jena, Germany

<sup>c</sup> Theoretical and Physical Chemistry Institute, National Hellenic Research Foundation, 48 Vassilios Constantinou Avenue, 11635 Athens, Greece

## ARTICLE INFO

### Article history:

Received 17 August 2015

Received in revised form 15 December 2015

Accepted 17 December 2015

Available online 16 January 2016

### Keywords:

Copper

Borate

Glass

Structure

Elastic moduli

Indentation toughness

## ABSTRACT

Copper–lead and copper–zinc borate glasses with different copper contents were prepared and studied for correlations between structure and mechanical properties, where the cations are used to tailor the intermediate-range speciation of borate groups. Structural characterization was done by optical absorption, electron spin resonance (ESR), Raman and infrared (IR) spectroscopy. The mechanical properties were investigated through in-depth instrumented indentation and mechanical resonance analyses. The zinc metaborate glass series shows a high disproportionation of metaborate into mainly trigonal pyroborate  $[B_2O_5]^{4-}$  and polyborate  $[B\emptyset_3]^{0-}$  units, while the lead borate glass series exhibits a network based on trigonal  $[B\emptyset_2O]^-$  and tetrahedral  $[B\emptyset_4]^-$  metaborate units and a minor PbO–pseudophase ( $\emptyset$  = bridging oxygen and O = non-bridging oxygen). For both glass types, the addition of copper oxide results in a more homogenous network containing  $[B\emptyset_2O]^-$  and  $[B\emptyset_4]^-$  metaborate units. This induces an enhancement of the elastic moduli and hardness in the lead borate glass series, but a decrease of these properties in the copper–zinc borate glasses, whereby copper–zinc borate glasses are stiffer and harder than copper–lead borate glasses.

© 2015 Elsevier B.V. All rights reserved.

## 1. Introduction

In glasses, transition metal oxides can act either as network formers or modifiers, depending on their redox state and coordination number. In Cu-containing oxide glasses molten in conventional atmospheric conditions, copper may be present as divalent  $Cu^{2+}$  (cupric), monovalent  $Cu^+$  (cuprous), and metallic copper  $Cu^0$  [1]. Such copper-doped glasses are increasingly studied for the strong effect of copper ions on the electrical, optical and magnetic properties.

It is known that the valence state of copper affects not only the physical and chemical properties but also the glass forming ability [2]. The copper redox behavior, which was investigated in copper–lead borate glasses [1,3], indicates that the replacement of  $Pb^{2+}$  by  $Cu^{2+}$  ions increases the  $Cu^+/Cu_{tot}$  ratio. For comparison, in typical silicate glasses, about one to two thirds of the Cu ions are indeed present in the reduced state, even when melted under air using an electric furnace [4,5]. As the network-forming boron species in glasses can be three- or four-fold coordinated by oxygen, depending on the concentration and type of the modifier oxide as well as on the conditions of glass preparation [6–16], such transitions can be used for intermediate-range tailoring of glass structure and, hence, mechanical properties [17,18]. In the above glasses, the fraction of trigonal  $[B\emptyset_2O]^-$  units increases as

$[B\emptyset_4]^-$  containing entities are converted into ring-type metaborate groups, and the hardness of the glasses is enhanced ( $\emptyset$  denotes bridging, and O non-bridging oxygen atoms). The average coordination number of lead ions in lead borate glass ranges from 5.1 to 5.8 for metaborate compositions with 40–50 mol% PbO, which indicates that the majority of the lead ions act as network modifier ( $PbO_6$ ) and only a minority acts as network former in the form of  $PbO_3$  trigonal pyramids [19]. Other studies showed that a PbO–pseudophase starts forming in the lead metaborate glasses, and develops upon increasing PbO content, leaving an undermodified borate network as part of the oxygen content is retained to form  $PbO_n$ -polyhedra [20–23].

In zinc borate glasses,  $Zn^{2+}$  ions can behave as network modifiers in six-fold coordination or as network formers in four-fold coordination with oxygen, whereby the coordination number depends on glass composition [6,24]. In  $xZnO-(100-x)B_2O_3$  glasses with  $x = 40$ –65 mol%, zinc atoms coordinate tetrahedrally with oxygen atoms. The neighboring borate structure transforms from tetrahedral to trigonal structure with increasing ZnO content [24]. In addition, the zinc metaborate glass shows liquid–liquid phase-separation below 50 mol% ZnO, while 53:47 ZnO: $B_2O_3$  typically yields clear homogenous glasses [6,25]. Zinc borate glasses are also prone to a high disproportionation of metaborate into pyroborate and polyborate units [26]. Some copper–zinc borate glasses have been investigated previously and it was found that the glass-forming regions are restricted to 40 mol%  $\leq B_2O_3 \leq 50$  mol%, 30 mol%  $\leq ZnO \leq 50$  mol%, and  $CuO \leq 30$  mol%. Mechanical testing showed that

\* Corresponding author.

E-mail address: [lothar.wondraczek@uni-jena.de](mailto:lothar.wondraczek@uni-jena.de) (L. Wondraczek).

the hardness increases with the increase of the packing density of glass and the decrease of the glass transition temperature  $T_g$ . With increasing CuO content, the Young's modulus decreases when  $B_2O_3$  is 50 mol% but increases when  $B_2O_3$  is 40 mol% [27].

In the present study, copper–lead borate glasses and copper–zinc borate glasses with 50 mol%  $B_2O_3$  and different copper contents are considered in detail. The structural changes which occur with the substitution of ZnO or PbO by CuO are related to the resulting changes in the mechanical properties. As governing parameters, the oxidation state, site environment and bonding characteristics of copper ions are also taken into account.

## 2. Materials and experimental methods

### 2.1. Synthesis of lead- and zinc-copper borate glasses

The glass samples of this study have the general chemical formula  $(50 - x)PbO - xCuO - 50B_2O_3$  ( $x$  from 0 to 30) and  $(50 - x)ZnO - xCuO - 50B_2O_3$  ( $x$  from 0 to 35). In the following, they are referred to as PCB\_x and ZCB\_x, where  $x$  is the CuO content in mol%. A list of all studied samples with selected physical properties is provided in Table 1. All glasses were prepared by melt quenching. High-purity CuO, PbO and  $B_2O_3$  powders were used as raw materials for the PCB\_x series, and CuO, ZnO and  $H_3BO_3$  for the ZCB\_x series.

Batches yielding 40 g of PCB\_x glasses were prepared by heating respective powder mixtures in air at 900 °C for 30 min, using platinum crucibles. The melts were subsequently quenched on a brass mold and crushed using a Retsch PM100 grinder apparatus before re-melting again at 900 °C for 30 min. The whole process was repeated twice to better homogenize the melt. Finally, the melts were poured onto an Inconel mold preheated at  $T_g$  for 1 h to avoid any residual stresses. No visible crystallization or phase separation was observed.

For the ZCB\_x series, powdered mixtures to yield 100 g of glass were heated in air at 1150 °C for 30 min using platinum crucibles. The melts were poured onto brass plates before annealing from about 610 °C to room temperature with a cooling rate of 30 °C/h. The 50:50 (mol%) glass composition showed liquid–liquid phase separation which resulted in a light phase containing primarily  $B_2O_3$  and  $H_3BO_3$  crystals encapsulating the clear vitreous bulk glass (see also [6]).

For characterization and analysis, glass plates and disks of different thicknesses (ranging from 2 mm to <0.2 mm) were cut and polished. Care was taken to sample only material from the homogeneous bulk glass phase for the ZCB\_x series. Fig. 1 shows a selection of less than 0.2 mm thick polished glass samples which were used for optical characterization. Binary lead borate and zinc borate glasses are transparent;

the color of the Cu-containing glasses varies from sky blue to dark green with increasing CuO content.

### 2.2. Structural and optical characterization

Both Raman and IR spectroscopy techniques were used to study changes of the glass structure as a function of composition. The measurements were carried out on polished samples. Raman spectra were obtained on a Renishaw inVia Raman microscope in the range from 100 to 3200  $cm^{-1}$  with a resolution of 2  $cm^{-1}$  using the 488 nm and 514 nm laser excitation lines, and a Near Excitation Tunable (NEXT) filter system for low-frequency Raman measurements in the 15 to ~600  $cm^{-1}$  range with excitation at 514 nm.

Infrared spectra were recorded in the specular reflectance mode on a vacuum Fourier transform spectrometer (Bruker, Vertex 80) and cover the range from 30 to 7000  $cm^{-1}$  with a resolution of 2  $cm^{-1}$ . The reflectance data were analyzed by Kramers–Kronig transformation to yield the spectral absorption coefficient [7]:

$$\alpha(f) = 4\pi f k(f) \quad (1)$$

where  $k(f)$  is the imaginary part of the complex refractive index and  $f$  is the infrared frequency in wavenumbers ( $cm^{-1}$ ).

Electron spin resonance (ESR) measurements were obtained for the selective study of the site geometry and bonding state of the paramagnetic  $Cu^{2+}$  ions. The experiments were conducted at the X-band frequency ( $G \sim 10$  GHz) on a Bruker instrument, which provided internal  $g$  and spin calibration. Polished samples of equal geometry (8 mm  $\times$  15 mm  $\times$  1 mm) were measured at room temperature, thus allowing for semi-quantitative analysis.

Ultraviolet–visible (UV–vis–NIR) spectroscopy was used in the transmission mode for the acquisition of the optical spectra of the samples. The obtained absorbance data was used to quantify changes in the  $Cu^{2+}$  concentration according to the Beer–Lambert law

$$A(\lambda) = \log_{10} \left( \frac{I_0(\lambda)}{I_t(\lambda)} \right) = \varepsilon(\lambda) \cdot c \cdot d \quad (2)$$

where  $A(\lambda)$  is the measured absorbance at a given wavelength  $\lambda$  (nm),  $I_0(\lambda)$  is the intensity of the incident light and  $I_t(\lambda)$  is the transmitted intensity,  $d$  (cm) the thickness of sample,  $c$  ( $mol \cdot L^{-1}$ ) the concentration of the absorbing ion and  $\varepsilon(\lambda)$  ( $L \cdot mol^{-1} \cdot cm^{-1}$ ) is the molar extinction coefficient at the wavelength  $\lambda$ . Optical absorption spectra were obtained in the range from 200 to 3000 nm on 0.16–0.18 mm thick polished, plane parallel glass samples. The absorbance values were normalized

**Table 1**  
Physical properties of glass samples;  $\rho$ : density;  $C_g$ : packing density;  $T_g$ : transition temperature; CTE: coefficient of thermal expansion;  $\langle U_o \rangle$ : molar energy;  $\langle U_o \rangle / \langle V_o \rangle$ : volume density of energy; E: Young's modulus; G: Shear modulus;  $\nu$ : Poisson ratio; K: elastic modulus.

Glass	$\rho$ ( $\pm 0.05$ g/cm <sup>3</sup> )	$C_g$ ( $\pm 0.002$ )	$T_g$ ( $\pm 5$ °C)	CTE ( $\pm 0.1 \times 10^{-6}$ K <sup>-1</sup> )	$\langle U_o \rangle$ (kJ/mol)	$\langle U_o \rangle / \langle V_o \rangle$ (Eq. (5), kJ/cm <sup>3</sup> )	$\langle U_o \rangle / \langle V_o \rangle$ (Eq. (4), kJ/cm <sup>3</sup> )	E ( $\pm 4$ GPa)	G ( $\pm 2$ GPa)	$\nu$ ( $\pm 0.01$ )	K ( $\pm 4$ GPa)
PCB_0	5.685	0.565	396	10.6	545.0	73.11	74.06	57.5	22.3	0.289	45.4
PCB_0.5	5.647	0.563	399	10.6	545.0	73.29	73.94	64.6	24.8	0.303	51.2
PCB_1	5.628	0.563	400	10.3	545.2	73.46	74.07	64.1	24.9	0.288	50.4
PCB_2	5.551	0.560	400	10.3	545.4	73.81	73.82	64.5	25.0	0.292	55.9
PCB_5	5.518	0.570	405	9.9	546.1	74.88	75.75	64.6	24.8	0.302	55.1
PCB_10	5.337	0.575	410	9.6	547.2	76.74	77.41	67.4	26.0	0.298	55.9
PCB_20	4.922	0.581	426	5.9	549.5	80.70	80.45	71.4	27.4	0.302	60.0
PCB_30	4.420	0.580	438	6.5	551.8	85.06	82.63	77.7	30.0	0.293	62.6
ZCB_0	3.435	0.577	571	5.2	554.5	90.61	88.29	80.9	30.4	0.330	79.3
ZCB_1	3.425	0.576	558	5.4	554.5	90.70	88.06	83.3	31.6	0.316	75.5
ZCB_10	3.402	0.575	538	5.3	554.9	91.50	87.71	86.7	33.0	0.315	78.1
ZCB_15	3.412	0.579	527	4.6	555.0	91.95	88.11	87.0	33.0	0.319	80.1
ZCB_20	3.419	0.581	518	5.5	555.2	92.40	88.43	86.4	33.0	0.309	75.4
ZCB_25	3.425	0.584	506	5.3	555.4	92.86	88.72	79.3	30.3	0.307	68.5
ZCB_30	3.388	0.580	498	5.5	555.6	93.32	87.91	81.1	31.1	0.304	68.9
ZCB_35	3.369	0.578	485	5.4	555.8	93.79	87.55	80.4	30.9	0.302	67.6

Download English Version:

<https://daneshyari.com/en/article/1480397>

Download Persian Version:

<https://daneshyari.com/article/1480397>

[Daneshyari.com](https://daneshyari.com)