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## 1 Environment dependence of $K_{Ic}$ of glass

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8

## 9 Abstract

10 **The** role of temperature ( $T$ ) and moisture on fracture toughness ( $K_{Ic}$ ) of glasses, as measured by the single-  
11 edge precracked beam method (**SEPB**), **is investigated**. The brittle to ductile temperature, **shown** by an  
12 increase of  $K_{Ic}$ , is  $\sim T_g$ . At  $T$  below  $0.9T_g$ , the decrease of the bond strength with  $T$  results in the decrease of  
13 both the fracture surface energy and Young's modulus, so that  $K_{Ic}$  decreases with  $T$ . From above  $T_g$  to below  
14  $1.1T_g$ , the work of fracture increases because of dissipative processes, including confined viscoplasticity and  
15 blunting at the crack front. From  $1.1T_g$ , viscous flow extends to the whole specimen and becomes more  
16 uniform, resulting in the macroscopic deformation of the specimen, eventually preventing against fracture.  
17 The results on humidity sensitive glasses show that both precracking and final fracture steps need to be  
18 performed in inert environment to meet the intrinsic  $K_{Ic}$  value, unless the test is fast enough.

19 **Keywords:** Fracture toughness, single-edge precracked beam (SEPB), environment dependence, brittle to  
20 ductile transition (BDT)

## 1. Introduction

Although the environment dependence of the fracture toughness ( $K_{Ic}$ ) of glasses and ceramics is important for their application in service conditions it is not well understood, and was scarcely reported. Most publications focused on the effect of temperature for ceramics [1–8], and of humidity for amorphous silica ( $a\text{-SiO}_2$ ) and window glass [9–11].

The SEPB test is a reliable and self-consistent method, which is based on the generation of a sharp precrack, with sharpness down to atomic scale [12–15]. However, due to inherent difficulties in specimen preparation and testing conditions, this method has not been used in environmentally controlled atmosphere so far.

In this work, the SEPB method is applied to glasses samples up to  $1.11T_g$ , and results are compared to previously published ones [10,11]. Both the precracking and the final fracture stages of the method are performed in controlled atmosphere.

Regarding the temperature dependence, four glasses from silicate, borate and oxynitride chemical systems were selected. As far as relatively small loading rates are applied (quasi-static regime), typically for  $dK_I/dt \leq 10 \text{ MPa}\cdot\sqrt{\text{m}}\cdot\text{s}^{-1}$ , which corresponds to strain-rates,  $\dot{\epsilon}$ , below  $10^{-2} \text{ s}^{-1}$ , the brittle to ductile transition temperature is expected to be at around  $T_g$ . For the environment dependence, four commercial glasses (silicate and borosilicate systems) were investigated. Cross-head speeds ranging from  $0.01 \mu\text{m}\cdot\text{s}^{-1}$  and to  $15 \mu\text{m}\cdot\text{s}^{-1}$  were applied during the SEPB bending experiment to investigate the possible influence of the crack velocity. Finally, results from previously published SEPB experiments in ambient atmosphere, where only the final fracture stage was conducted in dry  $\text{N}_2$  atmosphere [14,15], and present results (both precracking and final fracture steps in dry argon atmosphere) are compared.

## 2. Experimental Procedures

The seven glass compositions that were used are given in Tables 1 and 2. Among these glasses four grades covering a large  $T_g$  range, from 673 K to 1207 K, were used to study the effect of temperature on  $K_{Ic}$  (Table 1). Four silica-rich (70-100 mol.%) grades were used to investigate the effect of humidity (Table 2). The density ( $\rho$ ) was measured using  $3 \times 4 \times 20 \text{ mm}^3$  specimens by means of Archimedes principle of buoyancy

in distilled water. The elastic moduli (Young's modulus,  $E$  and shear modulus,  $G$ ) and Poisson's ratio ( $\nu$ ) were determined by means of ultrasonic echography using 10 MHz piezoelectric transducers:

$$G = \rho V_T^2 \quad (1)$$

$$E = \rho \frac{3V_L^2 - 4V_T^2}{(V_L/V_T)^2 - 1} \quad (2)$$

$$\nu = \frac{E}{2G} - 1 \quad (3)$$

Where  $V_L$  and  $V_T$  are the longitudinal and transverse wave velocities respectively.

### 2.1. $K_{Ic}$ at elevated temperatures

High temperature  $K_{Ic}$  measurements (SEPB method) were performed at  $0.35T_g$ ,  $0.93T_g$ ,  $T_g$ ,  $1.03T_g$ ,  $1.05T_g$ ,  $1.07T_g$  and  $1.11T_g$ . In order to use the SEPB technique, parallelepiped bars were cut from glass batches using a diamond saw to get  $3 \times 4 \times 20$  mm<sup>3</sup> bars, which were further polished down to 3  $\mu$ m diamond paste. A series of 10 N Vickers indents, each distant by 200  $\mu$ m to the adjacent ones, were aligned at the center of the  $3 \times 20$  mm<sup>2</sup> tensile face, along with broadness ( $B = 3$  mm) as detailed in Ref. [15]. Specimens were then set in a bridge-flexure anvil [16] allowing for a precrack to be generated, as long as about half of the specimen width ( $W = 4$  mm). During the bridge-flexure test, the indented specimen experiences a tensile stress at the lower part (near the indented surface) and a compressive one at the upper part. In such a situation, the precrack starts from the indents, grows and stops at around the center of the beam where it meets the compressive field. The precracked specimens were finally fractured at elevated temperatures with an aluminum oxide three-point bending device with a span length of 15 mm. A heating rate of 12 K·min<sup>-1</sup> was used and a thermocouple was positioned close ( $\sim 1$  mm) to the center of the specimen. After cooling down to room temperature, the precrack length was measured (fractography), and  $K_{Ic}$  was calculated from the maximum load [15]. All experiments were conducted in ambient atmosphere ( $\sim 60$  %) with a cross-head speed of 15  $\mu$ m·s<sup>-1</sup> (loading rate of about 10 MPa· $\sqrt{m}$ ·s<sup>-1</sup>), and the test temperature was known with an accuracy better than  $\pm 1$  K.

### 2.2. $K_{Ic}$ in dry argon gas atmosphere

Samples from the four glass grades in Table 2 were characterized both in dry argon gas ( $T = 20\text{ }^{\circ}\text{C}$ ; RH  $\sim 0$ ) and in ambient atmosphere ( $T = 20\text{ }^{\circ}\text{C}$ ; RH = 60 %). In the case of SEPB experiments conducted in dry argon gas, both precrack and final fracture steps were performed in a glove box filled with high purity dry argon. After indentation in ambient conditions (to ease the precrack formation), the bar specimens were placed in the anvil for precracking inside a glove box (**Figure 1**) and loaded by means of a portable uniaxial testing machine (Deben, UK). A camera focused on the middle of the specimen (where indentation was performed) was used to follow in-situ the precracking stage and to observe the pop-in of the precrack. The machine was manually stopped once the precrack appeared. The precracked specimen was then loaded in three-point bending (span length of 15 mm) **set-up positioning in a homemade uniaxial machine**, and the load was monitored by means of a 50 N capacity load cell (K25, Scaime Company, France) with an accuracy better than 0.001 N. The broken specimens were then taken out of the argon gas box to measure the precrack length and  $K_{Ic}$  was calculated from the maximum load and the measured precrack length (see **ref. [15] for details**). In ambient conditions (RH = 60 %), it was previously shown that the results derived from unstable tests (that is where the load-displacement curve exhibits some disruption or fast unloading once the maximum load is passed) are free from environment incidence (no slow crack growth) as they are associated to large crack velocities. Unstable test in ambient conditions were obtained at a cross-head speed between 5 and  $15\text{ }\mu\text{m}\cdot\text{s}^{-1}$ . The cross-head speed for the experiments in the glove box was set at  $0.05\text{ }\mu\text{m}\cdot\text{s}^{-1}$ , but for 1 extra experiment on a SLS specimen where a cross-head speed of  $5\text{ }\mu\text{m}\cdot\text{s}^{-1}$  (100 times faster than for other experiments) was chosen for comparison.

### 3. Results

#### *3.1. SEPB test evaluation*

Among one hundred thirty five tests, nine were found invalid and were discarded because either (i) the precrack was too short (less than 25% of the width,  $W$  in **Figure 2**) or too long (more than 75% of  $W$ ), or (ii) the precrack front was uneven between both sides of the broadness,  $B$  in **Figure 2** (more than 10% difference between the average precrack length and any measurement at 25%, 50% and 75% of  $B$ , i.e.  $|(a - a_1)/a| > 0.10$  as shown in **Figure 1**), or (iii) the angle between the precrack and the final fracture was larger than  $10^{\circ}$  (**Figure 3**). These unsuitable conditions lead to over- or under-estimated values for  $K_{Ic}$  [14,15]. During the

bridge-compression stage (**Figure 2a**), the precrack can be stable or unstable [15]. In our case, the precrack is unstable and is referred to as a pop-in precrack, i.e. the precrack suddenly occurred just after the onset of extension from the indents, as shown in **Figure 2**. **Figure 2b** shows the load-displacement curve during the pop-in precrack formation which is observed in **Figures 2c** and **2d**. An example of post-fracturing investigation is shown in **Figure 3**. The precrack length used in the  $K_{Ic}$  determination is measured from **Figure 3a**, and the angle between the precrack and the final fracture is measured from **Figure 3b**. The measured angles used in this Results section are between 0 and 4°.

### 3.2. Temperature dependence of $K_{Ic}$

The dependence of  $K_{Ic}$  on temperature is illustrated in **Figure 4** (data taken from **Table 2**). At high temperature, viscous flow induces some energy dissipation at the vicinity of the crack front (confined viscoplasticity) from  $T_g$  to  $1.05 T_g$  and then at a larger scale at higher temperature, where viscoplastic flow eventually extends through the overall thickness of the specimen depending on the loading rate, and preventing against fracture. As a result of this energy dissipation, the experimental values for  $K_{Ic}$  are no longer intrinsic in this temperature range. Recall that the intrinsic toughness is related to Young's modulus and to the fracture surface energy (intrinsic),  $\gamma$ , following:

$$K_{Ic}^{intrinsic} = \sqrt{2\gamma E'} \quad (4)$$

where  $E' = E$  in plane stress and  $E' = E/(1-\nu^2)$  in plane strain. Since both  $E'$  and  $\gamma$  decrease upon heating (consistently with the weakening of the interatomic bond strength),  $K_{Ic}$  is also expected to decrease. This is actually what is observed from RT to  $\sim 0.8T_g$ . However, experimental investigation reported on glasses (as well as on any material on approaching the brittle to ductile transition, if any) mostly show a rapid increase of  $K_{Ic}$  above  $T_g$  [10,11,17], but for a-SiO<sub>2</sub> glass [9,10], which exhibits little de-structuration and a weak decrease of the viscosity coefficient through the  $T_g$  range. This is because as temperature gets close to  $T_g$  the characteristic relaxation time constant become comparable to the experimental time, which allows for viscous stress relaxation to occur at the crack front. As a matter of fact,  $K_{Ic}$  becomes also loading-rate dependent above  $0.8T_g$ . A transition temperature is observed above which crack tip blunting occurs: this is the brittle-ductile transition (BDT) [11]. The loading rate dependence of the effective fracture toughness ( $K_{Ic}(T)/K_{Ic}(T_{RT})$ ) is illustrated in **Figure 4a** for SLS. With a loading rate of  $2 \text{ MPa} \cdot \sqrt{\text{m}} \cdot \text{s}^{-1}$ , the BDT of SLS

glass is at  $\sim 0.89T_g$  and with a loading rate of  $4 \text{ MPa}\cdot\sqrt{\text{m}}\cdot\text{s}^{-1}$ , it is at  $\sim 0.97T_g$  [11]. With the loading rates of 5 and  $8 \text{ MPa}\cdot\sqrt{\text{m}}\cdot\text{s}^{-1}$ , the BDT is at  $\sim T_g$  [10,11]. With the loading rate of  $10 \text{ MPa}\cdot\sqrt{\text{m}}\cdot\text{s}^{-1}$ , the BDT of SLS is  $\sim 1.05T_g$ . The temperature dependence on  $K_{Ic}$  for the four studied glasses at the rate of  $4 \text{ MPa}\cdot\sqrt{\text{m}}\cdot\text{s}^{-1}$  is shown in **Figure 4b**, together with additional results for SLS (window glass) and SiNaMgO at  $10 \text{ MPa}\cdot\sqrt{\text{m}}\cdot\text{s}^{-1}$ . The BDT for all glasses at the rate of  $4 \text{ MPa}\cdot\sqrt{\text{m}}\cdot\text{s}^{-1}$  are  $\sim 0.8T_g$  for N-Glass and  $0.9T_g$  for the other compositions. At the rate of  $10 \text{ MPa}\cdot\sqrt{\text{m}}\cdot\text{s}^{-1}$ , the BDT is  $\sim 1.05$  for both SLS and SiNaMgO.

### 3.3. Environment dependence of $K_{Ic}$ at room temperature

The cross-head speed (CHS) dependence on  $K_{Ic}$  of SLS, a-SiO<sub>2</sub>, Borofloat and BK7 is shown in Table 3. In ambient conditions,  $K_{Ic}$  is found to depend much on the CHS. With a CHS of  $0.5 \mu\text{m}\cdot\text{s}^{-1}$ , the test is stable and  $K_{Ic} \sim 0.5 \text{ MPa}\cdot\sqrt{\text{m}}$  for all glass compositions. On the other hand, with a CHS of  $5 \mu\text{m}\cdot\text{s}^{-1}$ , the test is unstable and  $K_{Ic}$  is as high as 0.70, 0.69, 0.65 and  $0.82 \text{ MPa}\cdot\sqrt{\text{m}}$  for SLS, a-SiO<sub>2</sub>, Borofloat and BK7, respectively. In the case of the unstable test (the load reaches a maximum value and then drops sharply as the crack suddenly extends) the crack velocity is fast enough to avoid moisture effects at the crack front, so that the experimental  $K_{Ic}$  value is not affected by stress corrosion (region 3 of the crack velocity- $K_I$  curve, after Wiederhorn [18]) [15]. Besides, there is no rate dependence in the case of experiments performed in argon atmosphere. In this latter case, values of  $K_{Ic}$  obtained with a CHS of  $5 \mu\text{m}\cdot\text{s}^{-1}$  agree with those obtained at a rate 100 times slower ( $0.05 \mu\text{m}\cdot\text{s}^{-1}$ ). It is thus concluded that dry argon atmosphere prevents stress-corrosion (also called static fatigue).

Values for  $K_{Ic}$  as measured by means of the SEPB method in different atmosphere or determined ab-initio by means of a simple theoretical approach (after Ref. [12]) is shown in **Table 4**. For all glasses, values measured in argon atmosphere are in agreement with those measured in ambient atmosphere using unstable tests (see ref. [15] for details) and are remarkably close to the theoretical ones [12]. In contrast, the average values measured in N<sub>2</sub> atmosphere are systematically a bit larger than the other values. This might result from the use of the 4-point bending device (in [14]) instead of the 3-point bending one (in this study). Recall that Quinn et al. [14] performed only the final fracture stage in dry N<sub>2</sub> while both precracking and final fracture stages were performed in dry argon in the present work. The agreement between these independent series of measurements suggests that the restricting environment controlled conditions solely to the final fracture stage

is enough to get rid of the stress corrosion effects. Besides, experiments can be done in ambient atmosphere providing the CHS is large enough to induce a crack velocity large enough to insure a fatigue-free behavior (region III of the Wiederhorn's v-K curve [18]).

## 4. Discussion

### 4.1. Temperature dependence of $K_{Ic}$

The fracture behavior of glass at elevated temperatures exhibits three regimes: elastic and brittle from RT to  $0.9 T_g$ , semi-ductile with some local viscoelasticity in the  $T_g$  range, and viscoplastic (ductile) above  $1.1 T_g$  as illustrated in **Figure 2** and corroborated by the absence of breakage in **Table 3** above  $1.1 T_g$ . Considering for example the loading rate of  $4 \text{ MPa} \cdot \sqrt{\text{m}} \cdot \text{s}^{-1}$ , regions I (Brittle), II (BDT) and III (Ductile) are associated with temperatures from RT to  $0.8T_g$ ,  $0.8T_g$  to  $0.93T_g$  and  $0.93T_g$  to above, respectively.

In region I and II,  $K_{Ic}$  decreases as the temperature is increased (**Figure 2**). This is because the bond strength and thus both  $E$  and  $\gamma$  decrease on heating, and so does  $K_{Ic}$  (Eq. 2). The temperature dependence of the elastic moduli of glasses from different chemical systems was previously reported [10,19–22]. In most cases but for amorphous silica ( $\alpha\text{-SiO}_2$ )  $E$  decreases on heating. In the case of  $\alpha\text{-SiO}_2$  (considered as an anomalous glass), a slight increase of  $E$  is observed below  $T_g$  and a light increase of  $K_{Ic}$  follows [9,10]. Nevertheless, for both normal and anomalous glasses, the fracture surface energy is expected to decrease as temperature is increased because of the weakening of the atomic bonding along the crack path. The decrease of the fracture surface energy ( $\gamma^{\text{loss}}$ ) is defined as:

$$\gamma^{\text{loss}} = \gamma - \gamma^T. \quad (5)$$

where  $\gamma$  is the surface energy at room temperature and  $\gamma^T$  the one at elevated temperature.

In the BDT region (II), taking  $E$  and  $\nu$  from Refs. [19,23],  $\gamma^{\text{loss}}$  of  $0.48 \text{ J} \cdot \text{m}^{-2}$ ,  $0.93 \text{ J} \cdot \text{m}^{-2}$  and  $0.34 \text{ J} \cdot \text{m}^{-2}$  for SLS, N-Glass, and BPbCuO were calculated, respectively. A simple theoretical model [12] led to the following expression for  $\gamma$ :

$$\gamma = \frac{1}{2} \left( \frac{\rho}{M_0} \right)^{2/3} N^{-1/3} \sum_i x_i n_i U_{0i}, \quad (6)$$



where  $M_0$  is the molar mass,  $N$  is the Avogadro number,  $x_i$  the stoichiometric fraction of the species involved in the  $i^{\text{th}}$  bonding energy  $U_{0i}$ . By neglecting the variation of  $\rho$  (with a large possible thermal expansion coefficient (of flat SLS glass) of  $9.5 \times 10^{-6} \text{ K}^{-1}$ , the volume change  $\Delta\rho = 2.2\%\rho$  at  $1.1T_g$ ),  $\gamma/\gamma^T = (\sum_i x_i n_i U_{0i}) / (\sum_i x_i n_i U_{0i})^T = 1.20, 1.24$  and  $1.21$  for SLS, N-Glass, and BPbCuO, respectively. Therefore, for the three glasses of concern, the mean bonding energy along the fracture path is about 83 % of its value at room temperature at the BDT. The same conclusion is met for a loading rate of  $10 \text{ MPa} \cdot \sqrt{\text{m}} \cdot \text{s}^{-1}$ . Furthermore, when the actual values of  $E$  and  $\nu$  at elevated temperature are used together with  $\gamma^T$  at the BDT temperature, the predicted value for  $K_{Ic}$  (Eq. 4) is in agreement with the experimental one.

In region III, the apparent toughness increases sharply from a value below  $K_{Ic}$  (RT) to over 1.5 times the initial value. In this range, fracture is eventually avoided due to viscoplastic relaxation, as seen in **Figure 5**. On the one hand, the crack tip becomes blunted (**Figure 5b**), which requires larger load to propagate the crack. On the other hand, from  $1.1T_g$ , the glass behaves in a more and more viscoplastic manner so that most of the mechanical energy is dissipated in the flow process. It is suggested that the load peaks for displacements of 0.15 and 0.4 mm correspond to onsets of crack extension steps but the load ultimately reach a slowly increasing plateau, which corresponds to the viscous flow. Indeed, a load between 15 and 20 N is associated with a stress ( $\sigma$ ) of about 10 MPa, and the imposed strain-rate ( $\dot{\epsilon}$ ), derived from the displacement rate ( $5 \mu\text{m} \cdot \text{s}^{-1}$  for a  $4 \text{ MPa} \cdot \sqrt{\text{m}} \cdot \text{s}^{-1}$  loading rate), is about  $0.5 \times 10^{-3} \cdot \text{s}^{-1}$ . This results in a viscosity coefficient,  $\eta = \sigma / (3\dot{\epsilon})$  of about  $0.7 \times 10^{10} \text{ Pa} \cdot \text{s}$ , which is in agreement with the glass viscosity at  $1.1T_g$ . It is noteworthy that, for most glasses  $\nu$  reaches values larger than 0.3 above  $1.1T_g$ , which also corroborates the occurrence of ductility as was recently discussed elsewhere [24].

#### 4.1.1. Pre-crack tip analysis

The crack front geometrical and physical characteristics are fundamental to understand the changes of the apparent toughness. For example, a diffuse damage zone at the vicinity of the tip was observed to give birth to relatively large apparent toughness values for metallic glasses, thanks to energy dissipation [25]. In such glasses, shear bands may occur and accommodate the singular tip stress field, especially in the case of glasses with large Poisson's ratio (over 0.33), where sliding predominates over volume change [26]. The

high Poisson's ratio together with high nanoductility has been shown on glasses with relatively low covalency interatomic bonding character and high structural disorder [27]. However, the present glasses lie at the opposite side, with low Poisson's ratio and high covalency (directional) bonds [28]. Consequently, no visible damage process zone (diffuse damage near the crack front) is observed in the present glasses at room temperature (**Figure 3**). Sharp crack tips produced by means of bridge-compression (see **Figure 1** and **2**) were observed by means of optical microscopes, and no blunting could be evidenced for testing temperature below  $T_g$ , as shown in **Figure 6a** and **6b** in the case of BPbCuO glasses. Nevertheless, some tip blunting occurs above  $T_g$  (**Figure 5** and **6c**). The crack is eventually completely healed at the highest temperature, where the beam deforms in a ductile manner as seen in **Figure 6d**. In such a case, the mechanical work is dissipated in the viscoplastic flow process. **Figure 5b** shows a confined viscoplastic flow region in a BPbCuO glass specimen tested at  $1.1 T_g$ . The analysis of the growth kinetics of the viscoplastic process zone would be of great interest to understand the physics of cracking and the BDT transition in inorganic glasses. The increase of the plastic zone size with increasing notch tip radius in metallic glasses was discussed in the light of a finite element simulation elsewhere [29], and this is definitely an interesting direction for future investigations on inorganic glasses. Another future investigation, as a key point to understand the crack blunting mechanisms occurring during crack propagation in high temperature, could be the nanocaracterization of crack tips in real time and in high temperature. However, such experiments are extremely hard to be performed.

#### 4.2. Environment dependence of $K_{Ic}$ at room temperature

In the ambient environment (20 °C, RH~60 %),  $K_{Ic}$  as measured with a CHS of  $0.05 \mu\text{m}\cdot\text{s}^{-1}$  is smaller than that obtained at  $5 \mu\text{m}\cdot\text{s}^{-1}$  because at low velocity water molecules in the ambience have the time to react with the oxide bonds at the crack front, mostly Si-O ones, which lowers the energy needed to propagate the crack. This phenomenon is known as stress corrosion [15,18,30]. Taking  $K_{Ic}$  values from Table 4 (0.69 and 0.47  $\text{MPa}\cdot\sqrt{\text{m}}$  for amorphous Silica measured at a CHS 5 and  $0.05 \mu\text{m}\cdot\text{s}^{-1}$  respectively) into Eq. 4, we reach values of 3.38 and  $2.15 \text{ J}\cdot\text{m}^{-2}$  for the fracture surface energy. The loss energy is about  $1.23 \text{ J}\cdot\text{m}^{-2}$ , which corresponds to a 60 % loss of the interatomic bonding energy in average along the crack path. In other word, by taking a new  $x_i$  of  $1 - 0.6 (= 0.4)$  and applying into Eq. 6 and then 4, we will obtain a value of  $\gamma$  of 2.15

$\text{J}\cdot\text{m}^{-2}$  and  $K_{\text{Ic}}$  of  $0.47 \text{ MPa}\cdot\sqrt{\text{m}}$  (the value measured with a CHS of  $0.05 \text{ }\mu\text{m}\cdot\text{s}^{-1}$ ). Using this loss assumption for SLS, Borofloat and BK7, we obtain  $K_{\text{Ic}}$  values of 0.53, 0.54 and 0.50, respectively, in good agreement with the experimental results (Table 4).

#### 4.2.1. Indentation crack pattern

The indentation cracking pattern can be studied from the indentation stage of the SEPB method as well as from the post-mortem fracture surface, since the precrack extends through the median plane of the Vickers indents. As discussed above, the precrack length is much greater than the crack created by the indentation, allowing us to avoid humidity influence in the SEPB results, even in the cases where the indentation step is performed in ambient conditions ( $20 \text{ }^{\circ}\text{C}$ , RH~60 %) with dwell time of either 15 s or 30 s. However, this difference in indentation dwell time allows us to observe the different indentation cracking pattern in one of the studied glasses, namely BK7. For sake of comparison, the cracking patterns (9.81 N load) of both Borofloat and SLS glasses are shown in **Figure 7**. Cone cracking is observed in the case of Borofloat (**Figure 7a**), quite similar to what is observed in silica glass [31]. This adds more complexity into the analysis of indentation cracking and mostly results in overestimated fracture toughness values as estimated from the radial/median indentation crack length [15]. Semi-elliptical cracks are observed in the case of SLS glass samples (**Figure 7b**). The indentation cracking pattern of the SLS glass was found independent on the dwell time. In contrast, BK7 shows normal radial/median cracks when indented with dwell time of 15 s, but a swollen pattern when indented with dwell time of 30 s. Long dwell time (as in our experiments) may facilitate the reaction of water vapor with the indent, causing some swelling, as seen in **Figure 7b**. It turns out that in the case of swelling, the corner crack length is ~5 to 10  $\mu\text{m}$  shorter.

## 5. Conclusion

The temperature and environment dependences of  $K_{\text{Ic}}$  of glasses from different chemical systems were studied by means of the SEPB method. Regarding the effect of temperature, we found that with a loading rate of  $4 \text{ MPa}\cdot\sqrt{\text{m}}\cdot\text{s}^{-1}$ , a transition from elastic-brittle to viscoplastic-ductile occurs at about  $0.9T_{\text{g}}$ . Regarding the effect of humidity, the following conclusions were drawn: (i) As long as both the precracking stage and the final fracture in bending are conducted within a one hour period, it is found sufficient to only perform the

final fracture stage (in bending) in the dry atmosphere to avoid stress corrosion; (ii) It is sufficient to perform the SEPB experiment in the ambient atmosphere once the cross-head speed (or crack velocity) is fast enough (e.g. a cross-head speed of more than  $5 \mu\text{m s}^{-1}$ ) to prevent against stress corrosion cracking effects on the toughness measurement.

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## Competing interests

The authors declare no competing financial interests.

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6

## 1 Tables

2 **Table 1:** Compositions, mechanical properties and transition temperatures. Results were obtained with a  
3 better than 0.005 g·cm<sup>3</sup>, 2 GPa, 0.01, 2 GPa and 5 K accuracy (experimental error) for  $\rho$ ,  $E$ ,  $\nu$ ,  $G$  and  $T_g$ ,  
4 respectively. <sup>1)</sup>Data of properties of SiNaMgO and N-Glass are taken from Refs [32] and [33]. <sup>2)</sup>Planilux  
5 (soda-lime silicate, SLS), Saint-Gobain Company.

Glass	compositions	$\rho$ (g.cm <sup>-3</sup> )	$E$ (GPa)	$\nu$	$G$ (GPa)	$T_g$ (K)
SiNaMgO <sup>1)</sup>	SiO <sub>2</sub> (80)Na <sub>2</sub> O(14)MgO(6)	2.396	66	0.17	28	773
SLS <sup>2)</sup>	SiO <sub>2</sub> (71)Na <sub>2</sub> O(13)MgO(6)CaO(10)	2.495	72	0.23	29	813
N-Glass <sup>1)</sup>	SiO <sub>2</sub> (56)Al <sub>2</sub> O <sub>3</sub> (14)Y <sub>2</sub> O <sub>3</sub> (24)Si <sub>3</sub> N <sub>4</sub> (6)	3.759	137	0.29	53	1207
BPbCuO	B <sub>2</sub> O <sub>3</sub> (50)PbO(49)CuO(1)	5.628	64	0.29	25	673

6



1 **Table 2:** Compositions and mechanical properties. Results were obtained with a better than 0.005 g·cm<sup>3</sup>, 2  
2 GPa, 0.01 and 2 GPa accuracy (experimental error) for  $\rho$ ,  $E$ ,  $\nu$  and  $G$ , respectively. <sup>1</sup>Planilux (soda-lime  
3 silicate, SLS), Saint-Gobain Company; <sup>2</sup>Silica (amorphous silica, a-SiO<sub>2</sub>), Corning Company; <sup>3</sup>Borofloat,  
4 Schott Company; <sup>4</sup>BK7, Schott Company.

Glass	Composition	$\rho$ (g cm <sup>-3</sup> )	$E$ (GPa)	$\nu$	$G$ (GPa)
SLS <sup>1</sup>	SiO <sub>2</sub> (71)Na <sub>2</sub> O(13)MgO(6)CaO(10)	2.495	72	0.23	46
a-SiO <sub>2</sub> <sup>2</sup>	SiO <sub>2</sub> (100)	2.200	70	0.15	30
Borofloat <sup>3</sup>	SiO <sub>2</sub> (81)Na <sub>2</sub> O(4)B <sub>2</sub> O <sub>3</sub> (13)Al <sub>2</sub> O <sub>3</sub> (2)	2.211	64	0.20	27
BK7 <sup>4</sup>	SiO <sub>2</sub> (70)Na <sub>2</sub> O(9)B <sub>2</sub> O <sub>3</sub> (11)BaO(2)K <sub>2</sub> O(8)	2.511	82	0.21	34

5

- 1 **Table 3:** Fracture toughness at different temperatures relative to  $T_g$  for two loading rates.  $K_{Ic}$  is in  $\text{MPa}\cdot\sqrt{\text{m}}$
- 2 and the accuracy is better than  $0.06 \text{ MPa}\cdot\sqrt{\text{m}}$ .

$T/T_g$	0.35	0.8	0.93	1	1.03	1.05	1.07	1.11
$dK_I/dt = 10 \text{ MPa}\cdot\sqrt{\text{m}}\cdot\text{s}^{-1}$								
$K_{Ic}(\text{SLS})$	0.73	/	0.66	0.64	0.63	0.63	/	Not broken
$K_{Ic}(\text{SiNaMgO})$	0.70	/	/	0.68	/	/	0.62	0.73
$dK_I/dt = 4 \text{ MPa}\cdot\sqrt{\text{m}}\cdot\text{s}^{-1}$								
$K_{Ic}(\text{SLS})$	0.73	/	0.67	0.79	/	/	/	Not broken
$K_{Ic}(\text{SiNaMgO})$	0.70	/	0.61	0.90	/	/	/	Not broken
$K_{Ic}(\text{N-Glass})$	1.04	0.86	1.05	1.08	/	/	Not broken	/
$K_{Ic}(\text{BPbCuO})$	0.43	0.36	0.37	0.44	/	/	Not broken	Not broken

3

1 **Table 4:** Fracture toughness of a window glass (SLS) in argon and ambient atmospheres for two different  
2 displacement rates (cross-head speed). The error interval is the standard deviation calculated from at three  
3 experiments. <sup>(1)</sup> Only one experimental result was found valid (due to premature failure).

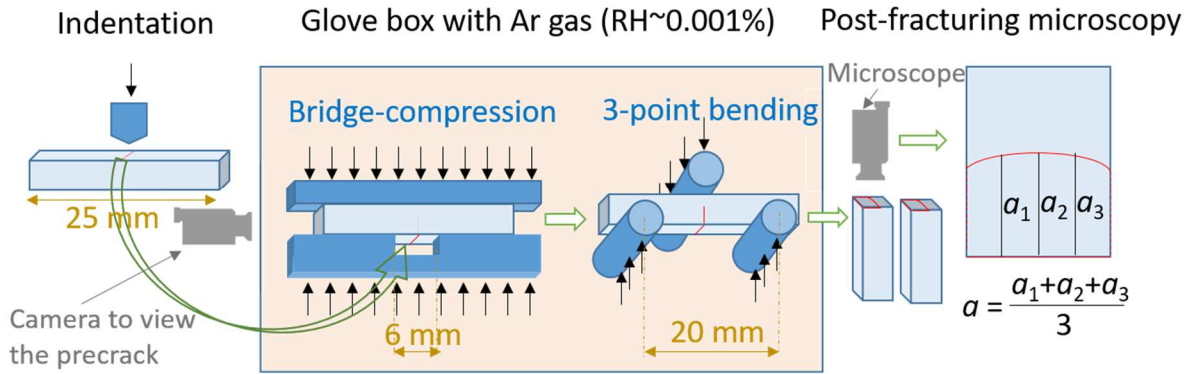
	Ambient atmosphere (20 °C, RH~60%)		Argon atmosphere (20 °C, RH~0%)	
CHS	5 $\mu\text{m}\cdot\text{s}^{-1}$	0.05 $\mu\text{m}\cdot\text{s}^{-1}$	5 $\mu\text{m}\cdot\text{s}^{-1}$	0.05 $\mu\text{m}\cdot\text{s}^{-1}$
SLS	0.70 $\pm$ 0.01	0.55 $\pm$ 0.02	0.70 $\pm$ 0.02	0.71 $\pm$ 0.03
a-SiO <sub>2</sub>	0.69 $\pm$ 0.02	0.47 $\pm$ 0.05	0.69 $\pm$ 0.04	0.71 $\pm$ 0.04
Borofloat	0.65 $\pm$ 0.03	0.52 $\pm$ 0.03	0.67 $\pm$ 0.02	0.66 $\pm$ 0.05
BK7	0.82 $\pm$ 0.02	0.47 <sup>(1)</sup>	0.81 $\pm$ 0.03	0.83 $\pm$ 0.04

4

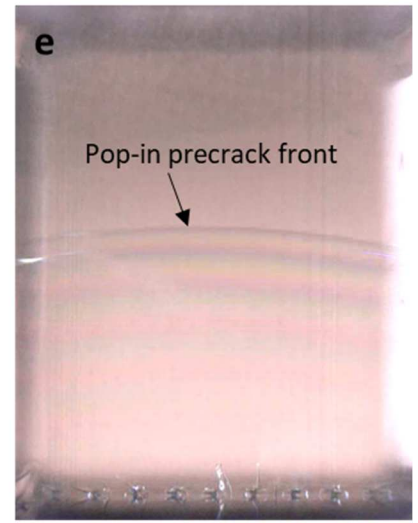
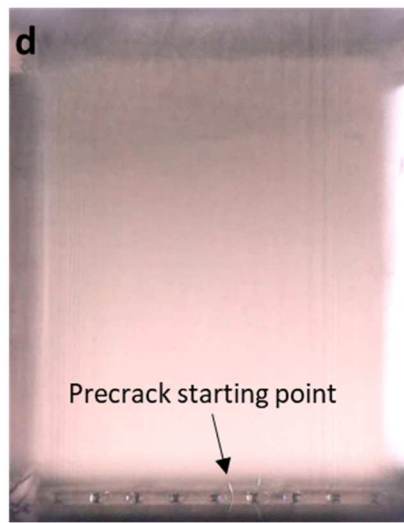
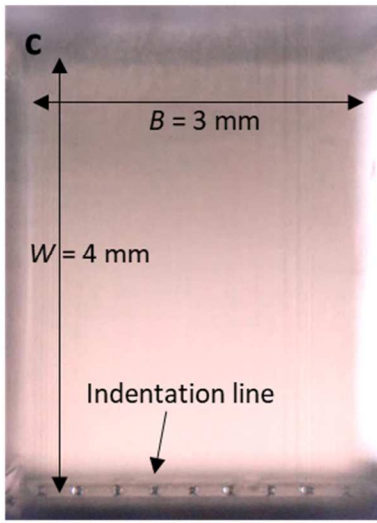
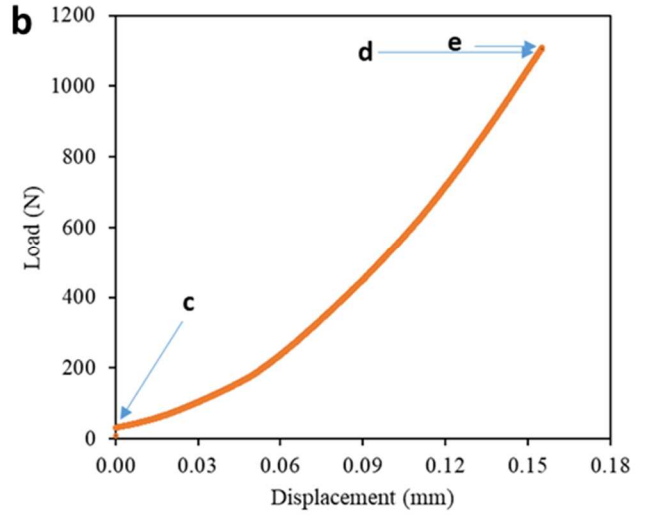
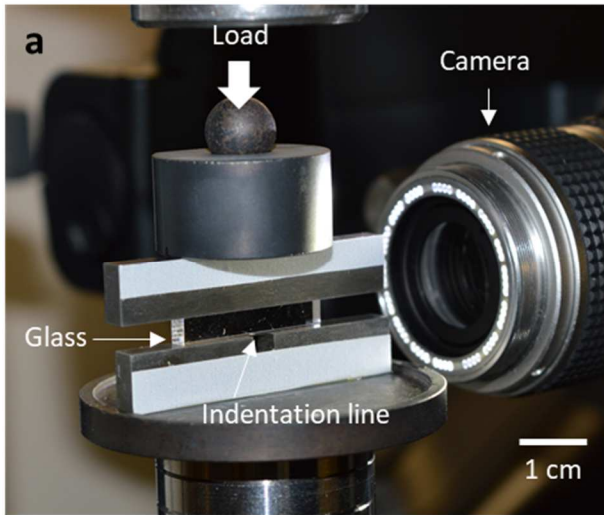
1 **Table 5:** Intrinsic fracture toughness,  $K_{Ic}$ , of the four studied commercial glasses: experimental values  
2 (SEPB) and theoretical prediction.  $\pm$ : standard deviation calculated from at least three experiments.

Materials	$K_{Ic}$ (MPa $\sqrt{m}$ ) by means of SEPB method and Theoretical values			
	Dry Argon atmosphere	Ambient atmosphere (unstable experiment)	Dry N <sub>2</sub> atmosphere [14] (4-point bending)	Theoretical Prediction [12]
SLS	0.71 $\pm$ 0.03	0.70 $\pm$ 0.01	0.76 $\pm$ 0.03	0.73 $\pm$ 0.01
a-SiO <sub>2</sub>	0.69 $\pm$ 0.04	0.69 $\pm$ 0.02	0.78 $\pm$ 0.06	0.72 $\pm$ 0.01
Borofloat	0.67 $\pm$ 0.02	0.65 $\pm$ 0.03	0.71 $\pm$ 0.03	0.72 $\pm$ 0.02
BK7	0.81 $\pm$ 0.03	0.82 $\pm$ 0.02	0.92 $\pm$ 0.05	0.85 $\pm$ 0.01

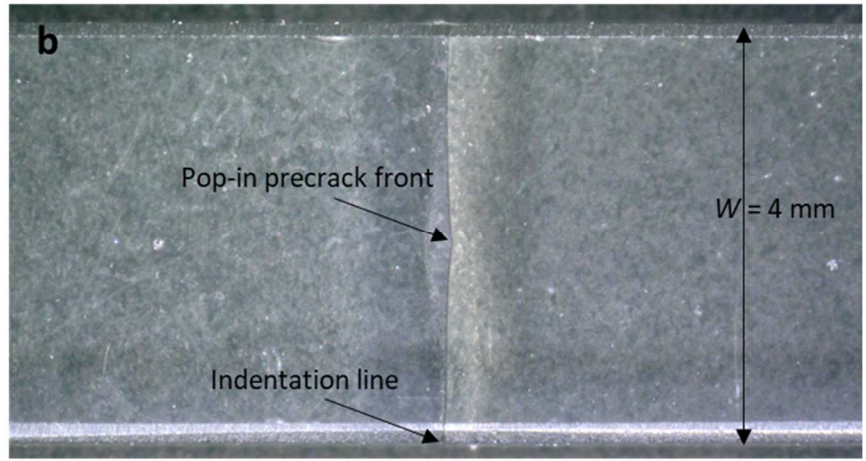
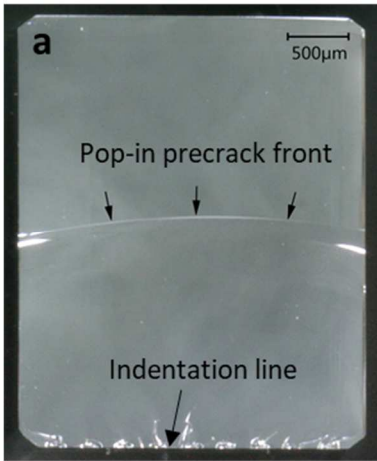
# Figures



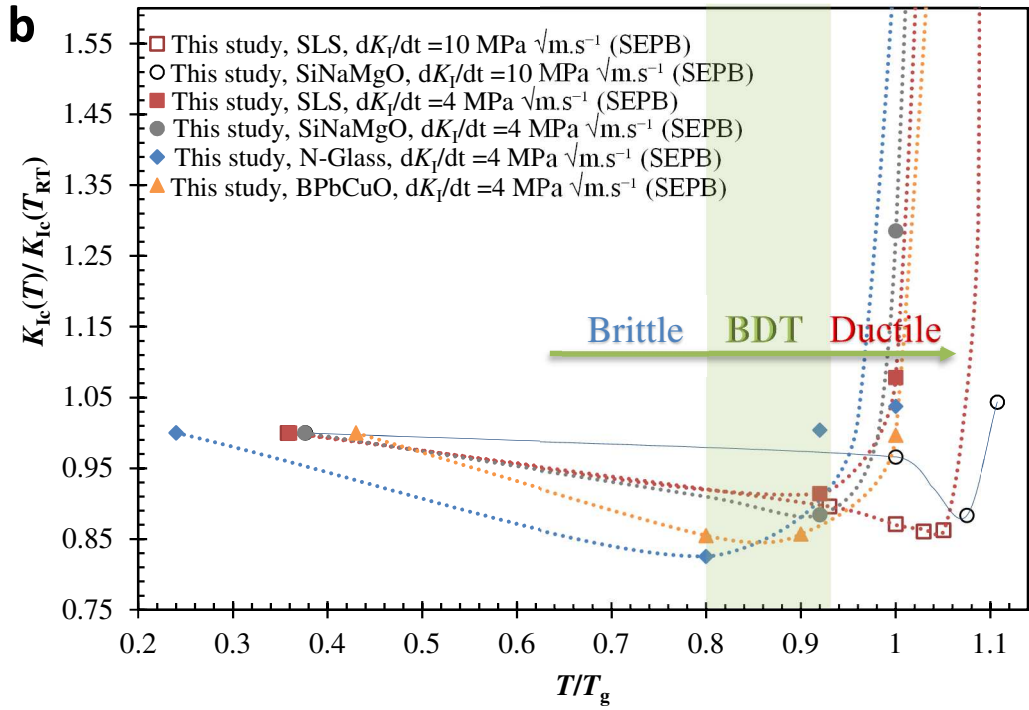
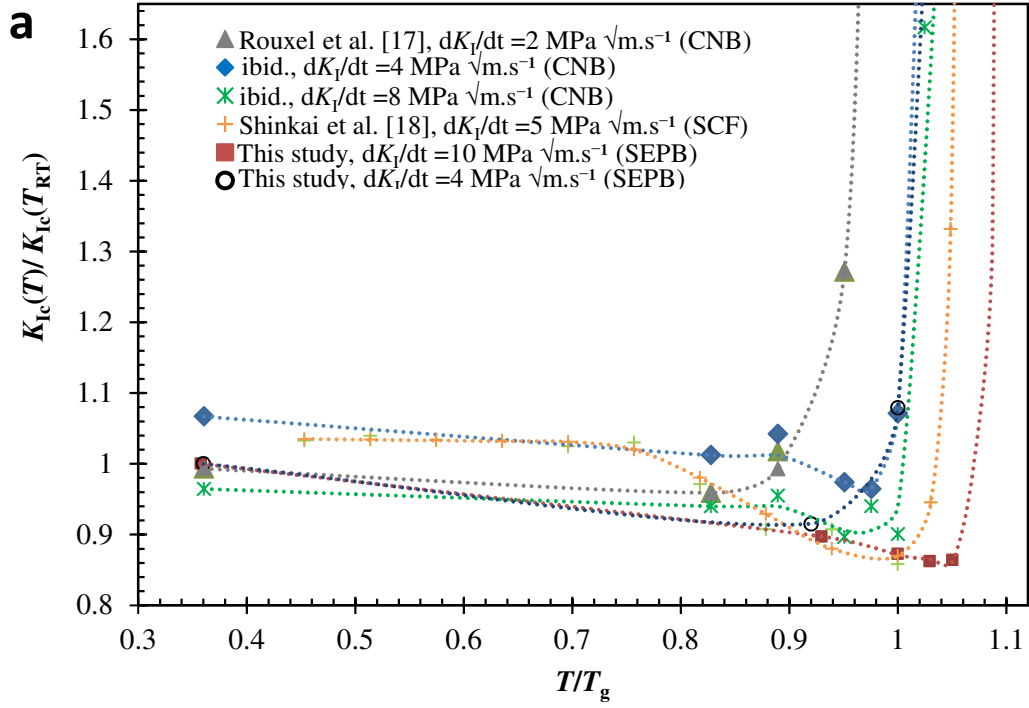
**Figure 1:** Schematic drawing of the SEPB experiment from indentation to precrack ( $a$ ) measurement. Both precracking (by bridge compression) and fracturing (by 3-point bending) were performed in the glove both to assure the non-humidity environment. It is noteworthy that although the indentation was performed outside the glove box, there would not be any humidity left after the precracking stage since  $a$  is ~100 times longer than the indentation depth. The black narrow, dark blue block and light blue block represents the applied load (or stress), the equipment and glass specimen, respectively. The red lines represents the indentation line and precrack front.



**Figure 2:** Precracking observation on a soda-lime-silica glass SEPB specimen. **a.** Bridge-compression fixture with an optical camera. **b.** The load-displacement curve from the bridge-compression test. The point c, d and e are according to **c.** The initial state of the SEPB specimen focused on the middle part, where the indentation line is located, with visible indentation line at the bottom. **d.** the precrack starting point from joint crack of two indents around the middle of the indentation line as shown by the black arrow. **e.** the precrack front; the precrack is visible in rainbow colors. The light orange color in the 2c, 2d and 2e is from the lamp installed in the room (the brightness at the right-hand side of 2c, 2d and 2e). The precracking observation on a non-transparent glass is made possible by positioning the camera on the sample side (perpendicular to the current position) as shown elsewhere [34].

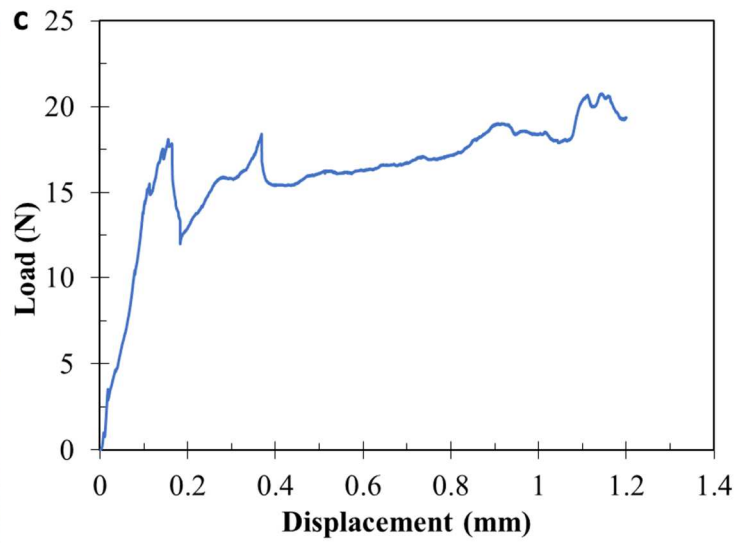
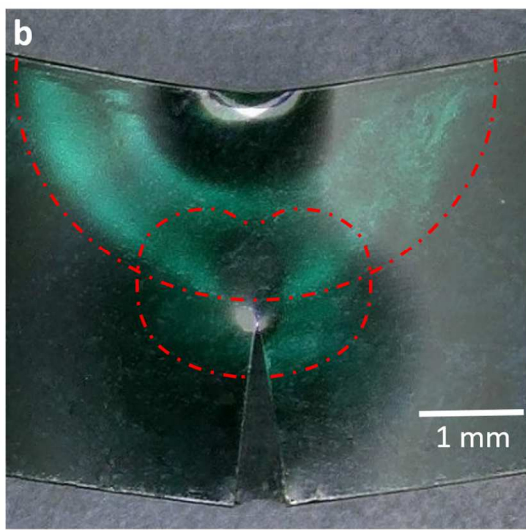


**Figure 3:** Post-fractography on the same glass specimen used in **Figure 2**. **a.** Typical image used for measuring the precrack length at 25%, 50% and 75% of the broadness,  $B$  (**Figure 2**). In this case, the precrack evenness (the difference between the average length and any measured length) is around 0.2%, i.e. valid precrack [15]. **b.** Typical side view of two broken pieces positioned close to each other and used to measure the angle of the fracture plan (the plan after precrack front). In this case, the angle is around  $1^\circ$ , i.e. valid test.

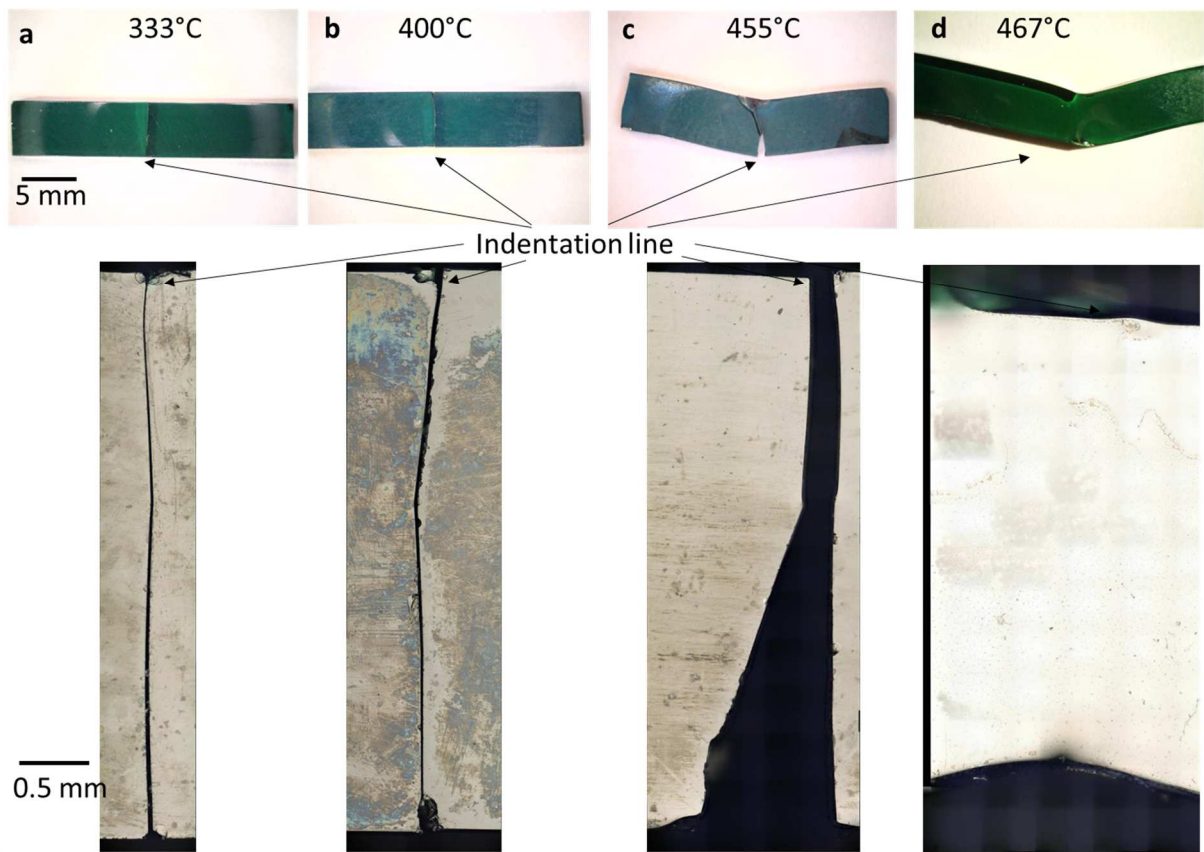


**Figure 4:** Temperature dependence of the apparent fracture toughness of **a.** soda-lime silicate (SLS) with different loading rates and **b.** all studied glasses with a loading rate of  $4 \text{ MPa} \cdot \sqrt{\text{m}} \cdot \text{s}^{-1}$ , and additional SLS and SiNaMgO with a loading rate of  $10 \text{ MPa} \cdot \sqrt{\text{m}} \cdot \text{s}^{-1}$ . Rouxel et al. [11] used chevron-notched beam (CNB) method and Shinkai et al. [10] used surface crack in flexure (SCF) method. The horizontal green narrow shows the brittle to ductile states of the four studied glasses when using the rate of  $4 \text{ MPa} \cdot \sqrt{\text{m}} \cdot \text{s}^{-1}$ .

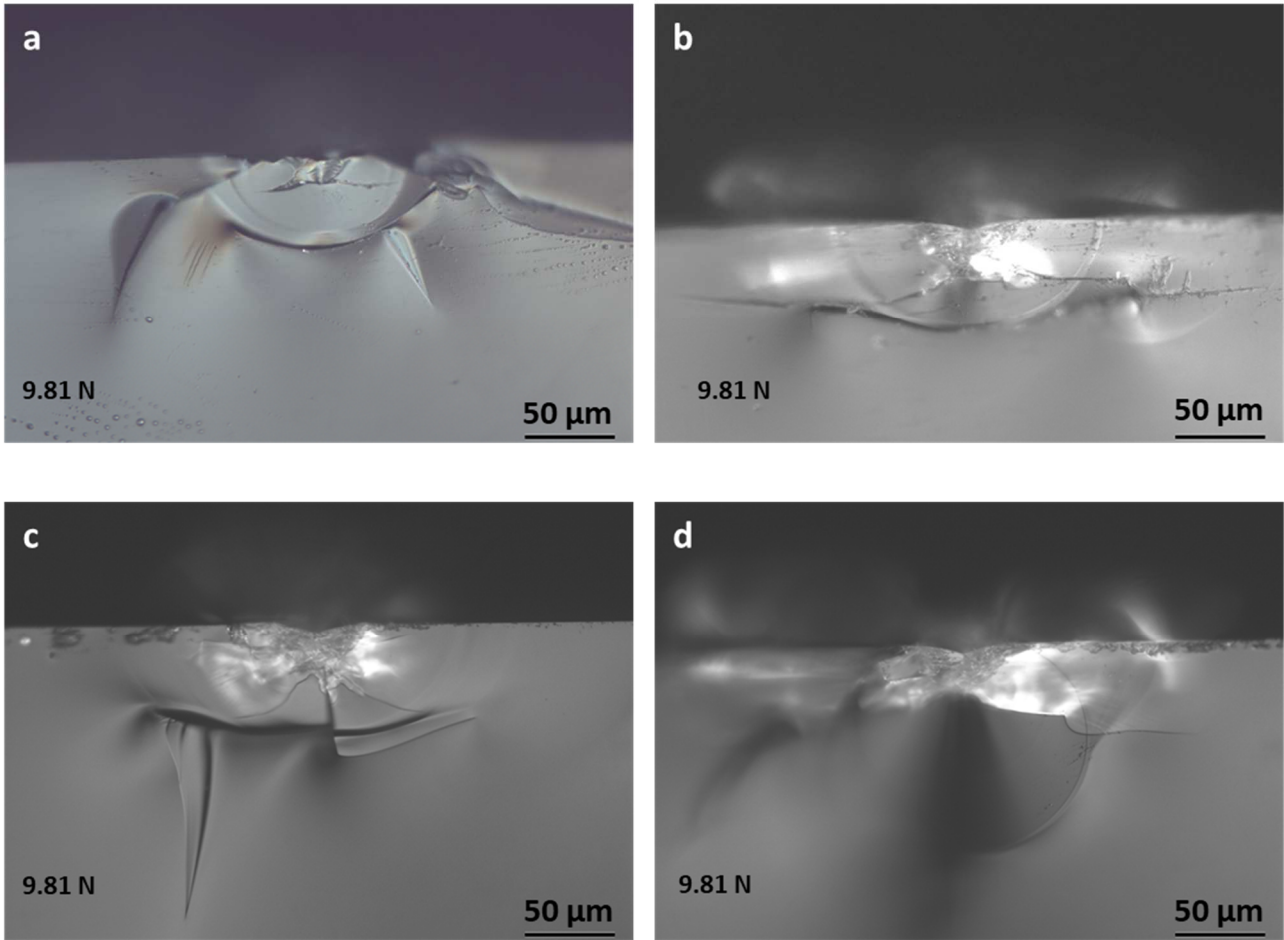




**Figure 5:** A BPbCuO glass specimen tested in bending at  $\sim 1.1T_g$  with a loading rate of  $4 \text{ MPa}\cdot\sqrt{\text{m}}\cdot\text{s}^{-1}$ , exhibiting viscoplastic deformation without fracture: **a.** after cooling down to room temperature; **b.** zoom around the crack tip (the red dashed line contour shows the shape of the confined viscoplastic zone around the crack front and just beneath the upper roller); **c.** corresponding load-displacement curve.



**Figure 6:** Pre-crack tip analysis on BPbCuO glasses tested in temperatures from 333°C to 467°C. Upper: 2 broken pieces of SEPb specimen with the indentation line at the bottom (black arrow). Lower: Zoom on the 3 fracture plane. The degradation on the surfaces were from the heating, cooling and storage processes.



**Figure 7:** Indentation pattern (cross section) observed from the indentation line in the post-fractured precrack image as shown in **Figure 3a**. **a.** Borofloat glass, **b.** SLS, **c.** and **d.** BK7. The different between **c** and **d** is the indentation dwell time. **c** use the dwell time of 15s and **d** of 30s.