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Nucleation kinetics of a $Li_2O{\cdot}2SiO_2$ glass based on a liquid model

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A liquid model was proposed wherein crystal embryos should exist in equilibrated melts at temperatures even above the melting point or liquidus temperature and the number density of embryos should decrease as the melting temperature increases. Crystallization behavior of a $Li_2O{\cdot}2SiO_2$ glass was studied. Secondary heat-treatment (600 °C for 20–60 min) of the $Li_2O{\cdot}2SiO_2$ glass induced different number of crystals depending upon the melting temperature in the range 1040°–1300 °C and duration of heat-treatment *t*. The number density of crystals *N* decreased with increasing temperature of melting. The number density of pre-existing embryos was estimated from ($N - t$) diagram and was found consistent with what the proposed model claims. © *1999 Kluwer Academic Publishers*

1. Introduction

Molten slag can be solidified as a glass when quenched at sufficiently high rate. Vitrification point T_v, defined as the lowest temperature from which slag glass can be obtained under a given quenching rate, decreased with increasing quenching rate [1]. Under insufficient quenching rate partial crystallization takes place in the glass. The amount of precipitated crystals in the slag glass was found to decrease with increasing melting temperature [1]. To explain these results Ota, Fukunaga and Yoshida [1] proposed a liquid model. The liquid model is based on the assumption that any liquid should contain crystal embryos at temperatures even above the melting point (liquidus temperature), and the number density of the embryos should decrease as the temperature rises. The liquid model is compared with the conventional phase diagram in Fig. 1. Fig. 1a represents the phase diagram of a system having a clear cut melting point T_m and no solid phase is existing at temperatures above T_m. Fig. 1b shows the schematically depicted liquid structure of the system after the liquid model at temperatures above and below the melting point. At the melting point solid phase (micro-crystals or crystal embryos) should be coexistent with the liquid phase and solid/liquid phase ratio must be 50/50. With increasing temperature, number density of crystal embryos and their volume fraction should decrease. In the present study some experimental work was carried out in order to prove the liquid model. $Li_2O{\cdot}2SiO_2$ compound was chosen because this compound melts congruently at melting point $T_m = 1034\,^{\circ}C$ [2] and $Li_2O{\cdot}2SiO_2$ composition lies off the phase separation zone (Li_2O less than 30.4 mol % at 600 °C) in the Li_2O-SiO_2 system [3]. $Li_2O{\cdot}2SiO_2$ glass has been known to exhibit a homogeneous nucleation [4]. The primary aim of the present study is to observe the number density of crystal embryos in the glass quenched from various temperatures and to demonstrate the temperature dependence of number density of pre-existing embryos and size distribution of the embryos.

2. Experimental

The experimental process for present study is shown in Fig. 2. Molten glass of $Li_2O{\cdot}2SiO_2$ composition was prepared from mixture of reagent grade lithium carbonate and silica powder by firing in a platinum crucible at 1300 °C for 2 h. Then the melt was moved to a temperature-controlled furnace of 1040°, 1050°, 1080°, 1100°, 1200° and 1300 °C and was kept there for 3 h or 20 h to achieve the structural equilibrium. The melt was then water quenched to preserve the equilibrated liquid structure. The resulted glass was inspected by optical microscopy or SEM observation of micro-crystals which must have developed from presumably pre-existing embryos in the melt. Since embryos could not be detected in the glass by SEM observation, the glass was subjected to additional heat-treatment (600 °C, 20–60 min) to make the pre-existing embryos grow to be observable by the optical microscopy. The surface of the heat-treated glass was polished and the number of the crystals in the interior of the glass was counted in the optical microscopic view (Fig. 3) and the number density N (particles/mm^3) was calculated. The diameter along the short axis of the largest crystals ever observed among the precipitated crystals was also measured as a function of melting temperature. Number density of embryos in melt prepared from $Li_2O{\cdot}2SiO_2$ crystals was compared with that prepared from batch-melting. $Li_2O{\cdot}2SiO_2$ crystals were prepared from $Li_2O{\cdot}2SiO_2$ glass ($T_g = 450\,^{\circ}C$) by heat-treatment 600 °C for 5 h.

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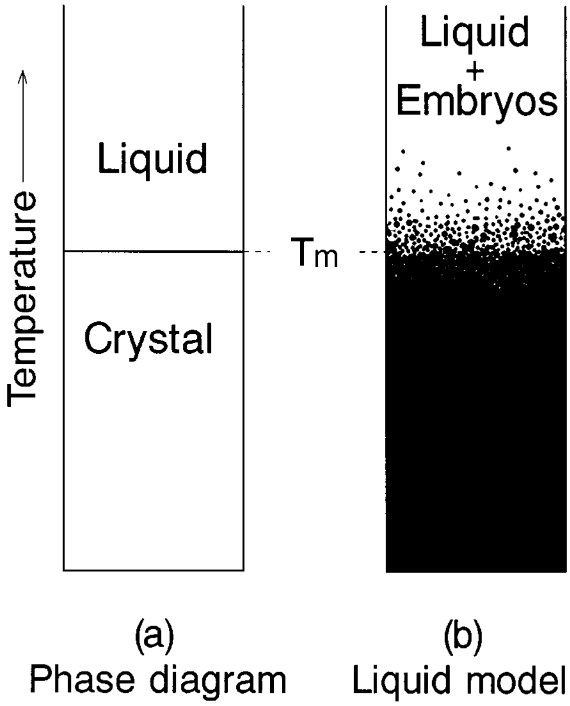
3. Results and discussion

3.1. Number density of micro-crystals and embryos

The number density of precipitated micro-crystals (particles/mm^3) in the heat-treated glass (600 °C, 30–60 min) from batch melting is shown in Fig. 4 as a function of melting temperature. Fig. 4a indicates N of batch-melting (1300 °C, 3 h) followed by heating at 600 °C for 30, 45 or 60 min. It is seen that after 30 min heating N stands at maximum 10 particles/mm^3 at melting temperature 1040 °C, which is close to $T_m = 1034$ °C, and N decreases to 1–2 particles/mm^3 at 1200°–1300 °C. However, it can be noticed that on prolonged heating for 45 min or 60 min, N increased with heating time but nucleation rate seems greater in higher temperature range (1100°–1300 °C) than in lower temperature range (1040°–1100 °C). Fig. 4b indicates the case of batch-melting (1300 °C, 20 h), followed by heating at 600 °C for 20, 30 or 60 min. From comparison between case (a) and (b) it is apparent that for the same melting temperature and after 600 °C–30 min heat-treatment, N turned out to be greater in case (b) than (a).



(a) Phase diagram

(b) Liquid model

Figure 1 Phase diagram of a compound (a) and liquid model (b).

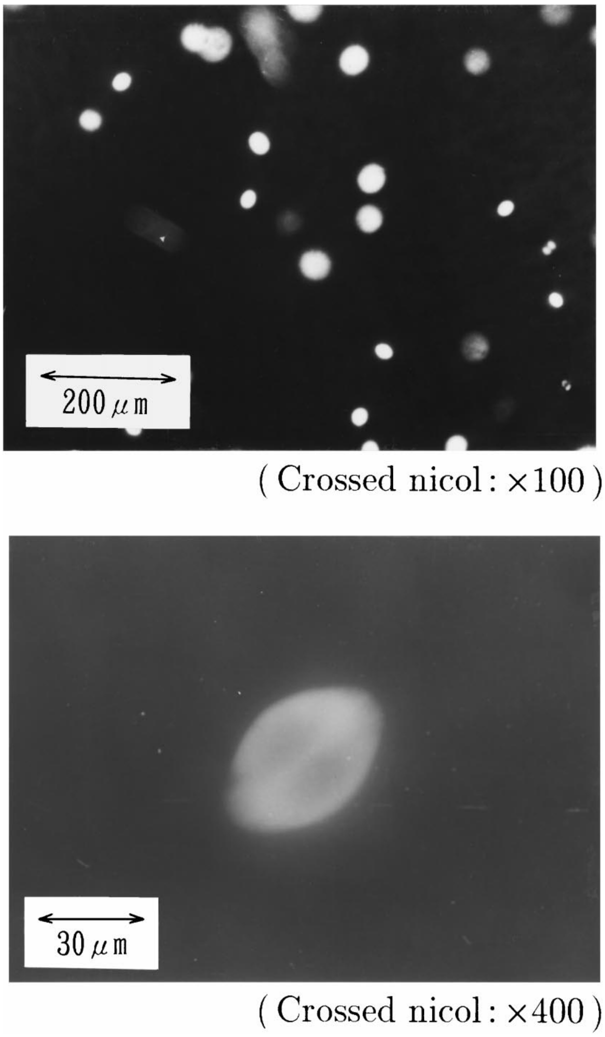


Figure 3 Optical micrographs of $Li_2O\cdot 2SiO_2$ crystal particles precipitated in the $Li_2O\cdot 2SiO_2$ glass prepared by melting at 1050 °C for 3 h and heat-treated at 600 °C for 30 min.

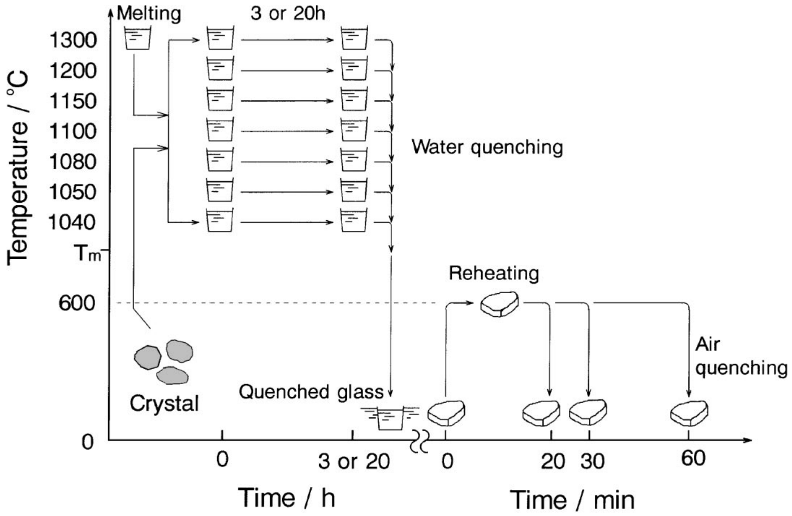


Figure 2 Experimental process for melting and heat-treatment of glass.

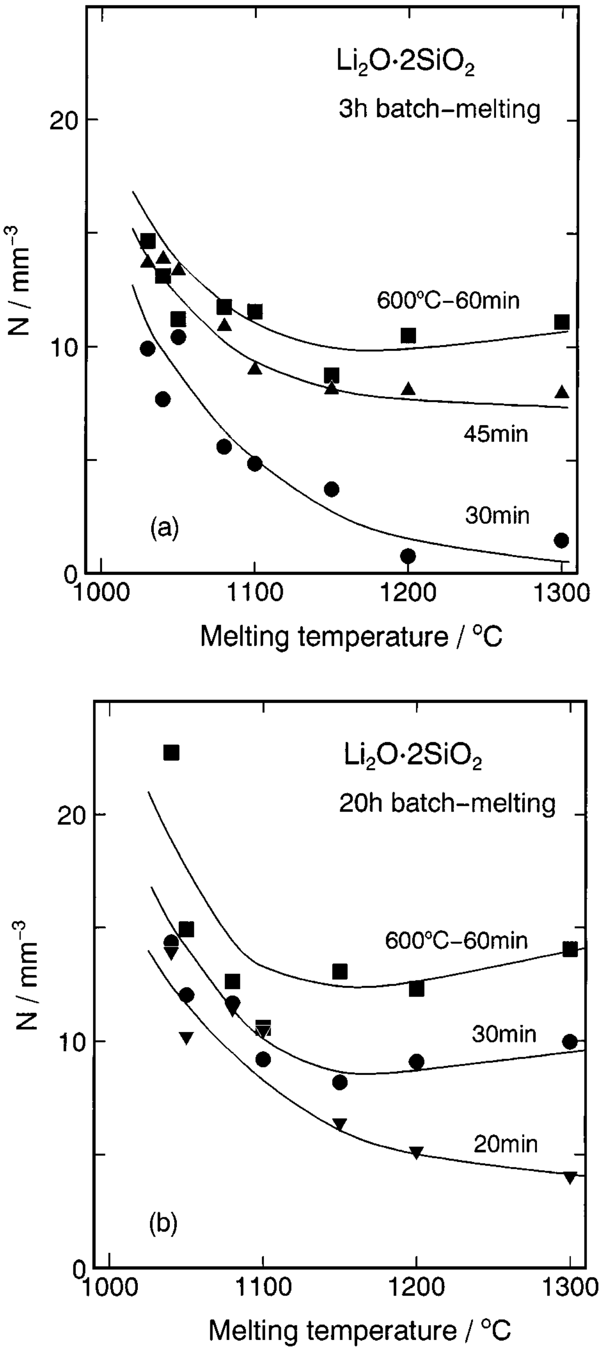


Figure 4 Number density N of $Li_2O{\cdot}2SiO_2$ crystal particles in batch-melted $Li_2O{\cdot}2SiO_2$ glass as a function of melting temperature. Melted for 3 h and heat-treated at 600 °C for 30 min (●), 45 min (▲) or 60 min (■) (a). Melted for 20 h and heat-treated at 600 °C for 20 min (▼), 30 min (●) or 60 min (■).

The number density of crystals in the heat-treated glass (600 °C, 30–60 min) from crystal melting (1300 °C, 20 h) is shown in Fig. 5 as a function of melting temperature. It can be noted that the temperature dependency of number density and change of number density with heating time look very much similar among the batch-melting (Fig. 4) and crystal-melting(Fig. 5).

Fig. 6a shows the change of N with heating time t for different melting temperatures. Fig. 6b indicates the nucleation rate dN/dt calculated from the slope of the $(N - t)$ diagram as a function of melting temperature.

The present liquid model could be validated by evaluating the values of number density of embryos N_0 corresponding to $t = 0$ values of the $(N - t)$ diagram

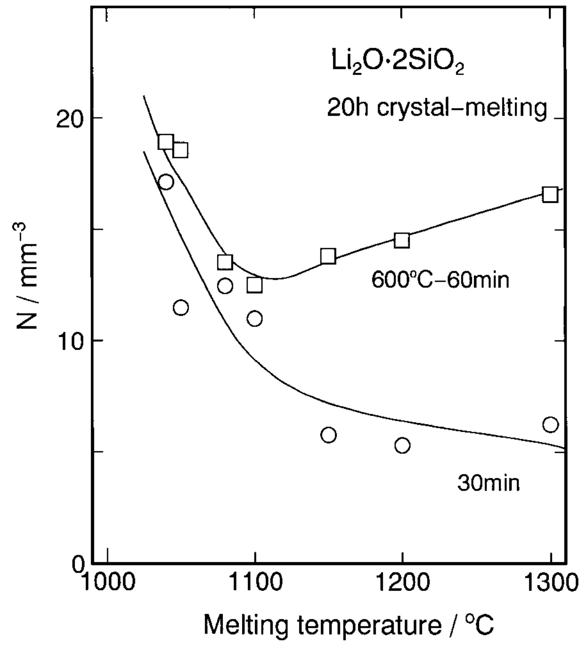


Figure 5 Number density N of $Li_2O{\cdot}2SiO_2$ crystal particles in crystal-melted $Li_2O{\cdot}2SiO_2$ glass as a function of melting temperature. Melted for 20 h and heat-treated at 600 °C for 30 min (○) and 60 min (□).

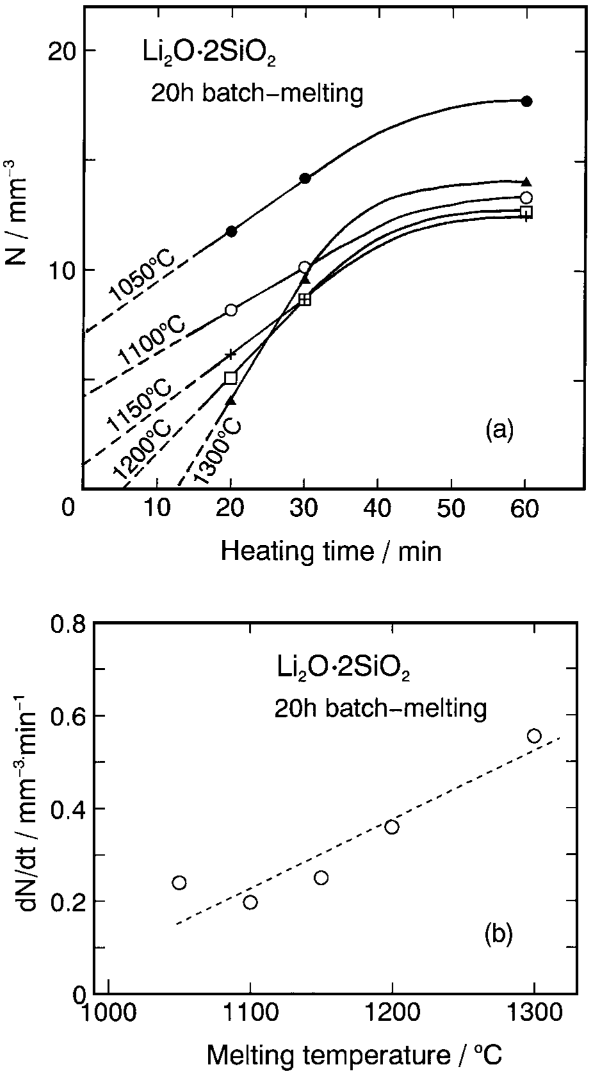


Figure 6 Number density N of $Li_2O{\cdot}2SiO_2$ crystal particles as a function of heating time at 600 °C (a). Figures indicate the melting temperatures. Nucleation rate dN/dt calculated from the slope of the number density N–heating time diagram.

(Fig. 6a). Obviously N_0 values are non-zero and are seen to decrease as melting temperature rises. Fig. 6b demonstrates that nucleation rate is higher in higher temperature range.

3.2. Size distribution of precipitated crystals

Radius R along the short-axis of the largest $Li_2O{\cdot}2SiO_2$ crystals was determined after heated at 600 °C for 20, 30 or 60 min as a function of melting temperature and is presented in Fig. 7. Fig. 7a shows that R decreases with increasing melting temperature (heating time 30 or 45 min) and so does Fig. 7b for heating time 20 or 30 min. The growth rate of precipitated particles seems to be enhanced in higher temperature range (1100°–1300 °C) as can be estimated between heating time 45 min and 60 m (Fig. 7a). It is seen that for the same melting temperature and 600 °C–30 min heat-treatment R is some 50% larger in 20 h-melting (b) than 3 h-melting (a).

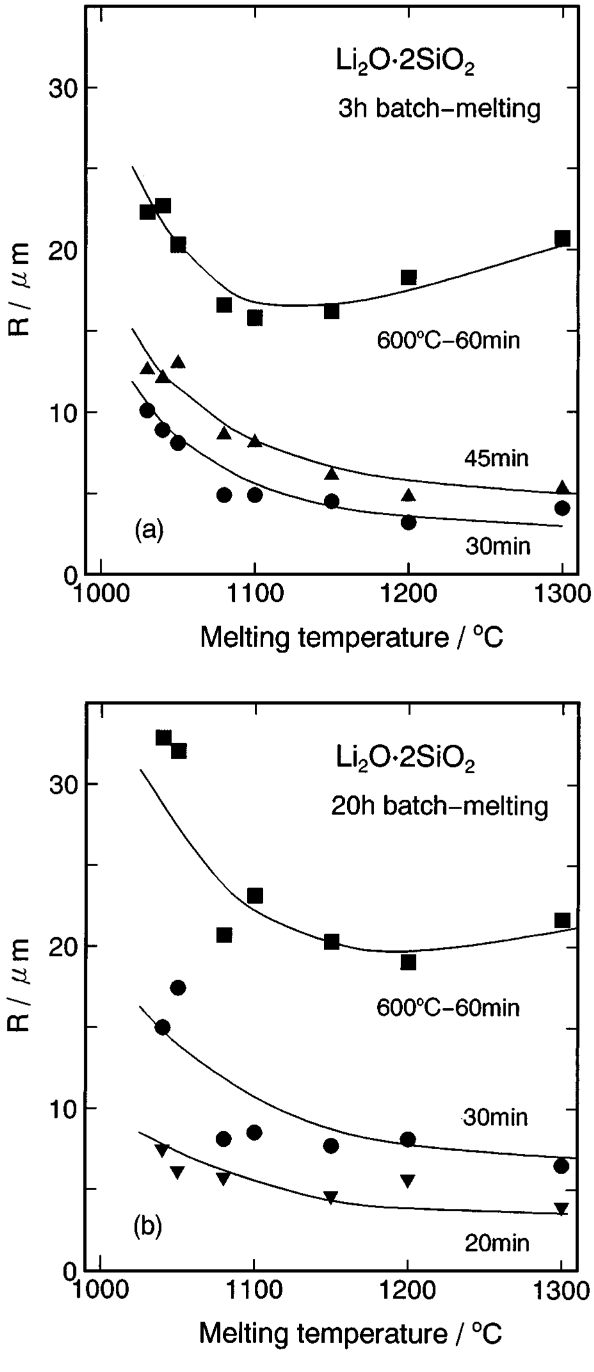


Figure 7 Particle size R of precipitated $Li_2O{\cdot}2SiO_2$ crystals as a function of melting temperature in batch-melted $Li_2O{\cdot}2SiO_2$ glass. Melted for 3 h and heat-treated at 600 °C for 30 min (●), 45 min (▲) and 60 min (■) (a). Melted for 20 h and heat-treated at 600 °C for 20 min (▼), 30 min (●) and 60 min (■) (b).

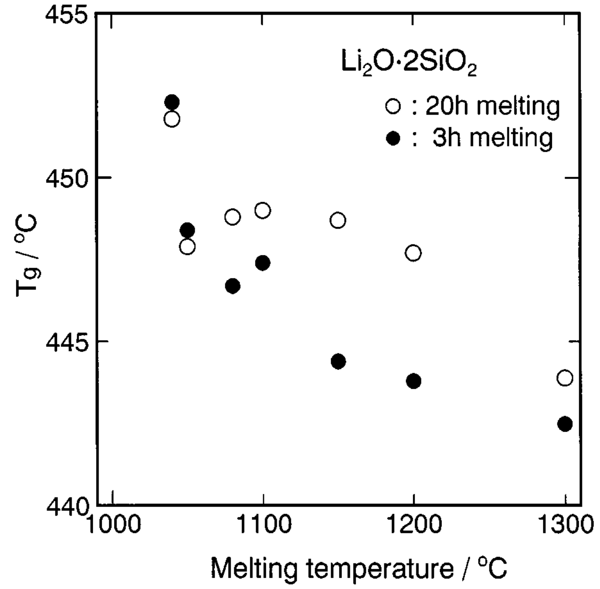


Figure 8 Glass transition temperature T_g of $Li_2O{\cdot}2SiO_2$ glass determined by the DTA method as a function of melting temperature. Melted for 3 h (●) and 20 h (○).

The experimental results shown above can be understandable if we regard the radius distribution of precipitated crystals is based on the radius distribution of pre-existing embryos in the melt. These results are in accordance with what the liquid model suggests.

3.3. Change of liquid structure with temperature

As demonstrated previously in Figs 4, 5 and 7, nucleation rate and growth rate are apparently higher in the higher melting temperature range. It is probable that glass assumes a lower fictive temperature as melting temperature increases [5]. To confirm this idea glass transition temperature T_g was determined by the DTA method. T_g variation is shown in Fig. 8 as a function of melting temperature. T_g decreases from 452 °C at 1040 °C to 442 °C at 1300 °C. Thus it was clearly shown that glass of higher melting-temperature assumes a higher fictive temperature and consequently a lower T_g and a lower viscosity.

4. Conclusion

To confirm a liquid model [1] “Number of crystal embryos may exist in liquids at temperatures even above the melting point (liquidus temperature) and the number density of the embryos should decrease as the temperature increases”, melt of $Li_2O{\cdot}2SiO_2$ composition was quenched from various temperatures and the resulted glasses were examined of their crystallization behavior on additional heat-treatment. The number density of the crystal embryos was estimated from the relationship between the number density of crystallized particles and heat-treating time. The crystal size of precipitated particles was measured as a function of melting temperature. The result is that number density of embryos and crystal size decrease as melting temperature increases. This result is in accordance with the liquid model. Increasing nucleation rate in higher temperature range can be regarded due to a decreased T_g or a decreased viscosity of the glass with melting temperature.

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