# ON SPINODAL DECOMPOSITION OF E-BEAM IRRADIATED BOROSILICATE GLASSES

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## ABSTRACT

Evidence is presented on instability of the electron beam irradiated glass 51.5$SiO_2$. 25.6 $B_2O_3$ 4.3 $Li_2O$ 8.6 $Na_2O$ 4$CeO_2$ 4$ZrO_2$ 2$Cr_2O_3$ (mol%). Irradiation of this glass in a TEM JEM 3010 by a 300 keV e-beam resulted in a phase decomposition characterised by a continuous variation of concentrations with diffuse interfaces formed and visible regularity of second phase distribution in size and spacing. In addition, the morphology for the separated second phase tends to be non-spherical with high connectivity, rather than isolated particles. All these characteristics are evidence for spinodal type phase decomposition generated under the electron beam. The spinodal decomposition of glass under the electron beam is assumed to be caused by radiation-induced effective bond breaking processes and increased cation mobility and glass fluidity under conditions of intensive electron irradiation.

## INTRODUCTION

Vitrification is the most effective immobilisation technology currently used to increase the safety of storage and disposal of radioactive wastes. Nuclear waste glasses are durable materials capable to withstand in a disposal environment for geological-scale times at a minimal impact to it. In addition vitrification significantly reduces the volume of liquid radioactive wastes. An important question is the limit of waste volume reduction for immobilising hosts. Further reduction of waste volumes increases the efficiency of waste repository use. However overloading of wasteforms with radionuclides implies compositional changes as well as potential radiation-induced effects which may impair retention properties. It was shown for example that inhomogeneities in distribution of radionuclides in insulating wasteforms may cause their mechanical decomposition [1] an effect which was experimentally observed for Pu-immobilising zircon [2]. Radiation-induced devitrification with formation of crystalline phases has not been observed in any borosilicate glasses used for immobilisation of high-level waste [3]. However spinodal-type decomposition of irradiated glasses was observed in conditions of electron-beam irradiation such as decomposition of a nuclear waste borosilicate glass into silica-reach and heavy-metal-reach phases [4-6] and electron-induced phase decomposition of alkaline earth boroalumionosilicate glass into two phases with different contents of B and alkaline earths [7].

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Although the dose rates required for such type effects are currently unrealistically high for vitrified radioactive wastes they show that radiation-induced effects imply limitations on radionuclide loadings.
Phase separation can result in substantial changes in physical and chemical properties of glasses. Similarly to technical glasses nuclear waste glasses are complex e.g. made of oxides which either exhibit complete miscibility or only metastable immiscibility. Above the liquidus temperature, $T_L$, liquid immiscibility is stable such as on formation of yellow phase on nuclear waste vitrification [8]. Both crystallisation and immiscible liquid phase separation are avoided in glasses using rapid cooling. Immiscibility may however occur metastable below $T_L$ such as in the $Na_2O$-$B_2O_3$-$SiO_2$ systems where immiscible glasses are restricted near the $B_2O_3$-$SiO_2$ edge e.g. in compositions used to produce Vycor and Pyrex glasses [9]. Most of nuclear waste immobilising glasses are based on $Na_2O$-$B_2O_3$-$SiO_2$ system which exhibits a broad range of immiscibility extending up to 16 mol% of soda and for nearly all silica compositions in excess of 20 mol%. Phase separation in this system results in one silica-rich and another silica-poor phase, the latter being rather chemically non-durable. Radiation-induced effects may accelerate the rate of metastable immiscibility however phase separation caused by radiation effects in borosilicate is poorly investigated.

In the present work, we attempt to examine the level of stability of a typical mixed alkali borosilicate simulated nuclear waste glass with a small number of representative waste simulants with a total of 10% molar loading. The glass 51.5$SiO_2$. 25.6 $B_2O_3$ 4.3 $Li_2O$ 8.6 $Na_2O$ 4$CeO_2$ 4$ZrO_2$ 2$Cr_2O_3$ (mol%) is subjected to a well defined cooling and annealing sequence and TEM specimens are finally exposed to 300 keV e-beam irradiation. The resulting phase separations will be described, consisting of both an irradiation independent precipitation of round nanoparticles, and – after irradiation - of a secondary phase decomposition showing characteristics of spinodal type phase decomposition, kinetically enabled by the electron beam.

## SPINODAL DECOMPOSITION

Glass is a metastable form of matter, decomposition of which to a more stable crystalline structure is kinetically impeded for extremely long times exceeding for oxide glasses the lifetime of universe [10]. Most often glasses are produced from melts which also can be either stable or metastable. The stability of a phase is determined by the increase of chemical potential of each component with its increasing density on infinitesimal composition or density changes [11, 12]. The curve that delimits the stable single phase composition from the two phase region (coexistence curve) is termed binodal with the highest binodal temperature termed consolute temperature, $T_c$. Inside the binodal the single phase can be either metastable or unstable depending on the curvature of the free energy curve. The temperature limit to the metastability has been called the spinodal. In a binary system the spinodal is determined by the second derivative of Gibbs free energy, G, with mole fraction of second component, c, $\partial^2 G / \partial c^2 = 0$. The single phase is either unstable when $(\partial^2 G / \partial c^2)_{T,P} < 0$ or metastable when $(\partial^2 G / \partial c^2)_{T,P} > 0$. Under the binodal the single phase is metastable whereas under the spinodal a single phase is in principle unstable and can decompose into two phases which differ in composition (Fig. 1).

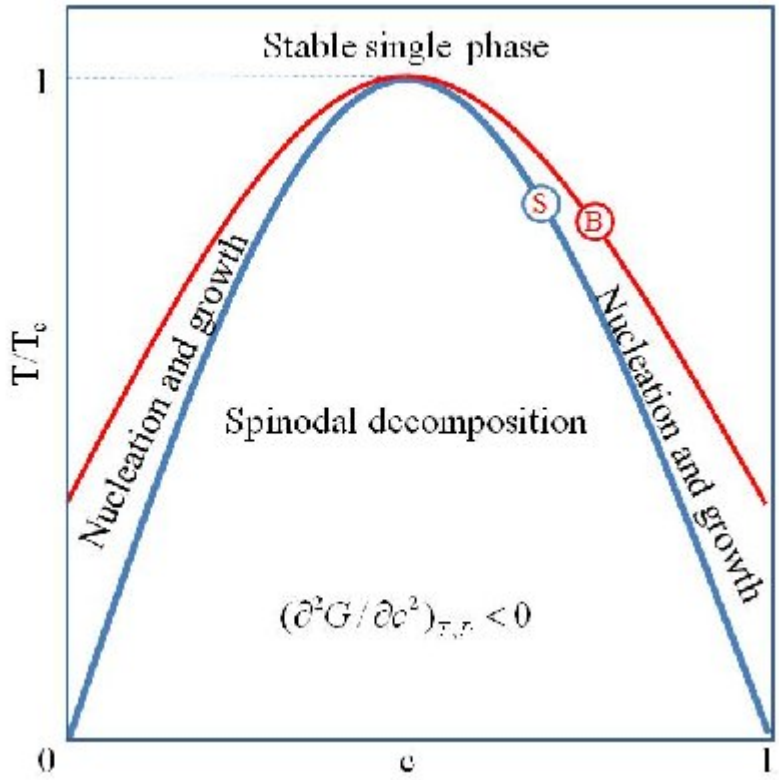


Fig. 1: Schematic phase diagram of a binary system. B – binodal or coexistence curve, above which the single phase is stable; S – spinodal, below which the single phase is unstable.

Phase separation in glasses can hence occur either by nucleation and growth (NG) or by spinodal decomposition (SD). The main factors that differentiate between NG and SD are [12]:
(i) invariance of second phase composition to time at constant temperature on NG versus continuous variation of both extremes in composition with time until equilibrium is achieved on SD;
(ii) interface between phases at same degree of sharpness on NG versus very diffuse interface which eventually sharpens on SD;
(iii) tendency for random distribution of particle sizes and positions in matrix on NG versus regularity of second phase distribution in size and position characterised by a geometric spacing on SD; and
(iv) tendency for separation of second phase spherical particles with low connectivity on NG versus tendency for separation of second phase as non-spherical particles, lamellae, or other high connectivity morphology on SD.

The kinetics of phase decomposition, however, can be impeded by low fluidity and metastability might only be revealed at relatively high temperatures such as typically present in compositions used to produce Vycor and Pyrex glasses. Radiation can in principle reveal the instability of a single phase composition at room temperature by enhancing the cation diffusion coefficients and by reducing the viscosity of glasses.

## EXPERIMENTAL

The glass of composition on oxide basis (mol%) 51.5$SiO_2$. 25.6 $B_2O_3$ 4.3 $Li_2O$ 8.6 $Na_2O$ 4$CeO_2$ 4$ZrO_2$ 2$Cr_2O_3$ has been melted as described previously [13-15], to result in the designed composition. The glass was batched from reagent grade powders of oxides and carbonates, melted at 1400°C for 5 h including 1 h stirring before pouring. Subsequently the melt was either quenched by pouring in water or annealed for 1 h at 570 °C with cooling into metal forms with rectangular block shape. Glass blocks of 300 g have been cut into slices from the inner material, and subsequently fractured and grinded by pestle-and-mortar into finest powders. After suspension of the powder in acetone to allow settling of the bigger particles, drops of the suspension have been dispersed on a Cu-grid with holey carbon film (Agar Scientific, Inc.).

Fig. 2 shows a ~300 nm diameter fragment of annealed glass irradiated by a ~600 nm diameter electron beam visible in Fig 2b by its contamination circle. Exposure has been at maximum intensity of the $LaB_6$ gun at largest condenser aperture and spot size of roughly around 150pA/$cm^2$ for a few minutes. We observe roundening in its top left corner, while at the same time all glass within undergoes phase separation in two equally interconnected phases of structure size of 5 – 8 nm. The results obtained evidence on spinodal phase separation in silica-rich and alkali-borate rich phases similar to that which occur in "Vycor"-type glasses, a process that typically requires temperatures above 700 $^oC$ and times of the order of several hours [9]. Note that additionally visible Ce-oxide nanophases, formed during cooling and described in detail in [14] do not participate in this transformation. The picture is valuable as it clearly excludes temperature rise as the main reason for either effects of shape transformation or phase separation. Our reasoning is based on the unchanged bottom left corner which is outside the electron beam, visible by its deposited carbon imprint, but which would share a similar equilibrated temperature after a few seconds.

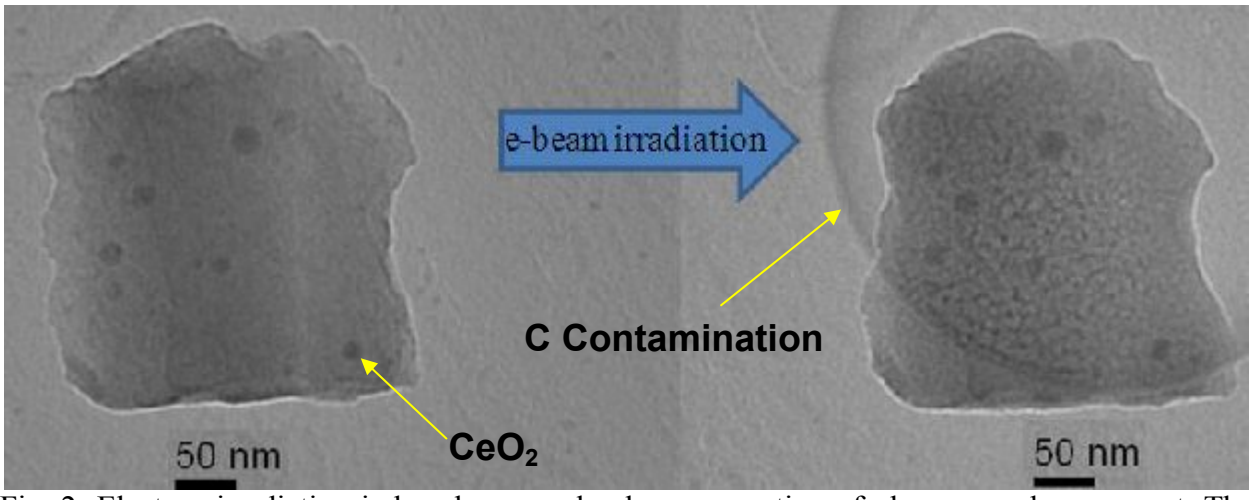


Fig. 2: Electron irradiation induced nanoscale phase separation of glass on carbon support. The electron beam (JEM 3010, 300kV) exposed region is visible by the circular carbon-deposited ring while the glass outside the beam remains unaffected.

## DISCUSSION

The phase separation observed on TEM (JEM 3010) 300 keV e-beam irradiation of glass $51.5SiO_2$. 25.6 $B_2O_3$ 4.3 $Li_2O$ 8.6 $Na_2O$ $4CeO_2$ $4ZrO_2$ $2Cr_2O_3$ is characterised by a continuous variation of concentrations with quite diffuse interfaces formed on decomposition. Moreover the phase separation is characterised by visible regularity of second phase distribution in size and position and geometric spacing. In addition there is seen a tendency for separation of second phase formed as non-spherical particles with high connectivity. All these characteristic are clearly evidencing that the phase decomposition observed in glass is of SD-type.

We assume that the effects observed are due to radiation-induced increase of diffusivity and glass fluidity under the electron beam as described in [15-18] rather than due to thermal effects. Fig. 3 shows liquid-liquid immiscibility boundaries depending on temperatures after [19] where we have approximately positioned the compositional area for the glass studied.

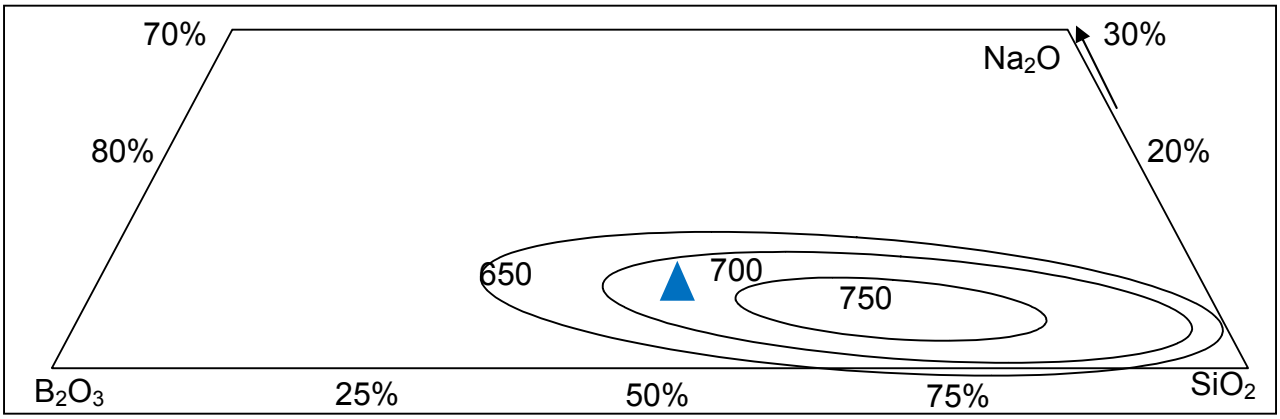


Fig. 3: Liquid-liquid immiscibility boundaries in the $Na_2O$-$B_2O_3$-$SiO_2$ system [after 19]. The possible contents of $Na_2O$, $B_2O_3$ and $SiO_2$ for the irradiated glass $51.5SiO_2$. 25.6 $B_2O_3$ 4.3 $Li_2O$ 8.6 $Na_2O$ $4CeO_2$ $4ZrO_2$ $2Cr_2O_3$ is shown by the blue triangle.

One can see that the glass irradiated is in the area of metastable immiscibility with potential phase decomposition at thermal treatment at temperatures exceeding 700ºC. The fluidity of glass at such temperatures remains low [9, 10] requiring thermal treatment durations longer than a few hours for formation of a phase decomposed glass. Therefore phase decomposition observed instantly under the electron beam is due to radiation-induced increase of glass fluidity rather than due to thermal effects.

Four main effects may lead to phase decomposition on irradiation: (i) radiation-enhanced diffusion; (ii) radiation-induced heating; (iii) formation of radiation products [3]; and radiation-induced fluidization at high dose rates [15, 17, 18]. The effects of radiation-induced heating and formation of radiation products were insignificant in our experiments, however, radiation-enhanced diffusion and radiation-induced fluidization play an important role. Irradiation of silicate glasses liberates cations from non-bridging oxygen (NBO) resulting in their mobilisation [16, 20-22]. A well-known effect related directly to radiation enhanced diffusion is marked

modification of the near-surface alkali concentrations in electron-irradiated glasses [20]. Irradiation also enhances ionic conductivity of glasses particularly if temperatures are not very high [21]. Mobilisation of alkalis in irradiated glasses is confirmed by experimental studies and molecular dynamic simulations [22] which demonstrate that the association with NBO confines the alkali to local motion, whereas the absence of a co-ordinating NBO allows the alkali ion to explore more easily its environment and to undergo long-range migration. Irradiation generates in glasses point defects in addition to those which are normally created by thermal fluctuations. Bond breaking processes and release of cations from the negatively charged NBO were described in details by Jiang and Silcox [7]. Radiation-induced diffusion is dominant when the concentration of defects created by irradiation, $C_{ir}$, is higher compared with concentration of thermally-induced defects, $C_{eq}$. The coefficient of radiation-induced diffusion for a cation can be written as [16] $D_{i,ir} \approx D_0 f_{ir} \exp(-H_{mi}/RT)$, where $D_0$ is the pre-exponential factor, $H_{mi}$ is the enthalpy of motion of cation in glass, $f_{ir} = C_{ir}/C_{sites}$ is the fraction of NBO created by irradiation from the available sites at concentration $C_{sites}$. The enthalpy of motion of a cation is analogous to the elastic strain energy and can be written as [23] $H_{mi} \approx \pi G(r_i - r_d)^2 \lambda_i$, where $G$ is the shear modulus of the glass, $r_d$ is the radius of network doorway related to the ionic porosity factor and $\lambda_i$ is the cation jump distance, $r_i$ is the radius of cation. Thus larger cations have higher activation energies and hence lower radiation-induced diffusion coefficients. For example the ionic radii are in nm [24]: $r_{Cs} = 0.170 > r_K = 0.138 > r_{Na} = 0.102 > r_{Li} = 0.068$. The mobility of cations is related to diffusion coefficient through Einstein relation: $\mu_{i,ir} = D_{i,ir}/kT$, thus larger cations have lower mobility. Experiments confirmed that Li is the easiest alkali to move through the irradiated glass and Cs is the most difficult one [13]. Intensive irradiation significantly reduces the viscosity and its activation energy [15, 17, 18]. The viscosity of irradiated amorphous materials is given by [17]: $\eta_R(T) = \eta(T)/\left[1 + \alpha_e I_e \left[1 + C\exp\left(D/RT\right)\right]\right]$, where $\eta(T)$ is the viscosity of an non-irradiated material $\alpha_e I_e$ is the dimensionless electron flux density. The higher the electron flux density the higher the increase of fluidity. Intensive electron beam irradiation changes the activation energy of viscous flow from characteristic high values at low temperatures to low values, which without irradiation are characteristic only at high temperatures. The electron-beam reduced viscosity of borosilicate glasses in our experiments was as low as $10^{11}$ Pa s [15, 18]. The kinetics of flow and viscosity-controlled processes at such high fluidity can be fast enough to be monitored on nano- and micro-scale.

## CONCLUSION

Irradiation of glass 51.5$SiO_2$. 25.6 $B_2O_3$ 4.3 $Li_2O$ 8.6 $Na_2O$ 4$CeO_2$ 4$ZrO_2$ 2$Cr_2O_3$ (mol%) in a TEM JEM 3010 by a 300 keV e-beam resulted in a phase decomposition characterised by a continuous variation of concentrations with diffuse interfaces formed and visible regularity of second phase distribution in size and spacing. The microstructure of the second phase formed appears non-spherical, which is best described as high connectivity of both primary and secondary phase, rather than particles in a matrix. All these characteristics support evidence that we observe spinodal type phase decomposition in this glass under the electron beam. One can suppose that the phase decomposition observed is due to effective bond breaking processes under the e-beam irradiation which lead to radiation-induced increase of cation mobility and glass fluidity which enable phase separation to occur.

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