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Electron Beam Transformation of Glass Nanoparticles

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Abstract. The phenomenon of electron irradiation induced quasi-fluid flow in solid amorphous silicates is examined. High-intensity electron beam irradiation of glass nanoparticles in TEM leads to a variety of transformations including rounding, bead formation, and phase separation. Evidence for possible rise in temperature, charging fields, and enhanced diffusion is collected and compared, while the latter effect (loosening of glass network) is shown to dominate.

1. Introduction
The deliberate or accidental irradiation of amorphous solid oxide materials has attracted major interest in a variety of research fields, including glass patterning for e.g. wave guide applications, modulated index or photochromic glass fabrication, nanoplasmonic glass/metal nanoparticle composites, and for radioactive material storage and disposal by vitrification \cite{1}. While laser, ion beam, and radioactive radiation sources have been widely used in the past to study glass-irradiation behaviour, we concentrate here on electron beam irradiation. Expected effects of the irradiation of an initially homogeneous glass would include: density changes (either up or down), diffusivity changes, phase separation, and precipitation of crystalline particles.

Relevant recent research findings include the \textit{in-situ} TEM nanomechanical testing of irradiated glass with ultra-soft plastic flow \cite{2}, point defects and high diffusion rates \cite{3}, while our preliminary work has found evidence for surface shape changing and pseudo-ductile behaviour of glasses in TEM \cite{4}. The finding that "solid", normally brittle, material appears mechanically soft when objects are of nanoscale dimensions and irradiated at high enough electron intensity, is often referred to as "Radiation Induced Fluidity" (RIF) or quasi-melting.

Here we aim at collecting evidence which could help decide between three basic mechanisms possibly underlying the RIF-observations of fine glass particles in TEM:

M1: The first possible option for mechanisms is the thermal "melting"-like transformation. Electron-beam induced sample heating could lift the particle to either above glass-transition, or further up to near melting temperature. The result would be some liquid-like glass behaviour with rough surfaces turning smooth and approaching overall spherical or at least round shapes by surface tension.

M2: The second option is charging and related ionic migration and atomic ablation due to local electric fields of varying strength \cite{5, 6}. Diffusion and Ablation rates would follow local field strength and contribute to enhanced flow and material removal (the latter preferentially at sharp corners with peaks in field strength)
M3: Radiation-induced fluidity (RIF) in the narrower meaning [2,3] involves neither change in temperature nor de-homogenisation by ion migration, but merely relies on high point defect generation rates triggering high diffusion rates, and allowing the glass particles to reconfigure according to surface tension "as if they were liquid-like", with a massively softened glass network.

In continuation of [4, 7-9], we present examples supporting or marginalising each of the mechanisms M1-M3, illustrated in Figure 1:
(a) centripetal surface tension with sphere formation under volume conservation,
(b) electric field enhancement at corners and ablation leading to rounding under volume loss;
(c) surface diffusion leading to rounding with overall shape conservation.

![Figure 1. Schematic of 3 possible glass particle transformation mechanisms by electron irradiation.](image)

2. Materials and Methods
Alkali-borosilicate glasses have been synthesised with varying boron content and with a variety of extra cations loaded, as part of earlier precipitation studies. Melting at 1300-1400°C followed by quenching in water generates a glass-frit which is ground into small micron or nano-sized fragments by pestle-and-mortar and suspended onto Cu-grid/C-film TEM specimens. Microscopy is performed at 200 or 300 kV (JEM 2010F or JEM 3010) with intensities varied via condenser focusing, normally at largest aperture. Occasionally very high intensities are achieved by removing any condenser aperture.

Glasses used include in particular:

| Glass | Compositions (mol.%) |
|-------|----------------------|
|       | B₂O₃ | SiO₂ | Na₂O | Li₂O | CeO₂ | Cr₂O₃ | ZrO₂ | CuO | ZnO |
| NBS   | 20   | 63.4 | 16.6 | 0    | 0    | 0     | 0    | 0   | 0   |
| NLBS-CCZ | 25.7 | 51.4 | 8.6  | 4.3  | 4    | 2     | 4    | 0   | 0   |
| Cu-NBS | 15   | 50   | 15   | 0    | 0    | 0     | 20   | 0   | 0   |
| Zn-BS  | 20   | 20   | 0    | 0    | 0    | 0     | 0    | 0   | 60  |

3. Results
3.1. Slow particle rounding
In Figure 2 (a, b) an original, randomly shaped, glass particle with sharp corners is irradiated and its transformation to round shape followed. This slow change is well controllable, and while the length of the anisotropic particle is clearly shrinking, the short aspect is growing. The latter points to volume conservation to a good degree, and proves materials flow. The alternative rounding mechanism by preferential ablation only can be excluded here, as it would result in a smaller particle the footprint of
which fits completely into the original shape. No signs of glass de-homogenisation (phase separation or precipitation) are seen, all evidence supports mechanism M3.

**Figure 2.** Example of slowly transformed (a, b) glass fragment (NBS-glass; JEM 2010F at 200 kV), and comparison to (c, d) rapidly transformed fragment (Cu-NBS glass [8]; JEM 3010 at 300 kV).

### 3.2. Fast bead formation.
The 2nd particle (Figure 2 (c, d)) shows distinctively different behaviour, as here a rapid not well controlled one-step transformation from the original rough and non-symmetric shape into a sphere is observed. While the compositions of the two glasses are not different enough to explain the behaviour, two details matter: The bead-formation is only observed for particles a few 100-nm large, and there is also a particularly sparse carbon-lace support visible at the particle location. Both details would trigger a much larger jump in temperature compared to Figure 2 (a, b), and might support a combination of mechanisms M1 and M3.

### 3.3. De-homogenisation.
Phase separation, particle precipitation and shape-rounding can all coincide, see Figure 3 (a, b). While only observed occasionally, the effect supports increased diffusion and assures glass homogeneity is preserved on the >10 nm scale (the composition near the corners is identical to the fragment centre), again supporting mechanism M3. Yet, electric field induced ion migration and ablation (M2) play a complementary role as evidenced in Figure 3 (c, d). Here, unlike in any other figure, the beam diameter used for irradiation was smaller than the glass fragment. Therefore, local charge-patterns and radial field distributions are generated. The response by the glass showing enhanced ablation (volume loss) and formation of two cation-enriched rings indicates mechanism M2 is dominant.

**Figure 3.** (a, b) Particle rounding with phase separation (NLBS-CCZ). (c, d) Field-induced ion migration alongside materials ablation and precipitation. Cu-NBS glass [8], JEM 3010; 300 kV.

### 3.4. Heating holder TEM.
Glass irradiation has been performed on a Zn-borosilicate glass [9], initially generating many Zn-nanoparticles (Figure 4 (a, b)) and some volume shrinkage. Subsequent heating up to 300° C in situ triggered changes in microstructure such as precipitation growth and particle-coagulation, while
intensities were kept low for imaging. However, no rounding or shape change due to heating is observed, and nearby un-irradiated particles did show neither rounding nor precipitation.

Figure 4. Zn-borosilicate (ZnBS) glass fragment subjected to irradiation (a, b) in JEM 3010 TEM at 300 kV and heating to 300º C (c, d) using a Gatan heating holder in the same TEM.

Our study aims at rank-ordering the three mostly quoted mechanisms to explain electron irradiation induced shape changes of glass nanoparticles, such as temperature, charging-fields, and radiation induced flow (RIF). Evidence has been found that generally all three mechanisms are at work and superimpose. However, in individual situations, one effect might dominate and dwarf the others. For small particles (<100 nm), temperature appears negligible and RIF explains all observations. For larger particles and where bad contact to carbon-supports is observed, beam-heating seems evident however without symptoms of true melting. In-situ TEM heating confirmed that at least up to 300ºC no temperature-related re-shaping occurs at all. The side-effects observed simultaneously alongside the main glass softening include phase separation and particle precipitation. Both prove that enhanced diffusion by irradiation generated defect concentrations is a shared underlying conditions of all effects observed. The relevance of the local irradiation in Figure 4d is that due to the flat and straight geometry of the fragment edge, surface tension is eliminated as driving force. For such localised focused irradiation of an impact area within a particle, charging and field-driven ion migration/ablation, effect M2, then becomes the lead-effect as M1 is effectively symmetry-cancelled.

4. Conclusions
The observed effects are of importance for glass-surface engineering (both smoothing and - via phase separation - roughening could be achieved), but also for improving wetting-behaviour, for defect healing (low-temperature “annealing”), or changing porosity characteristics in nanoporous glasses, and ultimately also for glass patterning and grating formation.

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