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Nanoparticle Formation in Borosilicate Glasses under Electron Irradiation

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Abstract

Here we examine Cu, Ag and Zn loaded alkali-borosilicate glasses. Nanoparticle formation in these glasses upon 200 keV and 300 keV electron beam irradiation is studied due to the excellent capability of transmission electron microscopy (TEM) to spatially confine irradiation in either stationary beam or line-scan irradiation modes with a variety of beam diameters. Nanoparticles of various shapes and sizes have been precipitated using different irradiation sequences. In particular, the formation of particle chains consisting of self-organized particle ordering have been observed along with some high intensity irradiation ablation of the glass matrix, which happens in parallel with the precipitation.

Keywords Line-scan irradiation; Nanoparticles; Oxide glasses; Patterning; TEM.

1. Introduction

Much attention has been paid to study the effects of electron beam irradiation in oxide glasses [1]. This is due to the fact that an electron beam of high energy can alter the properties, structure and composition of the glass [2], such as inducing any combination of phase separation and precipitation/crystallisation, volume expansion or shrinkage along with change of external particle shape, and the more TEM-specific effects of oxygen-bubble formation and alkali migration out of the irradiation zone [3, 4]. Borosilicate glasses have been widely studied for durability and structural stability under a variety of ion, gamma, and electron radiations in the context of radionuclide immobilisation [1]. On the other hand, in optical communication and solar energy device materials, patterning of transparent matrix materials has attracted much interest, and irradiation with lasers or particle beams is one method to add modern functionalities to glasses. It has also been shown that the non-linear optical properties of glasses can be improved by inserting nanoparticles. Electron irradiation-induced formation of metallic nanoparticles in amorphous materials has been reported variously [2,5], and this paper extends upon the authors' previous work [6].

2. Materials and Results

Table 1 shows three oxide glasses used in this study. They are melted from their raw materials at appropriate temperatures and varying crucibles. TEMs used here include JEM 3010 at 300 keV with thermal gun, and JEM 2010F at 200 keV with field emission gun and electron energy loss spectrometer (EELS). In this work, TEM serves for simultaneous materials patterning, line-scan irradiation by slow scanning beam, imaging and *in-situ* observations. Fig. 1 shows three different irradiation experiments conducted on glass-1. Fig. 1a,b show irradiation of a glass fragment by non-focused electron beam of diameter > 200 nm using largest condenser aperture and spot size. We find nanoparticles of diameter of about 1-5 nm (mostly circular shape) precipitating after 3 min irradiation, in addition to a chain of nanoparticles at the edge of the glass fragment. Fig. 1c shows irradiation with no aperture inserted to get a maximum current density. Irradiation using such conditions resulted in forming nanoparticles of diameter of about 50-190 nm. Fig. 1d,e show that irradiation using focused electron beam has generated a ring in the glass fragment. Such irradiation made the ions migrate toward the electron beam edge and accumulate there, except one nanoparticle, which remains at the centre, in accordance with [3].

Table I. Compositions of glass (Mol%).

Glass		Composition (Mol%)									
		SiO_2	B_2O_3	Na_2O	K_2O	CeO_2	Fe_2O_3	Nd_2O_3	CuO	Ag_2O	ZnO
1	Cu-BS	50	15	15	---	---	---	---	20	---	---
2	Ag-BS	60	15	---	15	4	3	2	---	1	---
3	Zn-BS	20	20	---	---	---	---	---	---	---	60

Fig. 2 shows results of glass-2. Line-scan irradiation of the glass rod (Fig. 2a) resulted in formation of nanoparticles of diameters of about 2-30 nm within the e-beam path (Fig. 2b). Stationary e-beam irradiation (Fig. 2c,d) on the other hand resulted in partial glass ablation and formation of circular nanoparticles of about 7 nm in diameter. EDX analysis revealed that the precipitated particles are silver rich. Fig. 3 shows results on glass-3. Prolonged irradiation using stationary electron beam resulted in formation of mostly spherical nanoparticles (Fig. 3a), while line-scan irradiation of the glass fragment (Fig. 3b) resulted in producing nanoparticles of size decreasing with distance from the e-beam (Fig. 3c) with very little glass ablation can be seen.

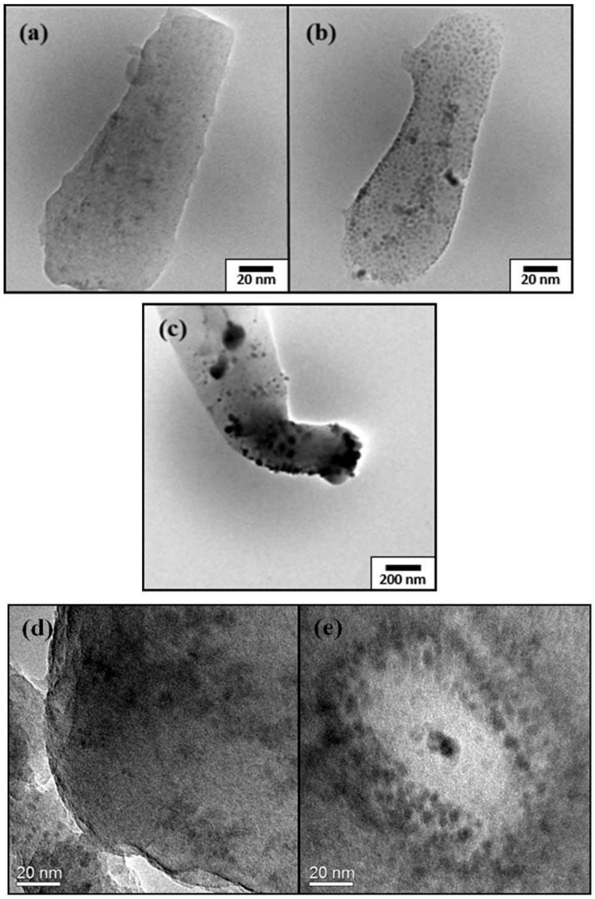

Figure 1. Glass 1 (Cu-rich) at different irradiation experiments; **(a-c)** using TEM 3010 at 300 keV; **(d,e)** using TEM 2010F at 200 keV.

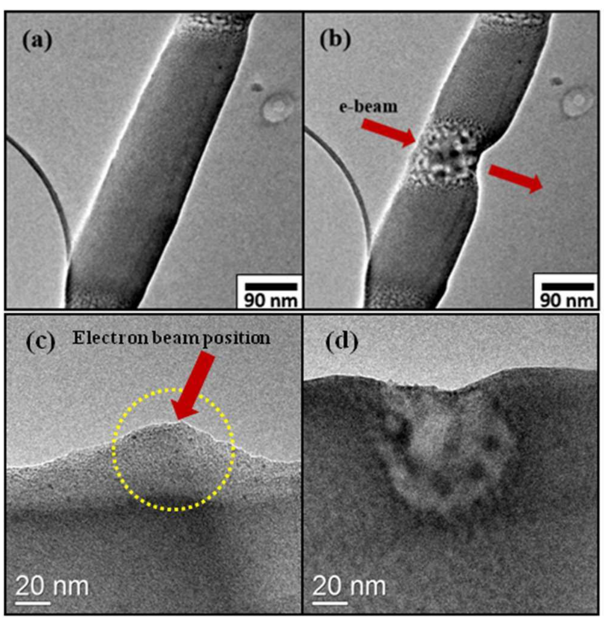

Figure 2. Glass 2 (Ag-doped); **(a, b)** before and after line-scan irradiation respectively (TEM 3010 at 300 keV); **(c, d)** before and after stationary irradiation respectively (TEM 2010F at 200 keV).

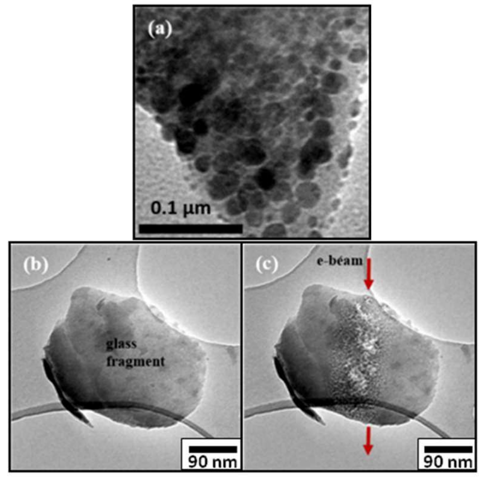

Figure 3. Glass 3 (Zn-rich); **(a)** after prolonged stationary irradiation (TEM 2010F at 200 keV); **(b, c)** before and after line-scan irradiation respectively (TEM 3010 at 300 keV).

3. CONCLUSIONS

From the preliminary results achieved in three borosilicate glasses, we can conclude that the method of electron-beam induced precipitation can operate on a very broad compositional range of cations added to the borosilicate network, including 1%, 20%, 60% of oxide. Therefore it applies to elements entering the glass matrix network (60%) as well as to non-network forming dopants (1%). The particle distribution can be tuned non-homogenously by beam positioning, and for the Ag and Zn-loaded glasses (less so for Cu) the boundaries between precipitated and non-precipitated areas are rather sharp, indicating a direct radiation mechanism rather than a beam-induced heating process. EELS and EDX results indicate all particles are metal for Zn, Cu and Ag. All experiments so far have been performed on rapidly cooled glass fragments to prevent possible precipitation before irradiation, therefore influence of pre-annealing will also be studied in future.

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