FR8704192

COMMISSARIAT A L'ENERGIE ATOMIQUE

CENTRE D'ETUDES NUCLEAIRES DE SACLAY
Service de Documentation
F91191 GIF SUR YVETTE CEDEX

CEA-CONF -- 9079

M2

RADIATION EFFECTS ON PHASE SEPARATION AND VISCOSITY OF GLASSES

Biron, I.; Barbu, A. CEA CEN Saclay, 91-Gif-sur-Yvette (France). IRDI, DTech

Communication présentée à : 2. International conference on the effects of mode[illegible]
of formation on the structure of glasses
Nashville, TN (USA)
15-18 Jun 1987

RADIATION EFFECTS ON PHASE SEPARATION AND VISCOSITY OF GLASSES

Isabelle BIRON, Alain BARBU
Centre d'Etudes Nucléaires de Saclay, Section de Recherches de Métallurgie Physique 91191 GIF SUR YVETTE CEDEX France

The effect of electron irradiations on the stability of B_2O_3-PbO glasses is studied by transmission electron microscopy. Rapid coagulation of pur lead particles is observed. By using the Smoluchosky's coagulation theory, it is shown that the viscosity of B_2O_3 is drastically reduced by several orders of magnitude under irradiation. The electron excitations are shown to play the dominant role in this phenomena.

1 - INTRODUCTION

Microstructural stability, diffusion and viscosity of glasses under irradiation are related topics. Structural stability under irradiation has been the subject of severals studies, mainly through transmission electron microscopy in situ experiments [1,2], but also ion irradiations [3].

Measurements of diffusion profiles of modifier under irradiation have been performed but are often difficult to explain because of the presence of a radiation induced electric field [4,5]. There is unfortunately no study of the mobility of glass-former elements under irradiation.

Concerning the viscosity of glasses under irradiation very little has been done. In 1960, G. Mayer and M. Leconte pointed out that the viscosity of fused silica irradiated at 60°C under a flux of 2.10^{12} fast neutrons/cm^2 is the same as at 600°C without irradiation [6]. Maxim et al. found a similar behaviour in alomino-silicates glasses always under neutron irradiation [7]. W. Primak reports that the stress relaxation of vitreous silica under irradiation can be understood by assuming a reduction of the viscosity ; he points out that this effect is observed also with low energy electrons which do not create atomic displacements [8,9]. We previously mentioned [10] that viscosity can be estimated by transmission electron microscopy in a B_2O_3-PbO glass exhibiting phase transformation. The aim of this paper is to show the ability of the method to study the effect of the irradiation parameters.

2 - EXPERIMENTAL PROCEDURE

The lead-borate glass containing 7,2 wt % PbO is melted in a platinium crucible. These foils are obtained by blowing clear glass bubbles from the melt.

The electron irradiation were perfortmed in situ by a transmission electron microscopy either at low energy (60 - 125 keV) with a conventional device or with a high voltage electron microscope at 1 MeV. The electron flux varies from $5{,}6.10^{17}$ to $4{,}5.10^{19}$ e^-/cm^2s^{-1}, in the temperature range 100 K - 780 K.

We want to emphasize that such a work under irradiation is meaningful only if the temperature rise under the beam ΔT is studied carefully. It was done by determining the reversible solid-liquid transition of small isolated Indium islands deposited at the surface of the sample. It is found that ΔT varie from 300 to 470 K depending on the electron flux.

3 - RESULTS

No contrast (or sometimes very faint) is observed in the as prepared glass. After a time depending on flux and temperature, but always short, spherical droplets appear. At high temperature and flux enough, it leaps the eye that those dark droplets are like being alive in the matrix.

The radius of the spherical particles increase with time (Fig. 1). As shown in Figure 2 it is clearly a coagulation mechanism which control the growth (and not Oswald ripenning).

a - Phase separation

The composition of our glass is in the miscibility gap of the amorphous B_2O_3 -PbO system. We assumed in our previous paper that the particles appearing under irradiation have the equilibrium composition (B_2O_3, 43 wt % PbO) [11]. Diffraction patterns under 600 K show clearly that they are in fact made of pur lead (Fig. 3) and at the matrix is almost pure B_2O_3. Furthermore oxygen bubbles have been observed only under low energy electron irradiation below 290 K. Some experiments performed at higher PbO concentration, outside the miscibility gap, show clearly lead particles too.

It is worth noticing that the cinetic of phase separation which is obviously not of the same nature is drastically faster inside irradiation than outside [10].

b - Viscosity

What we observe looks like the Brownian motion of lead particles in a low viscosity matrix [10].

Assuming that their is no interaction between particles, the viscosity of B_2O_3 can be calculated by using the Smoluchowski model of coagulation. It can be shown within, the hypotheses of the self preserving size distribution of particles, that the number of particles per cubic centimeters N is given by the relation :

$$1/N = - AkTt/3\mu$$

Where t is the time, T the temperature and μ the viscosity. A is related to the integral of the distribution of the particles.

The evolution of the histogram of size shows that the self preserving hypothesis is valid and that $A \simeq 4$, the value obtained for homogeneous hydrosol [12].

By scaling 1/N versus t the viscosity μ can be calculated. As shown in Figure 4, 1/N is not actually linear in time on the whole time scale : two slops can be seen, one at short time (small particle sizes) and another for longer time (large particle sizes). We believe that this behaviour is an effect of thin foils which appears when the particle size is no longer negligible compared to the thickness of the foil. The following results are relevant to the short time linear part of the curve, but the second part give qualitatively the same behaviour.

For the entire energy range (60 - 125 keV and 1 MeV) and the electron flux range a drastic reduction of the viscosity under irradiation (Fig. 5) is observed. At low energy (125 keV) the viscosity can only be estimated above 470 K, with an activation energy equal to that of the liquid. On the other hand, the viscosity under high energy electron irradiation exhibits an athermal behaviour between 320 and 570 K. In the medium temperature range the same features as at low energy are observed.

4 - DISCUSSION

The stability on the B_2O_3-PbO glass under irradiation shows the same features as silicate glasses. The PbO component is reduced under irradiation, as in many common glasses [1,2], free oxygen either agglomerates to give bubbles or leaves the thin foils depending on the temperature. Pb ions (or atoms) probably less mobile than Na in alkali silicates give colloïds.

It is precisely those colloïds or lead particles which render possible the evaluation of the viscosity of B_2O_3. It must be understood that the measurement of μ, using the previously described techniques cannot be precised but because of the tremondous effect it does not really matter. As shown in the Figure 5 electron irradiation drastically reduces the viscosity of B_2O_3.

Because such an effect is observed even at 60 keV, an electron energy which cannot induce atomic displacements, it is clear that the origin of this effect must be sought in electronic excitation.

The lack of microscopic model of viscosity of glass even outside irradiation renders difficult any deep discussion of the effect of irradiation. However the decrease of the viscosity with increasing temperature can be intuitively understood as a consequence of the weakening of the bonds. The higher the temperature, the higher the number of brooken bonds. Under irradiation the electronic excitations, hole and electron pairs eventually trapped on trap, result in weakenning of bonds. The highest efficiency of 1 MeV electron irradiation could seem surprising because the higher the electron energy the lower the cross section for electronic excitation. However it can be proposed than the effect observed is due to the high atomic displacement rate under 1 MeV irradiation leading to a great amount of point defects (at saturation) able to trap electronic defect such as the well known E' centers in silica glass [13,14]. On the other hand the low energy irradiation does create such traps and cannot sustain a very high level of electronic defects.

BIBLIOGRAPHY

1 - M. ANTONINI and A. MANARA - Rad. Effects 65, 55 (1982)

2 - J.F. De NATALE and D.G. HOWITT - Nuclear Instruments and Methods in Physics Research B1, 489 (1984)

3 - J.F. De NATALE, D.G. HOWITT and G.W. ARNOLD - Rad. Effects 98, 63 (1986)

4 - P. MAZZOLDI and A. MIOTELLO - Rad. Effects 98, 39 (1986)

5 - P. REGNIER, Y. SERRUYS, A. ZEMSKOFF - Phys. Chem. Glasses 27, 185 (1986)

6 - G. MAYER et M. LECONTE - Le Jounral de Physique et le Radium 21, 846 (1960)

7 - I.V. MAXIM and D. APOSTOL - J.N.M. 42, 49 (1972)

8 - W. PRIMAK - J. Appl. Phys. 35, 1342 (1964)

9 - W. PRIMAK - J. Appl. Phys. 53, 7331 (1982)

10- I. BIRON et A. BARBU - Appl. Phys. Lett. 48, (24), 1645 (1986)

11- J. ZARZYCKI and F. NAUDIN - Phys. Chem. Glasses 8, 11 (1967)

12- D.L. SWIFT and S.K. FRIEDLANDER - J. Collo. Sci. 19, 621 (1964)

13- P.W. LEVY - SPIE Vol. 541, Radiation effects in optical materials (1985)

14- D.L. GRISCOM - Same ref. us [13]

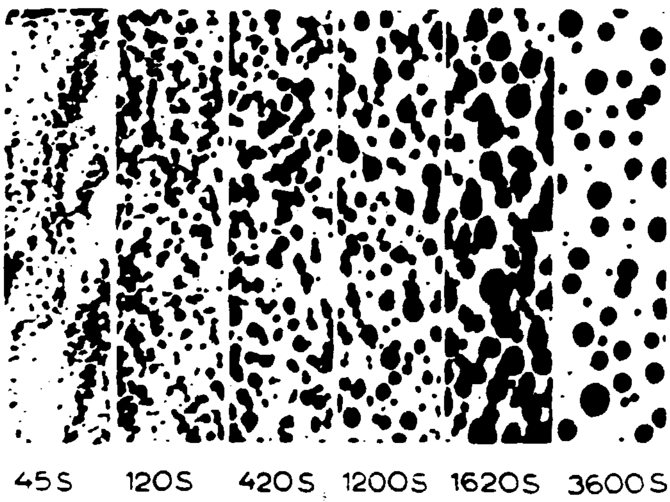

FIG. 1 : Kinetic of coagulation at 670 K and 4.8 10^{18} e^{-}/cm^{2} s

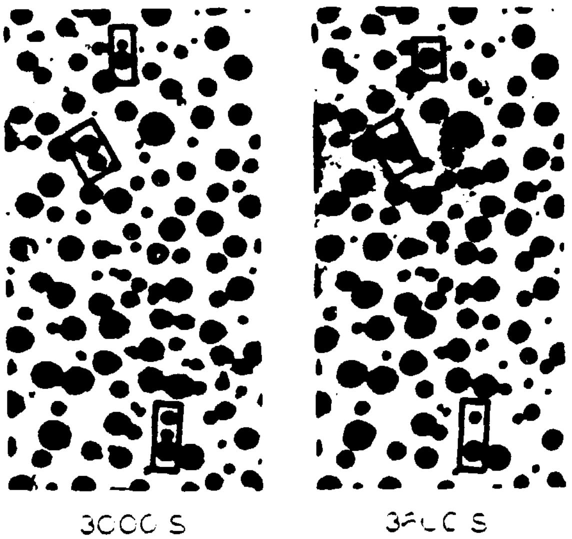

FIG. 2 : An example pf a coagulation event shown in the dark framework.
T = 670 K
ϕ = 4.8 10^{18} e^{-}/cm^{2} s

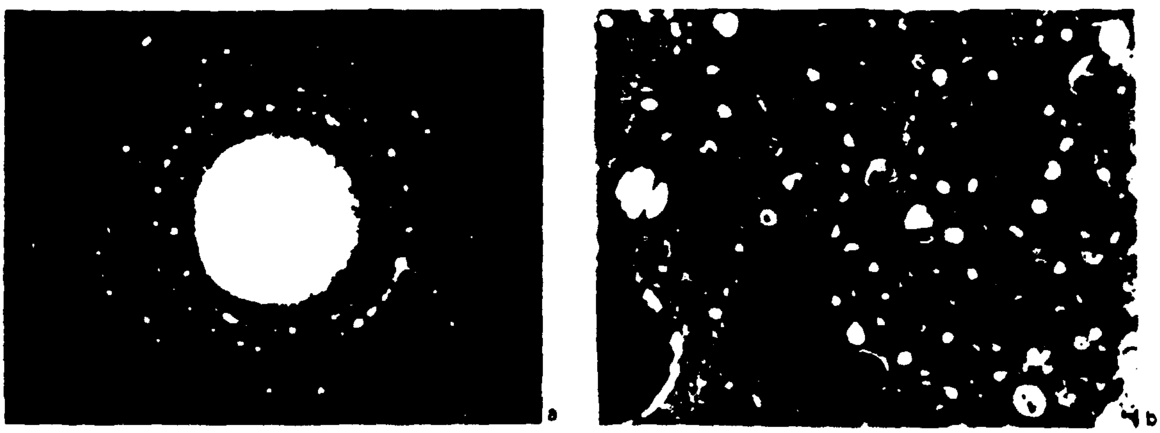

FIG. 3 : The particles are pur lead. a) Diffraction pattern.
b) Dark field picture showing twinned particles.

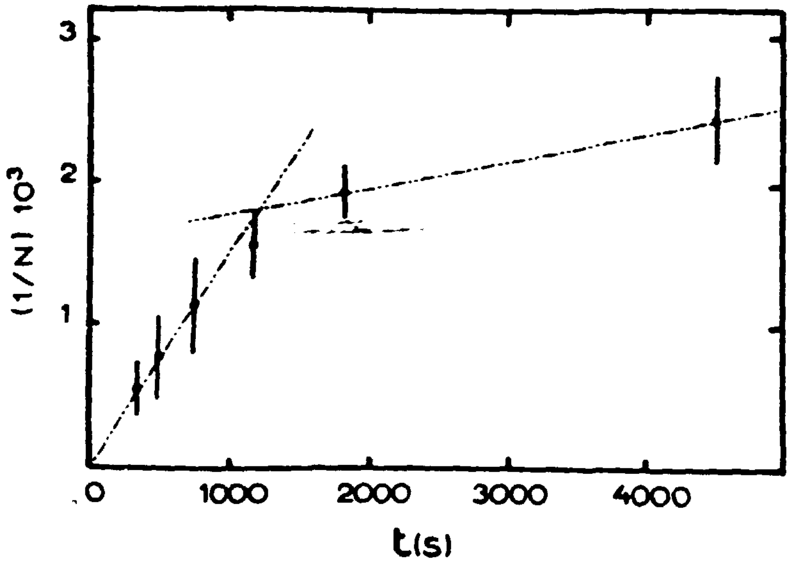

FIG. 4 : The evolution of the number of lead particles versus time at 600 K, 5.6 10^{18} e^-/cm^2 s.

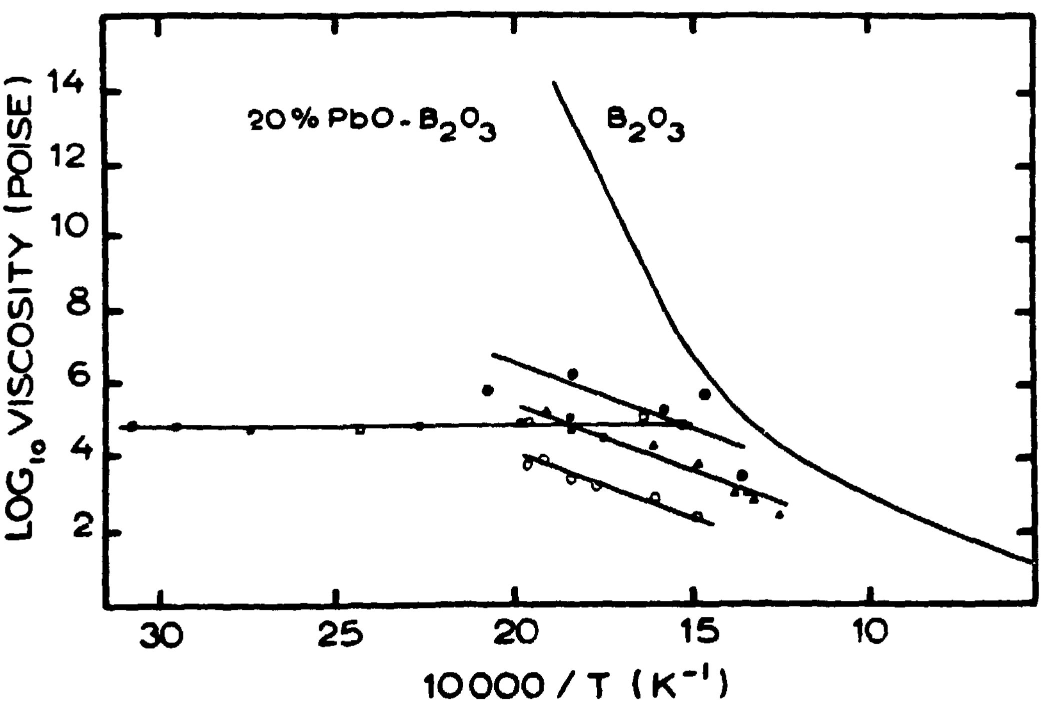

FIG. 5 : The viscosity of B_2O_3 under e^- irradiation. The right hand side curve : viscosity outside irradiation measured by a macroscopic method (10).

● 125 keV, 5.6 10^{17} e^-/cm^2 s ; ▲ 125 keV, 5.6 10^{18} e^-/cm^2 s

○ 125 keV, 1.1 10^{19} e^-/cm^2 s

□ 1 MeV, 1.4 10^{19} e^-/cm^2 s ; ■ 1 MeV, 4.5 10^{19} e^-/cm^2 s