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Metal atom clustering in reduced lead-, bismuth- and antimony-silicate glasses: a comparative molecular dynamics study

AGNIESZKA WITKOWSKA, JAROSŁAW RYBICKI, JAROSŁAW BOŚKO

Department of Solid State Physics, Faculty of Technical Physics and Applied Mathematics, Technical University of Gdańsk, ul. Narutowicza 11/12, 80–952 Gdańsk, Poland, and TASK Computer Centre, ul. Narutowicza 11/12, 80–952 Gdańsk, Poland.

SANDRO FELIZIANI

INFM UdR Camerino, Istituto di Matematica e Fisica, Università di Camerino, Via Madonna delle Carceri, Camerino (MC), Italia.

We report on the results of molecular dynamics (MD) simulations of the formation of metallic granules in totally reduced lead-, bismuth- and antimony-silicate glasses of composition x Me $(1-x)$ SiO_2, Me = Pb, Bi, Sb, $x = 0.25$, 0.5. The simulations were performed in the NVE ensemble, with two-body Born–Mayer–Huggins interaction potential. For all the glasses considered a strong tendency of heavy metal atoms to agglomerate was observed. In this contribution we compare the distributions of the sizes of Pb, Bi and Sb granules and their packing.

1. Introduction

Binary silicate glasses containing heavy metal oxides, such as PbO, Bi_2O_3 or Sb_2O_3 show many interesting and useful properties, finding applications as low-loss wave-guide materials which operate at wavelengths >3 μm [1], and as the active medium of Raman-active fibre optical amplifiers and oscillators [2], [3]. These glasses, submitted to the reduction process (*e.g.*, in hydrogen atmosphere or proton bombardment), undergo dramatic changes in their optical properties [4], and electrical surface conductivity [5]. Reduced glasses contain metallic granules and/or neutral Pb/Bi/Sb atoms [6], [7], reveal a very high secondary emission coefficient, and find application in the production of electron channel multipliers [8].

In the present contribution we report on the results of molecular dynamics simulations of the structure of totally reduced lead-, bismuth- and antimony-silicate glasses of composition x Me $(1-x)$ SiO_2, Me = Pb, Bi, Sb, $x = 0.25$, 0.5. In Section 2 we describe in brief our numerical experiment. The results are presented and discussed in Sec. 3. Section 4 contains concluding remarks.

2. Molecular dynamics simulations

The molecular dynamics simulations have been performed in the microcanonical (NVE) ensemble (*e.g.* [9]). The atoms were assumed to interact by a two-body potential (Born–Mayer repulsive forces, and Coulomb forces due to ionic charges, calculated with the aid of the standard Ewald technique). The Si–Si, Si–O, and O–O interaction parameters were taken from [10], Pb–Pb and Pb–O from [11], and Bi–Bi and Sb–Sb from [12]. The Bi/Sb–O, and Bi/Sb–Si interaction parameters were calculated as suitable averages of the Bi/Sb–Bi/Sb and O–O, and Bi/Sb–Bi/Sb and Si–Si interactions, respectively, using the Lorenz–Berthelot mixing rule. Full ionic charges Si^{+4} and O^{-2} were used, whereas the metal atoms were neutral. All the samples were initially prepared in a well equilibrated molten state at 8000 K, and then cooled down to 300 K. The structures discussed below were obtained at the average cooling rates of $2 \cdot 10^{13}$ K/s. The numbers of atoms within the simulation box are presented in the Table.

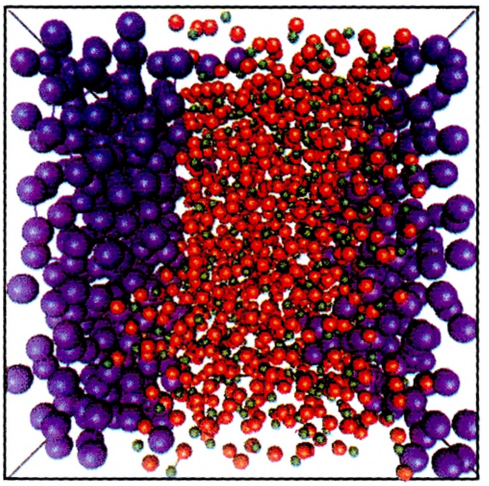
Table. Numbers of atoms within the simulation box.

	$x = 0.25$	$x = 0.5$
Pb/Bi/Sb	250	500/5000
Si	750	500/5000
O	1500	1000/10000

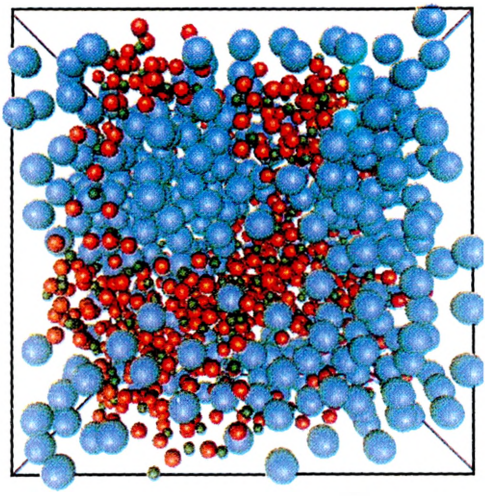
3. Results and discussion

Figure 1 shows the snapshots of the atom configurations in the last simulation step of the 2000-atom calculations for the $x = 0.5$ lead-, bismuth-, and antimony-silicate glasses. As results from a series of simulations performed for various initial conditions and cooling rates, the images are quite typical for the materials considered: in lead-silicate systems a full phase separation occurs, whereas the separation between the metal phase and silica is less pronounced in bismuth- and antimony -silicate glasses. In order to describe quantitatively the compactness of the metallic phase we calculated the fractions of the metal atoms that have the metal–metal co-ordination not less than n, where n is an integer. High fraction of highly co-ordinated metal atoms means that there are many bulk metal atoms, *i.e.*, the granules are rather compact. On the other hand, low fraction of highly co-ordinated metal atoms might suggest that the granules have a rather high surface to volume ratio, and/or are interconnected by narrow paths of metal atoms. In what follows, such co-ordination data will be used to compare the "agglomeration tendencies" of various metals in the silica matrix.

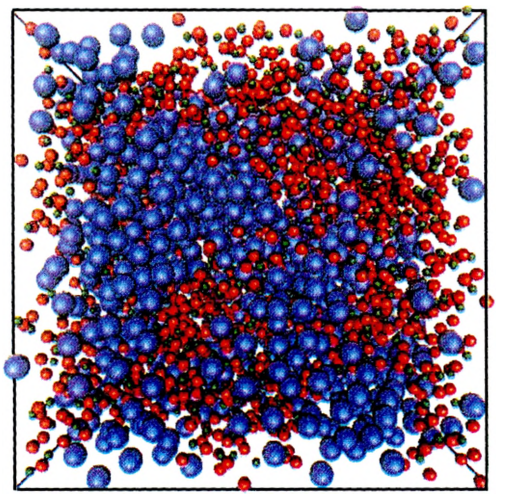
As can be easily seen from Figure 2, the agglomeration tendency for lead system is much more distinct than for bismuth or antimony systems: lead granules are more compact than bismuth or antimony granules. The latter two elements show almost identical clustering behaviour. The differences between the distributions of co-



$0.5Pb\ 0.5SiO_2$

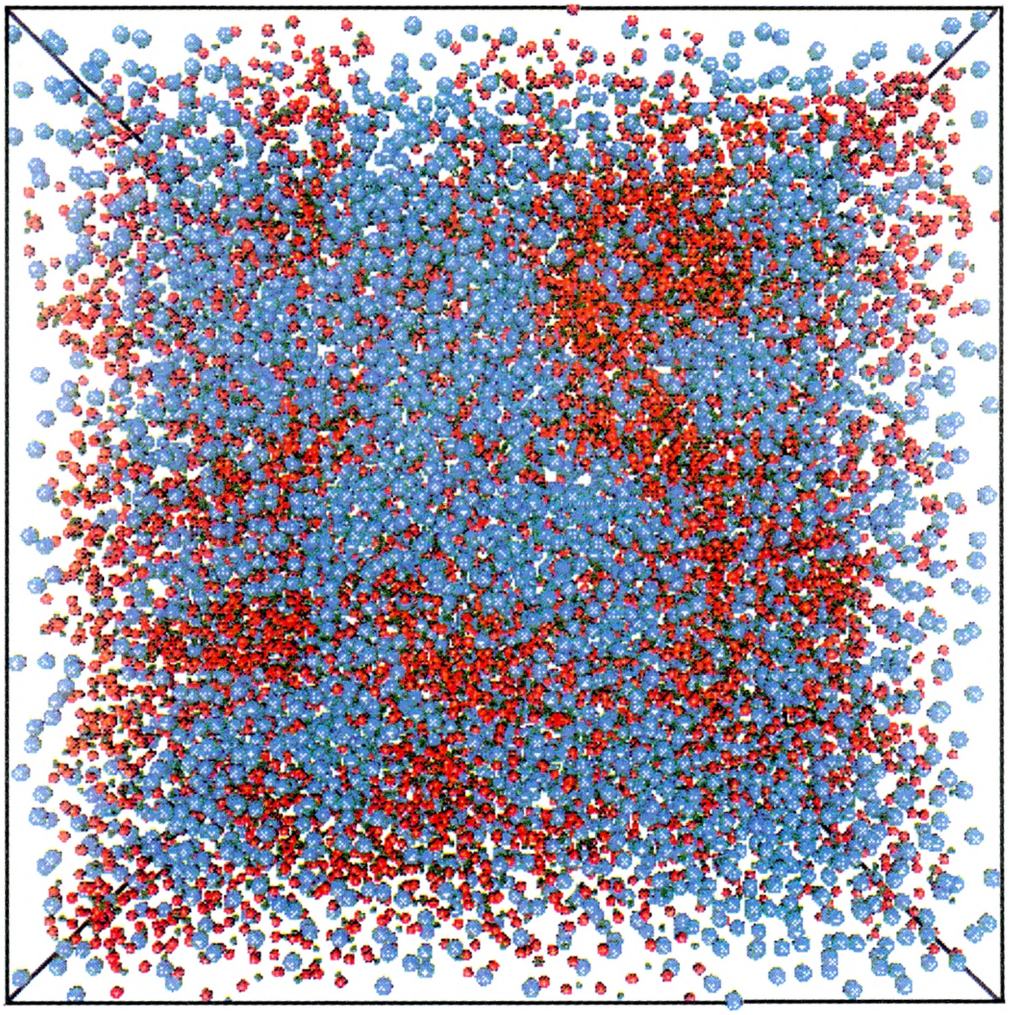


$0.5Bi\ 0.5SiO_2$



$0.5Sb\ 0.5SiO_2$

Fig. 1. Snapshots of atom configurations in the last simulation step for 0.5 Me 0.5 SiO_2 systems. Me = Pb, Bi and Sb. Red balls – oxygen atoms, green balls – silicon atoms, big bluish balls – lead, bismuth, and antimony atoms. 2000 atoms in the simulation box (500 Me atoms, 500 Si atoms, 1000 O atoms).



$0.5Bi\ 0.5SiO_2$

Fig. 3. Snapshot of atom configuration in the last simulation step for 0.5 Bi 0.5 SiO_2 system. Red balls – oxygen atoms, green balls – silicon atoms, bluish balls – bismuth atoms. 20000 atoms in the simulation box (6000 Bi atoms, 5000 Si atoms, 10 000 O atoms).

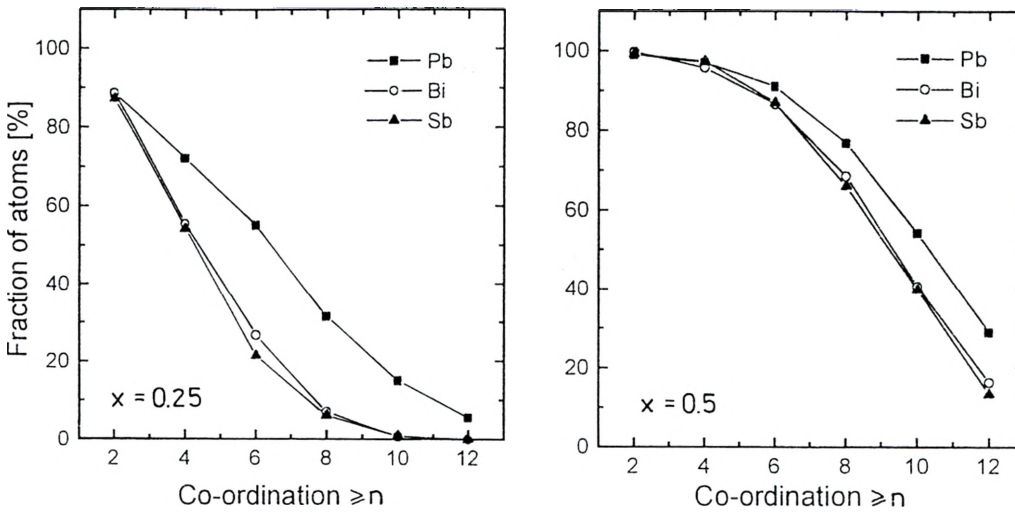


Fig. 2. Fractions of Me atoms of the Me–Me co-ordination higher than n, Me = Pb, Bi, Sb.

ordination numbers of lead and bismuth/antimony are more pronounced for lower metal contents. For example, in the $x = 0.25$ systems about 80% of Bi/Sb atoms have co-ordinations lower than 6, while in the case of the lead system this percentage amounts to only about 45%. Comparing the distributions of the co-ordination numbers as a function of x for various glasses one sees that the agglomeration tendency increases with increasing contents of neutral metal atoms for all the glasses under consideration. For $x = 0.25$ about 10% of the metal atoms (Pb, Bi, Sb) are separated or occur in pairs, whereas for $x = 0.5$ practically no isolated atoms or pairs of atoms are detected.

The clustering properties described above can be related to the diffusion coefficients D of metal atoms. The coefficient D has been calculated in a standard way from the average square displacements of metal atoms (*e.g.*, [9]). It turns out that:

– the diffusion coefficient is higher at higher metal contents for each of the compounds considered,

– for a fixed stoichiometry (x = const.) diffusion coefficients of Bi and Sb are similar to each other ($D_{Bi} \approx D_{Sb} \approx 10^{-8}$ m^2/s), while the diffusion coefficient of Pb is higher by one order of magnitude.

Thus, the higher the diffusion coefficient, the bigger and more compact the granules appear.

The question arises of whether and/or to what extent the clustering data presented are dependent on the size of the simulation box. Figure 3 shows a snapshot of the atom configuration for the 20000-atom calculation for the $x = 0.5$ bismuth-silicate glass, and this image is to be compared with the corresponding picture for the 2000-atom calculation (Fig. 1). It is difficult to answer the question directly from the inspection of the figures. However, the co-ordination data similar to those used in the previous section indicate that no significant size effects are present (see Fig. 4).

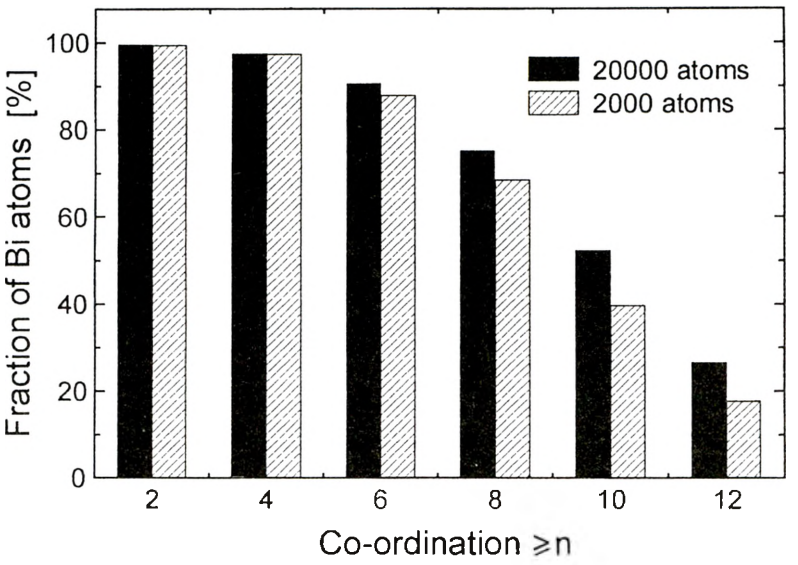


Fig. 4. Effect of the simulation box size on the agglomeration process for 0.5 Bi 0.5 SiO_2 glass.

4. Conclusions

Using classical MD simulations it has been shown that the Pb neutral atoms are more mobile in the silica matrix than the Bi or Sb atoms. Although each metal reveals a tendency to agglomerate into clusters, the Pb granules are the most compact ones. As a result, in $x\,Pb\,(1-x)\,SiO_2$ systems one can expect the appearance of rather spherical and well separated granules caged in the silica matrix, whereas in $x\,Bi\,(1-x)\,SiO_2$ and $x\,Sb\,(1-x)\,SiO_2$ systems the granules are more irregular and interconnected with paths of weakly co-ordinated Bi or Sb atoms, forming a kind of infinite cluster. Such a result seems to be compatible with the experimental fact that the electrical conductivity is hardly influenced by the reduction process, whereas the conductivity of the reduced bismuth glasses increases even by 10 orders of magnitude in respect of unreduced glasses [13]. However, since a very simplified form of interatomic interactions has been applied in our simulations, the above conclusions still require validation from simulations performed with more sophisticated force fields.

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