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ABSTRACT

Molecular dynamics simulation is applied to an europium doped sodosilicate glass containing silver $[(Na–Ag)_2O–SiO_2–Eu_2O_3]$. The silver is implanted in substitution of Na, simulating an ionic exchange. For ionic interactions a modified Born–Mayer–Huggins potential was employed. For the Ag–Ag interaction, a Lennard-Jones (LJ) potential is applied, while for the Eu–Ag interaction, a modified LJ potential is introduced. The particle size increases with the annealing treatment and follows a lognormal law. After 75 ps the average particle size reaches 5.8 atoms (4.8 for Ag and 1.0 for Eu), and it is found that the europium is preferentially situated on these nanoclusters.

1. Introduction

The application of metallic nanoparticles as a modifier of optical properties of liquid and solid state media is very a nowadays subject on the side of nanophotonics [1–3]. It is important to mention that, in the solid state case, the absence of long range order turns the glasses out to be natural candidates to host metallic nanoparticles [4–9]. In the case of lanthanide ions (Ln^{3+}) doped glasses containing silver nanoparticles, the spectroscopic behaviour still lack interpretations, e.g., what really is the effect of the plasmon band on the Ln^{3+} luminescence or from what size the plasmonic oscillations do interact with transitions between levels [10–16]. Further, the importance of such a kind of study can be verified through very recent applications of silver nanoparticles, which include the antibacterial activity, clinical diagnostics and dental restoration [17–22].

Molecular dynamics (MD) has been largely employed to simulate structure and properties of glasses, rare-earth doped glasses (see e.g., [23]) as well as the nanoparticles growing process in glasses [24–28]. MD has become an important tool, because just by typing and keeping the potentials of interaction within physically acceptable ranges, predictions can be made and one try to envisage non evident experimental or theoretical local features.

In this work a MD study of a europium doped sodosilicate glass containing silver nanoparticles is developed, with the aim of obtaining Ag–Eu nanoalloy. To this end, for all ionic interaction, a modified Buckingham potential is employed and, for the Eu–Ag metallic interaction, it is introduced a modified Lennard-Jones (LJ) potential.

2. MD procedures

For all ionic interaction a modified Buckingham potential was employed which consists of a repulsive exponential and an attractive dispersion part represented by $-C/r^6$. The erfc term corresponds to the real component of the Ewald sum modelling screened coulombic interactions.

$$V_{ij}(r_{ij}) = A_{ij}\exp\left(-\frac{r_{ij}}{\rho_{ij}}\right) + \frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}}\,\mathrm{erfc}\left(\frac{r_{ij}}{\beta_{ij}}\right) - \frac{C_{ij}}{r_{ij}^6} \quad (1)$$

where A_{ij} is the short range repulsion term, β_{ij} and ρ_{ij} are adjustable parameters used to reproduce correct bond lengths, r_{ij} is the distance between atoms i and j, and q_i is the ionic charge of atom i [24]. In the case of silicon and oxygen interactions a 3-body potential was also used to insure better angle distribution functions and better statistic for defects (tetrahedral silica rings statistics) [29].

In order to simulate the growth of silver nanoparticles a Lennard-Jones potential between Ag atoms is introduced [24]. The same Lennard-Jones potential with a corrective coefficient was also used for the Ag–Eu interaction as follows

$$V_{ij}(r_{ij}) = 4A_{ij}\left[\left(\frac{\rho_{ij}}{r_{ij}}\right)^{12} - \left(\frac{k_{ij}\rho_{ij}}{r_{ij}}\right)^{6}\right] \quad (2)$$

The corrective coefficient k_{ij} means that the Eu^{3+} is attracted by the silver nanoparticles, because the strong cation induces a negative charge on it. k_{ij} is set to 1 for Ag–Ag interactions.

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Table 1
Composition of the simulated samples.

Atoms	Eu	Ag	Na	Si	O
Eu–glass	656	–	32 112	32 440	81 920
Eu–Ag–glass	656	3280	28 832	32 440	81 920

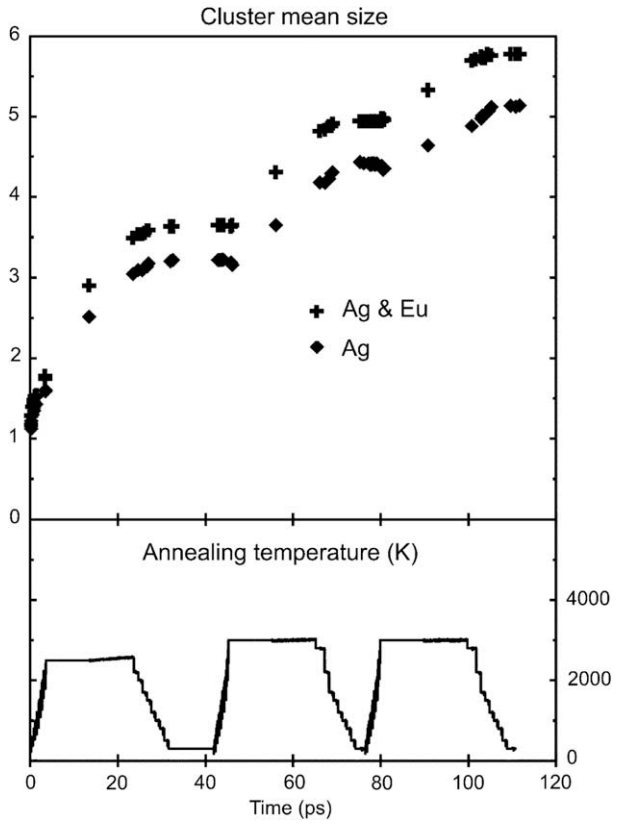

Fig. 1. Temperature (bottom) and mean particle size (top) as a function of the annealing time.

Firstly, the europium doped-glass is prepared by simulating a sample of 147 128 atoms. The percentage of europium is 0.45 at.%. This percentage is kept in the final composition of the glass containing silver. The sample containing silver is obtained by substitution of Na^+ by Ag^0, simulating both an ionic exchange and the silver reduction. The percentage of silver is 2.23 at.% (Table 1). This simulates a glassy density of 2.616 g/cm^3 within a box of $14.5 \times 14.5 \times 10.1$ nm^3.

Several stages have been performed in order to get glass samples with silver and europium nanoclusters. Firstly, the europium doped sodosilicate glass is obtained by cooling from the melt. Secondly, sodium ions are substituted by silver. Thirdly, three successive numerical annealings are performed at temperatures that are roughly half the melting temperature of the glass (Fig. 1). It should be notice that the simulated temperatures (several thousand of degrees during 30 ps) are not realistic but correspond to values often encountered in MD simulations of glasses [30].

3. Results and discussion

In a sodosilicate glass, the mixing of sodium and silicon oxide is good. Sodium is a network modifier, breaking numerous Si–O bonds and thus allowing a lower melting temperature for the sodosilicate glass than for silica. The substitution of randomly chosen sodium ions by silver ions insures a good homogeneity for the process. This can be seen on the first snapshot (Fig. 2a). One can see a homogeneous repartition of silver atoms and no cluster. In this initial configuration, less than 16% of the Ag atoms belong to a cluster of size three or more. Table 2 shows the cluster size distribution per number of Ag atoms as a function of the Ag atoms before annealing. The size distribution before annealing shows that essentially one-atom-particles is grown, which confirms the observation in Fig. 2a.

The annealing process reduces the viscosity of the glass, the silver atoms can now migrate and the mean size of clusters increases with the annealing time. In Fig. 1b one can see the snapshot after an annealing of 100 ps and the mean particle size is plotted with respect to the annealing time (Fig. 1). One can then depict that

Table 2
Cluster size distribution before annealing.

Size (atom per cluster)	1	2	3	4	5	6
Size × number/total number (%)	64.0	20.7	8.8	3.7	1.5	1.2

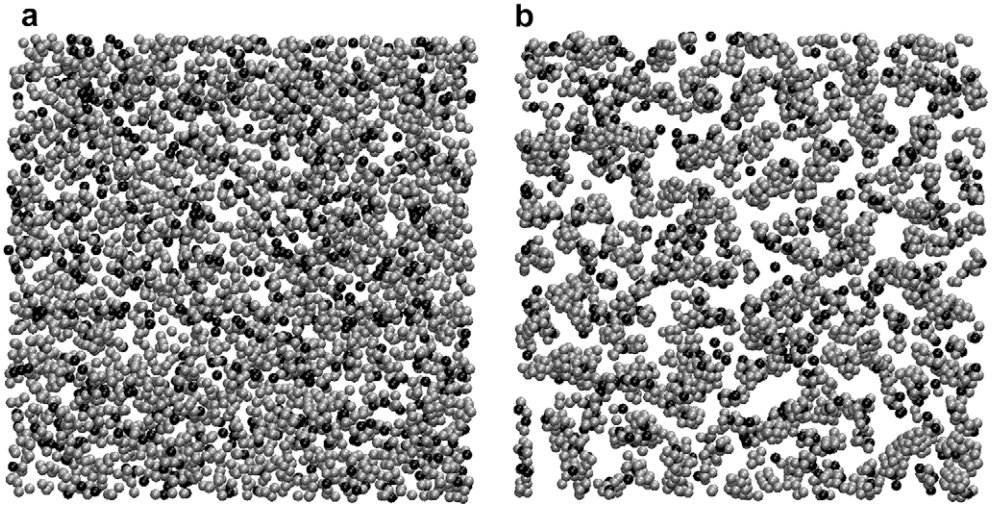

Fig. 2. Snapshots of the simulated microscopic structures. Eu^{+3} ions are in black and Ag atoms in grey. For clarity Si, Na and O are not drawn. (a) Snapshot before annealing, showing a homogeneous repartition of silver atoms and no cluster; and (b) after the annealing procedure pure Ag particles and Ag–Eu nanoalloys have been simulated.

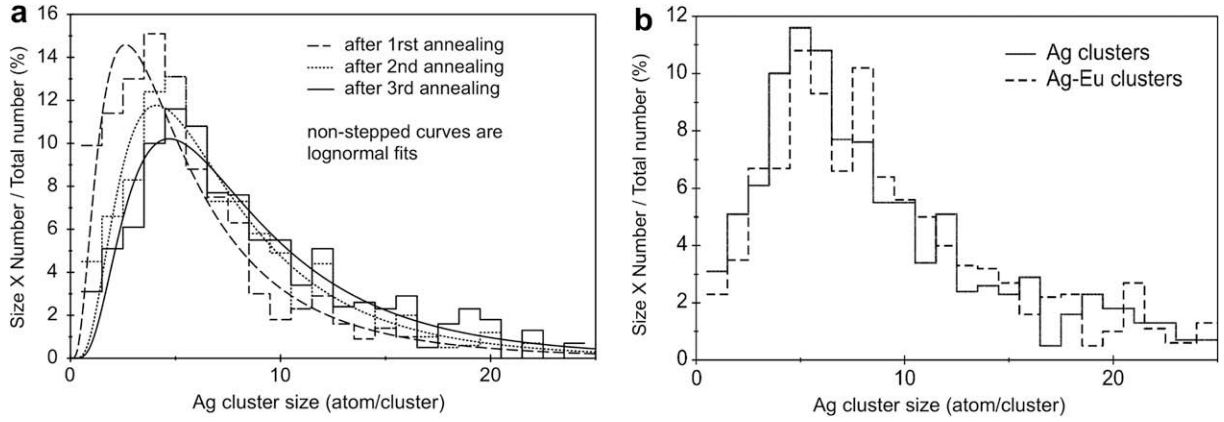

Fig. 3. Particle size distributions (a) after each annealing; lognormal fitting curves are drawn; and (b) comparison of Ag clusters distribution and Ag–Eu clusters distribution after the 3rd annealing.

before the heat treatment only very few clusters of 2 or 3 atoms have grown can be observed. After the annealing procedure (Fig. 2b) pure Ag as well as Ag–Eu nanoalloys are formed, with different sizes. This nanoalloy composition is explained because the silver nanoparticles are neutral and should attract the strong metal cation Eu^{3+} by induction. As one can note in Fig. 1, the mean particle contains 5.8 atoms, being 5.2 for Ag and 0.6 for Eu in average ($Ag_{5.2}Eu_{0.6}$), which reproduces satisfactorily the experimental Ag_5Eu composition after EDAX measurements [11]. These latter measurements have been performed in a fluoroborate ($B_2O_3 + CaF_2$) glass and using the Sb_2O_3 for silver reduction proposes.

After annealing processes lognormal curves should fit the particle size distributions (Fig. 3a). The point to be considered is in Fig. 3b. If only Ag particles are considered, lognormal curves always fit the particle size distributions. However, as Ag–Eu nanoparticles are present, lognormal curves does not fit the particle size distribution anymore. Then, at least two systems or a very inhomogeneous system of nanoparticles should grow. This has been observed before in a fluoroborate glass without Sb_2O_3 [13].

From the photonic point of view, the Ag–Eu proximity should be observed, because the spectroscopic behaviour of Ln^{3+} containing glasses is clearly modified. Local electric field enhancement or Ag - ↔ Eu energy transfer are the phenomena invoked to explain the spectroscopic changes [12,14,15].

4. Concluding remarks

Based on the fact that the growth and optical properties of silver particles in glass are not completely understood, molecular dynamics simulation has been employed to simulate the growth of Ag nanoparticles in a sodosilicate glass containing Eu^{3+} ions. The known potentials for all kind of interactions in glasses and for growing silver particles have been used, and a modified Lennard-Jones potential was successfully introduced to create attraction between the silver particles and the Eu^{3+}. The simulated nanoalloy mean composition $Ag_{5.2}Eu_{1.3}$ is satisfactorily close to the experimental average composition Ag_5Eu, obtained after EDAX measurements. Further, the size distributions after heat treatment have been fitted by lognormal curves.

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