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Changes in irradiated LnSiAlO(N) glasses at a microscopic scale

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Abstract

Six oxide and oxynitride glasses from three different M–Ln–Si–Al–O(–N) systems (where M is an alkaline-earth and Ln a rare earth) have been irradiated by Kr, Ni and S ions, with different energies varying from 350 to 700 MeV. Neither micro-bubble formation nor crystallisation are evidenced, but the irradiated glasses exhibit an anisotropic deformation under the ion beam. The main crack mode developed during scratching is shifted from radial for the pristine glasses to lateral for all the irradiated glasses. The hardness of each glass decreases when irradiated for all the incident ions used. This decrease appears to be in close relation with the electronic stopping power of the incident particle, and is associated with a change in the indentation mechanism (from normal to anomalous behaviour). The evolution of the scratches in the material depth confirms the change in deformation mechanism and the strong dependence between the hardness of the irradiated material and the electronic stopping power of the incident ion. Three phenomena can be the source of the changes in the properties: the creation of internal stresses during irradiation, the creation of point defects and the cross-linking of the silicate network.

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1. Introduction

In radioactive waste management, transmutation appears as an alternative to a potential disposal in a deep geological site [1] but it requires the insertion of the separated wastes in a matrix. Up to now, mainly ceramics were tested as transmutation matrices but most of them become amorphous under irradiation in the transmutation conditions, among which are heavy-ions bombardments (ions of a 100 MeV and a 100 amu simulate atoms generated during transmutation) [2–4]. However the mechanism of this amorphisation is not well understood yet.

The various allotropic forms of silica, such as quartz, trydimite, and fused silica, lead under irradiation to a unique amorphous compound [5,6] of which structure and properties differ from the one of fused silica [7]. Thus it is interesting to examine amorphous materials' evolution under heavy-ion irradiation and Si–Al–O–N glasses were chosen as suitable materials for such a study.

M–Si–Al–O(–N) glasses have been studied for more than 30 years now, and even if their structure is not extensively known, particularly in terms of medium range order, numerous studies gave information on the first coordination sphere of each cation involved in the network [8–21]. In M–Si–Al–O(–N) system, Si is a tetrahedrally coordinated structural network former, forming rather covalent bonds with oxygen or nitrogen. Metals are modifiers forming rather ionic bonds mostly with oxygen, creating non-bridging oxygen (NBO) in the formative network.

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Aluminium is an intermediate cation and either can be network former or network modifier.

Rare earth aluminosilicate glasses exhibit high mechanical properties and high characteristic temperatures. The substitution in this system of oxygen by nitrogen to produce oxynitride glasses leads to even better properties [22–29]. Ab initio calculations of Young's modulus [30] and considerations on the cationic field strength of different network modifiers led to the choice of three different vitreous systems (Ln–Mg–Si–Al–O–N, with Ln = Y or Nd and La–Y–Si–Al–O–N), to study glass behaviour towards irradiation. The authors have reported about the properties and structure of those glasses in a former study [31]. The most noticeable compositional effect on properties is the partial substitution of the oxygen by nitrogen. However, cationic substitution is not negligible as the amount of non-bridging oxygen (NBO) plays a key-role in glass properties. In order to check the influence of nitrogen and of NBO content on the glasses' behaviour under irradiation, they were exposed to swift heavy-ion bombardment. Particular attention was paid to the evolution of their hardness after irradiation.

2. Experimental

2.1. Glass synthesis and characterization

Compositions of the glasses are summarized in Table 1. SiO_2, Ln_2O_3, $MgSiO_3$, Al_2O_3 powders (reagent grade) were dried at 800 °C for 12 h. Powders were weighted and mixed for 1 h in a glass bottle. As AlN is less likely to decompose at high temperatures than Si_3N_4 [32,33] it was consequently used to introduce nitrogen in the compositions. The raw mixtures were molten for 1 h in a molybdenum crucible in an induction furnace under high purity nitrogen atmosphere. The melt was quenched and then crushed in coarse pieces. Glass powders of a granulometry <20 μm were obtained by milling and sieving. The powders were pressed to pellets (30 mm diameter, 4 mm thickness) by uniaxial hot pressing in a carbon mould. The mould was heated with a heating rate of 10 °C/min to the pressing temperature ($T_g + 50$ °C). Ten megapascal pressure was applied for 45 min before 1 h annealing at the glass transition temperature followed by a slow decrease to room temperature (2 °C/min). This shaping stage allowed to obtain homogeneous and stress free pellets, which were then cut and mirror polished with a diamond paste.

Table 1
Composition (at.%) of the studied glasses

Composition	Y	Nd	La	Mg	Si	Al	O	N
YMG	4.6			6.1	15.8	11.5	61.9	
YMGN	4.7			6.3	16.2	11.8	54.9	5.9
NDMG		6.8		5.9	14.9	10.6	61.8	
NDMGN		7.0		6.1	15.3	10.9	55.3	5.5
LAY	5.3		5.3		15.8	10.5	63.2	
LAYN	5.4		5.4		16.0	11.0	57.0	5.4

XRD powder diagrams were recorded for each glass after quenching and pressing. All the glasses are amorphous according to the X-ray diffraction pattern. Morphology studies by SEM additionally evidenced that the glasses were free of crystalline impurities. The nitrogen and oxygen contents were measured by combustion analysis (LECO apparatus) and the cationic contents were determined by chemical analysis (wet chemistry). The experimental compositions of the glasses are in good agreement with their nominal compositions, indicating no significant loss occurred during synthesis.

2.2. Irradiation

Bulk glasses ($4 \times 3.5 \times 30$ mm) and wafers ($4 \times 0.3 \times 20$ mm) were irradiated at the CIRIL-GANIL (Caen, France). A part of each sample was masked by a 200 μm thick aluminium foil to keep a pristine part as a reference. The ions' projected penetration range R_p and the average electronic and nuclear stopping powers ($\langle S_e \rangle$ and $\langle S_n \rangle$) calculated using the SRIM software [34] are summarized in Table 2 with the corresponding ions and energies.

Kr ions were used as they provide a realistic simulation of fission products generated during transmutation. Ions of lower mass (S and Ni) were also chosen as incident particles to examine the electronic stopping power influence on the irradiation damage of the material ($S_{e_{Kr}} > S_{e_{Ni}} > S_{e_S}$).

2.3. Hardness measurement

The hardness H (Meyer's definition) was measured from Vickers indentations, and calculated using the following equation:

$$H = \frac{2P}{d_{app}^2}, \tag{1}$$

where P is the applied load and d_{app} the indentation trace diagonal. Ten indentations were performed all along the surface of each sample in order to obtain an average value. The experimental standard deviation of ±0.1 GPa is considered as the measurement error.

Elastic recovery [35,36], surface energy contribution, load for the initiation of permanent plastic deformation, tip radius of the indentor [37] or pile-up phenomena [38] are as much parameters to explain the ceramics', alloys' or glasses' hardness decrease with the increase of the applied load, the so-called indentation size/load effect (ISE). This load/size dependence effect was investigated by increasing the indentation load (from 0.49 to 9.81 N) on NDMGN before and after irradiation (2×10^{13} cm^2 Kr, 365 MeV).

2.4. Scratching experiments

Scratching allows to screen in a rapid and clear way the different damaging modes appearing in glasses