

MD STRUCTURAL STUDY OF $23Y_2O_3\text{-}77Al_2O_3$ AND $23La_2O_3\text{-}77Al_2O_3$ GLASSES

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Submitted November 7, accepted January 28, 2009

Keywords: Molecular dynamics, Ab initio, Structure, Yttrium/lanthanum-aluminate glass

The ab-initio molecular dynamics (MD) calculations of the yttrium aluminate and lanthanum aluminate binary systems $23R_2O_3\text{-}77Al_2O_3$ ($R = Y, La$) were performed with help of the Vienna ab-initio simulation package VASP. Both the R-O equilibrium distances and R/O and Al/O coordination numbers calculated from the partial pair radial distribution functions (PP RDF) obtained for MD simulated glass at the temperature of 300 K are in a reasonably good agreement with the published neutron diffraction and X-ray diffraction studies. The structural differences between glasses studied by MD calculation were attributed to the higher network modifying activity of the lanthanum oxide which comes from the higher electropositivity and bigger ionic radius of lanthanum in comparison with yttrium.

INTRODUCTION

Binary yttria-alumina and lanthana-alumina glasses and melts attract a significant attention of both glass science and ceramics technology [1]. Alumina and yttria are used as additives for liquid phase sintering of Si_3N_4 , SiC, and SiAlON ceramics, yttrium-aluminum garnet ($YAG\text{-}Y_3Al_5O_{12}$) has broad industrial applications (e.g. laser technology), and $YAG\text{-}Al_2O_3$ eutectic is a promising candidate for the production of fibers for reinforcement of ceramics and metals. From the theoretical point of view structures of these glasses attract an attention due to the phenomenon of polyamorphic transitions, i.e. transitions between high-density and low-density amorphous phases [2]. On the other hand, due to the high tendency to crystallization the experimental synthesis of yttria - alumina and lanthanum – alumina glasses in a broader compositional range needs special contemporary experimental techniques allowing extremely high cooling rate of melt [3]. Thus the experimental studies devoted to $Y_2O_3\text{-}Al_2O_3$ and $La_2O_3\text{-}Al_2O_3$ glasses were relatively scarce in the past. Among the structural studies the ^{27}Al magic angle spinning nuclear magnetic resonance (MAS NMR) spectroscopy and X-ray and neutron diffraction studies [2, 4-6] have to be mentioned. The presence of AlO_4 , AlO_5 and AlO_6 coordination polyhedra were found by ^{27}Al MAS NMR spectroscopy in studied glasses. From X-ray and neutron diffraction data of these glasses it was

found the average Al/O coordination a little bit higher than 4.0 and pair correlation function peaks close to 1.80 Å. The values close to 7.0 were obtained for both Y/O and La/O coordination. First peak positions at PP RDFs for Y/O and La/O were found at (2.27-2.52) Å. These results imply the prevailing tetrahedral Al/O coordination and octahedral Y/O coordination in the structure of the studied glasses.

Among simulations the classical MD simulation [7, 15] and our *ab-initio* MD study of $23Y_2O_3\text{-}77Al_2O_3$ melt at 2500K should be mentioned [8].

The present paper deals with the *ab-initio* MD study of the $23R_2O_3\text{-}77Al_2O_3$ ($R = Y, La$) glass at 300 K. The motivation for this structural study is the need of the direct connection between the structural features on one side and the glass forming ability on the other. The obvious future extension of the present work will reside in enlarging the study to broader compositional range.

COMPUTATIONAL DETAILS

The *ab-initio* MD calculations, using the Hellmann-Feynman forces, of the bulk yttrium/lanthanum aluminate systems were done with help of the Vienna ab-initio simulation package VASP [9]. The projector augmented wave (PAW) pseudopotentials [10] were used. The pseudopotentials can be found in the VASP pseudopotential PAW_PBE database as: Al, Y_sv, La_sv, and O_s. The potential energy calculations were performed with a default plane-wave cut-off (213 eV)

Paper presented at the Czech and Slovak Conference on Glass, Luhačovice, November 5-7, 2008.

and Brillouin-zone sampling was restricted to the Γ -point only.

The $23R_2O_3\cdot 77Al_2O_3$ ($R = Y, La$) systems were simulated by *ab-initio* MD. The systems contained 160 atoms: 49 Al, 15 R, and 96 O. Both MD models were prepared in a similar way as in our previous works [8, 11-14]. Atoms were randomly placed into the cubic computational box with side length corresponding to experimental density [6]. First, the systems were thermodynamically equilibrated and structurally relaxed for 2 picoseconds (ps) at 5000 K. Then, the temperature was decreased to 4000 K, 2500 K, 1000 K and finally to 300 K. At each temperature the systems relaxed for 10 ps. Temperature was rescaled in every 20 time-steps. The time-step of the numerical integration of the equations of motion was 0.002 ps. Atom positions were recorded in every 20 time-step and later used in calculations of radial distribution functions (RDF) and coordination numbers.

RESULTS AND DISCUSSION

The radial distribution function (RDF) together with the Al/O and R/O PP RDFs for the both studied systems, $23R_2O_3\cdot 77Al_2O_3$ ($R = Y, La$), i.e. AY23 and AL23, are plotted in Figures 1 and 2. The equilibrium distances for the Al-O bond (1.81 Å) and for the Y-O bond (2.28 Å) in the AY23 were found as positions of maxima of PP RDF's in Figure 1. These values agree well with the experimental data obtained with X-ray and/or neutron scattering experiments: Al-O bond (1.81 Å in AY20 and 1.79 Å in AY25 [4]) and Y-O bond (2.28 Å in AY20 and AY25 [4] and 2.27 Å in AY27 and YAG glasses [6]). Integration of the PP RDF's in Figure 1 provided the average coordination numbers of 4.55 for Al/O coordination, and 7.07 for Y/O. These results agree (within uncertainty limits) with the experimental values [4] of 4.38 ± 0.22 in AY20 and 4.16 ± 0.21 in AY25 for Al/O coordination. The Y/O coordination number obtained via

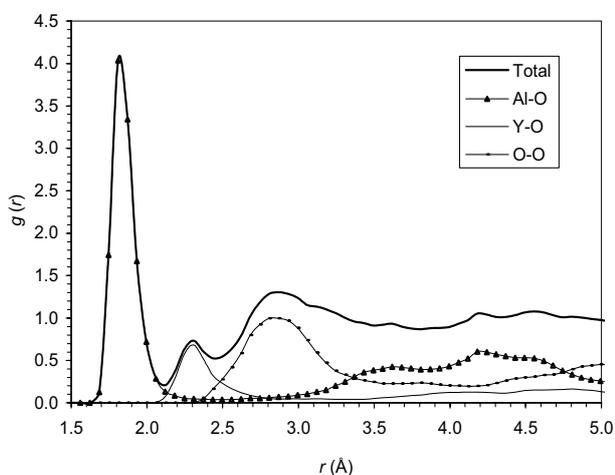


Figure 1. Total RDF (thick line) and PP RDF's (thin lines) of $23Y_2O_3\cdot 77Al_2O_3$ (AY23) glass at 300K.

MD simulation (7.07) is close to the experimental value of 6.90 in AY27 (value of 6.10 in YAG glass is lower) [6].

In the lanthanum AL23 system the data obtained from PP RDF's in Figure 2. are the equilibrium distances for the Al-O bond (1.80 Å) and for the La-O bond (2.41 Å) and corresponding coordination numbers, 4.48 for Al/O and 7.92 for La/O pairs. These values we can compare with X-ray and/or neutron scattering experimental data: Al-O bond (1.79 Å in AL25 [4]) and La-O bond (2.50 Å in AL25 and 2.52 Å in LAG glasses [4, 6]) and corresponding coordination numbers, 4.55 ± 0.25 for Al/O in AL25 and 7.0 ± 0.1 for La/O in LAG glass. The difference between experimentally obtained R/O coordination numbers for LAG and YAG ($CN(La/O, LAG) - CN(Y/O, YAG) = 7.0 - 6.1 = 0.9$) is almost the same as the difference between the MD results obtained for AL23 and AY23 ($CN(La/O, AL23) - CN(Y/O, AY23) = 7.92 - 7.07 = 0.85$). The higher coordination number obtained for lanthanum in comparison with yttrium corresponds well to bigger radius and higher electropositivity of lanthanum ion and thus its higher network modifying activity.

In Table 1 we present in detail the Al/O coordination in MD simulated AY23 and AL23 glasses and in real AY24 glass [5]. It can be seen both MD results and the experimental results obtained for Y_2O_3 glass provide significant abundance of three types of Al/O coordination. The experimental result gives the AlO_4 amount higher of about 17 %. The MD gives the broader distribution of the coordination polyhedra that may be (as usually) attributed to the extremely high cooling rate applied in MD simulations. The experimental data for the lanthanum

Table 1. Distribution of Al/O coordination numbers in MD simulated AY23 and AL23 glasses at 300K and in real AY24 glass studied with ^{27}Al MAS NMR spectroscopy [5].

	MD AY23	MD AL23	Exp. AY24
$Al^{[4]}$	50.5	56.9	67.5
$Al^{[5]}$	44.2	37.9	24.5
$Al^{[6]}$	5.3	5.3	7.8

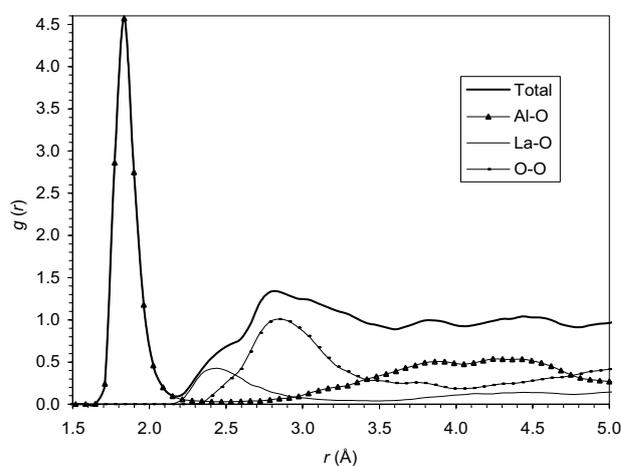


Figure 2. Total RDF (thick line) and PP RDF's (thin lines) of $23La_2O_3\cdot 77Al_2O_3$ (AL23) glass at 300K.

glass are not accessible. But we can suppose the same trend as in case of yttrium glass. On the other hand when MD results obtained for yttrium glass are compared with those for lanthanum glass a little bit higher amount of four-coordinated Al atoms can be found in the latter case. This is in harmony with the assumption of higher network-modifying activity of La_2O_3 . Thus, lanthanum glass is “shifted” closer towards the per-alkaline region where the four-coordinated aluminum is expected.

The O-Al coordination is similar in both MD studied glasses, see Table 2. The relatively high content of triclusters $\text{O}^{[3]}$ can be attributed to the octahedral aluminum coordination. On the other hand, due to the tricluster formation a significant amount (13-14%) of single aluminum coordinated oxygen is formed. In fact these oxygen atoms form bonds to the yttrium/lanthanum atoms.

Table 2. Distribution of O/Al coordination numbers in MD simulated AY23 and AL23 glasses at 300K.

	MD AY23	MD AL23
$\text{O}^{[1]}$	12.9	13.9
$\text{O}^{[2]}$	45.2	49.0
$\text{O}^{[3]}$	39.0	31.4
$\text{O}^{[4]}$	3.0	5.7

Table 3 reports Y/O and La/O coordinations in MD simulated glasses in detail. It can be seen that in harmony with the bigger atomic radius and the assumption of stronger network modifying activity of lanthanum, the distribution of La/O coordination polyhedra is shifted to the higher coordination numbers (7-9) when compared with those of yttrium (5-8).

Table 3. Distribution of Y/O and La/O coordination numbers in MD simulated AY23 and AL23 glasses at 300K.

	MD AY23	MD AL23
$\text{Y}^{[5]}$	6.3	$\text{La}^{[5]}$ 0.0
$\text{Y}^{[6]}$	8.3	$\text{La}^{[6]}$ 1.3
$\text{Y}^{[7]}$	57.2	$\text{La}^{[7]}$ 27.9
$\text{Y}^{[8]}$	28.1	$\text{La}^{[8]}$ 47.9
$\text{Y}^{[9]}$	0.1	$\text{La}^{[9]}$ 22.6
$\text{Y}^{[10]}$	0.0	$\text{La}^{[10]}$ 0.2

CONCLUSIONS

Both the R-O equilibrium distances and R/O and Al/O coordination numbers calculated from the partial pair radial distribution functions (PP RDF) obtained for MD simulated glass at the temperature of 300 K are in a reasonably good agreement with the published neutron diffraction and X-ray diffraction studies. The structural differences between glasses studied by MD calculation were attributed to the higher network modifying activity

of the lanthanum oxide which comes from the higher electropositivity and bigger ionic radius of lanthanum in comparison with yttrium. Further MD study of broader compositional range of both studied systems is needed.

Acknowledgement

This work was supported by Agency for Promotion Research and Development under the contract APVV-20-P06405, and by the Slovak Grant Agency for Science under the grant VEGA 1/3578/06 and by the Grant Agency of the Czech Republic through the Grants No 104/07/P420 and 104/06/0202. This study was also a part of the research programme MSM 6046137302 preparation and research of functional materials and material technologies using micro and nanoscopic methods and the project No 2A-ITP1/063, „New glass and ceramic materials and advanced concepts of their preparation and manufacturing“, realized under financial support of the Ministry of industry and trade. The Supercomputing Centre of Czech Technical University contributed with SGI Altix 3700 supercomputing facility.

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