

Oxygen 2*p* partial density of states in a typical oxide glass B₂O₃

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1 Introduction

The partial structures of B₂O₃ glass were investigated by Suzuya *et al.* [1] using a combination of high-energy x-ray diffraction, neutron diffraction, and reverse Monte Carlo modeling. As predicted by Zachariasen [2], the BO₃ triangle building blocks are connected with each other to form the network structures by sharing the O atoms.

Due to improvements of high-flux x-ray and neutron sources, information on nearest neighbor atomic configurations becomes much reliable even in binary or multi-component glasses. However, positions of second-neighboring atoms are still hardly determined because second peaks in pair distribution functions available from diffraction data are rather blurred and contain multiple pair contributions. XAFS does not help to solve this difficulty due to the short lifetime of the x-ray-excited electrons and rather fluctuated interatomic distances between the central and the second-neighboring atoms in glasses. Thus, another experiment is necessary to determine bond angles in glasses.

Information on O 2*p* partial density of states (DOS) is helpful to discuss bond angles around O atoms in oxide glasses since they are highly affected by O 2*s*-2*p* hybridizations, such as *p* (90°), *sp*³ (109°), *sp*² (120°), *sp* (180°). Soft x-ray emission spectroscopy (SXES) is a photon-in photon-out method, *i.e.*, a charging-free technique, and element- and quantum-number-sensitive. Therefore, SXES is a very powerful tool for obtaining valence-band DOS for insulating materials [3].

We have performed O 2*p* SXES measurement on the B₂O₃ glass. In addition, soft x-ray absorption spectra (SXAS) were measured around the O *K* absorption edge simultaneously. To examine the validity of these experimental results and for the further discussion on the bond angle distribution around the O atoms, *ab initio* molecular dynamics (MD) simulations were carried out. Details of the results are given elsewhere [4].

2 Experimental and theoretical procedure

SXES and SXAS experiments were carried out at BL-2C of the PF-KEK. Synchrotron radiation from a linear undulator insertion device was monochromatized using a varied-line-spacing plane grating with a line density of

1000 lines/mm. The SXES spectra were measured using a Rowland-type monochromator with a spherical grating with a radius of 5 m and a line density of 1200 line/mm and a photon detector with a CsI-coated multichannel plate. The total energy resolution of SXES was ~0.5 eV.

SXES spectra of O 2*p* valence-band partial DOSs were obtained with incident photon energies of about 560 eV, more than 20 eV above the corresponding 1*s* absorption edge (~ 537 eV). The SXAS spectra were measured around the O 1*s* absorption edge in O *K* partial fluorescence mode. The energy resolution of SXAS was ~ 0.1 eV. The SXES and SXAS experiments were carried out at room temperature. Clean sample surfaces were obtained by scraping *ex situ*, after which the samples were immediately loaded into the vacuum chamber. The experiments were carried out under ultrahigh vacuum condition of less than 10⁻⁷ Pa.

The *ab initio* MD simulation was based on the density functional theory with the generalized gradient approximation (GGA) for the exchange-correlation energy. Projector augmented wave potentials were employed for the electron-ion interaction with valence electron configurations 2*s*²2*p*¹ and 2*s*²2*p*⁴ for B and O, respectively. The electronic wavefunctions and the electron density were expanded using plain wave basis sets with cutoff energies of 30 and 250 Ryd, respectively. Only the Γ point was used to sample the Brillouin zone of the cubic MD supercell. We used 120 atoms (48 B and 72 O) with periodic boundary conditions with a side length of 1.149 nm corresponding to the number density of this system. The constant-temperature MD simulations were performed at 300 K for 4,000 steps in time steps of 1.21 fs (totally 4.84 ps). The initial configuration was obtained from the simulation for the liquid state at 4,000 K, and then, it was gradually cooled down (for more than 26 ps) to 300 K.

3 Results and Discussion

Figure 1 shows the SXES and SXAS spectra, *i.e.*, O 2*p* partial valence- and conduction-band DOS, of glassy B₂O₃ given by solid and dashed curves, respectively. The characteristic structures of the spectra indicated by

arrows, may be assigned, i.e., bonding states with B sp^2 hybrids at -12 and -9.5 eV, non-bonding states at -4 eV, and anti-bonding states with B sp^2 hybrids at 5-6 eV.

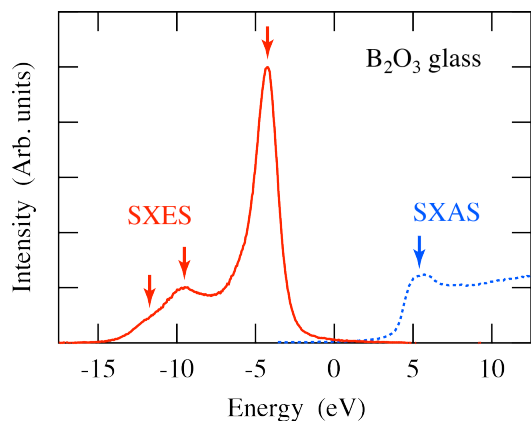


Fig. 1: SXES (solid curves) and SXAS (dashed curves) spectra of glassy B_2O_3 . The figure is taken from Ref. [4].

Figure 2 shows again the O $2p$ SXES spectra (circles) and O $2p$ partial DOS obtained from *ab initio* MD simulation (solid curves) for the comparison. Although small differences are seen, such as in the peak heights, the peak positions of the spectral structures in non-bonding and bonding states are in good agreement with each other. Thus, it is concluded that the present *ab initio* MD simulation successfully reproduces the atomic and electronic structures of glassy B_2O_3 with the existing experimental data.

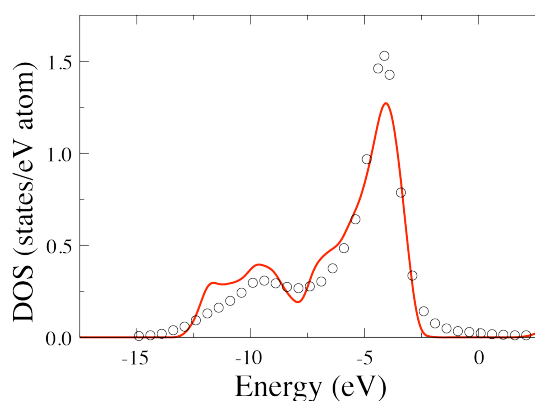


Fig. 2: The O $2p$ SXES spectra (circles) and O $2p$ partial DOS obtained from *ab initio* MD simulation (solid curves). The figure is taken from Ref. [4].

As mentioned in the introductory section, the O $2p$ partial DOS is correlated with the θ_{BOB} distributions in this glass. To examine this relation theoretically, the bond angle dependence of the O $2p$ partial DOS is calculated and the θ_{BOB} in glassy B_2O_3 is $130^\circ \pm 5^\circ$.

There have been naive arguments on the fraction of B atoms in boroxol B_3O_3 rings, f , in the glassy B_2O_3 network. The boroxol rings were considered to play an important

role in this glass, quite different from that in the crystalline forms.

A quantitatively sensitive probe to determine the local structure in B_2O_3 glass is NMR. Jellison *et al.* [5] measured ^{11}B and ^{17}O NMR spectra and concluded $f = 0.75 - 0.90$ using a boroxol model, where it was obtained that 55% of O atoms are contained in the ring with $\theta_{BOB} = 120^\circ$ and 45% of O atoms are located between the rings with $\theta_{BOB} \sim 130^\circ$, and the average value, $\langle \theta_{BOB} \rangle$, is $\sim 125^\circ$. Hannon *et al.* [6] analyzed their well accurate neutron diffraction data, and concluded that f is 0.80 ± 0.05 . There, the θ_{BOB} value for the sharing O atoms was fixed to be 130° , i.e., $\langle \theta_{BOB} \rangle = 124^\circ$.

On the contrary, a combination of x-ray and neutron scattering with help of RMC modeling was investigated [7], and the models containing large amounts of boroxol rings ($f > 0.3$) show significantly large deviations from the experimental data than those with small fraction ($f \leq 0.2$). The theoretical f values could be directly obtained from the atomic configurations, which indicated generally very small values, such as 9.4% by Umari and Pasquarello [8] and 19% by the present study. The $\langle \theta_{OBO} \rangle$ values were mostly 120° indicating highly planar BO_3 triangles, and the θ_{BOB} values for inside and outside of the boroxol rings were 120° and slightly smaller than 135° , respectively.

From the combination of the present SXES data and *ab initio* MD simulation, the $\langle \theta_{BOB} \rangle$ value should be $130^\circ \pm 5^\circ$. The RMC analyses may have too small $\langle \theta_{BOB} \rangle$ values although $f \sim 0.2$. Since the *ab initio* MD simulations always exhibited the planar rings, it is necessary to include the *electronic* contributions to the structure.

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