

Mg K-Edge XANES Spectra in Crystals and Oxide Glasses: Experimental vs. Theoretical Approaches

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Abstract. Experimental Mg K-edge XANES spectra were obtained for crystals and synthetic glasses. To interpret the experiments, two different *ab initio* XANES calculation methods were employed. The first one is based on multiple-scattering calculations and muffin-tin potentials (FEFF package). The second uses a plane-wave basis set, norm-conserving pseudo-potentials, periodic boundary conditions. The resulting calculations for reference models with three different Mg coordinations are used to derive the best way to analyze the experimental XANES spectra for the glasses.

Keywords: XANES, Mg K-edge, glass, minerals, *ab initio* calculations, pseudo-potentials, multiple-scattering calculations.

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INTRODUCTION

Magnesium is an earth-alkaline that is often present in industrial and natural silicate glasses (from a few wt. % up to 30 wt. %). The presence of magnesium in the glasses influences significantly properties as viscosity, glass transition temperature and chemical durability [1]. It was shown [2] that the weathering rate of nuclear waste glasses is significantly increased when Mg is present.

In order to investigate the structural role of Mg in oxide glasses, X-ray Absorption Near Edge Structure (XANES) spectroscopy was employed at the Mg K-edge. XANES provides information about the local structures of magnesium in glasses, which is otherwise difficult to study with other methods [3]. The interpretation of the XANES spectra is not straightforward and *ab initio* calculations are needed to obtain the required information. In this paper, we present *ab initio* XANES calculations computed using two different packages: PARATEC including the XANES calculation implementation described in references [4,5] and FEFF [6]. The *ab initio* calculations are compared with the experimental

spectra to find the best conditions for simulating the XANES spectra at the Mg K-edge.

EXPERIMENTAL DETAILS

Synthetic silicate glasses, with composition XMS3 (in which X stands for either Li₂O, Na₂O, K₂O, Rb₂O or Cs₂O, M for MgO and S for SiO₂) and aluminosilicate glasses with different Aluminium Saturation Index ($ASI = Al_2O_3/(Na_2O + K_2O)$) (Table 1) were prepared from powdered oxides and carbonates. The starting materials were dried overnight, weighted, mixed in an agate mortar and placed in a platinum crucible. The crucible was heated up to 600°C in 30 minutes and held at this temperature for one hour to start the decarbonation of the mixture. The temperature was then elevated at 1550°C in one hour and maintained at this temperature during one hour to obtain a homogeneous melt. The bottom of the crucible was quickly poured into water to quench the melt into a glass. To ensure ASI glass homogeneity, the procedure was repeated 2-3 times. Compositions were checked by electron microprobe analysis (CAMPARIS, Univ. Paris 6, France). Three natural crystalline compounds containing Mg in 4-fold, 5-fold

and 6-fold coordination were selected: spinel (Mg_2AlO_4) [7], grandierite ($(\text{Mg,Fe})\text{Al}_3\text{SiBO}_9$) [8] and diopside ($\text{CaMgSi}_2\text{O}_6$) [9], respectively.

TABLE 1. Composition of ASI glasses.

Oxides	ASI=0.6	ASI=1	ASI=1.2
Al_2O_3	10.77	12.95	14.65
SiO_2	72.18	73.79	72.82
K_2O	8.26	6.04	5.7
Na_2O	5.44	3.92	3.7
MgO	3.35	3.3	3.14

Mg K-edge XANES spectra were collected on the LUCIA beamline of the SOLEIL facility [10], currently located at the Swiss Light Source, with an injected electron energy and current of 2.4 GeV and 350 mA, respectively. A two-crystal beryl (1010) monochromator was used as well as KB mirrors to focus the beam to $10\text{ }\mu\text{m} \times 15\text{ }\mu\text{m}$ (vertical and horizontal). The first inflection point of the Mg K-edge of metallic Mg at 1303 eV was used to calibrate the monochromator in energy. XANES spectra were recorded between 1280 and 1550 eV with energy steps of 0.2 eV in the edge region and with a counting time of 1 second per point. XANES spectra were collected in the fluorescence mode with a silicon drift diode detector. To increase the signal to noise ratio, three spectra per sample were averaged together. Samples were placed perpendicular to the beam and the detector was placed at 73° of the beam to minimize as much as possible self-absorption effects (found to be negligible). Spectra were deadtime corrected. Mg K-edge XANES spectra were normalized in absorbance using conventional methods (xafs package [11]).

RESULTS AND DISCUSSION

Normalized XANES spectra of glasses and models are presented in Figures 1 and 2, respectively. The XANES spectra of the glasses (Fig. 1) can be described by four features labeled (A' , A, B and C). When the alkaline ions are substituted, the relative intensities of these features vary (Fig. 1 (a)). The “pre-edge” feature A' is the highest for the smaller alkalis (Li, Na). Features A and B are almost identical for all glasses. In contrast, feature C increases with increasing alkali ionic radius. In CsMS3, feature C is split into 2 components (C_1 and C_2). XANES spectra of glasses with variable polymerization degree (XMS2 vs XMS3) do not show any differences (not reported here). On the contrary, the relative intensities of features A and B vary with the ASI (Fig. 1 (b)). Moreover, the feature C varies when the ASI changes from 0.6 to 1.2 and is more intense for ASI=0.6. However the “finger print” method is not sufficient to extract structural information from the XANES spectra

of glasses. *Ab initio* calculations are needed and should be tested on model compounds first.

Two methods were used to simulate the XANES spectra for the spinel, grandierite and diopside. The first method is a self-consistent full-potential approach: it uses a plane wave basis set, norm-conserving Trouillier-Martins pseudo-potentials and periodic boundary conditions. It reconstructs the all-electron wave function using the Projector Augmented Wave method [12] and computes the cross section as a continued fraction [4,5]. The second method uses the more widely used full multiple scattering formalism, based on self-consistent muffin-tin potentials (FEFF8.2 code) [6].

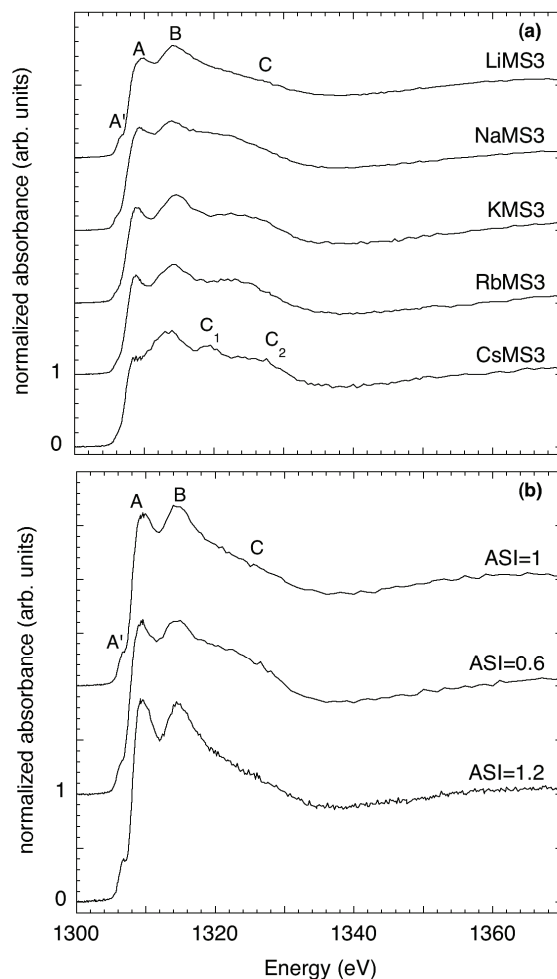


FIGURE 1. Normalized Mg K-edge XANES spectra of silicate glasses of composition XMS3 (a) and alumino-silicate glasses with variable ASI (b).

In the plane-wave method, supercells were built, including a 1s core-hole on one of the Mg atom: a $2 \times 2 \times 2$ trigonal supercell for spinel, a $1 \times 1 \times 2$ orthorhombic supercell for grandierite and a $1 \times 1 \times 2$ monoclinic supercell for diopside (containing 112, 120

and 80 atoms, respectively). The self-consistent potential was obtained in the local density approximation [13] with an energy cut-off of 60 Ry for the plane-wave expansion of the wave-functions, and a $2 \times 2 \times 2$ k -point grid. The cross section was calculated using a $4 \times 4 \times 4$ k -point grid. The continued fraction was calculated with a constant broadening parameter of 0.5 eV.

In FEFF8.2, muffin-tin exchange and correlation Hedin-Lundqvist potentials were used. Self-consistency calculations were refined with a radius of 4.0 Å around the central Mg. For the Full Multiple-Scattering calculations, we have chosen a radius of ~6.5 Å to obtain about 100 atoms in the simulated cluster. To simulate the central excited atom we used

the Z+1 approximation (otherwise FEFF fails to reproduce adequately the spectra).

Figure 2 shows the experimental and calculated XANES spectra for the three crystalline models and the two packages. For the three structures, the full-potential computed spectra (Fig. 2a) are in good agreement with experiment. Relative positions and intensities for the various features present in the three compounds modeled are reproduced. The results obtained with FEFF are in relatively fair agreement with the experimental spectra (Fig. 2b), for the spinel and the diopside, despite some high-energy shift. But, the calculation for the granddierite is not in agreement with the experiment.

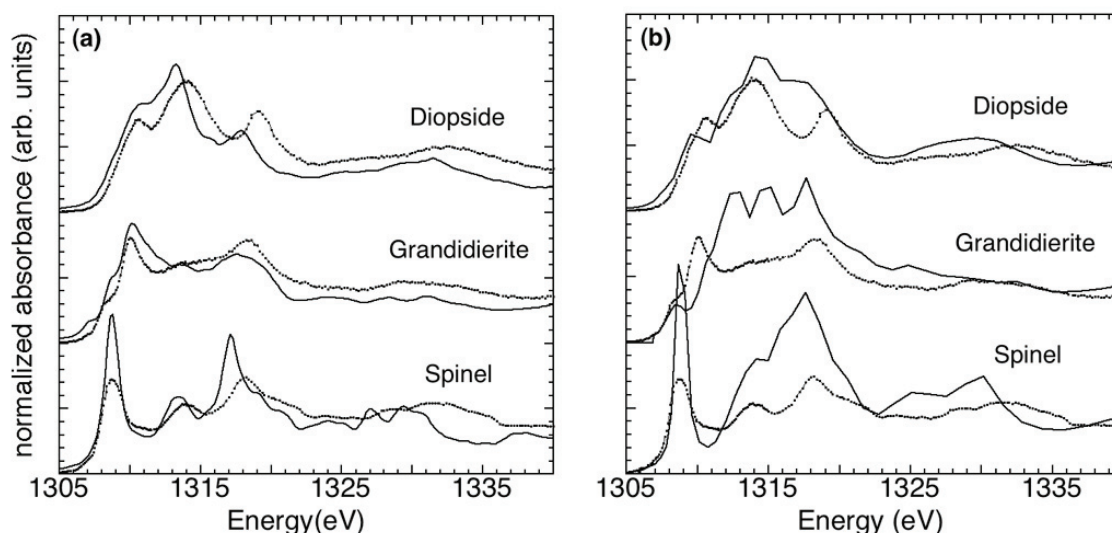


FIGURE 2. Comparison between experimental (dotted line) and calculated (full line) Mg K-edge XANES spectra of spinel (4-fold coordinated Mg), granddierite (5-fold coordinated Mg) and diopside (6-fold coordinated Mg): (a) full-potential plane-wave approach, (b) full multiple-scattering approach.

CONCLUSION

We have presented two different approaches to simulate the XANES spectra for reference models with the aim to understand the XANES collected for the oxide glasses. The most promising approach appears to be the plane-wave approach. Molecular dynamics simulations are underway to provide 3D models of the Mg-bearing glasses. *Ab initio* XANES calculations from these MD simulations will then be compared to the experimental spectra in order to better understand the influence of the alkali size and ASI on the XANES spectra.

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