Pressure-induced changes in local electronic structures of SiO$_2$ and MgSiO$_3$ polymorphs: Insights from ab initio calculations of O K-edge energy-loss near-edge structure spectroscopy

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ABSTRACT

Despite its important geophysical implications, direct probing of the local electronic structure of mantle minerals, such as MgSiO$_3$ perovskite and post-perovskite is experimentally challenging. Recent advances in ab initio calculations have allowed us to explore the details of the local electronic bonding structure around oxygen in MgSiO$_3$ polymorphs in Earth’s interior. Here, we calculate the O K-edge energy-loss near-edge structure (ELNES) spectra for SiO$_2$ and MgSiO$_3$ polymorphs (i.e., α-quartz, stishovite, enstatite, ilmenite-type MgSiO$_3$, MgSiO$_3$ perovskite, and post-perovskite) using ab initio calculations based on the full-potential linearized plane wave (FP-LAPW) method. The calculated O K-edge ELNES spectra for SiO$_2$ and MgSiO$_3$ polymorphs show characteristic oxygen K-edge features caused by distinctive local atomic configurations and topology around oxygen, and are in good agreement with previous experimental O K-edge X-ray Raman scattering (XRS) results. The O K-edge ELNES spectra for α-quartz and enstatite show similar edge features at ~538 eV, which is characteristic of corner-sharing oxygen sites (4Si-O-4Si). The spectra for stishovite and ilmenite-type MgSiO$_3$ show edge features with double peaks at ~537–538 and ~541–543 eV due to an electronic excitation from an oxygen in edge-sharing topology. The spectrum for MgSiO$_3$ perovskite shows a broad peak spanning from ~538 to ~543 eV, which results from corner-sharing oxygen with two six-coordinated silicon (6Si-O-6Si). The calculated O K-edge ELNES spectrum for MgSiO$_3$ post-perovskite shows a predicted main feature at ~543–545 eV, approximately 3 eV higher than that of MgSiO$_3$ perovskite. These O K-edge features systematically shift to higher energy with increasing degree of densification in atomic arrangement in the polymorphs (from enstatite, ilmenite, perovskite, to post-perovskite), indicating an increase in the energy of unoccupied oxygen 2p-state with pressure. The calculated O K-edge spectra also show the effect of densification on the changes in the edge features for the crystallographically distinct oxygen sites: the features for the corner-sharing oxygen move to higher energy from enstatite, perovskite, to post-perovskite. A drastic peak shift for edge-sharing O atoms in ilmenite-MgSiO$_3$ and post-perovskite is also observed. These results confirm that the oxygen K-edge features at ~540–550 eV for MgSiO$_3$ glass at pressures above ~20 GPa can be due to densification of the atomic configurations around oxygen in melt networks associated with enhanced proximity between oxygen atoms. The current method also shed light on a unique opportunity to probe the pressure-induced electronic bonding transitions and topology in diverse simple and complex oxides in Earth’s interior using ab initio calculations of O K-edge ELNES spectra.

Keywords: MgSiO$_3$ polymorphs, X-ray Raman scattering, energy-loss near-edge structure, high pressure, ab initio calculations

INTRODUCTION

Knowledge of the electronic and atomic structure of MgSiO$_3$ polymorphs is essential in understanding their elasticity, thermodynamic, and transport properties, but also in providing atomistic origins of the evolution and dynamics of the mantle in Earth’s interior (e.g., Hemley 1998; Price 2007 and references therein). Advances in in-situ high-pressure high-temperature experimental techniques combined with brilliant synchrotron X-ray radiation and theoretical calculations have allowed us to explore details of the atomic structures of crystalline MgSiO$_3$ polymorphs at high pressure (e.g., Hemley et al. 1998; Hirose 2006; Jeanloz and Williams 1998; Mao and Hemley 1998; Mao and Mao 2007; Mao et al. 1991, 2006a, 2006b; Oganov 2007; Oganov et al. 2010; Ohtani et al. 2005; Prewitt and Downs 1998; Shim 2008; Stixrude et al. 1998; Wentzcovitch et al. 2010; Xu et al. 2008 and references therein). For instance, the phase transition between MgSiO$_3$ perovskite (Pv) and post-perovskite (PPv) near the core-mantle boundary at ~125 GPa provides atomistic insight into the structure and heterogeneity in the D’ layer and ultralow-velocity zone (ULVZ) at core-mantle boundary (see Hirose 2006; Irfune and Tsuchiya 2007; Mao et al. 2006b; Murakami et al. 2004; Oganov and Ono 2004; Shim 2008 and references therein). Although the atomic structures of the MgSiO$_3$ phases at high pressure are well understood, direct