Atomistic origins of pressure-induced changes in the O *K*-edge x-ray Raman scattering features of SiO₂ and MgSiO₃ polymorphs: Insights from *ab initio* calculations

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Despite its fundamental importance in condensed matter physics and geophysical implications, establishing the systematic and direct link between the pressure-induced structural changes in crystalline and noncrystalline low-z oxides and their corresponding evolution in O K-edge core-electron excitation features under extreme compression has been challenging. Here we calculated the site-resolved partial density of states and O K-edge x-ray Raman scattering (XRS) spectra for two of the important oxide phases in the Earth's lower mantle, MgSiO₃ bridgmanite and post-bridgmanite, up to 120 GPa using *ab initio* calculations, revealing the electronic origins of the O K-edge features for oxides under compression. The absorption threshold (E_A) and band gap increase *linearly* with a decrease in the O-O distance in diverse SiO₂ and MgSiO₃ high-pressure phases [$E_A(eV) \approx$ $-10.9d_{O-O}(Å) + 34.4$], providing a predictive relationship between the E_A and the O-O distances in the oxide at high pressure. Despite densification, upon isobaric phase transition from bridgmanite to post-bridgmanite at 120 GPa, a decrease in band gap results in a decrease in edge energy because of an increase in O-O distance. The oxygen proximity is a useful structural proxy of oxide densification upon compression, as it explains the pressure-induced changes in O K-edge XRS features of crystalline and amorphous SiO₂ and MgSiO₃ at high pressures. These results can be applied to studies of the pressure-bonding transitions in a wide range of oxides under extreme compression.

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I. INTRODUCTION

Direct probing of the detailed bonding nature of crystalline and noncrystalline oxides at high pressure are among the fundamental and challenging questions in condensed matter physics. Particularly, the pressure-induced changes in atomic configurations in SiO₂ and MgSiO₃ at high pressures are critical in clarifying the chemical and physical evolution of the Earth's crust and mantle [1-3] and the atomistic origins of the seismic heterogeneities near the core-mantle boundary at a depth of $\sim 2850 \text{ km}$ [4–9]. In situ synchrotron x-ray Raman scattering (XRS) is a unique experimental method that probes the element-specific local electronic structures around low-z elements (e.g., O, B, Li, and C) and that has been used to explore the direct electronic bonding transitions of low-z oxides and silicates under extreme compression [10-14]. In particular, O K-edge XRS has provided insights into the changes in the bonding transitions of H_2O [15], SiO₂ [15–18], GeO₂ [19], B₂O₃ [20]; alkali borate [21–23] glasses; and diverse silicate glasses such as MgSiO₃ [24–26], CaMgSi₂O₆ [27], and multicomponent glasses [28]; as well as molecular solids and fluids, such as H₂O [29-33], and solid O_2 [34] phases at ambient and high pressure up to ~ 70 GPa. In addition to the first excitation shell (i.e., K edge) for low-z elements, L- and M-edge XRS processes for low- and high-z elements (e.g., Si $L_{2,3}$ -edge and Fe $M_{2,3}$ -edge XRS) have also been used to probe the pressure-induced changes in electron spin transition, oxidation states, and local coordination in Si, SiO₂, FeO, Fe₂O₃, FeCO₃, and FeS [15,35-39]. We also note that recent progress in x-ray emission spectroscopy has provided improved insights into electron-spin-state transition in the Fe 3*d* state in diverse crystalline and amorphous $(Mg,Fe)SiO_3$ phases ([40–45] and references therein).

While a detailed review of the previous experimental efforts to explore the O K-edge feature of crystalline and noncrystalline silica and silicates can be found elsewhere [10], a brief summary of these efforts is called for. The XRS experiment on SiO₂ glasses at high pressures up to \sim 51 GPa revealed the pressure-induced changes in the O K-edge XRS spectra [17]. A comparison of α -quartz (consisting of a 6-coordinated Si atom, ^[4]Si) and stishovite (high-pressure polymorph, consisting of ^[6]Si) with the characteristic O K-edge XRS spectra attributed the formation of $^{[6]}$ Si to the emergence of stishovitelike excitation features (at \sim 544 eV) of the O K-edge XRS spectra of the SiO₂ glasses at high pressures [17]. Oxygen triclusters (^[3]O; triply coordinated O atoms) have been suggested as the structural origin of the formation of \sim 544–545-eV features in the earlier O K-edge XRS spectrum for the densified MgSiO₃ glasses up to 39 GPa [25]. Though minor, pressure-induced shift in O K-edge energy was observed in the XRS spectrum for shockcompressed multicomponent quaternary oxide glasses [28]. A recent O K-edge XRS study of CaMgSi₂O₆ glasses under compression up to ~ 20 GPa reported the formation of a similar feature at \sim 544–545 eV. The formation of ^[6]Si has been attributed to the structural origin of the feature [27].

Despite these experimental efforts, establishing the direct link between the changes in the XRS features observed in extreme high-pressure conditions and the corresponding local atomic configurations of crystalline and noncrystalline materials has been experimentally challenging because of the limitations of *in situ* high-pressure XRS experiments (the highest pressure of 70 GPa in the literature) and the difficulties in resolving crystallographically distinct and, thus, site-specific structural information [10,11]. Consequently,

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probing the electronic bonding nature of two of the important oxide phases in the Earth's lower mantle, MgSiO₃ bridgmanite (stable up to \sim 130 GPa) and post-bridgmanite (stable near the core-mantle boundary), at a pressure of $\sim 120-135$ GPa [6,46–48], is challenging using current *in situ* high-pressure XRS experiments. Input from theoretical calculations is indeed necessary for the analysis of XRS features in order to interpret XRS edge features properly [10,16,18,24,34]. Ab initio calculations have been effective in predicting the coreelectron excitation spectrum, including XRS, electron energy loss spectroscopy (EELS), and x-ray absorption near-edge structure (XANES), for low-z oxides and silicates [49-51]. Particularly, ab initio calculations of O K-edge XRS spectra for oxides at high pressure overcome the current difficulties of in situ high-pressure experiments, providing insight into the pressure-induced structural transitions in oxides under compression [10,11,24]. For example, the calculated O p^* DOS and Si s^* and d^* DOSs were also used to account for the O K-edge (due to O $1s-2p^*$ transition) and Si $L_{2,3}$ -edge (due to Si 2p- $3s^*$ and $-3d^*$ transitions) XRS spectra of diverse SiO₂ high-pressure phases [10,18,24]. Successive phase transitions and corresponding structural changes around oxygen in diverse crystalline oxides leads to pressure-induced changes in the calculated O K-edge XRS features [24]. A recent theoretical study explored the pressure-induced changes in the O K-edge features of amorphous SiO₂, where the formation of highly coordinated Si atoms has been suggested to be the emergence of the high-pressure XRS features at \sim 544 eV [16].

Whereas the aforementioned advances and progress shed light on unknown details of the pressure-induced bonding transitions in oxide, there are several fundamental unsolved questions regarding the origin of O K-edge XRS features in both crystalline and amorphous oxides upon compression. First, although the simple short-range structure [coordination number and local structures, nonbridging oxygen (NBO) and bridging oxygen (BO)] in oxide glasses has been linked to observed peaks and features [10,16-19,25,34,38], those XRS features in the O K edge are often broad and span $\sim 20-30 \,\mathrm{eV}$. The interpretation is further complicated by the overlaps among the XRS features that are due to multiple crystallographic sites and their long-range topological variations. Consequently, the origin of 544–545-eV features in the O Kedge XRS spectra for oxide glasses at high pressure has been controversial: Previous experimental and theoretical studies have provided distinct structural origins for the emergence of the high-pressure feature in the O K-edge XRS spectra for oxides, which includes the densification of the network involving the formation of highly coordinated Si atoms [16], a transition similar to that of stishovite with ^[6]Si [17], formation of ^[3]O and related changes in the medium-range order [25], and overall topological variation (Si-O, Mg-O, O-O, bond angle, etc.), similar to pressure-induced structural transitions in crystalline oxides [24]. Therefore, further theoretical confirmation has been anticipated. Second, the quantitative and systematic relationships between the local oxygen configurations and O K-edge XRS features (edge energy) in both crystalline and noncrystalline oxides remain to be established. While it has been previously confirmed that an increase in structural densification upon phase transition leads to a systematic increase in O K-edge energy [24], the comparison has been made between polymorphs at their corresponding pressure condition at the onset of phase transition (e.g., bridgmanite at 25 GPa and post-bridgmanite at 120 GPa). Therefore, the remaining fundamental question includes whether structural densification within a stability field of a single phase can result in pressureinduced changes in O K-edge XRS spectra. Furthermore, the effect of onset of isobaric phase transition on O K-edge XRS features (i.e., MgSiO₃ bridgmanite at 120 GPa and coexisting post-bridgmanite at 120 GPa) is not known. Third, it is expected that band gap may increase with increasing pressure, contributing to changes in the O K-edge feature of oxides upon compression. Indeed, the effect of the Si-O bond on the band gap in SiO₂ polymorphs (α -quartz, β -quartz, β -tridymite, α -cristobalite, β -cristobalite, keatite, coesite, and stishovite) up to ~ 10 GPa has been reported [52]. However, the systematic effect of pressure and topological changes, such as Si-O and O-O distance in silicate crystals on the band gap and its effect on O K-edge XRS features up to pressure ranges that are relevant to the core-mantle boundary (~120-130 GPa) has not been explored. The information from XRS on densificationinduced changes in electronic bonding nature has fundamental implications in condensed matter physics and it could highlight the utility of O K-edge XRS as a unique structural probe of the electronic structure of diverse oxides at high pressure.

Recent advances in ab initio calculations provide an opportunity to calculate the site-specific XRS spectra of crystalline oxides at high pressures [21,24], which are difficult or impossible to achieve with current experimental XRS techniques [10,11]. Therefore, this study's objectives are to reveal the atomistic and electronic origins of the O K-edge features for oxides using ab initio calculations and to further determine the general relationship between the densification in oxygen environments and the O K-edge energy features of diverse oxides under extreme compression. Specifically, we calculate the site-resolved partial density of states (PDOS) and the O K-edge XRS spectra for bridgmanite and postbridgmanite MgSiO₃ high-pressure phases based on the fullpotential linearized augmented plane wave+local orbitals (FP-LAPW+lo) method [53], and examine the atomistic origins for the pressure-induced changes in the calculated results. In particular, we explore the effect of pressure-induced changes in the band gap on the O K-edge XRS features. The MgSiO₃ bridgmanite has a significantly wide range of stability, from \sim 25 to \sim 120 GPa [6,46,54], and it provides a rare opportunity to reveal the unknown effect of pressure-induced changes in structural densification in the same phase. Based on the results calculated in the present study and the results from a previous study [24], we also seek to find a simple structural and spectroscopic proxy to the densification around the oxygen atoms in low-z oxide glasses and crystals under extreme compression.

II. AB INITIO CALCULATIONS

A. Crystal structures

The crystal structures of the bridgmanite and postbridgmanite MgSiO₃ high-pressure phases used in this study were obtained from previous experimental and theoretical studies (bridgmanite synthesized at ~25 GPa [46], bridgmanite at 45 GPa [55], 79 GPa [56], 90 GPa [55], 120 GPa [48], and

TABLE I.	Space groups,	lattice parameters,	and internal	variables of	MgSiO ₃	bridgmanite a	nd post-ł	oridgmanit	e. A 2	$\times 1 \times 1$	supercell	l (total
40 atoms) was	s used in the XI	RS calculations for	the bridgma	anite and pos	t-bridgm	anite phases.						

		Post-bridgmanite						
Name	25 GPa ^a	45 GPa ^b	79 GPa ^c	90 GPa ^d	120 GPa ^e	120 GPa ^f	121 GPa ^g	
System Space group			Orthorhombic Pbnm (62)			Rhombohedral <i>Cmcm</i> (63)		
Cell parameters	(Å)							
a	4.7019	4.5659	4.4449	4.3552	4.2890	2.4550	2.4560	
b	4.8704	4.7903	4.6648	4.6528	4.5570	8.0510	8.0420	
с	6.7827	6.6288	6.4544	6.3619	6.2640	6.0990	6.0930	
Si-O bond lengt	hs (Å)							
Avg. Si-O	1.7695	1.7430	1.6971	1.6762	1.6505	1.6853	1.6576	
Si-O1 (×2)	1.7725	1.7316	1.6860	1.6611	1.6500	1.6312	1.6443	
Si-O2 (×4)	1.7681	1.7488	1.7027	1.6837	1.6508	1.7123	1.6643	
O-O distances	Å)							
Avg. 0-0	2.5025	2.4648	2.3999	2.3703	2.3342	2.3835	2.3434	
01-02 (×8)	2.5035	2.4607	2.3959	2.3649	2.3340	2.3646	2.3395	
O2-O2 (×4)	2.5005	2.4731	2.4080	2.3812	2.3345	2.4213	2.3514	
Mg-O distances	(Å)							
Avg. Mg-O	2.1669	2.0977	2.0424	2.0168	1.9811	1.9496	1.9604	
Avg. Mg-O1	2.0382	1.9583	1.9067	1.9032	1.8484	1.8686	1.8377	
Avg. Mg-O2	2.2098	2.1441	2.0877	2.0547	2.0253	1.9766	2.0014	
Si-O-Si bond an	gles (deg)							
^[6] Si-O1- ^[6] Si	146.1407	146.2943	146.3000	146.4572	143.2781	138.3689	135.7544	
^[6] Si-O2- ^[6] Si	146.3562	142.1901	142.1896	142.2701	142.7830	91.5940	95.0964	
Volume of the Si	$O_{6}(A^{3})$							
SiO ₆	7.3849	7.0535	6.5108	6.2719	5.9938	6.3675	6.0458	
Crystal densities	$s(amu/Å^3)$							
ρ	2.5856	2.7700	3.0008	3.1152	3.2802	3.3315	3.3371	

Note. A $2 \times 1 \times 1$ supercell (total 40 atoms) was used in the XRS calculations for the bridgmanite and post-bridgmanite phases. ^aX-ray diffraction (XRD) at 15 GPa, from Sugahara *et al.* [46].

^bModified from the bridgmanite at 79.7 GPa in Fiquet *et al.* [56] by rescaling its lattice parameters according to the lattice compressibility suggested by Fiquet *et al.* [55].

^cIn situ XRD experiments using the in situ high-temperature diamond anvil cell (DAC) at 79.7 GPa and 1681 K; see Fiquet et al. [56].

^dModified from the bridgmanite at 79.7 GPa in Fiquet *et al.* [56] by modifying its lattice parameters according to the lattice compressibility suggested by Fiquet *et al.* [55].

^eAb initio calculations; see Iitaka et al. [48].

^f*Ab initio* calculations; see Iitaka *et al.* [48].

^gMurakami et al. [47].

a post-bridgmanite phase at 120 GPa [48], or 121 GPa [47]). The crystal structures of the bridgmanite and post-bridgmanite phases at 120 GPa were obtained from a theoretical study [48]. The structures of bridgmanite at 45 and 90 GPa were rescaled from bridgmanite at 79 GPa according to the lattice compressibility of bridgmanite [55]; thus they have the same fractional atomic coordinates. Table I provides details of the crystal structures, including the lattice parameters, bond lengths, interatomic distances, and bond angles. The crystal structures of the bridgmanite and post-bridgmanite were visualized using VESTA [57]. The electronic structures and corresponding O K-edge XRS spectra of the bridgmanite and post-bridgmanite under high pressure were calculated without additional optimization of the lattice structure. Both the bridgmanite and post-bridgmanite and post-bridgmanite and post-bridgmanite and post-bridgmanite and post-bridgmanite methyles and post-bridgmanite and post-bridgmanite and post-bridgmanite and post-bridgmanite under high pressure were calculated without additional optimization of the lattice structure. Both the bridgmanite and post-bridgmanite and post-bridgmanit oxygen atoms—those are O1 and O2 atoms. The oxygen atoms have only corner-sharing topologies in bridgmanite as apical corner-sharing O1 atoms (^[6]Si-O1-^[6]Si) and planar corner-sharing O2 atoms (^[6]Si-O2-^[6]Si) connecting the SiO₆ octahedra, while the post-bridgmanite phase exhibits both corner- and edge-sharing topologies as corner-sharing O1 atoms (^[6]Si-O1-^[6]Si) and edge-sharing O2 atoms (^[6]Si-O2-2^[6]Si), as shown in Fig. 1. Here, we attempt to calculate O *K*-edge spectra for these crystallographically distinct oxygen sites in the crystals. While the site-specific O *K*-edge XRS calculations have only been utilized for a few previous studies (e.g., [21,24]), a similar calculation of site-specific information has been used for the other element specific experimental probes including ¹⁷O NMR where the previously unknown details of oxygen environments (e.g., corner-sharing oxygen:



FIG. 1. Crystal structures of (a) bridgmanite at 25 GPa and (b) post-bridgmanite at 120 GP. Crystallographically inequivalent oxygen atoms in the unit cells are labeled O1 and O2. There are two crystallographically distinct oxygen sites in MgSiO₃ bridgmanite at 25 GPa: an apical oxygen atom, ^[6]Si-O1-^[6]Si (O1, ^[6]Si-O1: 1.7725 Å, ^[6]Si-O1-^[6]Si angle: 146.14°, average Mg-O1: 2.0382 Å), and a planar oxygen atom, ^[6]Si-O2-^[6]Si (O2, average ^[6]Si-O2: 1.7681 Å, ^[6]Si-O2-^[6]Si angle: 146.36°, average O2-O2 distance: 2.5005 Å, average Mg-O2: 2.2098 Å). The oxygen environments in post-bridgmanite at 120 GPa include a corner-sharing oxygen atom, ^[6]Si-O1-^[6]Si (O1, ^[6]Si-O1: 1.6312 Å, ^[6]Si-O1-^[6]Si angle: 138.37°, Mg-O1: 1.8686 Å) and an edge-sharing oxygen atom, ^[6]Si-O2-^[6]Si (O2, average ^[6]Si-O2: 1.7123 Å, average O2-O2 distance: 2.4213 Å).

^[4,5,6]Si-O-^[4]Si, ^[4,5,6]Al-O-^[4]Si, ^[4,5,6]Al-O-^[4]Si; nonbridging oxygen: Mg-O-^[4]Si; and metal-bridging oxygen: Pb-O-Pb) in a range of amorphous oxides at ambient and high pressure were revealed [58–64].

B. Calculations of the electronic structure and the O *K*-edge XRS spectra

The PDOSs and O K-edge XRS spectra of the bridgmanite and post-bridgmanite at high pressures were calculated using the WIEN2K based on the FP-LPAW+lo method [53]. Because the FP-LAPW+lo method describes all the electronic states without additional approximations of the core orbitals, it is suitable for calculating the core-level spectroscopy [49,50,65]. In the FP-LAPW+lo method, the electronic states of an atom are classified into three regions (core states, valence states, and semicore states). These distinct electronic states are calculated using different basis sets to improve the efficiency of the self-consistent field (SCF) calculations. The Perdew-Berke-Ernzerhof for the solid (PBESOL) scheme based on the generalized gradient approximation (GGA) method was used as the exchange-correlation functional to describe the short-range electronic interactions [66]. The muffin-tin radii $(R_{\rm MT})$ for Mg, Si, and O were 1.7–1.9 Å, 1.54–1.67 Å, and 1.54–1.67 Å, respectively. The cutoff energy for the separation of the core and valence states (E_{CUT}) was set to -7.0 Ry, and the Si 2p state was included in the valence state. The $E_{\rm CUT}$ value was chosen to prevent leakage of core electrons from the muffin-tin spheres because the leaked core electrons generate semicore states that increase the convergence time for the SCF calculations. However, negligible differences were observed between the calculated PDOSs with varying E_{CUT} values (i.e., -6.0 and -7.0 Ry). Including the Si 2p state in the core state does not lead to a significant change in the PDOS pattern. RK_{MAX} [the scalar product of the minimum value of $R_{\rm MT}$ and the largest plane wave cutoff vector ($K_{\rm MAX}$)] for the bridgmanite and post-bridgmanite is 5.0, which is suitable for describing sp-orbital elements from the Mg, Si, and O atoms in the unit cell. The G_{MAX} (i.e., the magnitude of the largest vector in the Fourier expansion of the charge density) was set to 12.0. The number of k points in the irreducible Brillouin zone for calculating the PDOSs and O K-edge XRS spectra was set to 18 and 36, respectively, while the Γ -point calculation (the center of the Brillouin zone) was sufficient for silicates and oxides [18,49]. The SCF calculations were carried out using the convergence criteria of 10^{-4} Ry for the total energy and $10^{-3} e$ for the charge [24]. The PDOSs of the bridgmanite and post-bridgmanite were calculated taking into consideration the core-hole effects with a $2 \times 1 \times 1$ supercell (see below for additional details of core-hole effect). The site-resolved PDOSs of the oxygen atoms were obtained from each crystallographically inequivalent oxygen atom (O1 and O2) in each unit cell. Calculated PDOSs for the Mg, Si, and O atoms are also resolved by the angular momentum of each electronic state (l-resolved PDOS). The calculated *l*-resolved PDOSs are presented from -30 to 30 eV with respect to the Fermi energy and are broadened with the full width at half maximum (FWHM) Gaussian-broadening factors of 0.02 Ry. The O K-edge XRS spectra for a series of bridgmanite and post-bridgmanite phases were calculated for the crystallographically inequivalent O1 and O2 atoms. In XRS processes, the O 1s electron is excited to the unoccupied states by incident x-ray photons, and the local electronic structures around the oxygen atoms are affected to an extent by this partially empty O 1s state [11,50,51,65]. This core-hole effect is significant in low-z elements, but it is less critical in high-z elements because the sufficient number of outer electrons in the high-z element can mitigate the effect of the partially empty core states [49,51,67]. Therefore, the core hole is applied to the target oxygen atom to obtain reliable O K-edge XRS spectra for both the bridgmanite and the post-bridgmanite phases. A single 1s core electron of the target oxygen atom is excited to the valence states as an extra background charge to preserve the total charge in the unit cell. This adjustment of the electronic occupation mimics the final state of the electronic transition because of the XRS process [49,50]. The O K-edge XRS spectra of the bridgmanite and post-bridgmanite were calculated with a $2 \times 1 \times 1$ supercell using WIEN2K from the transition matrix of relativistic double differential scattering cross section (DDSCS) under dipole-allowed transitions as well as monopole, quadrupole, and octupole-allowed transitions [53,67,68]. The calculated O K-edge XRS spectra are presented up to 45 eV above the absorption O K-edge energy of 528.25 eV. Here the values for energy loss (i.e., energy of scattered photon-elastic energy) in the calculated O K-edge features are estimated by adding 528.25 eV to $E - E_F$ (where E_F is the highest occupied energy state for oxygen). All the calculated O K-edge XRS spectra were broadened with 0.5 eV of the FWHM Gaussian-broadening factors so they are visually similar to the experimental XRS spectra.



FIG. 2. Crystal densities (i.e., the total atomic mass divided by unit cell volume) of the SiO₂ (α -quartz, coesite, and stishovite) and MgSiO₃ [enstatite, ilmenite-type MgSiO₃, bridgmanite (BR), and post-bridgmanite (PBR)] high-pressure phases with respect to average Si-O bond lengths (a) and average O-O distances (b); average O-O distances (c), and average Si-O bond lengths (d) of SiO₂ and MgSiO₃ high-pressure phases with increasing pressure. The black line refers to the trend for all the phases studied here, whereas a blue trend line is for the bridgmanite phase only. The linear relationships between crystal densities (ρ) and average O-O distances (d_{0-O}) are described as ρ (amu/Å³) $\approx -5.1d_{0-O}$ (Å) + 15.3 ($R^2 = 0.9$) for all the phases and ρ (amu/Å³) $\approx -4.0d_{0-O}$ (Å) + 12.6 ($R^2 = 1.0$) for the bridgmanite phase only. The linear relationship between average O-O distances and pressures for the bridgmanite phase is described as d_{0-O} (Å) $\approx -0.002P$ (GPa) + 2.6 ($R^2 = 0.8$). The linear relationship between average Si-O bond lengths and pressures for the bridgmanite phase is described as d_{Si-O} (Å) $\approx -0.001P$ (GPa) + 1.8 ($R^2 = 1.0$).

III. RESULTS AND DISCUSSION

A. Effect of pressure on crystal structures and PDOS of the bridgmanite and post-bridgmanite

Table I lists the lattice parameters and internal variables of the bridgmanite and post-bridgmanite. The interatomic distances of the bridgmanite change significantly with increasing pressure from 25 to 120 GPa: The average Si-O1 bond length decreases by 6.9% (from 1.7725 to 1.6500 Å), and the average Si-O2 bond length decreases by 6.6% (from 1.7681 to 1.6508 Å). The average O1-O2 and O2-O2 distances also decrease by 7.3% (from 2.5035 to 2.3340 Å) and 7.11% (from 2.5005 to 2.3345 Å), respectively (see Fig. S1 in the Supplemental Material [69]) [46,48]. Figure 2 presents the crystal densities (i.e., the total atomic mass with respect to the unit cell volume) of the SiO₂ and MgSiO₃ high-pressure phases with respect to the Si-O bond lengths and O-O distances. The Si-O bond lengths of the SiO2 and MgSiO3 high-pressure phases (consisting of SiO₆ octahedron, ^[6]Si) were negatively correlated with the crystal density [Fig. 2(a)]. A strong negative and linear correlation between the crystal densities and O-O distances of the SiO₂ and MgSiO₃ high-pressure phases was observed, regardless of the Si coordination numbers (^[4]Si and ^[6]Si) [Fig. 2(b)], indicating that the O-O distance can describe the pressure-induced densification of the SiO₂ and MgSiO₃ phases well. Figure 2(c) shows the effect of pressure on Si-O bond length in SiO₂ and MgSiO₃ phases. As expected, upon phase transition to high-density polymorphs, Si-O bond length increases. Within a stability field of the polymorph, Si-O bond length tends to decrease with increasing pressure. Figure 2(d) also shows that O-O bond distance decreases systematically with increasing pressure. Given the strong correlation between O-O distance and crystal density [Fig. 2(b)], the results indeed confirm that O-O distance can be effectively used to describe the densification of SiO₂ and MgSiO₃ phases.

Because the O K-edge XRS features arise primarily from the O $1s-2p^*$ transition [11], the unoccupied O PDOSs of the crystallographically distinct O1 and O2 atoms in the MgSiO₃ phases with increasing pressure are calculated to account for the atomistic origins of the changes in O K-edge spectra. Figure 3 shows the *l*-resolved O PDOSs (for unoccupied states) of O1 [Fig. 3(a)] and O2 [Fig. 3(b)] for MgSiO₃ bridgmanite and post-bridgmanite, where the systematic pressure-induced changes in the PDOS are demonstrated. Pressure-induced changes in each *l*-resolved DOS show unique information on the evolution of electronic state with pressure. Pressureinduced broadening in O PDOS in the empty states is prevalent primarily in d states, whereas the pressure-induced broadening is not clearly demonstrated for s and p states. Figure 4 also shows the DOS threshold energy in unoccupied states for the oxygen s state, p state, and d state for O1 and O2 in the MgSiO₃ bridgmanite with varying average O-O distance. Here, the



FIG. 3. *l*-resolved oxygen PDOS (for unoccupied states) of O1 (a) and O2 (b) for MgSiO₃ bridgmanite (BR) and post-bridgmanite (PBR) with varying pressure. The Gaussian-broadening FWHM for PDOS is 0.02 Ry (red solid, oxygen *s* state; blue solid, oxygen *p* state; green solid, oxygen *d* state; black solid, total DOS of oxygen).

DOS threshold of each *l*-resolved DOS was estimated from the energy transfer value with the largest change in slope near the absorption edge of the spectrum. This threshold energy increases *linearly* with an increase in pressure and, thus, a decrease in O-O distance. A decrease in O PDOS threshold is also observed upon phase transition from bridgmanite to post-bridgmanite at 120 GPa. The systematic changes in O PDOS indicate an increase in band gap with O-O distance and/or pressure. Figure 5(a) presents the changes in the band gap (E_G) of the SiO₂ and MgSiO₃ high-pressure phases with respect to the O-O distance (see Supplemental Material [69] for the total and PDOS of the bridgmanite phase for the valence state with which the band gap was estimated (Fig. S2)] [24]). The band gaps of the diverse



FIG. 4. DOS threshold energy for oxygen *s* state (red), oxygen *p* state (blue), and oxygen *d* state (green) for O1 (a) and O2 sites (b) in MgSiO₃ bridgmanite (BR; closed circle) and post-bridgmanite (PBR; open circle), with varying average O-O distance. The linear relationships between DOS thresholds (E_{DOS}) of and average O-O distances (d_{O-O}) for the bridgmanite structures are described as E_{DOS} (O1-*s*) (eV) $\approx -20.8d_{O-O}$ (Å) + 58.3 ($R^2 = 1.0$) for the O1 *s* state, E_{DOS} (O1-*p*) (eV) $\approx -21.1d_{O-O}$ (Å) + 59.7 ($R^2 = 1.0$) for the O1 *p* state, E_{DOS} (O1-*d*) (eV) $\approx -19.9d_{O-O}$ (Å) + 65.5 ($R^2 = 1.0$) for the O1 *d* state, E_{DOS} (O2-*s*) (eV) $\approx -22.8d_{O-O}$ (Å) + 63.3 ($R^2 = 1.0$) for the O2 *s* state, E_{DOS} (O2-*p*) (eV) $\approx -22.1d_{O-O}$ (Å) + 61.8 ($R^2 = 1.0$) for the O2 *p* state, and E_{DOS} (O2-*d*) (eV) $\approx -21.2d_{O-O}$ (Å) + 59.4 ($R^2 = 1.0$) for the O2 *d* state, respectively.

SiO₂ and MgSiO₃ high-pressure phases decrease linearly with decreasing O-O distance (d_{O-O}) , regardless of phases or the Si coordination number [i.e., $E_G(eV) \approx -14.1 d_{O-O}(\text{\AA}) +$ $42.6 (R^2 = 0.8)$]. The pressure-induced decrease in the E_G of the bridgmanite phase alone can also be well described with the relationship $E_G(eV) \approx -22.7 d_{O-O} (\text{\AA}) + 63.9 (R^2 =$ 1.0). Note that the E_G does not correlate strongly with the Si-O bond length. Figure 5(b) also shows the changes in the E_G of the SiO₂ and MgSiO₃ high-pressure phases with increasing pressure. The E_G of MgSiO₃ bridgmanite increases with increasing pressure up to 120 GPa, which is consistent with previous theoretical studies for the MgSiO₃ enstatite at relatively low pressures up to 2 GPa, where a positive correlation between the E_G and pressures is demonstrated [70]. Upon phase transition between the bridgmanite and postbridgmanite, at ~ 120 GPa the E_G decreases from 11 to 8.3 eV, as expected from a decrease in O PDOS (Figs. 3 and 4), consistent with earlier PDOS calculation of bridgmanite and post-bridgmanite without applying the core-hole effects on target oxygen atoms [71]. This result indicates that short-range



FIG. 5. Band gap of the SiO₂ (α -quartz, coesite, and stishovite) and MgSiO₃ [enstatite, ilmenite-type MgSiO₃, bridgmanite (BR), and post-bridgmanite (PBR)] high-pressure phases, with varying average O-O distance (a) and pressure (b). The linear relationship between band gaps and average O-O distances is described as E_G (eV) \approx $-14.1d_{O-O}$ (Å) + 42.6 ($R^2 = 0.8$) for all the phases and E_G (eV) \approx $-22.7d_{O-O}$ (Å) + 63.9 ($R^2 = 1.0$) for the bridgmanite phase only.

electronic repulsion is mitigated upon phase transition in $MgSiO_3$ (from bridgmanite to post-bridgmanite), while overall electronic interaction should increase with increasing pressure. This observed change in the calculated XRS confirms that the overall densification in medium- to larger-length scale beyond the first coordination environments also contributes to the changes in O *K*-edge spectra.

B. O *K*-edge XRS spectra of the bridgmanite and post-bridgmanite phases

Figure 6 shows the calculated O *K*-edge XRS spectra and the *l*-resolved PDOSs for the unoccupied states of the oxygen atoms in bridgmanite at 25 and 120 GPa. Figure 6(a) shows the O *K*-edge XRS spectra for the O1 and O2 sites in the MgSiO₃ bridgmanite at 25 GPa, where broad peaks centered at ~540 eV, which is characteristic of oxygen atoms linking two ^[6]Si atoms (i.e., corner-sharing ^[6]Si-O-^[6]Si), with fine features at ~537.5, ~539.5, and ~541.4 eV. Note the calculation results for bridgmanite at 25 GPa have been reported previously [24], but they are shown here to provide comparison between those at 25 GPa and 120 GPa. Figure 6(b) shows their site-resolved PDOSs for the unoccupied *s*, *p*,



FIG. 6. (a) Site-resolved and total O K-edge XRS spectra [blue solid, O1, apical corner-sharing oxygen; red solid, O2, planar cornersharing oxygen; black solid, total (O1 : O2 = 1 : 2)] for bridgmanite (BR) at 25 GPa. (b) *l*-resolved O DOSs (for unoccupied states) of each orbital (red solid, s state; blue solid, p state; green solid, d state; black solid, total O DOS) for bridgmanite at 25 GPa. (c) Site-resolved and total O K-edge XRS spectra [blue solid, O1, apical corner-sharing oxygen; red solid, O2, planar corner-sharing oxygen; black solid, total (O1 : O2 = 1 : 2) for bridgmanite at 120 GPa. (D) *l*-resolved O DOSs (for unoccupied states) of each orbital (red solid, s state; blue solid, p state; green solid, d state; black solid, total O DOS) for bridgmanite at 120 GPa. The Gaussian-broadening FWHM for PDOSs and O K-edge XRS spectra are 0.02 Ry and 0.5 eV, respectively. The experimental O K-edge XRS spectra of bridgmanite (open black circles with a black solid line) [25] were compared with the calculated O K-edge XRS spectra for the bridgmanite at 25 GPa.

and *d* states of the oxygen atoms at 25 GPa. Figure 6(c) shows the calculated O *K*-edge XRS spectrum for MgSiO₃ bridgmanite at 120 GPa, where the features at ~539.6, ~541.9, and ~544.2 eV are observed. Note that there are systematic pressure-induced shifts in the overall features (~2–4 eV) from 25 GPa to 120 GPa. Furthermore, there is a noticeable change in the overall spectral pattern with increasing pressure, indicating that a small change in topology with a fixed crystal symmetry contributes the changes in the XRS pattern in the phase. Figure 6(d) shows the site-resolved PDOSs for the oxygen atoms in the bridgmanite at 120 GPa, where the positive peak shifts that are due to enhanced electronic interactions are demonstrated. These results confirm that the calculated O *K*-edge XRS spectra arise primarily from the contribution of the unoccupied oxygen 2*p* state of PDOS.

Figure 7 shows the pressure-induced changes in the calculated O K-edge XRS spectra for MgSiO₃ polymorphs

[enstatite (at 1 atm), ilmenite-type MgSiO₃ (i.e., akimotoite, at 22 GPa), bridgmanite (from 25 to 120 GPa), and postbridgmanite (at 120 GPa)]. The site-resolved O K-edge XRS spectra of the crystallographically inequivalent oxygen atoms (e.g., O1, O2, and O3) [Fig. 7(a)] and the total O K-edge XRS spectra [Fig. 7(b)] are shown. The calculated O K-edge XRS spectra for the enstatite and ilmenite-type MgSiO₃ were from our previous study [24]. Previous experimental and theoretical studies have confirmed that the main feature of enstatite at \sim 538 eV (σ^* transition) is due to the transition of core electrons to the unoccupied 2p state in oxygen atoms, hybridized with neighboring ${}^{[4]}$ Si atoms [24,25]. The distinct nonbridging apical oxygen (O1, ${}^{[6]}$ Mg-O1- ${}^{[4]}$ Si), nonbridging basal oxygen (O2, ^[6]Mg-O2-^[4]Si), and corner-sharing bridging oxygen (O3, ^[4]Si-O3-^[4]Si) in the crystal show characteristic patterns that arise from distinct short- to medium-range structures around the oxygen [24]. Peculiar features with two peaks at \sim 536.4 and \sim 540.1 eV are observed in the O K-edge XRS spectrum for ilmenite-type MgSiO₃, which is consistent with previous experimental results [25]. These double-peak-like features are characteristic of the edge-sharing oxygen (^[6]Mg ^[6]Si - ^[4]O - ^[6]Mg ^[6]Si, with the average ^[6]Si-O bond length of 1.7989 Å, the ^[6]Si - ^[4]O - ^[6]Si bond angle of 99.23°, the O-O bond length of 2.3316 Å, and the average Mg-O distance of 2.0765 Å) [24,25].

The O *K*-edge XRS spectrum of bridgmanite at 120 GPa shows the characteristic feature near 541.7 eV, which is mostly from the O2 atom, and the other features at ~539.9 and ~543.9 eV are from both the O1 and O2 atoms. Those features shift to a higher-energy region with increasing pressure from 25 to 120 GPa. The O *K*-edge XRS spectrum for MgSiO₃ post-bridgmanite at 120 GPa shows complex features that span up to ~20 eV and are due to a corner-sharing oxygen atom, ^[6]Si-O1-^[6]Si, and an edge-sharing oxygen atom, ^[6]Si-O2-2^[6]Si. For example, the spectrum for the O2 site shows two characteristic peaks at ~537.8 and 540.5 eV, similar to the double-peak features for the edge-sharing oxygen in illmenite-type MgSiO₃.

The results calculated here provide previously unknown details about the effect of the bonding nature around oxygen on the O K-edge XRS features. For example, the characteristic features at \sim 536.7 eV in the total O K-edge XRS spectrum of bridgmanite at 25 GPa are caused primarily by the contribution of the O1 atom. The significant increase in the relative peak intensity of \sim 541.5 eV in the O K-edge features of bridgmanite at 120 GPa is due primarily to the contribution from the atomic configurations around the O2 atom. Although the features can be related to certain structural units, they are broad, overall, and span 10-20 eV, so care should be taken to assign the narrow features to specific atomic environments (e.g., NBO and BO), as has often been done in analyses of the XANES spectra for the oxide glasses (see [72,73] for the review of XANES analysis of glasses). Finally, a similar systematic shift of the σ^* features in the O K-edge XRS spectra for the MgSiO₃ polymorphs has been observed for both π^* and σ^* in the (O₂)₄ cluster in the ε phase [34]. A similar trend in the pressure-induced edge energy shift has been reported for simple elements (e.g., O, Ne, and Cl), suggesting a pressure-induced increase in mean excitation energy [74] (see below for further discussion).



FIG. 7. Site-resolved (a) and total (b) O K-edge XRS spectra of high-pressure MgSiO₃ [enstatite, ilmenite-type MgSiO₃, bridgmanite (BR), and post-bridgmanite (PBR)] polymorphs. Those for crystallographically inequivalent oxygen sites [O1 (black), O2 (red), and O3 (blue)] are shown. The spectra of the enstatite and ilmenite-type MgSiO₃ are from a previous study [24]. The Gaussian-broadening FWHM for O K-edge XRS spectra is 0.5 eV. (C) Direct comparison of the calculated O K-edge XRS pattern for bridgmanite and post-bridgmanite at 120 GPa.

Figure 7(c) shows the calculated O K-edge XRS spectra for bridgmanite and post-bridgmanite structures at 120 GPa. The differences between the O K-edge features for MgSiO₃ bridgmanite and post-bridgmanite stem from their differing local atomic configurations-packing of the SiO₆ octahedra with the emergence of an edge-shared topology for the bridgmanite and coexisting post-bridgmanite at 120 GPa: The latter has the longer average Si-O bond lengths (1.6505 vs 1.6853 Å), longer average O-O distances (2.3342 vs 2.3835 Å), a larger volume of SiO₆ octahedra (5.9938 vs 6.3675 Å^3), shorter average Mg-O distances (1.9811 vs 1.9496 Å), and shorter Si-Si distances [the Si-Si distance in the Si-O1-Si direction (an apical corner-sharing oxygen atom in bridgmanite, and a c-axis direction in the unit cell) decreases from 3.1320 to 3.0495 Å, and Si-Si distances in the Si-O2-Si direction (planar corner-sharing and edge-sharing oxygen atoms in bridgmanite and post-bridgmanite, respectively-a- and b-axis directions in the unit cell) decrease from 3.1290 to 2.4550 Å]. Thus, there is a higher overall density in the post-bridgmanite (from 3.2802 to 3.3315 amu/Å^3). The significant differences in absorption thresholds, in particular-a decrease in edge energy at 120 GPa upon phase transition-indicates less electronic repulsion between the Si and O atoms in the Si-O bond in post-bridgmanite than in bridgmanite, as expected from the longer Si-O bond length and O-O distances even with the shorter Mg-O and Si-Si distances (particularly in the direction of SiO₆ polyhedra constructing the edge-sharing topology in post-bridgmanite—a- and b-axis directions in the unit cells). In contrast to previous studies, which have revealed a systematic increase in edge energy features upon phase transition [24], an isobaric phase transition can result in a negative shift in the absorption threshold (mainly because of a decrease in band gap upon densification).

The calculated O K-edge spectra for the SiO₂ and MgSiO₃ polymorphs show the effects of densification on the O K-edge features for the crystallographically distinct oxygen sites [24]. A similar trend in pressure-induced edge energy shift has been reported for solid oxygen and archetypal single-component oxide glasses [10,16,34]. The changes in the O K-edge features upon phase transitions suggest that a densification of crystalline silicates (via formation of highly coordinated Si and enhanced proximity between oxygen atoms) shifts edge features into a higher-energy region [24]. Furthermore, the current results reveal that, without significant changes in topology and coordination number, there is systematic shift to a higher energy with pressure, which is due in part to a pressure-induced increase in band gap. A slight difference in the crystal structure of post-bridgmanite from ab initio calculations [48] and experiments [47] results in a slight but non-negligible change in the XRS features, indicating that the



FIG. 8. Absorption threshold energies in the O *K*-edge XRS of SiO₂ phases (α -quartz, coesite, and stishovite) and MgSiO₃ [enstatite, ilmenite-type MgSiO₃, bridgmanite (BR), and post-bridgmanite (PBR)] polymorphs with varying crystal density (a), average Si-O bond lengths (b), and average O-O distance (c). The black line refers to the trend for all the phases studied here, whereas a blue trend line is for the bridgmanite phase only. The absorption threshold for SiO₂ phases, enstatite, and ilmenite-type MgSiO₃ phases were obtained from a previous study [24] and that for the result of SiO₂ coesite will be presented in a future contribution. The linear relationships between absorption threshold energies (E_A) and average O-O distances (d_{O-O}) are described as E_A (eV) $\approx -10.5d_{O-O}$ (Å) + 33.7 ($R^2 = 0.7$) for all the phases and E_A (eV) $\approx -21.5d_{O-O}$ (Å) + 60.4 ($R^2 = 1.0$) for the bridgmanite structures, respectively.

XRS features at high pressure are sensitive to the small changes in topology and crystal symmetry (see Supplemental Material, Fig. S3 [24]).

Figure 8 presents the absorption threshold of the O K-edge XRS spectra of diverse SiO₂ and MgSiO₃ high-pressure

phases with respect to the Si-O bond lengths, crystal densities, and O-O distances. Each absorption threshold of the calculated O K-edge XRS spectrum was determined from the energy at which the O K-edge feature increases most rapidly (i.e., from the slope of calculated O K-edge XRS spectrum). The absorption threshold energies of the diverse SiO₂ and MgSiO₃ high-pressure phases may not be closely correlated with either the Si-O bond lengths or Si coordination numbers [Fig. 8(a)], but there is a moderate degree of correlation between the absorption threshold energies and the crystal densities [Fig. 8(b)]. In Fig. 8(c), the absorption threshold energies (E_A) are correlated *linearly* with the O-O distances (d_{O-O}) . This result can be represented by the simple relationship, $E_A(eV) \approx -10.5 d_{O-O}(\text{\AA}) + 33.7 (R^2 =$ 0.7). E_A of bridgmanite decreases with d_{O-O} with the following relationship, E_A (eV) $\approx -21.5 d_{O-O}$ (Å) + 60.4 ($R^2 =$ 1.0). Taking into consideration the quality of the fits, much stronger correlation between E_A and d_{O-O} is achieved within a single-phase polymorph (e.g., overall fit with R^2 of 0.7 and the fit only for bridgmanite with R^2 of 1.0). While this indicates that in addition to O-O distance, additional structural and chemical changes indeed affect the evolution of O K-edge features with pressure, it is also clear that regardless of the chemical compositions (SiO₂ and MgSiO₃) and Si coordination numbers (^[4]Si and ^[6]Si), O-O distance is a useful structural proxy of oxide densification upon compression. This correlation reveals a trend similar to that between the band gap and the O-O distance shown in Fig. 3, so the absorption threshold and the band gap energies are *linearly* correlated $(E_G \approx -1.2E_A - 1.4)$. The results presented here provide a quantitative relationship between the structural parameter and the changes in the O K-edge XRS features of the diverse SiO₂ and MgSiO₃ high-pressure phases. The oxygen proximity is a useful structural indicator of oxide densification upon compression, explaining the pressure-induced changes in the O K-edge XRS features of crystalline and amorphous SiO₂ and MgSiO₃ at high pressures.

C. Origins of the characteristic O *K*-edge XRS features of MgSiO₃ glasses at high pressures

It has been shown that the characteristic O K-edge XRS features of crystalline and amorphous SiO₂ at high pressures can be explained in part by the formation of highly coordinated Si atoms with increasing pressure [16,17]. Because the formation of highly coordinated Si atoms in the fully polymerized SiO₂ glasses is associated with the formation of ^[3]O (e.g., ^[4]Si -^[3]O -2^[4]Si) and the topological changes around O atoms, the change could be due to the formation of ^[3]O, as suggested by the O *K*-edge XRS spectra for MgSiO₃ glass at high pressure [25]. The current study and previous studies have also shown that the O K-edge XRS features of SiO₂ and MgSiO₃ polymorphs depend on the local oxygen and topology beyond the short-range structures [24,25]. It is also clear that successive phase transitions lead to changes in the O K-edge XRS features with pressure, resulting in a shift in edge energy features (and the absorption threshold) [24]. The current study of bridgmanite (from 25 to 120 GPa) adds additional insights into the origin of the O K-edge features in that, even without phase transition (and, thus, within



FIG. 9. Calculated O *K*-edge XRS spectra for the bridgmanite (BR) structures with the O *K*-edge XRS features of bridgmanite and MgSiO₃ glasses [25]. The black and red solid lines with open circles indicate the experimental O *K*-edge XRS features of the MgSiO₃ glasses at 1 atm and 39 GPa, respectively, and the blue solid line with open circles indicates the O *K*-edge XRS features of the bridgmanite. The black, blue, and red solid lines at the bottom of the figure refer to the calculated O *K*-edge XRS spectra for the bridgmanite structures at 25, 79, and 120 GPa, respectively.

identical crystal symmetry, topology, and cation and anion coordination environments), densification in the crystal can lead to significant changes (mainly systematic peak energy shifts) in the O K-edge XRS spectrum, resulting primarily from an increase in band gap with pressure. These results can help to clarify the atomistic origins of pressure-induced changes in diverse O K-edge features for complex oxide glasses. Figure 9 presents the calculated O K-edge XRS features for bridgmanite and the experimental O K-edge XRS spectra of MgSiO₃ glasses and bridgmanite [25]. While the calculations reproduce most of the features, the calculated XRS intensity above \sim 550 eV (i.e., \sim 15–20 eV from the E_F) was underestimated to a degree: Although the FP-LAPW+lo method typically calculates the ground-state density of electrons well, the intensity of unoccupied states far from the Fermi level may not be properly estimated because of the insufficient basis sets in these unoccupied state regions [49–51,75]. The underestimated XRS cross section can be improved using the additional basis sets for the high-energy regions far from the Fermi level [75]. This has also been suggested due to the fact that energy-independent exchange-correlation functionals used in the DFT method are too strong close to the ionization threshold [29,76]. We also note that background subtraction in x-ray absorption spectroscopy (or XRS) is not trivial and can partly contribute to the observed differences in the O K-edge features between the experiment and calculation. Figure 9 also shows the O K-edge XRS features of the MgSiO₃ glasses, where significant changes in the XRS features with increasing pressure are prevalent. Distinct spectral features at \sim 545 eV appear at 39 GPa, whereas overall spectral features shift with a broadening of FWHM to a higher-energy region. While the O K-edge XRS of the noncrystalline $MgSiO_3$ at high pressures remains to be calculated, in our previous experimental study of the O K-edge XRS of MgSiO₃ glass at high pressure (up to 40 GPa), it has been suggested that the formation of oxygen triclusters (oxygen coordinated with three Si frameworks; ^[3]O) and changes in the short- to medium-range structures that are associated with the formation of ^[3]O upon densification can contribute significantly to the formation of the ~545-eV feature [25]. Recent ab initio MD simulation of cold-compressed MgSiO₃ glasses confirms the presence of a considerable fraction of oxygen triclusters at high pressure $\sim 40 \,\text{GPa}$ [77], indicating that the formation of the ^[3]O can partly contribute to the emergence of the high-pressure O K-edge feature. Nevertheless, the O K-edge XRS spectra of the bridgmanite are also comparable to those in the O K-edge XRS features of the MgSiO₃ glasses with increasing pressure. Therefore, while the formation of $^{[3]}O$ and the associated decrease in O-O distance can explain the emergence of ~545-eV features in the spectra, the current results suggest that the formation of ^[3]O in the glasses may not be uniquely attributed to the formation of the 545-eV features. The current study shows that densification with no cation and anion coordination transformation can explain the feature at 545 eV. Therefore, the observed changes in the 545-eV features can be primarily due to a reduction in O-O distance. The formation of ^[3]O, the Si coordination number, and the shortening of the Mg-O distance lead to a decrease in the O-O distance in silicates and the emergence of high-pressure features in the O K-edge XRS spectra. Whereas the observed changes in the XRS pattern for the crystalline bridgmanite are prevalent in a very large pressure range, the pressure-induced spectral broadening is not clearly manifested: While the dispersion in d DOS with pressure can contribute to overall broadening, the O K-edge XRS features are largely controlled by the O-2p DOS. As shown in Fig. 9, the XRS spectra for the MgSiO₃ glass at 39 GPa are wider than that of the crystalline analog (e.g., approximately 8 and 12 eV for MgSiO₃ glass at ambient pressure and 39 GPa, respectively, while the width of O K-edge features of crystalline bridgmanite is $\sim 6-7 \, \text{eV}$ in the whole pressure range; see Fig. 9). While the detailed discussion will be provided in the future calculation of XRS spectra for the noncrystalline phases at high pressure, the difference indicates a larger O-O distance distribution (and thus a larger structural disorder) in the glasses.

Crystalline and noncrystalline MgSiO₃ at high pressure have strong geophysical and geochemical implications for the mantle minerals and melts in Earth's and other planets' interiors [1,5,78,79]. The band-gap and absorption threshold energies of the SiO₂ and MgSiO₃ high-pressure phases [Figs. 5(a) and 8(c)] show a *linear* negative relationship with the O-O distances, including the bridgmanite and post-bridgmanite MgSiO₃ high-pressure phases that exist near the core-mantle boundary. These changes result from the topological changes around the oxygen atoms from shortto medium-range structures (i.e., the Si-O bond lengths, the O-O, and Mg-O distances, and the Si coordination numbers). These results suggest changes in the chemical reactivity of the SiO₂ and MgSiO₃ high-pressure phases because chemical reactions that include electron transfer are assessed in terms of their relative differences in energy between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). Although the changes in the chemical reactivity of the SiO₂ and MgSiO₃ high-pressure phases are difficult to comprehend fully from the current results, the smaller band gap of post-bridgmanite suggests more efficient electron transfer than bridgmanite at 120 GPa and, thus, higher chemical reactivity.

IV. CONCLUSION

Despite earlier efforts to reveal the atomistic origins of the O K-edge XRS features, the relationship between the structures (e.g., the formation of highly coordinated Si atoms, the formation of oxygen triclusters and associated changes in medium-range structures, and the enhanced oxygen proximity) and the emergence of high-energy features in the O K-edge XRS spectra have not been fully explained because of the intrinsic overlaps of O K-edge features in the crystalline and noncrystalline

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network structures and the current experimental limitations of synchrotron XRS up to 60–70 GPa [10]. The present study carried out quantitative analysis of the O K-edge XRS spectra of the diverse SiO₂ and MgSiO₃ high-pressure phases up to 120 GPa to determine the relationship between the changes in electronic structures and the topological changes in the shortto medium-range structures around oxygen atoms. The study determined the linear relationships between the O-O distances and the absorption threshold and band gap of the SiO₂ and MgSiO₃ high-pressure phases, along with their simple predictive models. The oxygen proximity is a useful structural proxy of oxide densification upon compression, as it explains the pressure-induced changes in O K-edge XRS features of crystalline and amorphous SiO₂ and MgSiO₃ at high pressures. This study can be applied to efforts to unravel the pressureinduced bonding transitions in more complex, multicomponent noncrystalline materials under compression via O K-edge XRS experiments, thus providing insight into the atomistic account of the structural heterogeneity in lower-mantle melts.

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