

CONDENSED-MATTER
SPECTROSCOPY

Study of Local Atomic and Electronic Structure of Titanium-Containing Forsterite Based on Analysis of X-Ray Absorption Spectra

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Abstract—The local atomic structure of titanium-containing forsterite is investigated based on analysis of X-ray absorption near-edge structure (XANES) spectra. The Ti *K*-XANES spectra of the mineral under study are calculated for several possible structural models. Theoretical analysis of the X-ray absorption spectra is performed based on the full-potential finite-difference method. The local geometry of the titanium environment is determined by comparing the experimental Ti *K*-XANES spectrum with the theoretical spectra calculated for different structural models. The structural model where titanium atoms substitute for silicon ones is found to be most likely for titanium-containing forsterite. The calculated partial densities of electron states of titanium near the bottom of the conduction band of titanium-containing forsterite are analyzed.

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INTRODUCTION

In this paper, we report the results of studying the atomic and electronic structure of titanium-containing forsterite. This mineral is the end member of the olivine group; its chemical formula is Mg_2SiO_4 . Pure forsterite is rarely encountered; it is observed more often as a component of olivine (92% forsterite and 8% fayalite (Fe_2SiO_4)). Forsterite may contain some microelements, in particular, titanium. Olivine is the most widespread mineral in the terrestrial mantle at depths up to 410 km. Its properties are important for understanding the physical (for example, rheological) processes occurring in the terrestrial mantle and such an urgent phenomenon as the propagation of seismic waves, which, in turn, determines the character of earthquakes.

At the same time, the content of water in the defect positions in minerals (such as olivine) in the terrestrial mantle is of the same order of magnitude as on Earth's surface. The presence of OH in these minerals even in small amounts affects significantly their physical properties. It has been shown recently that OH is bound with titanium atoms in the upper mantle [1]. Thus, determination of the atomic positions of titanium is important for understanding the processes of water accumulation in olivine.

Having generalized the aforesaid, one can state that the study of Ti-containing olivine is important for understanding the solubility of titanium and the processes of water accumulation in the terrestrial mantle [1, 2]. Study of the atomic geometry of minerals is an important step on this path. Despite the great interest

in the titanium-containing forsterite, the fine details of its atomic structure are known incompletely. Thus, the investigation of the atomic structure of this mineral is an interesting and urgent problem.

When studying the local atomic structure, the choice of the analytical method is of radical importance. The X-ray absorption near-edge structure (XANES) spectroscopy [3–5] is a widely recognized effective method for studying the atomic and electronic structures of condensed-state materials, including those exhibiting no long-range order in the atomic arrangement. Recently, XANES spectroscopy has been successfully applied to analyze the atomic geometry and the features of the electron subsystem of different geological materials [6–11]. For example, the atomic and electronic structures near titanium atoms in ilmenite were theoretically analyzed based on the XANES data [6]. The local atomic structure of the materials entering the anatase group was investigated by analyzing the preedge features of XANES spectra after the *K* edge Ti [7]. The content of trivalent iron with respect to the total amount of iron in minerals of the garnet–omphacite–phengite system was analyzed by micro-XANES spectroscopy [8]. XANES analysis was also applied to the environment of iron (II) in some ferrosilicates, including fayalite [9]. The coordination of Ti atoms in different materials, including forsterite, can be determined by X-ray absorption spectroscopy. X-ray absorption spectra after the Ti *K* edge have a preedge feature, which is due to the $1s \rightarrow 3d$ electronic transition [12]. This transition is forbidden in the octahedral coordination but can be allowed in a low-symmetry environment as a result of the mix-

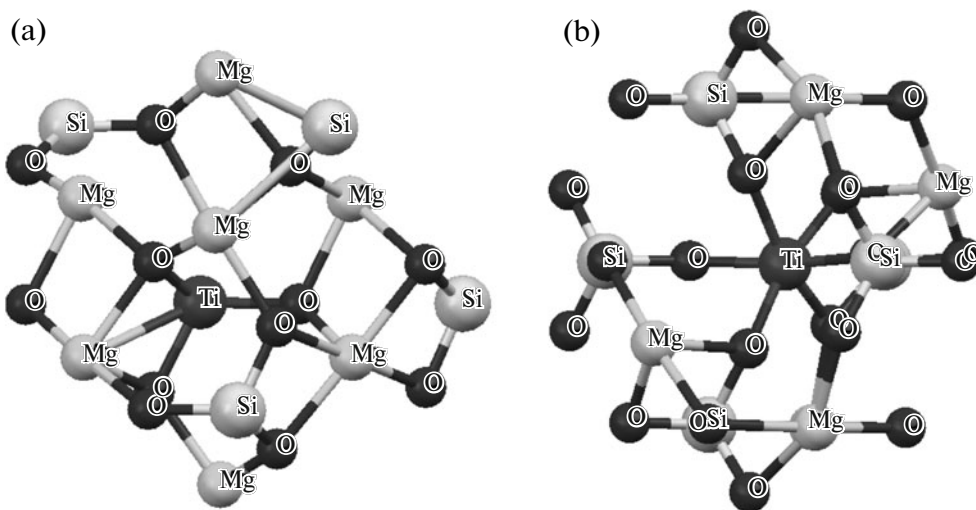


Fig. 1. Schematic structure of titanium-containing forsterite with titanium atoms substituting for (a) silicon and (b) magnesium atoms.

ing of p and d orbitals. The intensity of the preedge peak is directly proportional to the coordination number of Ti [13, 14], and this peak is blue-shifted with an increase in the Ti coordination number. Therefore, titanium-containing materials with titanium coordination numbers of 4, 5, or 6 can be distinguished by the intensity of the preedge feature and its energy position [15]. Analysis of the preedge features of the XANES spectra after the Ti K edge makes it possible to determine the coordination of Ti atoms in amorphous materials and in crystals, although coordination is not the only factor affecting the preedge peak. It was shown in [16] that preedge features depend on various geometric parameters, such as the coordination number, symmetry, lengths of Ti–O bonds, and bond angles.

In this paper, we report the results of studying the local atomic structure of the titanium environment in titanium-containing forsterite based on the analysis of X-ray absorption spectra after the Ti K edge. The partial densities of electron states (DOSs) of titanium were calculated to investigate the electronic properties of the mineral studied.

EXPERIMENTAL

A sample of titanium-containing forsterite was synthesized from powdered MgO, SiO₂, and Ti_xSi_{1-x}O₂ ($x \ll 1$) crystals. The powders were mixed using a technique ensuring uniform distribution of titanium atoms in the sample. Then, the material was pressed into pellets and calcined at 1400°C for 24 h. The Ti content was determined using a Cameca Camebax electron microprobe. The XANES spectra after the Ti K edge were recorded at the Synchrotron Radiation Center (KEK Photon Factory, Tsukuba, Japan)—one of the first large-scale specialized syn-

chrotron radiation sources. The electron energy in the storage ring reaches 2.5 GeV at a current of 450 mA. The XANES spectra after the Ti K edge were recorded in the range of 4955–5200 eV with steps of 0.2 (at energies from 4955 to 5015 eV) and 0.25 eV (at energies above 5015 eV).

CALCULATION METHOD

Structural simulation of possible defects in Ti-containing forsterite was performed based on the density functional theory (DFT) [2]. It was assumed that forsterite with incorporated titanium atoms forms a lattice with the parameters $a = 9.63$ Å, $b = 10.38$ Å, and $c = 12.18$ Å. Figures 1a and 1b show schematically the structural models where silicon and magnesium atoms, respectively, are replaced by titanium.

The theoretical XANES spectra after the Ti K edge for several structural models of titanium-containing forsterite were calculated based on the finite-difference method, implemented in the FDMNES 2010 code [17]. The finite-difference method is widely used to solve numerically differential equations through searching for a solution on a grid of points. In the case of XANES spectra, it is the Schrödinger equation for a fairly large region around an absorbing atom that is of interest. Calculations in the FDMNES code are performed using the so-called full potential, i.e., without any approximations for the potential shape, thus avoiding the problem characteristic of the classical muffin-tin approximation. The potential was calculated applying the model of exchange potential of the Hedin–Lundqvist type. The calculations were performed taking into account the core vacancy formed by the electronic transition. The best agreement with the experimental XANES spectrum for the preedge

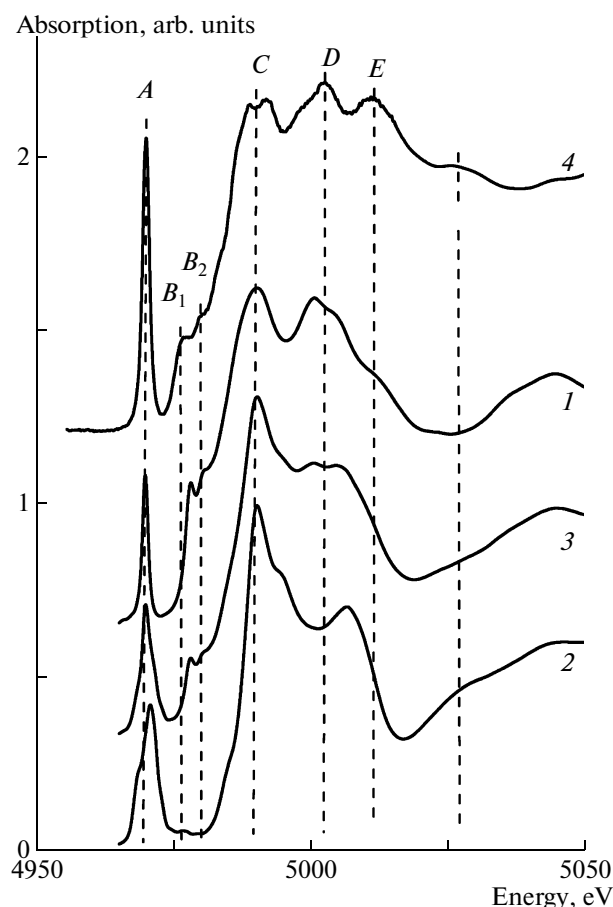


Fig. 2. Comparison of the (4) experimental X-ray absorption spectrum of forsterite after the Ti *K* edge with the theoretical spectra calculated for three structural models: titanium atoms substitute for (1) silicon and (2) magnesium atoms and (3) titanium atoms substitute for silicon and magnesium atoms in equal parts. The theoretical spectra were calculated using the FDMNES code.

range was obtained for the calculations taking into account both dipole and quadrupole transitions.

RESULTS AND DISCUSSION

The basic elements of the forsterite structure are the anionic group SiO_2^{4-} and two Mg^{2+} cations. Silicon is the central atom in the anionic group SiO_2^{4-} . Each oxygen atom is bound with silicon by a covalent bond. Since oxygen atoms in the anionic group are negatively charged, the distance between them should be fairly large. Thus, the optimal geometry for this group is a tetrahedron. Cations occupy two different octahedral positions, which form ionic bonds. The forsterite crystal structure is characterized by the orthorhombic (*Pbnm*) space group. Incorporation of titanium atoms into the forsterite structure leads to break of symmetry, because titanium replaces magnesium or silicon atoms

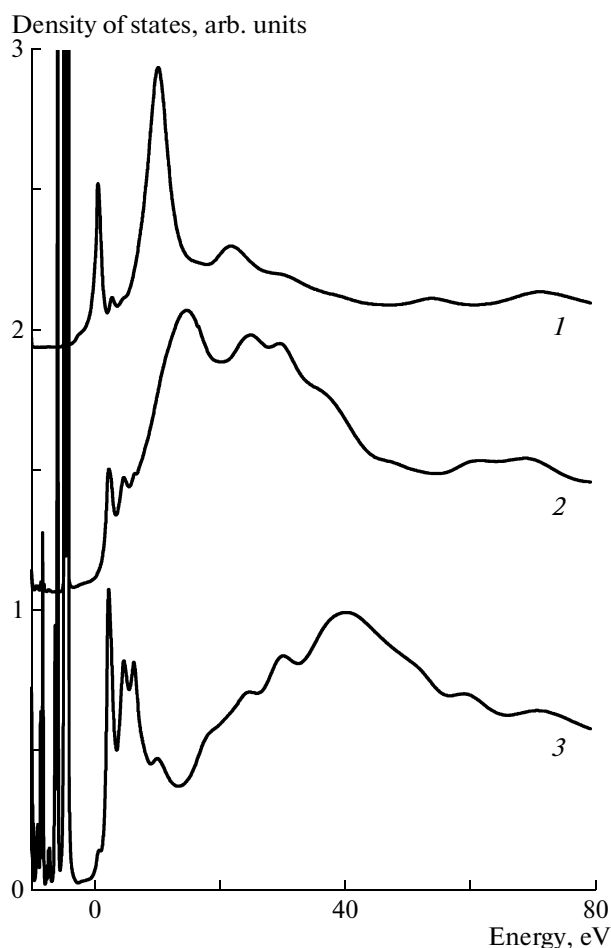


Fig. 3. Partial DOS spectra of Ti in Ti-containing forsterite: densities of (1) *s*, (2) *p*, and (3) *d* states. The calculations were performed for the structure where titanium atoms substitute for silicon; the Fermi level is at -7.6 eV.

(Fig. 1). We investigated the local structure near titanium atoms in titanium-containing forsterite by analyzing the XANES range. To determine the forsterite local structure, we considered three structural models with (i) titanium atoms replacing silicon atoms (Fig. 1a), (ii) titanium atoms replacing magnesium atoms (Fig. 1b), and (iii) titanium atoms replacing silicon and magnesium atoms in equal parts. In Fig. 2 the experimental Ti *K*-XANES spectrum of forsterite is compared with the theoretical spectra calculated for the above-described structural models based on the full-potential finite-difference method. Spectrum 3 for the third structural model was obtained by summing spectra 1 and 2 for the first and second structural models, taken with equal weights (0.5). It can be seen in Fig. 2 that spectrum 2 does not reproduce the features of the experimental spectrum (B_1 , B_2 , and E). Spectrum 2 is also inconsistent with the experimental one in the position of the peak D . Spectrum 3 reproduces the features B_1 and B_2 but does not exhibit the feature E . In addition, the intensity ratio for the peaks

C and D in spectrum 3 differs significantly from their experimental intensity ratio. The data in Fig. 2 suggest that the experimental XANES spectrum is in the best agreement with the first structural model, which implies replacement of silicon atoms by titanium ones.

Thus, analysis of the X-ray absorption spectra after the Ti K edge suggests that the most likely structural model of titanium-containing forsterite is that where silicon atoms are replaced by titanium.

To investigate the electronic structure of Ti-containing forsterite, we calculated the partial densities of unoccupied electron states of titanium near the bottom of the conduction band. Calculations were performed for the structure with Ti atoms substituting for Si atoms in the forsterite (Mg_2SiO_4) lattice. The obtained partial DOS spectra are shown in Fig. 3.

CONCLUSIONS

The X-ray absorption spectra after the Ti K edge in titanium-containing forsterite were calculated for several possible structural models. A comparison of the experimental XANES spectrum after the Ti K edge with the theoretical spectra calculated for different structural models made it possible to determine the local atomic structure of titanium environment in the material under study. The structural model of titanium-containing forsterite where silicon atoms are replaced by titanium ones is found to be most likely.

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