

The Ti environment in natural hibonite: XANES spectroscopy and computer modelling

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Abstract. The local atomic structure around Ti in Ti-bearing hibonite (CaAl_2O_9) was studied using X-ray absorption near-edge structure (XANES) spectroscopy and computer modelling. Structural models of the direct substitution of Al by Ti^{3+} , Al by Ti^{4+} charge balanced by the coupled substitution of Mg^{2+} for Al, and small Ti clusters were considered. The Ti *K*-XANES spectra of natural hibonite with different Ti concentration were recorded. Theoretical Ti *K*-XANES spectra for structural models of hibonite were calculated. It was shown that the theoretical Ti *K*-XANES spectra for a model with Ti at the five-coordinated M2 site are in agreement with the experimental XANES spectra of hibonite with low concentrations of Ti, while the theoretical spectra for a structural model of clustered Ti are in agreement with the experimental spectra of hibonite with higher Ti contents.

1. Introduction

Hibonite (CaAl_2O_9) is a mineral found in calcium-aluminum-rich inclusions (CAIs) of chondritic meteorites. CAIs are among the oldest materials in the Solar System [1], so, hibonite has the potential to record conditions that were present when the Solar nebula condensed to form the Solar System. In particular, hibonite has potential to be used to study the oxygen fugacity ($f\text{O}_2$) due to the incorporation of polyvalent elements such as Fe, V, Cr and Ti in its structure. The $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio can be used to determine the $f\text{O}_2$ of terrestrial materials, but it is not suitable for CAIs because the highly reduced conditions of formation result in the presence of metallic iron. In the case of CAIs, the $\text{Ti}^{3+}/\text{Ti}^{4+}$ ratio may be an alternative means of determining $f\text{O}_2$ (e.g. [2]).

The goal of the present study was to investigate the local atomic structure around Ti in Ti-bearing hibonite.

X-ray absorption near-edge structure (XANES) spectroscopy allows to study the electronic structure and 3D atomic geometry (bond lengths and bond angles) around an absorbing atom at a defect site (i.e. without long-range order) [3]. Recently, XANES spectroscopy was used successfully to investigate the local environment of Ti at defect sites in minerals [4-5]. But the method of extracting information from experimental XANES spectra is not direct and requires computer modelling.

Computer modelling of different Ti defects in Ti-bearing hibonite was recently undertaken using density functional theory (DFT) [6]. In this investigation we used Ti *K*-edge XANES spectroscopy to



verify the structural models of Ti-bearing hibonite obtained on the basis of computer modelling. We present the experimental Ti *K*-XANES spectra of natural hibonite with different Ti concentration and compare these to theoretical spectra simulated for the first time.

2. Experiment and methods of calculation

Ti *K*-edge XANES spectra of natural and synthetic hibonite with different Ti concentrations were recorded at I18 of Diamond Light Source (United Kingdom). Natural hibonite samples with low and high Ti concentrations contain a mixture of Ti³⁺ and Ti⁴⁺. In this paper we present Ti *K*-edge XANES spectra of natural hibonite; the spectra of synthetic samples will be presented elsewhere.

Hibonite has a hexagonal structure (e.g. [7]) that is dominated by polyhedral layers perpendicular to the *c*-axis. Ca occupies a 12-coordinated polyhedron and Al occupies five M sites. The cation site multiplicity and their coordination numbers can be described as ^[12]Ca^[6]M1^[5]M2^[4]M3₂^[6]M4₂^[6]M5₆O₁₉ [6]. Here the multiplicity of the site is subscripted and the coordination numbers are superscripted in brackets.

Modelling of Ti defects in hibonite was undertaken using DFT implemented in the SIESTA code, which uses a strictly localized atom-like basis set and pseudopotentials to achieve good computational performance for large systems. The structure of CaAl₁₂O₁₉ determined in [7] was used as the starting point for modelling the Ti defects. The structural models of direct substitution of different Al positions by Ti³⁺, the substitution of Al sites by Ti⁴⁺ coupled to a charge balancing substitution of Mg for Al, and small Ti clusters were considered [6].

Theoretical Ti *K*-XANES spectra for the structural models were calculated on the basis of two approaches.

First, self-consistent real-space full multiple scattering (FMS) theory, within the muffin-tin approximation for the potential shape, implemented into the electronic structure code FEFF9 [8-9] was used. XANES spectra were calculated for atomic clusters of 7.0 Å around absorbing Ti atoms. The influence of different types of exchange-correlation potentials on the Ti *K*-XANES was checked. For the calculation of spectra of hibonite with low Ti concentrations, the exchange-correlation potential of Dirac-Hara with Hedin-Lundqvist imaginary part was used. To calculate the XANES spectra of hibonite with high Ti concentrations, the Hedin-Lundqvist exchange-correlation potential was used.

Second, the full-potential finite difference method (FDM) to solve the Schrödinger equation with the Hedin-Lundqvist exchange-correlation potential realized in the FDMNES code [10] was applied. The main advantage of this method is the possibility of a totally free potential shape, thus avoiding the limitations of the muffin-tin approach. Because of the higher computational demands of FDM, the Ti *K*-edge XANES spectra were simulated for atomic clusters of 5.6 Å around the absorbing Ti atom.

All Ti *K*-XANES spectra of hibonite were calculated taking into account the core hole created by the electronic transition. Spectra for the structural models of small Ti clusters (a cluster of two Ti³⁺ defects on adjacent face sharing six coordinate M4 sites, and a cluster of two Ti⁴⁺ defects charge balanced by two Mg²⁺ defects) were obtained as a sum of the spectra calculated for the two Ti positions.

3. Results and discussion

Experimental Ti *K*-XANES spectra of natural hibonite samples with low (0.1 Ti per formula unit, pfu) and high Ti (0.55 Ti pfu) concentration are shown in Figures 1 and 2, respectively. The main difference in the experimental spectra is the intensity of the pre-edge feature marked as A. The pre-edge feature is more intense in the spectrum of the sample with the lower concentration of Ti, which suggests a lower coordination number [11].

In the first instance, the modelling of Ti defects in hibonite was guided by the results of DFT. It was found that the model with Ti on the five-coordinated M2 site is the lowest energy for substitution as an isolated cation on a M site [6]. For higher Ti concentrations, the lowest energy model was a small Ti cluster (two Ti atoms on adjacent face sharing six-coordinate M4 sites) [6]. The cases of Ti³⁺

and Ti^{4+} defects (the latter charge balanced by Mg^{2+} defects) were both considered. Upon optimization an increase in the Ti-O distances was observed.

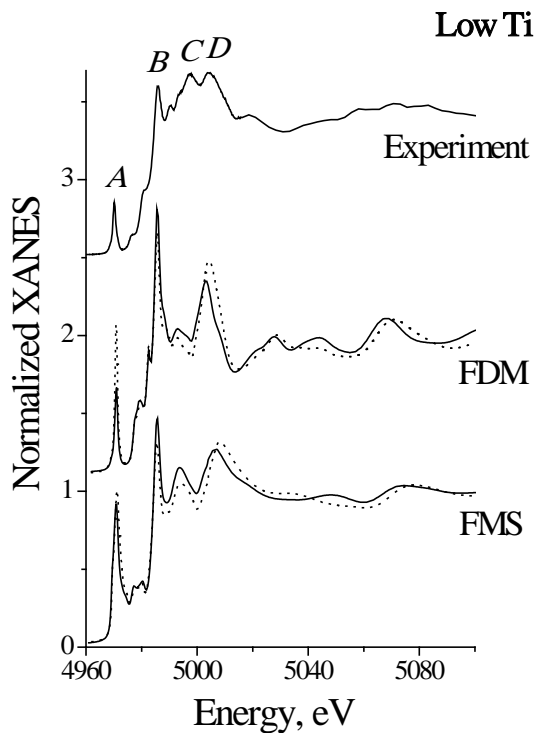


Figure 1. Comparison of the experimental Ti *K*-XANES spectrum of natural hibonite with low Ti concentration (0.1 Ti pfu) and theoretical spectra calculated for a structural model with Ti on the M2 site. Theoretical curves are the sum of spectra for a model of Ti^{3+} on the M2 site (20 %) and a model of Ti^{4+} on the M2 site charge balanced by Mg^{2+} on the M3 site (80 %). Theoretical spectra are shown for the non-optimized structure (dotted lines) and after structure optimization (solid lines). Theoretical spectra were simulated using the FMS (FEFF9 code) and FDM (FDMNES code) methods.

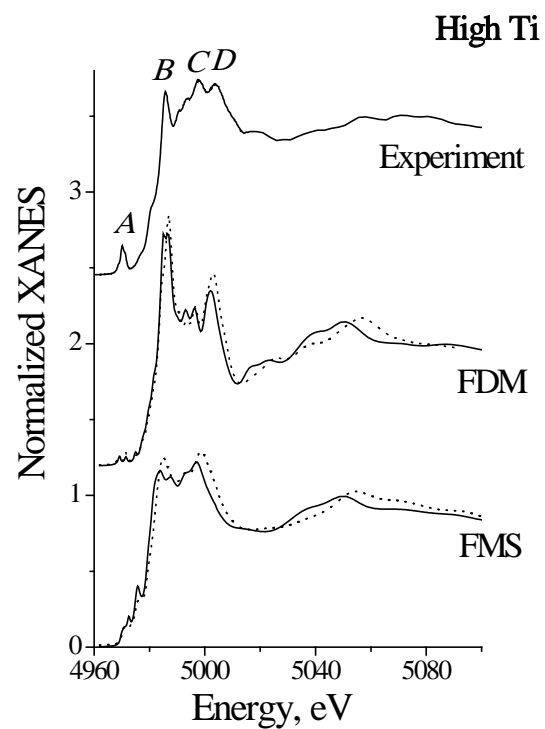


Figure 2. Comparison of the experimental Ti *K*-XANES spectrum of natural hibonite with high Ti concentration (0.55 Ti pfu) and theoretical spectra calculated for a structural model with 20% of clustered Ti^{3+} on adjacent face sharing M4 sites and 80 % of a small cluster of two Ti^{4+} defects charge balanced by two Mg^{2+} defects. Theoretical spectra are shown for the non-optimized structure (dotted lines) and after structure optimization (solid lines). Theoretical spectra were simulated using the FMS (FEFF9 code) and FDM (FDMNES code) methods.

The theoretical Ti *K*-XANES spectra were calculated for these structural models using the FMS and FDM methods implemented in the FEFF9 and FDMNES codes, respectively.

As some natural (meteoritic) hibonite contains about 80% of Ti as Ti^{4+} and 20% as Ti^{3+} [12], the sum of the theoretical spectra for the models of a single Ti^{3+} defect on the five-coordinated M2 site and a single Ti^{4+} on the M2 site, charged balanced by Mg^{2+} on the M3 site, with weights of 0.2 and 0.8, respectively, was used to compare to the experimental spectrum of natural hibonite with low Ti concentration (see Figure 1). The sum of the theoretical spectra for the models of small clusters of two Ti^{3+} on adjacent face sharing six coordinate M4 sites and two Ti^{4+} defects on M4 sites charge balanced by two Mg^{2+} defects (with weights of 0.2 and 0.8) was used for comparison with the experimental spectrum of hibonite with higher Ti concentrations (see Figure 2).

Figures 1 and 2 show that the theoretical spectra are in good agreement with the experimental ones. Both FDM and FMS result in adequate predictions of the shape of the experimental spectra, but FDM gives higher intensity of the peak marked as *B* for both samples. Relaxation of the atomic geometries of the Ti defects results in a decrease in the energy difference between spectral maxima (e.g. between *B* and *D*) as well as a decrease in the intensity of the pre-edge feature for the sample with low Ti concentration. The decrease in the intensity of pre-edge feature, *A*, with increasing Ti concentration indicates a change in Ti coordination that is attributed to clustering [11].

4. Conclusions

Ti *K*-edge XANES spectroscopy and computer modelling were used to study the atomic structure around Ti in Ti-bearing hibonite. Structural models of direct substitution of Al by Ti (Ti^{3+} and Ti^{4+} charge balanced by substitution of Mg^{2+} for Al) and small Ti clusters were considered. Modelling of Ti defects in hibonite was performed using density functional theory implemented in the SIESTA code. Experimental Ti *K*-XANES spectra of natural samples of hibonite were recorded. Theoretical analysis of the Ti *K*-XANES spectra was done using FMS and FDM theory, which both give results that are in good agreement with the experimental spectra. We conclude that Ti on the five-coordinated M2 position is the most probable for low concentrations of Ti in hibonite, while clustered Ti on the six-coordinated M4 site is most probable for higher Ti concentrations.

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