American Mineralogist, Volume 96, pages 100–109, 2012

X-ray absorption near edge structure (XANES) study of the speciation of uranium and thorium in Al-rich $CaSiO_3$ perovskite

Steeve Gréaux,[1,*] François Farges,[1,†] Laurent Gautron,[1] Nicolas Trcera,[2] Anne-Marie Flank,[2,3] and Pierre Lagarde[2,3]

[1]Laboratoire des Géomatériaux et Géologie de l'Ingénieur, EA 4119, Université Paris-Est Marne la Vallée, 5 Bd Descartes, Champs s/ Marne, 77454 France
[2] SOLEIL Synchrotron, L'Orme des Merisier, BP 48, F-91192 Gif-sur-Yvette, France
[3]Paul Scherrer Institut, Swiss Light Source, Villigen-PSI, CH 5232, Switzerland

Abstract

X-ray absorption spectroscopy was used to investigate the oxidation state of uranium in various U- and Th-bearing Al-rich $CaSiO_3$ perovskite samples synthesized at high-pressure and high-temperature using a multi-anvil press apparatus. X-ray absorption near edge spectroscopy (XANES) spectra collected at the U L_{III}- and Th L_{III}-edges using both micro- and macro-focused beams show U^{4+} in the Al-rich $CaSiO_3$ perovskite. The structure of the U- and Th-bearing Al-rich $CaSiO_3$ perovskite samples have been cross-checked by XANES spectra collected at the Ca *K*-, Al *K*-, and Si *K*-edges. Al *K* and Si *K* spectra suggest that Al incorporates exclusively on the Si site of the $CaSiO_3$ perovskite. Ca *K* spectra of the (U,Th)-bearing Al-rich $CaSiO_3$ perovskite samples were succesfully compared to FEFF8.2 ab initio models of a tetragonal $CaSiO_3$ perovskite with space group *P*4/*mmm*.

Our results confirm previous assumptions of the coupled substitution of $CaSi_2$ by UAl_2 in $CaSiO_3$ perovskite and that U and Th can be incorporated separately or together in $CaSiO_3$ perovskite by means of this mechanism. The possible occurrence of the U- and Th-bearing Al-rich $CaSiO_3$ perovskite are discussed as a potential candidate to locally host a large amount of actinides in the Earth's deep mantle. The study of a phase that can act as a storage mineral for heat-producing actinide elements such as uranium and thorium is fundamental to the understanding of the geodynamics and thermal behavior of Earth.

Keywords: Speciation, uranium, thorium, perovskite, X-ray absorption, deep mantle