

Electronic structure and local environment of substitutional V³⁺ in grossular garnet Ca₃Al₂(SiO₄)₃: K-edge X-ray absorption spectroscopy and first-principles modeling

**AMÉLIE BORDAGE,^{1,*} CHRISTIAN BROUDER,¹ ETIENNE BALAN,¹ DELPHINE CABARET,¹
AMÉLIE JUHIN,¹ MARIE-ANNE ARRIO,¹ PHILIPPE SAINTAVIT,¹ GEORGES CALAS,¹
AND PIETER GLATZEL²**

¹Institut de Minéralogie et de Physique des Milieux Condensés, UMR CNRS 7590, Université Pierre et Marie Curie, Université Paris Diderot, IRD UMR 206, IPGP, 140 rue de Lourmel, 75015 Paris, France

²European Synchrotron Radiation Facility, 6 rue Jules Horowitz, BP 220, 38043 Grenoble Cedex, France

ABSTRACT

The V *K*-edge spectrum of a V-bearing grossular garnet (tsavorite) single crystal has been measured by high-energy resolution fluorescence detected X-ray absorption spectroscopy (HERFD-XAS). First-principles calculations based on the density functional theory (DFT) reproduce the experimental spectra well, including the angular dependence of the pre-edge. The latter arises from pure electric quadrupole transitions since vanadium is incorporated in a centrosymmetric site, which inhibits the electric dipole transitions. An interpretation of the spectral features is given using a mono-electronic description of the transitions involved in the X-ray absorption process. The assignment of experimental pre-edge peaks in terms of *1s-3d* transitions makes it possible to determine the magnitude of the *3d*-splitting, which is similar to the 10 Dq crystal-field value determined from optical absorption spectroscopy. DFT calculations also indicate a full structural relaxation around V³⁺ substituting Al³⁺ in the garnet structure. The angular dependence only causes weak variations of the pre-edge intensity, which supports the use of V-bearing grossular garnet as a reference compound for octahedral V³⁺.

Keywords: Vanadium, garnet, HERFD-XAS, DFT calculations, *K* pre-edge, angular dependence, structural relaxation, crystal-field splitting