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Structural relaxation around substitutional Cr^{3+} in pyrope garnet

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ABSTRACT

The structural environment of substitutional Cr^{3+} ion in a natural pyrope $Mg_3Al_2Si_3O_{12}$ has been investigated by Cr *K*-edge extended X-ray absorption fine structure (EXAFS) and X-ray absorption near edge structure (XANES) coupled with first-principles computations. The Cr-O distance is close to that in knorringite $Mg_3Cr_2Si_3O_{12}$, indicating a nearly full relaxation of the first neighbors. The local C_{3i} symmetry of the octahedral Y site is retained during Cr-Al substitution. The second and third shells of neighbors (Mg and Si) relax only partially. Site relaxation is accommodated by strain-induced bond buckling, with angular tilts of the Si-centered tetrahedra around the Cr-centered octahedron, and by a deformation of the Mg-centered dodecahedra.

Keywords: Cr-pyrope, relaxation, XAS, ab initio, trace elements and REE, chromium, crystal structure, garnet, quantum mechanical calculations