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Synchrotron Mössbauer study of Fe-bearing pyrope at high pressures and temperatures

ZHU MAO,[1,*] JUNG-FU LIN,[1] SHU HUANG,[2] JIUHUA CHEN,[2] YUMING XIAO,[3] AND PAUL CHOW[3]

[1]Department of Geological Sciences, Jackson School of Geosciences, The University of Texas at Austin, Austin, Texas 78712, U.S.A.
[2]CeSMEC, Department of Mechanical and Materials Engineering, Florida International University, Miami, Florida 33172, U.S.A.
[3]HPCAT, Geophysical Laboratory, Carnegie Institution of Washington, Argonne, Illinois 60439, U.S.A.

ABSTRACT

Iron-bearing pyrope, an abundant silicate mineral in the Earth's upper mantle, exhibits the largest quadrupole splitting (QS) in Mössbauer spectra among all common Fe-bearing rock-forming silicate minerals at ambient conditions, with a value of ~3.5 mm/s. Knowledge regarding the hyperfine QS of mantle minerals at relevant pressures and temperatures (*P*-*T*) is needed to aid our understanding of the electronic spin and valence states of iron and local site distortion in major mantle silicate minerals. The latter, in turn, is relevant for coherent model of electronic and mechanical properties of the Earth's mantle. Here we have measured synchrotron Mössbauer spectra (SMS) of the high-spin Fe^{2+} in Fe-bearing pyrope garnet with two distinct compositions, $(Mg_{0.8}Fe_{0.2})_3Al_2Si_3O_{12}$ (py80alm20) and $Fe_3Al_2Si_3O_{12}$ (alm100), up to 30 GPa and 750 K. Analyses of the SMS spectra revealed that the high-spin Fe^{2+} ions in the distorted dodecahedral site exhibit extremely high QS of ~3.4–3.6 mm/s and relatively high chemical shifts (CS) of ~1.2–1.3 mm/s at high *P*-*T*, indicating that the Fe^{2+} ions remain in the high-spin state. An increase in the Fe content in the pyrope-almandine series only slightly decreases the QS and CS of the Fe^{2+} ions. To decipher the energy separation (Δ) between the two lowest energy levels of the 3*d* electrons of the Fe^{2+} ions in the sample, the d_{xy} and d_z^2 orbitals, the QS values of py80alm20 at high *P*-*T* were further evaluated using Huggins model. Our modeled results show that the Δ of the Fe^{2+} ions in py80alm20 is ~156 meV at high *P*-*T*, and may be correlated to the change of the crystal-field energy splitting (Δ_C). Comparison of the QS, Δ, and Δ_C values of Fe^{2+} ions in the distorted dodecahedral sites of pyrope and silicate perovskite indicates that the high-spin Fe^{2+} with the extremely high QS can remain stable at high *P*-*T* conditions, consistent with recent theoretical predictions. Our results thus contribute to our current understanding of the hyperfine parameters and spin and valence states of iron in the mantle silicate minerals at high *P*-*T*.

Keywords: Fe-bearing pyrope, Mössbauer spectroscopy, high pressure, high temperature, hyperfine parameters