Vibrational spectroscopy of pyrope-majorite garnets: Structural implications

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ABSTRACT

Infrared reflectance, thin-film absorbance, and polarized Raman spectra were acquired from ~100 to $\sim 4000 \text{ cm}^{-1}$ from polycrystalline garnets along the pyrope (Py = Mg₃Al₂Si₃O₁₂)-majorite [Mj = Mg₃(MgSi)Si₃O₁₂] join. We measured Py₁₀₀, Mj₃₉, Mj₄₅, Mj₈₀, and natural single-crystal, nearly endmember pyrope. Consistency is obtained between measured absorption spectra and absorption coefficients calculated through Kramers-Kronig analysis of reflectivity (R) data, if R-values are scaled to account for losses through scattering. The widths of the lattice modes double from each end-member toward the middle of the binary, whereas frequencies are nearly independent of composition. Strong polarization of Raman peaks of all our samples except pyrope shows that the space group is reduced from cubic, even for the Al-rich majorites. The largest number of IR or Raman peaks is observed for Mi_{80} . The number of peaks for Al-rich majorites lies between those seen for cubic pyrope and $I4_1/a$ majorite. The behavior of symmetry-breaking modes supports the I4₁/acd space group, which was inferred from X-ray data for Mj contents near 30 to 45% (Nakatsuka et al. 1999a). Also, the internal mode types that are expected for isolated SiO₄ tetrahedra in any garnet-like structure do not fully describe the patterns of peaks seen for some intermediate compositions along the Py-Mj join. The appearance of Si_{oct}-O-Si_{tet} bending modes in the available spectral data for Mj contents near 30-40 and 80-90%, but not near 45-50%, is attributed to two-mode behavior. Specifically, disruption of the $structural\ chain\ -Si_{oct}-O-Si_{tet}-O-Si_{oct}-O-Si_{tet}-in\ Si-rich\ majorites\ by\ units\ such\ as\ -Si_{oct}-O-Si_{uc}-O-Mg\ alters$ the electrostatic balance so that the internal modes are not entirely described by motions of isolated SiO₄ tetrahedra. Short chains are formed at both high and low Al contents, promoting coupling of Si octahedral and tetrahedral vibrations. Near M₅₀, each tetrahedron is linked (on average) to four octahedra containing two Al-, one Si-, and one Mg, and the Sioct-O-Sitet bending modes disappear. Order-disorder in majorite garnets is characterized not only by increased peak widths, but also by the presence of modes due to the bridging O atoms, whereas splittings and the appearance of new peaks indicate the space group for non-cubic garnets.