Mn5O8 nanorods were prepared by a topotactic conversion of γ-MnOOH nanorod precursors in nitrogen at 400 °C. The as-prepared Mn5O8 nanorods crystallized in a monoclinic structure (space group C2/m) with unit cell dimensions a = 10.3784(2) Å, b = 5.7337(7) Å, c = 4.8668(6) Å, and β = 109.491(6)°, having a compositional formula Mn2+Mn3+O8. The structure allowed 18 Raman-active modes (10 Ag + 8 Bg); 10 of these contributed were observed at 262, 300, 391, 429, 475, 533, 576, 615, 647, and 789 cm⁻¹. An intensive Ag mode at 647 cm⁻¹ was identified, representing a clear signature for probing the Mn5O8 materials via Raman scattering. X-ray photoelectron spectroscopy studies revealed the distinctive spectral features of the Mn5O8 due to the coexistence of divalent and tetravalent Mn ions. Magnetic measurements confirmed further that Mn5O8 was a mixed valence oxide with an antiferromagnetic transition at about 133 K. The decreased Nel temperature of the Mn5O8 nanorods suggested the possible presence of the finite size effect, which accounted also for the red-shift of the corresponding Raman bands in comparison with those of the bulk counterparts.