

Optical spectroscopic study of tuhualite and a re-examination of the beryl, cordierite, and osumilite spectra

MICHAEL N. TARAN^{*,†} AND GEORGE R. ROSSMAN

Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, California 91125-2500, U.S.A.

ABSTRACT

Polarized optical absorption spectra of a rare Fe²⁺, Fe³⁺-bearing silicate mineral, tuhualite, (Na,K)₂Fe₂²⁺Fe₂³⁺Si₁₂O₃₀, were measured at room temperature in the range 350–4000 nm (ca. 28500–2500 cm⁻¹). The spectra display a number of strongly pleochroic absorption bands in the visible and NIR range, which are attributed to ferric and ferrous ions distributed over octahedral and tetrahedral sites in the structure. No absorption bands caused by H₂O or OH stretching vibrations have been observed in the 3000 to 4000 cm⁻¹ range. A narrow, weak absorption line at ~422 nm ($\gamma \approx \beta$) is attributed to the ⁶A_{1g} → ⁴A_{1g}, ⁴E_g spin-forbidden transition of six-coordinated Fe³⁺ ions that occupy the octahedral Fe2 position of the tuhualite structure.

A broad, intense band at ~573 nm ($\gamma > \beta \gg \alpha$) is assigned to a Fe²⁺/Fe³⁺ intervalence charge transfer transition (IVCT) between tetrahedral Fe²⁺ and octahedral Fe³⁺. Together with the high-energy absorption edge, the band at 573 nm causes the intense violet color and spectacular pleochroism ($\gamma > \beta \gg \alpha$) of tuhualite. An intense band at ~1040 nm ($\gamma > \beta \gg \alpha$) and a much weaker band ~2150 nm (α) are attributed to spin-allowed *dd* transitions of Fe²⁺ in the strongly distorted tetrahedral Fe1 sites.

On the basis of the data obtained for tuhualite, optical spectra of the structurally related minerals beryl, cordierite, and osumilite are discussed and re-assigned. The spectra are re-interpreted on the basis of the distribution of Fe²⁺ in these minerals over structural octahedral and tetrahedral positions.