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

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ABSTRACT

Polarized optical absorption spectra of a rare Fe²⁺, Fe³⁺-bearing silicate mineral, tuhualite, \((\text{Na, K})_2\text{Fe}^{2+}\text{Fe}^{3+}\text{Si}_{12}\text{O}_{30}\cdot\text{H}_2\text{O}\), 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 (\(\gamma = \beta\)) is attributed to the \(^6\text{A}_{1g} \rightarrow ^4\text{A}_{1g}, ^4\text{E}_g\) 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 (\(\alpha\)) 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.

INTRODUCTION

The site occupancy of Fe²⁺ in ring silicates such as beryl and cordierite is controversial. In addition to occupation of an octahedral site, arguments have been presented in favor of additional Fe²⁺ being located in both an interstitial channel site and in a tetrahedral site. Tuhualite, a rare IVFe²⁺, VIFe³⁺-bearing chain silicate found only in the comendites of Mayor Island, New Zealand, provides an opportunity to experimentally address this controversy. Hutton (1956) described the occurrence, physical properties, morphology and chemical composition of tuhualite. Merlino (1969) refined the crystal structure and proposed the formula, \((\text{Na, K})_2\text{Fe}^{2+}\text{Fe}^{3+}\text{Si}_{12}\text{O}_{30}\cdot\text{H}_2\text{O}\).

According to Merlino (1969), the structure of tuhualite (Fig. 1) consists of six-repeated double chains of silicon tetrahedra and chains of edge-sharing alternating Fe²⁺ tetrahedra and Fe³⁺ octahedra, labeled Fe1 and Fe2, respectively. Sodium atoms are found in an irregular sixfold coordination in open structural channels aligned parallel to the a axis. Water molecules were also assumed to occupy the channel sites. Merlino proposed that the structure of tuhualite was closely related to that of osumilite, formulated as \((\text{Na, K})(\text{Mg, Fe}^{2+})(\text{Al, Fe}^{3+})\text{Si}_{12}\text{O}_{30}\cdot\text{H}_2\text{O}\) at that time.

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FIGURE 1. The view of a fragment of the tuhualite structure viewed down the a axis, based on the structural data of Merlino (1969). A zigzag-like chain of Fe²⁺ octahedra and distorted, edge-shared Fe³⁺ tetrahedra is parallel to the c axis. Six-coordinated Na⁺ ions are located in the structural channels.