*American Mineralogist, Volume 91, pages 1794–1801, 2006*

# Titanium incorporation and $^{VI}Ti^{3+}$ -$^{IV}Ti^{4+}$ charge transfer in synthetic diopside

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## ABSTRACT

A series of Ti-doped diopside samples synthesized by fluxgrowth methods under reducing conditions were investigated by microanalytical methods and optical absorption spectroscopy, to assess Ti incorporation mechanisms, valence states, and related electronic transitions. Chemical characterization show that Ti occurs both in the tri-and tetravalent states, with $Ti^{4+}$ preferentially ordered to the tetrahedral position whereas $Ti^{3+}$ is restricted to the M1 position. Charge-balance is maintained by incorporation of Na and minor B, stemming from the flux compound. Polarized optical absorption spectra reveal three major absorption features. Two relatively narrow bands centered at 18 500 and 15 700 $cm^{-1}$, mainly polarized in the crystallographic **c**-direction, display absorbance values that correlate with the calculated $Ti^{3+}$ (M1) concentration, and are assigned to spin-allowed d-d transitions in $Ti^{3+}$. A broader band centered around 24 500 $cm^{-1}$ displays absorbance values that are well correlated with the product of $^{VI}Ti^{3+}$ and $^{IV}Ti^{4+}$. Based on the spectral characteristics of this band, including a strong polarization in the crystallographic **b**-direction, we assign this band to an $^{M1}Ti^{3+}$-$^{T}Ti^{4+}$ intervalence charge transfer process.

**Keywords:** Crystal synthesis, diopside, optical spectroscopy, pyroxene, major and minor elements, Ti in pyroxene, order-disorder