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 flux growth 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$^{4+}$ (M1) concentration, and are assigned to spin-allowed d-d transitions in Ti$^{4+}$. 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 $^{VI}$Ti$^{3+}$-$^{IV}$Ti$^{4+}$ inter-valence charge transfer process.

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

INTRODUCTION

Titanium normally occurs in the tetravalent state in terrestrial minerals, whereas the presence of Ti in the trivalent state is known from the more reduced environments representative for lunar rocks and meteorites. Pyroxenes from occurrences containing Ti$^{4+}$ have earlier been studied by optical absorption spectroscopy (OAS), but the scarcity of good-quality samples of relatively simple compositions has made the interpretation of the spectral features difficult. The studied samples have almost invariably contained additional cations of Fe, which increases the number of possible interactions that have to be considered to cause absorption in the UV-VIS range. These interactions include single-ion d-d transitions in the ions Fe$^{3+}$, Fe$^{2+}$, and Ti$^{4+}$, as well as charge-transfer interactions involving Fe$^{2+}$-Fe$^{3+}$, Fe$^{2+}$-Ti$^{4+}$, and Ti$^{3+}$-Ti$^{4+}$ pairs. An exceptional sample in this respect has been the virtually Fe-free but Ti-rich “fassaite” (calcic subsilicic titanooan aluminian pyroxene) from the Allende meteorite, which has been investigated in several OAS studies (Dowty and Clark 1973a, 1973b; Burns and Huggins 1973; Mao and Bell 1974). The causes of the absorption bands in spectra of this sample has been debated, and the spectral features were interpreted by Strems et al. (1982) to be caused by electronic transitions involving Ti$^{3+}$ single-ions, exchange-coupled Ti$^{4+}$-Ti$^{3+}$ pairs, and Ti$^{4+}$-Ti$^{4+}$ charge transfer.

The aim of this study was to investigate substitutional mechanisms connected with Ti$^{3+}$ and Ti$^{4+}$ incorporation in clinopyroxene, and to further explore the possible electronic transitions involving Ti$^{3+}$ in the diopside structure by OAS. For these purposes, a series of diopside single-crystal samples with different Ti contents and Ti$^{3+}$/Ti$^{4+}$ ratios were synthesized by flux-growth methods under low oxygen fugacities. In addition, single crystals of a synthetic end-member NaTiSiO$_4$ clinopyroxene (Ohashi et al. 1982) were studied for reference purposes.

EXPERIMENTAL METHODS

Crystal synthesis and sample preparation

The diopside single crystals investigated in this study were produced by the flux-growth technique using Na$_2$B$_4$O$_7$ as a flux compound. The diopside components were weighed out as oxides (analytical grade powders), which were mixed with the flux compound in proportions that allowed the oxides to dissolve at the highest temperature of the experiment. About 5 g of these mixtures were thoroughly ground and transferred to 15 mL platinum crucibles, which were covered by lids. The crucibles were suspended in a vertical tube furnace equipped with a gas-flow system. The typical time-temperature path of the experiments consisted of a relatively fast rise in temperature to 1100 °C, a 24 hour plateau at this temperature to allow dissolution and homogenization, and then a linear cooling path of 2 or 4 °C/h down to 700 °C, from which the samples were allowed to cool more quickly down to room temperature. Before the temperature plateau was reached, an H$_2$-CO$_2$ gas flow was started, with H$_2$-CO$_2$ proportions in the range 1:1 to 5:1, which correspond to log fO$_2$ values equal to +0.5 to –1 relative to the Fe-wüstite solid buffer. The oxygen fugacity during the runs was monitored via a zirconia electrolyte sensor. The synthesis products consisted of many euhedral diopside single crystals embedded in residual glass. The diopside single crystals were recovered after dissolving the glass phase in warm diluted HCl. The crystals are elongated along the c-axis with dimensions up to 1 × 1 × 5 mm and are normally clear but contain occasional cracks and minor melt inclusions. The Ti-doped crystals range in color from gray to grayish brown. For the most Ti-rich compositions (Di-80 and Di-72), rod-shaped rutile crystals are abundant. The size of the rutile crystals varies, from a few to 100 μm in the smallest dimension and lengths from 30 μm to 3 mm.

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