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CHARGE-TRANSFER INTERACTIONS AND THE ORIGIN OF COLOR IN BROWN VESUVIANITE

P. G. MANNING

Canada Centre for Inland Waters, P.O. Box 5050, Burlington, Ontario L7R 4A6

ABSTRACT

Visible-region spectra of brown ferrous-rich vesuvianite crystals from Templeton, Quebec, and from near Great Slave Lake are described. Spectra of the Ti-rich Templeton crystals reveal a broad, complicated, shallow envelope centered at ~20,000 cm^{-1} (500 nm). The envelope seems to comprise two bands, one of which is strongly polarized in $E\perp c$ spectra, where *E* represents the vibration direction of the electric vector of incident light: the band is assigned to $Fe^{2+} \rightarrow Ti^{4+}$ intervalence charge-transfer. The spectrum of the Ti-poor Great Slave Lake material shows only the low-energy limb of ultraviolet-centered oxygen → Fe charge-transfer. It is suggested that substitution of Fe^{2+} and Fe^{3+} into the five-coordinated *B*-site is a major cause of brown and yellow coloration in vesuvianite.

SOMMAIRE

Parmi les spectres (dans le visible) de cristaux bruns de vésuvianite riches en fer, ceux des cristaux, de Templeton (Québec), riches en titane, révèlent une large enveloppe peu profonde et compliquée, centrée à ~20,000 cm^{-1} (500 nm). L'enveloppe semble comprendre deux bandes, dont l'une est fortement polarisée en spectres $E\perp c$, où *E* est le vecteur électrique de la lumière incidente: la bande est attribuée au transfert de charges intervalentiel $Fe^{2+} \rightarrow Ti^{4+}$. Le spectre des cristaux de la région du Grand lac des Esclaves, pauvres en titane, ne présente que la mince bande de faible énergie du transfert de charges oxygène → Fe dans l'ultraviolet. On émet l'hypothèse qu'une substitution de Fe^{2+} et Fe^{3+} en site *B* de coordination 5 est une des causes principales de la coloration brune et jaune de ces cristaux.

(Traduit par la Rédaction)

INTRODUCTION

Published optical-absorption studies of vesuvianite crystals from Wakefield, Quebec, describe a band at 11,000 cm^{-1} (909 nm) polarized in $E\perp c$ (Manning & Tricker 1975), where *E* represents the vibration direction of the electric vector of incident light. The same band is observed (unpublished work of the author) in optical-absorption spectra of reddish brown vesuvianite from Templeton, Quebec, which material is of similar color and of similar composition (*e.g.*, 2.7% FeO, 3% TiO_2) to the Wakefield. The Mössbauer-effect spectra of the Wakefield crystals (Manning & Tricker 1975) and of the Templeton crystals (unpublished work) are also similar. The 11,000 cm^{-1} Wakefield band was assigned to $Fe^{2+} \rightarrow Fe^{3+}$ intervalence charge-transfer (IVCT) between ions located on adjacent edge-sharing Al/Fe- and Ca(3)-centered polyhedra, which positions lie at approximately the same height along *z* (Rucklidge *et al.* 1975). Mössbauer-effect spectra of the Templeton and Wakefield crystals both show the presence of major amounts of Fe^{2+} and Fe^{3+} ions on Al/Fe. Crystallochemical arguments suggest that Ti^{4+} ions should also substitute into Al/Fe, but no band marking $Fe^{2+} \rightarrow Ti^{4+}$ IVCT at ~20,000 cm^{-1} was observed in the optical spectra of the Wakefield crystals. Part of the reason for this failure undoubtedly lies in preparing a section of the crystal of the optimum thickness to reveal the expected broad shallow IVCT feature that would be superimposed on the low-energy wing of a steeply sloping ultraviolet-centered charge-transfer absorption.

Progressive thinning and optical-spectral measurement of the Templeton material yielded the spectra presented in Figure 1; a broad shallow band is observed in both $E\perp c$ and $E/\!/c$ orientations at ~20,000 cm^{-1} (500 nm). The net envelope, representing absorption above a projected background, is considerably broader and more intense in the $E\perp c$ mode than in the $E/\!/c$. Moreover, the center of the net envelope is located at a significantly higher energy in the $E\perp c$ mode (centered at ~20,250 cm^{-1}) than in the $E/\!/c$ mode (at ~19,250 cm^{-1}). The $E\perp c$ envelope is best fitted with two Gaussian peaks: one, centered at ~21,250 cm^{-1} (470 nm), is strongly polarized in $E\perp c$, and the other, centered at 19,250±250 cm^{-1}, is weakly polarized with maximum intensity in $E\perp c$.

The 21,250 cm^{-1} band is the fifth vesuvianite band that is completely polarized in either $E/\!/c$ or $E\perp c$ (Manning 1975, 1976; Manning &

Tricker 1975). On the basis of polarization and of energy, the band appears to mark $Fe^{2+} \rightarrow Ti^{4+}$ IVCT between ions on, respectively, Ca(3) and Al/Fe positions. This assignment lends support to that of the 11,000 cm^{-1} band. The 21,250 cm^{-1} band is the sixth IVCT band found in spectra of different vesuvianite crystals. The origin of the 19,250 cm^{-1} band is not obvious: its polarization properties are similar to those of the Fe^{2+} $^5T_2 \rightarrow {}^5E(D)$ crystal-field bands described in the spectra of the Wakefield material (Manning & Tricker 1975), and it may therefore mark $^2T_2 \rightarrow {}^2E(D)$ transitions in Ti^{3+} on Al/Fe. Assuming an extinction coefficient of 20 l mole^{-1} cm^{-1} for the latter transition, the Ti^{3+} concentration in the Templeton crystal would be ~10% of total Ti, if this assignment is correct.

Figure 2 presents the visible-region spectra of a brown vesuvianite crystal from near Great Slave Lake. Electron microprobe analysis gave 4.6% FeO and 0.2% TiO_2 (Rucklidge *et al.* 1975). Spectra in the near-infrared show strong ferrous crystal-field bands; in contrast, the 21,600 cm^{-1} $^6A_1 \rightarrow {}^4A_1\,{}^4E(G)$ ferric band appears as a weak "blip". The extinction coefficient of the ferric band is ~1.5 l mole^{-1} cm^{-1} (Manning 1976), from which it is calculated that <20% of total Fe is ferric iron on Al/Fe. No absorption is observed at 20,000 cm^{-1} in the Great Slave Lake spectrum, reflecting the low Ti concentration: the brown color of this material is caused mainly by $O^{2-} \rightarrow Fe^{2+}/Fe^{3+}$ charge-transfer.

The $O^{2-} \rightarrow M^{n+}$ charge-transfer absorption makes a greater contribution to the colors of the mainly-ferrous Templeton, Great Slave Lake, and yellow Leurel crystals (see Manning 1975) than it makes to the green color of the ferric-rich Lowell crystals (5.65% Fe_2O_3, 0.10% TiO_2, Manning 1976). A "Ti-substitutional effect" (Robbins & Strens 1972; Faye *et al.* 1974) may be partly responsible in the Templeton crystal, but this is unlikely to be the case for the low-Ti Great Slave Lake crystal. For a given site, and assuming similar next-nearest neighbor compo-

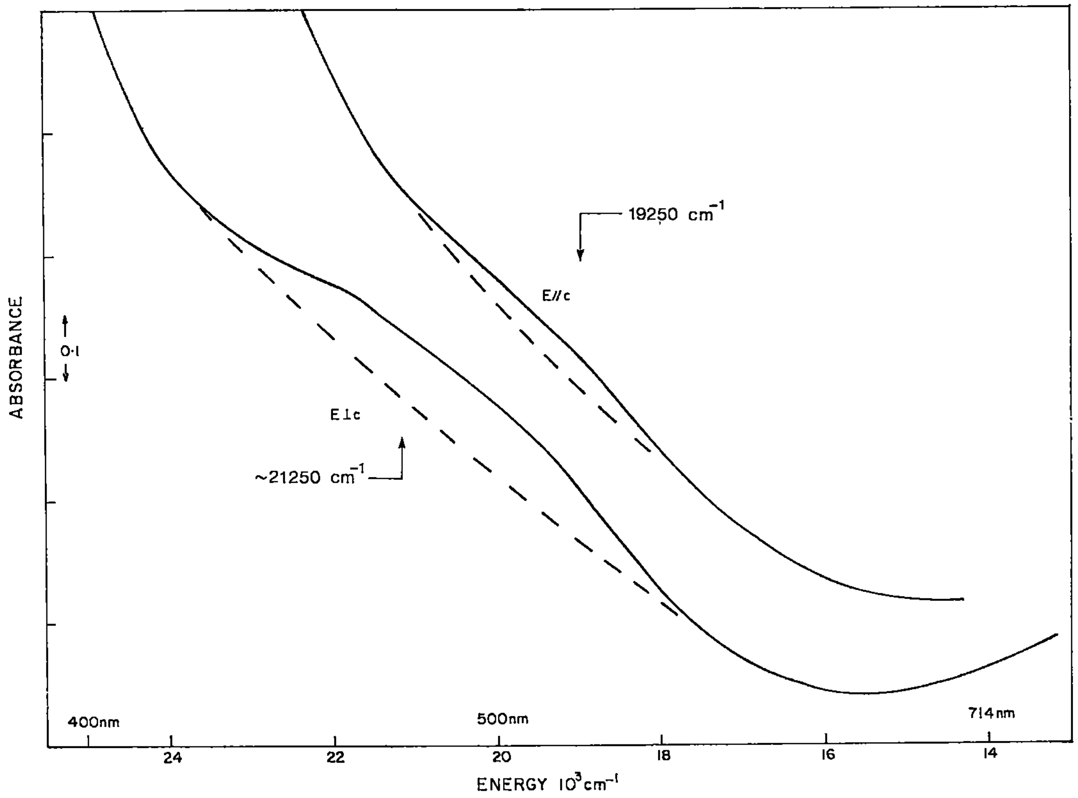

FIG. 1. Optical-absorption spectrum of a vesuvianite crystal from Templeton, Quebec. Specimen thickness 0.063 cm. Crystal is visually weakly pleochroic, and is reddish brown in *E*//*c* and brown in *E*⊥*c*. Dashed line represents an estimated background, the position of which is difficult to define accurately.

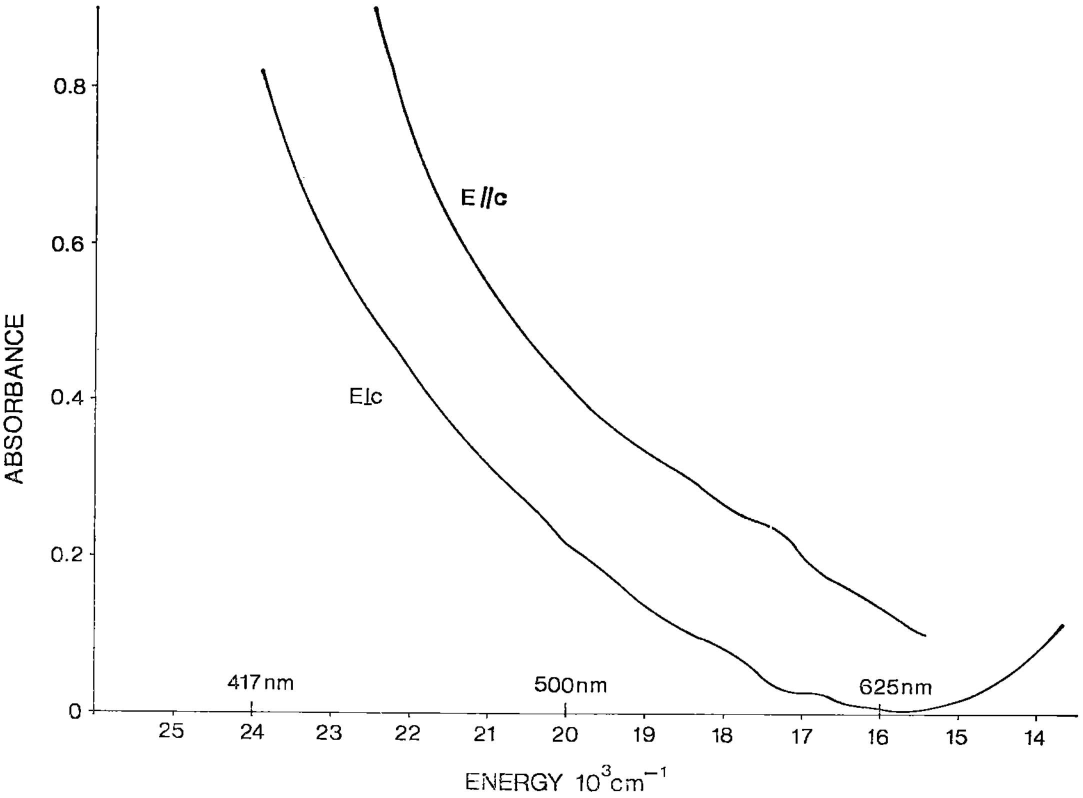

FIG. 2. Optical-absorption spectrum of a vesuvianite from near Great Slave Lake, Northwest Territories. Sample thickness 0.048 cm. Crystal is pleochroic, and is brown in $E/\!/c$ and yellow-brown in $E\perp c$. The near-infrared spectrum is similar to those of the Templeton and of the Wakefield crystals, comprising bands at 9000 cm^{-1}, 11000 cm^{-1} and 12500 cm^{-1}.

sitions, oxygen → Fe^{3+} charge-transfer is expected to occur with greater probability and at lower energy than oxygen → Fe^{2+} (Loeffler *et al.* 1974). Mössbauer-effect spectra of the Templeton, Leurel and Wakefield crystals all show evidence for Fe^{2+} on 5-coordinate *B*-sites and, significantly, the bonding O_{10} ion is not attached to Si, although it is not known whether O_{10} is bonded to a proton. Increased charge-density on O_{10} will promote $O^{2-} \rightarrow Fe^{2+}$ charge-transfer, which would account in large measure for the brown and yellow hues of Fe^{2+}-bearing vesuvianites.

The large number of IVCT bands in vesuvianite spectra shows that Fe^{2+}, Fe^{3+}, and Ti ions can be distributed over several of the available cation positions. In all likelihood, therefore, the optical-absorption and Mössbauer-effect spectra of vesuvianites will show considerable diversity. The following loose classification in terms of color and transition-metal chemistry is proposed:

(i) Blue, pink, and lilac crystals in which the origin of color lies mainly in *d-d* transitions in Cu^{2+}, Mn^{3+} and Cr^{3+} (see Deer *et al.* 1962).

(ii) Green crystals in which Fe^{3+}, seemingly on Al/Fe, is the main chromophore. This group is typified by crystals from Lowell, Vermont, from Pakistan (Manning 1976) and from Sanford, Maine (Ito & Arem 1970). Oxygen → Fe^{3+} charge-transfer is suppressed, possibly because of high OH content: the Lowell material contains 2% H_2O.

(iii) Ferrous-rich vesuvianites of various hues of brown and yellow. Crystals can be Ti-rich (>1% TiO_2) or Ti-poor (<0.2% TiO_2). Fe^{2+} occupation of Ca positions is of a minor proportion (Manning & Tricker 1975) compared with occupation of *B* and Al/Fe.

(iv) Vesuvianite crystals may contain transition-metal ions in sites of unusual coordination, for example Fe^{3+} in 5- or 8-coordination, and in major amounts, say 10 to 20 percent of total metal. Such substitutions may be coupled to some other substitutional process. These crystals, containing Fe^{2+} and Fe^{3+} ions located, at least partly, on *B*-sites are likely to be brown.

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