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Fe^{2+}-Ti^{4+} vs. Fe^{2+}-Fe^{3+} charge-transfer and short-range order in single chains of face-sharing octahedra: ellenbergerite and dumortierite

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In zoned pyrope megacrysts from the Dora-Maira UHP terrane, new, dark-violet colour varieties of the hexagonal, high-pressure silicate ellenbergerite extend the range of known Fe contents for this mineral from 0–0.1 to 0–0.4 atom pfu, for Ti contents commonly in the range 0.2–0.4 pfu. The new varieties show an extremely intense pleochroism, colourless for E perpendicular to c to deep Prussian blue for E//c, as compared to colourless to lilac or reddish purple for classical Fe-poor ellenbergerite. These features were the incentive for an electronic absorption spectroscopic study and a reappraisal of the interpretation of the charge transfers (CT), colour and ordering schemes in this group and the structurally related borosilicate dumortierite. Both structures are characterized by the presence of infinite single chains of face-sharing, partly vacant octahedra along the 6-fold screw axis and pseudo-hexad axis, respectively, in which the Fe and Ti atoms are partitioned.

In the spectra of Fe-poor ellenbergerite, the presence of a single Fe^{2+}-Ti^{4+} CT band near 19000 $cm^{\breve{}1}$ was taken as evidence for complete short-range ordering of Mg(Fe), Ti and vacancies in the octahedral single chain [1]. The E//c spectra of Fe-rich ellenbergerite show the same absorption band near 19000 $cm^{\breve{}1}$ but consistently flanked by another CT band near 14000 $cm^{\breve{}1}$, the intensity of which increases with total Fe content. The latter is similar to the 12400 $cm^{\breve{}1}$ CT band observed as the single feature in E//c spectra of the isotructural (Ti-free and Fe-bearing) phosphoellenbergerite, and clearly assigned to Fe^{2+}-Fe^{3+} CT in the octahedral single chain [1].

The same colour pattern occurs in the dumortierite group, with red Fe-poor, Ti-rich crystals showing a single CT band near 20000 $cm^{\breve{}1}$, blue Ti-poor crystals showing a single CT band near 16500 $cm^{\breve{}1}$, and violet Fe- and Ti-rich crystals showing a combination of the two bands [2]. In the light of the new data, we reinterpret the dumortierite colour scheme as due to both Fe^{2+}-Fe^{3+} (16500 $cm^{\breve{}1}$) and Fe^{2+}-Ti^{4+} (20000 $cm^{\breve{}1}$) CT, rather than to Fe^{2+}-Ti^{4+} CT only with two extreme types of Fe-Ti dimers [- v - Fe^{2+} - Ti^{4+} - v -] and [- M - Fe^{2+} - Ti^{4+} - v -], where v stands for vacancy. We discuss the implications in terms of energy and of short-range ordering of vacancies in the octahedral single chains of the ellenbergerite and dumortierite groups. Optical spectroscopy appears as a very sensitive structural probe of minor or trace elements.

[1] Chopin C. & Langer, K. (1988): Fe^{2+}-Ti^{4+} charge transfer between face-sharing octahedra: polarized absorption spectra and crystal chemistry of ellenbergerite. Bull. Minéral., 111, 17-27.

[2] Platonov, A.N., Langer, K., Chopin, C., Andrut, M., Taran, M.N. (2000): Fe^{2+}-Ti^{4+} charge-transfer in dumortierite. Eur. J. Mineral., 12, 521-528.