

SPINELS RENAISSANCE: THE PAST, PRESENT, AND FUTURE OF THOSE UBIQUITOUS MINERALS AND MATERIALS

Color of Mn-bearing gahnite: A first example of electronic transitions in heterovalent exchange coupled ${}^{\text{IV}}\text{Mn}^{2+}$ - ${}^{\text{VI}}\text{Mn}^{3+}$ pairs in minerals†

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ABSTRACT

A natural yellow and transparent crystal of Mn-bearing, Mg-rich gahnite (ZnAl_2O_4) from Nordmark (Sweden) was studied by electron microprobe, single-crystal X-ray diffraction and optical absorption spectroscopy. The empirical structural formula of the crystal, ${}^{\text{T}}(\text{Zn}_{0.52}\text{Mg}_{0.34}\text{Mn}_{0.08}^{2+}\text{Al}_{0.06})_{\Sigma 1.00}{}^{\text{M}}(\text{Al}_{1.88}\text{Mn}_{0.06}^{3+}\text{Fe}_{0.01}^{3+}\text{Mg}_{0.04}\text{Mn}_{0.01}^{2+})_{\Sigma 2.00}\text{O}_4$, shows that Mn^{2+} and Mn^{3+} are almost completely ordered at the T and M sites, respectively. The electronic absorption spectrum of the spinel shows, in addition to a strong UV-absorption edge (O^{2-} - Mn^{3+} and O^{2-} - Fe^{3+} ligand-metal charge transfers) and two broad ${}^{\text{VI}}\text{Mn}^{3+}$ -bands, a set of relatively narrow absorption bands at energies comparable to those caused by spin-forbidden electron transitions in tetrahedrally coordinated Mn^{2+} in oxide spinel. However, the set of bands in the present spectrum is shifted to lower energies and they are intensified by approximately an order of magnitude compared to those recorded for spin-forbidden ${}^{\text{IV}}\text{Mn}^{2+}$ -bands in spinel. These characteristic differences in combination with the determined cation distribution in the present gahnite demonstrates that electronic transitions in exchange coupled ${}^{\text{IV}}\text{Mn}^{2+}$ - ${}^{\text{VI}}\text{Mn}^{3+}$ pairs cause its color.

Keywords: Gahnite, crystal structure, electronic spectra