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Galaxite, $MnAl_2O_4$, a spectroscopic standard for tetrahedrally coordinated Mn^{2+} in oxygen-based mineral structures

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Abstract

Chemical analyses, crystal structure refinement, cation order determination, and single-crystal optical absorption spectrum of synthetic galaxite are presented. New optical absorption spectra of natural Mn-bearing willemite, rhodochrosite, Mn-rich forsterite, and tephroite are reported for comparative purposes.

The structure of a synthetic galaxite end-member is characterized by a relatively large unit-cell edge, a_0 = 8.2104(3) Å, a *u*-parameter equal to 0.26588(7), a T-O distance of 2.0034(6) Å, and an M-O distance of 1.9310(5) Å. Mn^{2+} is strongly ordered at the tetrahedral T-site as demonstrated by the refined structural formula $^{T}(Mn^{2+}_{0.90}Al_{0.10})^{M}(Mn^{2+}_{0.10}Al_{1.90})O_4$.

The optical absorption spectrum of galaxite in the range 300–800 nm shows a set of five relatively sharp bands at 20 300, 22 250, 23 390, 25 970, and 27 780 cm^{-1} marking spin-forbidden transitions in Mn^{2+} at the tetrahedral site. The molar absorption coefficient of the field-independent $^6A_1(S) \rightarrow {}^4E_g^4A_{1g}(G)$ absorption band at 23 390 cm^{-1} equals 1.90 L/(mol·cm), which is approximately an order of magnitude higher than for corresponding bands in spectra of compounds that contain isolated Mn^{2+}-centered octahedra.

The calculated crystal field splitting, 10Dq, for Mn^{2+} at the T-site in galaxite equals 5290 cm^{-1}. This compares well with derived 10Dq-values of 5860 and 5510 cm^{-1} for Mn^{2+} at the tetrahedral T1- and T2-site in Mn-bearing willemite. In agreement with theory, the 10Dq for Mn^{2+} in MnO_4 tetrahedra is ca. 30% smaller than corresponding values in MnO_6 octahedra. The lower Racah B-parameters of the spectroscopic data indicate that the degree of covalency of Mn^{2+}-O bonds is higher in tetrahedra than in octahedra.

Keywords: Crystal structure, galaxite, optical spectroscopy, willemite, tephroite, forsterite