

EPR of V⁴⁺ and Cu²⁺ ions in single crystals of pyrovanadates: β -Mg₂V₂O₇, α -Zn₂V₂O₇

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The EPR spectra for the V⁴⁺ and Cu²⁺ ions were recorded in single crystals of β -Mg₂V₂O₇ and α -Zn₂V₂O₇ at X-band (9.6 GHz) at 120 and 295 K. Vanadium-mixed oxides (V-Mg-O, V-Zn-O) are important in catalytic processes, such as oxidative dehydrogenation of hydrocarbons and selective catalytic reduction of NO by ammonia, synthesis of supported V₂O₇ catalyst, insulin-mimetic agents and rechargeable Li batteries. The electrical conductivity of Mg and Zn pyrovanadates strongly depends on the impurity ions and thermal treatment, which governs the formation of V⁴⁺ defects. [V.A. Ioffe, V.S. Grunin, Z.N. Zonn, S.E. Ivanov, I.S. Yanchevskaya, *Izv. Akad. Nauk SSSR, Neorg. Mater.*, 1977, 13, 1484.] Therefore, investigation of defect centers in these compounds is a very important topic. The point symmetry of both Mg and V ions is C_i in triclinic β -Mg₂V₂O₇ crystals, and there exist two magnetically inequivalent sites for Mg and V ions. The EPR spectra of the V⁴⁺ and Cu²⁺ ions are observed in only one of the two magnetically inequivalent positions in β -Mg₂V₂O₇. One V ion is 4-fold tetrahedrally coordinated, while the VO₄ tetrahedron of the second V ion is distorted due to bonding with the fifth oxygen ion. There is only one magnetically inequivalent site for V⁴⁺ ions in monoclinic α -Zn₂V₂O₇, with the point symmetry being C_i, in trigonally bipyramidal fashion. The Cu²⁺ ion is 6-fold octahedrally coordinated in β -Mg₂V₂O₇, while it is 5-fold tetrahedrally coordinated in α -Zn₂V₂O₇ in a trigonally bipyramidal fashion. A rigorous least-squares fitting of EPR line positions in three mutually perpendicular planes to spin-Hamiltonian (SH) parameters, enabled determination of the orientations of the principal axes of the Zeeman and HF interaction matrices. The SH parameters of V⁴⁺ ions in β -Mg₂V₂O₇ and α -Zn₂V₂O₇ at 295 K are:

	g _z	g _x	g _y	A _z (GHz)	A _x (GHz)	A _y (GHz)
Mg ₂ V ₂ O ₇	1.930	1.977	1.996	0.480	0.185	0.147
Zn ₂ V ₂ O ₇	1.928	1.971	2.014	0.504	0.189	0.170

In β -Mg₂V₂O₇ and α -Zn₂V₂O₇ the SH parameters of V⁴⁺ ions are similar. The Mg and Zn ions are differently coordinated in these host crystals, therefore the Cu²⁺ ion, substituted for these ions, has quite different from each other SP parameters: g_z = 2.000 < g_x = 2.283, g_y = 2.355, A_z = 0.25 GHz > A_x, A_y ≈ 0.05 GHz (unresolved EPR lines) in β -Mg₂V₂O₇ and g_z = 2.388 > g_x = 2.123, g_y = 2.050, A_z = 0.24 GHz > A_x, A_y ≈ 0.05 GHz (unresolved EPR lines) in α -Zn₂V₂O₇. Formation of defect centers V⁴⁺ is related to local distortion of stoichiometry and impurity ions.