

Magnetic resonance study of phases from Sb-V-O and Sb-V-Mo-O systems

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Electron paramagnetic resonance (EPR) study of selected phases formed in the Sb-V-O and Sb-V-Mo-O systems has been carried out in the 3-300 K temperature range. The following compounds were investigated: SbVO_5 , $\text{Sb}_3\text{V}_2\text{Mo}_3\text{O}_{21}$, and six samples containing phase type solid solutions of MoO_3 in SbVO_5 . As the catalytic activity of these materials depends crucially on the concentration and type of defect center, EPR technique will be used to provide this important information. In powder samples of SbVO_5 three kinds of paramagnetic defect centers involving vanadium ions were found: one center involving a mobile electron hopping along a $\text{V}^{4+}\text{--O--V}^{5+}$ bond producing a broad EPR line without hyperfine structure, the second centre is formed by VO^{2+} ions in octahedral coordination with a tetragonal compression, and the third complex is a dimer composed of two interacting VO^{2+} ions. Study of thermal decomposition products of SbVO_5 revealed in EPR spectrum a broad component arising from vanadium(IV) clusters present inside the micrograins forming powder sample, and a narrow component due to vanadium(IV) ions located on the surface of these grains. EPR spectra of $\text{Sb}_3\text{V}_2\text{Mo}_3\text{O}_{21}$ registered in the 4-290 K temperature range represent a very broad line that has been decomposed on three anisotropic components. The temperature dependence of these components has been studied revealing a strong change of that component connected with the z axis of vanadium cluster. Only 11.3% of all vanadium ions in $\text{Sb}_3\text{V}_2\text{Mo}_3\text{O}_{21}$ are magnetic and could be revealed by EPR method. In the case of $\text{SbVO}_5\text{:MoO}_3$ solid solutions the problem of charge compensation could be resolved by EPR study. The dominating mechanism of compensation of an excessive charge of Mo^{6+} ion is realized by cation vacancy formation, although a significant part (~25%) of Mo^{6+} ions takes part in valence state reduction of V^{5+} ions.