

SbVO₄ Catalyst Structure Determination using Electron, X-ray and Neutron Diffraction

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SbVO₄ series of compounds could be used as oxidation catalysts of industrial interest yielding 20% cheaper acrylonitrile by the ammoxidation of propane compared to current method producing 8×10⁶ton/year based on propylene as starting reactant.

In the non-stoichiometric series described as Sb_{0.9}V_{0.9+x}0.2-xO₄ (0≤x≤0.2), cation vacancies () are introduced in the basic rutile type-structure following the mechanism: 4V³⁺→3V⁴⁺ + , while antimony remains as Sb⁵⁺. The reduced phase richest in V³⁺ has been reported to be Sb_{0.9}V_{1.1}O₄, which shows by electron diffraction (ED) superlattice reflections characteristic of a 2-fold rutile superstructure along *c* and the following unit cell: *a* = *b* = √2*a*_r, *c* = 2*c*_r. (subindex *r* refers to the basic rutile unit cell: *a*_r = 4.6085(1), *c*_r = 3.0867(1) Å, S.G. *P4*₂/*mmn* from X-ray powder diffraction data). Its space group, *I4*₁*md*, was determined by means of CBED [1]. A structural model based on alternating Sb and V cations ordering along *c* in the chains of edge-sharing octahedra was proposed. No cation vacancies have been observed for this reduced phase, see Figure 1, while for the compounds synthesized in oxidizing conditions the presence of vacancies has been confirmed. In fact, ED experiments have shown that vacancies order in the basic rutile structure giving rise to a modulated structure on the other end member of the series, namely Sb_{0.9}V_{0.9}O₄ [2], see Figure 2.

On the other hand, we have observed for the first time in this system the onset of magnetic ordering [3], see Figure 3. Due to the unique property of the neutrons to interact with ordered magnetic moments, the magnetic scattering coming from the V spins could be constrained to its crystallographic position, giving more information than at first glance could be expected by its almost null nuclear scattering. Thus, using neutron diffraction we try to determine the magnetic structure of reduced SbVO₄ coming from the ordering of vanadium magnetic moments, which certainly takes place at T_N ~50K, and to study how the substitution of V³⁺(S=1) by V⁴⁺(S=½), while the synthesis conditions become more oxidizing, affects the spin arrangement in Sb_{0.9}V_{0.9+x}0.2-xO₄. This order seems to be destroyed by the appearance of vacancies and the chemical disorder in the cations positions, on agreement with the nuclear structures proposed. Furthermore, it is possible to measure the intensity in an absolute scale and perform simultaneous Rietveld refinement of multipattern X-ray and neutron powder diffraction data, taking advantage of the neutron scattering length for oxygen location and higher contrast for the cations involved which is achievable with neutron diffraction compared with X-rays. The fact that V coherent scattering length for neutrons is rather small should give us an obvious advantage to determine the superstructure due to alternating Sb-V occupation of two crystallographic positions split from the substructure.

References

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2. A. Landa-Cánovas, J. García-García, S. Hansen, Catal. Today: 156, 2010
3. J. Hernández-Velasco, J. García-García, A. Landa-Cánovas, Acta Cryst. A67, C428, 2011

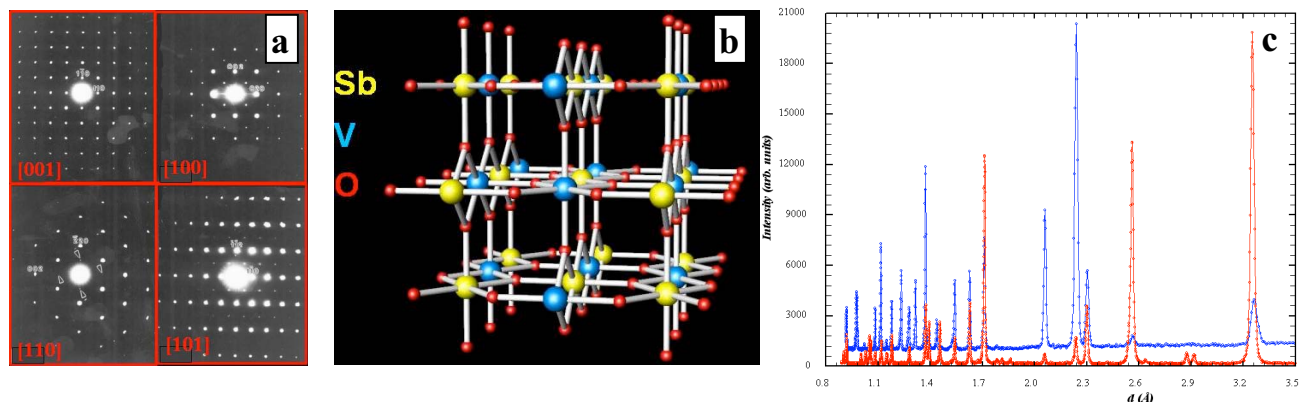


Figure 1. *Fig.a*) SAED patterns of reduced phase $\sim\text{Sb}_{0.9}\text{V}_{1.1}\text{O}_4$ along 4 high symmetry directions. *Fig.b*) Structure model proposed for the rutile-superstructure seen approximately along c -axis. *Fig.c*) Neutron (blue) and X-ray powder data (red) on d spacing corresponding to reduced SbVO_4 .

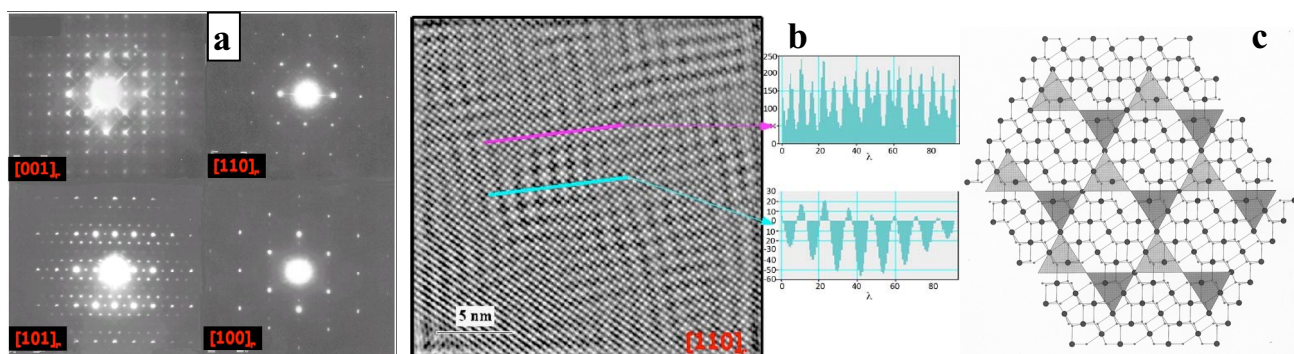


Figure 2. (a) SAED patterns of modulated oxidized SbVO_4 along four different crystallographic orientations. (b) HRTEM image of a crystal of oxidized SbVO_4 oriented along the $[1\ 1\ 0]$ rutile direction. The white dots correspond to basic rutile cation positions and the superimposed dark bands to sinusoidal waves of cation vacancies. The magenta and blue lines indicate the line scans whose intensity is displayed at the right of the figure. Magenta line runs across the cationic positions while the blue line runs mainly across the cation vacancy waves. (c) Possible model for vacancy ordering of oxidized composition close to $\text{Sb}_4\text{V}_3\text{O}_{16}$

Figure 3. Neutron diffraction patterns (I vs 2θ) of reduced SbVO_4 collected at the E6 diffractometer (HMI-Berlin) at 60K (blue) and 1.5K (red). Difference curve at the bottom (green line) corresponds to pure magnetic scattering. Inset shows the intensity evolution with temperature of a selected magnetic reflection marked by arrows ($T < 50\text{K}$).

