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$FeSbO_4$ and other rutile type mixed-oxides revealing nano-structural flexibility

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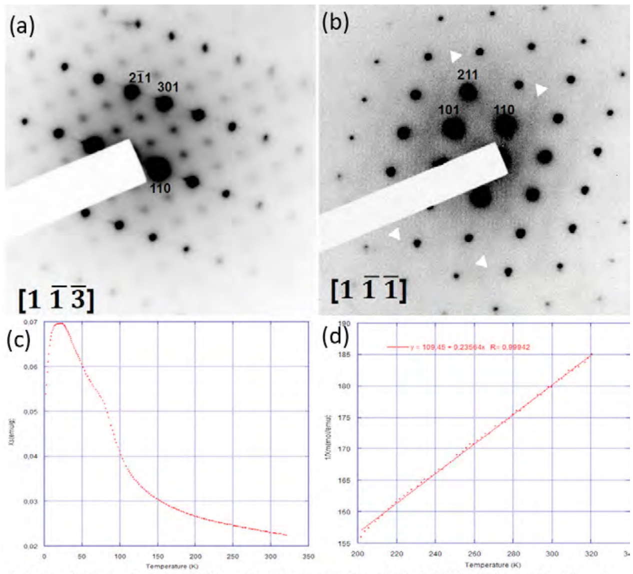
There are many examples of rutile-type mixed oxides that are active and selective catalysts for the ammoxidation of propane into acrylonitrile [1] ($VSbO_4$, $FeSbO_4$, $FeVSbO_6$, $CrSbO_4$ …). In this way, many studies have focused on the structural flexibility shown by rutiles when different cations and oxidation states are added.

$Fe_{0.5-x}V_{2x}Sb_{0.5-x}O_2$ ($0 < x < 0.4$) solid solutions were prepared by solid-state reaction from their raw oxides (Fe_2O_3, Sb_2O_3 and V_2O_5), using an air or argon atmosphere depending on the composition. The obtained samples were characterized by powder x-ray diffraction, electron diffraction, XEDS analysis, EELS spectroscopy, micro-Raman spectroscopy and magnetic susceptibility measurements.

Even though $FeSbO_4$ has been deeply studied [2], some doubts remain about the iron oxidation state and cation ordering. In this sense, electron diffraction patterns reveal a reciprocal lattice where diffuse reflections suggest a 3-fold trirutile along *c*-axis. The weak intensity of these reflections may indicate that only small clusters of the crystal are ordered into a trirutile type superstructure, the rest of the crystal is still crystallizing as a simple rutile. It is argued that only the presence of Fe^{2+} can produce this superstructure. Thus, EELS spectroscopy analysis and magnetic susceptibility measurements were made in order to find out if Fe^{2+} is present. The obtained results do not exclude this hypothesis.

With the purpose of keeping on studying the structural modification of rutile type oxides, vanadium was partially substituted in $FeSbO_4$ preparing the next composition series: $Fe_{0.5-x}V_{2x}Sb_{0.5-x}O_2$. Due to the difficulty of three cations have to be ordered in the same atomic position [3], no superstructure reflections are observed by electron diffraction. However, in the compounds with high iron contents, weak diffuse intensity indicative of short-range order (SRO) phenomena is found by electron diffraction.

In conclusion, these compounds, which are studied due to their catalytic properties, show very interesting order-disorder phenomena because of the extraordinary structural flexibility of these phases. The different characterization of each compound and its particular structural order will be reported.



Selected area electron diffraction patterns for FeSbO4 (a) and $Fe_{0.4}V_{0.1}Sb_{0.5}O_2$ (b). Magnetic susceptibility as function of T (c) and (d)

References:

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