

Changes of structural, optical and vibrational properties of WO_3 powders after milling and mixing with ReO_3 .

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The mixing of monoclinic tungsten oxide ($m - WO_3$) with cubic rhenium oxide ($c - ReO_3$), followed by high temperature treatment, induces changes in the phase composition and the coloration of the mixture.

A set of samples with different compositions ($W_{1-x}Re_xO_{3-y}$), starting from $x = 0$ up to $x = 0.9$, has been synthesized, by the following procedure. A mixture of $(1 - x)$ mol.% of $m - WO_3$ and (x) mol.% of $c - ReO_3$ was finely ground and closed under vacuum in a quartz ampoule; the ampoule was successively heated at $T = 450^\circ C$ for 17 hours (h) and at $T = 600^\circ C$ during 73 h: thus the obtained powders were gray to black in colour.

The room-temperature XRD spectra of these mixed samples indicate that they consist of orthorhombic-type WO_3 and ReO_2 phases which in pure state, are stable at high temperatures (above $300^\circ C$). Note that the ReO_2 phase appears in the mixture due to decomposition of $c - ReO_3$ at $400^\circ C$ during the preparation procedures. The positions of all peaks in XRD patterns well correspond to the sum of *ortho* - WO_3 and *ortho* - ReO_2 and no presence of any new phase, due to the mixing, was observed. Note that since W and Re are neighbours in the Periodic Table of Elements, the XRD cannot distinguish whether $W(Re)$ ions are partially incorporated within $ReO_2(WO_3)$ phase or not. However, the X-ray-absorption study on the W and Re L_3 edge shows that tungsten and rhenium ions are preferentially present in WO_3 and ReO_3 phases, respectively.

The Raman spectroscopy, more sensitive to the orientational changes of the $W - O$ bonds, confirms that picture: in fact, the $W - O$ stretching frequency at 800 cm^{-1} , is not affected by the mixing with rhenium oxide, but the low frequency spectrum, related to external modes of librational character, undergoes a spectral shape modification and turns out very similar to that of *ortho* - WO_3 , usually observed at temperatures above $330^\circ C$. Moreover, the total Raman scattering intensity abruptly decreases of a factor higher than 20 in passing from the pure WO_3 to the mixed composition with 10% of rhenium oxide. Finally, no spectral feature related either to formation of a new

A quite similar colour modification, accompanied by a strong quenching of the Raman scattering, is actually observed also for WO_3 powders undergoing a nonreactive grinding: the intensity of the Raman signal decreases progressively with the time duration of the milling, starting from few minutes to several hours. Here the XRD technique reveals a broadening of the peaks associated with a decrease of the average grain size, and the Raman intensity exhibits an intensity decrease similar to that induced by the mixing with the rhenium oxide. It is interesting to remark that in this second case changes of the colour and the Raman intensity decrease disappear with relaxation times of the order of some weeks: this process can be also fastened by a sample heating in air.

A comparative analysis between $W_{1-x}Re_xO_{3-y}$ and ground WO_3 suggests that the observed modifications of the electronic structure, henceforth of the optical properties of WO_3 , occur at the grain boundaries (WO_3/ReO_2) and open surface of WO_3 crystallites. In the meanwhile the electronic and vibrational properties of WO_3 bulk phase remain unchanged, as revealed by the substantial invariance of the Raman spectral shape. The open-surface/grain-boundaries effect can be well attributed to tungsten ions having the effective charge $5+$, whose presence at the surface of pure WO_3 has been recently confirmed by scanning tunneling spectroscopy (1).

REFERENCES

1. F.H. Jones, K. Rawlings, J.S. Foord, P.A. Cox, R.G. Egdell, J.B. Pethica and B.M.R. Wanklyn, Phys. Rev. B, **52**, R14392 (1995).