

Changes of structural, optical and vibrational properties of WO_3 powders after non-reactive milling and mixing with ReO_3

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INTRODUCTION

Many interesting aspects of its phase transitions sequence and the phenomenology of defect creation in WO_3 remain to be better clarified. Aim of this work is a more extensive analysis of the structural transformations and the optical changes as a function of the milling parameters, strength, used materials, DURATION OF THE TREATMENT.

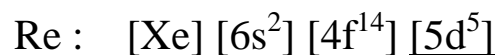
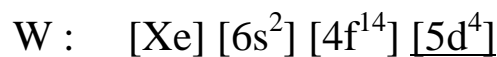
1) Difference between moderate mechanical treatments (like manual grinding) and stronger treatments (long times milling):

a) Phases and phase transitions of the commercial powders

b) Change of color of WO_3 :

2) Comparison of the observed coloration effects and structural transformations with the similar effects obtained by mixing of tungsten oxide with oxides having a different electronic configurations.

The rhenium oxide appears as an interesting candidate in this attempt, because of its electron in excess with respect to the WO_3 configuration



The addition of even small fractions of ReO_3 to WO_3 powders, induces a coloration phenomenon, after a proper thermal treatment of the mixture .

EXPERIMENTAL

Sample preparation:

Milling experiments:

The starting material for the present study is a commercial powder, with a nominal purity of 99.9%, produced in USSR, which appear of a yellow color. In the following this powder will be labeled as “VIRGIN POWDER”.

Commercial powder after a moderate mechanical treatment, consisting of a manual compression in a mortar of agate for a few minutes. In the following this kind of powder will be labeled as “TREATED POWDER”

Strong mechanical treatments have been performed on the *virgin powder* by using a ball milling machine Retschmuele, with three balls of agate:

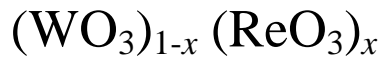
- one with diameter of 0.5 cm and weight of 0.17 g
- two with diameter of 1 cm and weight of 1.09 g

Milling frequency of the order of 1 Hz (50-70 cycles per minute) for VARIABLE TIMES OF MILLING, ranging from a few minutes up to 21 hours. The samples made by the powders after this treatment will be called “GROUND POWDERS”.

Sample preparation :

Mixed powders :

The *mixed samples* are indicated by the general formula



with x the relative molar fraction of ReO_3 at the beginning of the mixing process (the use of this notation does not imply the formation of a new phase of mixed crystal or a solid solution)

Components:

- WO_3 virgin powders, as defined above
- ReO_3 , produced in USSR from metallic rhenium, (same structural characteristics of commercial rhenium oxide with 99.9% purity)

Mixing procedure :

The starting materials have been finely ground in air by manual grinding for some minutes, and later sealed under vacuum in a quartz ampoules. These closed containers have been heated for 17 h at 450 °C and later for 73 h at 600 °C. After such thermal treatments, the powders have been ground in air again.

Mixed powders of seven different compositions have been obtained, ranging from $x = 0.1$ to $x = 0.9$, whose color varied from gray to black.

EXPERIMENTAL SET-UP

XRD :

X-ray diffractometer model Bragg-Brentano, made by Italstructures, working with the Cu K α line (Trento, Italy)

The samples for XRD have been prepared by deposition on a Millipore filter of the powder from an aqueous suspension driven by a vacuum pump.

XAS

Experimental X -ray absorption spectra of the W and Re L₃-edge were recorded in transmission mode at the LURE DCI (Orsay, France) storage ring on the EXAFS-3 beam line located at the bending magnet.

Raman spectroscopy

Micro-Raman configuration: Jobin-Yvon HG-2S double monochromator with holographic gratings (2000 grooves/mm) interfaced to an Olympus BE microscope. Photomultiplier detection. Back-scattering geometry. Spectral resolution was of the order of 3 cm^{-1} .

No difference of spectral shape between HV and VV polarization setting. The exciting light provided mostly by Argon laser (514.4 nm and 488 nm) or a Krypton laser (647.1 nm and 530.9 nm) lines. Laser beam power below 10 mW at microscope entrance.

Sample preparation methods for the Raman spectroscopy

Deposition on a microscopy cover glass of some droplets of a suspension of WO_3 powders in acetone. After the necessary time for solvent evaporation the deposited powders show a good adhesion to the substrate and allow a good Raman signal detection.

For the temperature dependence study, a standard macro-Raman configuration has been used, with a right angle scattering geometry, and the same monochromator and detection equipment. In the case of high temperature study the powder samples have been sealed in a quartz square cuvette.

RESULTS AND DISCUSSION

Ground powders

1) A preliminary investigation on the phase transitions sequence of our powder samples, by temperature dependence of the Raman spectra evolution (down to 32 K and up to 1073 K):

In the low temperature range, our samples, starting from the triclinic phase, do not show the transition to the second monoclinic structure, of polar and piezoelectric character, reported by Salje for monocrystals [Acta Crystallogr. A **31**, 360 (1975)]

Instead, the Raman spectra give some evidence of a diffuse transition in the range 30-150 K, for at least a fraction of the powders, quite similar to that observed in microcrystals by Arai *et al.* [Solid State Comm. **75** , 613 (1990)]

2) Thermal cycling and mild mechanical treatments:

Phase transition from the monoclinic phase (*virgin powders*) to the triclinic structure (*treated powders*) after quite moderate milling (few minutes) or after manual compression in a mortar of agate; they maintain this latter structure at room temperature for long times (months).

Raman study of monoclinic-triclinic phase transition

The transformation of the powders from monoclinic to triclinic structure can be observed following small modifications of XRD patterns, but a clearer evidence is given by the evolution of the low frequency bands (up to 100 cm^{-1}) of the Raman spectra; they correspond to lattice modes of librational nature and are particularly responsive to the transitions between the low symmetry phases of WO_3 , which involves mainly collective reorientations of the basic WO_6 octahedral units (XRD patterns are more sensible to the changes of W atoms distances, scarcely affected by these transitions).

The phase transition can be monitored, in particular, by following the relative intensity decrease of the 34 cm^{-1} peak (typical of the monoclinic phase) and the simultaneous increase of the 41 cm^{-1} peak (typical of the triclinic phase).

The transformation induced in such way can be reversed only by thermal annealing processes at high temperatures (at least $>300^\circ\text{C}$).

The spectral evolution for increasing times of manual grinding is quite similar to that observed for powder samples after different cooling times in liquid nitrogen, from few minutes up to a maximum of two hours. WO_3 powders undergoing mild mechanical treatments do not show evident coloration effect, and the final triclinic phase appears to be well defined, by XRD and Raman measurements.

Stronger mechanical treatments.

At fixed milling frequency of about 1 Hz, increasing times of milling have been analyzed: after about 1 hour a change of color is observed, from the pale yellow of the monoclinic or triclinic powders toward a greenish color; a strong blue coloration is reached by increasing the times of milling up to many hours.

Structural evolution for varying milling times

For the longest times no well defined diffraction peaks are observed, and the remaining broad XRD features reveal a quite disordered structural configuration, which can be consistent with the hypothesis of coexistence of different crystalline phases or else with a general amorphisation of the structure.

Raman spectral evolution of the ground powders

After a first transformation into the triclinic phase, observed for shortest times of milling, low frequency Raman peaks broaden remarkably for longer milling times, in such a way to make impossible the assignment to a well defined crystal phase.

In some step of the structural evolution (sample after 1 h milling) new peaks appears as shoulders in various region of the spectrum, at 143 cm⁻¹, 643 cm⁻¹ and 680 cm⁻¹, characteristic of the low temperature monoclinic phase (polar and piezoelectric), which has not been observed in the low temperature spectra collected on the same starting powders. Also XRD characteristic peak of this phase appear in the same sample.

A general change in the Raman spectra of the powders undergoing milling is the strong decrease of the total intensity, measured on all the collected spectral region of interest (20-900 cm⁻¹). This effect seems to be connected to the changing optical absorption properties, rather than to the structural transformation.

The longest milling times induces increasing crystal shear deformations and smaller average sizes of the grains. Most of the point defects created by crystal shear and responsible for the optical absorption are probably localized at the grain surface.

In fact, an interesting correlation is observed between the relative microcrystal size, measured via XRD methods, and the total Raman intensity: both are decreasing versus the milling time in a quite similar way.

A spectroscopic evidence of the increasing fraction of surface configurations is the appearance of a Raman band centered at

about 950 cm^{-1} , whose relative intensity increases versus the milling duration

Such higher energy vibration is characteristic of the so called W=O double bond, and does not exist in the virgin powders; it is associated to the creation of terminal oxygen at the grain surface.

The deep modifications induced in the powders by long milling processes, with defect creation, color changes and strong Raman intensity decrease, are not long-lasting, contrarily to the structural phase transition induced by weak mechanical treatments: after days or weeks, depending from the amount of the coloration, the ground powders return back to the original color.

High temperature treatments in the normal atmosphere strongly accelerate this bleaching phenomenon, while similar thermal treatments in inert gases (N_2 or Argon) leaves the blue coloration invariant. Raman measurements, performed on the ground powders after 6 months in air at room temperature or after some hours in air at high temperatures, show a good restoration of the Raman intensity to the values before the milling.

RESULTS AND DISCUSSION

Mixed samples

Phenomena of color changing, irreversible against oxidizing atmosphere, have been observed on mixed samples indicated as $(\text{WO}_3)_{1-x} (\text{ReO}_3)_x$.

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 coloration of the mixture, from the pale yellow typical of bulk WO_3 toward a green-blue coloration, similar to that induced by cation intercalation.

The integrated Raman intensity decreases strongly versus the x value in the mixture, and this trend cannot be justified by the decreasing content of WO_3 : in fact, the intensity decrease is of about a factor 20 in passing from the pure WO_3 to the mixed composition with 10% rhenium oxide, a further minor decrease is observed for other composition at increasing x ; for the sample with $x = 0.9$, no Raman scattering signal can be appreciated.

All the observed vibrational modes in the frequency region 20-900 cm^{-1} , for all the mixed samples, can be assigned to tungsten oxide dynamics. The Raman spectra for higher x seem rather similar to the spectra of monoclinic pure WO_3 at temperatures above the room temperature.

The introduction of rhenium oxide does not induce any new band in the spectrum. This fact suggests that no chemical combination or solid solution occur in the bulk of the particle of the mixture. Comparison of EXAFS spectra (L_3 edge) of W and Re among the various mixed samples fully confirms this view.

Low temperature spectra, down to 32 K, have the same evolution as the ones of the pure WO_3 , and no contribution of the rhenium oxide dynamics is found. The only appreciable difference is the stronger intensity of two new bands at 785 and 685 cm^{-1} , satellites for the stretching modes at 800 and 714 cm^{-1} , respectively: they reveal the new phase already observed in microcrystals and also in our temperature dependence study on the pure WO_3 powders. The coexistence of two oxides seems to catalyze the low temperature transition toward this new phase of WO_3 .

The XRD spectra for different compositions, indicate the coexistence of two compounds: a pure WO_3 phase, monoclinic but similar to the high temperature range of this phase, approaching the orthorhombic structure (a XRD evidence for this view is the doubling of the relative intensity of one of the diffraction peak of the triplet at about $2\theta = 30^\circ$), and a pure ReO_2 phases with rutile-like structure and orthorhombic space group. Some defect of oxygen can be postulated, corresponding to a non-stoichiometry of the order of 2%.

Note that the ReO_2 phase, appearing in the mixture due to decomposition of *c*- ReO_3 at 400 °C during preparation, is stable, in pure state, only at high temperatures (>300 °C).

The persistence of the Raman spectrum of *bulk* WO_3 in all the samples suggest a model of segregation where particles of pure tungsten oxide, with unperturbed crystal structure, are surrounded by zones of ReO_2 . The electron excess of Re with respect to W

originates the population of the charged defects, preferentially localized at the interfaces.

The color changes due to the mixing are quite stable against the oxidizing action of the normal atmosphere. This fact lead to discard the hypothesis that the coloration is only due to vacuum induced reduction at high temperature during the mixing process.

A spectroscopic indication of the presence of deformed WO_6 octahedra associated to the defects is given by the appearance of a Raman band in the range $950\text{-}1000\text{ cm}^{-1}$ for the mixed samples.

The mean frequency of this Raman band is about 980 cm^{-1} , higher than the usual values of about 950 cm^{-1} observed in the pure ground sample. This difference in the bond strength suggests a different nature of the defects created in the mixed samples, which can depend on the presence of the rhenium atoms as electron donor. The Raman resonant behavior of this band in the mixed samples, not observed in pure WO_3 , suggest that the stronger bond at the phase boundary is also concerned with the electron excess responsible for the optical absorption.

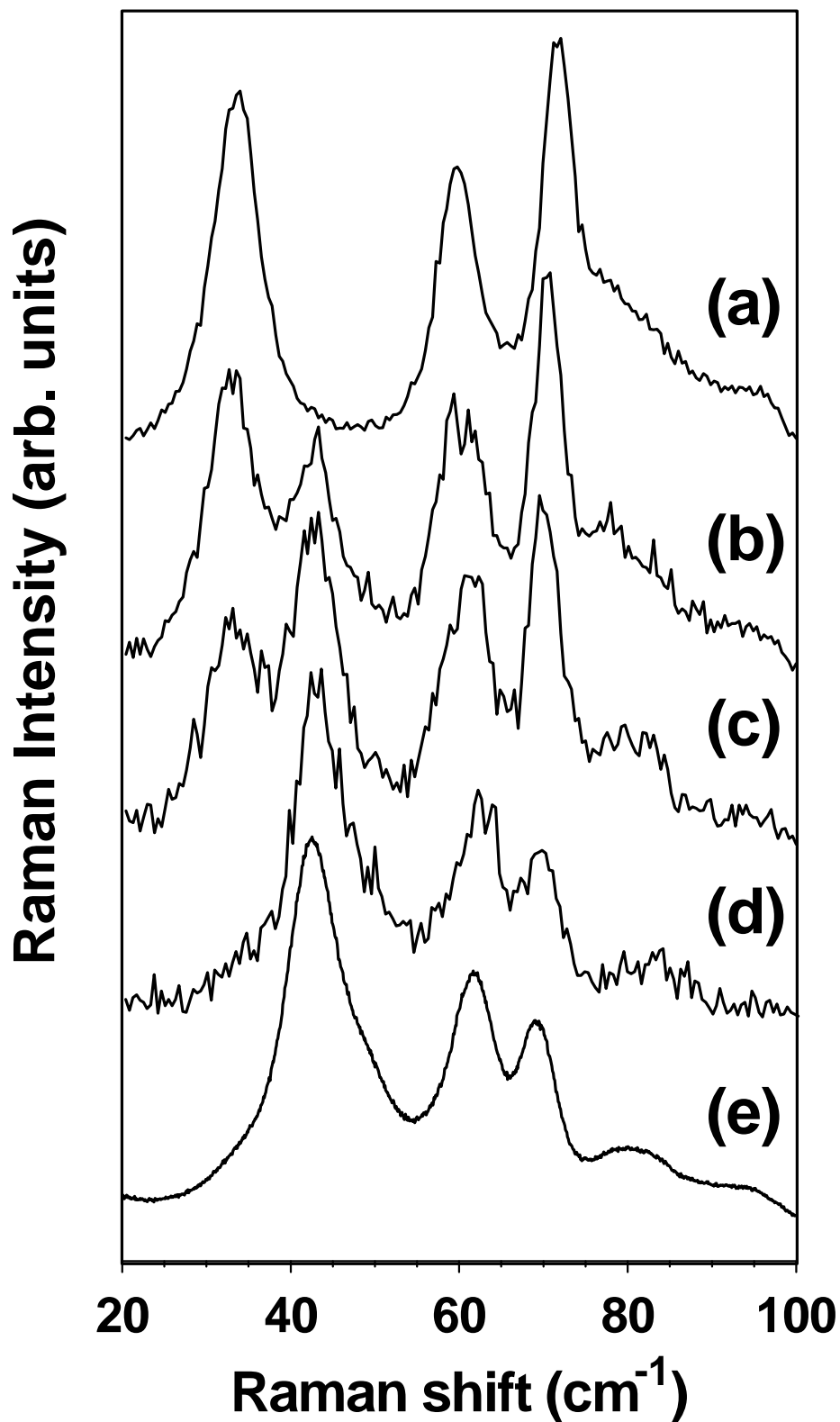
CONCLUSIONS

The bulk electronic and vibrational properties of WO_3 phase remain mainly unchanged, as revealed by the substantial invariance of the Raman spectral shape.

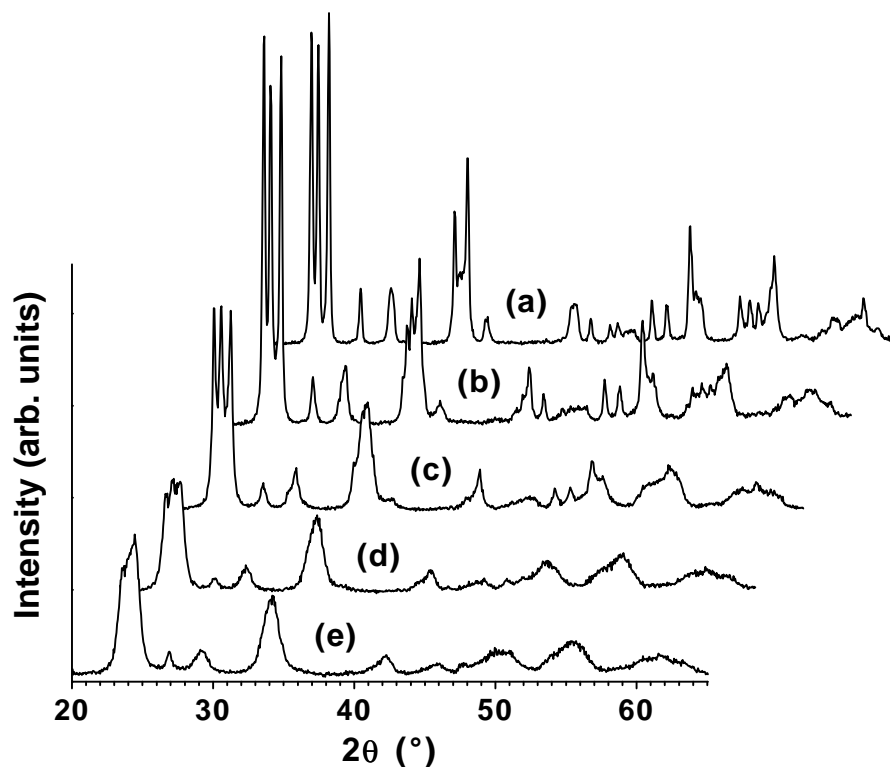
A general comparative analysis between mixed samples and ground pure WO_3 suggests that the observed modification of the electronic structure, henceforth of the optical properties of WO_3 , occurs at the grain boundaries (WO_3/ReO_2), in the mixed samples, and in the open surface of WO_3 crystallites, in the case of pure ground powders. Models of the color centers consistent with the experimental findings can be proposed both for pure WO_3 and for mixed samples.

In the first case the presence of W^{5+} ions and terminal oxygens (well separated) at the surface has been confirmed recently by scanning tunneling microscopy. [J. K. Rawlings *et al.*, Phys. Rev. B **52**, R143 (1995)].

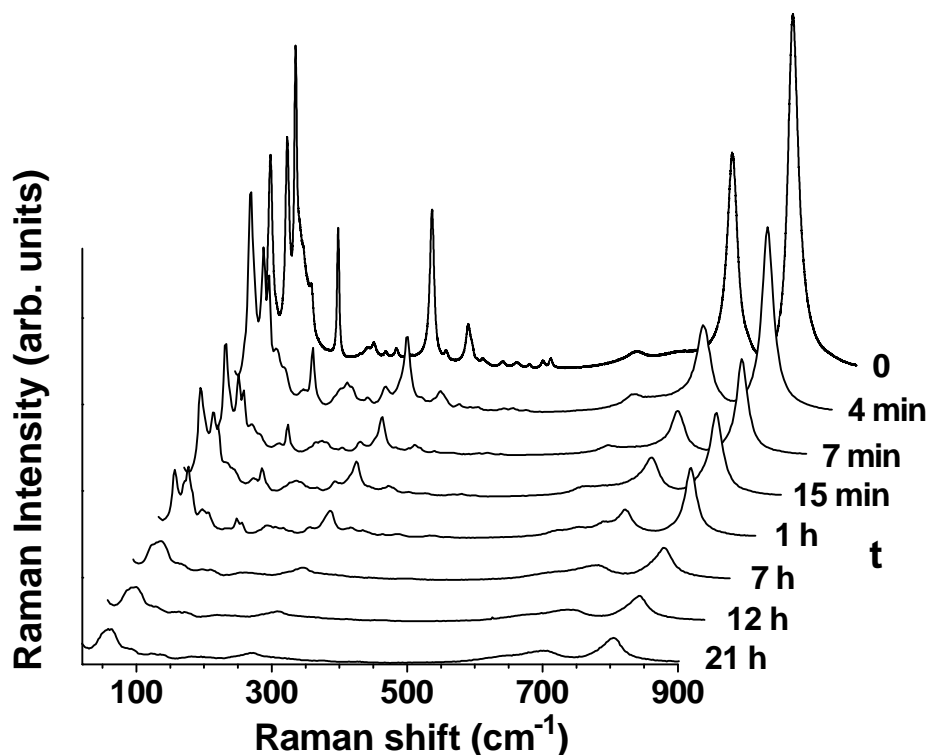
For the mixed samples the electronic excess charge is associated to a peculiar W-O bond at the grain-boundaries, as it is suggested by the Raman resonance effect on the band at 980 cm^{-1} .



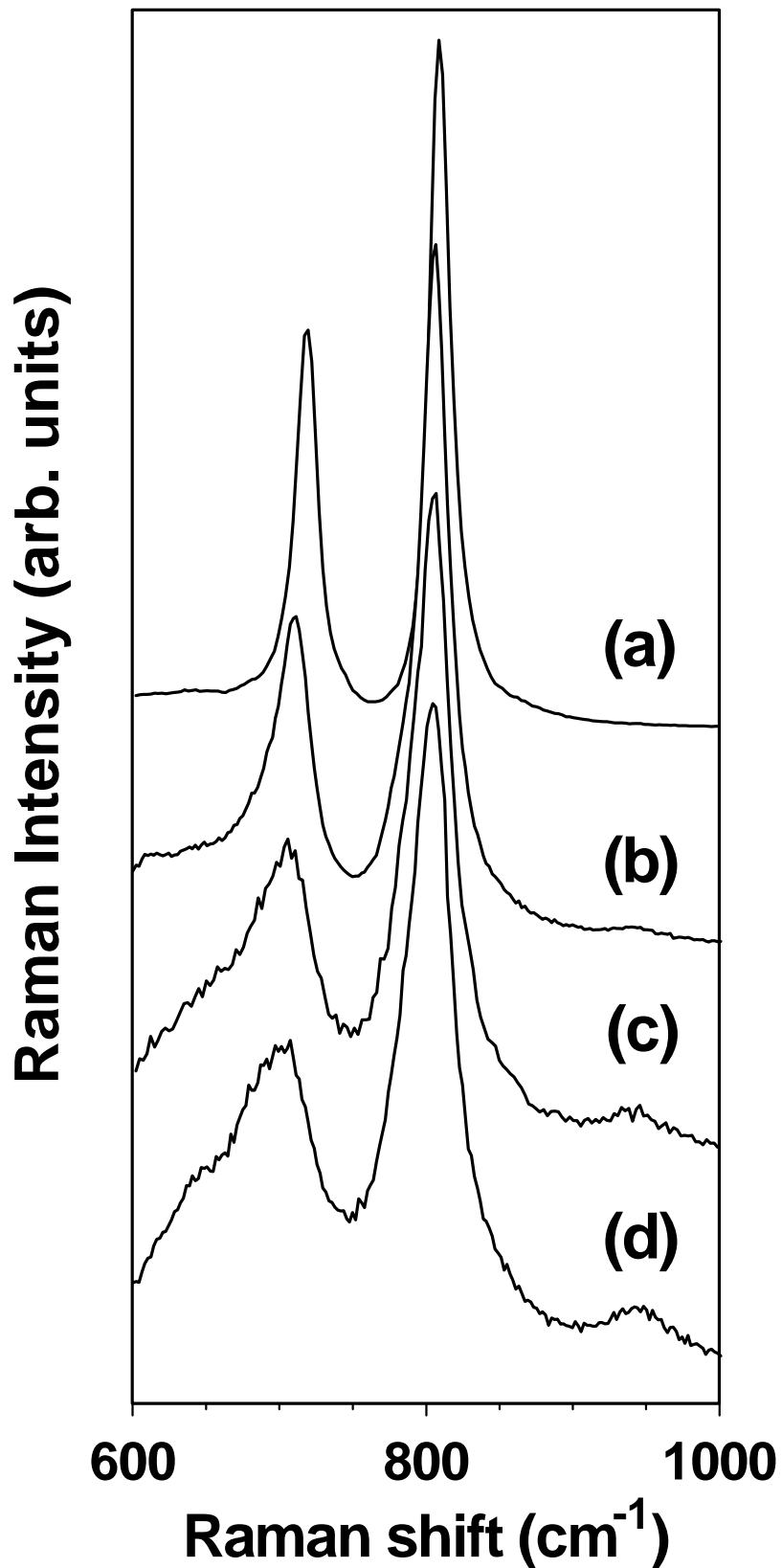
Raman spectra of tungsten oxide collected in the range 20-100 cm^{-1} from (a) reference “virgin” powder, monoclinic structure, (b) the same powder after manual pressure for 5 s, (c) manual pressure for 10 s (d) 2 min, (e) reference “treated” powder, triclinic



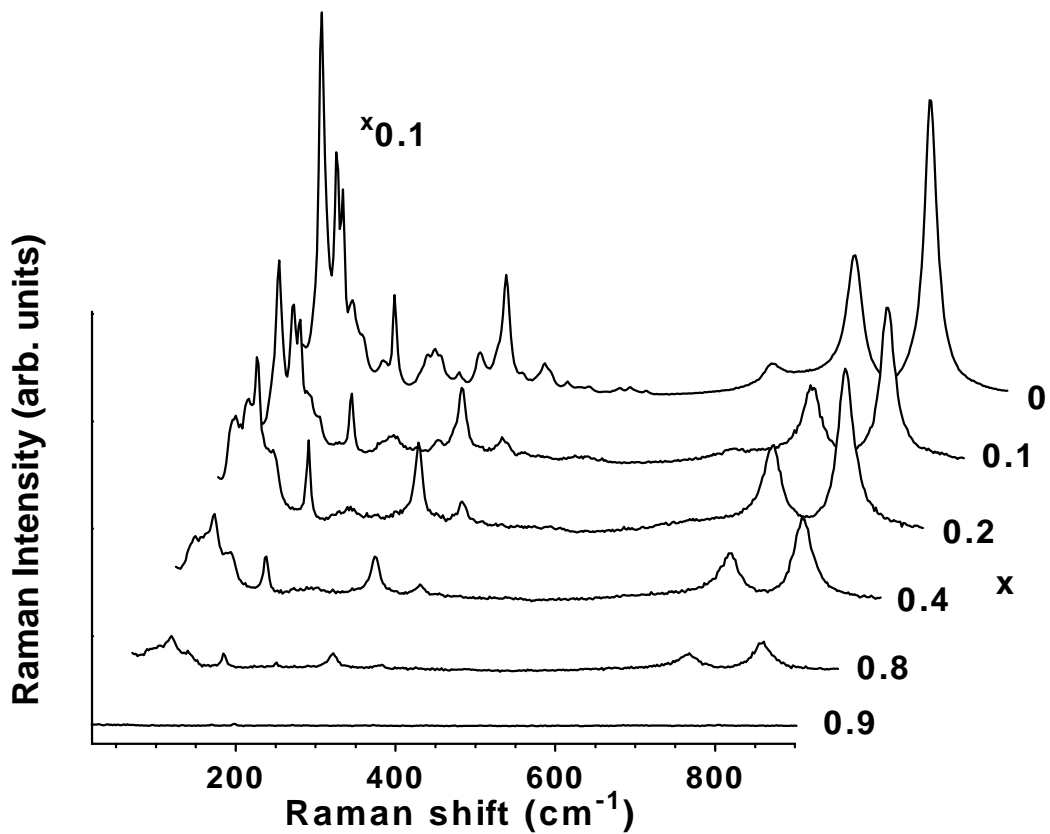
XRD patterns of tungsten oxide powder as a function of the milling time: (a) “virgin” powder, (b) 2 min milling, (c) 15 min milling, (d) 2 h milling, (e) 21 h milling.



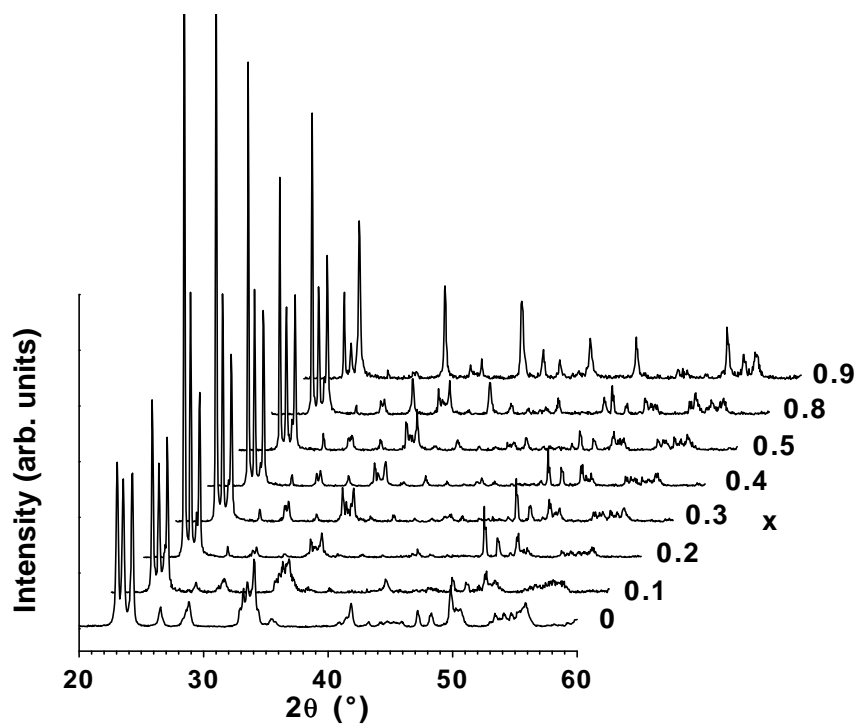
Total Raman spectra of WO_3 (frequency range 20-900 cm^{-1}) as a function of the milling time t . Exciting wavelength 530.9 nm. Note that the spectrum at $t=0$ corresponds to the “virgin” WO_3 (see experimental section for details).



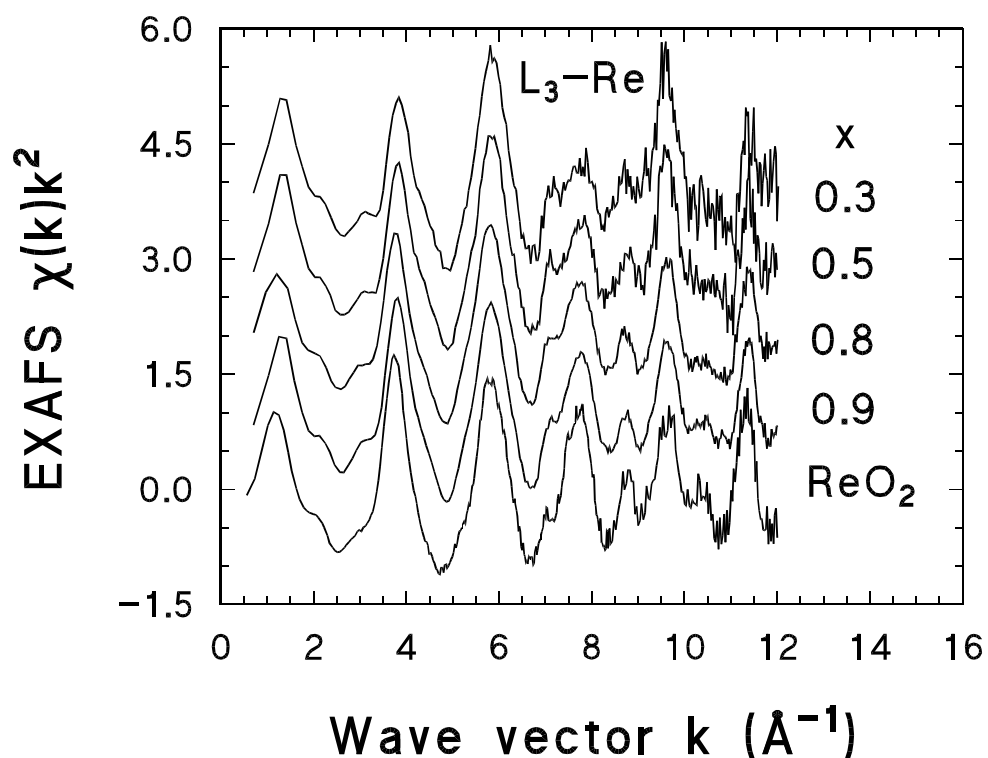
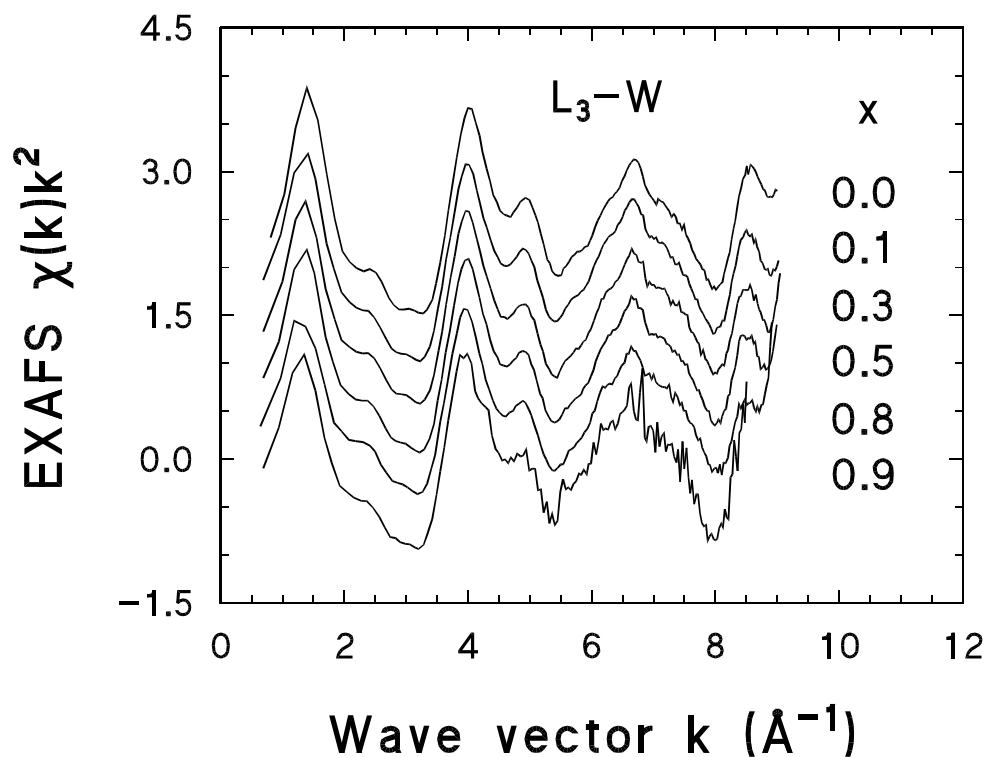
Variation of the Raman band at 950 cm^{-1} in ground WO_3 powders as a function of milling time in comparison with the stretching modes at 800 cm^{-1} and 710 cm^{-1} : (a) “virgin” powder, (b) 15 min milling, (c) 2 h milling, (d) 21 h milling.



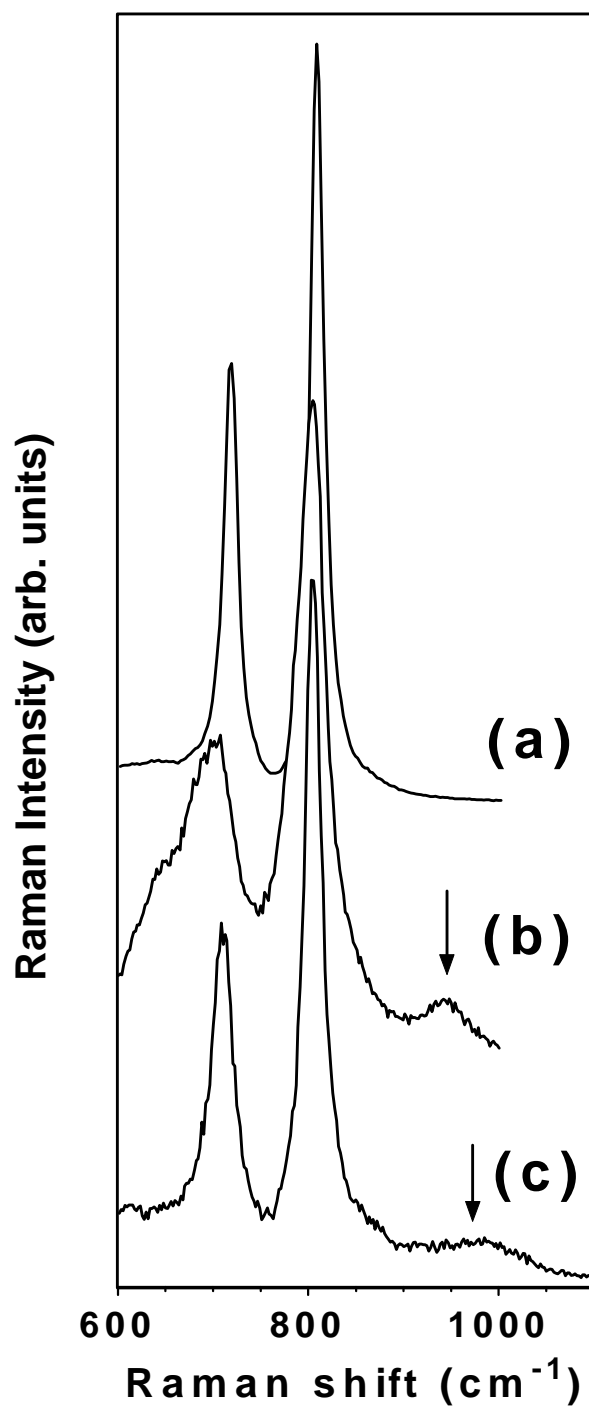
Raman spectra of $W_{1-x}Re_xO_{3-y}$ mixed compounds for various compositions x . The top spectrum is plotted on a full scale 10 times larger than the other spectra. Exciting wavelength 530.9 nm. Note that the spectrum at $x=0$ corresponds to the “treated” WO_3 (see experimental section for details).



XRD spectra of $W_{1-x}Re_xO_{3-y}$ mixed compounds for various compositions.

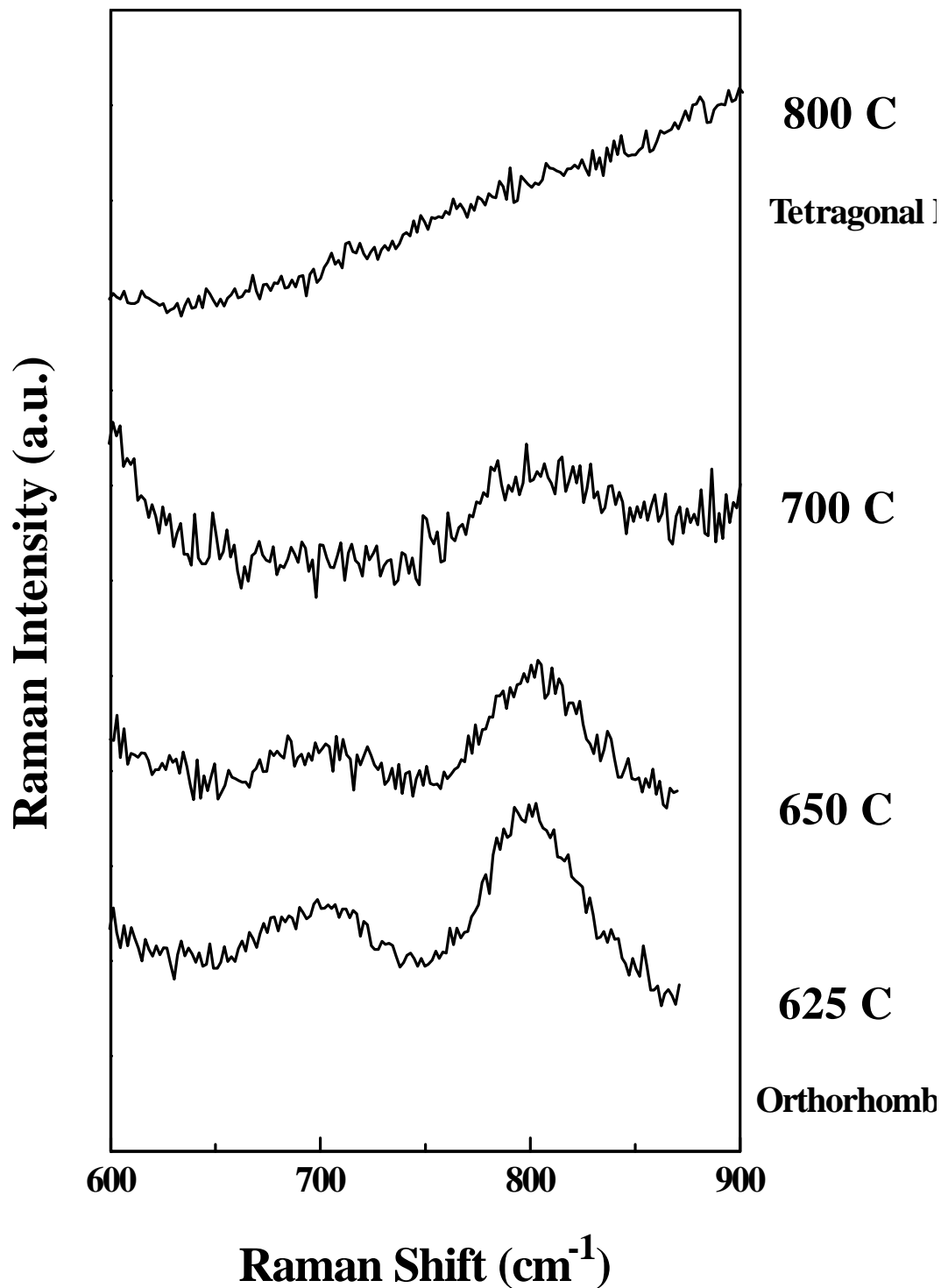


Experimental EXAFS $\chi(k)k^2$ spectra of the W and Re L_3 -edge in $W_{1-x}Re_xO_{3-y}$ mixed compounds. The data for pure WO_3 ($x=0$) and ReO_2 crystals are shown for comparison.



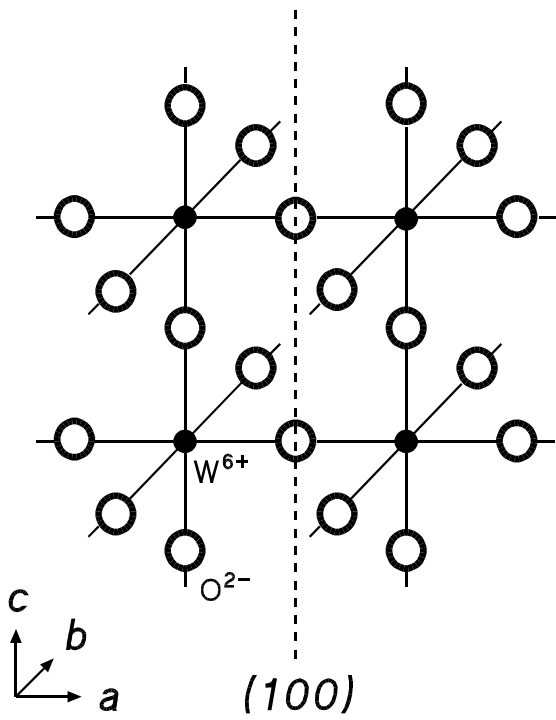
Raman spectra of high-frequency stretching modes in (a) “virgin” WO_3 powder, (b) pure WO_3 powder ground for 21 h, (c) mixed sample with $x = 0.1$. The low intensity Raman band at 950 cm^{-1} in (b) and 980 cm^{-1} in (c) is attributed to the presence of short and strong W-O bonds.

Orthorhombic - Tetragonal Phase Transition



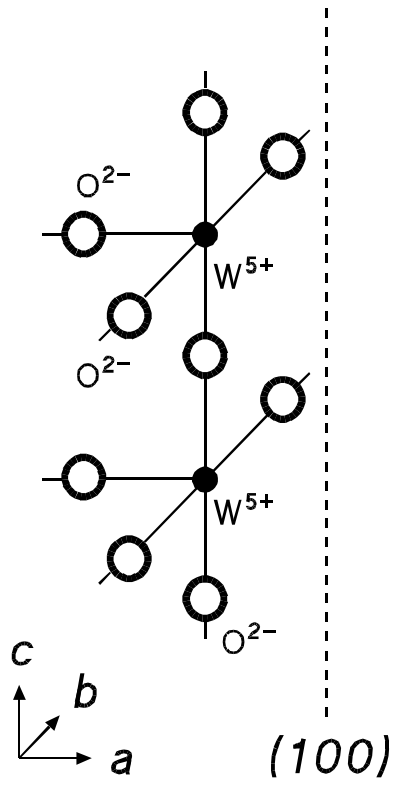
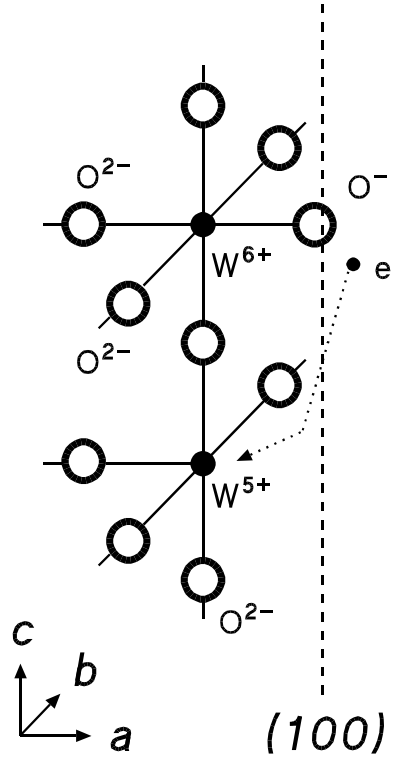
Temperature dependence of Raman active WO_3 stretching modes across the orthorhombic-tetragonal phase transition. Note that the lower frequency mode at about 700 cm^{-1} disappears below the transition temperature (740 C) while both the modes are not detectable in the tetragonal phase.

Fracture line

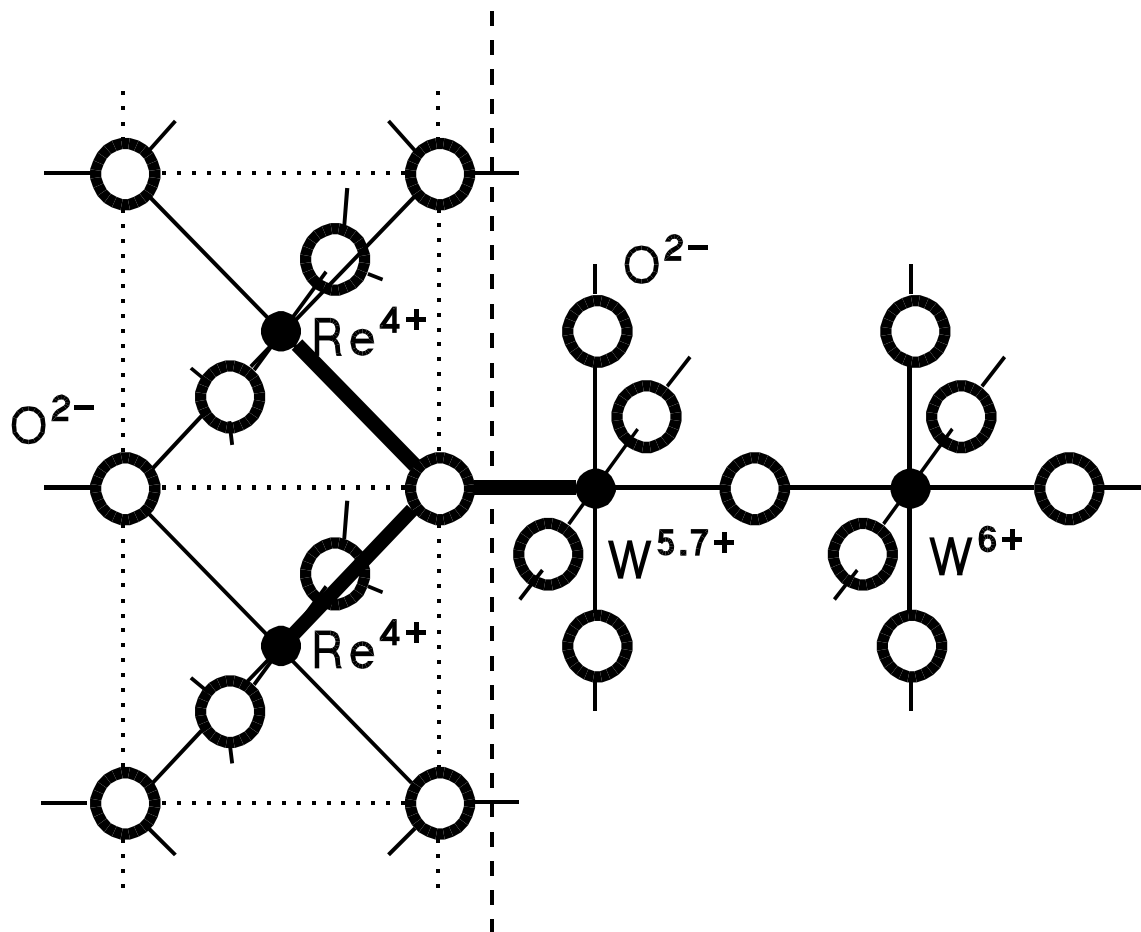


(1)

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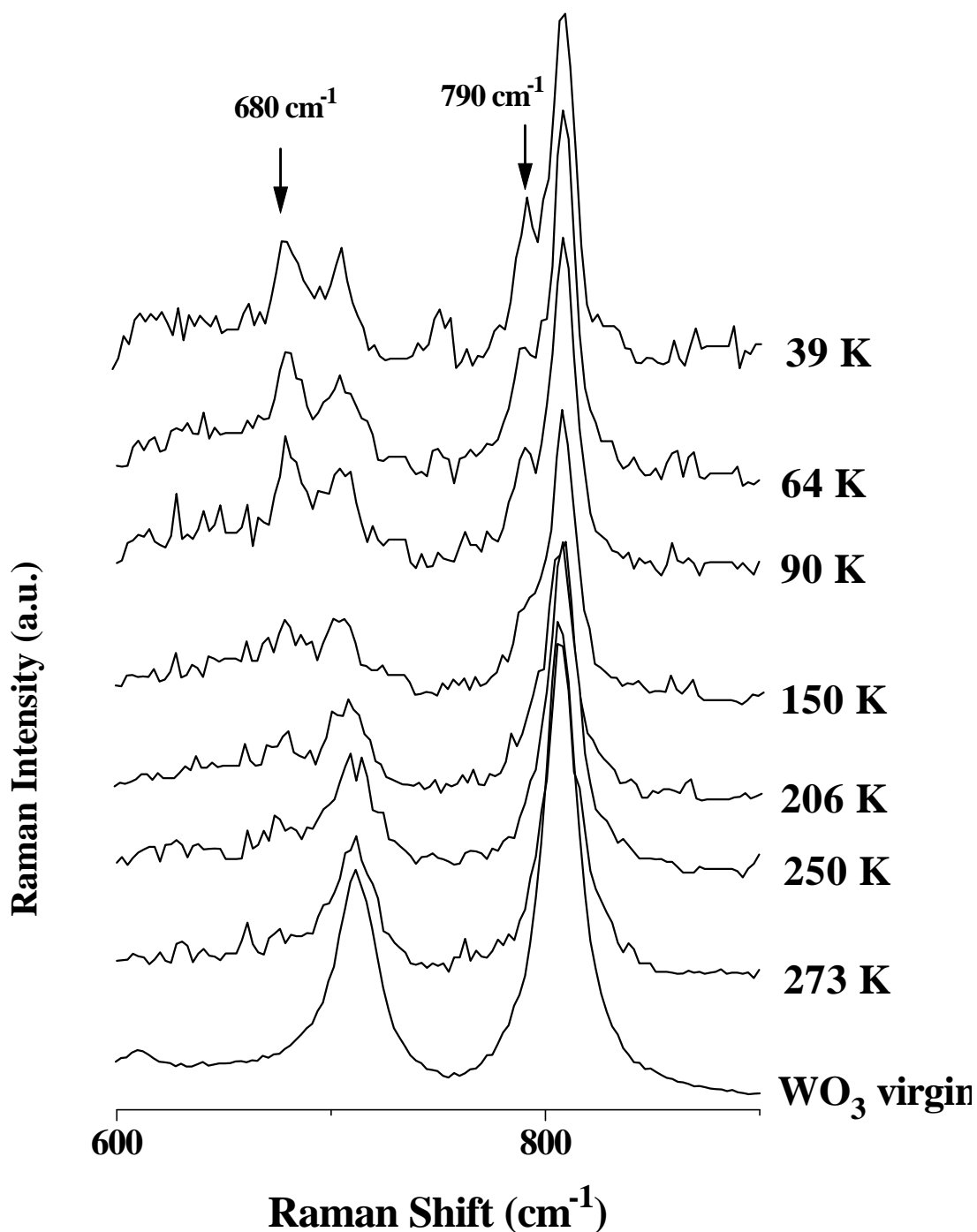
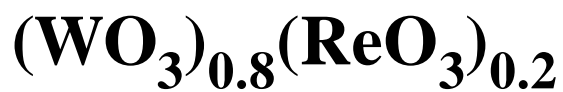


Models of grain surfaces after fracture along the (100) plain.



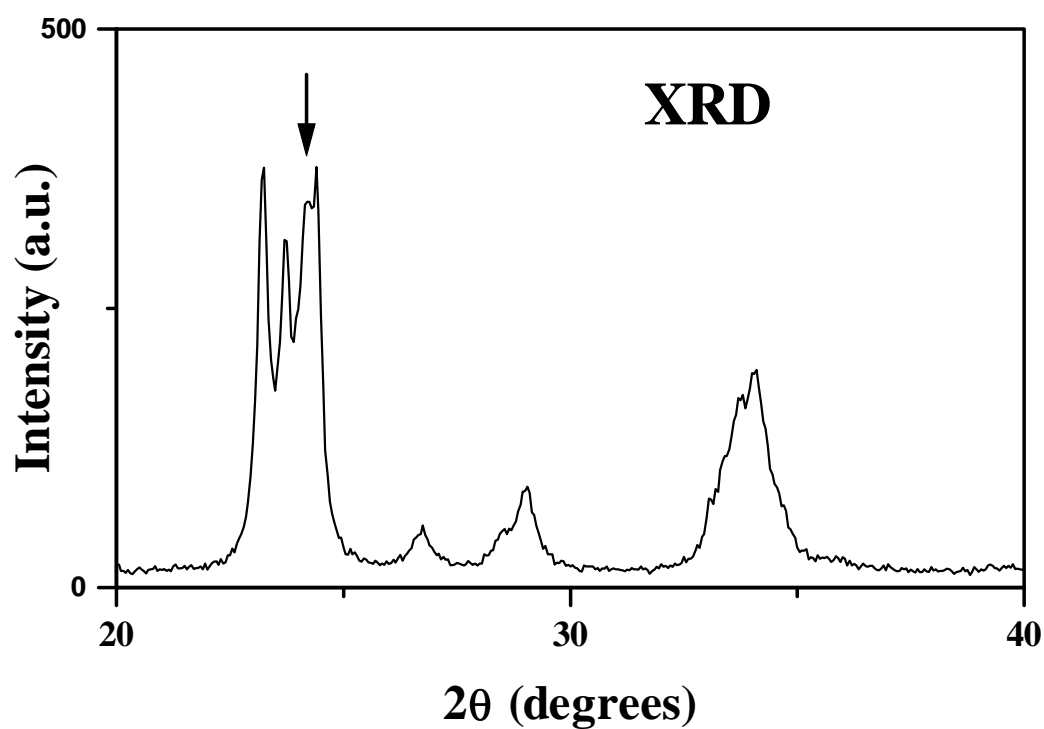
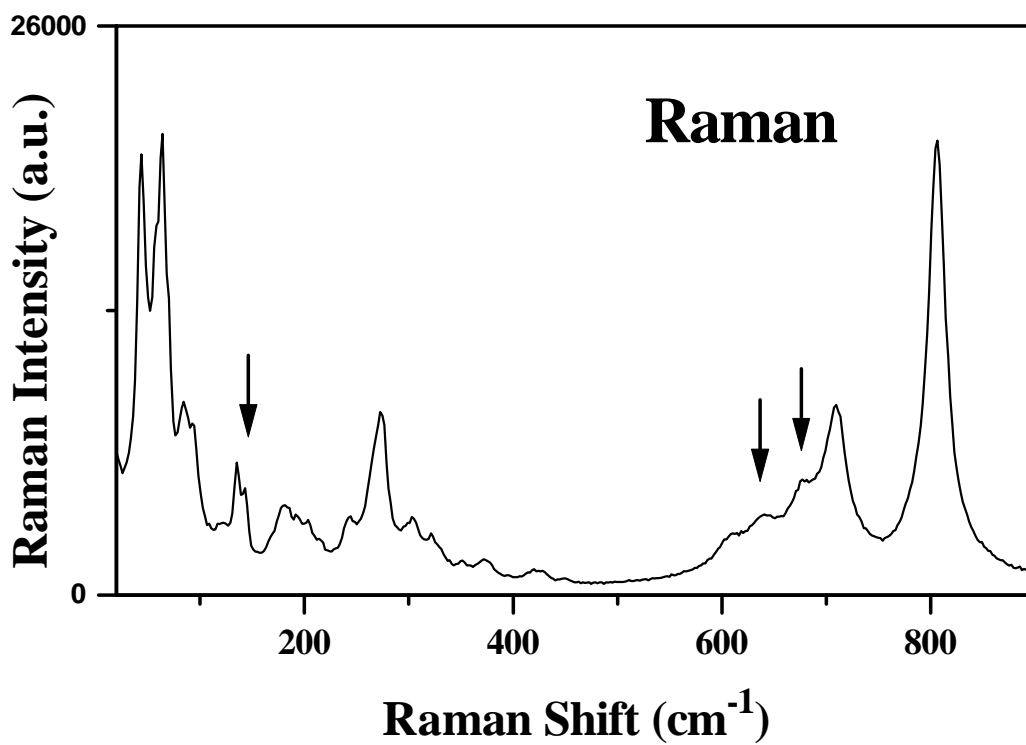
*$\text{ReO}_2 - \text{WO}_3$
grain
boundary*

Model of the ReO_2 - WO_3 grain boundary.

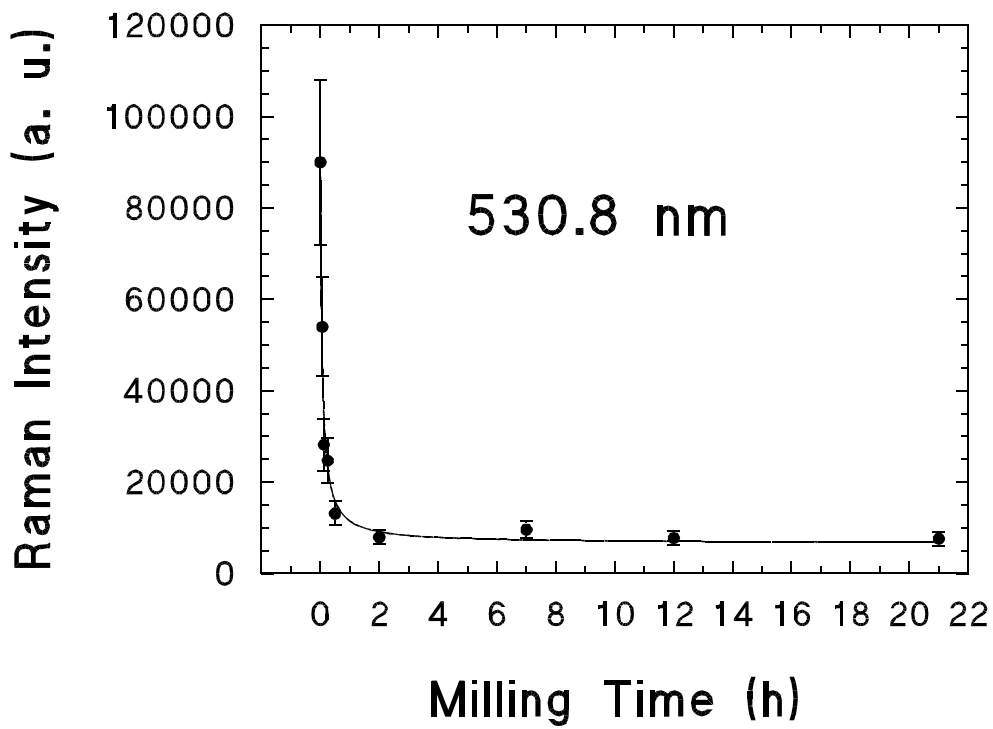
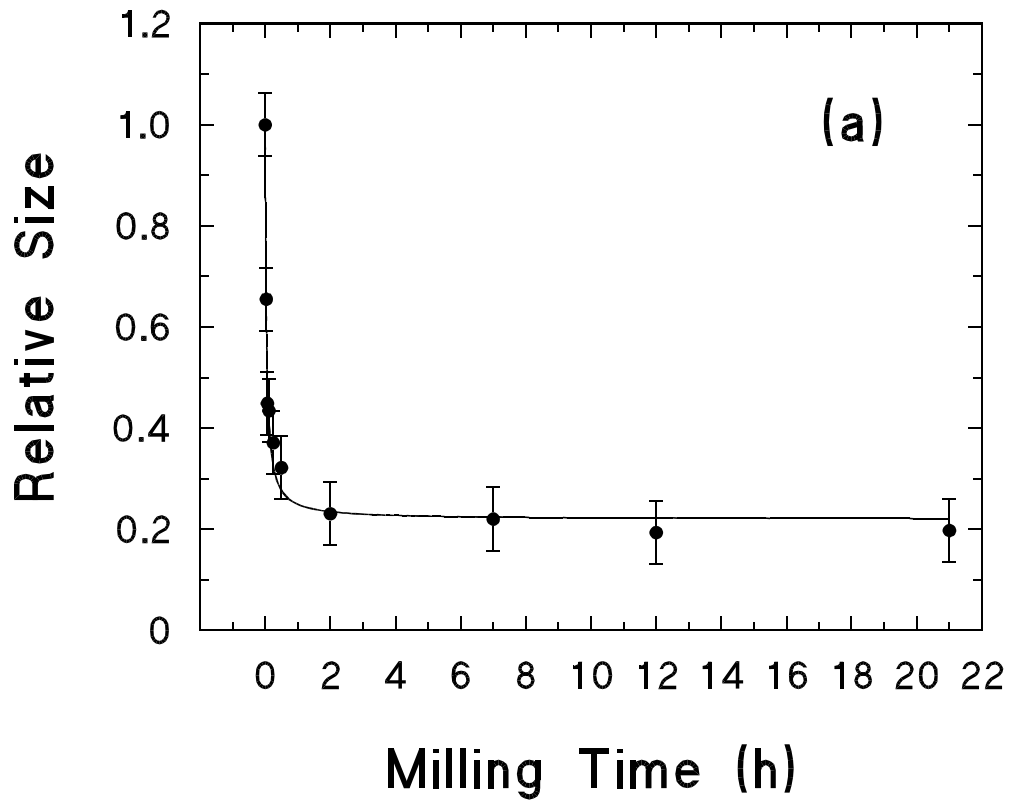


Low temperature evolution of WO_3 Raman spectra in mixed compounds. Satellite peaks (see arrows) are more evident in this sample than in pure WO_3 .

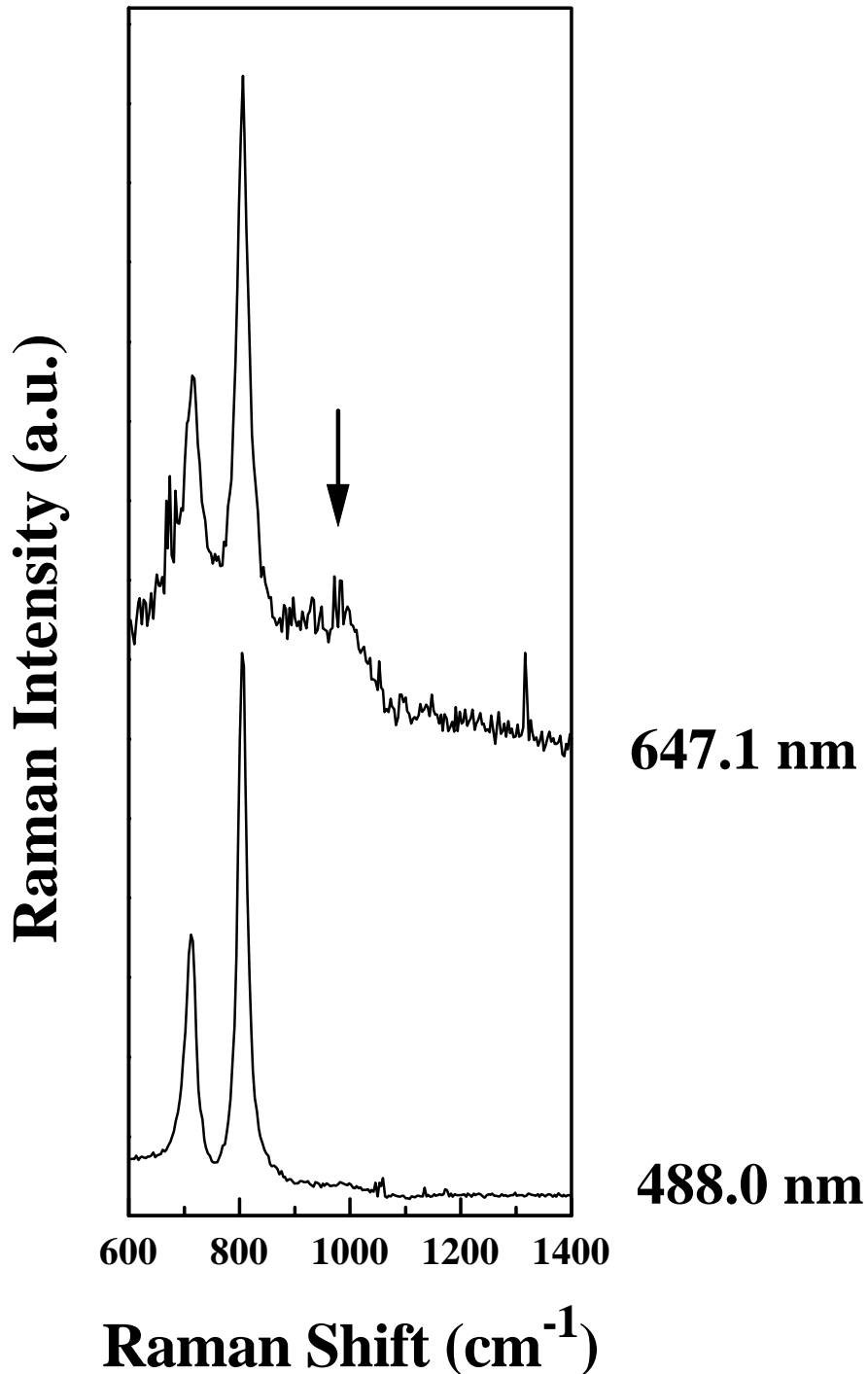
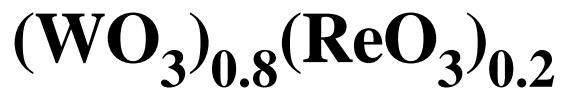
WO₃ 1h milling



Raman and XRD evidences for the formation of the monoclinic (II) polar phase at room temperature after milling.



Similarity in the behavior of relative microcrystal size and total Raman intensity vs. milling time.



Resonance effect for the relative intensity of the Raman band at 980 cm^{-1} in mixed compound. Note that in pure WO_3 after milling the correspondent 950 cm^{-1} band exhibits no change in its relative intensity vs. excitation wavelength.