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Selectivity and composition dependence of response of wolframite-based gas sensitive resistors $(MWO_4)_x([Sn–Ti]O_2)_{1-x}$ $(0<x<1$; $M=Mn$, Fe, Co, Ni, Cu, Zn)

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The response to carbon monoxide, methane, ammonia and water of gas-sensitive resistors fabricated from wolframite-based solid solution compounds $(MWO_4)_x([Sn–Ti]O_2)_{1-x}$ $(0<x<1$; $M=Mn$, Fe, Co, Ni, Cu, Zn) has been studied. The conductance and the activation energy for conductance vary systematically with composition, reflecting the energy and number density of 3d-transition metal states which depend upon the nature of the transition metal ion and its concentration. Tungsten tended to be strongly surface segregated. The surface trap-limited conductivity model can explain, at least partially, the switch from resistance decreasing to resistance increasing response to reducing gases if assumptions are made about the local state occupancy and the energy of these states with respect to the energy associated with O adsorbed on the surface. The sign of response to water was not always consistent with that expected with the other reactive gases. The sign of resistance change associated with adsorption of water can be explained in terms of the surface OH trap energy relative to the $O_{ads}{}^{2-}$ trap state. There appear to be surface binding sites for water vapour which are specifically associated with particular transition metal ions.

Introduction

Semiconducting oxide gas sensors have been primarily used for the detection of combustible gases such as carbon monoxide and hydrocarbons. The response mechanism, described in detail elsewhere,[1,2] relies on the bulk resistance of porous solids mainly depending on ionosorbed oxygen species acting as electron traps. Thus, the interaction of a gas with these surface species results in a change in their surface concentration, which consequently affects the solid resistance. Systematic cation substitution in solid-solution materials as a way of understanding the gas response mechanism linked to the surface chemistry has been previously studied for $Cr_{2-y}Ti_yO_{2+x}$,[3,4] $Ba_6Fe_xNb_{10-x}O_{30}$,[5] $(CrNbO_4)_x$-$(Sn_{1-y}Sb_yO_2)_{1-x}$,[6] and $FeNbO_4$–$CrNbO_4$–TiO_2[7] and the effects of stoichiometry, microstructure, gas concentration gradients, and surface segregation on gas sensitivity have been observed. Analysis of the variation of conductivity with reactive gas concentration implies that the surface trap state is formally $O_{ads}{}^{2-}$. We have recently shown that this state can be described as an oxygen molecule adsorbed on a surface oxygen vacancy—reduced cation complex.[8] Oxides can be classified according to the sign of resistance change to reducing gases, as 'n' (resistance decrease) or 'p' (resistance increase). A model which rationalises the effects of bulk donor doping has been developed[9] which predicts a switch from n- to p-type response and conductance minimum at some value of the surface acceptor state density dependent on the bulk donor density.

Previous work[3,8] has considered solid solution series with transition metal ions in high oxidation states. The present work considers solid solution series with transition metal ions in low oxidation states. The divalent transition metal tungstates, $AWO_4(A=Mn$, Fe, Co, Ni, Cu, and Zn), also referred to as $NiWO_4$-type tungstates, are members of a large family of structurally related compounds with small cations which crystallize with the wolframite structure.[10] The structure is monoclinic with $Z=2$ and space group $P2/c$ $(C_{2h}{}^4)$. For pure $FeWO_4$ (feberite), $a=4.730$, $b=5.703$, $c=4.952$ Å and $\beta=90°05'$.[11] The structure consists of a hexagonal close-packed oxygen array in which one-half of the octahedral holes are occupied. The cation distribution in the octahedral interstices gives rise to zigzag chains of skew-edge linked octahedra extending along the *c*-axis, and in any single chain there is only one type of cation. The zigzag chains are arranged in alternating layers, perpendicular to the *a* direction. Between layers, the chains are connected by corner-sharing octahedra so that no chain of one type of cation is linked to another of the same cation. The structural similarity between wolframite and rutile implied the possibility of solid solution series of SnO_2 or TiO_2 with the transition metal tungstates, which would allow the systematic investigation of effects of d-electron population on gas sensitivity. Such a study would give a further test of the general model for gas response given earlier and, by comparison of the effects of different gases, might reveal particular effects attributable to some specific chemistry of the surface. The present paper reports this study.

Tungstates have been investigated for other technological applications. Single crystals of zinc tungstate have, in particular, received much attention because of their potential technological significance in applications such as scintillation detectors, photoanodes and masers. Several studies have reported a wide range of properties of these materials. Watterich *et al.*[12] have investigated the properties of paramagnetic defects in $ZnWO_4$ single-crystals induced by electron-irradiation. Intrinsic paramagnetic defects in undoped zinc tungstate crystals have been observed by electron paramagnetic resonance (EPR) after electron irradiation. The only hole-type defect was attributed to a hole trapped at an O^{2-} ion near a zinc vacancy. Two electron-excess centers were due to a single electron trapped at an oxygen vacancy where the defects differed in the oxygen vacancy position. Ti(III) centers in reduced $ZnWO_4$–Ti single crystals were also examined[13] by EPR methods which resulted in the characterization of a new Ti^{3+} centre expressed as $[Ti^{3+}–H]$.

The dc electrical conductivity and thermoelectric power of $CuWO_4$ have been measured[14] in the temperature range 300–700 K on single crystals and on polycrystalline pellets. It has been found that $CuWO_4$ is an n-type semiconductor. The intrinsic nature of the compound is observed above 455 K with an activation energy of 1.06 eV for polycrystalline pellets. Other authors have reported that $CuWO_4$ can be considered as an intrinsic semiconductor with a band gap of 1.52 eV.[15]

Measurements of ac and dc electrical conductivity of nickel tungstate indicated[16] that $NiWO_4$ has a band gap of 2.10 eV. The conduction mechanism above 500 K (with high resistivity: $\approx 10^9\ \Omega$ cm and $E_A = 1.5$ eV) was proposed as an electron transfer from one Ni^{2+} to an adjacent Ni^{2+} ion. Such a transfer would lead to the formation of Ni^{3+} ions ($Ni^{2+} + Ni^{2+} \rightarrow Ni^{3+} + Ni^{+}$) which would require high energy as both Ni^{3+} and Ni^{+} ions are less stable than Ni^{2+}.

Conductivity measurement in $CoWO_4$ single crystals showed[17] that cobalt tungstate is a p-type semiconductor. The solid exhibited extrinsic behaviour up to 750 K ($E_A = 0.64$ eV) and intrinsic behaviour above this temperature ($E_A = 1.4$ eV) implying a band gap of 2.80 eV.

Single crystals and polycrystalline samples of $FeWO_4$ were prepared and characterized by Sieber *et al.*[18] From high temperature paramagnetic data, the presence of high spin state iron(II) $3d^6$ was confirmed. Qualitative Seebeck measurements indicated p-type conductivity, and the room temperature resistivity of single crystals was $\approx 100\ \Omega$ cm with an activation energy of 0.16 eV. The p-type conductivity was interpreted as caused by a small amount of iron(III) being present, due to the formation of a small quantity of Fe_2WO_6, which is able to form a solid solution with $FeWO_4$. Another study by Bharati *et al.*[19] suggested that the solid exhibited extrinsic behaviour up to 900 K ($E_A = 0.27$ eV) characteristic of conductivity governed by impurities or defects, and intrinsic behaviour above this temperature ($E_A = 0.64$ eV).

Electrical conductivity of a single crystal of $MnWO_4$ in the temperature range 300–1200 K has been reported.[20] It was found that the dominant charge carriers are holes (p-type material) over the entire temperature range studied. A break in the Arrhenius plot (σ *vs.* $1/T$) occurred around 600 K. The activation energy below and above this break temperature was estimated as 0.53 and 0.57 eV respectively.

The A(II)B(VI)O_4 tungstates are potential compounds for use as photoelectrodes for the photoassisted decomposition of water using sunlight, and as gas detectors because these materials have the possibility of being either p- or n-type semiconductors. p-Type behavior could be observed when a small amount of one of the transition metals is oxidized, *e.g.*, the introduction of a small amount of iron(III) as Fe_2WO_6 in iron(II) tungstate. In addition, n-type behavior might be produced when one of the metals in the structure is reduced to a lower oxidation state, *e.g.*, the reduction of W(VI) to W(V). Thus, the ABO_4 tungstates have potential use as either photocathodes or photoanodes in the photoassisted decomposition of water.[21,22] Some metal tungstates and their composites with carbonates have also been investigated for application to semiconductor-type sensors capable of detecting nitrogen oxides at elevated temperature.[23]

The present study was concerned with the synthesis of some new wolframite-based oxides over the complete range of solid solution: $(MWO_4)_x([Sn\text{–}Ti]O_2)_{1-x}$ ($0<x<1$; M = Mn, Fe, Co, Ni, Cu and Zn), and the exploration of their use as gas sensitive resistors. The effect of changing the transition metal ion from the wolframite on the electrical properties and sensing behavior to carbon monoxide, ammonia and methane has been examined. As indicated previously wolframites can be n- or p-type while SnO_2 and TiO_2 are n-type, therefore an n–p transition can be expected at some value of composition. The aim was to elucidate any systematic trends in behavior caused by systematic change of the composition of the oxide.

Experimental

All chemicals were high-purity laboratory reagent grade from Aldrich. The wolframites MWO_4 (M = Mg, Mn, Fe, Co, Ni, Cu, and Zn) were prepared by precipitation from aqueous metal nitrate solution by addition of ammonium tungstate solution. The correct preparations were confirmed by X-ray powder diffractrometry using Cu-Kα radiation (Siemens D5000 in transmission, with incident beam monochromator). The electrical resistivity of these preparations was extremely high ($R > 10^9\ \Omega$ cm at elevated temperature >500 °C). The wolframites were miscible in the solid state with SnO_2 and TiO_2. The complete range of solid solutions $(MWO_4)_x$-$(M'O_2)_{1-x}$ ($0<x<1$; M = Mg,Mn, Fe, Co, Ni, Cu and Zn; M′ = Sn or Ti) was successfully prepared by classical solid state synthesis from mixed powders of the tungstate with SnO_2 or TiO_2, with a range of calcination temperature $1000 < T < 1300$ °C and confirmed by X-ray powder diffraction. Overall, a small quantity (<5%) of impurity phase content Fe_2WO_6 and Cu_2WO_4 were detected in the $FeWO_4$- and $CuWO_4$-substituted materials.

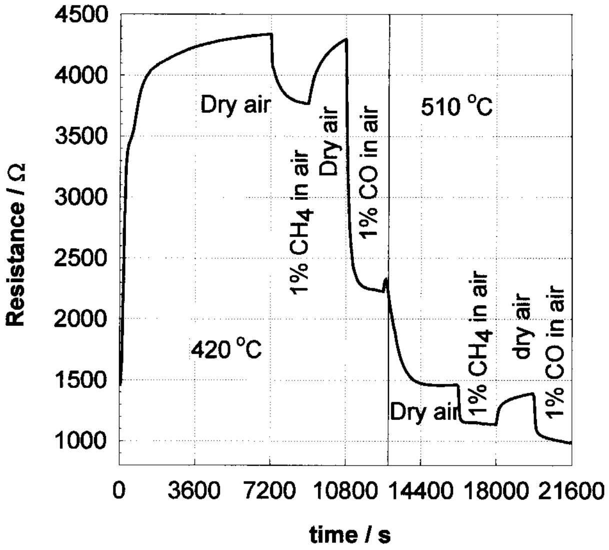

Fig. 1 Resistance *vs.* time upon exposure to 1% CO and CH_4 in air with a $(FeWO_4)_{0.1}(SnO_2)_{0.9}$ pellet at 420 and 520 °C.

Gas sensitivity and selectivity measurements were studied on compressed, sintered pellets (13 mm diameter, ≈ 2 mm thick, pressed between gold foils in a silica tube; two-terminal resistance measurement with a digital multimeter) as previously described.[3–7] The electrical resistance of the pellets was first stabilized in dry air at 400 °C for 2 h. Carbon monoxide, ammonia and methane at low concentration in air were introduced into the rig and the pellet resistance measured at 400 and 500 °C. Fig. 1 illustrates the typical experimental routine used, and results obtained. Gas sensitivity, S, was calculated as $S = \Delta\sigma/\sigma_0 = (R_0 - R)/R$, where σ denotes conductivity and R resistance (σ_0, R_0 in pure dry air). Hence, a resistance decreasing response is recorded as a positive value and a resistance increasing response as a negative one.

X-Ray photoelectron spectroscopy (XPS) was performed (VG ESCALAB 220i XL), for the Fe and Co series only, using focused (300 μm spot size) monochromatised Al-Kα radiation. The scans were acquired with a step size of 100 meV and the spectrometer pass energy was 20 meV. The binding energies were referenced to the hydrocarbon C 1s peak at 284.80 eV and the sample charging was controlled with a 3 eV flood gun.

Results

Electrical properties and gas sensing characteristics

The compounds studied covered the range from d^5 to d^{10} with TiO_2 (d^0) and SnO_2 (d^{10}) as end members. Fig. 2 shows electrical resistivity as a function of composition at 400 °C.

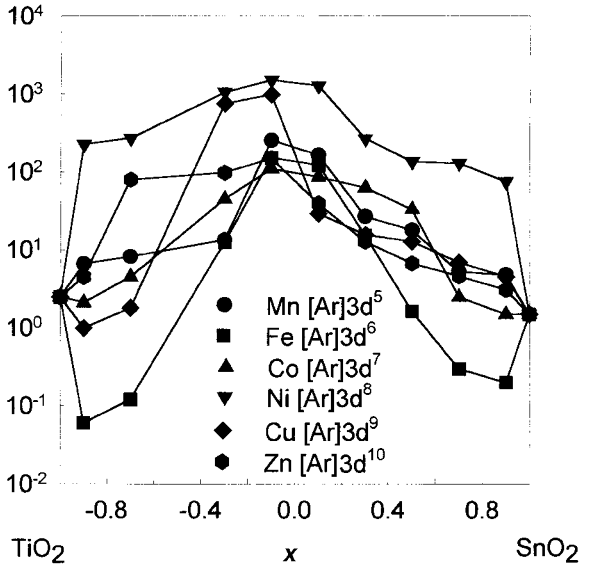

Fig. 2 Electrical resistivity of $(MWO_4)_{1-x}(M'O_2)_x$ at 400 °C (M = Mn, Fe, Co, Ni, Cu, Zn; M′ = Sn, Ti).

Even small substitutions of Ti or Sn ($x = 0.1$) brought the resistivity into a measurable range ($5.10^4 \leqslant \rho/\Omega\,\mathrm{cm} \leqslant 2.10^6$). It is notable that small substitutions of $FeWO_4$ into either TiO_2 or SnO_2 greatly decreased the resistivity. The behaviour is in contrast to the effect of a direct substitution of Fe, which causes a marked resistivity increase. For small substitutions of $NiWO_4$ into TiO_2 and SnO_2, the resistivity increased by a factor of two and remained high upon further substitution. Substitutions of the other tungstates gave resistivities clustering in a fairly narrow band well separated from either of these two extremes.

A rough estimate of the activation energies for conduction E_A, was calculated from the resistivities of the materials at 400 and 500 °C (Fig. 3). Overall, the activation energies were higher for SnO_2-substituted materials than TiO_2, which is consistent considering the band gaps of pure TiO_2 and SnO_2 to be respectively, 3.0 and 3.6 eV. The $NiWO_4$- and $FeWO_4$-substituted materials respectively exhibited the highest and lowest activation energy values, which tends to agree with the literature results given in the Introduction. All activation energies for the rest of the substituted materials were clustered between these values. There was an obvious and quite general pattern of variation of E_A with composition for all the compounds: a marked change in activation energy with small substitutions at either end of the series, and a monotonic but relatively small variation with composition between these limits.

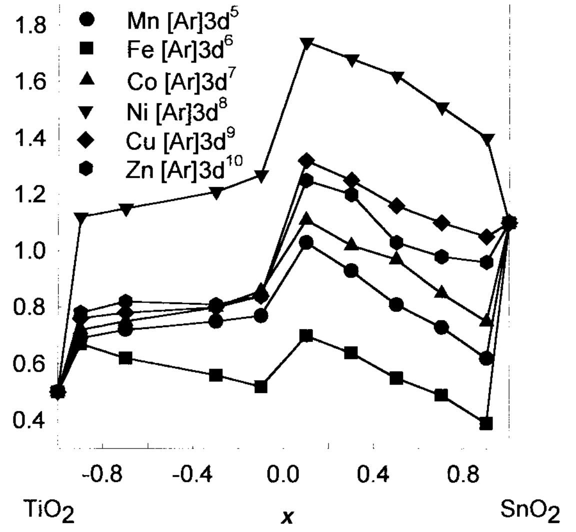

Fig. 3 Conductance activation energy for $(MWO_4)_{1-x}(M'O_2)_x$ for the temperature range 400–500 °C (M = Mn, Fe, Co, Ni, Cu, Zn; M′ = Sn, Ti).

Table 1 Sign of resistance changes of $(MWO_4)_x(M'O_2)_{1-x}$ (M = Mn, Fe, Co, Ni, Cu, Zn; M′ = Sn, Ti) upon exposure to wet air, 1% CO, 0.1% NH_3, and 1% CH_4 in air ('+' means resistance increase on change of gas from dry to wet air or from dry air to dry air containing the test gas) and sensitivity to water vapour $|S_{H_2O}| = |(R_{dry} - R_{wet})/R_{wet}|$(dry→100% relative humidity at 20 °C)

		$TiO_2 \leftarrow X_{wolframite} \rightarrow SnO_2$									
		0.1	0.3	0.7	0.9	1	0.9	0.7	0.5	0.3	0.1
Mn	Gas	−	+	+	+		+	+	−	−	−
	H_2O	−	−	−	−		−	−	−	−	−
	$\lvert S_{H_2O}\rvert = 0.04 \pm 0.03$										
Fe	Gas	−	−	−	+		+	−	−	−	−
	H_2O	−	−	+	+		+	+	+	+	−
	$\lvert S_{H_2O}\rvert = 0.1 \pm 0.07$										
Co	Gas	−	−	+	+		+	+	+	−	−
	H_2O	−	−	+	+		+	+	+	−	−
	$\lvert S_{H_2O}\rvert = 0.11 \pm 0.06$										
Ni	Gas	−	−	−	−		−	−	−	−	−
	H_2O	−	−	+	+		+	+	+	−	−
	$\lvert S_{H_2O}\rvert = 0.2 \pm 0.1$										
Cu	Gas	−	−	−	−		−	−	−	−	−
	H_2O	−	−	−	−		−	−	−	−	−
	$\lvert S_{H_2O}\rvert = 0.2 \pm 0.1$										
Zn	Gas	−	+	+	+		+	−	−	−	−
	H_2O	−	+	+	+		+	+	−	−	−
	$\lvert S_{H_2O}\rvert = 0.44 \pm 0.2$										

	TiO_2	SnO_2
Gas	−	−
H_2O	−	−
S_{H_2O}	0.2	1.4

Table 1 shows the resistance changes of $(MWO_4)_x(M'O_2)_{1-x}$ (M = Mn, Fe, Co, Ni, Cu, Zn; M′ = Sn, Ti) upon exposure to wet air, 1% CO, 0.1% NH_3, and 1% CH_4 in air ('+' means resistance increase on change of gas from dry to wet air or from dry air to dry air containing the test gas). Table 1 also shows the magnitude of the sensitivity to water vapour, calculated as $|S_{H_2O}| = |(R_{dry} - R_{wet})/R_{wet}|$, where R_{wet} denotes the resistance in air saturated with water vapour at room temperature (≈20 °C). The reactive gases CO, CH_4 and NH_3 were consistent in their classification of the materials as n- or p-type (Fig. 4–6, wherein $S_{gas} = (R_0 - R_{gas})/R_{gas}$ meaning that a resistance decrease gives a positive sign for S). However, the sign of response to water vapour was not always consistent. The effect of even small substitutions of the tungstates was greatly to decrease the sensitivity of SnO_2 to water vapour, $|S_{H_2O}|$ shifting typically from 1.4 to <0.2 for all the tungstate substituted materials. The magnitude of the response to water vapour varied systematically along the transition series: Mn < Fe,Co < Ni,Cu < Zn. The cases where the sign of the electrical response to water is different to that of the other gases demonstrate that the mechanism of response to water may be different to that of the other gases.

Several points are worth noting concerning the effect of composition on sensitivity. As expected, a notable feature is that, with change in composition along both series, the behaviour for some materials changes from 'n-type' (resistance decrease in the presence of the reducing gas) to 'p-type' (gas causes a resistance increase). Only the Ni- and Cu-based materials remained n-type along both series (SnO_2 and TiO_2). These two sets of materials did show a minimum in sensitivity across the range. For the Ni series, the minimum was on the TiO_2 side, whereas for the Cu series it was on the SnO_2 side. The n-type compounds exhibited much higher sensitivity to

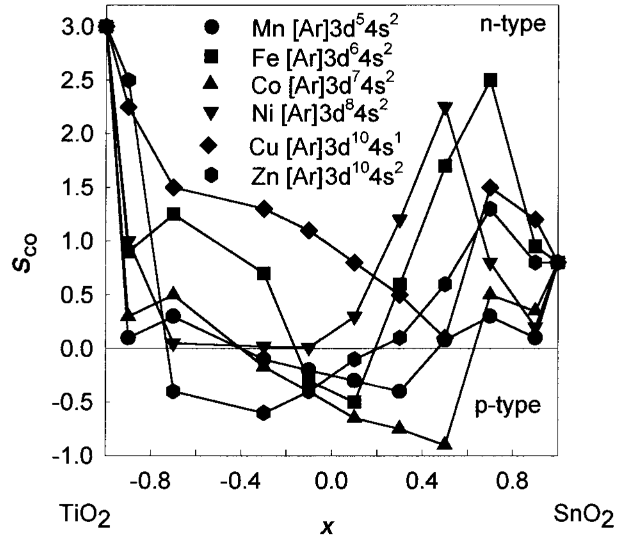

Fig. 4 Sensitivity, S_{CO} (defined in the text) of $(MWO_4)_{1-x}(M'O_2)_x$ to 1% carbon monoxide in dry air, measured at 400 °C (M = Mn, Fe, Co, Ni, Cu, Zn; M′ = Sn, Ti).

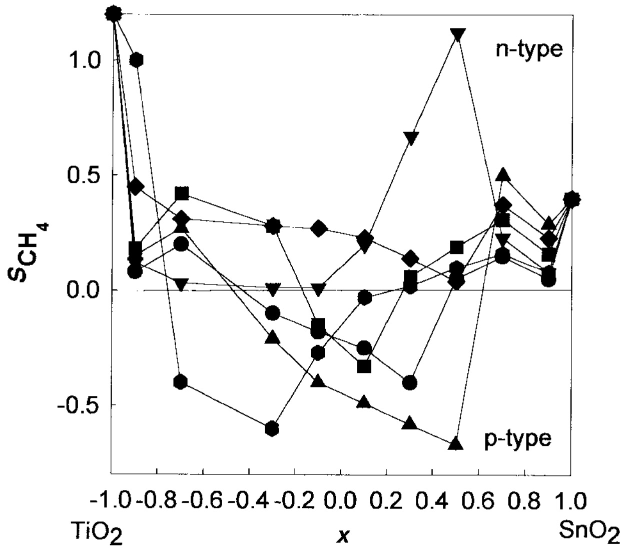

Fig. 5 Sensitivity of $(MWO_4)_{1-x}(M'O_2)_x$ to 1% methane in dry air, measured at 400 °C (M = Mn, Fe, Co, Ni, Cu, Zn; M′ = Sn, Ti) (●; Mn[Ar] 3d^5 4s^2, ■; Fe[Ar] 3d^6 4s^2, ▲; Co[Ar] 3d^7 4s^2, ▼; Ni[Ar] 3d^8 4s^2, ◆; Cu[Ar] 3d^{10} 4s^1, ⬢; Zn[Ar] 3d^{10} 4s^2).

CO than the p-type materials but for CH_4 the differences between n- and p-type materials were not so marked. The Co series was notable in showing a rather strong p-type sensitivity to CH_4 on the SnO_2 branch, just before the n–p transition. The n–p transition was found over the same composition range for all the reactive gases. Considering the mole fraction of tungstate, *y*, at which the n–p transition takes place, the sequence along the TiO_2 branch is Zn < Mn, Co < Fe and along the SnO_2 branch is Co < Mn < Zn, Fe, so the zinc compound was notable in showing asymmetrical behaviour with respect to the two end members. There was a remarkable maximum in the sensitivity to CO at $y = 0.3$–0.5 along the SnO_2 branch, for the Fe, Ni, Cu and Zn series, but not for the Mn or Co series. Any such maximum along the TiO_2 branch was not nearly so marked. For sensitivity to methane, a similar maximum was observed, but only for the Ni series. The Ni series on the SnO_2 side was interesting because small substitutions produced a decrease in sensitivity to both CO and CH_4 then further substitution caused a marked increase in sensitivity (n-type) to the maximum.

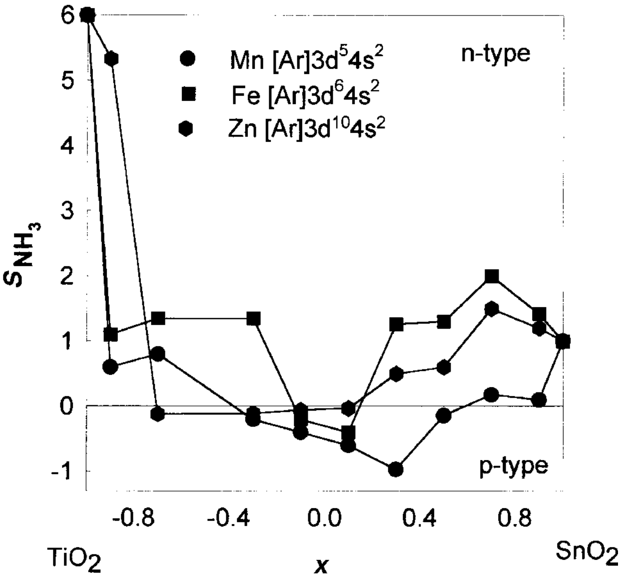

Fig. 6 Sensitivity of $(MWO_4)_{1-x}(M'O_2)_x$ to 1% ammonia in dry air, measured at 400 °C (M = Mn, Fe, Co, Ni, Cu, Zn; M′ = Sn, Ti).

The carbon monoxide-methane selectivity of all the compounds determined at 400 °C is given in Fig. 7, and the carbon monoxide-ammonia selectivity with the Mn, Fe and Zn compounds in Fig. 8. The Mn, Co, Ni and Cu compounds showed a very stable CO/CH_4 selectivity along both branches (Fig. 7) varying from 1 for Mn to 5 for Cu. For Fe and Zn the selectivity remained stable along the TiO_2 branch, but then went through a strong maximum along the SnO_2 branch, increasing by a factor up to 10. The Mn and Fe compounds showed a stable CO/NH_3 selectivity ($0 < S_{CO}/S_{NH_3} < 1$) along both series. The Zn compounds however exhibited a different behavior with a high selectivity (up to 7) along the TiO_2 branch (Fig. 8).

Surface composition

Fig. 9 and 10 give the surface concentration (atom%) *vs.* TiO_2 and SnO_2 mole ratio obtained by XPS surface analysis for the Fe- and Co-based materials. It is quite clear from these diagrams that the switch from n- to p-type gas sensitivity

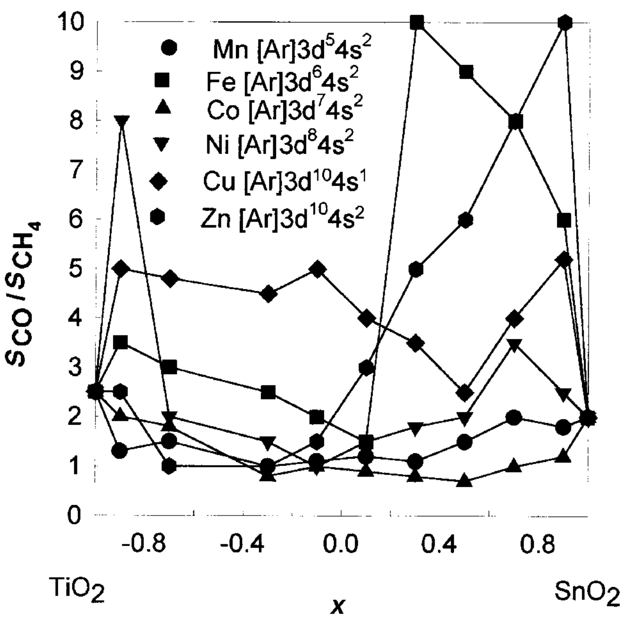

Fig. 7 Carbon monoxide/methane selectivity in dry air, S_{CO}/S_{CH_4}, of $(MWO_4)_{1-x}(M'O_2)_x$ measured at 400 °C (M = Mn, Fe, Co, Ni, Cu, Zn; M′ = Sn, Ti).

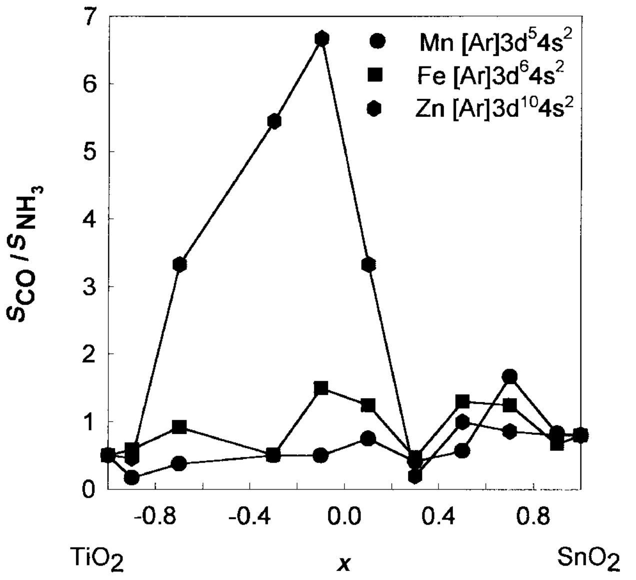

Fig. 8 Carbon monoxide/ammonia selectivity in dry air, S_{CO}/S_{NH_3}, of $(MWO_4)_{1-x}(M'O_2)_x$ measured at 400 °C (M = Mn, Fe, Co, Ni, Cu, Zn; M′ = Sn, Ti).

appeared to occur when the surface concentration of Ti and Sn started to decrease significantly. For both series there was a clear segregation of W to the surface corresponding to the suppression of the other cation, particularly the transition metal cation. This segregation was not found for the pure MWO_4. Titanium seemed to be present at the surface more or less in the concentration expected from the bulk composition. In the n-type range, Sn was repelled from the surface in the Fe-series; the effect was not so marked in the Co-series.

Discussion

The first level of interpretation comes from the idea that the transition metal ion from the wolframite provides localised d-states, split by the octahedral crystal field, in the band gap. The electronic structure of 3d-transition metal compounds is complex. The 2s and 2p oxygen orbitals strongly overlap with the 4s and 4p orbitals of the 3d-transition metal ions in 3d-transition metal oxides. Owing to this overlap, there exists a strong hybridisation, which leads to a large energy band gap between the top of the 2p band and the bottom of the 4s and 4p bands. The 3d bands associated with transition metal cations lie within this energy gap.[24] In these oxides, the five-fold degeneracy of d-orbitals is removed partially by the crystal field splitting and exchange splitting. The 3d-orbital splits into a lower triplet of t_{2g} symmetry (xy, xz and yz orbitals) and a higher doublet of e_g symmetry (x^2-y^2 and z^2 orbitals). Hence, the energy and number density of these states would depend upon the nature of the transition metal ion and its concentration. Furthermore, substitution of the transition metals as tungstates means that the lattice remains neutral without the need to change the oxidation state of Ti or Sn. Since W(VI) is d^0, and the tungstates are wide band-gap materials and are not reduced, then the transition metal d-states should be the only localised gap states to consider. The literature evidence (generalising from the case of $FeWO_4$[18]) is that where there is a choice the compounds are high spin. Thus, for Mn, Co, Fe, the unoccupied t_{2g} states could act as acceptors from the valence band and the occupied e_g states as donors to the conduction band. For Ni and Cu the t_{2g} states are all filled so the most likely case for these series is that the e_g states would act as donors to the conduction band. For Zn, all the d-states are filled and the effects should be dominated by defects and by Zn s-states at the conduction band edge.

There are certain caveats that must be placed on interpretations derived from results of measurements on porous pellets. Both resistivity and gas response are expected to depend upon microstructure. So comparisons require a consistent microstructure. We believe that this was achieved, based on microscopic examination and the systematic variation of behaviour across the different series that was observed, and upon our general experience of consistency of behaviour across repeat preparations, but cannot be certain that there was not some subtle influence which we did not control. The interpretation of measurements of activation energy deduced from variation of conductance over a limited temperature range is fraught with difficulty, also, especially for porous pellets where charge carrier activation from surface states as well as from bulk donors and across the band gap all contribute to the measured conductivity. Here again, we rely on the systematic variation of behaviour to support our interpretation.

Firstly, it is important to notice that, generally, the resistivity (see Fig. 2) of all the materials was higher along the TiO_2 than the SnO_2 series and decreased steadily for each family of compounds with increasing amount of TiO_2 or SnO_2. At the same time all p-type compounds exhibited higher resistivities than the n-type ones. In order to account for the variations with composition, one has to consider that all the behaviour is due to e_g states acting as donors. This leads to a formal oxidation of the cations which seems more reasonable than a formal reduction. Hence, the behaviour just reflects how far away the e_g states are from the conduction band edge. The activation energy for conduction (Fig. 3) gives an indication on where the localised d-states lie with respect to the conduction or the valence band. Hence, for small concentrations of Fe in $FeWO_4$-substituted compounds, the high conductivity and the low activation energy (Fig. 2 and 3) could be interpreted by the e_g states being near the conduction band edge for SnO_2 and TiO_2. For $NiWO_4$-substituted compounds, if the e_g states were far away from the conduction band or the valence band, the conductivity would be low and the activation high as observed. As far as the other materials are concerned, both the conductivity and the activation energy lie in between the two extremes with, interestingly, no apparent systematic variation with d-electron number. Overall, the activation energies increase with decreasing TiO_2 or SnO_2 content which indicates that positions of the d-states with respect to the conduction band edges change across the series which is consistent with the changes of conductivity.

Difficulties in interpreting the results could arise if there were surface segregation of one of the constituents. The behaviour would, then, reflect the variation of the surface composition, but not that of the bulk. The results (Fig. 9 and 10) show that a general tendency is observed for segregation of W to the surface and an inverse segregation of the transition metal away from the surface. Another complication, which is hard to quantify, is the effect of minor amounts of unreacted compounds or of other phases.

Using the simple model of a surface trap-limited conductivity,[6,9] the switch from n- to p-type response to reducing gases can be interpreted, at least in part, if one makes some guesses about the local state occupancy and the energy of these states with respect to the energy associated with an oxygen atom adsorbed on the surface. Ni- and Cu-based materials were the only two families of compounds, which remained n-type across both series. If the partially occupied e_g states in the Ni and Cu series lie above the oxygen surface state for all compositions, then these materials would always be n-type. For the Mn, Fe and Co series, however, at high mole fraction of tungstate, the d-states must all lie below the oxygen surface state to give the observed p-type behaviour whereas at low mole fraction of tungstate, the oxygen surface state must move above the e_g states. For Zn-based materials we would expect the behaviour to be different again, which is what is observed : for the Co, Mn, Fe series, the n–p transitions

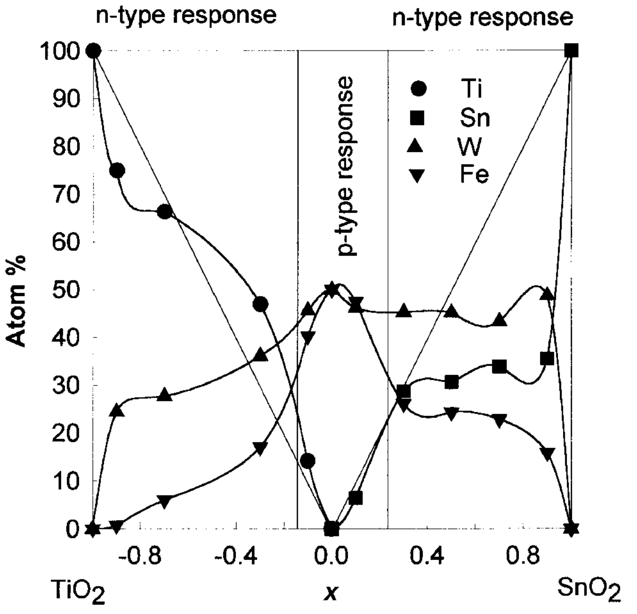

Fig. 9 Surface cation concentration as a fraction (%) of total surface cation concentration, determined by XPS, for $(FeWO_4)_{1-x}(M'O_2)_x$ (M′=Sn, Ti).

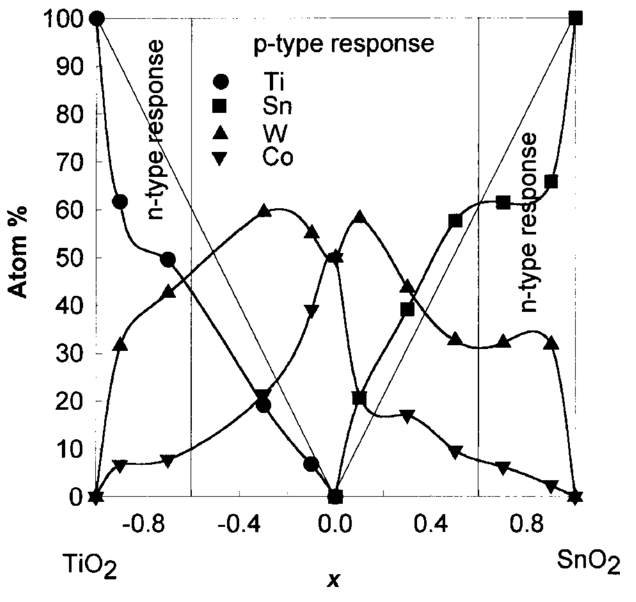

Fig. 10 Surface cation concentration as a fraction (%) of total surface cation concentration, determined by XPS, for $(CoWO_4)_{1-x}(M'O_2)_x$ (M′=Sn, Ti).

occur at similar compositions along both the TiO_2 and SnO_2 branches, whereas for the Zn series they do not.

The next question is why there should be a maximum in response with composition on the SnO_2 branch for some series but no corresponding maximum on the TiO_2 branch. We showed earlier in ref. 25 that, for the case where the gas response could be described in terms of a surface trap-limited process and interpreting the effect of a reactive gas as a decrease of N_S (the surface trap concentration, that is: the concentration of adsorbed oxygen species which mediate the gas response), the gas sensitivity could be written approximately as:

$$S \approx \frac{1}{N_S}\left(\frac{1-\alpha}{1+\alpha}\right)$$

$$\text{with } \alpha = \frac{\mu_e K_1 (N_A + N_D)^2}{\mu_p K_2 N_S{}^2}$$

where N_A denotes the bulk acceptor state density; N_D the bulk donor state density; K_1 the equilibrium constant for electron excitation between surface acceptors and conduction band; K_2 that for equilibrium between surface acceptors and valence band and μ_e, μ_p respectively the mobility of electrons and holes. With $\alpha < 1$, the conductivity decreases with decrease of N_S: this is a 'p'-type response. With $\alpha > 1$, conductivity increases with decrease of N_S: this is an '*n*'-type response. For an *n*-type oxide, if substitution increases the bulk state density, $(N_A + N_D)$, then the sensitivity should increase (in the absence of effects caused by the space charge layer at the surface being thinner than the crystallite size). This is observed for the SnO_2 branch of the series studied here. Then, if on further substitution, K_1/K_2 decreased, the response would go through a maximum then decrease and switch to p-type, again as observed on the SnO_2 branch. Dependent on the change of K_1/K_2 with composition compared with that of $(N_A + N_D)$, then the maximum in response might not be marked or might be absent, as observed on the TiO_2 branch.

In our previous discussion of the SnO_2 (n-type)–$CrNbO_4$ (p-type)–TiO_2(n-type) series,[6] we interpreted the p–n transition on the TiO_2 branch by the energy of the oxygen surface state moving closer to the conduction band edge as the Ti content increased. This statement is equivalent to postulating a marked change of K_1/K_2 with TiO_2 content, and so is consistent with the interpretation presented here for the difference in behaviour between TiO_2 and SnO_2 branches. The interpretation of the variation in conductance with composition presented above is also consistent with the postulate that K_1 decreased (that is, the energy difference between conduction band edge and surface acceptor state energy increased) with increase of wolframite concentration.

It remains to discuss the relative selectivity S_{CO}/S_{CH_4}, S_{CO}/S_{NH_3} observed, and the different effects of water vapour along the different series in comparison with the effects of the reactive gases. The notable effects on selectivity are the maximum in S_{CO}/S_{CH_4} for the Fe and Zn series along the SnO_2 branch, the uniformly higher selectivity S_{CO}/S_{CH_4} for the Cu series across the whole range and the maximum in S_{CO}/S_{NH_3} for the Zn series along the TiO_2 branch. Previous work has shown that the selectivity of porous pellets can be altered as a consequence of changes in the rate of surface catalysed combustion of the different gases. To explain the observed maximum in this way would require that the combustion rate of CO was drastically decreased for these particular compositions. Another explanation might be that there are two different types of oxygen surface state mediating the response, and that, for the series showing the maxima, the relative proportions of these two states change. This last interpretation is supported by comparing surface concentration for the Co and Fe series along the SnO_2 branch, these two series showing different behaviour in the way surface composition changes with bulk composition.

As stated earlier, all the reactive gases were consistent in their classification of the materials as n- or p-type. However, the sign of response to water vapour was not always consistent. Overall, the Co-, Cu- and Zn-based materials response to water behaved as expected as n- or p-type materials. Clearly, there were some differences between water and the other gases for Mn-, Fe- and Ni-based compounds. The sign of the resistance change associated with adsorption of water by the oxides can be discussed[6,7] in terms of the surface hydroxide trap energy; in particular its position relative to the $O_{ads}{}^{2-}$ trap state. For the n-type oxides which exhibit a resistance decrease upon exposure to water vapour or the p-type oxide which exhibit a resistance increase, the effect could be explained by assuming dissociative adsorption of water with the OH_{ads} trap state produced lying higher in energy than the $O_{ads}{}^{2-}$. The opposite behaviour, where materials which otherwise behave as p-type give a resistance decrease with water means that the OH_{ads} state must lie *lower* in energy than O_{ads}. The fact that the introduction of some transition metal ions causes a change in sign of response to water vapour without causing a change in sign of response to other gases implies that there are surface binding sites for water vapour which are specifically associated with these substituents. Fig. 9 shows that the behaviour may be associated with the surface excess of tungsten over tin, and there is the possibility that tungsten could be present on the surface in a lower oxidation state. In this sense, the results parallel those found for the effects of Sb(III) segregation.[8]

Since the compounds that contain the wolframites exhibit smaller sensitivity to water than SnO_2 (typically $S_{H_2O} \leqslant 0.5$), the energies of the acceptor states $O_{ads}{}^-$ and OH_{ads} on the substituted compounds must be closer together than for pure SnO_2. The magnitude of the response to water vapour can certainly be correlated with the cationic composition of the surface. The presence of Sn and to a lesser extent Zn on the surface seems to lead to a larger signal to water vapour.

Conclusion

The conductance and the activation energy for conductance of solid solution compounds $(MWO_4)_x(M'O_2)_{1-x}$ $(0<x<1$; $M=Mn$, Fe, Co, Ni, Cu, Zn; $M'=Sn$, Ti) vary systematically with the energy and number density of 3d-transition metal states, dependent upon the nature of the transition metal ion and its concentration. The resistivity behaviour of all the compounds can be interpreted as due to e_g states of the transition metal cation acting as donors. The surface trap-limited conductivity model can explain, at least partially, the switch from resistance decrease to resistance increase response to reducing gases if assumptions are made about the local state occupancy and the energy of these states with respect to the energy associated with O adsorbed on the surface. The switch in behaviour could be speculatively correlated with a decrease in the surface concentration of Sn or Ti below a critical value. The sign of response to water was not always consistent with that expected with the other reactive gases. The sign of resistance change associated with adsorption of water can be explained in terms of the surface OH trap energy relative to the $O_{ads}{}^-$ trap state. There appear to be surface binding sites for water vapour which are specifically associated with the transition metal ions.

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